

Defect Engineering in Metal Oxide Through Laser Irradiation

by

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Examining Committee Membership

The following served on the Examining Committee for this thesis. The decision of the Examining Committee is by majority vote.

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

This thesis consists of a literature review (Chapter 2) and three chapters containing research data which are written in the manuscript format (Chapter 3-5). At the time of submission, 7 papers have been published (5 published as the first author) and their contributions to this thesis are stated in Chapter 7. I am the primary author of these manuscripts and all related manuscripts were modified to fit the style of this thesis. Dr. Norman Zhou and Dr. Peng Peng are corresponding authors of these manuscripts who have reviewed and approved each chapter in this thesis. Other co-authors of these manuscripts and their contributions are described below.

Chapter 3

Shuo Zheng, Walter Duley, Peng Peng, and Norman Zhou. "Laser Modification of Au-CuO-Au Structure for Improved Electrical and Electro-Optical properties." *Nanotechnology*, 33 (2022): 245205.

Walter Duley helped conceptualize the idea and provided editorial support. Peng Peng provided guidance and editorial support. Norman Zhou provided guidance and editorial support. The device fabrication, material characterization and manuscript writing were done by myself.

Shuo Zheng, Xiaoye Zhao, Walter Duley, Norman Zhou, and Peng Peng. "Laser Engineering of ITO/ZnO/ITO Structures for Enhanced Photodetection in Visible Region." *Journal of Laser Applications*, 34 (2022): 032006.

Xiaoye Zhao helped conduct the photodetection. Walter Duley provided editorial support. Norman Zhou provided guidance and editorial support. Peng Peng provided guidance and editorial support. The device fabrication, material characterization, data acquisition and manuscript writing were done by myself.

Chapter 4

Shuo Zheng, Zuolong Chen, Walter Duley, Yimin Wu, Peng Peng, and Norman Zhou. “Engineering the defect distribution in ZnO nanorods through laser irradiation.” *Nanotechnology*, 34 (2023): 495703.

Zuolong Chen prepared the material and conducted the photocatalytic measurements. Walter Duley helped conceptualize the idea and provided editorial support. Yimin Wu provided financial support. Peng Peng provided guidance and editorial support. Norman Zhou provided guidance and editorial support. The material characterization, heat transfer simulation, electrochemical measurements and manuscript writing were done by myself.

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Abstract

Metal oxides such as copper oxide (CuO), titanium dioxide (TiO₂) and zinc oxide (ZnO) are one of the most important and broadly studied classes of semiconductors. Their nano-materials have shown great potential in the development of functional nano-devices. In metal-oxide nano-materials, zero-dimensional point defects are believed to play a central role in the control and optimization of their properties because they would be strongly determined by nature, concentration and arrangement of these point defects. Therefore, tailoring the properties of metal-oxide nano-materials for targeted applications through engineering these characteristics of defects is of growing interest.

Laser irradiation, as one of the emerging technologies, has shown the ability of engineering point defects in metal-oxide nano-materials through. However, the information on the characteristics of these laser-induced defects remains limited and further investigations are highly required to understand the defects related properties and how the defects can be introduced. In this thesis, the following research works were demonstrated.

The CuO nanowires (NWs), one of the most popular p-type metal-oxide nano-materials, were prepared by thermal oxidation and irradiated by ns laser. The produced defects resulted in intragap energy levels that narrow the bandgap of CuO, which gives rise to improved absorption in the visible region. The concentration of defect centers after laser irradiation increases electrical conductivity by a factor of two at a forward bias of 15 V and enhances photo-conductivity of the Au/CuO/Au structure, tripling the optical gain of these structures. Besides, the concentration of defects was also successfully tailored in ZnO, an n-type metal oxide. The defect-to-lattice ratio of oxygen species can be tuned in a range between 0.24 and 0.61. The increased concentration of defects in ZnO thin films resulted in narrowed bandgap energies and extended the photo-response of these ZnO thin films into the visible region.

Next, the control over the distribution of these defects was explored. CuO NW films were grown and surface defects were introduced through laser irradiation, which were verified by electrochemical measurements. Further control over the arrangement of the defects was

demonstrated in ZnO NWs. ZnO NWs with abundant defects locating at the surface regions (within 1.5 nm from the surface) and residing in the region as deep as 6 to 12 nm were obtained, respectively. The surface-to-bulk ratio of defects in ZnO NWs can thus be modulated by tuning the laser fluence and exposure time. ZnO NWs with abundant surface defects showed enhanced photodegradation rate of dye molecules while the ZnO NWs with more bulk defects exhibited less efficiency.

Lastly, the type of defects was tailored in Cu₂O and ZnO thin films through laser irradiation under different atmosphere conditions. Either oxygen-rich or oxygen-poor ambient conditions were provided during laser irradiation so that corresponding cationic or anionic vacancies can be generated. The formation of V_O in Cu₂O and V_{Zn} in ZnO thin films leads to the abnormal conductivity types in these materials, resulting in n- and p-type doping respectively. Thin film transistors with complementary conducting channels were then fabricated in Cu₂O and ZnO thin films with laser induced defects to show the efficacy of this laser doping process.

Overall, the investigation of defect engineering in metal-oxide nano-materials through laser irradiation is still limited and requires more effort. Some of the remaining research questions and potential research studies are stated in the last chapter of this thesis to inspire future research activities.

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Nomenclature

ALD	Atomic layer deposition
Au	Gold
Ar	Argon
AZO	Al-doped ZnO
CaH ₂	Calcium hydride
CMOS	Complementary metal-oxide semiconductor
CuO	Copper oxide
Cu ₂ O	Cuprous oxide
CVD	Chemical vapor deposition
CZ	Czochralski
DC	Direct current
DRS	Diffused reflection spectroscopy
EDS	Energy dispersive X-ray spectroscopy
EPR	Electron paramagnetic resonance
Fs	Femtosecond
GaAs	Gallium Arsenide
GILD	Gas immersion laser doping
LPCVD	Low pressure chemical vapor deposition
MEMS	Micro-electromechanical systems
MSM	Metal-semiconductor-metal
NaBH ₄	Sodium borohydride
NaOH	Sodium hydroxide
N ₂ H ₄	Hydrazine
NW	Nanorod
Ns	Nanosecond
NW	Nanowire

N ₂	Nitrogen
O ₂	Oxygen
PECVD	Plasma enhanced chemical vapor deposition
PL	Photoluminescence
PLD	Pulsed laser deposition
PLFL	Pulsed-laser fragmentation in liquids
PLML	Pulsed-laser melting in liquids
Ps	Picosecond
PVD	Physical vapor deposition
RF	Radio frequency
Si	Silicon
TFT	Thin film transistor
TiO ₂	Titanium dioxide
V _{Cu}	Copper vacancy
V _O	Oxygen vacancy
VTC	Voltage transfer characteristics
V _{Zn}	Zinc vacancy
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray diffraction analysis
UV	Ultra-violet
ZnCl ₂	Zinc chloride
ZnO	Zinc oxide

Chapter 1 Introduction

1.1 Background

The past decades witnessed the rapid growth of the semiconductor industry and the prosperity of abundant electronic devices. The continuous demand for device miniaturization to pursue better performance using less resources and energy has pushed the size of these devices into atomic and nanometer scales. The semiconductor materials in their nanoscale forms thus received lots of investigations in recent decades. Metal oxides such as copper oxide (CuO), titanium dioxide (TiO₂) and zinc oxide (ZnO) are one of the most important and broadly-studied classes of semiconductors. Their nano-materials have shown great potential for playing critical roles in the development of functional nano-devices. For instance, the unique physical and chemical properties of metal-oxide nano-materials make them compelling for applications in emerging technologies such as nano-electronics, nano-photonics, solar cells, detectors, etc.¹⁻⁶ A schematic showing some of these applications is displayed in Figure 1.1 (a).⁷ To meet the requirement of various functionalities, metal-oxide nano-materials need to be engineered to obtain desired properties. In metal-oxide nano-materials, the factor that plays a central role in the control and optimization of these materials is the defect.

Defects are imperfections in the atomic structure that all crystalline materials above absolute zero will contain, their presence is almost inevitable. If these imperfections are intentionally introduced into the material, they are extrinsic defects. Otherwise, the defects such as vacancies, self-interstitials and antisites are intrinsic defects. Defects in the materials can be zero-dimensional point defects, one-dimensional line defects, two-dimensional planar defects or bulk defects.⁸⁻¹⁰ Figure 1.1 (b) shows the schematic of some crystalline defects.¹¹ It is intuitive to perceive that defects weaken the properties of the material, however, it is not always true. For instance, planar defects were normally considered to deteriorate the mechanical properties of the semiconductor materials¹²⁻¹⁴, but recent studies showed that they can also improve the Young's Modulus at some circumstances^{15,16}. The roles of defects may

differ from case to case, but it is now broadly accepted that the properties of semiconductors are strongly dependent on the characteristics of defects. The importance of defects becomes even more pronounced as the feature size of devices reaches nanoscale. It is therefore clear that a better understanding of defect characteristics and how to modulate the properties of metal-oxide nano-materials for targeted applications through defect engineering is an area of growing interest. The scope of defect engineering is to prevent the generation of those “harmful” defects and to create defects which enhance the performance of the devices. Nowadays, defect engineering in metal-oxide nano-materials typically involves manipulating the type, concentration, and distribution of defects using various techniques such as electron irradiation,¹⁷ ion implantation,^{18–20} annealing,²¹ chemical solution method,^{22,23} and ambient-dependent physical deposition.

Recently, laser irradiation has emerged as another important technique to engineer the defects in metal-oxide nano-materials. A major advantage of laser irradiation is that the high-localization and high-precision nature of laser make it possible to engineer the defects in constrained regions to achieve anisotropic distributions and the sequential exposures enable the maskless patterning of defect-engineered regions. Meanwhile, laser irradiation also has the flexibility of switching from focused to de-focused beam to obtain universal manipulation of defects in large areas, suggesting great potential for mass production. The modification of point defects through laser irradiation has been successfully achieved in both n- and p-type metal-oxide nano-materials.^{24–27} One of the strategies tailors the defects by exposing the metal-oxide nano-materials to pulsed laser irradiation in liquid.^{28,29} For example, Lau et al.³⁰ demonstrated that pulsed laser irradiation upon ZnO and TiO₂ nanoparticles triggers both pulsed-laser melting in liquids (PLML) and pulsed-laser fragmentation in liquids (PLFL). Both PLML and PLFL processes generated defects in these nanoparticles and result in improved photocatalytic activities.³⁰ On the other hand, previous studies also reported that laser irradiation of metal-oxide nano-materials in air can produce defects because of photodissociation of bonds in the irradiated material.^{31–35} These laser-engineered metal-oxide nano-materials have shown outstanding performance in optoelectrical, photocatalytic and electrochemical applications.

Although progress has been made with regard to laser-induced defect engineering in metal-oxide nano-materials, there are still many remaining research questions to answer to expand the understanding beyond the existing knowledge. For instance, the relation between the concentration of defects and laser processing parameters were not investigated thoroughly, the distribution of laser-induced defects was not discovered, the strategies to produce the desired type of defect through laser irradiation were not demonstrated.

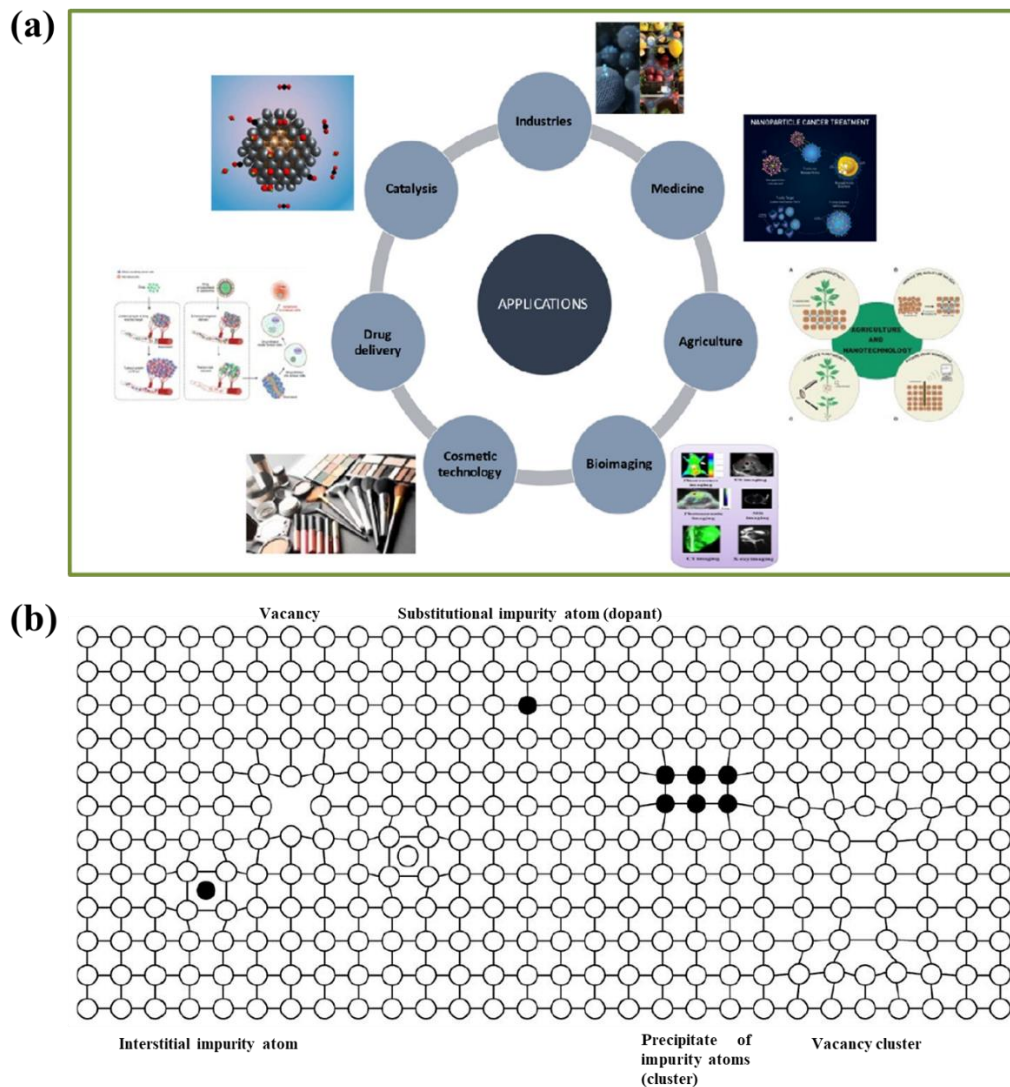


Figure 1.1 (a) A schematic showing the applications of metal-oxide nano-materials. Reprinted with permission.⁷ (b) A schematic showing the examples of defects in the crystalline. Reprinted with permission.¹¹

1.2 Objectives

The objective for this research is to advance the knowledge about the defects tailored through laser irradiation and utilize the laser-engineered metal-oxide nano-materials to fabricate functional nano-devices. The relation between the concentration of defects in metal-oxide nano-materials and the parameters of laser irradiation was first determined, the distribution of laser-induced defects was unraveled and the strategies to create desired doping in metal-oxide nano-materials through defect engineering were proposed. Particularly, the following sub-objectives for this research were set:

(1) The concentration of defects is the most straightforward property that can be readily characterized. Therefore, this research starts with the exploration of the relation between the concentration of defects in metal-oxide nano-materials and the parameters of laser irradiation. CuO is a typical p-type metal oxide semiconductor which is suffering from low current amplitude. The aim is to increase the concentration of defects to improve the electrical conduction in CuO nanowires (NWs) and enhance their current response under light illumination through laser irradiation. To further validate this laser processing technique, the concentration of defects in n-type ZnO thin films is tuned as well. The introduction of additional defects in ZnO thin films is expected to improve their electrical and optical properties.

(2) After determining the laser processing parameters for the production of defects, it is desired to reveal the distribution of these defects introduced through laser irradiation and establish strategies to control the distribution. Defects were first generated by laser irradiation in CuO NWs and their impacts on the electrochemical properties are examined. Most of the electrochemical measurements rely on the redox reactions on the surface of the material, which are affected by surface defects rather than bulk defects. Therefore, the improvements in the electrochemical properties of CuO NWs are perceived as the indication of the production of surface defects. The distribution of the defects is further investigated in ZnO NWs and the arrangement is described as the surface-to-bulk ratio. The goal is to reveal the relation between

the depth profile of defects in ZnO NWs and the parameters of laser irradiation then optimize the surface-to-bulk ratio in ZnO NWs for enhanced photocatalytic applications.

(3) Lastly, the target is to produce the desired type of defects through laser irradiation. Previous studies revealed that the dominant species of defects in metal-oxide nano-materials often possesses the lowest formation energy which can be controlled by the ambient conditions during the production of these defects. For example, the generation of oxygen vacancies are more favorable in oxygen-poor environment while the cationic vacancies are often obtained in oxygen-rich environment. However, this approach has never been examined for the defects produced by laser irradiation. Cuprous oxide (Cu_2O) and ZnO thin films are immersed in diverse gaseous environments during laser irradiation to obtain the desired type of defects. As an example of the efficacy of this laser processing technique, laser-induced defects are used to dope the thin films for transistor applications.

At the end of this research, the objective is to achieve a comprehensive understanding of the characteristics of the defects in metal-oxide nano-materials produced by laser irradiation. The strategies to tailor the concentration, arrangement as well as the types of these defects are investigated systematically and their impacts on diverse applications are discussed. To demonstrate the achievement of these objectives, this research thesis is split into the chapters described in the next section.

1.3 Organization of the Thesis

Chapter 1 contains an introduction covering the background, research objectives, and the organization of this thesis.

Chapter 2 is the literature review. A review of defects engineering in Si is presented first to show how they inspire the investigations in metal-oxide nano-materials. Then, the characteristics of defects are introduced based on their types, concentration and distribution. Subsequently, techniques used for defect engineering in metal-oxide nano-materials are reviewed and the applications of these laser-engineered materials are demonstrated.

Chapter 3 demonstrates the strategy to tailor the concentration of defects in CuO NWs and ZnO thin films. It is shown that laser irradiation in air can introduce additional defects in both p-type CuO and n-type ZnO. The existence of defects is confirmed by ultraviolet-visible (UV-Vis), x-ray photoelectron spectroscopy (XPS) and Raman results and their presence has improved multiple electrical and optoelectrical properties. These improved properties show great potential for applications such as photodetection and resistive switching devices.

Chapter 4 explores the possibility of modulating the distribution of defects in CuO and ZnO NWs. The defects are identified by transmission electron microscopy (TEM), x-ray diffraction analysis (XRD), Raman, UV-Vis, photoluminescence (PL) and the depth profiles of laser-induced defects are displayed. Their impacts on the electrochemical properties are also measured. The correlation between laser irradiation and the distribution of defects will be established and a heuristic mechanism to trace the effect of laser on the distribution of defects will be proposed. To validate the efficacy of this laser processing approach, glucose sensing using laser-processed CuO NWs is conducted and photodegradation of Rhodamine B is carried out using laser-modified ZnO NWs as the catalysts.

Chapter 5 shows the method to deliberately control the laser-generated defect types in Cu₂O and ZnO thin films. The vacancies produced by laser are characterized by UV-Vis and XPS. The controlled production of vacancies results in different conduction types in Cu₂O/ZnO thin films, which is revealed by obtaining homogeneous p-n junctions in these thin films. It will be demonstrated that both n-channel and p-channel thin film transistors (TFTs) can be obtained in Cu₂O/ZnO thin films and a novel inverter structure exploiting these complementary TFTs is discovered.

Chapter 6 gives the summary of this research and discuss the future works.

Chapter 7 displays the author's research contributions.

Chapter 2 Literature Review

This chapter reviews the properties of defects, the engineering techniques of defects and the related applications of these defect-engineered materials.

2.1 Defect Engineering in Silicon

As the knowledge of semiconductor physics develops, defects in semiconductor materials receive more and more investigations. The exploration of the defects was further stimulated by the prosperity of the Si-based electronic devices in recent decades. To achieve the best device performance, the monocrystalline silicon used for modern electronics must undergo appropriate process steps during their growth to eliminate the undesired defects. One of these practical methods was demonstrated by Dash in 1959.³⁶ He showed that the dislocations can be removed during the Czochralski (CZ) method growth of silicon crystal by creating a neck region at the beginning.³⁷ The pictures showing the process steps of CZ growth of silicon are shown in Figure 2.1 (a).³⁸ This is one of the earliest attempts to modulate the unwanted defects in semiconductor materials. As the time moves to 1980s and 1990s, the idea of engineering the defects such as the oxygen precipitates and agglomerated intrinsic point defects in CZ single crystalline silicon started to prevail.³⁷ Much of the work in the 1980s focused on the modulation of the interstitial oxygen and its precipitation in Si.³⁷ It is believed that the oxygen can precipitate excessively during the thermal treatments associate with the growth of Si as well as the subsequent fabrication processes. The oxygen precipitates, if formed in the surface region, would cause the device failure while the oxygen precipitates in the bulk regions can be beneficial for trapping the metal impurities that may contaminate the Si wafer.³⁷ It is therefore critical to control the depth profile of oxygen precipitates and it was achieved by manipulating the oxygen concentration during the growth of Si and performing thermal treatments to diffuse the oxygen out of the surface regions.³⁷ In the 1990s, the focus shifted to the engineering of the intrinsic point defects in Si. Vacancies and self-interstitials are the two major types of point defects that influence the properties of Si. During the CZ growth of Si, Frenkel pairs of

interstitials and vacancies are continuously produced close to the melt interface and they will be re-distributed due to the temperature-dependent diffusion as the crystal cools down, resulting in the predominating of one species of defects in particular regions. Understanding and controlling these behaviors of defects then became a major challenge for researchers. A breakthrough was made by Voronkov et al.,³⁹ who proposed that the dominance of interstitials and vacancies is governed by the ratio of the growth rate to the axial thermal gradient at the melt interface.

Rather than the aforementioned methods that modulate the defects during the growth of Si, defect engineering by post-treatments also received extensive investigations.^{11,40–43} One most widely used technique to introduce substitutional defects in Si is ion implantation, whose debut can be traced back to the 1950s.⁴⁴ A schematic showing the configuration of an ion implanter is given in Figure 2.1 (b).⁴⁵ The ion implantation typically employs radio frequency (RF) or direct current (DC) electric fields to accelerate the ionized volatile dopant atoms and direct them at the target Si. The dopant atoms enter the crystal lattice, colliding with the lattice atoms and finally stopping at some depth within the Si solid. Two of the most critical applications of ion implantation in Si are the doping of boron and phosphorous ions, which results in p- and n-type conductivities, respectively.^{46–48} A schematic showing these dopants in Si can be seen in Figure 2.1 (c).⁴⁹ During the collisions between implanted atoms and the lattice atoms, Frenkel pairs of vacancies and self-interstitials are also generated and they will diffuse in the lattice, reacting with themselves and other atoms so that more defects occur.^{47,50} It is believed that these point defects introduced in ion implantation also influence the diffusivity of dopants significantly. For instance, excess self-interstitials in Si enhance the diffusivity of boron dopants by several orders of magnitude.⁵⁰ Subsequent high temperature annealing is often necessary to repair the damage caused by the ion implantation as well as electrically activate the implanted dopants.^{51,52} Point defects can be removed from the active region of the device during the annealing so that better device performance can be achieved.⁵⁰ Another similar technique replaces the ion source with the electron beam.^{53–55} High energy electrons displace the lattice atom in Si so that vacancies and interstitials are produced. For example, Wada et al.

determined the production rates of point defects by electron irradiation in n-type Si and revealed the energy levels of these defects.⁵⁴

The rapid development of photovoltaic devices and field effect transistors requires the production and restraint of doping area in the shallow surface of Si, which can hardly be achieved by ion implantation nor high energy electron irradiation. A resolution proposed by researchers is the GILD process.⁵⁶ The GILD process takes advantage of UV laser irradiation to melt the silicon surface in a containment chamber while immersed in the gaseous dopant precursors. A schematic showing this process is displayed in Figure 2.1 (d).⁵⁷ The gaseous dopant precursors can be chemisorbed on the molten Si surface and partially incorporated during the recrystallization of Si so that doping can be realized.^{58–60} For instance, Kerrien and his coworkers⁵⁶ demonstrated ultra shallow doped junctions can be formed within 14 nm to 65 nm in depth. The doping profiles are also box-like, indicating a highly localized manner of laser doping.

The last 50 years witnessed the substantial development of knowledge about defects in Si and it is still of interest. But a more important trend in the modern semiconductor industry is the dramatically increased sophistication of heterogeneous integration of diverse devices with different functionalities. One of such examples is the integration of complementary metal-oxide semiconductor (CMOS) and micro-electromechanical systems (MEMS).^{61,62} As the functionalities of devices greatly expand, Si is no longer capable of meeting the requirements of all these functions and other semiconductor materials are making more and more contributions to the industry.^{63–65} Therefore, exploring the information of defects in these semiconductor materials other than Si is of great importance. Even though the characteristics of defects in compound semiconductor materials can be different from Si, the experience and techniques used for defect engineering in Si are great cornerstones that can be extended to the studies of defects in other semiconductors. For instance, ion implantation is also broadly adopted for doping in metal oxides,^{18,66} III-V compounds,^{67,68} graphene,^{69,70} etc. Among these semiconductor materials, we particularly explore the defect engineering in metal-oxide nano-materials in this research thesis. Unlike covalently-bonded Si, most of the metal oxide

semiconductors have a high degree of ionic bonding, indicating that the energies required to break these ionic bonds may be higher.⁷¹ Nevertheless, many of the properties of defects remain similar. The characteristics as well as the engineering techniques of defects in metal-oxide nano-materials are reviewed in detail in the following sections.

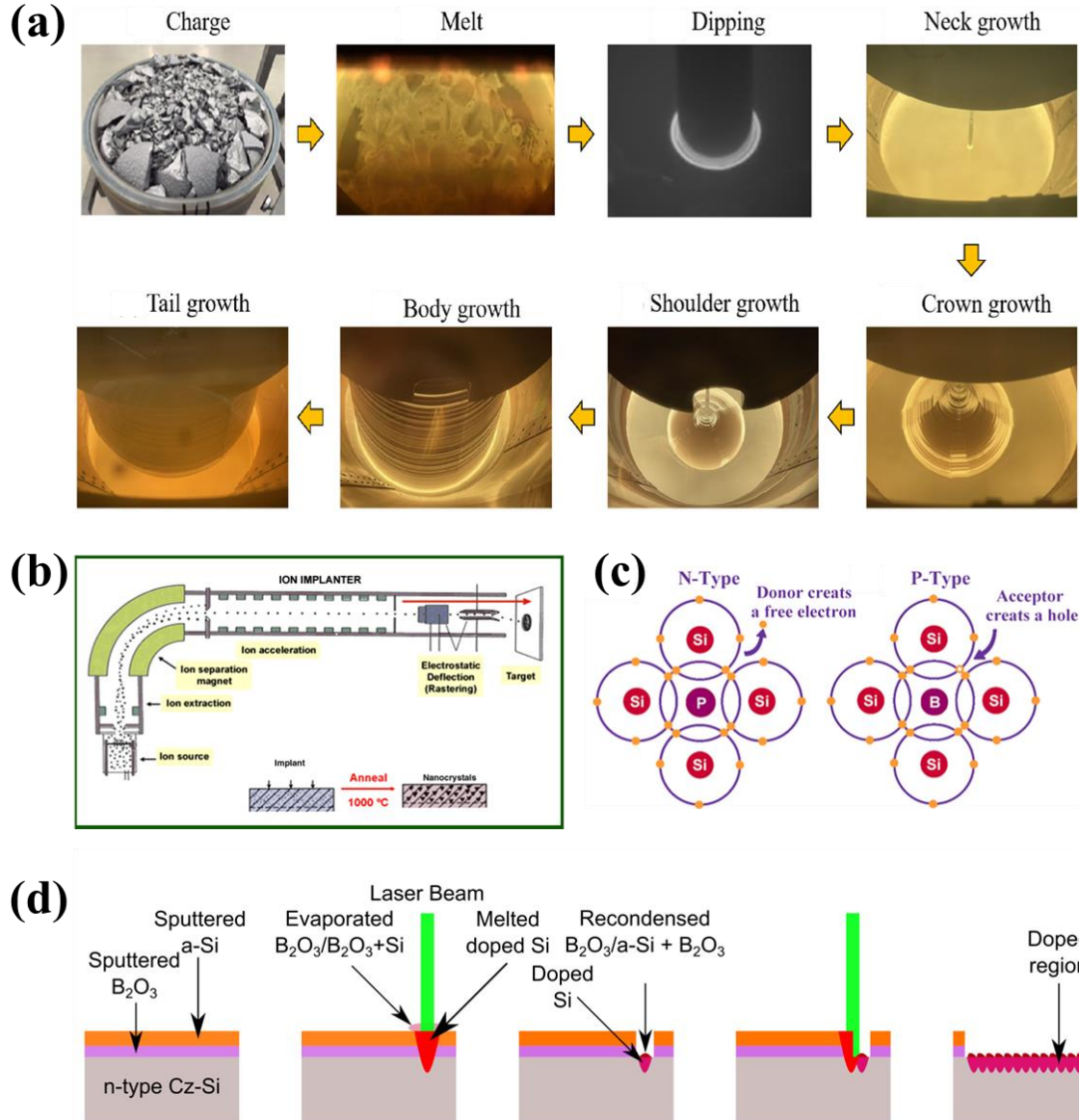


Figure 2.1 (a) The pictures showing the process steps of CZ growth of single crystal silicon. Reprinted with permission.³⁸ (b) The schematic showing the experimental configuration of the ion implantation. Reprinted with permission.⁴⁵ (c) A schematic of boron and phosphorous dopants in Si. Reprinted with permission.⁴⁹ (d) A schematic showing the process of GILD in Si. Reprinted with permission.⁵⁷

2.2 Defects in Metal-Oxide Nano-Materials

This research focuses on point defects in metal-oxide nano-materials and the defects in the following context indicate the native point defects if not specified otherwise. Nowadays, the type, the distribution and the concentration of these defects are three major aspects that received the most investigations.

2.2.1 Types of Point Defects

One critical property of defects in metal-oxide nano-materials is the type of these defects. Semiconductors are generally split into two major categories: intrinsic and extrinsic. Intrinsic semiconductors are the ones with no doping and the extrinsic semiconductors are doped with impurity atoms or vacancies. Because of the existence of many native defects in the lattice, most metal oxides are naturally extrinsic semiconductors. Based on the type of impurities, extrinsic semiconductors are often classified as: n-type or p-type semiconductors. In an n-type semiconductor, the current is carried by electrons which are the majorities of free carriers. On the other hand, free holes outnumber electrons in a p-type semiconductor. Typical n-type metal oxides include TiO_2 , ZnO , etc. And metal oxides such as CuO and Cu_2O are examples of naturally p-type semiconductors. The origin of these conduction types is often believed to be related to the native defects in metal oxides.⁷²⁻⁷⁴ In metal-oxide nano-materials, the native defects typically include vacancies, self-interstitials and antisites. An example of the schematic showing these defects in the lattice of ZnO is given in Figure 2.2. Their presence in metal-oxide nano-materials is often investigated through theoretical approaches. First-principles studies based on DFT with LDA or GGA have been reported previously to calculate the formation and migration energies of these defects.⁷⁵⁻⁷⁹ For instance, the formation energy of the oxygen vacancy in ZnO can be calculated by removing one oxygen atom from the supercell and is therefore expressed as follow:⁷⁵

$$E^f(V_O^q) = E_{tot}(V_O^q) - E_{tot}(\text{ZnO}) + \mu_O + n(E_F + E_v) \quad \text{Eq. (2.1)}$$

where $E_{tot}(V_O^q)$ is the total energy of the supercell containing the oxygen vacancy in the charge state n , $E_{tot}(V_O^q)$ is the total energy of a ZnO perfect crystal in the same supercell, μ_O is the oxygen chemical potential, E_F is the Fermi level and E_v is the valence band maximum. The chemical potential μ_O often depends on the ambient conditions, which can be either zinc rich, oxygen rich or in between, indicating that the formation of a particular type of defect can be modulated by controlling the ambient environment. Previous studies demonstrated that the defects with the lowest formation energy will dominate the population in the metal oxides and the formation energy often varies under different atmospheres. For example, Figure 2.2 (a) and (b) show the formation energy of different types of native defects in the CuO under oxygen-rich and oxygen-poor conditions, respectively.⁸⁰ It can be seen that the dominant species of the defect varies as the oxygen environment changes. Figure 2.3 (a) shows that copper vacancies (blue lines) always have formation energies lower than oxygen vacancies (pink lines) in oxygen-rich environment, but oxygen vacancies can possess comparatively lower formation energies in oxygen-poor environment as illustrated in Figure 2.3 (b). Figure 2.3 (c) and (d) illustrate the formation energy of different types of native defects in the ZnO under oxygen-rich and oxygen-poor conditions, respectively.⁸¹ It can be seen that oxygen interstitials often have lowest formation energies in oxygen-rich environment while oxygen vacancies often possess lowest formation energies under oxygen-poor conditions. And it can be concluded from Figure 2.3 (a)-(d) that V_O is more favored under oxygen-poor conditions rather than oxygen-rich conditions. These theoretical calculations were validated by Wang et al. with their experimental results in CuO.⁸⁰ They demonstrated that treating Cu₂O in various atmosphere resulted in different dominant species of defects, which was characterized by XPS results shown in Figure 2.3 (e). It can be seen that the peak associated with V_O changed as the ambient environment varied, indicating that its dominance can be tailored. Figure 2.4 (f) showed the residual weight of CuO after the treatment. It can be seen that CuO formed in air has a residual weight (pure Cu) ratio of $\sim 80.04\%$, which is close to the value of stoichiometric CuO. CuO formed in the mixed N₂/O₂ gas (N/O $\approx$ 9) gas didn't change this ratio significantly. On the other

hand, CuO formed in O₂ gas has a lower residual weight of 79.03% which indicates a less stoichiometric Cu that can be attributed to the formation of V_{Cu} .

Oxygen vacancies and metal interstitials are now often considered as electron donors so naturally many researchers believed that they are responsible for n-type conductivity in metal oxides. However, many early studies suggested that the oxygen vacancies are deep donors that can hardly be ionized thus contribute little to the n-type conductivity. These works were based on the assumption that oxygen vacancies in the neutral state are the most stable ones.⁸⁶ A most recent study demonstrated by Liu et al. showed that these previous works are wrong with regard to the oxygen vacancies in ZnO.⁸⁷ They demonstrated that the oxygen vacancies in ZnO are mostly +2 charged rather than neutral thus they are shallow donors that can be responsible for the n-type conductivity. Nowadays it still remains controversial that if oxygen vacancies are indeed the shallow donor levels that contribute the most to the n-type conductivity in metal oxides such as ZnO and TiO₂.^{87,88} Unlike the n-type metal oxides, a consensus is almost achieved that the conduction in p-type metal oxides such as CuO are attributed to metal vacancies and oxygen interstitials. Though Luo et al. demonstrated that oxygen vacancies on the surface of CuO can stimulate and trap electrons readily so that free holes giving rise to p-type conducting characteristics can be produced,⁸⁹ more researchers believed that the copper vacancies are the dominant defects contributing to the p-type conductivity. However, there was little experimental evidence to prove this idea because of the difficulties in identifying the copper vacancies. The role of copper vacancies was finally confirmed by a study conducted by Wang et al. in 2019.⁸⁰ In their study, they related the existence of copper vacancies to the generation of lattice oxygen in CuO so that it provides a simple method to identify the copper vacancies. In a word, the type of defect significantly impacts the properties of metal oxides thus it is highly required to provide strategies to produce certain types of defects selectively.

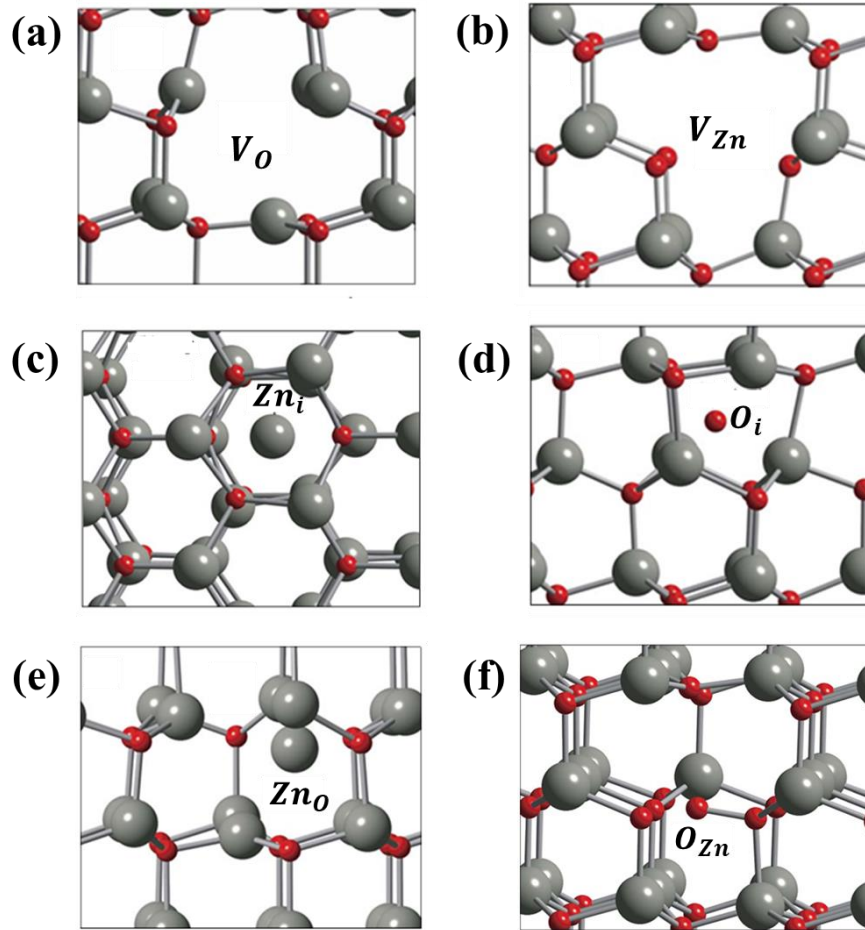


Figure 2.2 A schematic showing the native defects such as (a) oxygen vacancies, (b) zinc vacancies, (c) zinc interstitials, (d) oxygen interstitials, (e) zinc antisites, (f) oxygen antisites in ZnO. Reprinted with permission.⁷⁵

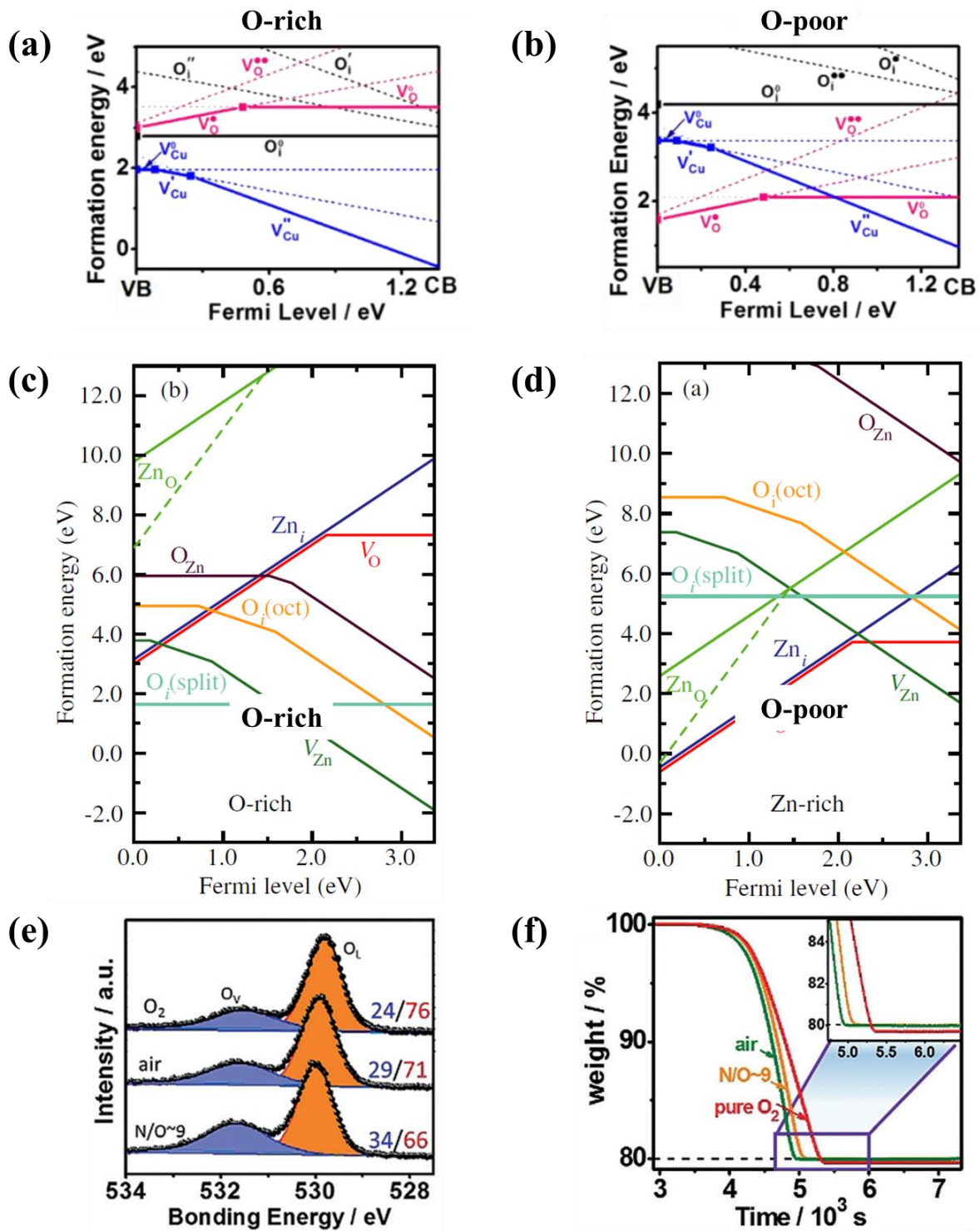


Figure 2.3 Calculated formation energies of different types of defects in CuO under (a) oxygen-rich, (b) oxygen-poor conditions. Reprinted with permission.⁸⁰ Calculated formation energies of various defects in ZnO under (c) oxygen-rich, (d) oxygen-poor conditions. Reprinted with permission.⁸¹ (e) The XPS of CuO in the O 1s region prepared in pure O_2 , air and mixed $N_2/$

O₂ gas (N/O $\approx$ 9). Reprinted with permission.⁸⁰ (f) The weight change of CuO prepared in pure O₂, air and mixed N₂/O₂ gas (N/O $\approx$ 9). Reprinted with permission.⁸⁰

2.2.2 The Concentration of Defects

Another important parameter of the defects in metal oxides is their concentration. The schematics showing the high concentration and a comparatively low concentration of oxygen vacancies in ZnO lattice sites are displayed in Figure 2.4 (a) and (b), respectively.⁹⁰ A straightforward way to characterize the concentration of defects can be achieved through XPS results. For instance, Huang et al. demonstrated that TiO₂ calcined at various temperatures lead to different concentration of V_O .⁹¹ As a result, the peak at ~ 531.6 eV in the O 1s region exhibited different intensities as illustrated in Figure 2.4 (c). Because defects are often considered as traps to capture free electrons or holes, the concentration of defects will thus influence the mobility as well as the density of carriers, both of which impact the electrical conductivity of the metal-oxide nano-materials.^{87,92-94} Many previous studies reported that the density of free carriers is proportional to the concentration of point defects.⁹⁵⁻⁹⁸ For instance, Menelaos et al. demonstrated that the conductivity of TiO₂ thin film is proportional to the concentration of V_O (Figure 2.4 (d)) and the electrical properties of TiO₂ can be enhanced with the presence of more V_O .¹⁰⁰ Nie et al. found similar phenomenon in ZnO thin films.¹⁰¹ They revealed that excimer laser irradiation can produce point defects in ZnO thin films and the concentration of these defects is a function of laser energy, which was reflected in PL results shown in Figure 2.4 (e). It can be seen that the intensity of the visible emission peak (1.9-2.6 eV) decreases as the laser energy increases. They also demonstrated that the electrical resistivity of ZnO decreases as the laser energy increases (Figure 2.4 (f)), which was attributed to the generation of more V_O at high laser energies. However, it is worth noting that only shallow donors in n-type metal oxides and shallow acceptors in p-type metal oxides can be ionized to contribute free carriers,⁸⁶ indicating that only the concentration of the defect that work as shallow donors/acceptors matters in terms of moderating the conductivity of metal-oxide nano-materials.

