

Size-Specific ZrO_2 and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ Nanoclusters and Their Magnetic and Nanodevice Applications

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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.

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Statement of Contributions

This thesis contains material from published journal paper that I authored or co-authored.

- The content in Chapter 3 has been published in

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Abstract

Nanoclusters, generally defined as assemblies of a discrete number of atoms or molecules in the size range of 1-10 nm, have attracted a lot of attention due to their unique properties that bridge the gap between isolated atoms or molecules and bulk materials. Nanoclusters possess distinct electronic, optical, magnetic, and catalytic characteristics, which are often profoundly different from those observed in bulk materials or even larger nanoparticles. These notable differences arise from quantum confinement effects, high surface-to-volume ratios, and the specific atomic arrangements in these nanoscale clusters that often include the presence of defects. The understanding and manipulation of these properties are pivotal for harnessing nanoclusters in diverse fields, ranging from nanoelectronics to catalysis, biomedicine, and advanced material design.

The oxides of group IV-B transition metals, notably ZrO_2 and HfO_2 , have attracted significant research interest due to their high dielectric constants, wide bandgaps, pronounced refractive indices, and superior thermal stability. Additionally, oxygen vacancy defects within these oxides, particularly in the nanocrystalline forms, contribute to the manifestation of intriguing phenomena. The present work delves deeply into the synthesis methodologies, precise characterization techniques, and the multifaceted application potential of the ZrO_2 and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($x \leq 1$) nanoclusters. Through this exploration, we aim to elucidate the intricate relationship between the defects in the physical structure of the nanocluster, composition, and their resulting macroscopic behaviors, with a special focus on the ferromagnetism, providing insights that could pave the way for future innovations in nanotechnology. Monosized ZrO_2 nanoclusters (NCs) are deposited over a large area by using gas-phase condensation followed by *in-situ* size selection by a quadrupole mass filter. These size-specific NCs exhibit sub-oxide photoemission features at binding energies that are dependent on the cluster size (from 3 to 9 nm), which are attributed to different oxygen vacancy defect states. These dopant-free ZrO_2 NCs also show strong size-dependent ferromagnetism, which provides distinct advantages in solubility and homogeneity of magnetism when compared to traditional dilute magnetic semiconductors. A defect-band hybridization-induced magnetic polaron model is proposed to explain the origin of this size-dependent ferromagnetism. This work demonstrates a new protocol of magnetization manipulation by nanocluster size control and promises potential applications based on these defect-rich size-selected NCs.

Using two metal targets in the gas-phase condensation technique, we synthesize, for the first time, size-specific hybrid $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($x \leq 1$) NCs that can be precisely tuned from 5 nm to 14 nm in size while adjusting the Zr and Hf composition. The crystallinity of the hybrid NCs is found to vary with the NC size obtained under specific deposition conditions, from amorphous for small NCs < 6 nm, to single crystalline for 6-10 nm NCs, to core-shell for NCs with higher Hf content and to polycrystalline for larger NCs > 10 nm with high Zr content. For the single-crystalline $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs, we observe, for the first time for NCs, the special orthorhombic ($Pca2_1$) structure found only in the HfZrO_2 film prepared under extreme conditions. Surprisingly, the measured bandgaps of these NCs are found to increase with the cluster size, in contrast to expected increasing band gap with decreasing NC size. The XPS spectra clearly show that the Zr 3d components can be attributed to oxygen vacancy defects and substitution of Hf for Zr in the lattice. A new model involving Hf induced polaron is proposed to describe the physical and electronic structures of these novel bimetallic hybrid oxide NCs. This work establishes a general formation protocol for other hybrid semiconductor NCs, while the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($x < 1$) NCs with novel phase and polarization could provide promising electrical properties for the next generation non-volatile memory device applications.

To understand the behavior of the electrons within the defects of these NCs and explore their electronic properties, we fabricate nano-electrodes, including nano interdigital electrodes and nanogaps. As one of the most crucial procedures in the electronic device fabrication, patterning is studied by comparing the results obtained by maskless optical lithography, electron beam lithography, and ion beam lithography with a gas field He ion source and with a SiAu liquid metal alloy ion source. Helium ion beam lithography is found to offer the most refined feature resolution, while the Si ion beam lithography demonstrates its fastest patterning speed in creating nanofeatures, particularly by taking advantage of its unique direct-write capability. Using ion beam lithography, a nano-IDE with a 43-nm gap is created with direct writing of Au^{++} ion beam on a Pt film. This technology also enables precise nanogap device production with sharp edges that are crucial for tunneling and electron hopping studies. The spacing of these nanogaps can be fine-tuned through ion beam exposure. We also fabricate a single-nanocluster device, for the first time, by integrating $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs into these nanogap devices. Such nano-electrodes serve as platforms for measuring the electronic properties of NCs, with promising potential for other nano and quantum device applications.

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Dedication

To my parents, **Leimei Wang** and **Shicheng Guan**,
only love should not be disappointed.

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List of Abbreviations

AC	alternating current
AFM	atomic force microscopy
amu	atomic mass unit
AL	aggregation length
BSE	backscatters electron
BMP	bound magnetic polaron
CTF	charge transfer ferromagnetism
CQDs-PEG1500 _N	carbon quantum dot with oligomeric poly (ethylene glycol) diamine
DC	direct current
DFT	density functional theory
DMO	dilute magnetic oxide
DMS	dilute magnetic semiconductor
DMSO	dilute magnetic semiconductor oxide
EBL	electron beam lithography
EDS	energy dispersive spectroscopy
FFE	full-face erosion
FFT	fast-Fourier transform
GFIS	gas field ionization ion source
GMR	giant magnetoresistance
GPC	gas phase condensation
HAADF	high-angle annular dark field
HER	hydrogen evolution reaction
HIM	helium ion microscope

HiPIMS	high-power impulse magnetron sputtering
HPLC	high-performance liquid chromatography
IBL	ion beam lithography
IDE	interdigital electrode
ISS	ion scattering spectroscopy
LMAIS	liquid metal alloy ion source
LUMO	lowest unoccupied molecular orbital
MACS	matrix assembly cluster source
MIBK	methyl isobutyl ketone
MPMS	magnetic property measurement system
NC	nanoclusters
NVPE	nano-Patterning and visualization engine
NG-YAG	neodymium-doped yttrium aluminum garnet; $\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$
PCL-MWCNT	polycaprolactone processed with multi-walled carbon nanotube
PMMA	polymethyl methacrylate
PPMS	physical properties measurement system
PSA	prostate specific antigen
P(VDF-TrFE)	poly(vinylidene fluoride–trifluoro ethylene) copolymer
REELS	reflection electron energy loss spectroscopy
RF	radio frequency
RKKY	Ruderman–Kittel–Kasuya–Yosida
RT-DMS	room temperature dilute magnetic semiconductors
SAXS	small angle X–ray scattering
SE	secondary electron

SEM	scanning electron microscopy
SQUID	superconducting quantum interference device
STEM	scanning transmission electron microscopy
STO	SrTiO ₃
TCO	transparent conductive oxide
TEM	transmission electron microscopy
TOF	time of flight
OER	oxygen evolution reaction
UV-Vis	ultraviolet–visible
UPS	ultra-violet photoelectron spectroscopy
VSM	vibrating sample magnetometry
WATLab	Waterloo Advanced Technology Lab
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

Chapter 1

Introduction

Atoms and molecules serve as the fundamental building blocks of our world. However, the manner and extent to which these blocks assemble can result in significant differences in the resulting matter, with properties transitioning from individual atoms or molecules to nano-objects to bulk materials, especially in or near the quantum regime. These “transition” materials, often termed nanoclusters, capture our primary research interest. The present work will center on the synthesis of zero-dimensional ZrO_2 and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoclusters, followed by an in-depth examination of their morphologies, structures, and electronic states. Based on their unique properties, we further investigate the potential use of these intriguing nanoclusters, with the emphasis on their electrical and magnetic applications. In this chapter, we provide an overview of nanoclusters, delving into their synthesis methods and size-dependent behaviors. We then discuss ferromagnetic semiconductors along with their origin. We close this chapter with a brief review of interdigital electrodes and nanogaps that serve as platforms for building future single-cluster devices.