Except for the electrical conductivity, the concentration of defects can also alter the electrical transport mechanism in the metal oxides. Lin et al. showed that the charge transport mechanism is defect-concentration dependent in CuO nanowires (CuO NWs).¹⁰² The I - V characteristics of CuO NWs with different defect concentrations are shown in Figure 2.4 (g)-(i). It can be seen that the conduction is ohmic when the applied voltages do not exceed the threshold value V_{on} (shown in the insets), and the conduction shift to a trap-filling process which results in non-linear I - V characteristics when the applied voltages are larger than V_{on} . They demonstrated that the different V_{on} values observed in Figure 2.4 (g)-(i) are due to the change in the concentration of defects in these samples. With a higher concentration of defects (Figure 2.4 (i)), the charged transportation mechanism is dominated by nearest-neighbor hopping, in which electrons are ionized from an occupied state to the nearest empty states. On opposite, trap-activation process, in which electrons transit from the valance band to the defect levels, dominates the transport mechanism in the CuO NW with a low concentration of defects (Figure 2.4 (g)).

In addition to the electrical properties, the concentration of defects is known to influence the thermal conductivity and photo-conductivity of the metal oxide as well. Ren et al. first proposed that the concentration of oxygen vacancies in particular metal oxides would influence the thermal conductivity but they failed to give a detailed relation.¹⁰³ Donovan and his coworker carry on the study and demonstrate the relation between the thermal conductivity and the concentration of defects (Figure 2.4 (j)).¹⁰⁴ In their investigation they showed that the interaction between the defects and the phonons in TiO_2 can dramatically disrupt the propagation of thermal carriers. At high defect concentrations, a significant reduction in the thermal conductivity and loss of the anisotropic thermal properties were observed.

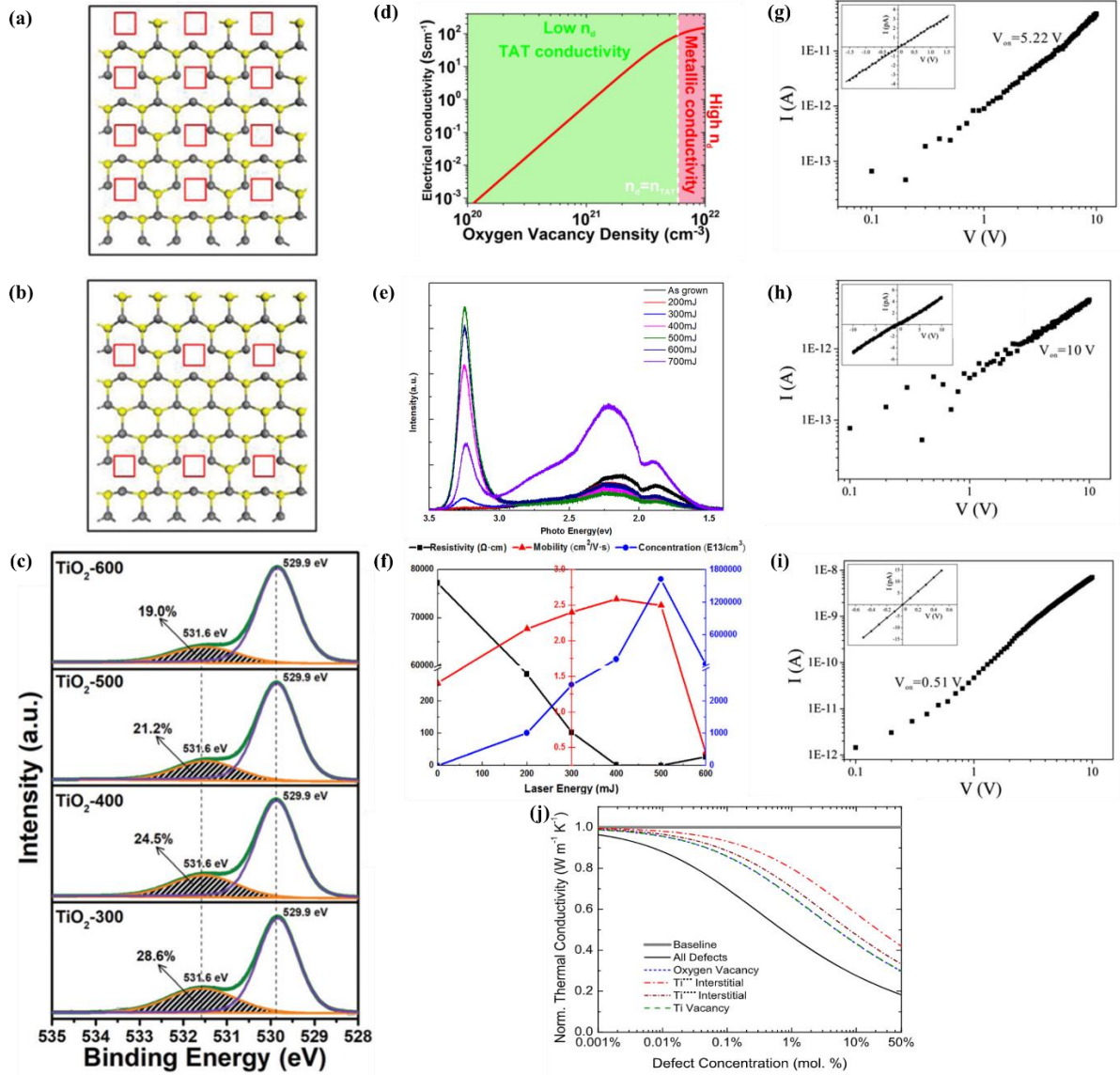


Figure 2.4 The schematic showing the oxygen vacancies in ZnO lattice with a (a) high concentration, (b) low concentration. The red box indicates the oxygen vacancy sites. Reprinted with permission.⁹⁰ (c) The XPS results of TiO₂ calcined at different temperatures. Reprinted with permission.⁹¹ (d) The electrical conductivity of the TiO₂ thin film as a function of oxygen vacancy density. Reprinted with permission.¹⁰⁰ (e) The PL spectra of ZnO thin films irradiated with different laser energies. Reprinted with permission.¹⁰¹ (f) The electrical properties of ZnO thin films as a function of laser energy. Reprinted with permission.¹⁰¹ The I - V characteristics of CuO NWs with (g) low, (h) medium, (i) high defect concentrations. Reprinted with permission.¹⁰² (j) The normalized thermal conductivity as a function of various defects at different concentrations in TiO₂. Reprinted with permission.¹⁰⁴

When exposed to light with sufficient photon energy, electrons in the valence band of metal oxides can be excited to the conduction band and leave holes behind in the valence band. And these free electrons in the conduction band, or holes in the valence band for p-type metal oxides, can be driven by the applied bias voltage to establish photo-current. Since there can be electrons trapped in the defects, similar excitation of electrons can also occur at defects sites.¹⁰⁷ From point of view on the band energy, defects are often believed to introduce intermediated energy levels in the band gap.^{108–112} These intragap energy levels allows the absorption of photons with energies smaller than the bandgap energy to excite electrons from valence band to occupy these intragap energy levels, or from these intragap energy levels to the conduction band. As a result, the metal-oxide nano-materials with defect-induced intragap energy levels can absorb a wider range of light, especially at longer wavelengths.^{113–117} Such information about the optical property is often revealed in the absorption spectra using ultraviolet-visible (UV-Vis) spectroscopy. For instance, Richa et al. presented the absorption spectra of ZnO nano-materials with various morphologies and compared the intensity of the absorption (Figure 2.5 (a)).¹¹⁸ They found that ZnO nano-flowers have exhibited the strongest absorption in the visible region, which was attributed to the abundance of V_O in this morphology. Similar results have been reported in TiO₂ nanoparticles by Kuriechen et al.¹¹⁹ They demonstrated that nitrogen doping results in the existence of additional V_O in TiO₂, leading to the red-shift of the absorption spectrum and enhanced intensity in the visible region, as displayed in Figure 2.5 (b). Furthermore, the bandgap energy of the metal-oxide nano-materials can be extracted explicitly from the Tauc plot which was converted from the absorption spectra. The direct bandgap energy, E_g , can be obtained from an extrapolation of the linear plot of $(\alpha h\nu)^2$ vs. $h\nu$ (Tauc plot), where α (cm⁻¹) is the optical absorption coefficient and $h\nu$ (eV) is photon energy. For example, Figure 2.5 (c) shows the absorption spectra of ZnO nano-powders prepared at different conditions and the corresponding Tauc plot is provided in Figure 2.5 (d).¹¹⁴ The shift in the absorption spectra and corresponding Tauc plot of the ZnO nano-powder due to different concentrations of defects can be observed. To be more specific, higher concentrations of V_O in ZnO nano-powder results

in the red-shifts of the absorption spectra and the corresponding bandgap energies calculated from the Tauc plots move towards smaller values. It is also worth noting that many previous studies demonstrated that the bandgap energy of the metal oxide can be increased if the concentration of defects is excessively high.^{120,121} At excess defect concentration, the Fermi level in the metal oxide is pushed towards the conduction band significantly thus many energy levels close to the conduction band edge will be occupied. Higher energies are then needed to excite electrons from valence band to conduction band, in other words, the bandgap energy is increased.

Since extra electrons can be excited from the defect sites, the concentration of defects also influences the concentration of carriers contributing to the photo-current. Many previous studies showed that the amplitude of photo-current is often proportional to the defect concentration in metal oxides. Syu et al. demonstrated the relation between the oxygen vacancies in the gallium-zinc-tin-oxide (GaZTO) and the photo-conductivity under periodic UV illumination of 280 nm at a bias of 10 V and their results are shown in Figure 2.5 (e)-(g).¹²² They found that the amplitude of the photo-current is enhanced as the concentration of oxygen vacancies increases. However, they also demonstrated that a higher concentration often affects the rise time. When illuminated with UV light, the electrons in oxygen vacancies can be excited to the conduction band so that these oxygen vacancies will capture the electrons again.¹²³ As a result, it takes longer time to reach the maximum of photo-current as the concentration of oxygen increases.

Overall, it can be concluded that the introduction of additional defects into the metal-oxide nano-materials can enhance many physical properties but this effect is not universal. The concentration of defects needs to be carefully controlled to get the optimal enhancement.

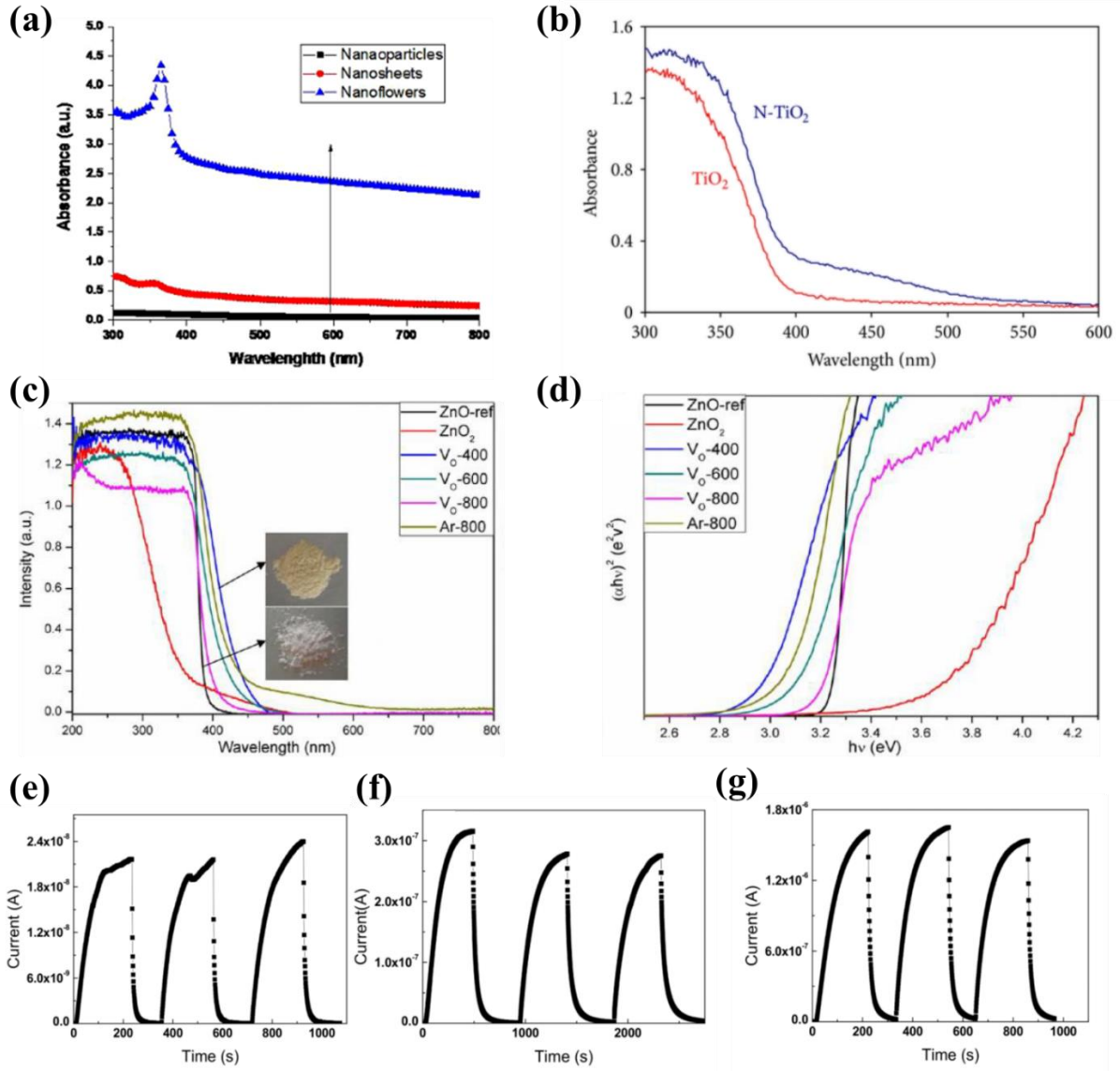


Figure 2.5 (a) Absorption spectra of ZnO nano-materials with various morphologies as indicated in the figure. Reprinted with permission.¹¹⁸ (b) Absorption spectra of TiO_2 nanoparticles before and after nitrogen doping. Reprinted with permission.¹¹⁹ (c) The shift of absorption spectra of ZnO nano-powders due to different defect concentrations. Reprinted with permission.¹¹⁴ (d) The corresponding shift in the Tauc plot of ZnO nano-powders due to different defect concentrations. Reprinted with permission.¹¹⁴ Time response of photo-current for GaZTO with a (e) low, (f) medium, (g) high defect concentration. Reprinted with permission.¹²²

2.2.3 The Distribution of Defects

In metal-oxide nano-materials, the distribution of native point defects is spontaneously non-uniform and this behavior can be explained well by theoretical models. The major category of such distribution is described based on the depth from the material surface, namely surface defects or bulk defects. Figure 2.6 (a) shows a schematic illustrating these vacancies residing in diverse regions in nanocerium. ¹²⁴ As mentioned in 2.2.1, the formation of defects can be calculated using theoretical approaches such as DFT. For instance, Deng et al. ¹²⁵ examined the diffusion of V_O in ZnO nanowires through calculating the formation energy of V_O and the corresponding migration barriers at different locations. They reported that the formation energy of V_O is always smaller in the surface regions than the bulk regions, indicating that surface V_O is spontaneously energetically favorable than the bulk V_O . They demonstrated that once the V_O is created in the host, the relaxation will occur subsequently to minimize the total energy of the system. And the vacancies have higher freedom to relax at the vicinity of the NW surface. Furthermore, they also showed that the migration of V_O from surface to bulk regions takes more energy than the reverse direction. As a result, they believed that the native surface V_O should be much abundant than the bulk V_O in the ZnO NW.

The location of the defects is critical because it influences the properties of the metal-oxide nano-material. ^{30,126–129} For instance, Kong et al. reported that the existence of bulk defects will jeopardize the photocatalytic efficiency in TiO_2 nanocrystals and their results are shown in Figure 2.6 (b). ¹²⁶ They found that decreasing the relative concentration ratio of bulk defects to surface defects can significantly improve the separation efficiency of photo-generated electrons and holes. As a result, the sample with the lowest bulk-to-surface ratio of defects (TiO_2 -480) produced the highest concentration of CO_2 during the photocatalytic oxidation of benzene. Yan et al. ¹²⁸ plotted the production rate of hydrogen as a function of surface-to-bulk ratio R during the photocatalytic activities in TiO_2 nano-powders (Figure 2.6 (c)). They explained that the photo-generated holes can be trapped by the bulk defects in TiO_2 through electrostatic interactions and these trapped holes are not available in photocatalytic reaction (Figure 2.6 (d)). Therefore, they suggested that it is better to create more surface defects to enhance the

photocatalytic activity. Zhang et al. also reported that bulk defects in TiO_2 showed quite low activity for photocatalytic hydrogen evolution but bulk defects can still enhance the charge separation efficiency and increase the light absorption in TiO_2 .¹²⁹ Though it seems that many studies supported the idea of eliminating bulk defects for improved photocatalytic activity, Hou et al. showed that bulk defects can still play a certain role to assist the photocatalytic activity.¹³⁰ They investigated the changes in solar hydrogen production of TiO_2 as a function of concentration ratio of bulk defects to surface defects and confirmed that the appearance of bulk defects within certain quantities is required to achieve the optimal performance.

Since the presence of vacancies is beneficial for attracting molecules from an ambient gas or liquid, they are also highly required for applications that exploit surface redox reactions. For instance, Huygh et al.¹³¹ revealed that the dissociation of CO_2 molecules is unlikely to occur on the anatase (001) surface if there are not sufficient V_O on the surface. Their schematics showing the different adsorption behavior of CO_2 on the anatase surface without and with V_O are given in Figure 2.6 (e) and (f), respectively. As can be seen from these schematics, the introduction of V_O results in more active sites with a stronger activation of the C-O bonds, leading to possible exothermic dissociation of CO_2 . A similar role of V_O in mesocrystalline CuO is revealed by Liang et al.¹³² Their CuO mesocrystal nanosheets exhibit an overpotential of 304 mV at 10 mA/cm² and deliver the OER current steadily for more than 15 h in the alkaline media. They attributed such excellent performance of CuO mesocrystal nanosheets to the abundance of the surface V_O which increases the surface-active sites and significantly improves electronic structure. In addition to the experimental results, they also calculate the Gibbs free energy for OER under alkaline conditions using CuO as the electrocatalyst and their diagram is shown in Figure 2.6 (g). It can be seen that the energies required in each step are often smaller in the case of CuO with surface V_O . Wang et al. also found a similar trend when CuO is used for glucose detection.¹³³ They reported that the CuO nanoflakes enriched with surface V_O obtained a low onset potential of +0.22 V and a high sensitivity of 4870 $\mu\text{A}\cdot\text{mM}^{-1}\text{cm}^{-2}$. The amperometric response of the CuO nanoflakes at 0.6 V with continuous addition of glucose in 0.1 M sodium hydroxide (NaOH) is displayed in Figure 2.6 (h). It can be seen that

the CuO with the most surface V_O (4h- CuO) shows the best performance. The believed that surface V_O increase the active sites on the surface of CuO meanwhile accelerate the adsorbed hydroxyl ions to promote the formation of Cu^{3+} species, which ultimately enhances the glucose oxidation.

In summary, it can be concluded that surface defects in the metal-oxide nano-materials are beneficial for enhancing the performance in many applications that are related to the reactions on the surface of metal-oxide nano-materials. On contrary, the bulk defects are often considered detrimental since they are traps that act to eliminate the carriers.

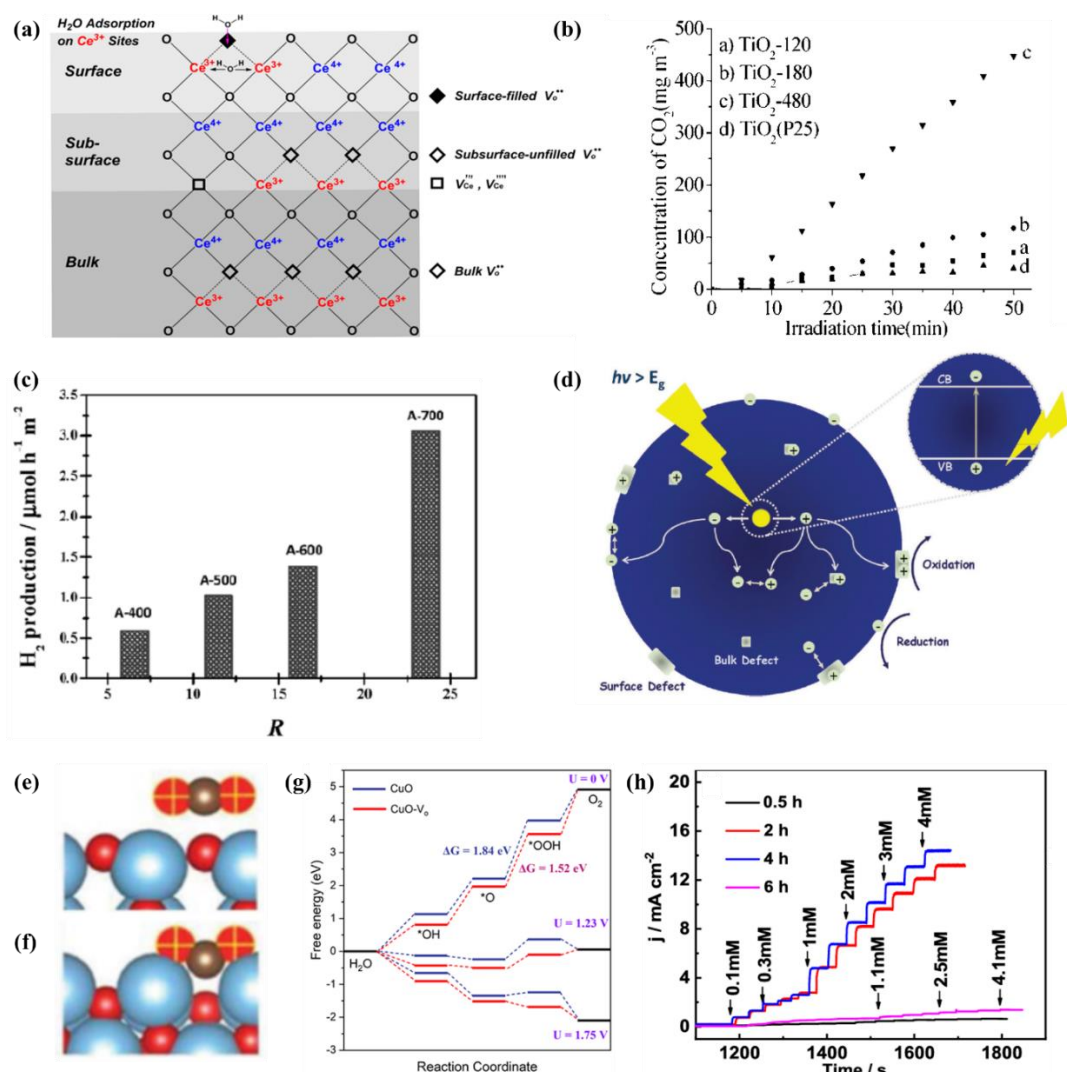


Figure 2.6 (a) A schematic showing the defects residing in different regions. Reprinted with permission.¹²⁴ (b) The specific rate of CO_2 production during benzene photocatalytic oxidation. Reprinted with permission.¹²⁶ (c) Correlation between the photocatalytic activities and the surface-to-bulk ratios of defects (R) of TiO_2 samples. Reprinted with permission.¹²⁸ (d) Recombination pathways of photo-generated electrons and holes in TiO_2 with surface and bulk defects. Reprinted with permission.¹²⁸ The schematics showing the adsorption of CO_2 on the anatase surface (e) without, (f) with V_O . The blue sphere represents titanium atom, the red sphere represents the lattice oxygen in TiO_2 , the red sphere with yellow plus sign is the lattice oxygen in CO_2 and the brown sphere is the carbon atom. Reprinted with permission.¹³¹ (g) The free-energy diagrams of OER at different reaction potentials. Reprinted with permission.¹³² (h) The amperometric response of the CuO nanoflakes at 0.6 V with continuous addition of glucose in 0.1 M NaOH. Reprinted with permission.¹³³

2.2.4 The Applications of Defect-Engineered Metal-Oxide Nano-Materials

The rapid development of semiconductor industry in recent decades is a witness to the dominance of Si-based electronics. However, the continuously growing demand for more sophisticated nanoscale devices may in some cases exceed the capability of Si, it is therefore necessary to explore various materials for diverse applications. Among all these semiconductors, metal-oxide nano-materials played a substantial role due to their abundance, low-cost and versatilities. Figure 2.7 shows a schematic depicting metal-oxide nano-materials, the defects in them as well as the potential applications. ¹³⁴ To meet the requirements of diverse devices, defect engineering has become a prevailing topic and a great motivation for material scientists since the properties of metal-oxide nano-materials are often largely determined by the defects. In this section, the progress on defect engineering and its roles in optimizing the device performance for diverse applications will be mentioned.

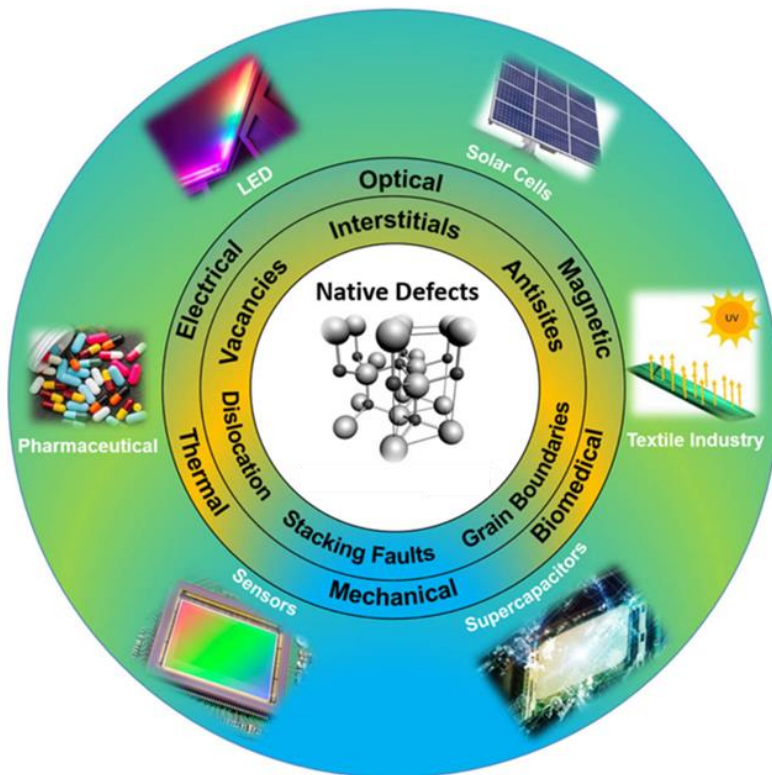


Figure 2.7 A schematic showing the examples of potential applications of defect-engineered metal-oxide nano-materials. Reprinted with permission. ¹³⁴

One of the major driving forces for defect engineering in metal-oxide nano-materials is to improve the properties of these materials for photocatalytic applications.^{113,135–139} Though the detailed mechanism of photocatalysis varies based on different pollutants, the primary mechanism is the interfacial redox reactions assisted by the electrons and holes that are produced during the light exposure.¹⁴⁰ As an example, Figure 2.8 (a) shows the degradation of RhB dye using ZnO as the photocatalyst and Figure 2.8 (b) shows the time evolution of the absorption spectra of the RhB.¹⁴¹ It is evident that the color of RhB fades as the time of exposure extends, indicating its gradual decomposition. The two major factors that determine the efficiency of photocatalysis are the light absorption and the life time of photogenerated electron hole pairs.^{138,142} Metal oxides such as TiO₂ and ZnO are known for their wide bandgaps, which significantly limit their absorption in the visible region.^{140,143} Therefore, one primary task for defect engineering in these materials is to narrow the bandgaps to facilitate the absorption upon visible light illumination. One of such efforts in TiO₂ was demonstrated by Yang et al.¹⁴⁴ They showed that the absorption of TiO₂ in the visible region is significantly enhanced with the existence of V_O (Figure 2.8 (c)). This is due to the fact that the existence of defects will introduce additional energy levels in the band gap, facilitating the absorption of light with lower energies. A schematic showing the intermediate band introduced by defects and the corresponding interband transitions is given in Figure 2.8 (d). With the existence of the intermediate band, visible light can promote electrons from valence and activate the redox reactions that is required for photocatalysis. Furthermore, the enhanced absorption caused by defects are also beneficial for photodetection applications.^{145–149} For instance, Reddy and his coworkers sputtered TiO₂ thin films and annealed them in vacuum.¹⁵⁰ Photodetectors based on these thin films were then fabricated and they were illuminated by an UV LED with a wavelength of 382 nm. The schematic to show the realization of these photodetectors is given in Figure 2.8 (e). The current responses in time domain before and after annealing are shown in Figure 2.8 (e) and (f), respectively. It is apparent that the photocurrent is about 1.4 times larger after the annealing of the film, which can be attributed to the generation of V_O . Another important application of defect-engineered metal-oxide nano-material is for sensing

applications. For instance, Figure 2.8 (g) shows the schematic diagram of $\text{SnO}_2/\text{SnO}_{2-x}$ gas sensing device fabricated by Wang et al.¹⁵¹ They found that additional V_O has significantly improved the sensing capabilities of SnO_2 for CO as the current responses are substantially increased (Figure 2.8 (h)). Overall, defects in metal-oxide nano-materials are usually considered beneficial for many applications but requires careful control.

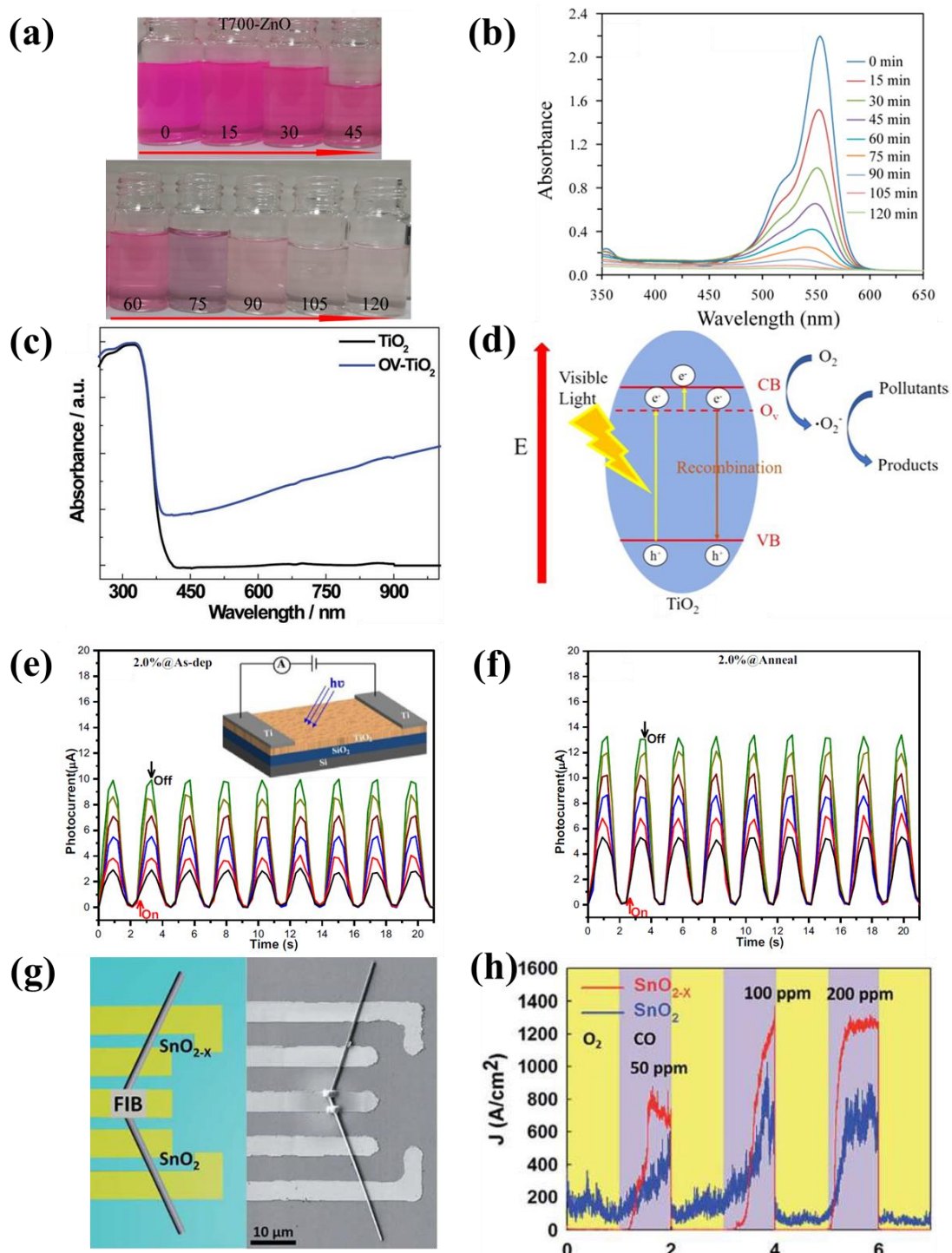


Figure 2.8 (a) The color change degradation of RhB dye using ZnO as the photocatalyst. Reprinted with permission.¹⁴¹ (b) The time evolution of the absorption spectra of the RhB. Reprinted with permission. Reprinted with permission.¹⁴¹ (c) The absorption spectra of TiO₂ NPs. Reprinted with permission.¹⁴⁴ (d) The schematic showing the intermediate band introduced by defects and the corresponding interband transitions. Reprinted with permission.¹⁴⁴ The current responses in time domain of the TiO₂ thin film (e) before, and (f) after thermal

annealing in vacuum. Reprinted with permission.¹⁵⁰ (g) The schematic and the SEM image of the $\text{SnO}_{2-x}/\text{SnO}_2$ NW device. Reprinted with permission.¹⁵¹ (h) Detection performance of O_2 and CO at 200 °C. Reprinted with permission.¹⁵¹

2.3 Techniques for Engineering Defects in Metal-Oxide Nano-Materials

Most of the early studies regarding defect engineering originated from its applications in silicon-based microelectronics as discussed in section 2.1. Though compound semiconductor materials like metal oxides are different from Si, the defect-engineering techniques may still apply. In general, there are two major strategies to engineer the defects in the materials, either during the synthesis process or through post-growth treatments. In this section, the current techniques for defect engineering in metal-oxide nano-materials will be reviewed and their characteristics are compared.

2.3.1 Chemical Solution Methods

Since defective metal-oxide nano-materials have proven superior properties,^{112,152–154} one major strategy for defect engineering in metal-oxide nano-materials is achieved through the facile preparation of these materials.^{112,118,155–157} One of such results was reported by Khokhra et al.,¹¹⁸ in which study they exploited simple solution method to prepare the ZnO nanostructures. They showed that an abrupt addition of Zinc chloride (ZnCl_2) precursor in NaOH results in the formation of ZnO NPs and these NPs can be transformed into nanosheets or nanoflowers by altering the synthesis parameters such as the molar ratio of OH^- to Zn^{2+} , the reaction time and the solvent. Figure 2.9 (a) - (c) shows the SEM pictures revealing the morphologies of these ZnO nanostructures prepared by them. The subsequent high resolution XPS investigation in the O1s region (Figure 2.9 (d) - (f)) illustrated that the concentration of V_O varies in these nanostructures, which was attributed to the diverse geometry. Similar results were reported in CuO/Cu₂O hybrid NPs by Wang et al.¹⁵⁸ They fabricated the hybrid cages by

solvothermal method and controlled the shapes by using lauric acid. The SEM images of the structures can be seen in Figure 2.9 (g) – (i) and the corresponding high resolution XPS data in the O1s region are displayed in Figure 2.9 (j) – (l). It is clear to see that the highest concentration of V_O was obtained in the octahedra structure. Overall, the results in these studies indicate that defects in metal-oxide nano-materials can be tailored by modulating the morphologies of these materials and this strategy was broadly adopted by many other researchers.^{22,102,132,159–162}

On the other hand, producing defects by chemical reducing agents became another widely explored method.^{163–167} For instance, Zhang et al. found that abundant V_O can be introduced in CuO nanoflakes after soaked and reduced by NaBH_4 .¹⁶⁸ The increased peak in the O1s region gives the explicit evidence of increasing concentration of V_O . Tan et al. also used NaBH_4 as the reducing agent to react with TiO_2 at high temperatures to obtain defects. The resultant TiO_2 turned black after the reaction, which is often considered as a distinct indication of defects in TiO_2 nano-materials.^{28,112,169–171} In fact, more hydrides such as sodium borohydride (NaBH_4), calcium hydride (CaH_2) and hydrazine (N_2H_4) as well as metals like Magnesium (Mg) and aluminum (Al) were proven to be efficient reducing agent to obtain defects in diverse metal-oxide nano-materials.^{166,167,172–174}

In addition to the two major aforementioned methods, many other methods such as basifying transition metal-oxide nano-materials with alkaline metal-oxide nano-materials were also reported to be feasible for engineering the defects. Overall, engineering the defects in metal-oxide nano-materials during their synthesis is a facile and low-cost way to tailor the properties of these materials. An interesting trend is that the products prepared by these methods are often low-dimensional NPs, the strategies to modulate the defects in thin film form of metal-oxide nano-materials are discussed in the following section.

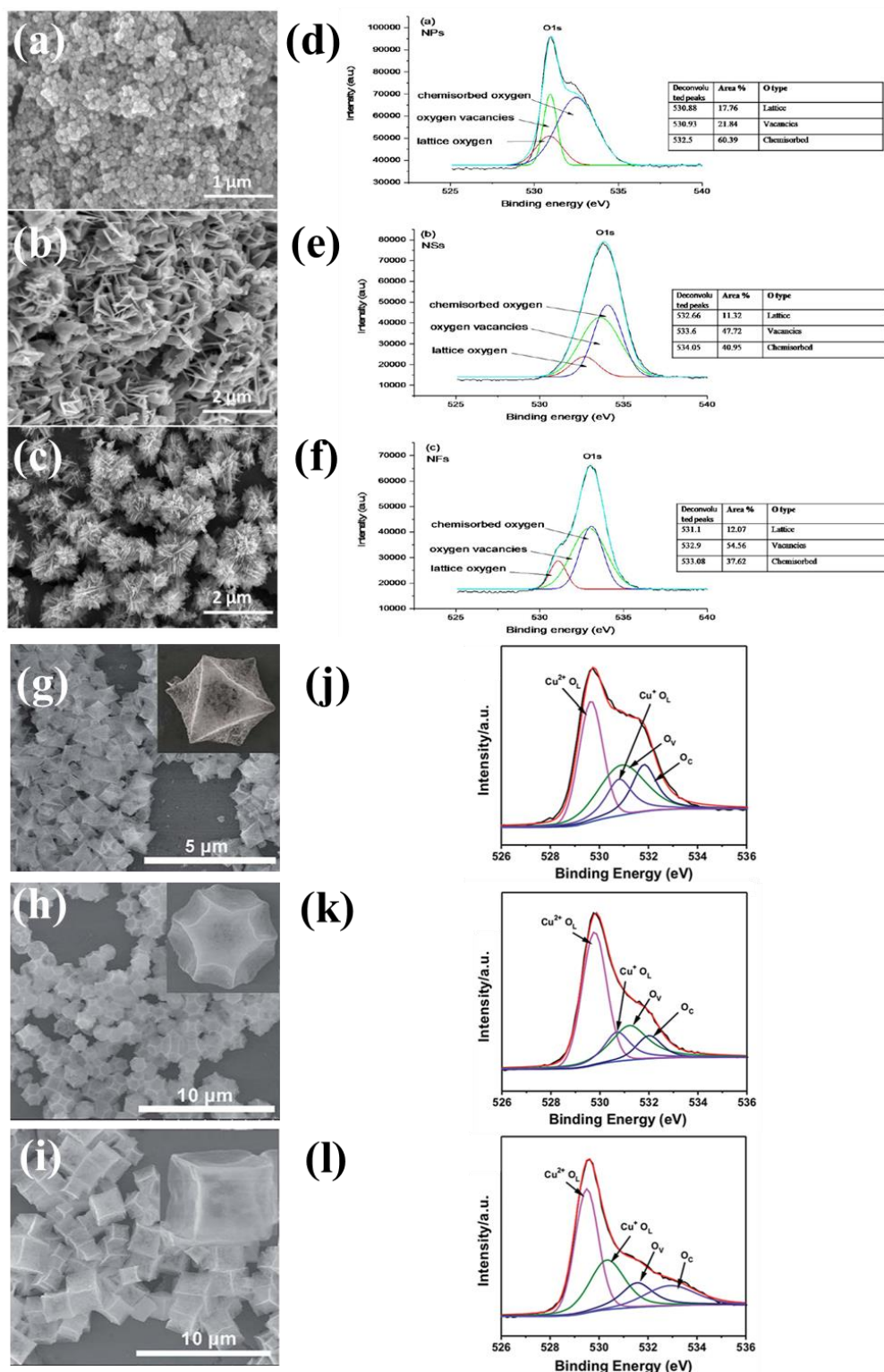


Figure 2.9 The SEM images showing the morphology of (a) ZnO NPs, (b) ZnO nanosheets, (c), ZnO nanoflowers and the corresponding high resolution XPS results of these samples in the O1s region are given in (e) – (f). Reprinted with permission.¹¹⁸ The SEM images showing the morphology of CuO NPs with the shape of (g) octahedra, (h) truncated octahedra (i) cube. The

high resolution XPS results of these samples in the O1s region are given in (j) – (l). Reprinted with permission.¹⁵⁸

2.3.2 Modulation of Growth Conditions

Vapor deposition is one of the most critical and widely-used vacuum deposition technology in modern semiconductor industry to produce high-quality and high-performance thin films.^{175–179} It can be generally divided into two major categories, physical vapor deposition (PVD) which vaporizes solid source species and deliver it to the target coating surface in a vacuum chamber, or chemical vapor deposition (CVD) whose source species is often in a gaseous form.¹⁸⁰ Evaporation, sputtering and pulsed laser deposition (PLD) are typical PVD techniques while plasma-enhanced chemical vapor deposition (PECVD), low pressure chemical vapor deposition (LPCVD) and Atomic layer deposition (ALD) are often recognized as CVD methods.^{181–183} The applications of these techniques in the growth of metal-oxide nanostructures were extensively investigated.^{184–191}

As discussed in section 2.2.1, the chemical potential μ_O in the equation for the formation energy is strongly determined by the ambient environment, which can be controlled readily in vapor deposition techniques as they are often carried out in vacuum chambers. Therefore, vapor deposition processes attracted much attention for defect engineering in metal-oxide nano-materials.^{192–196} One major strategy is to modulate the ambient conditions during the deposition. For instance, Hong et al. demonstrated the effects of oxygen partial pressure on the properties of ZnO films during the sputtering.¹⁹² They showed that ZnO films deposited at high oxygen pressure shows weaker PL emission intensities in the visible regions between 500 and 700 nm as seen in Figure 2.10 (a). Many previous studies reported that the intensity of this broad peak in the visible region is proportional to the concentration of defects centers such as V_O and zinc interstitials.^{197–199} A similar research from Ramakrishnan et al. sputtered CuO thin films under different oxygen partial pressure to engineer the cation vacancy defects, i.e. V_{Cu} , rather than V_O .²⁰⁰ They investigated the elemental composition of CuO thin films sputtered under various oxygen partial pressure by energy dispersive X-ray spectroscopy (EDS) (Figure

2.10 (b) and (c)) and revealed that the copper content reduces as the oxygen partial pressure increases, indicating that copper deficient phases (V_{Cu}) were formed when the ambient environment is filled with more oxygen. Similar controls over the ambient partial pressures during the deposition have also been applied in many other deposition methods for defect engineering.^{201,202} For instance, Heo et al.²⁰¹ deposited ZnO thin films by molecular beam epitaxy (MBE) which employs a RF plasma atomic source to supply oxygen while using a high-purity Zn metal as the source for Zn flux. They fixed the oxygen pressure and studied the properties of ZnO as a function of Zn pressure and discovered that the increase of Zn pressure leads to improved carrier concentration (Figure 2.10 (d)), which attributed to the increase of the defects such as V_O and Zn interstitials. Lin et al. reported that V_O is more likely to be created at low oxygen partial pressure conditions when TiO_2 thin films were deposited by pulsed laser deposition (PLD).²⁰³ In addition to the control over the gas flow, Venkatachalapathy et al. showed that the ratio of Zn/O vapors delivered to the sample surface can also be tuned by changing the deposition temperature.²⁰⁴

Atomic layer deposition (ALD) is another critical process to fabricate metal-oxide nano-materials and engineer their defects as it provides precise control down to sub-nanometer levels. ALD deposits the material layer-by-layer thus can achieve extremely precise thickness through self-limited reaction using cycle numbers.²⁰⁵ It is therefore not surprising that the defects in metal-oxide nano-materials can be modified by changing the cycle numbers during ALD. Chaaya et al. demonstrated the successful tailoring of defects using this method in ZnO thin films on Si substrate by altering the cycles from 100 to 1000. They discovered that higher cycle numbers yield lower O to Zn ratios, which may result from the improved stoichiometry of the ZnO crystalline. The atomic force microscopy (AFM) images showing the surface of ZnO with diverse deposition cycles are shown in Figure 2.10 (e). Since O/Zn ratio is always greater than one, they believed that their ZnO films possess oxygen-rich stoichiometry, indicating that V_{Zn} and oxygen interstitials are dominant species of defects. On the other hand, Guzewicz et al. demonstrated that the concentration of V_O in ZnO can be tuned by changing the temperature during ALD.²⁰⁶ The O/Zn ratio decreases significantly when the growth temperature raises,

indicating that the generation of V_O is more favorable at higher temperatures during ALD process. Although defects in metal-oxide nano-materials are preferable for many applications, the non-stoichiometry can also cause increased surface roughness and unwanted vacancy clusters which deteriorates the quality of the film. Therefore, elimination of defects is sometimes desirable. Want et al. reported that H_2O_2 precursor during ALD process is efficient to suppress the generation of V_O in ZnO thin films and gives rise to a much smoother surface.²⁰⁷ An interesting trend is that the quantity of investigations focusing on engineering V_O in metal-oxide nano-materials during their synthesis is substantially larger than the studies on cation vacancies, which is partially due to the much less characterization methods for cation vacancies.