1.1 Nanoclusters

Nanoclusters (NCs) are aggregations of atoms or molecules that are typically smaller than a few tens of nanometers in size.¹⁻³ In this special size regime, the electronic structure retains distinct individual states instead of merging into bands. The high surface area-to-volume ratio (or specific surface area) and quantum confinement effect could lead to unique properties and novel phenomena, which could be significantly different from those observed in bulk materials. Currently, there are huge varieties of nanoclusters generated in metals and metal oxides as well as their mixtures. The noble metal NCs with their high-temperature stability and strong local surface plasma resonance have found applications in light illumination,⁴ bio-sensing^{5,6} and fuel cells.⁷ In the last two decades, there has been a growing interest in the investigation of nanoclusters of transition metals and their oxides. These NCs not only exhibit marked changes in their bandgaps from their bulk forms arising from the “size effect”, they also often contain discernible oxygen vacancy defects, resulting in various oxidation and mid-gap states within the NCs. The presence of mid-gap states and the diverse structures composed of ordered arrays and assemblies make these materials promising candidates as catalysts in photoelectrochemical water splitting^{8,9} and CO_2 reduction reactions,¹⁰ and as various

sensors.^{11–13} More interestingly, the high specific surface area could also introduce novel phases that are not readily observable at room temperature, and these new (metastable) phases could exhibit other fascinating properties, like ferromagnetism, not found in stable phases.² In short, NCs hold the key to unraveling the evolution of electronic structure and other properties, providing insights into the mechanisms underlying the properties that bridge the bulk phase and the atomic world.

A well-known “bottom-up” strategy of synthesizing NCs involves building from atoms or molecules with precise size control in order to achieve better control over their structures and functionalities.¹⁴ To date, there are many methods for synthesizing metal and metal oxide nanoclusters, including hydrothermal method,¹⁵ self-assembly,⁴ wet-chemistry impregnation method,¹⁰ and gas-phase condensation.^{2,8,16} With the development of the cluster beam method, the gas-phase condensation technique coupled with size selection using a mass filter has emerged as a powerful approach for synthesizing NCs. In this section, we will focus on this popular NC synthesis technique via gas-phase condensation with post size selection and provide an overview of the latest research on NCs so produced and their size-dependent properties.

1.1.1 Basic Steps of Gas-Phase Condensation Technique

Gas-phase condensation technique has been used to synthesize NCs since the 1980s.¹⁷ In this technique, the target material is vaporized into the gas phase by an energy or particle beam or some other means. The resulting gaseous atoms or molecules are then carried by a buffer gas, usually Ar or He, through a cool condensation chamber following the pressure gradient. In the chamber, the gaseous target atoms collide with one another, lose their thermal energy, and condense into nanoclusters. With the explosive development of nanotechnology in the past decades, gas-phase condensation has become more advanced and is now capable of generating a wide variety of novel NCs. This technique consists of the following four basic steps:^{2,18}

- Target material evaporation:

Target material evaporation is the first step of the gas-phase condensation technique. It involves generating the target material into gas phase. High vacuum condition is required to ensure that the gas-phase target remains of high purity. There are several common methods to evaporate the target materials, including seeded supersonic nozzle source, thermal gas condensation, sputtering sources, pulsed arc cluster ion source and laser ablation sources, shown in Figure 1.1.¹⁹ The seeded supersonic nozzle source has an advantage of producing a high flux NC beam, but it is not compatible for targets

with high melting points. The laser ablation source has the flexibility of target selection, but it also introduces complexity into the system. Among these sources, the sputtering source, especially the magnetron-based sputtering source, is widely used and it has been considered as the most promising source due to its wide range of target selection, ease of operation, and ability to finely tune the gas-phase target generation rate.²⁰ Additionally, co-sputtering of several target materials simultaneously or sequentially can be easily achieved by magnetron sputtering to generate different types of nanoparticle clusters, such as alloy, bimetallic and trimetallic NCs, with various core-shell structures.^{17,21–24}

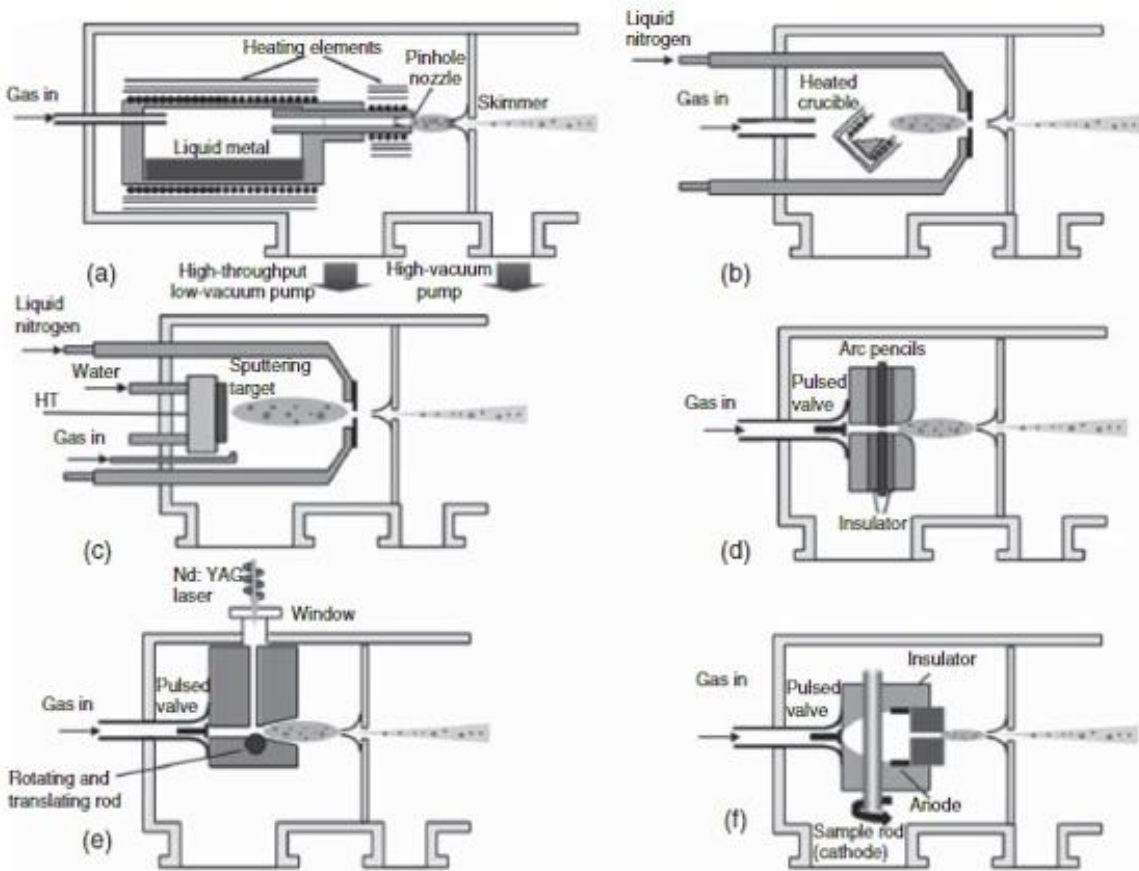
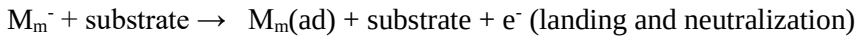
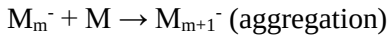
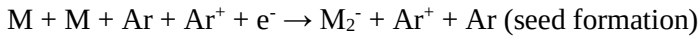


Figure 1.1 Basic layout of sources for the gas-phase condensation technique: (a) seeded supersonic source: a high pressure inert carrier gas takes the vapor of low melting point target material into the condensation chamber, while the sudden expansion of the gas cools down the target vapor into clusters; (b) thermal evaporation source: a heated crucible is used to evaporate the target for further cluster condensation; (c) sputtering source: a magnetron sputtering source is used to generate the

target gas vapor; (d) pulsed-arc cluster ion source: the evaporated plume is produced by a pulse arc coinciding with the gas burst; (e) laser ablation source: a Nd-YAG laser pulse focused onto the target to evaporate the target material; and (f) microplasma cluster source: a pulse of high pressure inert carrier gas is introduced to promote the sputtering yield.*

- Condensation and cluster growth:

In Figure 1.2a, an aperture along a pressure gradient is used to condense the gas-phase target germs into clusters. To help with the condensation, an inert gas (usually Ar) is introduced, not only for sputtering the target material but also to facilitate seed formation.²⁵ The formation and growth of the NCs by gas-phase condensation technique involve the following simplified mechanism, schematically presented in Figure 1.2a using the example of size-selected ZrO₂ NCs synthesis:



where Ar is the buffer gas, M_m (m = 2,3,..., n) is a free metal cluster species of m atoms, M_m(ad) is a metal cluster adspecies on the substrate.