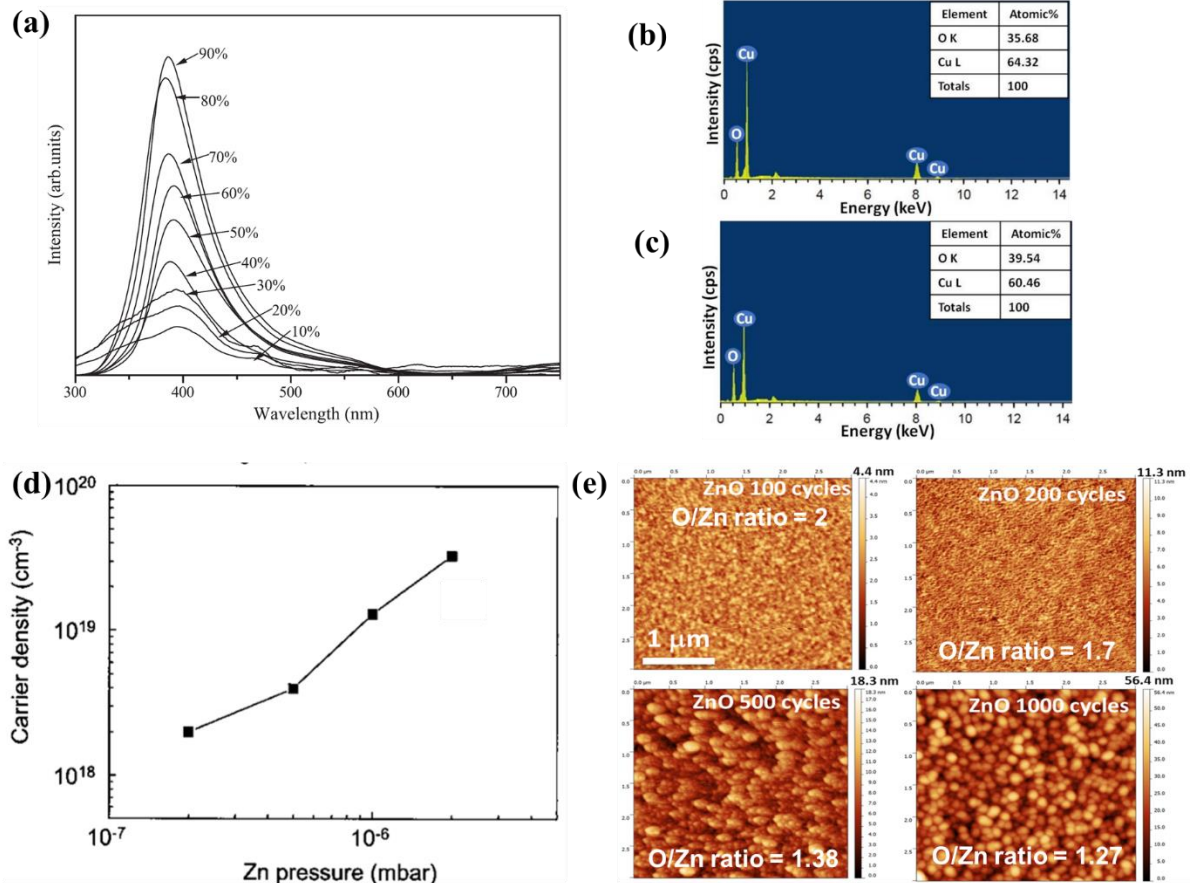


Figure 2.10 (a) The photoluminescence spectra of ZnO films sputtered under different oxygen partial pressure. Reprinted with permission.¹⁹² EDS spectra of $Cu_{2-x}O$ films grown at (b) 2 % and (c) 6 % oxygen partial pressure. Reprinted with permission.²⁰⁰ (d) The carrier concentration of ZnO film grown as a function of Zn pressures at 500°C. Reprinted with

permission.²⁰¹ (e) AFM images of ZnO deposited by ALD with different cycles. Reprinted with permission.²⁰⁸

2.3.3 Annealing

One of the most important strategies to engineer the defects in metal-oxide nano-materials after their synthesis is through heat treatments. The elevated temperature often boosts the kinetic energy of atoms in the material thus the total energy is increased as well. From Eq. (2.1) it can be seen that an increase in the material's total energy results in the decrease of the formation energy of defects, indicating that the generation of defects should be facilitated at high temperatures. Thermal annealing is a conventional heat treatment that is widely used in material processing for centuries.²⁰⁹ One of the earliest attempts to apply this technique in metal-oxide nano-materials was conducted by Radecka et al in early 1990s.²¹⁰ They studied electrical and optical properties of TiO_{2-x} thin films and observed different properties when they were annealed at diverse temperatures. However, due to the limited characterization methods for the defects in TiO_2 , they were not able to show the correlation between the annealing process and the defects characteristics at that time. The explicit correlation between defects and the post-growth annealing temperature was later revealed by Kang et al.⁹⁸ In their study, they investigated the influence of annealing temperature on the properties of ZnO thin films and observed that the green emission (490 ~ 530 nm) intensity was increased as the increase of annealing temperature (Figure 2.11 (a)). They attributed this evolution of green emission to the presence of more V_O . However, the measured resistivities of the films increase as the annealing temperature raise, suggesting a lower concentration of carriers after annealing at high temperatures. They perceive that this is because the V_O produced by thermal annealing are mostly singly-ionized V_O that is not contributing to the carrier density.

A similar trend was also reported in p-type CuO thin films in which holes are the major carriers. Peng et al.²¹¹ studied the physical characteristics of CuO films annealed at various temperatures and they demonstrated the carrier concentration, carrier mobilities and resistivity of the film as a function of annealing temperatures (Figure 2.11 (b)). They observed that the

carrier concentration, which indicates the concentration of V_{Cu} , decreases as the annealing temperature hikes to 700 °C. In addition to the concentration of defects, the type of defects can also be tailored during annealing since thermal annealing process is often achieved in the furnace in which the ambient condition can be readily modulated. One of such efforts made by Tu et al.²¹² showed annealed ZnO NRs in an oven at 350 °C for 1 hour under either nitrogen (N_2) or oxygen (O_2) environment had low defects from the high-resolution XPS data in the O1s region in Figure 2.11 (c), while the peak associated with V_O significantly increased after annealing in N_2 , and the area percentage of this peak rose from 27.2% to 35.8%. Conversely, this peak changed little after annealing in O_2 because the generation of V_O was suppressed in an oxygen-rich environment. Zhang and his coworkers achieved a more sophisticated control of defects in TiO_2 by thermal annealing.¹²⁹ They figured out that the concentration of V_O can be tailored by controlling the annealing temperature. The occurrence of V_O was examined by electron paramagnetic resonance (EPR), which is a sensitive method to detect the paramagnetic species with unpaired electrons. They found that the TiO_2 samples cleaned by different ways (TW and TC in Figure 2.11 (d)) did not exhibit active EPR response before thermal annealing. On the other hand, samples annealed at 500 and 700 °C (TH500, TH700 in Figure 2.10 (d)) exhibited strong EPR signals at $g = 2.002$. They believed that the more intense EPR signal of the TiO_2 annealed at 700 °C was a result of more V_O . Furthermore, they tailored the defects in TiO_2 by changing the gas flow from H_2/N_2 to pure N_2 and determined the distribution with the assistance of Raman spectroscopy. They believed that Raman spectra excited by a laser of 473 nm provide the information in the bulk region of the sample while the information in the surface region can be obtained by switching the exciting laser wavelength to 325 nm, their results are shown in Figure 2.8 (e) and (f). It can be seen that the E_g peak of TiO_2 annealed at 700 °C in N_2 (TN700) exhibit a clear blue shift compared with the unprocessed sample (TC) in Figure 2.11 (e), indicating the presence of V_O in the bulk region. Conversely, the blue shift appeared in Figure 2.11 (f) suggests that surface V_O was produced when TiO_2 was annealed at 700 °C in the H_2/N_2 mixed gas.

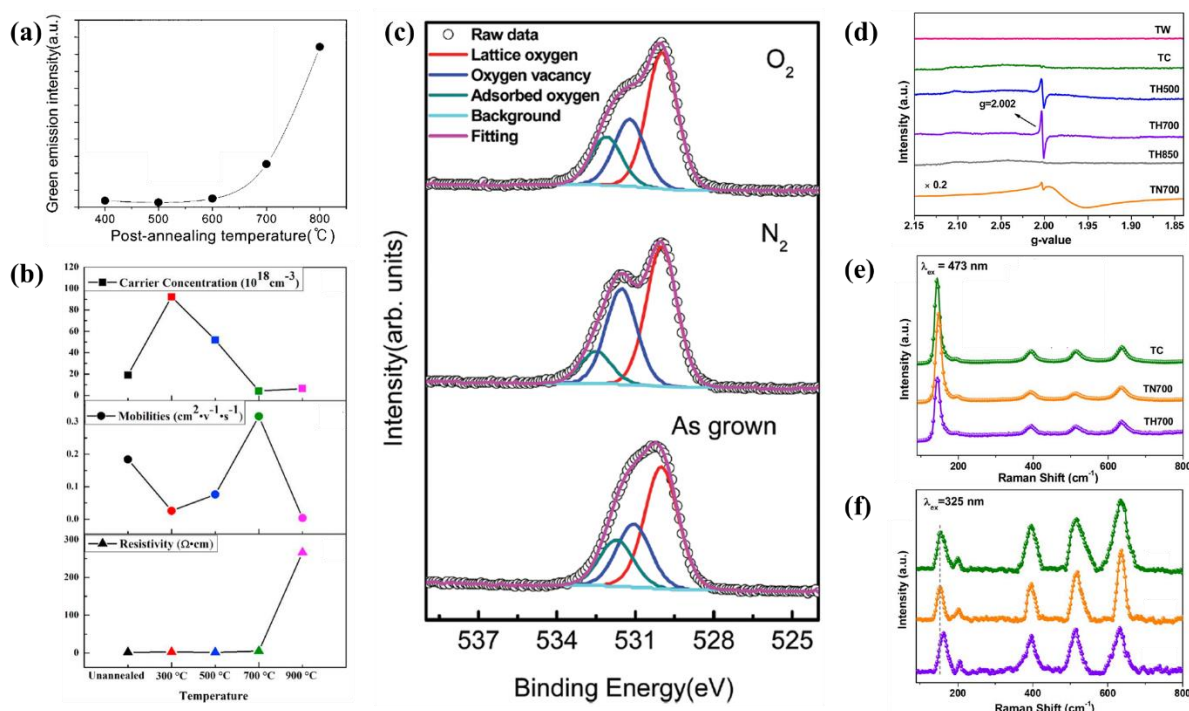


Figure 2.11 (a) The evolution of green emission intensity as a function of annealing temperatures. Reprinted with permission.⁹⁸ (b) The carrier concentration, carrier mobilities and resistivity of the CuO film as a function of annealing temperatures. Reprinted with permission.²¹¹ (c) High-resolution XPS results of ZnO nanorods annealed in diverse atmosphere. Reprinted with permission.²¹² (d) EPR spectra of the TiO_2 samples prepared under different conditions. Reprinted with permission.¹²⁹ The Raman spectra of various TiO_2 samples using an exciting wavelength of (e) 473 nm, and (f) 325 nm. Reprinted with permission.¹²⁹

2.3.4 High Energy Particle Bombardment

Annealing is an efficient and convenient post treatment to engineer the defects, however, it may not be applicable for some substrate materials with low thermal budgets. To avoid this limitation, an alternative method to form the defects in metal-oxide nano-materials is through high energy particle bombardments and these particles can either be ions or electrons. As discussed in 2.1, ion implantation is one of the most widely-used method to achieve doping in modern semiconductor industry. The injected ions do not only displace the lattice atoms and substitute them but also create vacancies and interstitials. For instance, Maldonado et al. simulate the electrical and structural properties of Al-doped ZnO supercells and predicted the

existence of defects along with Al dopants from the theoretical aspect.²¹³ Their prediction was later confirmed by Rottela et al.,²¹⁴ who studied the roles of vacancy defects in aluminum-doped ZnO (AZO) thin films and characterized the vacancies with the assistance of PL. A more comprehensive research on the defects induced during ion implantation was conducted by Das and his coworker.²¹⁵ Their XPS results in the O1s region showed the increase of V_O after Li doping in ZnO explicitly as the peak associated with V_O hiked (Figure 2.12 (a) and (b)). On the other hand, they also observed the formation of V_{Zn} as indicated by the PL data. Therefore, they simulated the formation of these defects and calculated the concentration of them. The plot showing the number of vacancies as a function the fluence of incident ions is given in Figure 2.12 (c). It can be seen that the numbers of both vacancies are proportional to the fluence of incident Li ions. Furthermore, the number of V_{Zn} is always higher than V_O , indicating that the type of vacancies can be determined by the dopant ions. This speculation is supported by many other investigations.^{216–219} For instance, Chen demonstrated that V_O dominates the phosphorus-implanted ZnO.²²⁰ In addition to the type and concentration, the distribution of defects may be controlled during ion implantation as well. Lv et al. showed that increasing H^+ implantation dose gives rise to defects formed at deeper regions.²²¹ It is worth noting that ion implantation conducted at high energies may produce very stable defects. For instance, the defects created during the implantation of nitrogen ions at 380 keV can only be removed by a thermal annealing performed at the temperature as high as 1100 °C.²²²

In addition to ions, the high energy particles can be replaced by electrons to bombard the surface of metal-oxide nano-materials for the generation of defects. For instance, Huang et al. applied an electron beam of 0.1 MeV to TiO_2 NRs and observed the formation of V_O .²²³ Their XPS results in the O1s region showed a clear correlation between the irradiation dose and the concentration of V_O . As can be seen in Figure 2.12 (d), the area percentage of the peak associated with V_O (O_s) expanded when the irradiation dose increased from 0 to 60 kJ/kg (EBI- TiO_2 -60). The electron beam irradiation was reported to obtain defects in many other metal-oxide nano-materials as well.^{224–227} However, an interesting trend in ZnO is that V_O can only be obtained at comparatively high irradiation dose. For instance, Siraj reported the formation

of both V_O and V_{Zn} was possible when the electrons possess energies as high as 15 MeV.²²⁸ Conversely, Yun et al.²²⁴ irradiated ZnO thin films with an energy of 1 MeV and they found that the elemental content of Zn reduced as the dose increased, indicating the formation of more V_{Zn} (Figure 2.12 (e)). Other studies employing electron beams with similar energies also observed the formation of V_{Zn} is dominant.^{229,230} Such selectivity of the formation of vacancies may be due to the fact that it requires less energy to displace Zn atoms than that of O.²³¹

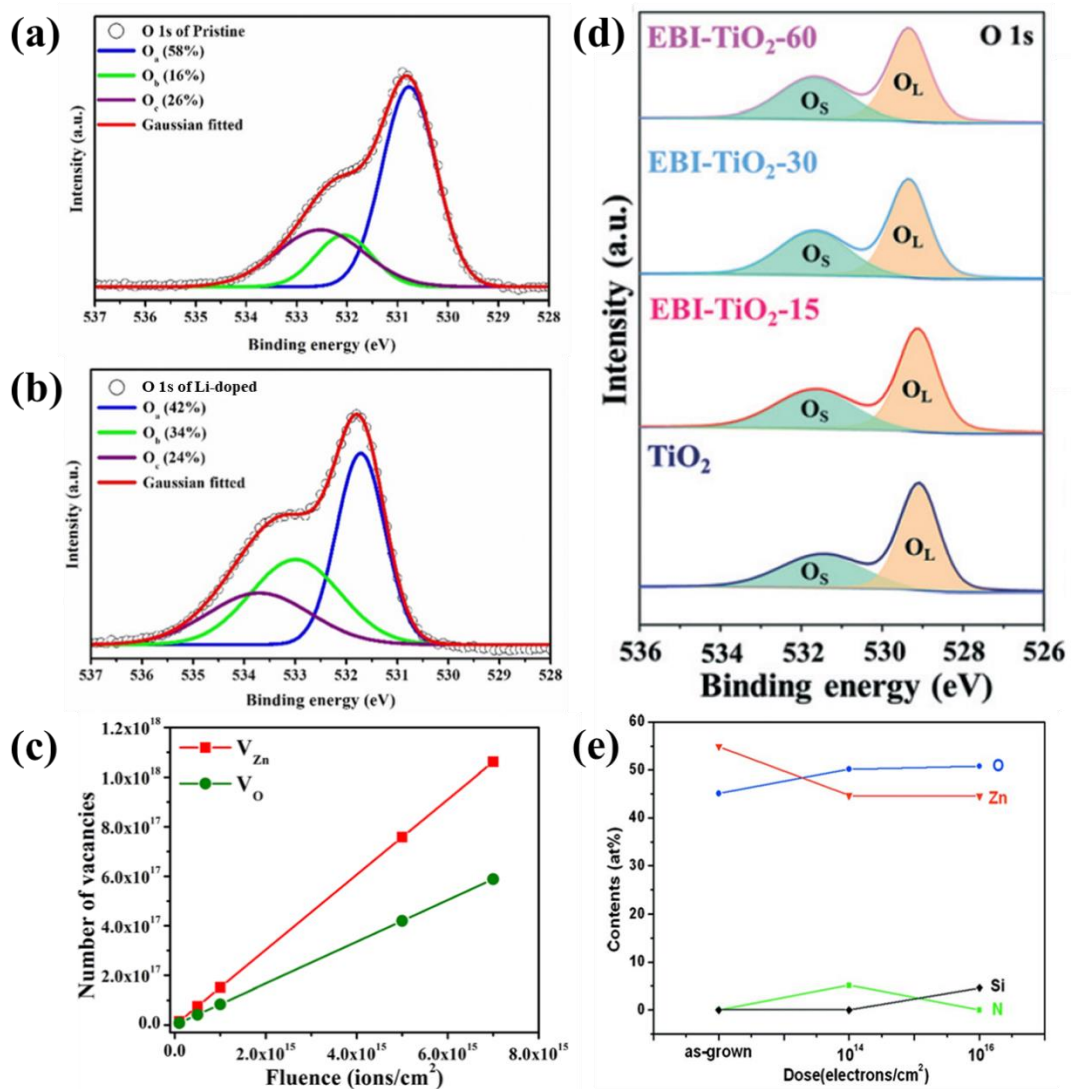


Figure 2.12 High resolution XPS results in the O1s region of (a) unprocessed and (b) Li-doped ZnO. Reprinted with permission.²¹⁵ (c) The number of vacancies as a function of the fluence of incident ions. Reprinted with permission.²¹⁵ (d) High resolution XPS results in the O1s

region of TiO₂ irradiated by electron beam at diverse doses. Reprinted with permission. ²²³ (e) The elemental contents in ZnO as a function of the electron beam dose. Reprinted with permission. ²²⁴

2.3.5 Laser Irradiation

Laser irradiation has emerged as a new compelling post-treatment technique for defect engineering in recent years, it was considered no more than a heat source because many early studies use excimer lasers whose wavelength is close to the absorption peak of many metal oxides. ^{232–234} Zhao and his coworkers were one of the first groups that noticed the introduction of defects in ZnO after laser irradiation. ²³⁵ They observed that the resistivity of undoped ZnO film was reduced after laser irradiation and this process can be reversed by thermal annealing. Hence, they predicted that oxygen vacancies may appear after laser processing. Nie et al. first confirmed the formation of oxygen vacancies after laser irradiation in ZnO films by attributing the visible emission peaks founded in the photoluminescence spectroscopy (PL) to the existence of various oxygen vacancies in ZnO. ¹⁰¹ Many efforts were made in the last decade to advance the understanding of how laser irradiation tailor the defects in different metal-oxide nano-materials. However, it is still a huge blank in terms of defect engineering in metal-oxide nano-materials through laser irradiation.

One of the major strategies tailoring the defects is through exposing the metal-oxide nano-materials to pulsed laser irradiation in liquid ^{28,29}. For example, Lau et al. ³⁰ demonstrated that pulsed laser irradiation upon ZnO and TiO₂ nanoparticles triggers PLML and PLFL. They demonstrated that vacancies in the bulk regions can be generated after irradiation by a nanosecond (ns) laser with a wavelength of 355 nm. And switching the laser source to a picosecond (ps) laser with a wavelength of 532 nm encouraged the diffusion of vacancies from the bulk region to surface regions. A schematic showing this mechanism is given in Figure 2.13 (a). A similar study was conducted by Kanakillam et al. in which they irradiated ZnO NPs in liquid using a ns pulsed laser. ²⁹ They showed that the ZnO NP powders turned black after laser irradiation, which is often considered an indication of abundant defects in ZnO. XPS mapping

on the surface of the thin films made by these ZnO NPs exhibited that the unprocessed surface of the ZnO NP thin film showed an almost universal blue color (Figure 2.13 (b)) but the excess oxygen appeared after laser irradiation (red areas in Figure 2.13 (c)), which was attributed to the introduction of V_O .

Another method is irradiating metal-oxide nano-materials in air. For instance, Lin et al. irradiated TiO₂ NWs with femtosecond (fs) laser and observed defects in the high resolution TEM image (indicated by yellow arrows in Figure 2.13 (d)).²³⁶ Xing et al. irradiated ZnO NWs with fs laser and observed the increase of oxygen vacancies after laser processing, which is supported by their XPS data in the O1s region (Figure 2.13 (e) and (f)).²⁶

Overall, the information of laser irradiation on defect engineering in metal-oxide nano-materials is still limited. For instance, gas immersion laser doping (GILD) in these materials was seldom mentioned and the processes to control the type of defects were not thoroughly investigated.

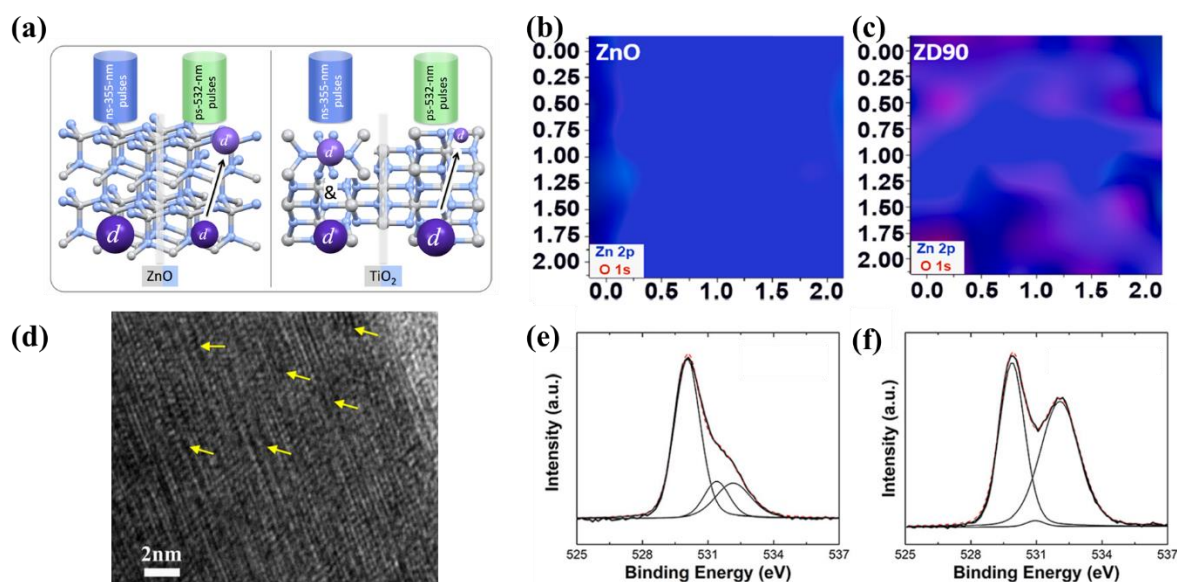


Figure 2.13 (a) A schematic showing the defects generated by irradiating ZnO and TiO₂ with a ns laser with a wavelength of 355 nm and a ps laser with a wavelength of 532 nm, respectively. Reprinted with permission.³⁰ XPS mapping of ZnO (b) before, and (c) after laser irradiation in liquid. Reprinted with permission.²⁹ (d) High resolution TEM image of the laser-irradiated TiO₂ NW, the defects are indicated by the yellow arrows. Reprinted with permission.²³⁶ High

resolution XPS data in the O1s region of ZnO NWs (e) unprocessed, and (f) irradiated at 82.1 mJ/cm². Reprinted with permission. ²⁶

Chapter 3 Tailoring the Concentration of Defects in CuO Nanowires and ZnO Thin Films

3.1 Introduction

The introduction of defects is often determined by the concentration of defects as it can be readily characterized. Therefore, tailoring the concentration of defects was first demonstrated to validate this laser processing technique before moving on to more comprehensive control over defects. Previous studies have demonstrated successful introduction of defects through laser irradiation in n-type metal oxides such as TiO₂ and ZnO, however, it is seldom discussed in p-type metal oxides. This work seeks to fill this void by tuning the concentration of defects in the versatile p-type CuO through laser irradiation. Nevertheless, the concentration of defects is also tailored in ZnO to further validate this laser processing technique.

In this chapter, the control over the concentration of defects in CuO NWs through ns laser pulses is first explored. The introduction of defects is evidenced by the results from UV-Vis spectroscopy, XPS and Raman spectroscopy. The impacts of the increased defect concentration on the electrical and optoelectrical properties of CuO NWs is examined by suspending these nanowires on interdigital Au electrodes to form metal-semiconductor-metal (MSM) bridged structures for the measurements. Photodetectors and optical memristors based on these MSM bridged structures with laser-engineered CuO NWs are demonstrated to illustrate the efficacy of this laser processing technique. On the other hand, the concentration of defects in ZnO thin films is also engineered through ns laser irradiation. The concentration of oxygen vacancies (V_O) in these films is characterized by the UV-Vis spectroscopy and XPS. Laser-engineered ZnO thin films are sandwiched by indium tin oxide (ITO) electrodes to investigate the electrical properties and photo-conductivities affected by the defects.

3.2 Experimental Section

3.2.1 CuO NWs Preparation and MSM Structure Fabrication

CuO nanowires were obtained by heating a clean copper foil at 500 °C for 4 h in air. The NWs were dispersed in ethanol for storage. Their average diameter is around 100 nm with lengths ranging from 2 to 5 μm . Interdigital gold (Au) electrodes with a 2 μm finger spacing were fabricated on a SiO₂/Si substrate using standard photolithography and lift-off techniques. Electrodes were first rinsed with high purity acetone and isopropanol then dried in flowing nitrogen gas before the deposition of CuO NWs. The solution containing CuO NWs was drop-cast on the gold electrodes and left to dry in air. The schematic showing this process is given in Figure 3.1.

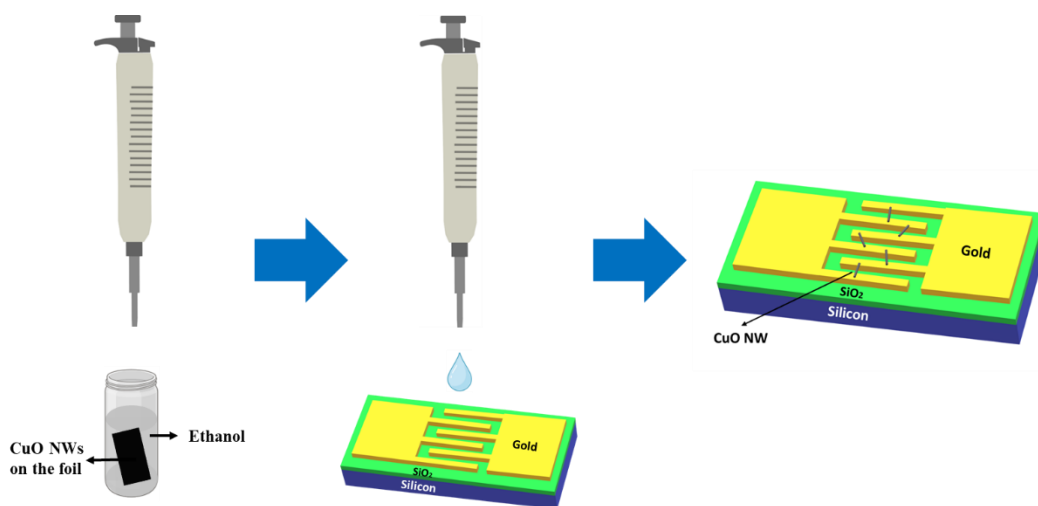


Figure 3.1 A schematic showing the deposition of CuO NWs on the Au interdigital electrodes.

3.2.2 ZnO Thin Films Deposition and Sandwich Structure Fabrication

For I-V characteristics measurement, Ag thin film was first deposited by RF sputtering (AJA ORION) onto a clean glass substrate held at room temperature. A mask was applied during the sputtering so that Ag lines with a width of 1mm and a thickness of 80nm were obtained. The RF power was 200W and the working pressure of argon was 5 mTorr at a flow rate of 12 sccm. ZnO thin films having a thickness of 50 nm were then deposited on top of this Ag layer by DC sputtering using the same system. During the deposition of ZnO, the power

was 200 W while the working pressure was maintained at 5 mTorr. The argon gas flow rate was 12 sccm while the oxygen gas flow rate was 0.5 sccm. The Ag thin film acting as a top electrode was deposited by RF sputtering using the same conditions as used for the lower electrode. The mask was applied and rotated by 90 degrees to form Ag lines perpendicular to the lines fabricated in the first step. The final configuration consisted of a three-layer-stacked crossbar structure with an overlapping area of 1 mm². Figure 3.2 (a) shows the schematic of this crossbar structure.

For optoelectrical applications, the photodetector sandwich must be transparent to optical radiation so the device configuration selected for photo-conductivity measurements utilizes transparent ITO to replace Ag as the electrode material. The fabrication process and the dimension of the structure remained the same. The RF power for the sputtering of ITO was 200W and the working pressure of argon was 5 mTorr at a flow rate of 10 sccm. A picture of the stacked structure from the top is displayed in Figure 3.2 (b).

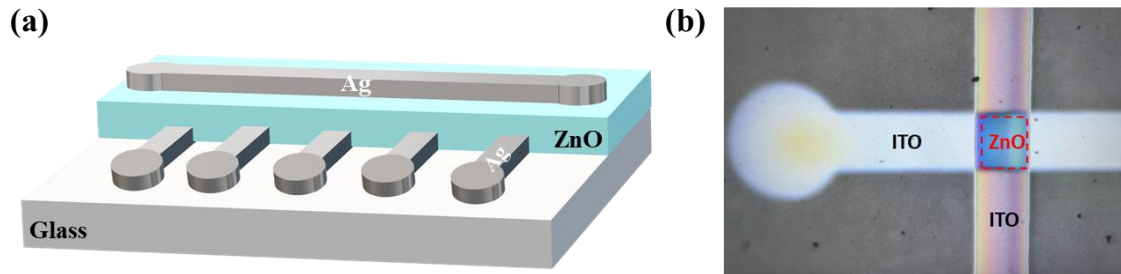


Figure 3.2 (a) The schematic of the Ag/ZnO/Ag vertically stacked structure. (b) A top-view picture of the ITO/ZnO/ITO stacked structure.

3.2.3 Laser Irradiation Set-up

CuO NWs were irradiated with 4 nanosecond (ns) pulses from a 1064nm neodymium-doped yttrium aluminum garnet (Nd: YAG) ns laser operating at 30 Hz. The laser fluences used for processing ranged from 180mJ/cm² to 300mJ/cm² and the exposure time is 3.5 min. A half-wave plate/neutral density (ND) filter combination was used for control over polarization and laser power. A convex lens was also used to produce a beam spot with a 1.25 mm diameter on the sample surface. The configuration of the laser is illustrated in Figure 3.3.

ZnO thin films were irradiated with the same apparatus and the same configuration. The laser fluences used for processing ranged from 240 mJ/cm² to 700 mJ/cm² while the exposure time remains 3.5 min.

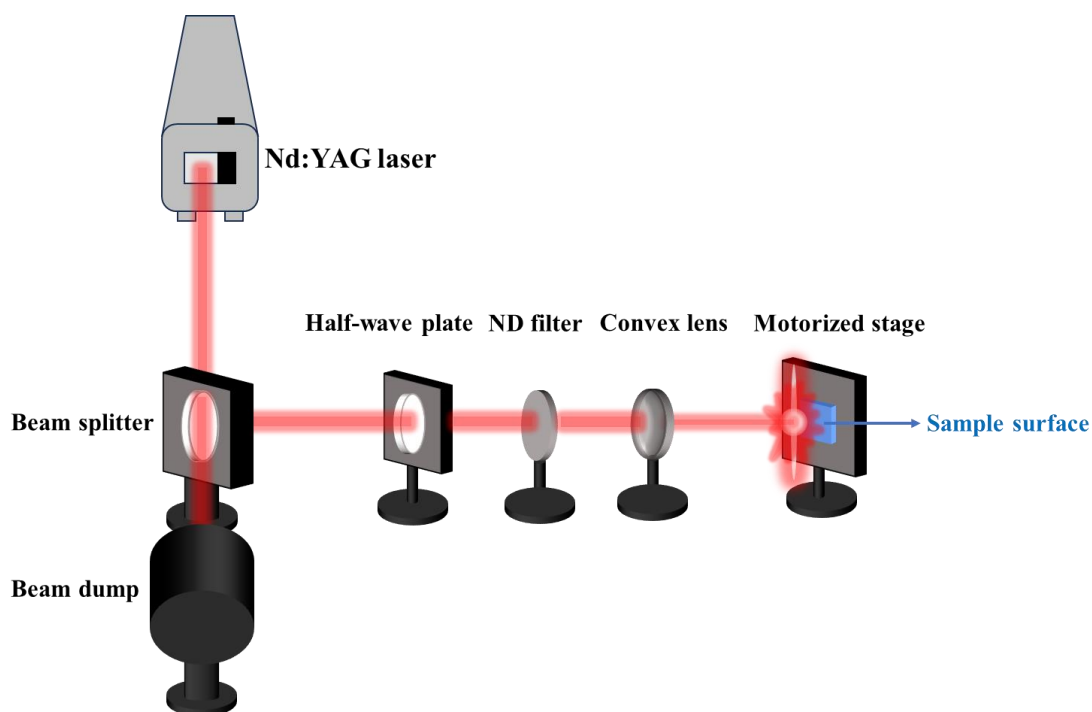


Figure 3.3 A schematic illustration of the laser beam path.

3.2.4 I-V Measurement and Photodetection

The electrical properties of Au/CuO NW/Au bridged structures were measured at room temperature using SMUs connected to a parameter analyzer (Keithley 4200A-SCS). A light-emitting-diode (LED) emitting at 460 nm was connected to a programmable DC power supply (Keithley Series 2200) to generate constant or intermittent blue light illumination with an intensity of $4.5 \times 10^{-2} \text{ W/cm}^2$ at the surface of the sample. The LED and the samples together with the measuring units were contained in an enclosure during the measurement to minimize the disruptions from the environment (Figure 3.4 (a)). The electrical characteristics and optoelectrical properties of the prepared samples were measured before laser irradiation to determine the baseline conditions.

The electrical properties of ZnO thin films were measured at room temperature using the same apparatus with the same experimental configuration (Figure 3.4 (b)). LEDs providing the illumination at UV (390 nm), blue (460 nm), green (570 nm) and red (620 nm) wavelengths were connected to a programmable DC power supply (Keithley Series 2200) to generate intermittent light illumination with an intensity of $2.8 \times 10^{-3} \text{ W/cm}^2$ at the surface of the sample.

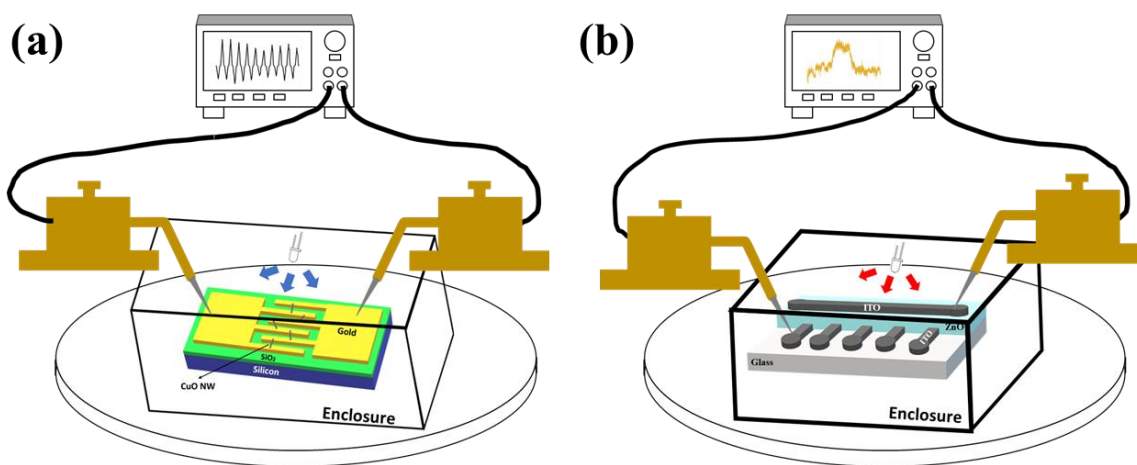


Figure 3.4 The schematic illustrations showing the experimental set-up for (a) Au/CuO NWs/Au bridged structures and (b) ITO/ZnO/ITO vertically-stacked crossbar structures.

3.2.5 Characterization Methods

Samples containing suspended CuO NWs were identified using both optical microscopy (Olympus BX-51) and scanning electron microscopy (SEM, Zeiss FESEM 1530) subsequently. The electrical characteristics of samples with suspended CuO NWs were measured at room temperature using source measure units (SMUs) that connected to a parameter analyzer (Keithley 4200A-SCS). The electrical and optoelectrical properties were measured with the same apparatus before and after laser irradiation. The elemental composition, chemical bonding and valence state of the atoms in CuO NWs before and after laser irradiation were determined by Raman spectroscopy (Renishaw micro-Raman spectrometer) with an excitation wavelength of 633nm and X-ray photoelectron spectroscopy (XPS, Thermo VG Microlab 350). The

presence of defects was inferred from ultraviolet-visible spectroscopy (UV-Vis, Shimadzu UV-2501).

The presence of defects in ZnO thin films was inferred from UV-Vis spectroscopy (Shimadzu UV-2501). The elemental composition, chemical bonding and valence state of the atoms in ZnO thin films before and after laser irradiation at different fluences were determined by XPS (Thermo VG Microlab 350).

3.3 Laser-Induced Defects in CuO NWs

3.3.1 Identification of Defects

The spectroscopic properties of the defects were obtained via UV-Vis absorbance spectroscopy. Figure 3.5 (a) shows the normalized absorption spectrum before and after ns laser irradiation with 9000 pulses at a fluence of 200 mJ/cm². It can be seen that the absorption edge has been extended from ~650nm to ~780nm after laser irradiation. This can be attributed to defect centers in the CuO NWs produced by laser irradiation. The bandgap energy can be extracted from a Tauc plot as shown in Figure 3.5 (b) where the direct bandgap energy, E_g , is obtained from an extrapolation of the linear plot of $(\alpha h\nu)^2$ vs. $h\nu$, where α (cm⁻¹) is the optical absorption coefficient and $h\nu$ (eV) is photon energy. This extrapolation shows that the bandgap energy changes from ~2.12 eV in unirradiated CuO NWs to ~2.02 eV after laser irradiation. The existence of the intermediate band facilitates the absorption of photons with lower energies, which causes the redshift in the absorption spectrum. A reduction in bandgap energy indicates that the presence of laser-induced defects is accompanied by the introduction of additional energy levels in the band gap. A schematic showing the intermediate band introduced by defects and the corresponding interband transitions is given in Figure 3.5 (c).

A variety of defect centers, including oxygen and copper vacancies as well as oxygen interstitials, are known to be present in intrinsic CuO NWs. The predominant defect is determined by the concentration of oxygen in the environment. Previous studies have shown that the formation energy of oxygen vacancies (~3 eV) is always much greater than that of copper vacancies (~1.96 eV) except in an oxygen-poor environment during equilibrium heating.

Since laser irradiation is carried out in an ambient air environment it is then possible that the dominant defects induced by ns laser irradiation are copper vacancies, although the strongly non-equilibrium excitation and heating/cooling conditions present during laser irradiation may result in the creation of oxygen vacancies.

The calculated change in the band gap (0.1 eV) after ns laser irradiation is also close to that reported (0.08 eV above the valance band) for the energy level of copper vacancies responsible for producing free holes. The valence states of Cu in pristine and ns laser irradiated CuO NWs have been investigated by XPS. High resolution XPS scans in the Cu 2p region before and after ns laser irradiation at a fluence of 200 mJ/cm² are shown in Figures 3.5 (d) and (e), respectively. In Figure 3.5 (d), the characteristic shake-up satellites near 943eV are a clear indication that Cu²⁺ is dominant in as-prepared CuO NWs. The double Cu²⁺ satellite peak disappears, and the proportion of the shake-up peak compared to the main Cu 2p_{3/2} peak at 934eV is significantly reduced after laser irradiation. This suggests that the concentration of Cu²⁺ in the CuO NWs may have been reduced after irradiation. This effect could arise if irradiation introduces a copper-deficient phase although the laser-induced reduction of CuO to Cu₂O would also reduce the concentration of Cu²⁺.

To further investigate the compositional changes in CuO NWs produced by ns laser irradiation, Raman spectra of CuO NWs before and after laser irradiation (Figure 3.6) are obtained. The peak at 298 cm⁻¹, corresponding to the A_g vibrational mode of CuO, is clearly present in both spectra but becomes increasingly asymmetric following ns laser irradiation. This asymmetry indicates that defect centers have been formed in the irradiation process. The appearance of the peaks at 149, 221 and 629 cm⁻¹ can be attributed to the LO infrared mode $\Gamma_{15}^{-(1)}$, the second order overtone and one TO mode $\Gamma_{15}^{-(2)}$ of Cu₂O.