Intense research has been directed towards understanding the growth mechanism of NCs within the condensation chamber, encompassing facets of nucleation and transportation. This realm of investigation can be categorized into two principal types of studies. The first category employs molecular dynamics to simulate the interactions between gas-phase atoms during collisions, yielding highly precise and accurate pictures of nanocluster growth.^{26–28} Based on this atomistic approach, Monte Carlo simulations have focused solely on pre-defined system transitions rather than the comprehensive trajectories of every individual particle.^{29–31} The second category of studies harnesses computational fluid dynamics to model the flow and transportation of nanoclusters within the condensation chamber.^{32–34} In particular, these later studies delve into the ramifications of gas flow rate and the positioning of the sputtering source, and examine such important variables as the distance

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between the source and the exit aperture, commonly referred to as the aggregation length. Both genres of inquiries, via molecular dynamics and computational fluid dynamics, have yielded noteworthy results. Indeed, these investigations underscore the pivotal roles played by the pressure within the aggregation chamber and the flow rate of the carrier gas. These factors significantly influence the dwell time of nanoscale aggregates, ultimately leading to variations in the NC size distributions.

- Mass-filtering and size-selection:

Both theoretical and experimental studies have provided ample evidence that NCs exiting the condensation chamber tend to follow a size distribution resembling a Gaussian profile.^{2,34} Consequently, to procure the size distribution of these NCs and selectively isolate NCs of desired mass (size) for further tasks such as *in-situ* deposition of monosized NCs onto appropriate substrates and *ex-situ* characterization, the integration of a mass filter becomes essential. Among the commonly employed mass filters for NC deposition are the quadrupole mass filter (Figure 1.2a) and the time-of-flight mass filter, both of which offer significant utility in this context.^{2,3,34} These mass filters are amenable to operation in both high-resolution and low-resolution modes, thereby enabling appropriate compensation for the beam flux. The time-of-flight mass spectrometer is noted by its remarkable resolution capabilities, extending up to 10^5 atomic mass units (amu), albeit with certain intricacies. On the other hand, the quadrupole mass filter exhibits a more streamlined configuration. Through a straightforward manipulation of the DC/AC ratio, the quadrupole mass filter can be effectively used to minimize any trade-off between flux and resolution.³⁵

- Deposition and on-substrate modification:

Monosized nanoaggregates are produced as they exit the mass filter and are ready for deposition. Ideally, the NC beam can be deposited onto any vacuum-compatible substrate.³⁶ However, conductive substrates are preferred if a thick NC film is required, in order to prevent charging from the negatively charged NCs. Additionally, the final NC deposition can be modified by applying a sample bias to control the landing energetics and/or changing the substrate temperature during the deposition process (e.g., by *in-situ* annealing).^{22,37}