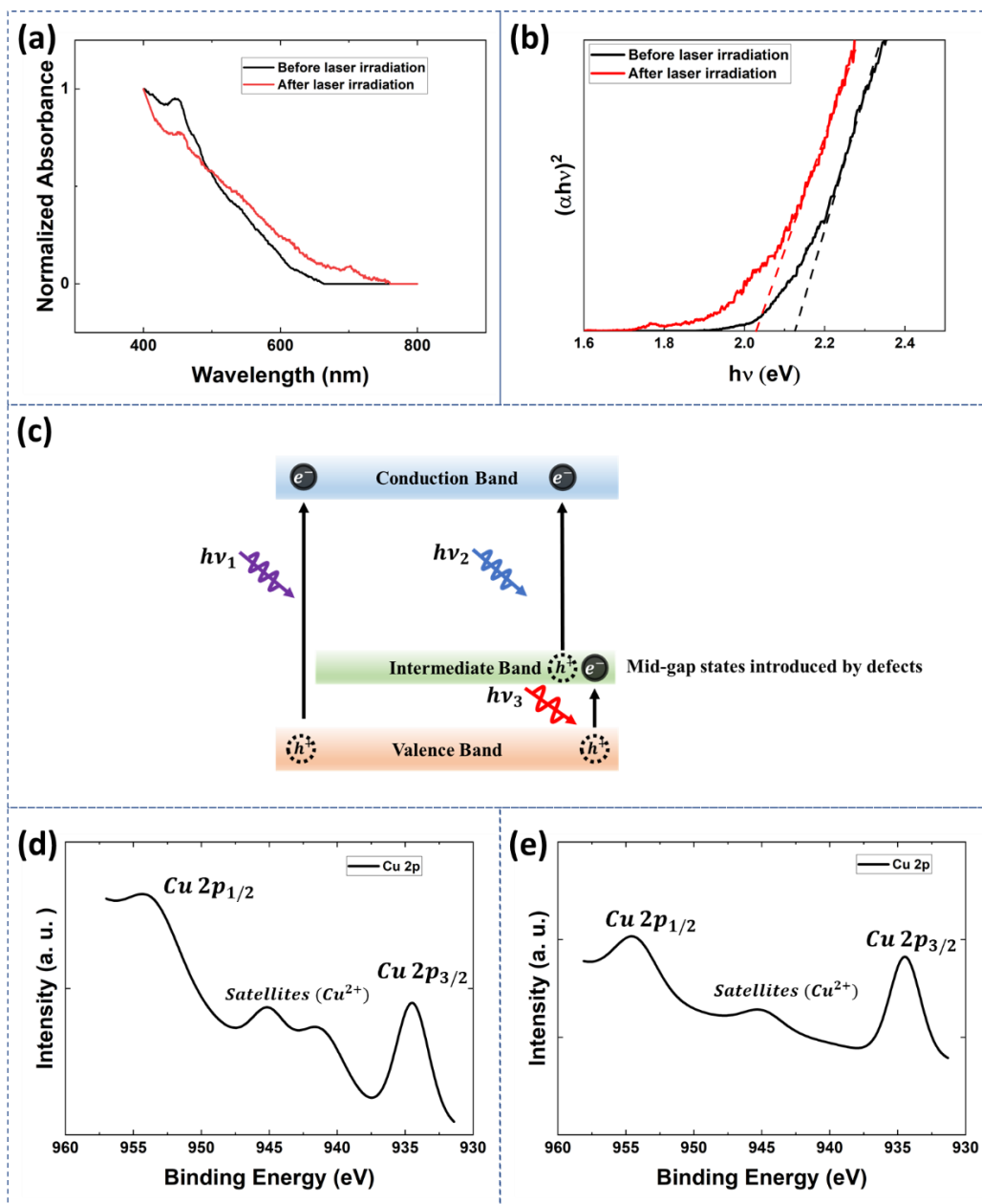


Figure 3.5 (a) Normalized absorption spectra for CuO NWs before (black line) and after (red line) ns laser irradiation (200 mJ/cm², 9000 pulses). The absorption edge shows a clear redshift after laser irradiation. (b) Tauc-plot of CuO NWs before (black line) and after (red line) ns laser irradiation. The intersections are at 2.02 eV (red) and 2.12 eV (black), respectively. (c) A schematic showing the intermediate band formed in the band gap due to laser-induced defects. Cu 2p XPS high-resolution spectra of CuO NWs taken (d) before and (e) after ns laser irradiation.

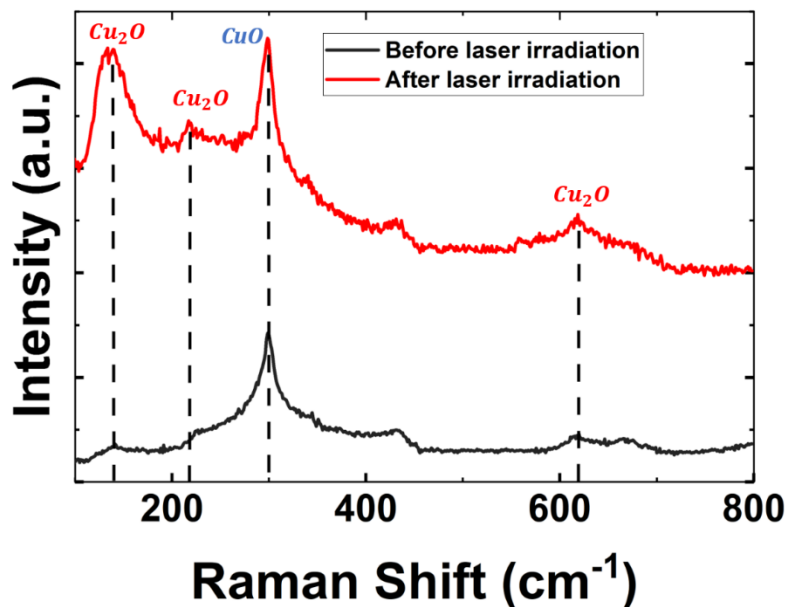


Figure 3.6 Raman spectrum of CuO NWs before (black) and after (red) ns laser irradiation. The strongest peak at 298 cm^{-1} corresponds to the Ag vibration of CuO while the weak peak at 150 , 220 and cm^{-1} arises from Cu_2O .

3.3.2 Defect-Dependent Conductivity

To study the influence of ns laser irradiation electrical conduction in the Au/CuO/Au bridged structure, I - V characteristics were measured using a voltage sweep from 15 V to -15 V under dark condition. Figure 3.7 (a) shows the I - V curve for the bridged structure containing a single nanowire before and after ns laser irradiation (200 mJ/cm^2 , 9000 pulses). The inset is an expanded view of the low bias response. The shape of the I - V curve indicates a Schottky type Au/CuO contacts formed. It is apparent that the overall conductivity was increased in both bias directions after ns laser irradiation. This is due in part to improvements in bonding at the Au/CuO interface, but changes in carrier concentration arising from defects generated by laser processing will also increase the conductivity. Before laser processing, the CuO NW was bonded to the Au electrodes by van der Waals forces giving a weak mechanical contact and the possibility of gaps between the electrodes and the nanowire. In this case, depletion regions at the contacting surfaces can be formed due to oxygen adsorbed on the nanowire surface. A potential barrier associated with a high concentration of adsorbed oxygen will therefore limit

the current density passing through the contacts. ns laser irradiation facilitates chemical bonding between Au and CuO and the formation of these metallurgical or covalent bonds will eliminate the adsorbed oxygen and result in a continuous structure. The potential barrier is then reduced and charge transfer across the junction area is enhanced. Previous study has shown that such variations in the height of the potential barrier can be inferred from the current amplitude in the low bias regime. The inset in Figure 3.7 (a) shows that the current at low bias increases after ns laser irradiation, indicating that the potential barrier height has been lowered and the carrier concentration in CuO has increased after laser processing. Similar improvement in charge transport was also reported due to an increasing concentration of defects in CuO NWs. To fabricate functional devices with reproducible performance and enhanced reliability, multiple CuO nanowires can be connected in parallel across the interdigital Au electrodes. Figure 3.7 (b) shows I - V curves for a bridged structure containing three nanowires before and after ns laser irradiation. It can be seen that the current amplitude is significantly enhanced compared to that obtained in the single nanowire system. The overall improvement in response on laser processing is similar to that seen in the single nanowire case. This suggests that the Au/CuO NW/Au configuration is scalable.

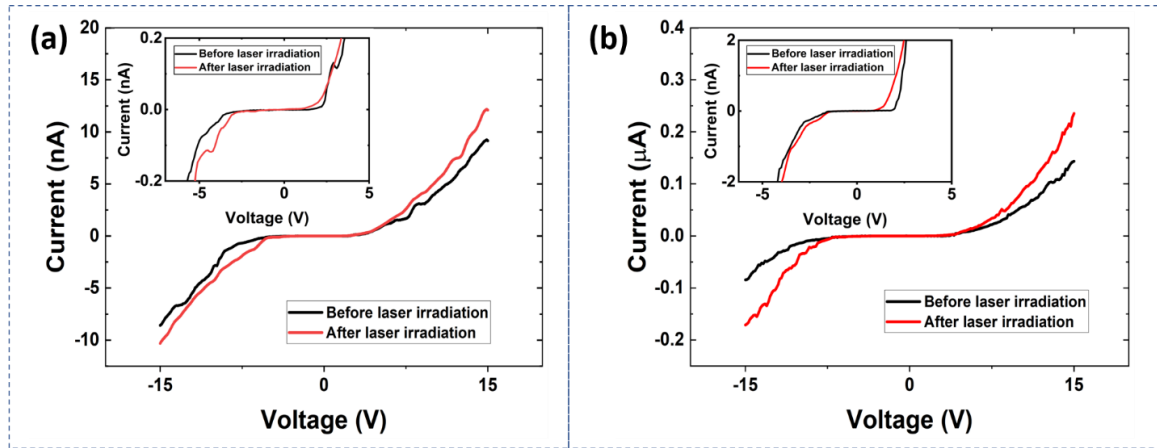


Figure 3.7 I - V curves for the Au/CuO NW/Au bridged structure (a) consisting of a single nanowire and (b) three nanowires before (black) and after (red) ns laser irradiation with 9000 pulses at a fluence of 200 mJ/cm^2 . The voltage sweep is $15 \text{ V} \rightarrow -15 \text{ V}$. The inset shows an expanded scale at low bias.

3.3.3 Defect-Enhanced Photodetection

Since the bandgap of CuO corresponds to the energy range of visible light, there have been many studies on the use of this material as a photodetector. In recent years, attention has focused on the use of CuO NWs in such applications. To investigate the role that ns laser irradiation might play in improving the electrooptical properties of the bridged Au/CuO NW/Au structure, the photo-current was measured before and after laser processing (Figure 3.8) using a blue LED (460nm) as a light source. Figure 3.8 (a) shows that both the dark current and the photo-current increase after ns laser irradiation. For instance, the dark current has been tripled and the photo-current has been doubled at a forward bias of 15V after laser irradiation. The increase in dark current follows the data shown in Figure 3.8 (a), while the increase in photo-current can be attributed to the lowered potential barrier at the Au/CuO interfaces as well as to the introduction of energy levels due to defects close to the junction area. It has been reported that a lowered barrier height at the metal-semiconductor interface can facilitate the direct tunneling of photo-generated carriers across the junction. Defects produced by ns laser irradiation near either of the Au/CuO interfaces can also introduce intragap states that liberate charge carriers on exposure to incident light. Figure 3.8 (b) shows the ON/OFF response of the photocurrent at a bias of -15 V. It can be seen that both ON and OFF currents are increased by 8 nA, but that there is essentially no change in the signal-to-noise ratio following ns laser irradiation. In all cases, the photocurrent initially increases rapidly (~ 0.1 s) upon illumination and then slowly increase towards saturation. A more robust photodetector, generating higher photocurrent, can be obtained by connecting multiple CuO NWs in parallel across the Au electrodes. Figure 3.8 (c) and (d) display the current response for a bridged structure consisting of four CuO NWs. Figure 3.8 (c) shows that the overall current amplitude for this system of multiple nanowires is ~ 2 orders of magnitude larger than that of the single nanowire. However, the I - V response is more asymmetric because the response of each Au/CuO NW/Au component is not identical as many previous studies reported. Changes in dark current and photo-current after ns laser irradiation are, however, consistent with that occurring in the single Au/CuO NW/Au system. Figure 3.8 (d) shows the time response of the photocurrent at a reverse bias of

15V, indicating that the difference between photo-current and dark current has been tripled after ns laser irradiation.

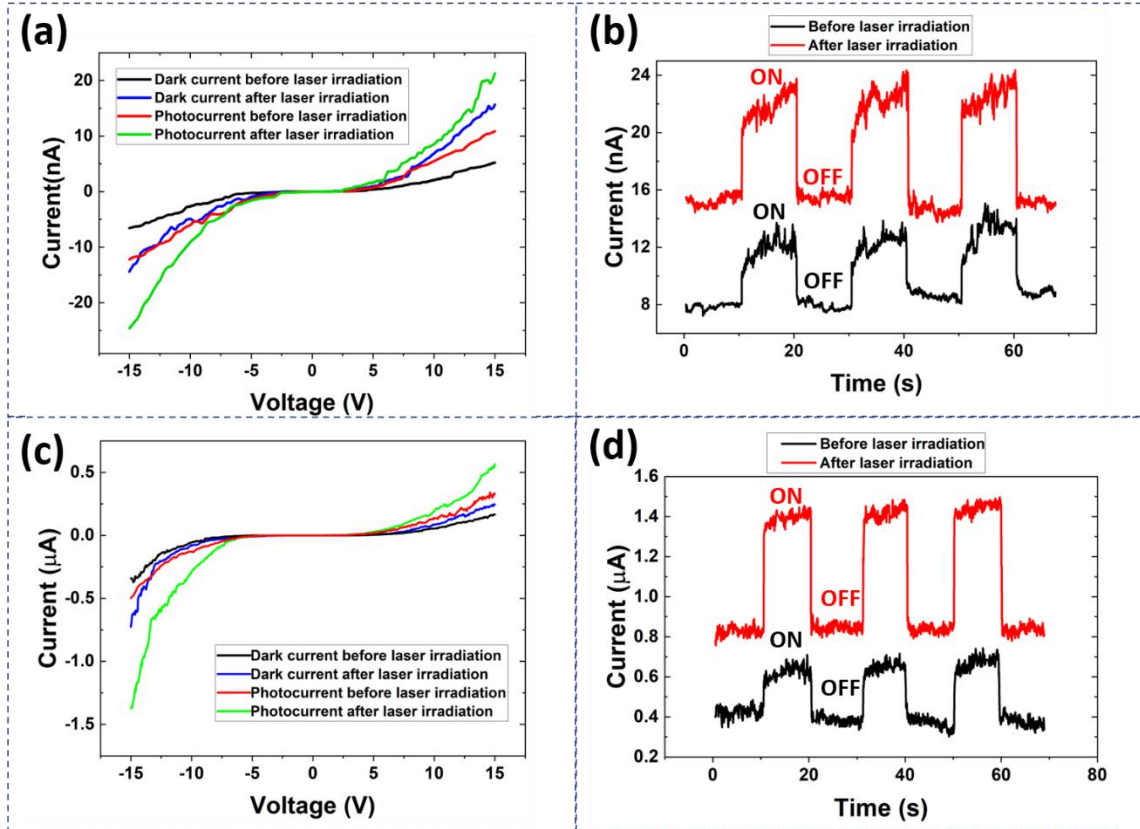


Figure 3.8 (a) Dark current and photocurrent of a bridged structure consisting of a single CuO NW connected across two Au electrodes before and after ns laser irradiation. The voltage sweeps from 15V to -15V. (b) Its ON/OFF response of the photocurrent before (black) and after (red) ns laser irradiation at a voltage of -15V. The time duration for both ON and OFF states is 10s and the ON/OFF times are ~0.1 s. (c) Dark current and photocurrent of a bridged structure consisting of four CuO NWs connected across two Au electrodes before and after ns laser irradiation. The voltage sweeps from 15V to -15V. (d) Its ON/OFF response of the photocurrent before (black) and after (red) ns laser irradiation. The duration for both ON and OFF states is 10s and the rise/fall times of the signals are ~0.1 s.

To quantitatively describe the performance of a photodetector, the responsivity, R , gain, G , and detectivity, D , were calculated as follows: ^{237,238}

$$R = \frac{I_p - I_d}{P_{in}} = \left(\frac{q\lambda}{hc} \right) G \quad \text{Eq.(3.1)}$$

$$D = \frac{R A^{\frac{1}{2}}}{(2qI_d)^{\frac{1}{2}}} \quad \text{Eq.(3.2)}$$

where I_p is the photocurrent, I_d is dark current, P_{in} is incident light power, η is the quantum efficiency, q is electron charge, λ is the incident light wavelength, h is Planck's constant, c is the speed of light and A is the effective area that absorbs incident light. A summary of these parameters calculated for the different configurations in this work are given in Table 3.1. These data indicate that all three characteristic parameters have improved after ns laser irradiation. For the single CuO NW configuration, the responsivity and the gain doubled meanwhile the detectivity is 1.4 times larger after ns laser irradiation. For the device consisting of four CuO NWs, all three parameters are one order of magnitude larger than the value in the single CuO NW case and ns laser irradiation further enhanced these values more than double. For comparison, Table 3.1 also lists the data from other studies which employed CuO nano-materials for photo-detection at similar wavelengths.

Table 3.1 A summary of resistivity, gain and detectivity obtained in our work and from other works.

Configurations	Wavelength (nm)	R ($\text{A} \cdot \text{W}^{-1}$)	G	D ($\text{cm} \cdot \text{Hz}^{1/2} / \text{W}$)	Reference
Single CuO NW before laser irradiation	460	3.5×10^2	5.3×10^2	3.5×10^{11}	This work
Single CuO NW after laser irradiation	460	7.0×10^2	1.1×10^3	5×10^{11}	This work
Four CuO NWs before laser irradiation	460	4.4×10^3	6.6×10^3	1.2×10^{12}	This work
Four CuO NWs after laser irradiation	460	1.3×10^4	2.0×10^4	2.5×10^{12}	This work
Single CuO NW	600	2×10^2	3.95×10^2	6.38×10^{11}	[⁸⁹]
Single CuO-Cu ₂ O core-shell NW	white light	1.1×10^3	-	1.99×10^{13}	[²³⁹]
CuO thin film	white light	15.3	-	1.08×10^{11}	[²³⁸]
CuO thin film	450	3.3×10^{-4}	1.00047	2.03×10^8	[²⁴⁰]

3.3.4 Defect-Enhanced Resistive Switching

Resistive switching in metal-oxide nanowires is another aspect of the electrical characteristics of these devices that has been the subject of many recent studies. It is now generally accepted that resistive switching in metal oxides is due to the formation of internal conductive filaments. In this model, when a “SET” voltage is applied, charged defects in the metal oxide assemble to form conductive filaments. This gives rise to the low resistance “ON” state. Subsequent application of a reverse bias (the “RESET” voltage) can “erase” these conductive filaments and return the material back to a high resistance “OFF” state. Defects in the metal oxide play a critical role and determine the detailed response involved in the resistive switching mechanism.

To study the influence of ns laser irradiation on the resistive switching behavior of the present Au/CuO NW/Au bridged structure, I - V characteristics have been obtained using a cyclic voltage sweep. To avoid problems with joule heating and thermal runaway in a single bridged structure subjected to multiple voltage sweep cycles, which can lead to breakage in the NW or contact region, these measurements were carried out using a bridged structure with seven CuO NWs. Figure 3.9 (a) shows the current response during a voltage cycle $0\text{V} \rightarrow 6\text{V} \rightarrow -6\text{V} \rightarrow 0\text{V}$ for this bridged structure before and after ns laser irradiation with 9000 pulses at a fluence of 200 mJ/cm^2 . The resulting I - V curves exhibit the hysteresis typically seen in resistive switching devices. Before ns laser irradiation, the current response shows a typical Schottky characteristic as the applied bias increases from 0 V to 3.1 V. The I - V curve is found to be linear in the voltage sweeps from 3.1 V to 6 V followed by the sweep from 6 V to 0 V. These characteristics can be attributed to the formation of conductive filaments due to the drift and accumulation of defect centers in the CuO NWs. Once the filaments are formed, the entire bridged structure transforms to a low resistance state (LRS) which is responsible for the linearity in the I - V curve.

When the applied bias is reversed, the existing conductive filaments in the CuO NW will be erased and the entire structure returns to a high resistance state (HRS). After ns laser irradiation, the current increased significantly in both bias directions as expected because

irradiation increases the conductivity of the bridged structure by introducing more defects in the nanowire as well as achieving better contacts between Au electrodes and CuO NWs. In addition, the onset of the linear part of the current response begins at a forward bias of 2.5 V rather than at 3.1 V in the unprocessed system. This indicates that the threshold for electroforming of the conductive filaments occurs at a lower bias voltage. This shift can be attributed to the presence of a higher concentration of defect centers following ns laser irradiation as well as to the lowering of the potential barrier at the CuO/Au junctions.

The ON/OFF ratio, given by the relative amplitudes of the current in the HRS and LRS conditions at a specific bias, is barely changed by ns laser processing. Stability is another major concern in resistive switching devices and is best assessed by measuring the current response for multiple voltage-sweep cycles. Figure 3.9 (b) shows the current response for the bridged structure shown in Figures 3.9 (a) as the number of cycles is extended to 10. It is seen that the peak current under both forward and reverse bias fluctuates significantly due to fluctuations in the Au/CuO NW contacts and the intrinsic instability of conductive filaments under high current flow. Figure 3.9 (c) shows the current response of the same structure after ns laser irradiation and indicates that much of this instability has been eliminated. It is also apparent that the peak currents in both forward and reverse bias conditions are significantly increased after ns laser processing. Similar improvements have been observed in the previous study.³⁵

Many recent studies have shown that the resistive switching effect can be enhanced upon light illumination. To investigate the influence of light illumination on the present bridged structure, the I - V characteristics have also been obtained using a cyclic voltage sweep while under constant illumination with blue light. Figure 3.9 (d) shows the current response under illumination during a voltage cycle $0V \rightarrow 6V \rightarrow -6V \rightarrow 0V$ for the same bridged structure consisting of seven CuO NWs mentioned above. The current response was measured both before and after ns laser irradiation with 9000 pulses at a fluence of 200 mJ/cm^2 . The corresponding I - V curves exhibit the typical hysteresis similar to Figure 3.9 (a) and the current amplitude in both HRS and LRS conditions has increased. However, the ON/OFF ratio under light illumination is not significantly changed from the ON/OFF ratio obtained under dark

conditions. This is due to the fact that the photo-generated carriers increase the carrier density leading to an enhanced current flow while having little effect on the concentration of defects. Figure 3.9 (e) shows the first 10 cycles of the current response for the bridged structure under blue light illumination as shown in Figure 3.9 (d). It is clear that illumination with blue light has little effect on current fluctuations caused by the instability of conductive filaments. Figure 3.9 (f) shows the first 10 cycles of the current response for the same configuration after ns laser irradiation and indicates that stability has been improved. In addition, the peak currents under both forward and reverse bias conditions are almost doubled after ns laser processing.

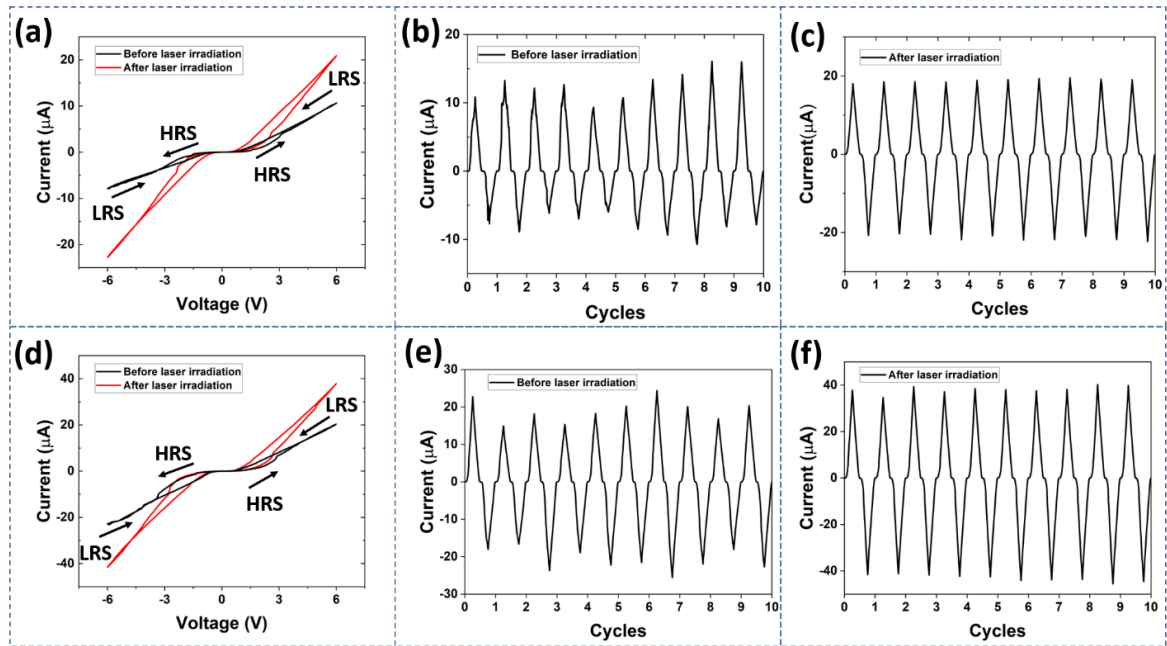


Figure 3.9 (a) $I-V$ response of a bridged structure consisting of seven CuO NWs bridging interdigital Au electrodes recorded under cyclic voltage sweeps for the same system before and after ns laser irradiation. The voltage sweep proceeds: $0V \rightarrow 6V \rightarrow -6V \rightarrow 0V$ (black arrows). The corresponding HRS and LRS conditions are as indicated. (b) Current response over 10 sequential voltage cycles ($0V \rightarrow 6V \rightarrow -6V \rightarrow 0V$) before ns laser irradiation. (c) Current response over 10 cycles as above after ns laser irradiation. (d) $I-V$ response of the bridged structure consisting of seven CuO NWs bridging interdigital Au electrodes illuminated with constant blue light under cyclic voltage sweeps for the same system before and after ns laser irradiation. The voltage sweep proceeds: $0V \rightarrow 6V \rightarrow -6V \rightarrow 0V$ (black arrows). The

corresponding HRS and LRS conditions are as indicated. (e) Current response under constant blue light illumination over 10 sequential voltage cycles ($0\text{V} \rightarrow 6\text{V} \rightarrow -6\text{V} \rightarrow 0\text{V}$) before ns laser irradiation. (f) Current response under constant blue light illumination over 10 cycles as above after ns laser irradiation.

To combine the enhanced electrical and opto-electrical properties, a light-assisted memristor that employs intermittent light illumination is demonstrated to further improve the ON/OFF ratio. Figure 3.10 (a) shows the current response of the same bridged structure consisting of seven CuO NWs mentioned in the above context. The I - V characteristics were taken after ns laser irradiation to exploit the advantages shown previously such as improved stability and enhanced current amplitudes. Instead of sweeping in cycles continuously ($0\text{V} \rightarrow 6\text{V} \rightarrow -6\text{V} \rightarrow 0\text{V}$), the voltage was kept at 6V while the blue light was turned on to achieve an optical “SET” process. The voltage was maintained at 6V for five consecutive measurements to ensure that the photo-current became stable. The voltage was then swept back to 0V and kept at this value for five consecutive measurements while the blue light was turned off. The voltage was then swept to -6V and maintained at this value to obtain similar results in the reverse bias direction. It can be seen that the differences between the HRS and LRS are magnified compared to the hysteresis loop shown in Figures 3.9 (a) and (d) especially in the regions between 2 and 6 V as well as -2 to -6 V . Figure 3.10 (b) shows the long-term performance of the structure over 50 consecutive cycles at a 2 V read voltage. The black line shows the current for the HRS while the red line shows the current for the LRS under voltage sweeps $0\text{V} \rightarrow 6\text{V} \rightarrow -6\text{V} \rightarrow 0\text{V}$ in the dark condition. In this case, the ON/OFF ratio is ~ 2 . On the other hand, for voltage sweeps as demonstrated in Figure 3.10 (a), the current in the LRS has been enhanced due to the presence of photo-generated carriers. Under these conditions, the ON/OFF ratio increases to 6.

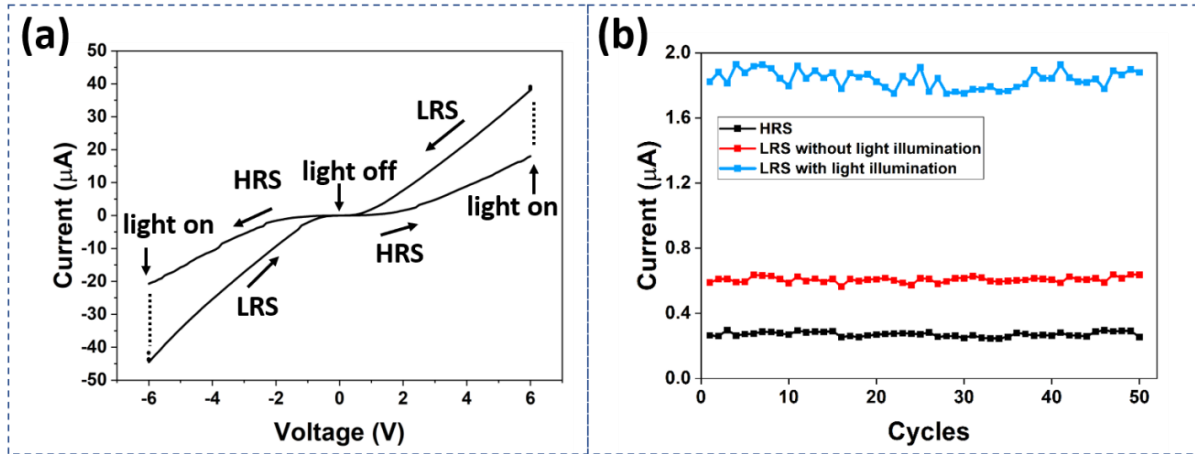


Figure 3.10 (a) The current response of a bridged structure consisting of seven CuO NWs under cycled voltage sweeps. The voltage first raises to 6V and then maintained at 6V for 5 consecutive measurements while the structure is illuminated with blue light. The voltage is then swept back to 0V and kept at 0V while the blue light was turned off. The subsequent voltage sweep repeated this process in the reversed bias direction. The sweep directions are as indicated by the black arrows on the corresponding HRS and LRS scans in (b) The long-term performance of the structure over 50 cycles at a 2V read voltage. The black line shows the current in the HRS while the red line shows the current in the LRS under dark conditions. The blue line shows the current in LRS under the same condition as shown in (a).

3.4 Laser-Induced Defects in ZnO thin films

3.4.1 Laser Fluence vs. Concentration of Defects

Figure 3.11 (a) shows the absorption spectrum before and after ns laser irradiation at different fluences ranging from 240 mJ/cm^2 to 700 mJ/cm^2 . The inset in this Figure shows the absorption spectrum at higher dispersion over the wavelength range between 400 and 800 nm. It has been well established that point defects can be introduced into materials after irradiation with high-intensity laser pulses and that the presence of these defects will increase absorbance over localized regions of the UV-Vis spectrum.^{241,242} The evolution of this effect in ZnO can be clearly seen in Figure 3.11 (a) and its inset where enhanced absorption can be observed between 400 nm and 700 nm after irradiation at laser fluences exceeding $\sim 350 \text{ mJ}/\text{cm}^2$. An increase in

the fluence to 480 mJ/cm² shifts the onset of the absorption edge from ~600 to ~620 nm and yields a strong absorption band peaking at ~480 nm. A further increase in laser fluence to 600 mJ/cm² shifts the absorption edge to ~700 nm and enhances interband absorption producing a strong peak near 500 nm. The absorbance of this band, measured at 500 nm, increases from 0.064 (a.u.) at 480 mJ/cm² to 0.086 (a.u.) at 600 mJ/cm². These effects can be attributed to the introduction of defects by laser irradiation of ZnO. However, when the fluence reaches 700 mJ/cm², the absorption spectrum returns to that of the unprocessed material indicating that the incident laser radiation has resulted in heating and the elimination of defects via annealing.^{101,243} Heating and annealing of ZnO is facilitated even though the absorption coefficient at the 1064 nm laser wavelength is very small, as multi-photon absorption is important at high laser intensity.^{244,245}

The direct bandgap energy, E_g , can be extracted from a Tauc plot of $(\alpha h\nu)^2$ vs. $h\nu$, where α (cm⁻¹) is the optical absorption coefficient and $h\nu$ (eV) is photon energy (Figure 3.11 (b)).²⁴⁶ An extrapolation of the linear part of this plot to its intersection with the photon energy scale gives the bandgap energy. This shows that the bandgap energy remains essentially unchanged after irradiation at low fluences. After irradiation at 480 mJ/cm², the bandgap energy changes slightly from ~3.15 eV in unirradiated ZnO to ~3.14 eV after irradiation at this fluence. A further narrowing of the bandgap to ~3.11 eV can be achieved after irradiation at 600 mJ/cm². This fluence-dependent reduction in bandgap energy indicates that the presence of laser-induced defects introduces additional energy levels in the bandgap.^{108-111,112} These defects are presumably related to the oxygen and zinc vacancies and zinc interstitials known to be present in intrinsic ZnO thin films.¹⁰⁶⁻¹¹⁶

The evolution of the chemical states of oxygen after laser irradiation at different fluences were investigated by micro XPS spectroscopy and are shown in Figure 2 (c)-(h). The O 1s peak was de-convolved using a fit with three Gaussians. Components with binding energies of ~530 eV and ~532 eV in ZnO are associated with lattice oxygen (O_L) and chemisorbed oxygen, respectively.^{248,212} The peak centered at ~531 eV, which is associated with the oxygen vacancy (V_O),^{249,250} increases in strength as the laser fluence goes from 240 mJ/cm² to 600 mJ/cm². A

further increase in laser fluence to 700 mJ/cm^2 , is accompanied by a decrease in the amplitude of the oxygen vacancy component at $\sim 531 \text{ eV}$ indicating that the lattice oxygen to oxygen vacancy ratio is close to that in the unprocessed sample. This confirms that laser irradiation at high fluences “overprocesses” the material by generating excess heat that can anneal the ZnO lattice reducing defect concentration.

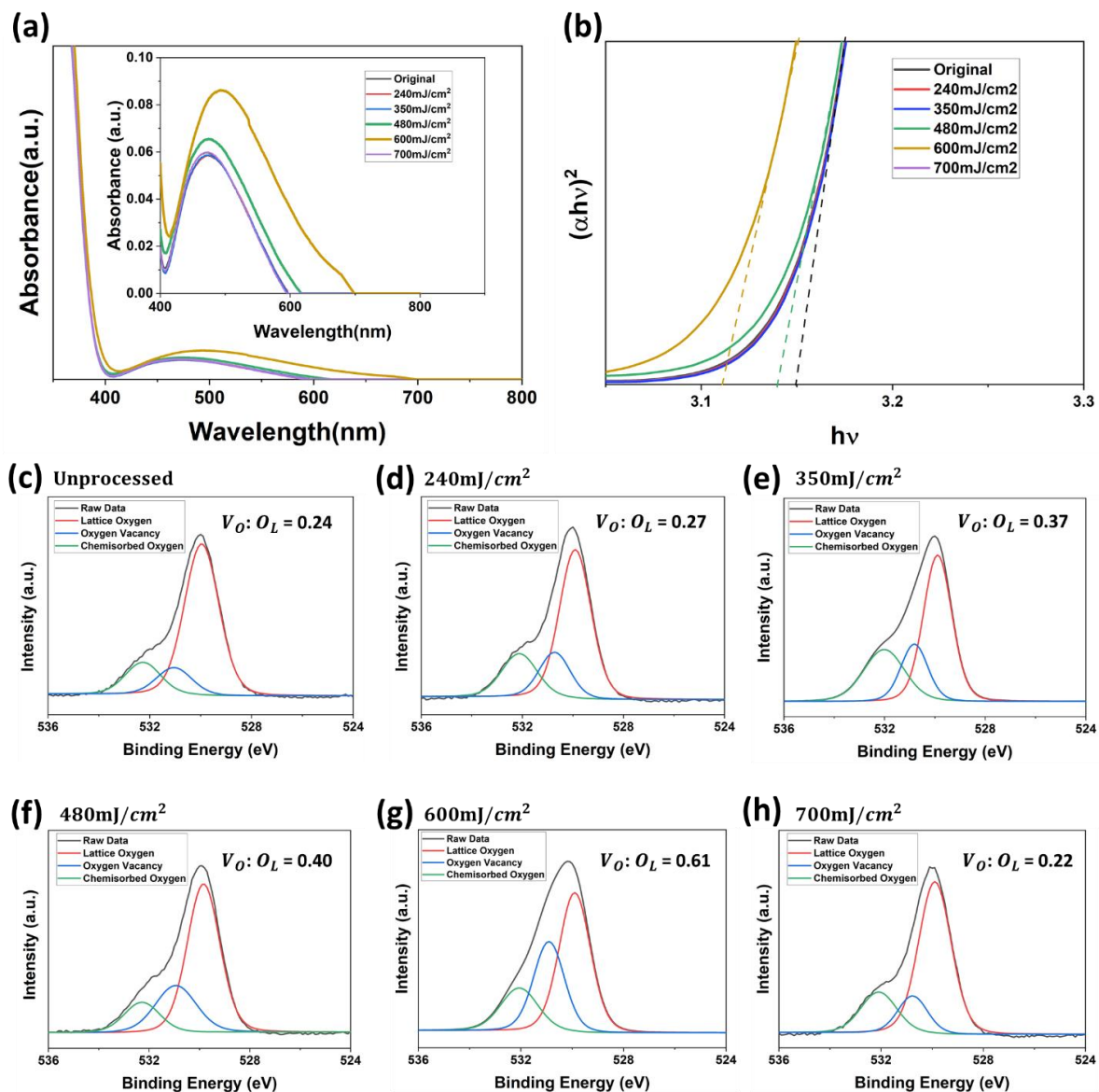


Figure 3.11 (a) The absorption spectra for ZnO thin films before and after ns laser irradiation at different fluences. The inset shows the visible region on an expanded wavelength scale. (b) Tauc-plot of ZnO thin films before and after ns laser irradiation at different fluences. The intersection of the linear extrapolation with the axis for unprocessed ZnO films and films irradiated at fluences $< 350 \text{ mJ/cm}^2$ is at 3.15 eV . After irradiation at 480 mJ/cm^2 and 600

mJ/cm², the intersections became 3.14 eV and 3.11 eV, respectively. High resolution XPS spectra in O 1S region for the ZnO film after laser irradiation at a fluence of (c) 0 mJ/cm², (d) 240 mJ/cm², (e) 350 mJ/cm², (f) 480 mJ/cm², (g) 600 mJ/cm², (h) 700 mJ/cm².

3.4.2 Defect-Dependent Conductivity

To study the influence of ns laser irradiation on the conductivity of ZnO thin films, Ag/ZnO/Ag sandwich structures were fabricated. The ZnO film was deposited on Ag and then irradiated at various laser fluences before the top Ag electrode was deposited. Following this procedure, I-V characteristics of the Ag/ZnO/Ag sandwiched structures were measured under dark conditions using a voltage sweep from 0.3 V to −0.3 V (Figure 3.12). It is apparent that little change in conductivity occurs when the laser fluence is below 480 mJ/cm². Irradiating at 480 mJ/cm² results in a slight increase in the current amplitude and the increase is amplified when the fluence reaches 600 mJ/cm², suggesting that more carriers were generated at a higher laser fluence. However, increasing the fluence to 700 mJ/cm² returns the conductivity to its baseline value because of thermal annealing of the defect concentration.

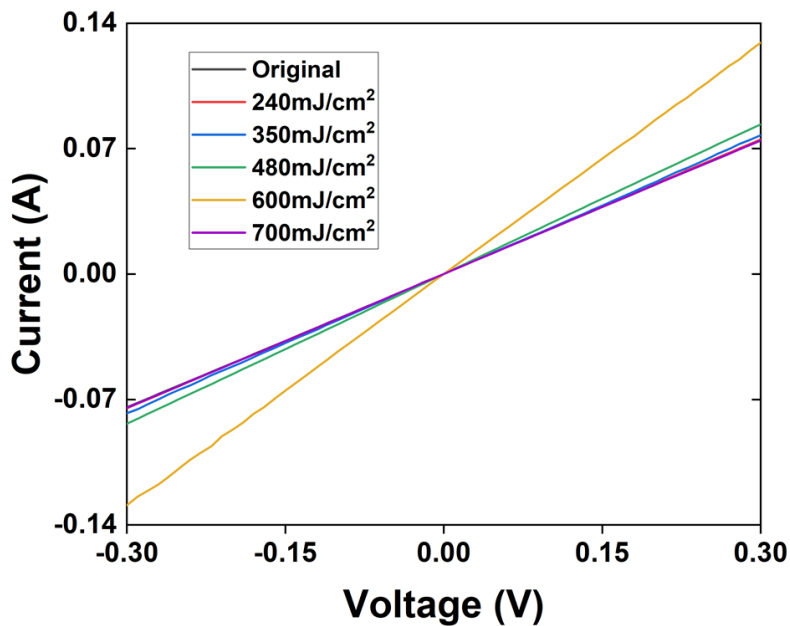


Figure 3.12 I-V characteristics of the Ag/ZnO/Ag stacked structures after laser irradiation at a range of fluences.

3.4.3 Defect-Enhanced Photodetection in Visible Region

To investigate the role of defects might play in improving the photo-conductivity under the illumination at different wavelengths, the transparent ITO/ZnO/ITO structures were fabricated and their photo-current was measured before and after laser irradiation using UV (390 nm), blue (460 nm), green (570 nm) and red (620 nm) LEDs as light sources. Figure 3.13 (a) shows the ON/OFF response of the photocurrent under UV illumination after laser irradiation at different laser fluences. The voltage bias was 10 V. The LED was turned on at the 20s after the measurement started and remained on for another 20s. It can be seen that, as the laser fluence increases, the amplitude of the photocurrent changes dramatically. In the unprocessed ITO/ZnO/ITO device, the ON current reaches saturation shortly after the UV light was switched on. However, the ON current does not become saturated over the same illumination time in laser-irradiated units. This may be due in part to the higher concentration of defects in irradiated devices, as an increase in defect concentration can raise the Fermi level producing a reduction of the width of the depletion region near the ITO/ZnO interface.²⁵¹ As a result, charge carriers find it easier to cross the depletion region through direct tunnelling and field emission. Therefore, photo-generated electron-hole pairs have a higher opportunity to recombine, so that the rise time to the saturation current is extended.²⁵²

In addition, laser-induced defects act as trapping centers so that the mobility of photo-generated carriers is decreased. A similar effect is found in the timescale for the decay of the photocurrent following termination of the light pulse. After illumination, photo-generated carriers are released from traps but, as this is a thermally activated process with an activation energy, the decay time can take many seconds at room temperature, especially when the trap energy levels associated with defect centers are deep.²⁵² Similar effects were reported in ZnO as well as in other metal oxides.^{122,253}

The difference between the amplitude of the photocurrent (ON current) and the background current in the absence of photoexcitation (OFF current) also changes after laser irradiation. For example, under UV irradiation, the ON/OFF difference was 0.12 mA in unprocessed devices. This becomes 0.32 mA when the ITO/ZnO/ITO structure was irradiated

with a fluence of 600 mJ/cm². Since the concentration of defects is increased after laser irradiation, more carriers are available to contribute to the current under UV illumination, leading to an enhanced ON current. Similar results are obtained under blue illumination (Figure 3.13 (b)). The conditions for illumination and the measurement of I - V characteristics were the same for excitation with UV and blue light. It can be seen that the effects of ns laser irradiation on the photo-response are similar to the UV LED results in Figure 3.13 (a). The only change is that the difference between the ON current and the OFF current has increased slightly in a device irradiated at a laser fluence of 600 mJ/cm². We also see an increase in the rise and fall times under these conditions. To quantitatively describe the performance of ITO/ZnO/ITO structures as photodetectors, the responsivity, R , and detectivity, D , were calculated using equations 3.1 and 3.2. The responsivity and detectivity under UV illumination and blue illumination for the ITO/ZnO/ITO structures before and after laser irradiation at different fluence are summarized in Table 3.2 and Table 3.3, respectively.

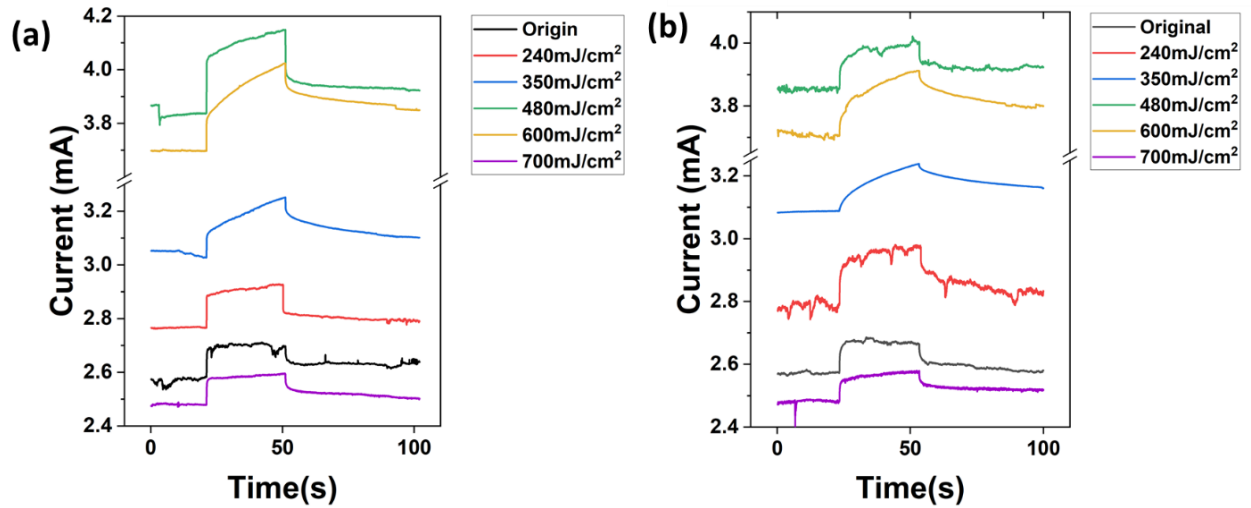


Figure 3.13 (a) The ON/OFF response of the photocurrent under illumination with a UV light source (390 nm) for the ITO/ZnO/ITO devices before and after ns laser irradiation at different fluences. (b) The ON/OFF response of the photocurrent under the illumination with a blue light source (460 nm) for the ITO/ZnO/ITO devices before and after ns laser irradiation at different fluences.

Table 3.2 The responsivity and detectivity under UV illumination for ITO/ZnO/ITO structures before and after laser irradiation at different laser fluence.

	Unprocessed	240 mJ/cm ²	350 mJ/cm ²	480 mJ/cm ²	600 mJ/cm ²	700 mJ/cm ²
R (A· W ⁻¹)	4.29	5.71	8.21	10	11.43	4.28
D(cm· Hz ^{1/2} / W)	1.50× 10 ¹⁰	1.91× 10 ¹⁰	2.63× 10 ¹⁰	2.85× 10 ¹⁰	3.32× 10 ¹⁰	1.47× 10 ¹⁰

Table 3.3 The responsivity and detectivity under blue illumination for ITO/ZnO/ITO structures before and after laser irradiation at different fluences.

	Unprocessed	240 mJ/cm ²	350 mJ/cm ²	480 mJ/cm ²	600 mJ/cm ²	700 mJ/cm ²
R (A· W ⁻¹)	3.75	5.35	5.71	6.07	7.14	3.57
D(cm· Hz ^{1/2} / W)	1.30× 10 ¹⁰	1.78× 10 ¹⁰	1.82× 10 ¹⁰	1.72× 10 ¹⁰	2.08× 10 ¹⁰	1.27× 10 ¹⁰

The response was quite different when the ITO/ZnO/ITO structures were illuminated with light from a green LED, and no photocurrent was observed in devices processed with fluences < 480 mJ/cm². Since photon energy in green light (2.17 eV) is not energetic enough to excite electrons from the valence band to the conduction band in ZnO, the residual photoresponse can be attributed to the excitation of electrons from the valence band to defect levels within the bandgap followed by thermal excitation into the conduction band.^{106,254} Another alternative would involve the photoexcitation of charged carriers from trap levels into the conduction band. Previous studies have found that the introduction of oxygen vacancies into ZnO is accompanied

by the appearance of absorption in the visible region in nominally transparent films.²⁵⁵⁻²⁵⁸ Singly-ionized oxygen vacancies (V_O^+) have been reported to introduce energy levels ~ 0.86 - 2.43 eV²⁵⁹⁻⁷³ below the edge of the conduction band while the doubly-ionized oxygen vacancy (V_O^{++}) generates energy levels ~ 0.95 eV²⁶¹ below the edge of the conduction band. It appears that the concentration of defect centers after irradiation with fluences < 480 mJ/cm² is not sufficient to yield a significant photocurrent on excitation with green light. However, when the fluence is increased to 480 mJ/cm² and 600 mJ/cm², a photocurrent can be generated under green light illumination (Figure 3.14 (a)). No photocurrent is detected on excitation with red light (620 nm) until the ITO/ZnO/ITO structure has been irradiated with a fluence of 600 mJ/cm² (Figure 3.14 (b)). A notable difference in this case is that the amplitude of the photocurrent as well as the time required for the current to fall back to the dark current under green and red-light illumination are much smaller than the values under UV and blue light illumination. This may be due to the fact that the density of photo-generated carriers in the conduction band is comparatively small under these conditions. Overall, the photo-response of ITO/ZnO/ITO stacked structures shows a strong correlation to the concentration of defects in ZnO thin films. These results tell us that optimizing the abundance of defects in ZnO through processing of the device with ns laser pulses can be used to extend the response to longer wavelengths.

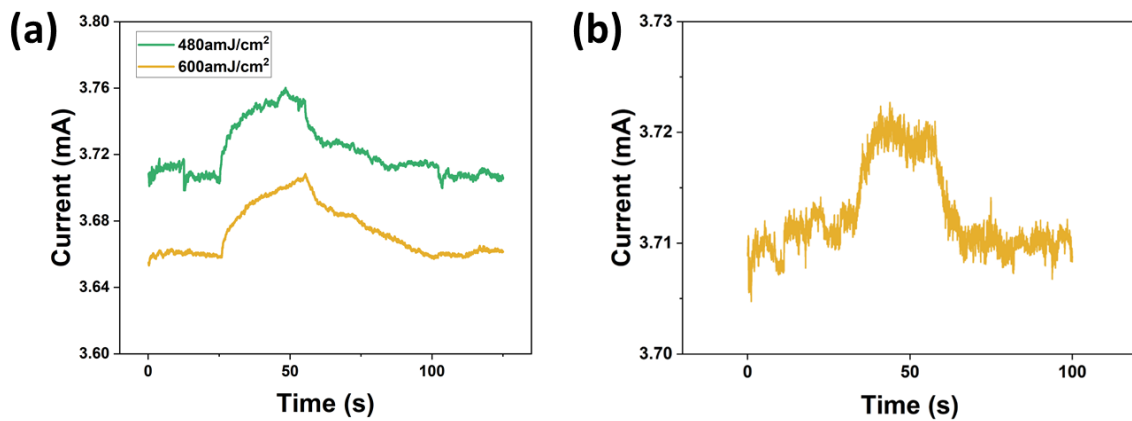


Figure 3.14 (a) The ON/OFF photocurrent response under illumination with green light (570 nm) for ITO/ZnO/ITO devices after ns laser irradiation at different fluence. (b) The ON/OFF

response with illumination at 620 nm for the ITO/ZnO/ITO device after ns laser irradiation at a fluence of 600 mJ/cm².

3.5 Summary

In this chapter, a new technique that utilizes ns laser irradiation to engineer the concentration of defects in both p-type CuO NWs and n-type ZnO thin films was demonstrated. Irradiation with intense ns pulses produces additional defects in the CuO NW, which is confirmed by UV-Vis spectroscopy, XPS and Raman. The presence of defects introduced new energy levels that narrows the effective bandgap. Electrical and opto-electrical properties of the Au/CuO NW/Au bridged structure were examined. Due to the increase in the concentration of defects, the electrical conductivity is significantly increased in the bridged structure. This is accompanied by enhanced photo-conductivity. The I-V characteristics for resistive switching in the CuO NW were also improved due to an increase in defect concentration generated through ns laser irradiation. To take advantage of this improvement in electrical and opto-electrical properties, it is shown that laser processing enables the use of the Au/CuO/Au device as a light-assisted memristor with an enhanced ON/OFF ratio.

On the other hand, the application of this technique in the ZnO thin film was also explored. The electrical conductivity of the ZnO thin film was studied by connecting them with top and bottom Ag electrodes to form vertically-stacked crossbar structures. The optoelectrical properties were measured using transparent ITO to replace Ag electrodes for this stacked structure. It is shown that improvements in the optical characteristics and electrical conductivity of these devices are obtained through tailoring the concentration of laser-induced defects in the ZnO film. These laser-induced defects were identified as oxygen vacancies and high-resolution XPS spectra in the O 1s region showed that the concentration of oxygen vacancies rises as the laser fluence increases when the laser fluence used for processing is below 700 mJ/cm². Once the fluence reaches 700 mJ/cm², thermal heating causes the annealing of the ZnO films and leads to a reduction in the defect concentration. Defects produced by laser

irradiation introduce new energy levels within the bandgap of ZnO that narrows the effective bandgap, extending photo-response of ITO/ZnO/ITO devices to longer wavelengths.

Overall, these preliminary results validate the efficacy of the engineering of defect concentration through laser irradiation in both p- and n- type metal-oxide nano-materials. However, the properties other than the concentration of these defects are still unknown, i.e. the distribution of defects. In recent years, defect engineering has become a prominent focus in the optimization of metal-oxide nano-materials for use in photocatalytic applications.^{129,138,262} Many previous studies perceived that the surface-to-bulk ratio of defects play a central role to influence the effectiveness in charge separation for photocatalytic reactions.^{129,263,264} Therefore, it is highly motivated to reveal how laser-induced defects arrange in metal-oxide nano-materials and it will be discussed in the next chapter.

Chapter 4 Tailoring the Distribution of Defects in CuO NWs and ZnO NWs

4.1 Introduction

Many previous studies have focused on tailoring the concentration of the defects in metal-oxide nano-materials but there is little information currently available on whether these laser-induced defects are located at the surface or within the bulk of the metal oxide.^{26,35} Such information is particularly critical in the optimization of these materials for the important applications such as photocatalysis and gas sensing applications.^{265,266} Photocatalytic applications often involve harvesting solar energy in metal oxides to excite electrons (e) to the conduction band and produce holes (h) in the valence band. These photogenerated e-h pairs then migrate from the bulk to the surface of the metal oxides, taking part in the redox reactions with the adsorbed species such as hydroxyl or organic pollutants.^{140,267} Defects are believed to play a key role in this process as they produce intragap energy levels which facilitates the generation of more e-h pairs.^{268,269} Furthermore, it is believed that bulk defects only serve as charge carrier traps where electrons (e) and holes (h) recombine, leading to less e-h pairs that are available for the photocatalytic reactions.^{126,127} Conversely, surface defects serve as charge carrier traps as well as adsorption sites where the separation of e-h pairs is improved so that they have a higher probability to participate the photocatalytic reactions.^{130,270} Therefore, it is highly motivated to unravel what is the arrangement of the laser-induced defects and endeavor to manipulate the surface-to-bulk ratio through tuning laser processing parameters.

In this chapter, the distribution of defects in both p-type CuO and n-type ZnO is going to be investigated. Their one-dimensional nanowires are selected so that large surface areas are obtained to improve the efficiency of surface redox reactions and help the discrimination of surface and bulk defects. CuO NWs are grown on copper foils through chemical solution method and defects are introduced in these CuO NWs through laser irradiation. The presence of defects is validated by XPS, diffuse reflectance spectroscopy (DRS) and Raman

spectroscopy. The copper foils with CuO NWs are also used as the working electrode for electrochemical measurements. Data obtained from Mott-Schottky and Nyquist plots shows that the surface adsorption of CuO NWs is improved after laser irradiation which can be attributed to the generation of surface defects. The role of these laser-induced surface defects on the non-enzymatic sensing of glucose has also been demonstrated.

A more detailed investigation is conducted in ZnO NWs. The defects after laser irradiation are identified by Raman, DRS, PL and XPS. It is found that both laser fluence and exposure time (number of applied pulses) affect the concentration of defects as well as the overall heat input and temperature rise in ZnO NWs. Since the migration of defects is limited by activation energies and is therefore temperature dependent,²⁷¹ we assume that additional thermal energy introduced during laser irradiation will assist the diffusion of defects. Laser irradiation is then a two-step process involving the creation of defects followed by control over the migration of defects after production. A combination of these two processes can then be used to tailor the defect distribution and properties of defects in ZnO NWs. As an example of the efficacy of this laser-engineering technique, the use of this process in preparing ZnO NWs for the photocatalytic degradation of Rhodamine B (RhB) dye have been evaluated.

4.2 Experimental Section

4.2.1 Preparation of CuO NWs

High purity copper foil (99.9%, Thermo Fisher Scientific) was cut into 1 cm × 2 cm pieces and then ultrasonically cleaned sequentially in ethanol ($\geq 99.9\%$, Sigma-Aldrich), 4 M hydrochloride acid (HCl) and isopropanol ($\geq 99.9\%$, Sigma-Aldrich). The foil was then immersed for 30 min in a mixed solution of 3.6 ml of DI water, 0.8 ml of 1 M ammonium persulfate and 1.6 ml of 10 M sodium hydroxide before being taken out to dry in air. The resulting blue foil was placed in a ceramic boat in a furnace at a temperature of 120 °C for 3 hours followed by further heating in the furnace for 2 hours at 180 °C. The blue foil turned black after this heat treatment, indicating that CuO NWs had been successfully grown on the surface. The SEM pictures showing the geometry of these NWs are given in Figure 4.1.

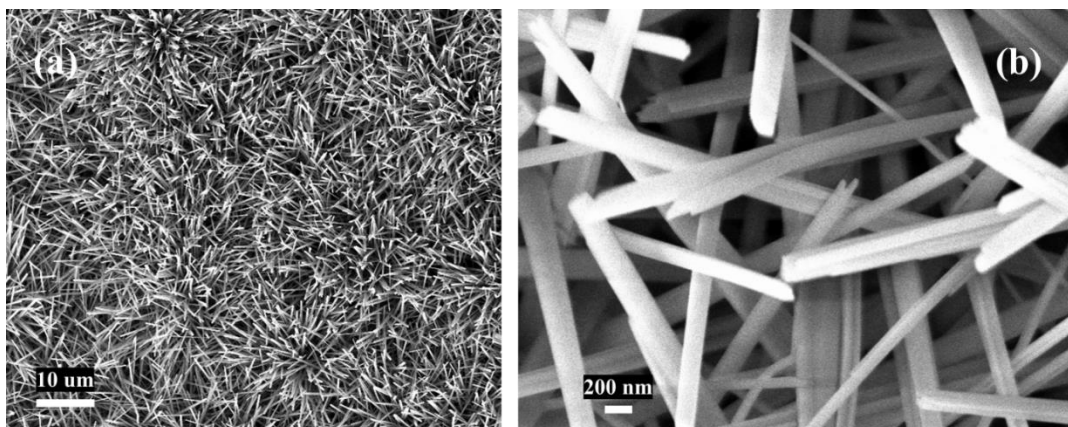


Figure 4.1 The SEM images of the as-prepared CuO NWs in a (a) low and (b) high magnification.

4.2.2 Preparation of ZnO NW Powders

20 mg of powder consisting of single crystalline ZnO nanowires (99.9%, US Research Nano-materials Inc.) was dispersed in 2 ml of ethanol ($\geq 99.9\%$, Sigma-Aldrich). The solution was sonicated for 10 minutes in an ultrasonic cleaner to achieve more uniform dispersion and then the mixture was deposited on a 2.5 x 2.5 cm quartz glass sheet by drop-cast.

4.2.3 Laser Irradiation Set-up

A Nd: YAG laser with a pulse duration of 4 ns and a wavelength of 1064 nm operating at 30 Hz was used for the irradiation of CuO NWs. The apparatus and its configuration are identical to the one shown in Figure 3.3 except that the diameter of the beam on the sample surface was ~ 2.5 mm. The foils were placed in a 3D-printed chamber sealed by an O ring and with a quartz glass window to facilitate laser irradiation in a nitrogen gas (Figure 4.2). The irradiation was conducted under this ambient environment to deliberately produce V_O in CuO NWs. The control over the types of defects will be discussed in Chapter 5 with more details. For fluences exceeding 200 mJ/cm^2 a large proportion of the CuO NWs on the surface are broken and/or ejected from the sample. However, laser fluences $< 160 \text{ mJ/cm}^2$ do not produce any significant changes in the properties of CuO NWs regardless of the exposure time. As a result, 180 mJ/cm^2 was determined to be the optimal fluence and irradiation conditions were

varied by varying the exposure time, i.e. number of pulses, at this fluence. Empirically it is found that an exposure time of 3.5 min is the optimized condition.

ZnO NWs were irradiated with the same apparatus with the same configuration. Indexing grids were drawn on the back of the quartz glass sheet to divide it into 64 individual 3 mm x 3 mm cells and the ZnO nanowires in each cell were then irradiated individually. The laser fluences were 200, 240, and 300 mJ/cm² while exposure times at each fluence were 1.5, 3.5, and 5 min. After laser irradiation, the irradiated nanorods were removed from the quartz glass sheet using a single-edged razor blade and collected in a petri dish.

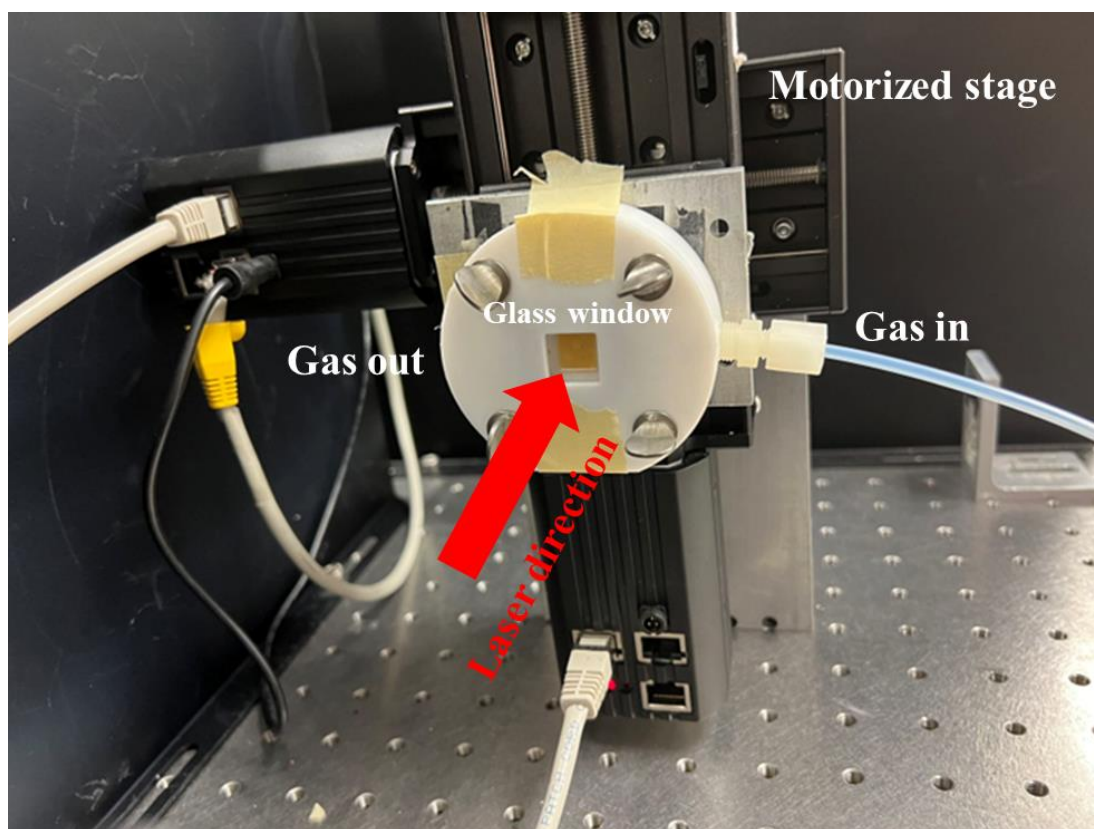


Figure 4.2 The picture of the 3D-printed chamber for laser processing.

4.2.4 Material Characterizations

Optical properties of samples before and after laser irradiation were determined from diffuse reflectance spectroscopy (DRS, Shimadzu UV-2501) incorporating an integrating sphere. For diffuse reflectance spectroscopy, the spectra were measured directly from the array of CuO NWs as grown on the copper foil before and after laser irradiation. The elemental

composition and chemical bonding in the CuO NW samples were obtained from Raman spectroscopy (Renishaw micro-Raman spectrometer) with an excitation wavelength of 633nm and XPS (Thermo VG Microlab 350).

The structural properties of the ZnO nanowires were examined by scanning electron microscopy (SEM, Zeiss FESEM 1530) and transmission electron microscopy (TEM, Talos 200X) while the optical properties were determined from diffuse reflectance spectroscopy with the integrating sphere installed (DRS, Shimadzu UV-2501) and photoluminescence spectroscopy with an excitation wavelength of 325nm (PL, Edinburgh Instruments FL920). The elemental composition and chemical bonding in the irradiated ZnO NWs were determined by Raman spectroscopy (Renishaw micro-Raman spectrometer) with an excitation wavelength of 633nm and XPS (Thermo VG Microlab 350). Baseline characterization of all parameters was carried out for each sample before laser irradiation.

4.2.5 Electrochemical Measurements

Electrochemical measurements were conducted using a standard three-electrode configuration. As-prepared foils with CuO NWs grown on the surface were used as the working electrodes, while a platinum electrode was used as the counter electrode and Ag/AgCl was used as the reference electrode. Electrochemical impedance spectroscopy (EIS) and amperometry were performed using a CH Instrument 660 electrochemical workstation with 50 ml of 0.1 M NaOH aqueous solution. EIS was carried out with the potential ranging from – 0.4 V to 1V with an increase rate of 0.05 V at a frequency of 1000 Hz. The Nyquist plots were captured within the frequency range of 0.1 Hz to 100k Hz. The amperometry was implemented with a potential of + 0.65 V. A rotator with an RPM of 300 was used during glucose sensing to facilitate electron transport. The glucose solution with various concentrations was added every 50 s. A schematic illustration of the experimental set-up is displayed in Figure 4.3. All measurements were carried out both before and after laser irradiation for each sample in a dark environment at room temperature.

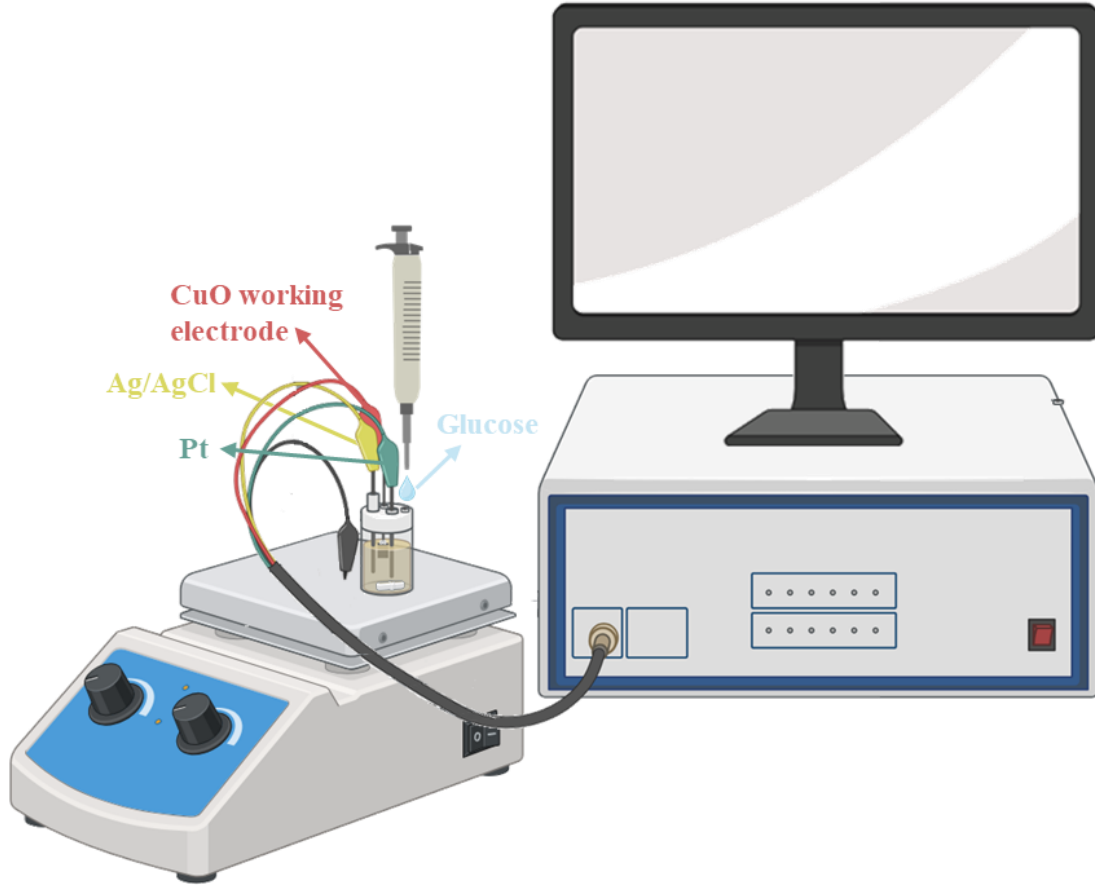


Figure 4.3 A schematic showing the three-electrode configuration using the foil with CuO NWs as the working electrode.

4.2.6 Simulation Methods for Temperature Estimations

To study the relation between the temperature in the ZnO NWs and the laser fluence, finite element method (FEM) simulations were conducted to estimate the temperature rise in the ZnO NWs due to laser irradiation. Since the pulse duration of the ns laser is much longer than the electron-phonon coupling time of ZnO, the lattice and the electronic systems are in thermal equilibrium during the laser pulse.^{272,273} It can then be assumed that incident laser energy is instantaneously converted into heat,^{274,275} so that heat transfer is described by the equation:

$$\rho \cdot C \cdot \frac{\partial T}{\partial t} = \nabla \cdot (k \cdot \nabla T) + Q(z, t) \quad \text{Eq. (4.1)}$$

where ρ (kg/m³) is the density of the material, C (J/kg·K) is heat capacity, T (K) is temperature, k (W/m·K) is the thermal conductivity and $Q(z, t)$ (W/m³) is the source term at a depth z (m)

in the material at time t (sec), which is obtained from the laser intensity distribution and the Lambert-Beer law:

$$Q(z, t) = \alpha \cdot I(z, t) \cdot (1 - R) \quad \text{Eq. (4.2)}$$

where α (m^{-1}) and R are the absorption coefficient and reflectivity of the material, respectively. $I(z, t)$ (W/m^2) is the laser intensity normal to the material surface at a depth z in the material at time t . This formalism assumes that an individual NW is irradiated with a plane wave incident normal to the long axis of the NW. Values of the relevant parameters used in simulations are given in Table 4.1.

Table 4.1 The parameters used in the simulation for the estimation of temperature rise in the ZnO NW during one pulse.

Parameters	Values
Fluence of laser	200, 240, 300 mJ/cm^2
Pulse duration of laser	$4 \times 10^{-9} \text{ s}$
Repetition frequency of laser	30 Hz
Initial temperature	293.15 K
Reflectivity of ZnO	0.0735
Absorption coefficient of ZnO	$1.1515 \times 10^6 \text{ 1/m}$
Extinction coefficient of ZnO	0.021528 1/m
Thermal conductivity of ZnO	6 $\text{W}/(\text{m} \cdot \text{K})$
Heat capacity of ZnO	$53.99 + T \times 7.851 \times 10^{-4} - T^2 \times 5.868 \times 10^{-5} - 127.5 \times T^{-0.5} + T^2 \times 1.9376 \times 10^{-6} / \text{molar weight}$
Volume of ZnO	$6.28 \times 10^{-20} \text{ m}^3$
Refractive index of ZnO	1.7435
Molar weight of ZnO	0.08138 kg/mol

4.2.7 Configurations for Photodegradation

5 mg of ZnO nanowire powder was weighted and deposited on the quartz glass first and their morphologies were examined by SEM. The size distribution was analyzed by ImageJ so that the average size and the content of the ZnO nanowires can be maintained approximately the same between different samples. The nanowire powder was then dispersed in a 30 ml RhB dye solution whose concentration was 5 ppm. The mixture was then sonicated for 30 sec and then placed in an enclosure for 30 min under dark conditions to reach the adsorption-desorption equilibrium.^{276,277} A magnetic stir bar was used to stir the mixture during this period. After 30 min, 1 ml of the mixture was taken from the solution and the UV-Vis absorption spectrum was measured by UV-Vis spectroscopy (Shimadzu UV-2501). Subsequently, the mixture was exposed to a xenon light source (PerfectLight). This illumination with broadband light was used for photocatalysis. During this procedure, the beaker containing the mixture was immersed in a water bath to minimize evaporation of the solution. 1 ml of the mixture was extracted from the solution every four minutes and subjected to centrifugation at 10000 rpm for 30 sec to precipitate the ZnO nanorods so that they did not affect the measurement of the optical absorption of RhB. The degradation of RhB dye was studied from an analysis of these absorption spectra. To relate these absorption spectra to the concentration of RhB, solutions containing 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm of RhB were prepared and evaluated.

4.3 Defects in CuO NWs

4.3.1 Identification of Defects

The presence of defects in CuO NWs is obtained by XPS spectrum in O 1s and Cu 2p regions. The O 1s peak generally has three components: a peak associated with lattice oxygen vacancies with binding energy ~ 531.4 eV, (V_O), a component with binding energy ~ 529.9 eV corresponding to lattice oxygen, (O_L), and a third peak associated with chemisorbed oxygen, (O_{Ch}), with a binding energy ~ 532.4 eV. O 1s XPS spectra for CuO NWs before and after laser irradiation are shown Figure 4.4 (a) and (b). Figure 4.4 (a) shows these data for the as-prepared CuO NWs samples S1 before laser processing. Figure 4.4 (b) shows the O 1s spectrum of S1

after laser irradiation in N_2 gas. This shows that the peak intensity of the V_O and O_{Ch} components rises dramatically while the ratio of the areas of the V_O and O_L features is seen to increase from 0.51 to 0.71, indicating that the concentration of V_O is enhanced after laser irradiation under this condition. It is also evident that the area of chemisorbed oxygen increased significantly in both Figure 4.4 (b), implying that the adsorption of oxygen on the surface of CuO NWs is enhanced after laser irradiation. Such enhancement in the adsorption indicates that the vacancies produced during laser irradiation are in the surface and sub-surface regions.

133,278

Additional insight can be obtained from XPS scans in the Cu2p region (Figure 4.4 (c)). High-resolution Cu 2p spectra can be deconvoluted into two major peaks, a $Cu2p_{3/2}$ peak positioned at ~ 933.8 eV and a $Cu2p_{1/2}$ peak positioned at ~ 953.8 eV, and two shake-up satellite peaks ~ 10 eV higher than these major peaks. It is evident that all peaks in the Cu2p region shifts towards lower binding energy by ~ 0.8 eV after laser irradiation, implying that there is increased electron density around the Cu core level as a result of the presence of V_O in CuO.¹³²

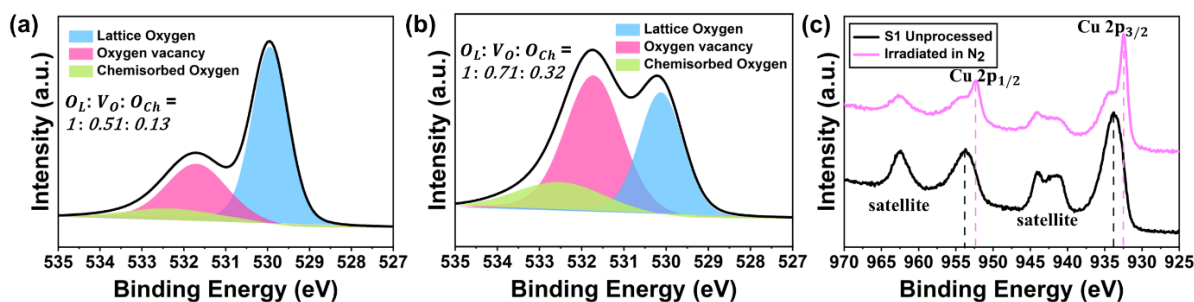


Figure 4.4 High-resolution XPS results in the O 1s region of (a) unprocessed CuO NWs on S1, (b) CuO NWs on S1 after laser irradiation, (c) High-resolution XPS results in the Cu 2p region of CuO NWs on S1 before and after laser irradiation.

The structural disorder and the presence of lattice defects in CuO can also be obtained from Raman spectroscopy. Figure 4.5 shows that Raman spectra of the unprocessed samples S1 is characterized by major peaks attributable to the A_g (273 cm^{-1}), B_g^1 (325 cm^{-1}) and B_g^2 (595 cm^{-1}) vibrations of CuO.^{279–281} The broad peak centered at 1100 cm^{-1} can be attributed to a combination mode arising from the presence of defects and attendant structural

disorder in the CuO NWs.²⁸² The Raman spectrum of S1 after laser irradiation shows a 1.5-fold increase in the intensity of the broad peak centered at 1100 cm^{-1} which is consistent with the generation of additional point defects in the CuO NWs. This is accompanied by a reduction in the intensity of the A_g vibrational mode compared to that in the unprocessed sample, suggesting that laser irradiation under these conditions introduces structural disorder. Furthermore, an additional peak appears at $\sim 800 \text{ cm}^{-1}$. This feature can be associated with peroxide or superoxide species adsorbed on the surface of CuO NWs,^{282–285} suggesting that defect centers created during laser irradiation locate at the surface areas.

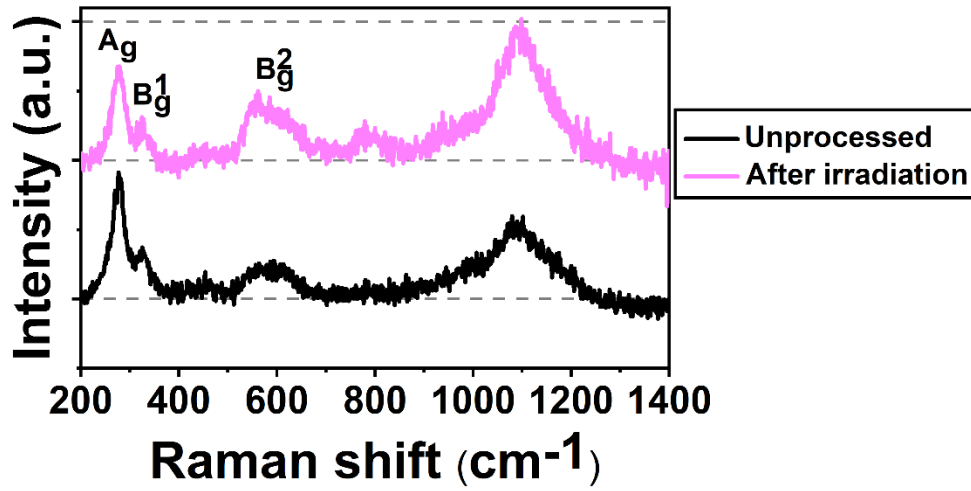


Figure 4.5 Raman spectra of CuO NW samples before and after laser.

4.3.2 Vacancy-Enhanced Electrochemical Properties

Mott-Schottky measurements (Figure 4.6 (a)) have also been used to study the electrochemical properties of CuO NW samples containing laser-induced vacancies. In this formalism, the carrier concentration N_A in CuO can be calculated from the measured capacitance C using the Mott-Schottky equation:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 A^2 e N_A} \left(V - V_{FB} - \frac{k_B T}{e} \right) \quad \text{Eq. (4.3)}$$

where ϵ is the dielectric constant of the semiconductor, ϵ_0 is the permittivity of free space, A is the interfacial area, e is electronic charge, V is the applied voltage, V_{FB} is the flatband potential, k_B is Boltzmann's constant and T is the temperature.^{286,287} The carrier

concentration N_A is then inversely proportional to the slope of the Mott-Schottky curve and the negative slopes of the plots in Figure 4.6 (a) indicate that p-type conductivity is dominant, with holes as the major carriers in these CuO NWs.^{288,289} As laser irradiation of CuO NWs increases the concentration of V_O centers which is known to act as hole traps²⁶⁰, the slope of the Mott-Schottky curve should increase relative to that for unprocessed samples. However, the slope of the Mott-Schottky curve for CuO NWs after irradiation actually decreased as shown by the pink curve in Figure 4.6 (a). This reduction in slope is attributed to the fact that laser-induced V_O is located at the surface of CuO NWs, increasing the adsorption of the electrolyte on the nanowire surfaces. Similar trends can also be obtained from the Nyquist plot (Figure 4.6 (b)).

Many previous studies have demonstrated that the Nyquist plot in the low frequency region is diffusion-controlled while the semicircle in the high frequency region is reaction-controlled.^{290–292} A smaller diameter of the semicircle often indicates a lower interfacial charge transfer resistance (R_{CT}) between the electrolyte and the CuO NWs.^{23,293,294} As can be seen in Figure 4.6 (b), R_{CT} of sample S1 was reduced after the irradiation, indicating that the charge transfer efficiency is enhanced due to the presence of V_O appeared at the interface, namely the surface of CuO NWs.

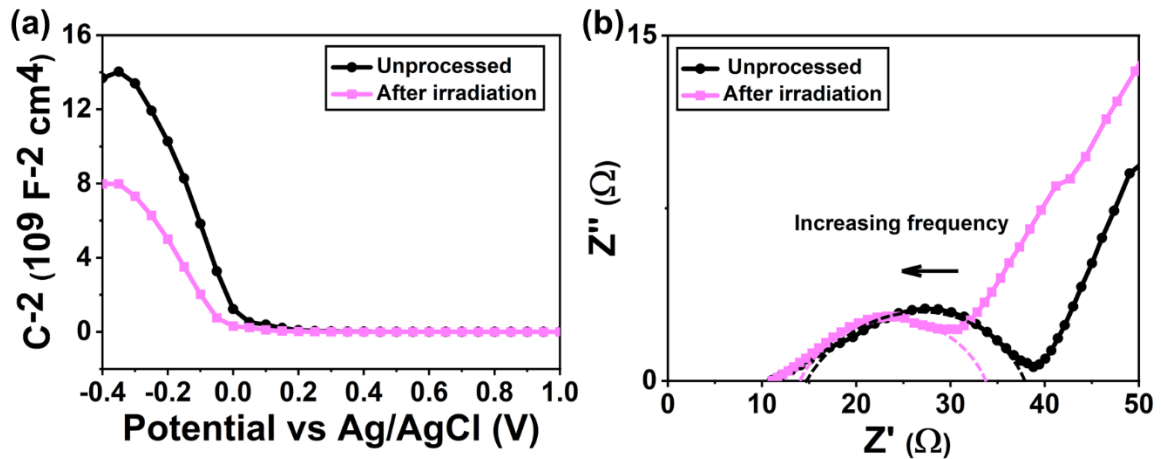
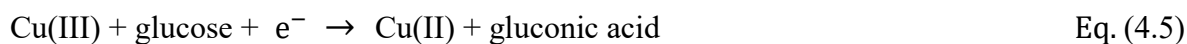


Figure 4.6 (a) Mott-Schottky plots of CuO NWs before and after laser irradiation. (b) Nyquist plot of CuO NWs before and after laser irradiation.

4.3.3 Enhanced Glucose Sensing with Surface Oxygen Vacancies

An important application of CuO is for use as an electrocatalyst enabled by the durability, relatively high sensitivity and low overpotential of this material.^{295–297} For example, there have been many studies of the use of CuO as the catalyst for non-enzymatic glucose detection.^{298–301} To study the roles of laser-induced vacancies on such detection applications, the amperometry was implemented using the foil with CuO NWs as the working electrode in a standard three-electrode configuration. Figure 4.7 (a) shows the amperometric signal from CuO NWs during the sequential addition of glucose as indicated in the figure. The current response of CuO NWs after laser irradiation increases substantially, implying that the presence of V_O centers improves the sensitivity for glucose detection. Although the exact mechanism for the oxidation of glucose using CuO-based electrodes in an alkaline environment is not well understood, many previous reports have suggested the following mechanism:^{302,303}



It was believed that the existence of a higher concentration of V_O on the surface of CuO ameliorates the adsorption and stabilization of the OH^- functional groups thus improves the non-enzymatic glucose sensing.¹³³ Therefore, the enhancement seen in Figure 4.7 (a) indicates that V_O produced by laser irradiation is supposed to reside on the surface of CuO NWs. As traditional blood-based glucose detection techniques are complex and unfriendly to users, non-invasive glucose detection technologies that can extract information from saliva, sweat and tears are in high demand and several devices with this protocol have been developed recently.^{304–306} These techniques generally require the detection of glucose at much lower concentrations (0.03–0.6 mM).³⁰⁷ Hence, amperometry of CuO NWs with glucose concentrations in the 0.5 μM to 50 μM range has been carried out using the present samples (Figure 4.7 (b)). It can be seen that a detection limit as low as 0.5 μM can be achieved with unprocessed CuO NW samples, and that the current response is enhanced after the introduction of laser-induced V_O centers.

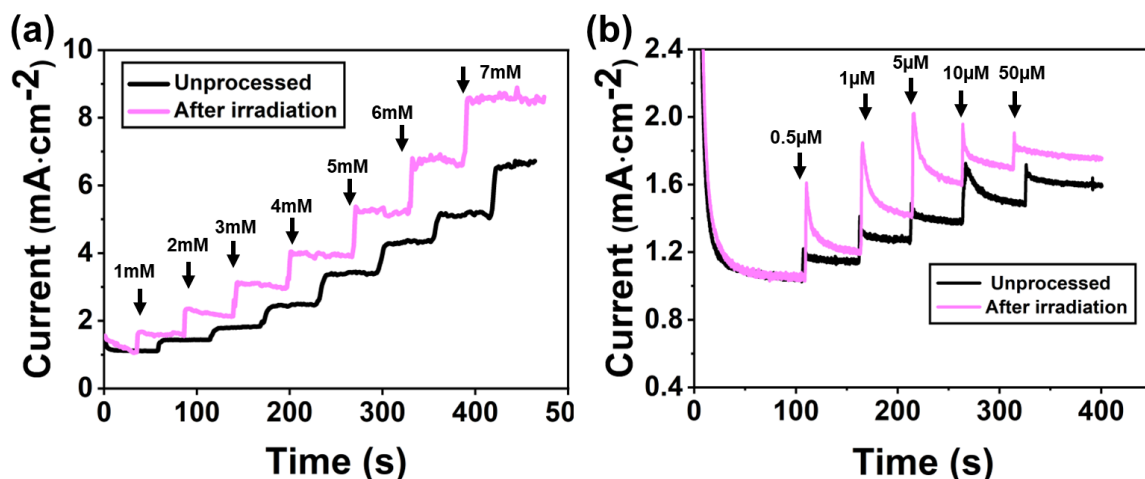


Figure 4.7 (a) The amperometry of CuO NWs in as prepared condition compared to the response of samples after laser irradiated. Measurements were carried out in 0.1 M NaOH and 1 mM, 2 mM, 3 mM ... to 7 mM of glucose were sequentially added into the solution. (b) Amperometry of unprocessed CuO NW samples compared to the response of samples after irradiation. The measurements were conducted in 0.1 M NaOH with the addition of low glucose concentrations as indicated in the figure.

4.4 Defects in ZnO NWs

4.4.1 Identification of Defects

The nature of defects in ZnO is first examined from optical spectra and absorption features associated with the defect states were characterized by DRS. The diffuse reflection data from DRS has been converted into absorption by using Kubelka-Munk equation.³⁰⁸ Figure 4.8 (a) shows the absorption spectrum of ZnO NWs irradiated at 200 mJ/cm² for different times. The effect of laser irradiation is to introduce broadband absorption between 360 and 700 nm which increases with exposure time. Similar enhancements in broadband absorption can also be observed when ZnO NWs are irradiated for 1.5 and 3.5 min at a fluence of 240 mJ/cm² (Figure 4.8 (b)). It can be seen that laser irradiation under these conditions increases the intensities of the absorption spectra in the visible region and shift the absorption edges to higher wavelengths, which are often considered as the result of increasing oxygen vacancies.²⁰⁵ However, these

enhancements in absorption virtually disappear when the exposure time is extended to 5 min. This effect can be attributed to thermal heating of the nanostructures by laser irradiation which enables the removal of defect centers via annealing. Absorption spectra of ZnO NWs irradiated at 300 mJ/cm² show some enhancement in broadband absorption when the exposure time is 1.5 min and this increases for an exposure of 3.5 min (Figure 4.8 (c)), but the broadband absorption between 360 and 700 nm has disappeared entirely at an exposure of 5 min. This behavior is postulated to arise as an equilibrium between the formation of defects by photo-absorption and the recombination of defects facilitated by thermal heating.

Bandgap narrowing caused by defects in ZnO and other oxides can be attributed to optical transitions involving charge carriers trapped at energy levels within the bandgap.^{113,256} The overall reduction in the effective bandgap can be obtained from a Tauc plot of $(\alpha(\nu)h\nu)^2$ vs. $h\nu$,³⁰⁹ where $\alpha(\nu)$ is the absorption coefficient (m⁻¹), h is Planck's constant and ν is the light frequency. Tauc plots calculated from the corresponding absorption spectra of unprocessed and laser irradiated samples are shown in Figures 4.8 (d)-(f). These show that the bandgap energy $E_g \sim 3.46$ eV in unprocessed ZnO NWs. Laser irradiation of ZnO NWs at 200 mJ/cm² for 1.5 min gives $E_g \sim 3.45$ eV but the bandgap energy is reduced to ~ 3.41 eV and ~ 3.39 eV for exposures of 3.5 and 5 min, respectively. When the laser fluence is increased to 240 mJ/cm², the effective bandgap energy decreases to ~ 3.37 eV and ~ 3.0 eV for exposures of 1.5 and 3.5 min, respectively. On the other hand, an exposure time of 5 min resets the bandgap energy to that of unprocessed material (~ 3.46 eV). A similar effect is observed for the ZnO NWs irradiated at 300 mJ/cm². Laser irradiation of the ZnO NWs for 1.5 and 3.5 min at this laser fluence gives $E_g \sim 3.39$ eV and ~ 3.44 eV, respectively. Extending the exposure time to 5 min again causes the effective bandgap energy to reset to ~ 3.46 eV.

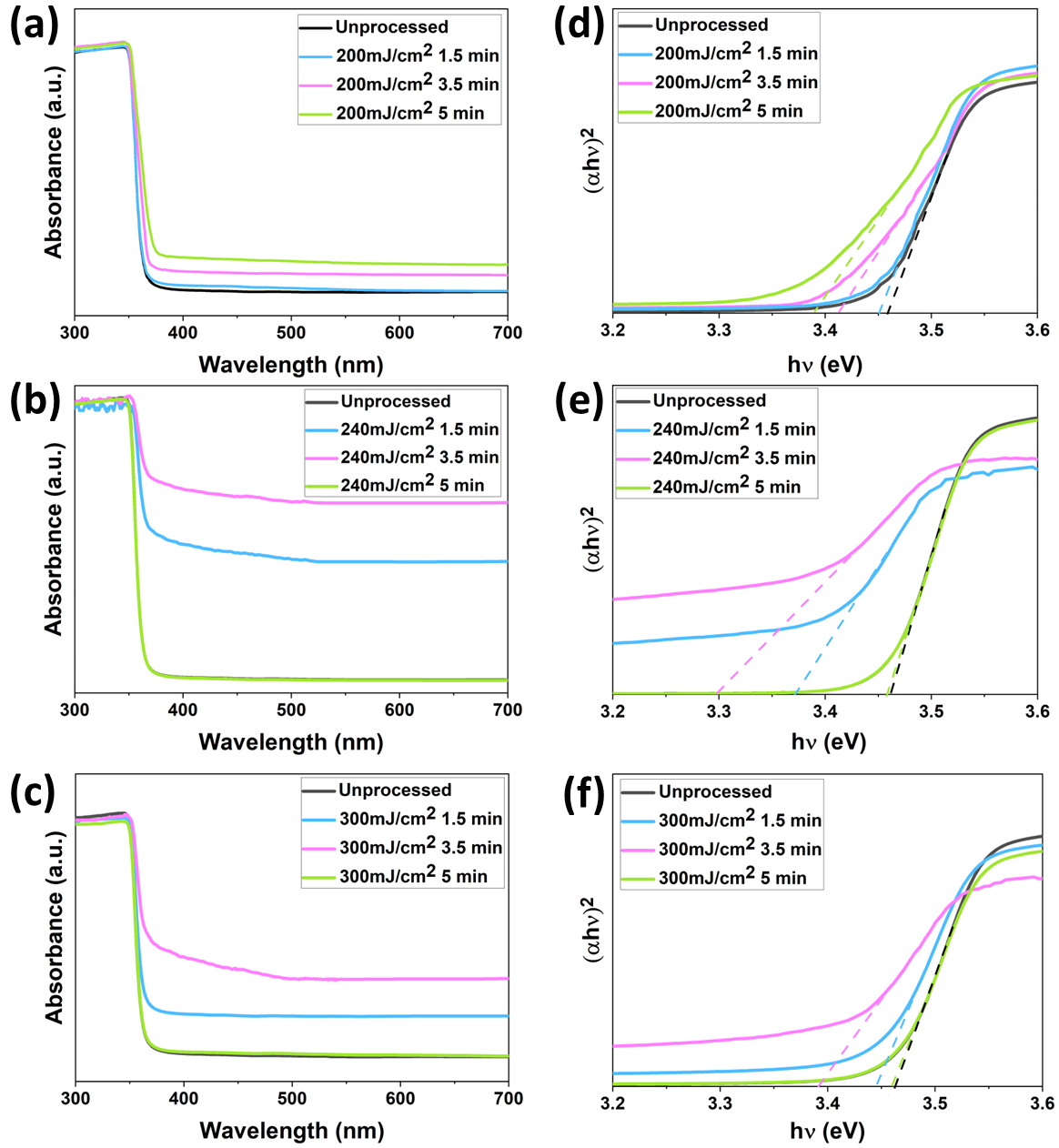


Figure 4.8 Absorption spectra of ZnO NWs samples before and after irradiation at fluences (a) 200 mJ/cm², (b) 240 mJ/cm² and (c) 300 mJ/cm² for different exposure times. Tauc plots showing the bandgap energy of the ZnO NWs before and after irradiation at fluences (d) 200 mJ/cm², (e) 240 mJ/cm² and (f) 300 mJ/cm² for different exposure times.

After examining the relation between the laser fluence as well as exposure time and the production of defects, Raman spectroscopy was also conducted and Raman spectra of ZnO NWs after laser irradiation under different conditions are given in Figure 4.9. The intense peak

at $\sim 439 \text{ cm}^{-1}$ represents the nonpolar E_2^{high} optical phonon mode associated with the hexagonal wurtzite structure,^{310,311} while the broad feature at $\sim 565 \text{ cm}^{-1}$ is typically ascribed to defect modes involving oxygen vacancies.^{312,313} The weak peak at $\sim 331 \text{ cm}^{-1}$ is the combination mode associated with the difference between E_2^{high} and E_2^{low} while the peak at $\sim 775 \text{ cm}^{-1}$ is the LA + LO mode with A1 symmetry. Previous studies have shown that a decrease in the strength of the E_2^{high} peak accompanied by a reduction in the energy of this peak indicates that the concentration of oxygen vacancies has increased.²⁹ It can be seen in Figure 4.9 (a) that the intensity of the E_2^{high} peak is reduced as the exposure time at a fluence of 200 mJ/cm^2 increases from 1.5 min to 5 min while the peak energy decreases by up to 2 cm^{-1} compared to that obtained in the unprocessed sample. This suggests that the concentration of oxygen vacancies continues to increase with exposure under these conditions.

When the fluence is increased to 240 mJ/cm^2 , the intensity of the E_2^{high} peak decreases as before up to an exposure of 3.5 min (Figure 4.19 (b)), then resets to a value close to that of the unprocessed ZnO NWs when the exposure time reaches 5 min. This indicates that exposure under this condition raises the temperature of the sample into the range where defects associated with oxygen vacancies can be annealed out. Increasing laser fluence further is supposed to generate more heat in ZnO NWs thus may amplify the annealing effects to remove all defects. However, the spectra shown in Figure 4.9 (c) indicates that this process does not occur when the fluence is raised to 300 mJ/cm^2 . While the intensity of the E_2^{high} peak decreases somewhat for exposures up to 3.5 min at this fluence, the intensity of this peak increases again for an exposure of 5 min. This complex behavior suggests that the oxygen vacancy concentration is the result of a balance between the defect formation rate driven by photo-absorption, and a reverse reaction involving thermally activated recombination. At high photo-absorption rates (high fluence), this equilibrium shifts toward a higher oxygen vacancy concentration while the rate of defect formation is compensated by the enhanced recombination rate at higher temperatures.

The recombination of defects in ZnO NWs has been shown to involve an activation energy associated with the migration of vacancies in the ZnO lattice.²⁷¹ In a low dimensional system such as an NW this migration likely involves the diffusion of defects towards the surface since the formation energy of the defects are often lower in the surface regions.¹²⁵ Recovery of the intensity of the E_2^{high} peak under high exposure conditions (300 mJ/cm², 5 min exposure) suggest that laser-induced annealing does not only require a high temperature, but that this increase in temperature also needs to be sustained for an extended period of time.

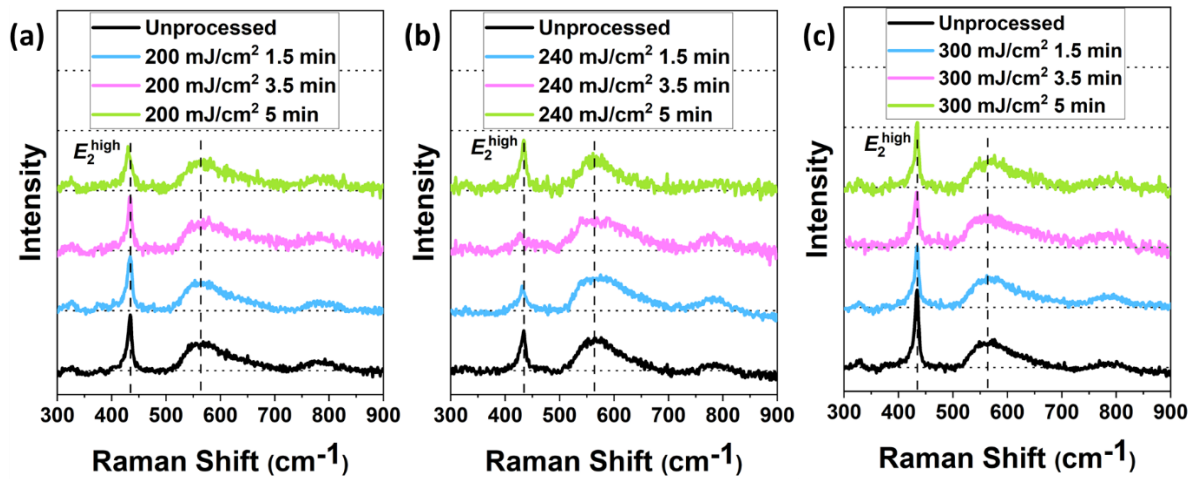


Figure 4.9 Raman spectra of ZnO NWs irradiated at (a) 200 mJ/cm², (b) 240 mJ/cm² and (c) 300 mJ/cm² for a selection of times.

Photoluminescence (PL) spectroscopy is also used to characterize states of defects in ZnO. The PL spectrum of ZnO nanostructures typically consists of a strong UV emission peak related to near-band edge transitions of excitons, together with a broad peak in the visible corresponding to emission from defect centers.^{197–199} Figure 4.10 shows PL spectra of ZnO NWs after laser irradiation under different conditions. To facilitate comparison, PL intensities are normalized to that of the UV emission peak. With this normalization, it is apparent that the intensity of the broad peak at visible wavelengths is only weakly affected by laser irradiation for 1.5 min at a fluence of 200 mJ/cm². The UV-to-vis ratio of the peak intensities decreases slightly from ~ 9.1 to ~ 8.3 . On the other hand, the intensity of the broadband peak is dramatically enhanced after laser irradiation for 3.5 min at 240 mJ/cm² and the UV-to-vis ratio

decreases significantly to a value of ~ 1.1 . This increase in intensity in the visible region is accompanied by a shift in the peak of the emission band from ~ 358 nm to ~ 361 nm, which is often considered as the near-band-edge emission.^{314,315} These changes are consistent with a significant increase in defect concentration under these conditions and a corresponding decrease in bandgap energy.^{154,316–318} Extending the exposure time to 5 min, while maintaining the laser fluence at 240 mJ/cm^2 decreases the amplitude of the broad PL peak due to a reduction of the defect concentration. An intermediate modification of the ZnO NW sample occurs after irradiation at a fluence of 300 mJ/cm^2 for 3.5 min. And the UV-to-vis ratio of the peak intensities decreases to 3.2.

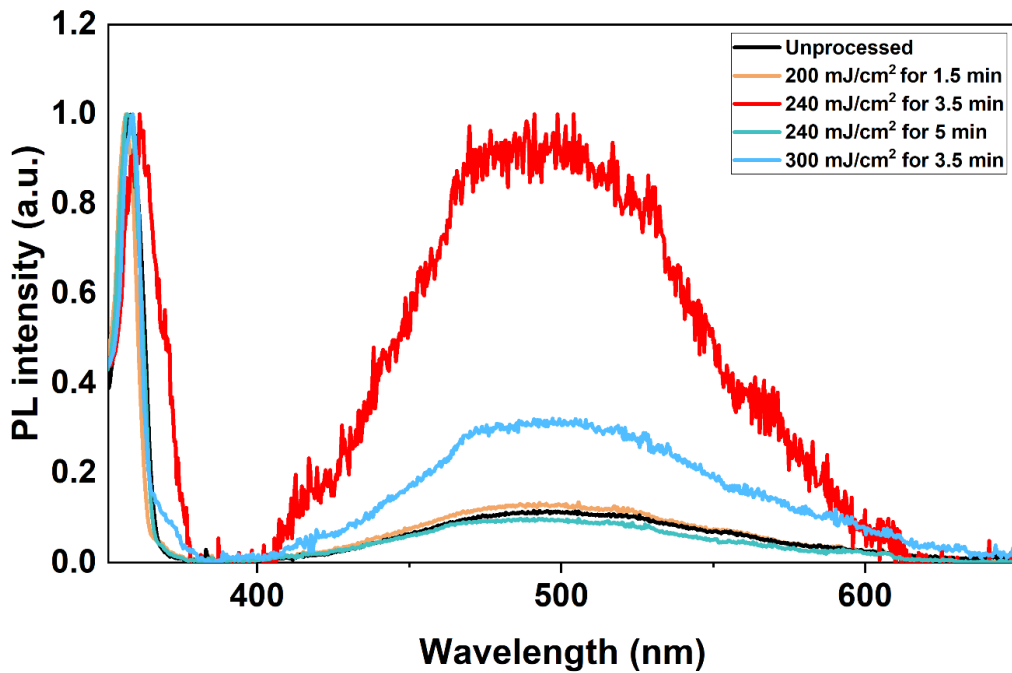


Figure 4.10 Photoluminescence spectra of ZnO NWs samples after laser irradiation under different conditions.

4.4.2 Effect of Laser Irradiation on Temperatures in ZnO NWs

As can be seen in previous section 4.4.1, the heat transferred from laser irradiation to ZnO NWs plays a critical role in determining the effects of laser. Previous studies have shown that quenching ZnO nano-materials after melting results in the production of many bulk defects,^{29,30} indicating that melting in ZnO nano-materials strongly influences the overall defect distribution. Melting in nanostructures is generally not uniform due to the concentration of

thermal energy in “hotspots” during laser irradiation, so it is important to examine the morphology of ZnO NWs after irradiation with different fluences and exposure times to determine the locations where melting has occurred.

Some SEM images of ZnO NWs after irradiation under different conditions are shown in Figure 4.11. It can be seen (Figures 4.11 (a) - (c)) that no significant melting of ZnO NWs occurs after irradiation for up to 5 min. at a fluence of 200 mJ/cm². On the other hand, ZnO NWs show little change in morphology after irradiation at 240 mJ/cm² for 1.5 (Figure 4.11 (d)) and 3.5 min (Figure 4.11 (e)) but extending the exposure time to 5 min generated globules at the end of some ZnO NWs (Figure 4.11 (f)). These globules are formed by localized melting at locations where the ZnO NWs experienced high temperatures excursions during laser irradiation. The delay in the appearance of melting (5 min vs. 3.5 min) indicates that repetitive application of laser pulses eventually raises the overall temperature of the NWs. This occurs because the temperature of individual NWs stacks between laser pulses and cannot reset to 300K.^{319,320} When the laser fluence is increased to ~ 300 mJ/cm², melting occurs even for exposure times as short as 1.5 min and many globules appear in the nanostructure (Figure 4.11 (g)). This happens when the instantaneous peak temperature during one laser pulse exceeds the melting temperature of ZnO NWs. This temperature is likely less than the melting temperature of bulk ZnO due to surface energy effects in such nano-systems.^{321,322} This conclusion is supported by the appearance of extensive melting in the following irradiation for 3.5 (Figure 4.11 (h)) and 5 min (Figure 4.11 (i)). Under these conditions (high fluence and long irradiation time) some of the short nanowires are completely melted while others exhibit significant changes in shape.

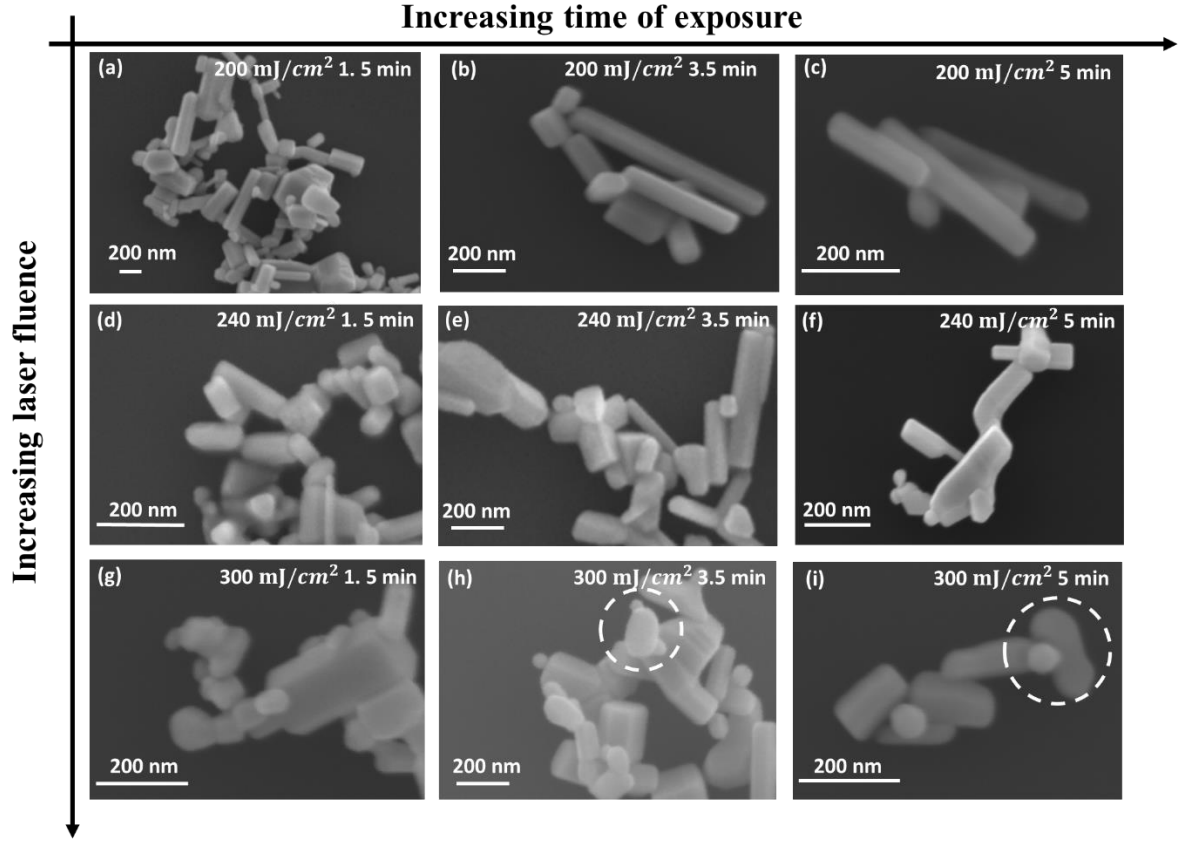


Figure 4.11 SEM pictures of ZnO NWs irradiated for a range of times at different laser fluence. The dashed circles in (h) and (i) indicate regions of significant melting and morphological change. These appear only under conditions of extreme exposure to incident laser radiation.

The time-dependent temperature in an isolated ZnO NW during one laser pulse at fluences of 200, 240 and 300 mJ/cm² is given in Figures 4.12 (a)-(c), respectively. In this approximation, which ignores the effect of aggregation of NWs and any concentration of the electric field in hotspots, the peak temperature within an individual ZnO NW reaches 1667 K at a laser fluence of 200 mJ/cm², 1907 K at a fluence of 240 mJ/cm², and 2248 K at a fluence of 300 mJ/cm² which reaches the melting temperature of bulk ZnO.³²³ Given the assumptions inherent in these simulations, these data can only be used to demonstrate that thermal heating to temperatures close to the melting point within a NW during laser irradiation increases along with incident laser fluence. As noted above, the overall ZnO NW structure will also accumulate heat between laser pulses,^{319,320} so that localized melting may occur at specific locations as seen in Figures 4.11 (h) and (i). The simulation results reflecting such accumulation of heat after multiple laser

pulses are given in Figure 4.13. It is obvious that the temperature in the ZnO NW elevates with the increase of exposure time.

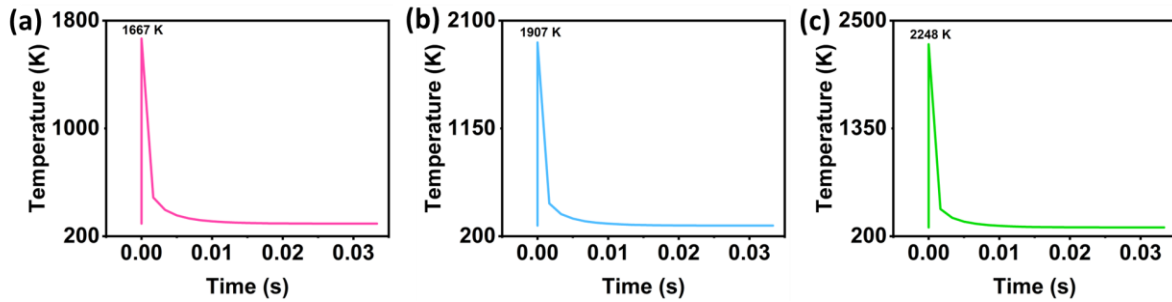


Figure 4.12 Simulated temperature rise in an ZnO NW during one laser pulse at laser fluence (a) 200 mJ/cm² (b) 240 mJ/cm² (c) 300 mJ/cm².

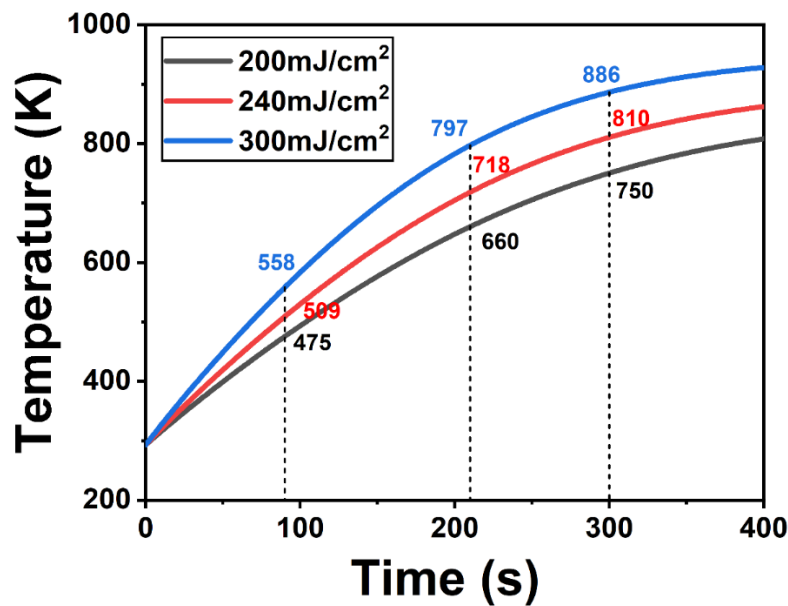


Figure 4.13 Simulated temperature rise in a ZnO NW after multiple laser pulses under a laser fluence of 200 mJ/cm², 240 mJ/cm² and 300 mJ/cm², respectively. The corresponding temperatures at 1.5 min, 3.5 min and 5 min under these conditions were labeled in the figure.

4.4.3 Temperature-Dependent Distribution of Defects

To explicitly investigate the distribution of defects in ZnO NWs irradiated under these conditions, TEM analysis was carried out and the high-resolution TEM (HRTEM) images are given in Figure 4.14. Figure 4.14 (a) shows the HRTEM image of the unprocessed ZnO NW

and it is well-crystallized without noticeable defects. Figure 4.14 (b) shows the HRTEM picture of the ZnO NW after irradiation at 240 mJ/cm^2 for 3.5 min. Many defects (vacancies) are clearly visible (indicated by the circle in the figure), however, their locations are limited to the surface and sub-surface regions. The crystalline structure in the regions deeper than 10 nm remains intact.

The HRTEM image of the ZnO NW irradiated at a fluence of 240 mJ/cm^2 for 5 min is shown in Figure 4.14 (c). A globule similar to the one shown in Figure 4.11 (f) can be seen at the end of the nanowire, which results from the localized melting at this location where the ZnO NW experienced high temperatures during laser irradiation. It is obvious that the defects barely exist and the crystalline structure is well-organized, indicating that the defects were possibly removed through the thermal annealing at this temperature. Figure 4.14 (d) presents the HRTEM image of the ZnO NW after irradiation at 300 mJ/cm^2 for 3.5 min. The slightly rougher surface of the ZnO NW might be the result of melting and re-solidification processes under this condition. The defects are apparent to see and they locate at regions as deep as 17 nm.

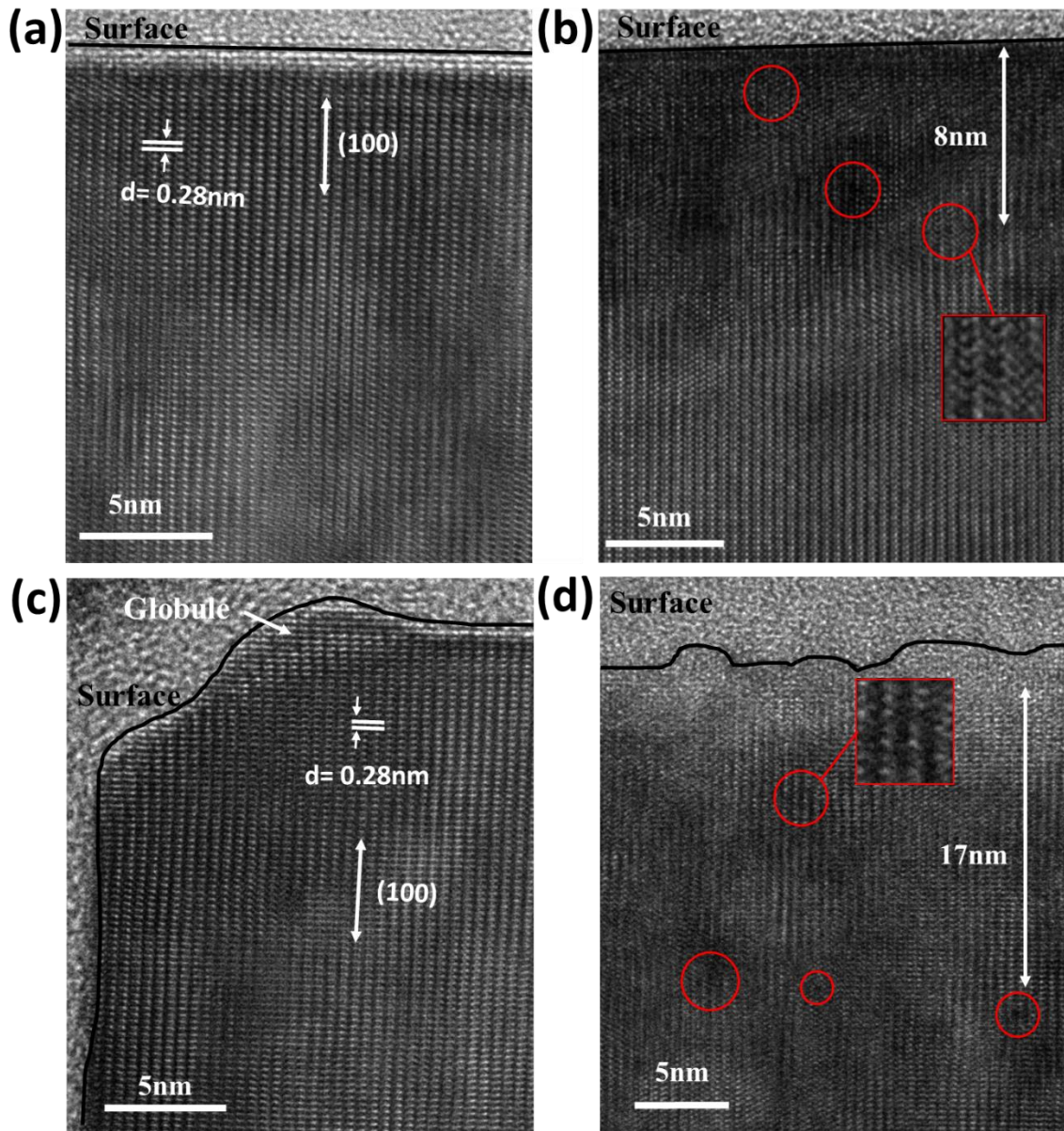


Figure 4.14 HRTEM images of (a) unprocessed ZnO NW, and ZnO NWs irradiated at (b) 240 mJ/cm^2 for 3.5 min, (c) 240 mJ/cm^2 for 5 min, and (d) 300 mJ/cm^2 for 3.5 min. The defects are indicated by the red circles in the figure.

The elemental composition of defects in ZnO NWs and their depth profile are obtained from XPS measurements. In the O 1s region, the major peak centered at $\sim 530.1 \text{ eV}$ corresponds that of oxygen bonded to Zn atoms i.e., lattice oxygen in the wurtzite structure.^{249,324} The second peak with binding energies of $\sim 532 \text{ eV}$ can be deconvoluted to two peaks at $\sim 531.6 \text{ eV}$ and $\sim 532.1 \text{ eV}$ which are associated with oxygen vacancies and chemically adsorbed oxygen

species in the ZnO, respectively.^{324–326} The information in the O1s region as a function of depth in the ZnO samples can be revealed by taking XPS results and etching surface layers repeatedly. As an example, XPS depth profiling results of unprocessed ZnO NW is shown in Figure 4.15 (a). The percentage of different oxygen atomic species at each depth of this unprocessed NW is obtained by calculating the area of each peak (Figure 4.15 (b)) followed by normalization.

Figure 4.16 (a) shows the percentage of oxygen atoms in each bonding environment at different depths in the ZnO after laser irradiation for 1.5 min at 200 mJ/cm². These data show that, while oxygen vacancies are concentrated in the surface (depth = 0 nm) and sub-surface regions (depth = 0.5 – 3 nm), they are also present deeper inside the samples (depth > 6nm). The effect of laser irradiation on the concentration of these oxygen vacancies throughout the samples is clearly evident. The distribution of oxygen vacancies throughout the ZnO samples after laser irradiation can be attributed to the fact that ZnO is only weakly absorbing at the laser wavelength (1064 nm) allowing laser radiation to penetrate inside the sample. Figure 4.16 (b) demonstrates the percentage of each oxygen species at selected depths in the ZnO after laser irradiation for 3.5 min 240 mJ/cm². The fraction of oxygen vacancies in the surface and sub-surface regions (depth < 3 nm) is higher than the corresponding values shown in Figure 4.16 (a). Under this set of laser irradiation conditions, the highest oxygen vacancy concentration (12.04%) appears at a depth of 1.5 nm. This is accompanied by a decrease in oxygen vacancy concentration at depths greater than 3 nm indicating that irradiated by laser under this condition is not effective in generating oxygen vacancies in the bulk region.

Figure 4.16 (c) shows the distribution of oxygen vacancies when ZnO is irradiated for 5 min at a fluence of 240 mJ/cm². It is apparent that the concentration of oxygen vacancies is reduced at all locations while the percentage of lattice oxygen is larger at all depths compared to the percentages recorded in Figures 4.16 (a) and 4.16 (b). This effect is consistent with thermal annealing of oxygen vacancies induced by laser heating. Variations in the concentration of chemisorbed oxygen in these samples reflect changes in the surface activity of ZnO related to the concentration of oxygen vacancies, as it is well known that surface and sub-surface defects facilitate surface adsorption of atmospheric oxygen^{29,327}. Irradiation of ZnO samples

at a higher fluence (300 mJ/cm^2) dramatically increases the concentration of oxygen vacancy centers at depths up to 24 nm indicating that more bulk oxygen vacancies were generated after laser irradiation under these conditions and that these defects survive annealing (Figure 4.16 (d)).

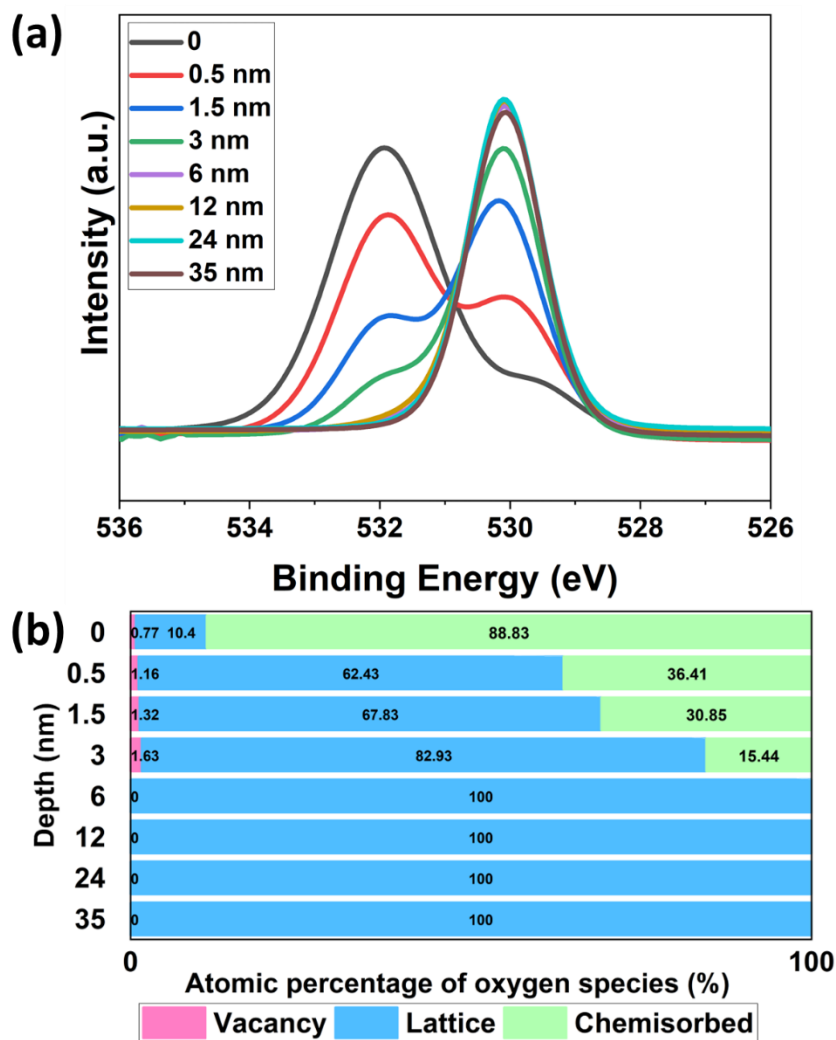


Figure 4.15 (a) XPS results of the unprocessed ZnO at various depth. (b) Depth profile showing the percentage concentration of oxygen species at different depths.

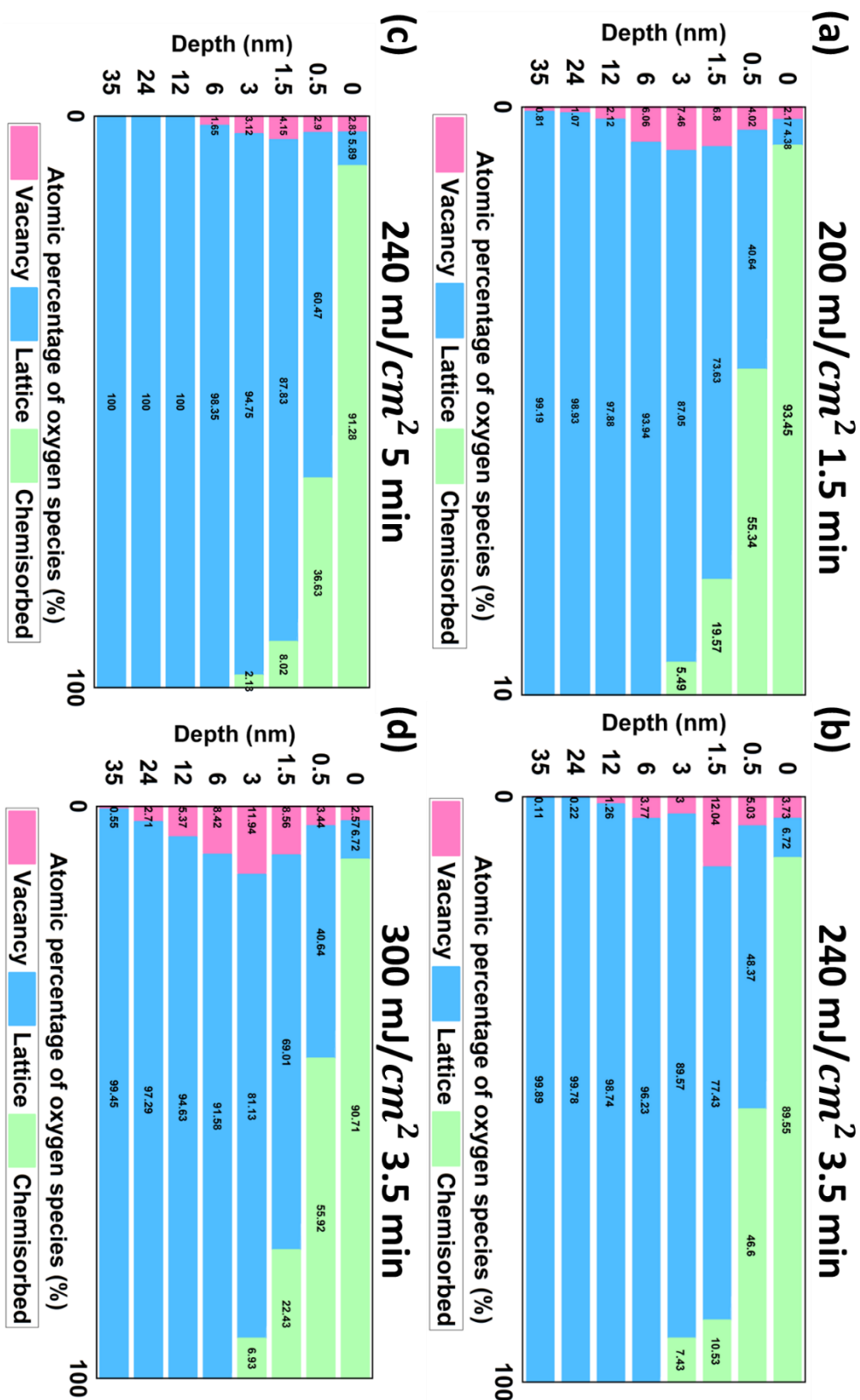


Figure 4.16 XPS depth profiling showing the percentage concentration of oxygen species at different depths in ZnO samples irradiated at (a) 200 mJ/cm² for 1.5 min, (b) 240 mJ/cm² for 3.5 min (c) 240 mJ/cm² for 5 min and (d) 300 mJ/cm² for 3.5 min.

4.4.4 Regimes of Laser Processing vs. Arrangements of Defects

Based on results shown in sections 4.4.1 and 4.4.3, a heuristic mechanism is developed to trace the effect of laser irradiation on the production and annealing of defects in ZnO. The effect of laser irradiation at different fluence and exposure times can be pictured as shown schematically in Figure 4.17. In the low excitation regime, the lattice temperature does not rise significantly (i.e., ZnO NWs processed at 200 mJ/cm^2 for 1.5 mins), intrinsic and laser-induced defect centers have limited mobility so that oxygen vacancies are distributed throughout the sample, both in the bulk and in the surface regions. When laser excitation is sufficient to exceed some thermal threshold such as the migration energy barriers of ZnO ($\sim 1.7 \text{ eV}$),¹²⁵ either through an increase in incident laser fluence or by prolonging the exposure time, migration and recombination of defects is facilitated via an Arrhenius activated reaction. The preferential migration of lattice defects toward the surface in ZnO NWs under these conditions is indicated by the study of Deng et al.¹²⁵ This process can be associated with the second processing regime in which surface defects are dominant (i.e. ZnO irradiated at 240 mJ/cm^2 for 3.5 mins). If laser irradiation then continues for a longer time (e.g. 5 min), the temperature in the ZnO rises to the point at which annealing removes both surface and bulk defects. The last processing regime occurs when the temperature reaches or surpasses the melting point of ZnO NWs (i.e., irradiated at 300 mJ/cm^2 for 3.5 min). In this case, the lattice is subject to localized softening or melting causing amorphization and a reduction in short range order,^{328,329} which causes redistribution of defects. Because of the rapid cooling that occurs following excitation with ns laser pulses, defects can be frozen in both the bulk and also the surface of the NWs. A summary of these effects, relating laser fluence and exposure time to defect distribution, is given in Figure 4.18.

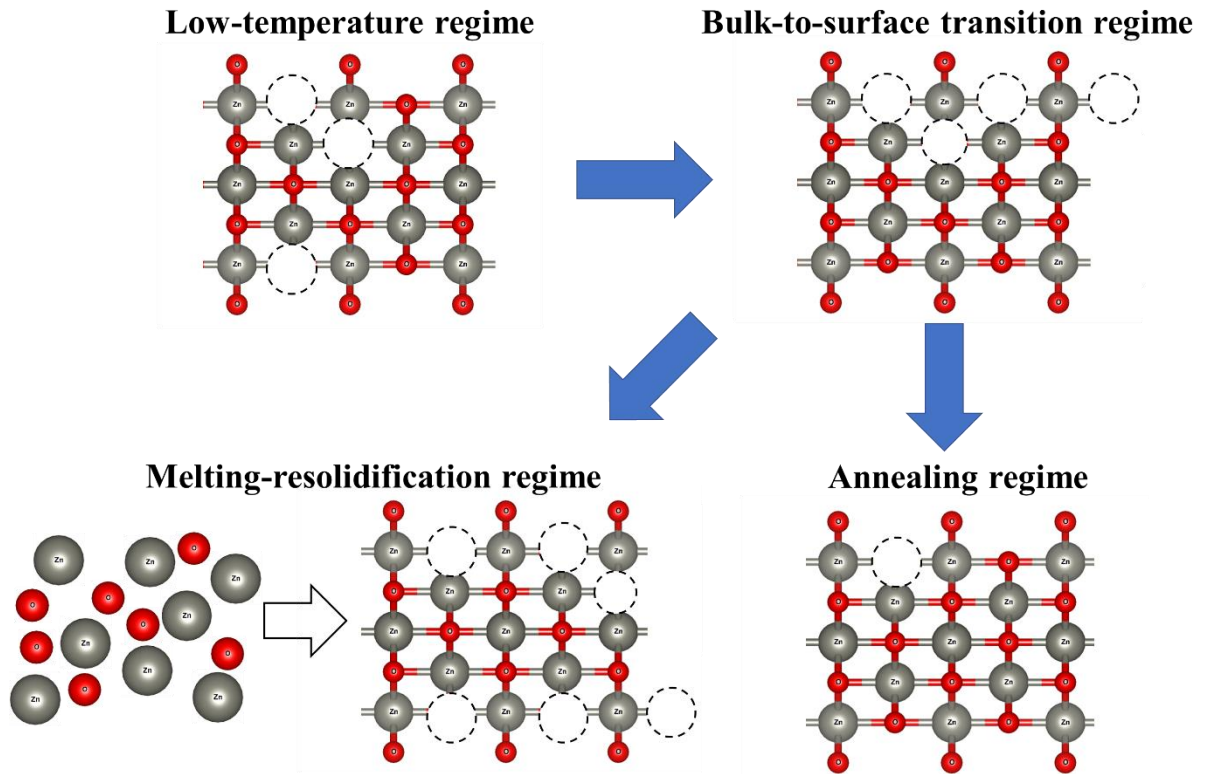


Figure 4.17 The distribution of defects with respect to different regimes.

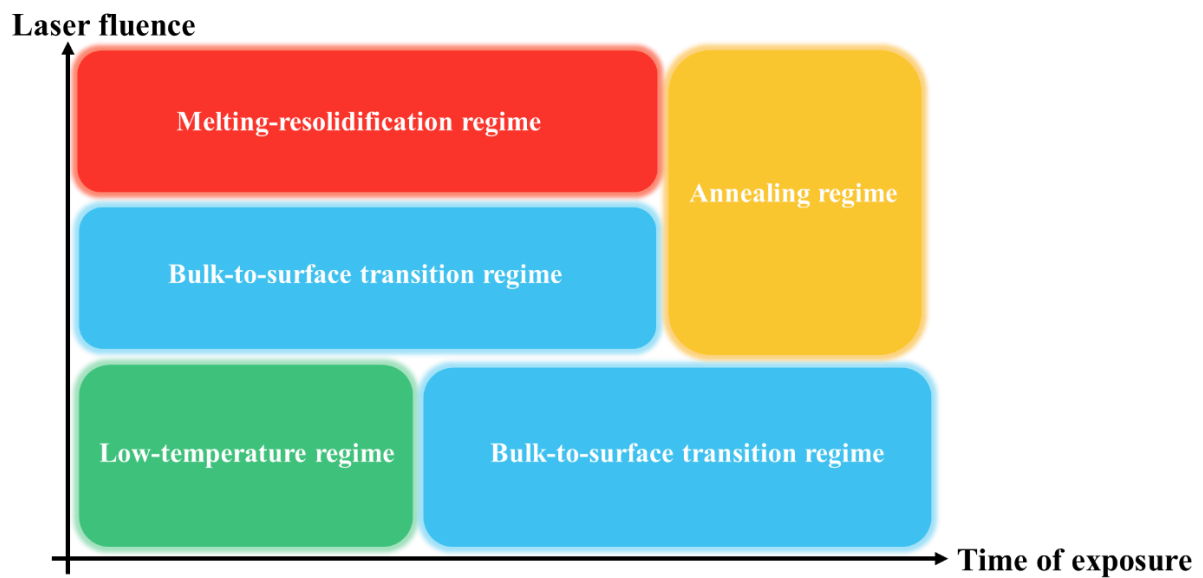


Figure 4.18 Correlation between laser parameters and the identified processing regimes for ZnO NW samples.

4.4.5 Photodegradation with Laser-Processed ZnO NWs

The large database on the properties of the dye RhB makes this material ideal for studying the mechanism of the photo-degradation of RhB in the presence of ZnO nano-materials.^{330,331} Upon illumination with broadband light, photo-excited electrons migrate to the surface and combine with adsorbed oxygen to form the anion O_2^- , while photo-generated holes will react with H_2O or OH^- to produce the $OH^\cdot$ radical. These species are then active in the degradation of RhB dye molecules forming a variety of chemical products. The lifetime of the electron-holes pairs, as well as their proximity to the surface, is critical in determining the overall efficiency of the photo-degradation reaction. The formation of oxygen vacancies during laser irradiation introduces additional energy levels into the bandgap thereby enhancing the production of photo-generated charge carriers that assist in the degradation process.²⁶² However, not all of the defects generated by laser processing assist in photocatalysis, as defect centers deeper in the ZnO NWs can act as traps for photogenerated carriers.¹²⁶ Given this limitation, it is expected that only defects in the surface or near-surface regions will provide the charge carriers that result in the formation of $OH^\cdot$ radicals and O_2^- anions at the surface. As a result, efforts have been made to adjust the defect concentration within the surface region relative to that of defects in the bulk region to obtain optimized performance in photocatalytic applications.^{332,333}

As can be seen in the sections above, the concentration and distribution of surface and bulk oxygen vacancies in ZnO NWs is temperature-dependent and can be controlled by laser irradiation parameters. The effect of laser irradiation on the photocatalytic properties of ZnO NWs has been evaluated by dispersing laser processed samples in 30 ml of a 5 ppm RhB solution. The photo-degradation of RhB can be ascertained by the effect on the visible absorption spectrum of this solution. Figure 4.19 (a) – (c) shows this effect in RhB: ZnO NWs solutions containing unprocessed ZnO NWs, ZnO NWs irradiated at 240 mJ/cm^2 for 3.5 min and ZnO NWs processed at 300 mJ/cm^2 for 3.5 min. Figure 4.19 (d) shows the decay of dye concentration vs. time for each of these laser processing protocols in terms of concentration. In this figure C_0 is the initial concentration of RhB and $C(t)$ is the concentration at time, t . It can

be seen that the rate of photocatalytic activity of ZnO NWs irradiated at 240 mJ/cm^2 is greater than that occurring with unprocessed nanorods, indicating that the presence of surface oxygen vacancies enhances photodegradation. Conversely, ZnO NWs irradiated for 3.5 min at 300 mJ/cm^2 were less effective in promoting the photodegradation of RhB presumably because this set of irradiation conditions increases the concentration of oxygen vacancies within the ZnO NWs that act to trap photogenerated charge carriers.

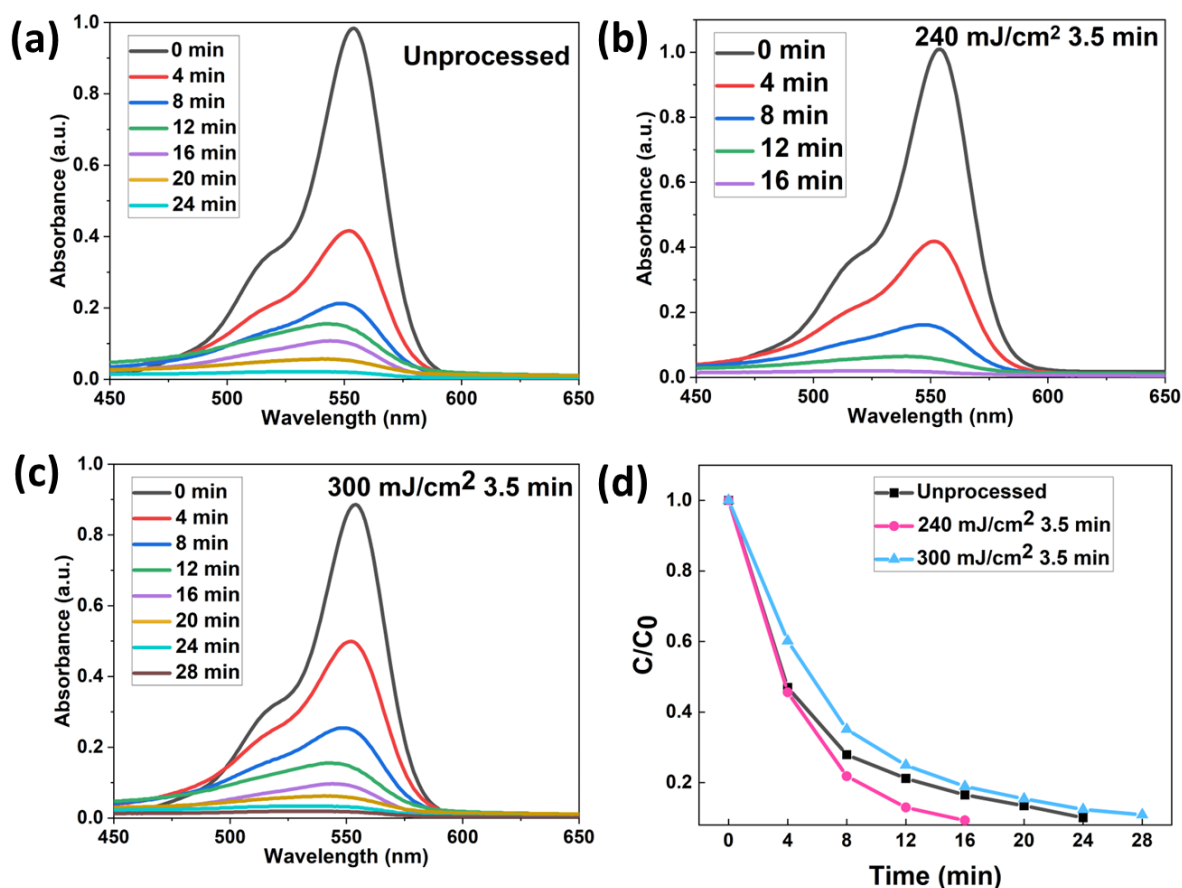


Figure 4.19 Absorption spectra of RhB dye solution containing (a) unprocessed ZnO NWs, (b) ZnO NWs irradiated at 240 mJ/cm^2 for 3.5 min, (c) irradiated at 300 mJ/cm^2 for 3.5 min. (d) Photocatalytic degradation efficiency for different samples.

4.5 Summary

In this Chapter, it was demonstrated that the distribution of defects can be tailored in both p-type CuO and n-type ZnO NWs. Irradiation with moderate ns pulses produces V_O in CuO NWs, which is confirmed by XPS results in O 1s and Cu 2p regions as well as Raman spectra. The XPS results showed that the oxygen adsorption is improved after laser irradiation, which is also reflected in the Raman spectrum as the rise of the peak associated with peroxide and superoxide species adsorbed on the surface of CuO NWs. Both of these features indicate that laser-induced V_O majorly resides at the surface and sub-surface regions in CuO NWs. This conclusion is further supported by electrochemical measurements. It was found that laser-induced V_O did not increase the slope of the Mott-Schottky curve as expected. On the contrary, the slope was decreased which can be attributed to the improved adsorption of the electrolyte on the nanowire surfaces due to the existence of surface V_O . The reduced charge transfer resistance revealed in the Nyquist plot also suggested the appearance of V_O in the surface regions. To explore the efficacy of this laser processing approach, CuO NWs are used as the catalyst for non-enzymatic glucose detection and amperometry was implemented. It was found that the presence of laser-induced surface V_O increased the current response, suggesting better glucose sensitivity.

To maneuver the distribution of defects, laser irradiation of ZnO NWs under controlled conditions was investigated. Control over the composition and distribution of lattice defect centers was obtained within a parameter space consisting of laser fluence and exposure time. It was shown that ns laser irradiation of ZnO NW samples in air produces discrete temperature-dependent distributions of oxygen vacancies in surface and bulk sites as well as changes in morphology. Using standard analytical techniques, we have determined that these changes arise from a combination of the photochemical generation of defect centers together with thermal heating induced by a series of overlapping laser pulses. Four distinctive regimes containing different ratios of surface-to-bulk oxygen vacancies have been identified in irradiated samples offering the possibility of laser engineering ZnO NW materials to enhance specific material

properties. As an example of this capability, the photo-degradation of RhB dye was carried out using laser-processed ZnO NWs as the catalyst. A laser processing window was identified that leads to substantial improvements in catalytic activity for the photodegradation of RhB in the presence of ZnO NWs. Overall, it can be concluded that laser irradiation with moderate fluence and exposure time majorly gives rise to surface defects. It requires extra heat to generate bulk defects and migrate surface defects to bulk regions, which indicates that extreme irradiation conditions are often needed in this case.

In Chapter 3 and Chapter 4, the modulation of defects with respect to their concentration and distribution were achieved. The results showed that laser-induced defects majorly reside on the surface of the metal-oxide nano-materials and the conductivity of these materials can be readily tailored through tuning the concentration of defects. Hence, it raised an intriguing question whether these defects can dope the metal-oxide nano-materials. Doping with extrinsic dopants is often constrained by the solubility of the dopant atoms and the compensation caused by intrinsic defects. As a result, doping with intrinsic defects is a compelling solution and received extensive investigations. It is now broadly-accepted that oxygen vacancies and metal interstitials act as electron donors which leads to n-type conductivity. Conversely, cationic vacancies and oxygen interstitials are often considered as electron acceptors that give rise to p-type conductivity. It is therefore necessary to unravel the types of defects produced by laser irradiation before they can be utilized for doping. In the following chapter, the objective is to manipulate the type of defects generated by laser irradiation and explore the feasibility of using them to dope metal-oxide nano-materials.

Chapter 5 Modifying the Type of Defects in Cu₂O and ZnO Thin Films

5.1 Introduction

Doping the metal oxides to meet the demand of vast applications emerged as one of the prevailing strategies.^{326,334,335} For instance, group III elements are often used to substitute Zn atoms to enhance the n-type conductivities in ZnO^{218,336} while Na-doped CuO exhibit improved p-type conductivities^{337,338} and the methods to dope metal-oxide nano-materials to enhance their normal conduction type have been widely demonstrated both during the synthesis and through post-treatments.^{339–342} On contrary, doping the metal-oxide nano-materials to achieve abnormal conduction properties still present a great challenge. For example, tremendous efforts were made to use group I and group V elements as the dopants to achieve p-type conductivity in ZnO but only limited success were achieved due to the issues such as the low solubility of extrinsic dopants and the compensation caused by the intrinsic defects.^{74,343,344} Though these pioneering attempts did not succeed, they have revealed that the native defects play a central role in determining the conduction type of the metal-oxide nano-materials.^{73,345,346} For example, Huang et al. demonstrated that V_{zn} must be coexisted so that Li dopants can transform the conductivity of ZnO to be p-type.³⁴⁷

Typical native defects in metal-oxide nano-materials are vacancies, interstitials and antisites,^{134,249,348} their effects on the conduction of metal-oxide nano-materials have long been debated. For instance, many early theoretical investigations perceived that V_O dominate among all donor-like defects in ZnO.^{83,86} However, they predicted that the V_O in ZnO are often in the neutral state thus can hardly be ionized to contribute to the n-type conductivity in ZnO. A later study reported by Liu et al. has proven experimentally that the dominant V_O in ZnO are actually doubly-ionized, which indicates that the V_O is indeed the origin of n-type conductivity in ZnO.⁷² Though some controversial issues still exist, it is now broadly accepted that oxygen vacancies and cation interstitials are the major sources of electron donors that

results in the n-type conductivity in metal-oxide nano-materials. On opposite, cationic deficiencies and oxygen interstitials are often considered as the origin of p-type conductivity in metal-oxide nano-materials since they generate shallow acceptor levels. As a result, producing targeted defects to achieve the desired type of conduction in metal-oxide nano-materials became a compelling resolution.

In this chapter, ns laser pulses are adopted to tailor the vacancy defects in both p-type Cu_2O and n-type ZnO thin films emersed in diverse gaseous environment to produce the desired type of vacancies which results in corresponding doping in these thin films. Cu_2O was selected over CuO in this study because n-type doping with V_O has been reported in Cu_2O which can be used as references. It was found that irradiating in O_2 gas leads to the generation of V_{Cu} in Cu_2O and V_{Zn} in ZnO thin films, which improves the p-type conductivity in these films. On the other hand, irradiating in argon (Ar) gas results in the production of V_O in both Cu_2O as well as ZnO thin films and n-type doping can be achieved. As an example of the efficacy of this laser-engineering technique, this process was utilized to fabricate both p-channel and n-channel TFTs and they were connected to realize complementary switching inverters.

5.2 Experimental Section

5.2.1 Thin Film Deposition and Device Fabrication

The Cu_2O thin films were sputtered (AJA ORION) on the surface of 5mm-by-5mm silicon substrates for the examination of XPS. They were sputtered on 2cm-by-2cm silicon-on-glass (SOI) substrates for the fabrication of TFTs. The sputtering was achieved at room temperature with a continuous supplying of mixed gas whose ratio is $\text{Ar}/\text{O}_2 = 12/0.5$. The time of sputtering is 10 mins for Cu_2O to reach a film thickness of ~ 25 nm. The ZnO thin films were sputtered using the same apparatus. The sputtering was achieved at room temperature with a continuous supplying of mixed gas whose ratio is $\text{Ar}/\text{O}_2 = 12/0.5$. The time of sputtering is 20 mins for ZnO to reach a film thickness of ~ 25 nm.

The fabrication process flow of electrodes used for the electrical measurements of p-n junctions characteristics is shown in Figure 5.1 (a). The Cu_2O thin film was first sputtered on

the SOI substrate to reach a thickness of 25 nm. The first electrode comprising Au and titanium (Ti) was then deposited by thermal evaporation. The patterns were defined by the laser direct writing (Heidelberg-MLA) and realized by a standard lift-off process. The electrode has a thickness of 100nm (90nm Au + 10nm Ti), a width of 50 μm and a length of 100 μm . The photoresist was then spin-coated again to define the patterns of the second layer of 25 nm Cu_2O thin film, which is deposited subsequently. Before the lift-off, the sample emerged in either O_2 or Ar gas was then irradiated by laser to dope the thin film with vacancies. The photoresist has a thickness of over 4 μm , which we believe is enough to attenuate the laser irradiation so that the areas beneath the photoresists remained unexposed. The photoresists were then removed by the standard lift-off process. Subsequently, the second electrode was deposited in parallel to the first one by thermal evaporation and the distance between the two electrodes is 5 μm . The dimension of these electrodes remained the same. The fabrication process flow of the electrodes used for the I-V characteristics and resistive switching measurements is displayed in Figure 5.1 (b). The Cu_2O thin film was first sputtered on the SOI substrate with a thickness of 25 nm. The coupled electrodes comprising Au and Ti was then deposited in parallel by thermal evaporation which both have a thickness of 100nm (90nm Au + 10nm Ti), a width of 50 μm and a length of 100 μm . The uncovered surface of the Cu_2O thin film between the electrodes (5 $\mu\text{m} \times 100 \mu\text{m}$) was then irradiated by laser irradiation under various conditions described previously. The structures used for the measurements in ZnO thin films repeated these fabrication steps by replacing Cu_2O with ZnO.

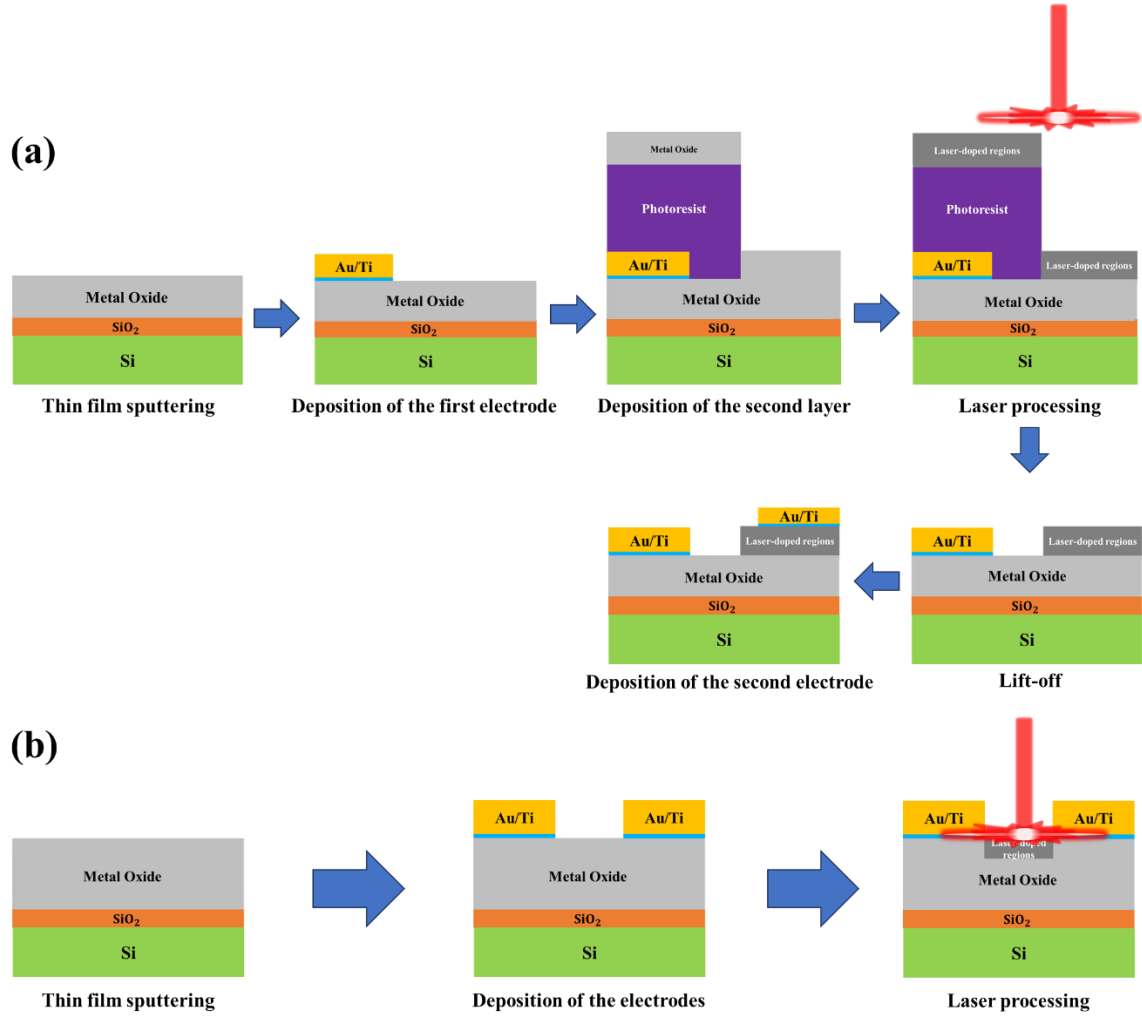


Figure 5.1 (a) The fabrication process flow of the electrodes used for the p-n junction I-V characteristics. (b) The fabrication process flow of the electrodes used for the I-V curve and resistive switching measurements.

The fabrication process flow of metal oxide TFTs is given in Figure 5.2. The metal oxide thin film (either Cu_2O or ZnO) was first sputtered on the SOI substrate to reach a thickness of 25 nm. The thin films were then irradiated by laser irradiation under various conditions to achieve desired doping in the surface and sub-surface areas in the thin films. In Cu_2O thin films, the films were irradiated at 180 mJ/cm^2 for 3.5 min while immersed in O_2 to produce V_{Cu} so that p-type regions can be obtained. On the other hand, immersing the films in Ar while irradiated at 180 mJ/cm^2 for 3.5 min generates V_{O} to dope the regions to be n-type. In ZnO thin films, the films were irradiated at 480 mJ/cm^2 for 3.5 min while immersed in O_2 to produce

V_{Zn} so that p-type regions can be obtained and the films were immersed in Ar while irradiated at 480 mJ/cm^2 for 3.5 min to create V_O . The source and drain electrodes comprising a combination of Au and Ti were then deposited by thermal evaporation. The patterns were defined by the laser direct writing (Heidelberg-MLA) and realized via a standard lift-off process. The electrodes have a thickness of 100nm (90nm Au + 10nm Ti), a width of $50 \mu\text{m}$ and a length of $100 \mu\text{m}$. The channel length of the TFT, which is defined as the distance between source and drain, is $5 \mu\text{m}$ and the channel width is $100 \mu\text{m}$. The gate dielectric (200nm silicon dioxide) was then patterned and deposited in the regions between the source and drain, followed by the subsequent deposition of the gate electrode (280 nm Au + 50 nm Ti). The TFTs with complementary channels were separated by 4 mm and they were connected by Au/Ti wires (280 nm Au + 50 nm Ti) to establish the inverter circuits.

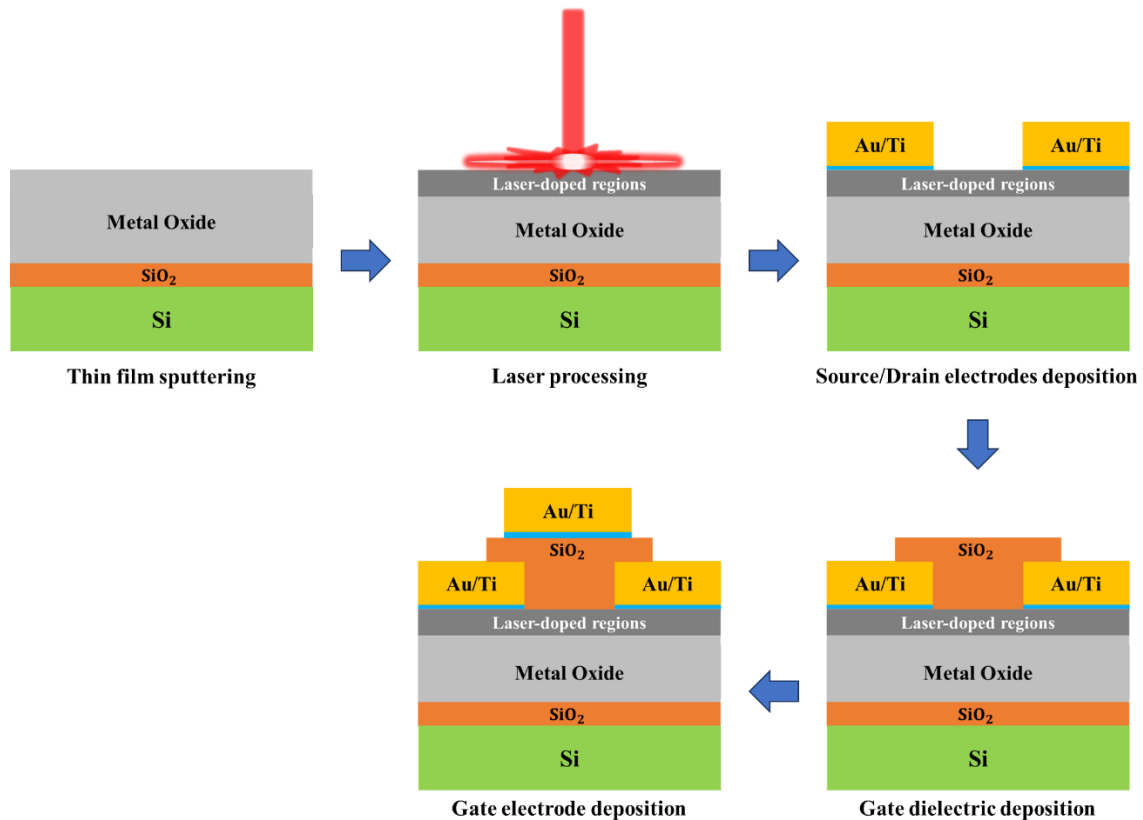


Figure 5.2 The fabrication process flow of the TFTs.

5.2.2 Laser Irradiation Set-Up

A Nd: YAG laser with a pulse duration of 4 ns and a wavelength of 1064 nm operating at 30 Hz was used for the irradiation. The diameter of the beam on the sample surface was ~ 2.5 mm. The apparatus and the configuration are identical to the one shown in Chapter 3.2.3. Laser fluence was typically 180 mJ/cm^2 for Cu_2O while the fluence for the irradiation of ZnO was 480 mJ/cm^2 . The time of exposure for both thin films was 3.5 min. The thin films were placed in a 3D-printed chamber with a quartz glass window (Figure 4.2) to facilitate laser irradiation in a controlled atmosphere. The ambient environment was controlled by supplying a continuous flow of either high purity (99.9%, 6.8 kPa, Praxair) O_2 or Ar gas during the irradiation.

5.2.3 Electrochemical Measurements

To fabricate the electrodes for electrochemical measurements, 100nm Cu_2O thin films were sputtered on both the front and the back side of the 1cm-by-3 cm copper foils first and the electrochemical measurements were then conducted using a standard three-electrode configuration. As-prepared foils with Cu_2O films sputtered on the surface were used as the working electrodes, while a platinum electrode was used as the counter electrode and Ag/AgCl was used as the reference electrode. Electrochemical impedance spectroscopy (EIS) was performed using a CH Instrument 660 electrochemical workstation with 50 ml of 0.1 M NaOH aqueous solution and it was carried out with the potential ranging from -0.5V to 0.6V with an increase rate of 0.05 V at a frequency of 1000 Hz. All measurements were carried out both before and after laser irradiation for each sample in a dark environment at room temperature.

5.2.4 Characterization Methods for Vacancies

Optical properties of samples before and after laser irradiation were determined from the diffuse reflectance spectroscopy (DRS, Shimadzu UV-2501). The elemental composition and chemical bonding in the thin film samples was obtained from XPS (Thermo VG Microlab 350). Baseline characterization of all parameters was carried out for each sample before laser irradiation.

5.3 Vacancies in Cu₂O Thin Films

5.3.1 Identification of Vacancies

The nature of defects in Cu₂O can be readily obtained from optical spectra, as defect states introduce energy levels between the valence and conduction bands^{109,250}. Absorption features associated with these defect states are characterized by DRS and the diffuse reflection data from DRS has been converted into absorption using Kubelka-Munk equation.³⁰⁸ Figure 5.3 (a) shows the absorption spectrum of Cu₂O thin films before and after laser irradiation at 180 mJ/cm² under various ambient atmosphere. As expected, absorption spectra of the two unprocessed samples S1 and S2 are essentially identical (Figure 5.3 (a)). However, a noticeable increase in absorption in the region between 500 nm and 900 nm can be observed in sample S1 after laser irradiation in O₂. This increase can be attributed to additional V_{Cu} centers produced during laser irradiation. In contrast, the absorption spectrum of the Cu₂O thin film on S2 has a slight blue shift and the absorption is reduced in the region between 500 nm and 600 nm after laser irradiation in Ar, which might be the outcome of the existence of additional V_O .

To explicitly examine the effect of laser irradiation on the direct bandgap in these Cu₂O thin films, the absorption spectra are converted to the Tauc plot.^{309,349,350} Tauc plots for unprocessed and laser irradiated Cu₂O thin film samples are shown in Figures 5.3 (b). Linear extrapolation indicates that the bandgap in unprocessed Cu₂O thin films (samples S1 and S2) is ~ 2.03 eV, which is close to the values reported previously.^{193,351,352} The introduction of additional V_{Cu} in Cu₂O thin film through laser processing in O₂ narrows the bandgap to ~1.9 eV, while laser processing in Ar and the presence of additional V_O has slightly widened the bandgap to ~2.11 eV. Such widening of the bandgap due to the V_O in Cu₂O has been reported previously. Anand et al. demonstrated the effects of V_O in Cu₂O theoretically using the DFT with the help of standard GGA.³⁵³ In their calculation, they found that the increasement of V_O in the Cu₂O supercell will shift the absorption peak and increase the bandgap energy. A similar result has been reported by Li et al.³⁵⁴ They determined the energy level of V_O in the nitrogen-doped Cu₂O and revealed that the formation of V_O will result in the bandgap widening.

Nakano et al. measured the optical absorption of Cu₂O doped with nitrogen and V_O experimentally and also confirmed the same increase in the bandgap energy.³⁵⁵

The presence of defects in Cu₂O thin film can also be characterized by the XPS spectrum in the O 1s and Cu 2p regions. The O 1s peak can be deconvoluted into two major components: a peak associated with lattice oxygen with binding energy ~ 530.6 eV, (O_L) and another peak associated with oxygen adsorptions (O_{ads}), with a binding energy ~ 532.4 eV. Many previous studies believed that the adsorption of oxygen is also strongly affected by the V_O thus this peak also indicates the concentration of V_O in Cu₂O.^{158,356} O 1s XPS spectra for Cu₂O thin film before and after laser irradiation are shown Figure 5.3 (c) – (f). Figures 5.3 (c) and (e) show these data for two as-prepared Cu₂O thin film samples, S1 and S2 before laser processing. The similarity of the percentage area of each oxygen species in both spectra indicates that samples are consistent within the same batch. Figure 5.3 (d) shows the O 1s spectrum of S1 after laser irradiation in Ar gas. This shows that the peak intensity of the O_{ads} component rises dramatically while the ratio of the areas of the O_{ads} and O_L features is seen to increase from 2.3 to 5.6, indicating that the concentration of V_O is enhanced after laser irradiation under this condition. Figure 5.3 (f) shows O 1s spectra for S2 after laser irradiation in O_2 gas. In this case, the intensity of the O_{ads} peak is slightly reduced and the ratio of the areas of the O_{ads} and O_L peaks decreases from 2.3 to 2.0. This indicates that the concentration of lattice oxygen has been enhanced. Previous studies have shown that the formation of V_{Cu} results in the appearance of additional lattice oxygen and an increase in voids in an oxygen-rich environment, these changes in the O1s spectrum in sample S2 are a clear indication of the production of V_{Cu} .

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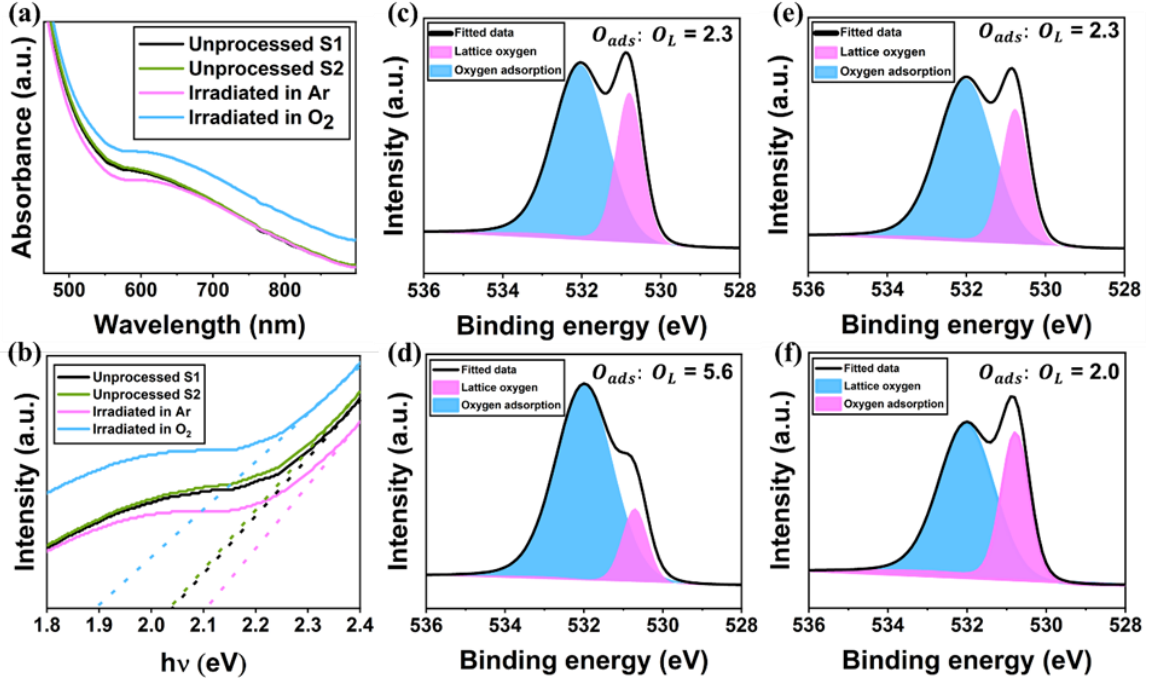


Figure 5.3 (a) Absorption spectra of Cu₂O thin films before and after laser irradiation in Ar and O₂ gas. (b) Corresponding Tauc plots calculated from the absorbance in figure (a). High-resolution XPS results in the O 1s region of (c) unprocessed Cu₂O thin film S1, (e) unprocessed Cu₂O thin film S2, (d) Cu₂O thin film after laser irradiation in Ar gas, (f) Cu₂O thin film after laser irradiation in O₂ gas.

5.3.2 Doping Cu₂O Films with V_{Cu} and V_O

After the identification of defects produced by laser irradiation, it is critical to figure out whether these laser-induced defects can be exploited for doping in the Cu₂O thin film, especially in the case of abnormal conduction type caused by V_O . One of the most straightforward ways to verify the type of doping is through the fabrication of p-n junction diode as the p-n junction diode is able to rectify the electric current and generate unique current-voltage (I-V) features.^{358,359} Figure 5.4 (a) shows the I-V characteristics of unprocessed Cu₂O thin films as well as thin films after irradiation, and a schematic of the configuration for the electrical measurement is also provided. After the deposition of the first Au electrode, a second layer of Cu₂O was sputtered. The photoresist was exploited as the mask so that only the second layer of Cu₂O was irradiated. The fabrication details are displayed in section 5.2.1.

It can be seen from the Figure 5.4 (a) that the two unprocessed samples exhibit almost identical linear I-V characteristics, indicating the good repeatability of the measurement and minimizing the dispute about the changes originated from the configuration of the electrical measurement. When the second layer of Cu_2O was irradiated in Ar gas, the I-V characteristics changed dramatically. Instead of being linear, the current was reduced first, reached a sub-linear region at ~ 2.5 V and increases linearly again at the voltage above 4 V in the forward bias direction. On the other hand, the current remained minimal until it reached an abrupt increase at ~ -4.5 V in the reverse bias direction, which is often recognized as the electrical breakdown of p-n junction diode. It is therefore reasonable to believe that the regions irradiated under Ar gas were doped with V_O to achieve an n-type conductivity. On the other hand, the measured current is larger than the unprocessed samples, suggesting an enhanced p-type conductivity attributed to the abundance of V_{Cu} in the second layer of Cu_2O after laser irradiation in O_2 gas.

To further study the roles of defects on the electrical properties of the Cu_2O thin film, the I-V characteristics were also measured in the case that the two electrodes were directly deposited on the film. Figure 5.4 (b) shows the I-V characteristics in this case with a schematic for the electrical measurement. The unprocessed samples again showed good consistency and can be used as references. Irradiating the regions between the electrodes in O_2 gas has enhanced the current amplitude, indicating that V_{Cu} generated by laser irradiation increased the major carrier density. On opposite, a significant reduction in the current amplitude can be seen when the regions between the electrodes was irradiated in Ar gas. Such decrease in the current often indicates the reduction in the available carrier in the system, either due to the removal of carriers caused by the annealing effect of laser or due to the compensation of the minor carrier. Since the I-V results of the sample irradiated in O_2 gas did not indicate thermal annealing, it is assumed that changing the ambient atmosphere from O_2 gas to Ar gas will not result in significant changes of heat to cause thermal annealing. Therefore, it is believed that the reduction of the current amplitude after laser irradiation in Ar gas is majorly due to laser-induced V_O which are electron donors that compensate the major carriers (holes) in the Cu_2O thin film.

Resistive switching in metal-oxide nano-materials is another aspect of the electrical characteristics that has been the subject of many recent studies. It is now generally accepted that resistive switching in metal oxides is due to the formation of internal conductive filaments. In this model, when a “SET” voltage is applied, charged defects in the metal oxide assemble to form conductive filaments. This gives rise to the low resistance state (LRS). Subsequent application of a reverse bias (the “RESET” voltage) can “erase” these conductive filaments and return the material back to a high resistance state (HRS). To study the influence of ns laser irradiation on the resistive switching behavior of the Cu_2O thin film, I-V characteristics have been obtained using a cyclic voltage sweep. Figure 5.4 (c) shows the current response during a voltage cycle $0\text{V} \rightarrow 40\text{V} \rightarrow -40\text{V} \rightarrow 0\text{V}$ before and after laser irradiation. The configuration was kept the same as indicated by the inset in Figure 5.4 (b). The resulting I-V curves exhibit the hysteresis typically seen in resistive switching devices. After laser irradiation in O_2 gas, the current increased significantly in both bias directions as an outcome of more V_{Cu} in the Cu_2O thin film. The ON/OFF ratio is significantly increased by laser processing, which results from the increased concentration of major carriers. On opposite, irradiating in Ar gas did not only cause the reduction of the current but also eliminate the difference between the HRS and LRS. We attribute this phenomenon to the generation of V_O under this Ar gas irradiation condition, which act as electron donors to recombine with the holes in the thin film thus jeopardizing the conductive filaments.

Mott-Schottky measurements (Figure 5.4 (d)) have also been used to study the electrochemical properties of Cu_2O thin film samples containing laser induced vacancies. The carrier concentration N_A in Cu_2O can be calculated from the measured capacitance C using the Mott-Schottky equation given in Eq. (4.3). The carrier concentration N_A is then inversely proportional to the slope of the Mott-Schottky curve. The negative slopes of the plots in Figure 5.4 (d) indicate that p-type conductivity is dominant, with holes as the major carriers in these Cu_2O thin film. The Mott-Schottky curves for the unprocessed Cu_2O thin film samples S1 and S2 are almost identical.

As laser irradiation of Cu_2O thin film in Ar gas increases the concentration of V_{O} centers which is known to act as hole traps, the slope of the Mott-Schottky curve should increase relative to that for unprocessed samples. However, the slope of the Mott-Schottky curve for Cu_2O NWs irradiated in Ar actually decreased as shown by the pink curve in Figure 5.4 (d). We attribute this reduction in slope to the fact that laser irradiation can modify the surface structure or chemistry of Cu_2O thin film, increasing the chemical adsorption of the electrolyte on the surface of the film. Furthermore, the slope of the curve became positive at region close to -0.5 V, forming a distinct inverse V-shape. Since the positive slope of the Mott-Schottky curve often indicate the n-type conductivity, many previous studies suggested that the existence of such V-shape can be attributed to the p-n junction in the thin film.^{360,361} The blue Mott-Schottky curve obtained for sample S2 after the irradiation in O_2 gas has a much smaller slope which indicates that the introduction of additional V_{Cu} centers leads to enhanced p-type conductivity.

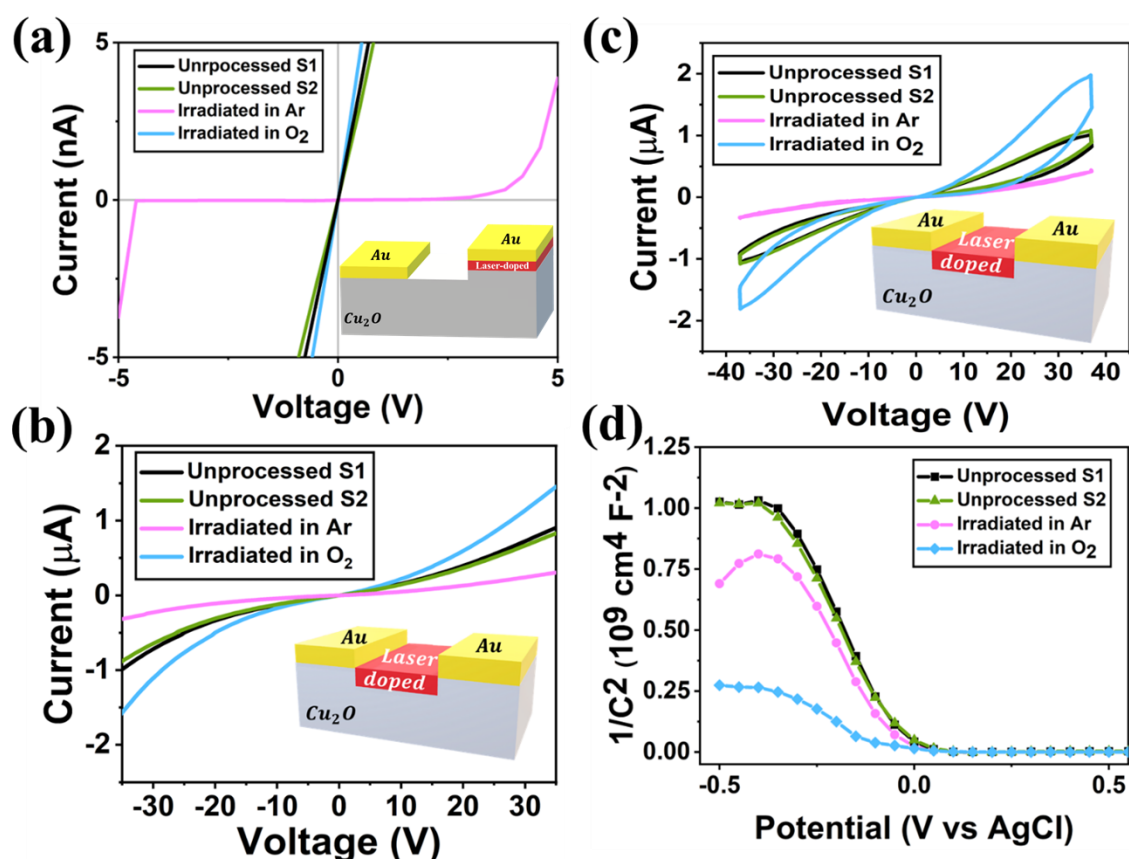


Figure 5.4 (a) I-V characteristics of the Cu_2O thin film measured using the configuration as indicated by the schematic in the figure. (b) I-V curves of the Cu_2O thin film measured using

the configuration as indicated by the schematic in the figure. (c) I-V response of the Cu₂O thin film under cyclic voltage sweeps for the same system before and after laser irradiation. The voltage sweep proceeds: 0V → 40V → -40V → 0V. (d) Mott-Schottky plots of the Cu₂O thin film irradiated under different conditions.

5.3.3 P-Channel Cu₂O TFTs

In short, the above results demonstrated that Cu₂O thin films can be doped with laser-induced V_{Cu} in O₂ rich environment to achieve enhanced p-type conduction while laser-induced V_O in O₂ lean environment (Ar gas) can dope Cu₂O thin films to obtain local n-type conduction. To explore the applications of this laser processing technique, Cu₂O thin film transistors (TFTs) were fabricated. The Cu₂O thin films were first irradiated by laser to dope the films with V_{Cu} and then electrodes were deposited subsequently on top of the laser-irradiated regions. The detailed fabrication process is shown in Figure 5.2. The corresponding electrical properties of Cu₂O TFTs are displayed in Figure 5.5. It can be seen that the Cu₂O TFT is initially in the depletion mode as the source-drain current was at its maximum when the gate potential is at 0V (Figure 5.5 (a))^{362,363}. The non-linear feature of the current in the region between the 0V and ~ -40V is likely due to the contact resistance between the Cu₂O thin film and the source/drain electrodes.^{364,365} The source-drain current decreases significantly as the gate potential increases from 0V to 50V, suggesting a transition of the Cu₂O TFT from “ON” to “OFF” state. This phenomenon is often seen in ordinary p-channel TFTs as the increasing positive gate potentials repel the holes away from the conducting channels underneath the gate, leading to a smaller source-drain current. On the other hand, a subsequent negative gate potential can increase the source-drain current to turn the TFT back to an “ON” state (Figure 5.5 (b)). These I-V characteristics suggest that laser-produced V_{Cu} did not change the conduction type of the Cu₂O thin film.

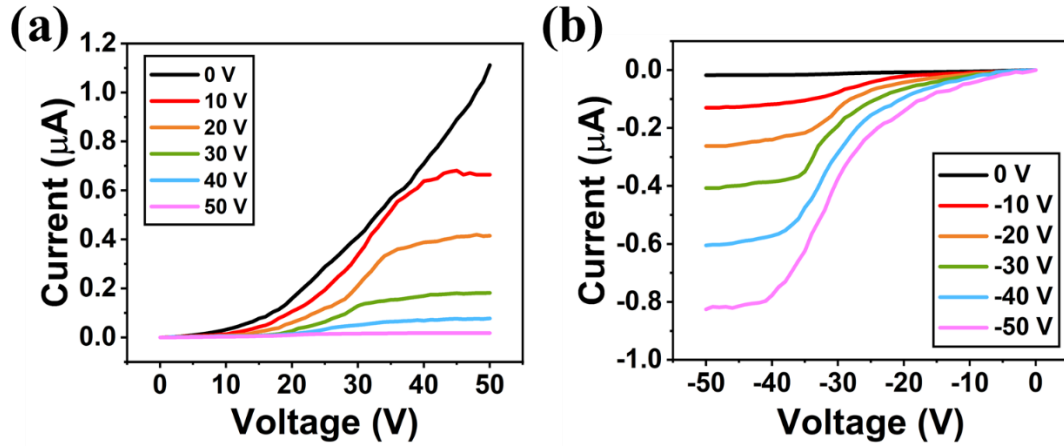


Figure 5.5 I-V characteristics of the Cu_2O thin-film transistor with a p-channel under (a) positive and, (b) negative gate potentials.

5.3.4 N-Channel Cu_2O TFTs

Interestingly, Figures 5.6 shows the n-type I-V characteristics of Cu_2O TFTs irradiated by laser irradiation in Ar gas, expecting with V_O . The TFT is still working in the depletion mode in this case since the source-drain current is not zero without the gate potential. The increasing negative gate potentials shown in Figure 5.6 (a) have suppressed the current between source and drain, which results from the fact that negatively charged defects such as V_O were repelled away from the gate so that the conducting channels between source and drain are broken. On opposite, Figure 5.6 (b) shows the I-V characteristics of this TFT when positive gate potentials were applied subsequently. It can be seen that the positive gate potentials have significantly promoted the source-drain current so that the TFT was switched to “ON” state. These current responses under various gate potentials are consistent with the ordinary TFTs with n-channels, suggesting that laser-induced V_O could be able to and have switched the conduction type from p to n locally in the surface and sub-surface regions.

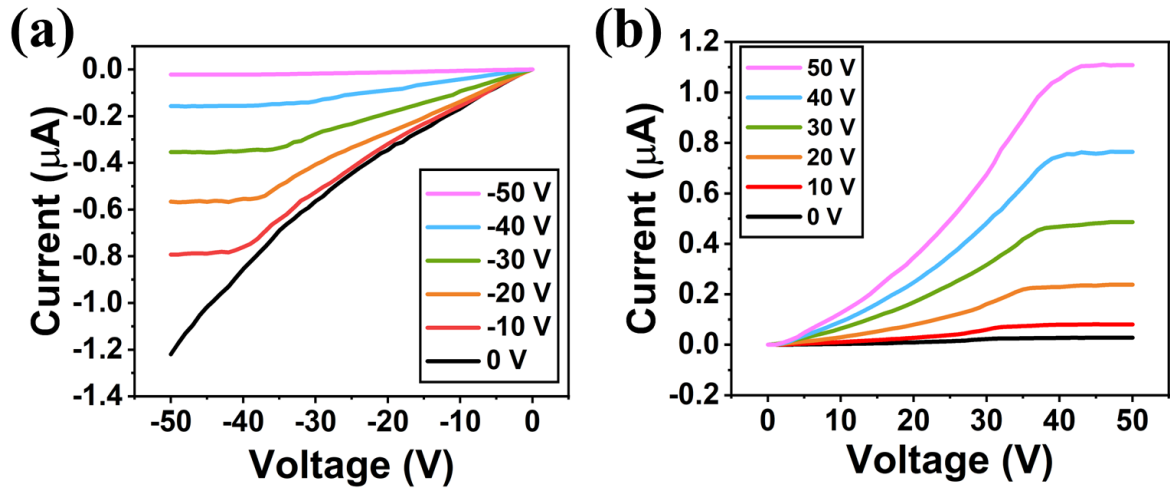


Figure 5.6 I-V characteristics of the Cu₂O thin-film transistor with a laser-generated n-channel under (a) negative and, (b) positive gate potentials.

5.3.5 Cu₂O TFTs with Complementary Channels and Inverters

The demands for transparent and wearable electronics for biomedical and display applications kept growing rapidly in recent years.³⁶⁶ The TFTs based on the flexible and transparent materials such as metal-oxide nanomaterials is one of the major solutions to achieve the integration of practical electronic circuits and the logic control circuits.^{367–369} However, most of these oxide-TFT-based devices were implemented by constructing the p-channel and n-channel TFTs with heterogeneous materials. For instance, Li et al.³⁶⁷ employed ZnO as the n-channel material and SnO as the p-channel material to achieve the flexible complementary oxide-TFT-based inverters. On the other hand, there is still limited information about the TFT logic circuits fabricated on the homogeneous metal-oxide materials due to the difficulties in obtaining the abnormal conduction type in these materials.

As demonstrated in the previous sections 5.3.3 and 5.3.4, the laser irradiation induced defects can readily dope the Cu₂O thin films to be either n- or p- channel TFTs. Therefore, both of these TFTs were fabricated and connected together to explore the feasibility of achieving the homogenous complimentary logic circuits. Figure 5.7 (a) shows the circuit diagram and a schematic illustration of the logic inverters employing n- and p- channel TFTs on the same Cu₂O thin film. During the operation, a supply voltage of V_{in} ranging from 0V to 50V is

applied to both gates simultaneously while a constant supply voltage V_{DD} is applied to the source of the p-channel TFT as indicated in the schematic. The source electrode of the n-channel was kept grounded all the time. Figure 5.7 (b) shows the VTC of the inverters employing n- and p- channel TFTs on the same Cu_2O thin films. When V_{in} equals to zero, the p-channel TFT is in the “ON” state while its n-channel counterpart is on the “OFF” state thus the output voltage V_{out} is the same as V_{DD} . As the gate potentials increases from 0V to V_{DD} , the p-channel TFT is gradually turned off while the n-channel TFT is switched to “ON” state. When the n-channel TFT reached “ON” state finally, the electrode collecting V_{out} is grounded so that the output voltage drops to zero. An additional curve showing the voltage transfer characteristics (VTC) of the inverter when V_{DD} equals to 40V is also provided. This suggest a full function of logic inverter circuit was realized in a single Cu_2O film through laser induced different types of defects for doping purpose.

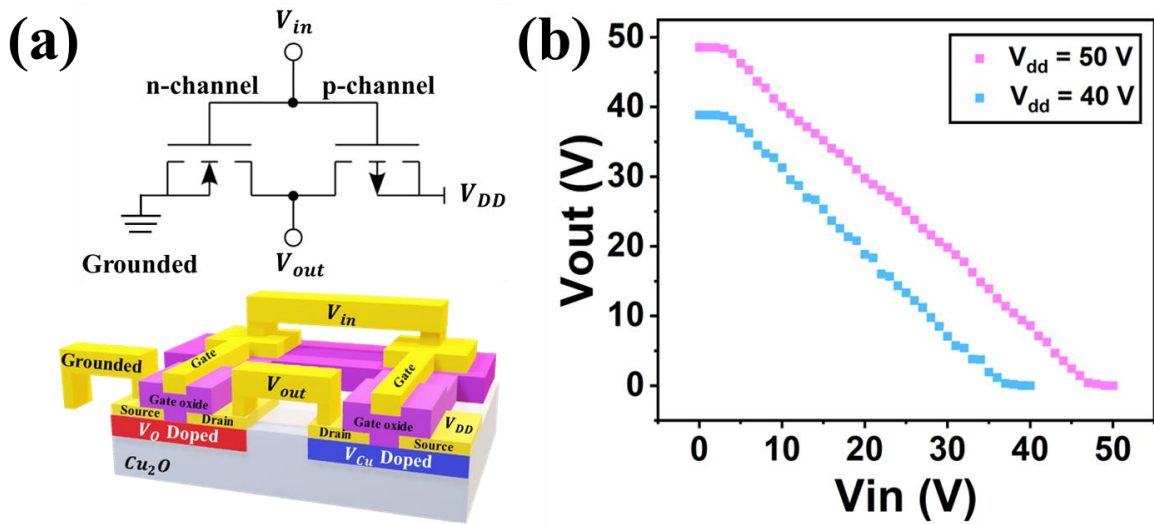


Figure 5.7 (a) The circuit diagram and the schematic of the logic inverter employing n- and p-channel TFTs on the same Cu_2O thin film. (b) Voltage transfer characteristics of the Cu_2O thin-film inverter fabricated based on the schematic shown in (a).

5.4 Vacancies in ZnO Thin Films

5.4.1 Identification of Vacancies

The characteristics of vacancies in ZnO are first determined by high resolution XPS in the O 1s region. As discussed in section 4.4.1, the O 1s peak can be deconvoluted into three major components: a peak residing at ~ 530.1 eV which is associated with the lattice oxygen, an V_O related peak at ~ 531.6 eV and a peak at ~ 532.1 eV which is corresponding to the oxygen adsorption (O_{ads}). The XPS results of ZnO thin films before and after laser irradiation under diverse conditions are displayed in Figure 5.8 (a) – (d). Figures 5.8 (a) and (b) show these data for the two unprocessed ZnO thin film samples Z1 and Z2, respectively. The similar percentage area of each oxygen component suggests good consistency in these films. Figure 5.8 (c) displays the XPS results of sample Z1 after laser irradiation at 480 mJ/cm^2 in Ar gas. It can be seen that the area percentage of the peak associated with V_O increases substantially which indicates a higher concentration of V_O after irradiation. Meanwhile, the intensity of the O_{ads} peak also rises as a result of the higher concentration of vacancies. Conversely, sample Z2 irradiated at 480 mJ/cm^2 in O_2 gas leads to minimal changes of the V_O peak. However, the area percentage of the O_{ads} peak rises dramatically. As stated in section 4.3.1, this peak is related to the loosely bounded oxygen species on the surface and the increasement of this peak often indicates the presence of additional surface vacancies. Since the small change in the V_O peak suggests that no additional V_O generated under this condition, it is therefore believed that such hiking of the O_{ads} peak is due to the presence of zinc vacancies (V_{Zn}).

The properties of these vacancies are further investigated by DRS. The reflection data was converted into absorption spectra using Kubelka-Munk equation³⁰⁸ and the absorption spectra are shown in Figure 5.8 (a). The absorption spectra of two unprocessed samples show little difference, suggesting a universal baseline of the data. Irradiating sample Z1 in Ar at 480 mJ/cm^2 for 3.5 min results in a substantial increase in the region between 400 nm and 900nm and a slight red-shift of the absorption spectrum. These changes are consistent with previous reports which showed that the presence of V_O improves the absorption of ZnO in the visible

region.^{113,138} Interestingly, sample Z2 after irradiation in O₂ at 480 mJ/cm² for 3.5 min also shows improved absorption intensities in the region between 400 nm and 900nm but with a smaller amplitude compared with that of irradiated in Ar. These results are in agreement with many previous studies which showed that both V_O and V_{Zn} improves the absorption of ZnO in the visible region.^{370,371} The information of the band structure of these ZnO samples is revealed by converting the absorption spectra into Tauc plot (Figure 5.8 (f)). The direct bandgap energy can be obtained from an extrapolating of the linear part of the Tauc plot as we discussed in section 5.3.1. It can be seen that irradiation in Ar gas results in a reduction of bandgap energy from ~ 3.15 eV to ~ 3.05 eV while irradiation in O₂ gas reduces the bandgap energy of ZnO from ~ 3.15 eV to ~ 3.1 eV. The bandgap is narrowed in both cases, which is consistent with previous observations.^{370,371}

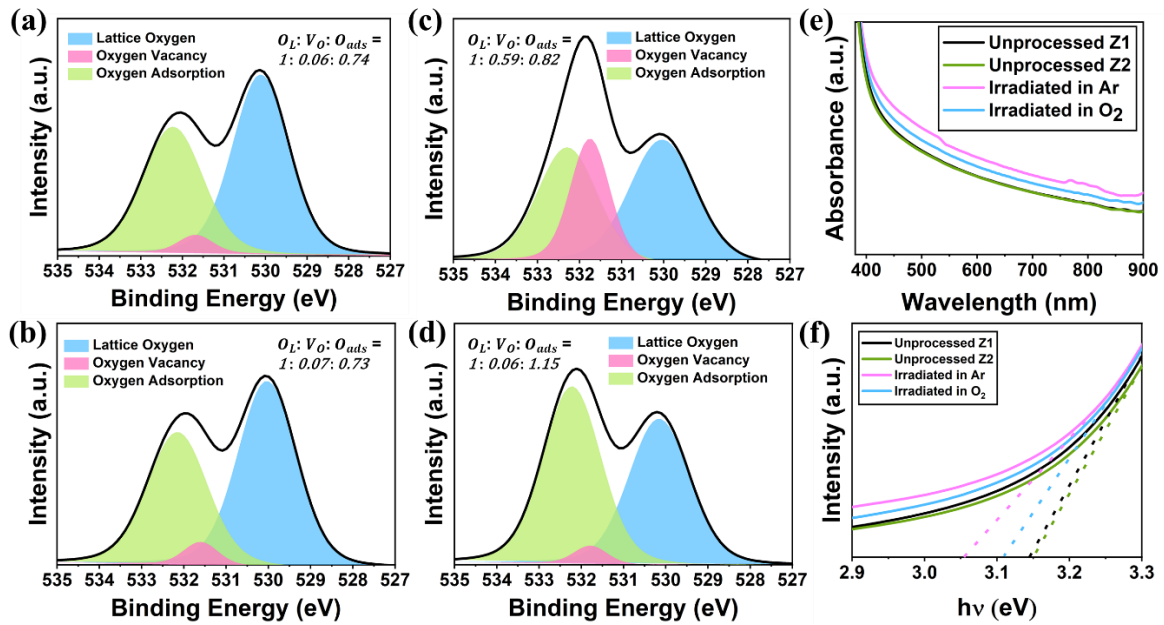


Figure 5.8 High-resolution XPS results in the O 1s region of (a) unprocessed ZnO thin film Z1, (b) unprocessed ZnO thin film Z2, (c) ZnO thin film after laser irradiation in Ar gas, (d) ZnO thin film after laser irradiation in O₂ gas. (e) Absorption spectra of ZnO thin films before and after laser irradiation in Ar and O₂ gas. (f) Corresponding Tauc plots calculated from the absorbance in figure (e).

5.4.2 Doping ZnO Films with V_{Zn} and V_O

The roles of V_{Zn} and V_O on the electrical properties of ZnO thin films are examined using similar approaches as discussed in section 5.3.2. Figure 5.9 (a) shows the I-V characteristics of unprocessed ZnO thin films as well as thin films after irradiation and an illustration of the configuration for the electrical measurement is provided. After the deposition of the first Au electrode, a second layer of ZnO was sputtered. The photoresist was exploited as the mask so that only the second layer of ZnO was irradiated. The fabrication details are displayed in Chapter 5.2.1. It is clear to see that the two unprocessed samples ZA1 and ZA2 exhibit almost identical I-V characteristics, indicating the good consistency of the samples within the same batch. When the second layer of ZnO was irradiated in Ar gas, the measured current increases compared with the unprocessed samples, suggesting an enhanced n-type conductivity attributed to the abundance of V_O after laser irradiation. On the other hand, the I-V characteristics of the sample irradiated in O_2 gas exhibit typical p-n diode features. The current first reduces and then hikes abruptly after reaching a “knee” point at ~ 2 V in the forward bias direction. In the reverse bias direction, the current remained minimal until it reached an abrupt increase at ~ -5 V, which is often recognized as the electrical breakdown of p-n junction diode. These p-n diode features indicate that the regions irradiated under O_2 gas were doped with V_{Zn} to obtain a p-type conductivity locally.

The I-V characteristics were also measured in the case that the two electrodes were directly deposited on the film. Figure 5.9 (b) displays the I-V characteristics in this case and the configuration of the structures for the electrical measurement is seen in the inset. The unprocessed samples again showed good consistency and can be used as references. Irradiating the regions between the electrodes in Ar gas has enhanced the current amplitude, indicating that laser-induced V_O increase the major carrier density. On opposite, the current amplitude is dramatically suppressed when the regions between the electrodes was irradiated in O_2 gas. This decrease in the current indicates the reduction of the concentration of major carriers, which results from laser-induced V_{Zn} which acts as acceptors to compensate electrons in the ZnO thin film.

The resistive switching behavior of the ZnO thin film irradiated at diverse conditions is also investigated and the results of the current response during a voltage cycle $0V \rightarrow 40V \rightarrow -40V \rightarrow 0V$ are illustrated in Figure 5.9 (c). The configuration was kept the same as indicated by the inset in Figure 5.9 (b). It is worth noting that the resulting I-V curves of the unprocessed ZnO thin films do not exhibit the typical hysteresis features. This is due to the fact that O_2 gas was supplied continuously during the sputtering of these ZnO thin films, which suppresses the concentration of V_O that is available for the electroforming of the conductive filaments. The hysteresis characteristics with noticeable HRS and LRS re-appear in the ZnO thin film after laser irradiation in Ar gas and the current increases in both bias directions, suggesting that laser-induced V_O significantly increases the carrier density under this condition. On opposite, irradiating in O_2 gas leads to the reduction of the current which indicates the elimination of major carriers due to V_{Zn} produced by laser irradiation.

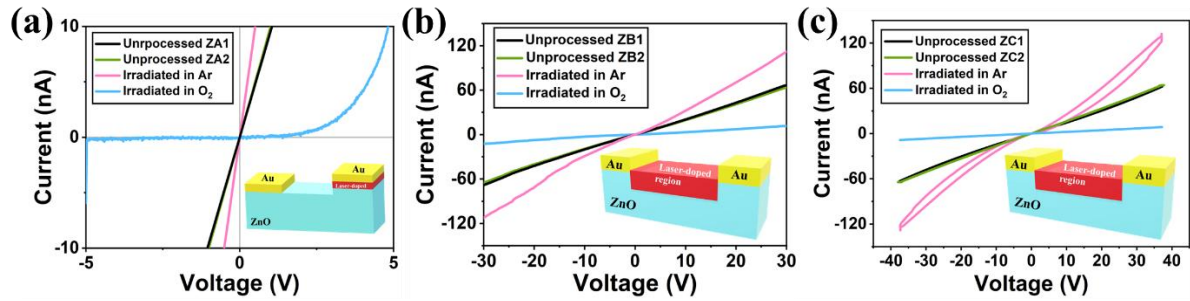


Figure 5.9 (a) I-V characteristics of the ZnO thin film measured using the configuration as indicated by the schematic in the figure. (b) I-V curves of the ZnO thin film measured using the configuration as indicated by the schematic in the figure. (c) I-V response of the ZnO thin film under cyclic voltage sweeps for the same system before and after laser irradiation. The voltage sweep proceeds: $0V \rightarrow 40V \rightarrow -40V \rightarrow 0V$.

5.4.3 N-Channel ZnO TFTs

The above results suggest that ZnO thin films can be doped with laser-induced V_{Zn} to achieve p-type conduction while laser-induced V_O can dope ZnO thin films to enhance n-type conduction. ZnO TFTs were also fabricated following the steps described in Figure 5.2. The ZnO thin film was irradiated in Ar gas at 480 mJ/cm^2 to dope with V_O . The corresponding

output characteristics of this laser-processed ZnO TFT are displayed in Figure 5.10. It is clear to see that the ZnO TFT is initially in the depletion mode as the source-drain current was at its maximum when the gate potential is at 0V (Figure 5.10 (a)).^{362,363} The source-drain current decreases dramatically as the gate potential increases reversely from 0V to -50V, suggesting a transition from “ON” to “OFF” state. The subsequent positive gate potentials increase the source-drain currents to switch the TFT back to an “ON” state (Figure 5.10 (b)). These I-V characteristics suggest that the conductive channel of this laser-processed ZnO thin film TFT remains n-type.

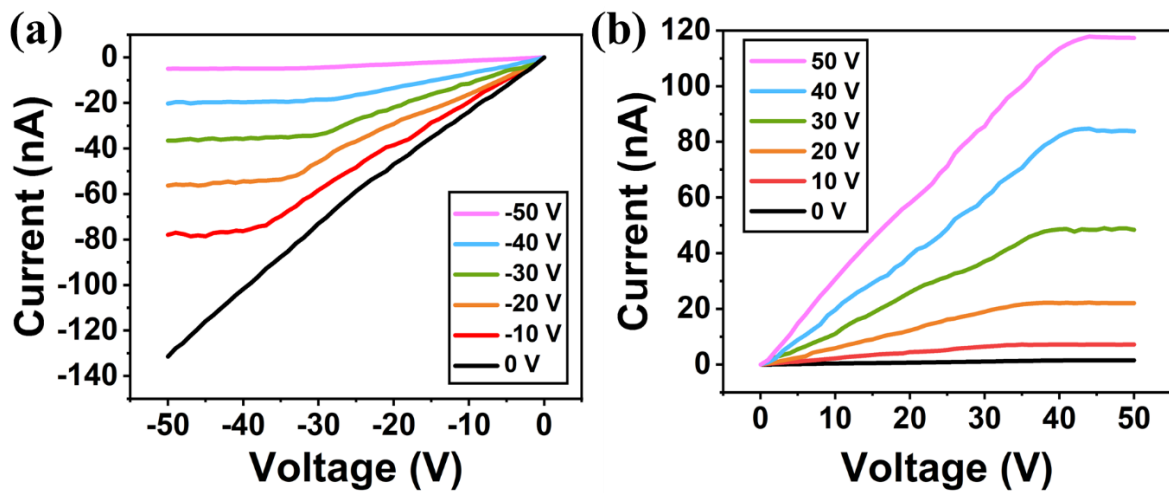


Figure 5.10 Output characteristics of the ZnO thin-film transistor with an n-channel under (a) negative and, (b) positive gate potentials.

5.4.4 P-Channel ZnO TFTs

Figures 5.11 shows the output characteristics of the ZnO TFT processed by laser irradiation in O₂ gas. The TFT is still working in the depletion mode in this case since the source-drain current is not zero without the gate potential. The increasing positive gate potentials shown in Figure 5.11 (a) have suppressed the current between source and drain, which results from the fact that positively charged acceptors such as V_{Zn} are eliminated in the channel region close to the gate. Figure 5.11 (b) shows the I-V characteristics of this TFT operating with subsequent negative gate potentials. The source-drain current is promoted significantly so that the TFT is switched back to “ON” state. These current responses under various gate potentials are

consistent with the ordinary TFTs with p-channels, indicating that laser-induced V_{Zn} have alter the conduction type from n- to p- in the conductive channel regions.

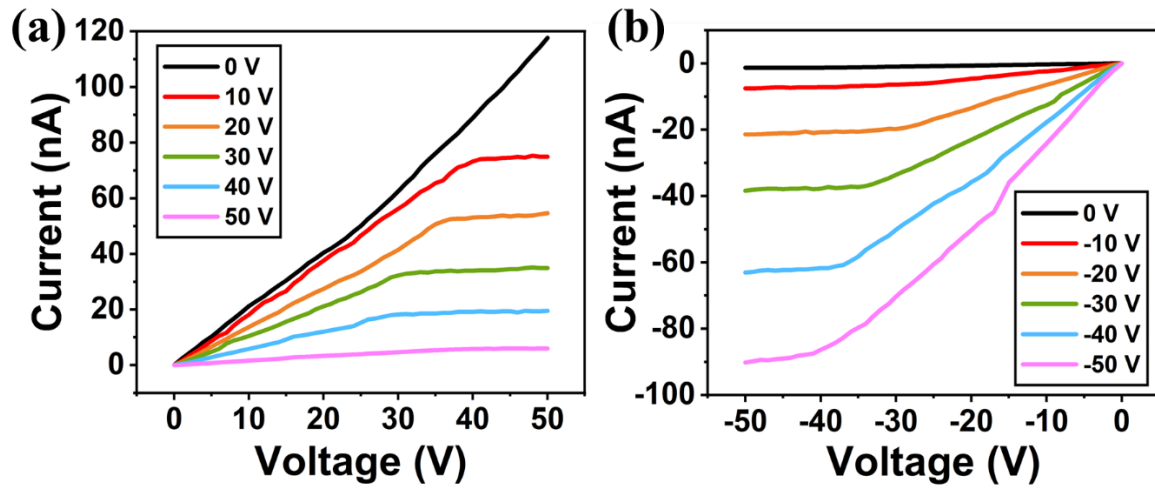


Figure 5.11 Output characteristics of the ZnO thin-film transistor with a p-channel under (a) positive and, (b) negative gate potentials.

5.4.5 ZnO TFT Inverters

Both of these TFTs were fabricated and connected together to explore the feasibility of achieving the homogenous complimentary logic circuits in ZnO thin films similar as Cu_2O in section 5.3.5. Figure 5.12 (a) illustrates the schematic of the inverter employing n- and p-channel TFTs on the same ZnO thin film. It can be seen that a supply voltage of V_{in} ranging from 0V to 50V is applied to both gates simultaneously while a constant supply voltage V_{DD} is applied to the source of the p-channel TFT as indicated during the operation. The source electrode of the n-channel was kept grounded all the time. Figure 5.12 (b) shows the VTC of the inverter fabricated based on the structures displayed in Figure 5.12 (a). When V_{in} equals to zero, the p-channel TFT is turned “ON” while its n-channel counterpart is on the “OFF” state thus the output voltage V_{out} is the same as V_{DD} . As the gate potentials increases from 0V to V_{DD} , the p-channel TFT is gradually turned off while the n-channel TFT is switched to “ON” state. When the n-channel TFT reached “ON” state finally, the electrode collecting V_{out} is grounded so that the output voltage drops to zero. An additional curve showing VTC of the inverter with a V_{DD} of 40V is also provided in Figure 5.12 (b). Therefore, starting from a n

type material, laser irradiation could also achieve the target n- or p- doping through engineering the defect types.

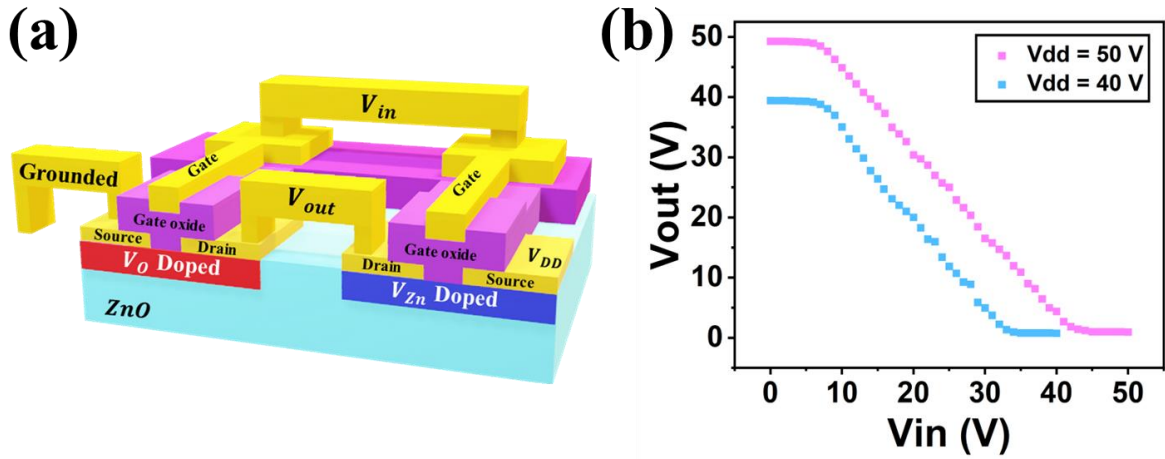


Figure 5.12 (a) The schematic of the inverter employing n- and p- channel TFTs on the same ZnO thin film. (b) Voltage transfer characteristics of the ZnO thin-film inverter fabricated based on the schematic shown in (a).

5.5 Summary

In summary, it was demonstrated that controlled amounts of V_{Cu} and V_O vacancy centers can be introduced in p-type Cu_2O thin films through laser irradiation under diverse ambient conditions. It was shown that adjusting the type of these vacancy centers using laser irradiation can have a significant effect on the optical absorption of Cu_2O thin-film samples. In particular, the introduction of V_O centers leads to a blue-shift in optical absorption in the spectral region between 500 and 600 nm and the corresponding bandgap is widened. Modification of the I-V response of the Cu_2O thin film is also achieved using laser irradiation via changes in the major carrier type. I-V characteristics combined with Mott-Schottky plots illustrate that laser-induced defects can dope the thin film to achieve either an enhanced regular conduction or an abnormal conduction. Cu_2O TFTs with both n- and p- channel were fabricated and characterized and as an example of the application for this laser processing technique, inverters made of n- and p-

type TFTs on the same Cu_2O thin films were fabricated and the voltage transfer characteristics were examined.

On the other hand, V_{Zn} and V_{O} were also introduced in n-type ZnO thin films to further validate this laser processing technique. The XPS results in the O 1s region showed the evidence of the production of V_{O} after irradiation in Ar gas and the hiking peak intensity associated with the oxygen adsorption indicate the generation of V_{Zn} after irradiation in O_2 gas. It was shown that both of these vacancies improved the optical absorption of ZnO thin films in the visible region and the corresponding bandgap energies are decreased. The I-V characteristics of the ZnO thin films were modified by laser-induced V_{Zn} and V_{O} and the abnormal conduction type can be achieved through the doping of V_{Zn} . ZnO TFTs with both n- and p- channel were fabricated and the voltage transfer characteristics of the inverter made of these TFTs on the same ZnO thin film were examined.

Overall, a general strategy employing gas immersion laser doping to produce desired types of vacancies and the effects of these vacancies on the electrical conduction of metal-oxide nano-materials were revealed. The efficacy of this approach makes it a promising technique to readily dope metal-oxide nano-materials for diverse applications and the exploitation of this approach on more ionic-bonded semiconductor materials worths further investigations.

Chapter 6 Conclusion and Outlook

6.1 Conclusions

This thesis focuses on the engineering of defects in metal-oxide nano-materials through pulsed laser irradiation and explores the applications of these defect-engineered materials. Three major aspects of the defects were tailored through laser irradiation and the progresses are presented from Chapter 2 to Chapter 5. First, the concentration of defects in CuO NWs and ZnO thin films were investigated. Second, the distribution of laser-induced defects was discovered and characterized in CuO NWs and ZnO NWs. Third, the strategies to produce desired types of defects in Cu₂O and ZnO thin films were explored, respectively. More detailed observations are shown below:

(1) A new technique that utilizes ns laser irradiation to engineer the concentration of defects in both p-type CuO NWs and n-type ZnO thin films was developed. Irradiation with intense ns pulses produces additional defects in CuO NWs, introducing new energy levels that narrow the effective bandgap. The decreased satellite peak associated with Cu²⁺ in the XPS results and the increased asymmetry of the A_g vibrational mode in Raman spectra both suggested the production of additional defects after laser irradiation. Due to the increasement in the concentration of defects, the electrical as well as photo-conductivity is significantly increased in the Au/CuO/Au MSM bridged structure. The electrical conductivity was doubled at a forward bias of 15 V and the optical gain of these structures was tripled after laser processing. The Au/CuO/Au device as a light-assisted memristor with an enhanced ON/OFF ratio was fabricated. Meanwhile, this laser irradiation is also applied to ZnO thin films to increase the concentration of V_O . The absorption spectra and XPS results in the O 1s region suggested that the concentration of V_O in these films can be readily controlled through changing the laser fluence. The V_O -to- O_L ratio was achieved in a range between 0.24 and 0.61. Additional V_O produced by laser irradiation improve the conductivity of the ZnO film and introduce new

intragap energy levels that narrows the effective bandgap of ZnO by approximately 0.04 eV, extending photo-response of ITO/ZnO/ITO devices to longer wavelengths.

(2) After achieving the modulation of the defect concentration, the distribution of these defect centers was further examined in CuO and ZnO NWs. Irradiation with moderate ns pulses produces V_O in CuO NWs, which is confirmed by XPS results in O 1s and Cu 2p regions as well as Raman spectra. The XPS results showed that the oxygen adsorption is improved after laser irradiation, which is also reflected in the Raman spectrum as the rise of the peak associated with peroxide and superoxide species adsorbed on the surface of CuO NWs. Both of these features indicate that laser-induced V_O majorly resides at the surface and sub-surface regions in CuO NWs. These results were reinforced by electrochemical measurements. It was found that laser-induced V_O resulted in a decrease in slope of the Mott-Schottky curve which was attributed to the improved adsorption of the electrolyte on the nanowire surfaces due to the existence of surface V_O . The reduced charge transfer resistance revealed in the Nyquist plot also suggested the appearance of V_O in the surface regions. To explore the efficacy of this laser processing approach, CuO NWs are used as the catalyst for non-enzymatic glucose detection and amperometry was implemented. It was found that the presence of laser-induced surface V_O increased the current response and achieved an improved detection limit as low as 0.5 μM , suggesting better glucose sensitivity. The control over the distribution, on the other hand, was obtained by tuning the laser fluence and exposure time and it was demonstrated in ZnO NWs. Ns laser irradiation of ZnO NW samples produces discrete temperature-dependent distributions of V_O in surface and bulk sites as well as changes in morphology. ZnO NWs with defects majorly locating in the areas within 1.5 nm from the surface and mostly residing in the bulk regions as deep as 12nm were both obtained, respectively. Using UV, Raman, PL and XPS, it was revealed that these changes arise from a combination of the photochemical generation of defect centers together with thermal heating induced by overlapping laser pulses. Four distinctive regimes lead to diverse distribution of V_O have been identified in irradiated samples. As an example of this capability, the photo-degradation of RhB dye was carried out using laser-processed ZnO NWs as the catalyst.

(3) Lastly, the strategy to generate desired types of vacancies was explored in both Cu_2O and ZnO thin films. Controlled amounts of either V_{Cu} or V_{O} vacancy centers can be introduced in Cu_2O thin films through laser irradiation under specific ambient conditions. Their existence was evidenced by XPS results and the absorption spectra. In particular, the introduction of V_{O} centers leads to a blue-shift in optical absorption in the spectral region between 500 and 600 nm and the corresponding bandgap is widened by approximately 0.05 eV. Conversely, laser-induced V_{Cu} gives rise to enhanced absorption and a narrowed bandgap. Modification of the I-V response of the Cu_2O thin film was obtained using laser irradiation via changes in the concentration of carriers. I-V characteristics combined with Mott-Schottky plots illustrated that laser-induced V_{Cu} can dope the thin film to achieve an enhanced p-type conduction while doping with laser-induced V_{O} gives rise to n-type conduction. Cu_2O TFTs with p- and n- channels were fabricated connected together to establish the inverter structure and the transfer characteristics of such inverters were determined. Similar studies were repeated in ZnO thin films to further validate this laser processing approach.

Overall, this research thesis shows a comprehensive study of defect engineering in metal-oxide nano-materials through laser irradiation. The strategies of engineering various properties of defects in metal-oxide nano-materials via tuning laser processing parameters are demonstrated and the knowledge of these defects produced by laser irradiation is advanced.

6.2 Outlooks

Since the investigation of defect engineering in metal-oxide nano-materials through laser irradiation is still in its early stages, it can be foreseen that many extra efforts are necessary to further advance the knowledge. This thesis proposes some of the potential research studies as listed below:

(1) Gas immersion laser doping in metal-oxide nano-materials is studied in this thesis, however, there are still many remaining questions to answer. For instance, the relation between the gas partial pressure and the production of desired defects was not discovered. The required laser energy as a function of the yield of defects has never been studied. In theory, the energy

transferred from laser to the metal-oxide nano-materials can be determined through calculations and the formation energy of defects can be determined by density functional theory. Hence, there must be some ways to be established to reveal the correlation between the targeted concentration of defects as a function of laser energy input.

(2) There are extensive experimental results for defect engineering achieved through laser irradiation, however, the theoretical study remains extremely limited. It is shown in this thesis that the formation energy of defects can be determined through DFT calculations while the energy transfer between laser and materials is governed by heat equations. It is therefore intriguing to discover whether these calculations can be combined to provide a solid theoretical understanding for the phenomena observed in the experiments.

(3) Another critical issue that is not revealed in this thesis is the charge states of these defects produced by laser irradiation. As stated in Chapter 2, V_O was not considered as the source of n-type origin in ZnO until the experimental results revealed that these V_O can be doubly-ionized which can act as shallow donors. It can be postulated from the experimental results in this thesis that laser irradiation often produces defects occupying shallow donor and acceptor levels. However, this assumption needs further investigations to validate.

(4) Even though the device performance was often improved after laser-induced defect engineering, the durability of the devices has seldom been examined. As defects are often vulnerable to the ambient environment, it remains unknown how durable the laser-engineered devices are and it is still challenging to keep the properties of these laser-engineered defects constant in a long period of time.

(5) The commercialization of laser-engineered devices. After the successful fabrication of prototype devices made of metal-oxide nano-materials and engineered by laser irradiation, whether these devices can be commercially available in the market remains a big question mark. Considering that laser irradiation has already been widely exploited in the semiconductor industry, it is expected that the laser processing techniques demonstrated in this thesis can be integrated with other state-of-the-art nanofabrication technologies for advanced electronic devices.

Chapter 7 Research Contributions

7.1 Articles Published in Refereed Journals

- (1) **Zheng, S.**, Duley, W., Peng, P., and Zhou, N. (2024) Engineering the defects in CuO NWs through laser irradiation: oxygen vacancy vs copper vacancy. *Applied Surface Science*. 642: 158630. (contribute to the content in chapter 4)
- (2) **Zheng, S.**, Chen, Z., Duley, W., Wu, Y., Peng, P., and Zhou, N. (2023) Engineering the defect distribution in ZnO nanorods through laser irradiation. *Nanotechnology*. 34: 495703. (contribute to the content in chapter 4)
- (3) Zhao, X., Yang, H., Duley, W., **Zheng, S.**, Guo T., and Zhou, N. (2023) A simple self-powered sensor for the detection of D₂O and other isotopologues of liquid water. *ACS Sensors*. 8: 3973.
- (4) **Zheng, S.**, Zhao, X., Duley, W., Zhou, N., and Peng, P. (2022) Laser Engineering of ITO/ZnO/ITO Structures for Enhanced Photodetection in Visible Region. *Journal of Laser Applications*. 34: 032006. (contribute to the content in chapter 3)
- (5) **Zheng, S.**, Duley, W., Peng, P., and Zhou, N. (2022) Laser Modification of Au-CuO-Au Structure for Improved Electrical and Electro-Optical properties. *Nanotechnology*. 33: 245205. (contribute to the content in chapter 3)
- (6) **Zheng, S.**, Duley, W., Peng, P., and Zhou, N. (2021) Formation of metal-semiconductor nanowire heterojunctions by nanosecond laser irradiation”, *AIP Advances* 11: 095207.
- (7) Xiao, M., **Zheng, S.**, Shen, D., Duley, W., and Zhou, N. (2020) Laser-induced Joining of Nanoscale Materials: Processing, Properties, and Applications. *Nano Today*. 35:100959.

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Figure 1.1



Advanced green approaches for metal and metal oxide nanoparticles synthesis and their environmental applications

Author: Gopika M. Nair,T. Sajini,Beena Mathew

Publication: Talanta Open

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by Chao-Chun Yen ^{1,†}, Anoop Kumar Singh ^{1,†} , Yi-Min Chung ¹, Hsin-Yu Chou ¹ and Dong-Sing Wu ^{1,2,3,*}  

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Unified Model for Laser Doping of Silicon from Precursors

by Mohamed Hassan ^{*} , Morris Dahlinger , Jürgen R. Köhler , Renate Zapf-Gottwick  and Jürgen H. Werner  

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Author: Richa Khokhra et al
Publication: Scientific Reports
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Date: Nov 8, 2017

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Oxygen Vacancy Induced Band-Gap Narrowing and Enhanced Visible Light Photocatalytic Activity of ZnO

Author: Junpeng Wang, Zeyan Wang, Baibiao Huang, et al
Publication: Applied Materials
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Effect of Oxygen Vacancy Ratio on a GaZTO Solar-Blind Photodetector

by Jhih-Chun Syu ¹, Ming-Hung Hsu ¹, Sheng-Po Chang ^{1,*} , Shouu-Jinn Chang ¹ and Lucent Lu ²

¹ Institute of Microelectronics & Department of Electrical Engineering, Center for Micro/Nano Science and Technology, Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 70101, Taiwan

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Figure 2.6



Surface, Subsurface, and Bulk Oxygen Vacancies Quantified by Decoupling and Deconvolution of the Defect Structure of Redox-Active Nanoceria

Author: Rashid Mehmood, Sajjad S. Mofarah, Wen-Fan Chen, et al

Publication: Inorganic Chemistry

Publisher: American Chemical Society

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Tuning the Relative Concentration Ratio of Bulk Defects to Surface Defects in TiO₂ Nanocrystals Leads to High Photocatalytic Efficiency

Author: Ming Kong, Yuanzhi Li, Xiong Chen, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Oct 1, 2011

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		End Page	10988
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 Author: Stijn Huygh, Annemie Bogaerts, Erik C. Neyts
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Engineering Oxygen Vacancies in Mesocrystalline CuO Nanosheets for Water Oxidation
 Author: Linfeng Liang, Ke-Yu Niu, Linjie Zhang, et al
 Publication: ACS Applied Nano Materials
 Publisher: American Chemical Society
 Date: Jun 1, 2021
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 Publication: Applied Surface Science
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From the journal *Nanotechnology Reviews*
<https://doi.org/10.1515/ntrev-2022-0035>

Figure 2.8

Open Access Article

Controllable Synthesis of ZnO Nanoparticles with Improved Photocatalytic Performance for the Degradation of Rhodamine B under Ultraviolet Light Irradiation

by Xinyue Ren ¹ , Yien Du ^{1,*} , Xinji Qu ² , Yumei Li ^{2,*} , Luxi Yin ¹ , Kaixin Shen ¹ ,
 Jingwen Zhang ¹  and Yufang Liu ¹ 

¹ Department of Chemistry and Chemical Engineering, Jinzhong University, Jinzhong 030619, China

² Qingdao Second Health School of Shandong Province, Qingdao 266308, China

* Authors to whom correspondence should be addressed.

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Visible and UV photo-detection in ZnO nanostructured thin films via simple tuning of solution method
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Evolution of microstructure and related optical properties of ZnO grown by atomic layer deposition

Adib Abou Chaaya^{1,§}, Roman Viter^{2,3,§}, Mikhael Bechelany^{1,†}, Zanda Alute², Donats Erts⁴, Anastasiya Zaleskaya², Kristaps Kovalevskis³, Vincent Rouessac¹, Valentyn Smyntyna² and Philippe Miele¹

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³Institute of Atomic Physics and Spectroscopy & Institute of Chemical Physics, University of Latvia, 19, Raina Blvd., LV 1586, Riga, Latvia,
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§ These authors contributed equally to the paper

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This article is part of the Thematic Series "Energy conversion applications of atomic layer deposition".

Guest Editor: J. Bachmann

Beilstein J. Nanotechnol. **2013**, *4*, 690–698. <https://doi.org/10.3762/bjnano.4.78>

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 Author: Marcus Lau, Sven Reichenberger, Ina Haxhija, et al
 Publication: ACS Applied Energy Materials
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