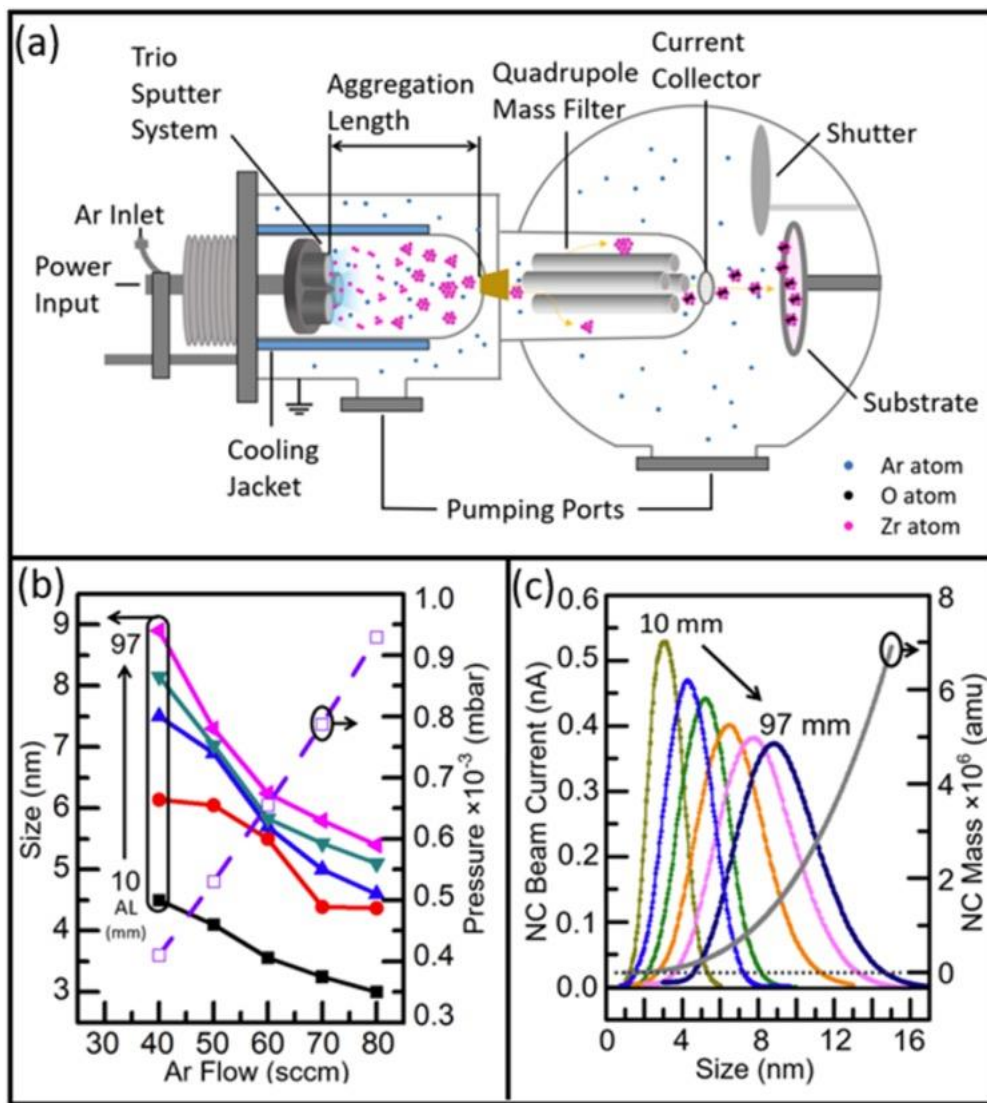


Figure 1.2 (a) Schematic representation of the Nanogen NC deposition system for producing a size-selected NC beam, which involves (i) generation of free atoms by DC magnetron sputtering, (ii) seed formation by collision and atom condensation into bigger clusters, and (iii) beam collimation via a 3 mm diameter entrance aperture and size selection of the NCs by a quadrupole mass filter. (b) Zr nanocluster mode size (in diameter, left axis) and the deposition chamber pressure (right axis) as a function of Ar flow rate (from 40 to 80 sccm in steps of 10 sccm) for different aggregation lengths or Als (10, 30, 50, 70, and 97 mm). The mode cluster size corresponds to the size (diameter) of the maximum in the cluster size distribution. (c) Zr nanocluster size distribution, as reflected by the beam current obtained at the collector of the quadrupole mass filter, for a fixed Ar flow rate (50 sccm) and

different Als (10, 30, 50, 70, 90, and 97 mm), along with the mass of Zr NCs (right axis) for different NC sizes.

1.1.2 NC Tuning

The magnetron sputtering-based gas-phase condensation technique, coupled with a quadrupole mass filter, offers a high degree of freedom to finely tune the NC beam with different sizes, phases, structures, and compositions.¹⁸ Based on the aforementioned synthesis mechanism, tuning can be performed in each step to affect the final form of the NCs. Tuning the source could provide different initiations for the subsequent condensation process. Simply adding more magnetron sputtering sources with different targets becomes a powerful and flexible solution to create a wider variety of NCs.^{22,38} By turning each sputtering source on and off individually in different time sequencing manners, bi-metallic (A+B) or alloy (AB) NCs can be synthesized from just two sources. Huttel *et al.* have also demonstrated that different core-shell structures can be precisely manipulated by controlling the position of each sputtering source (i.e., each source has its own aggregation length).¹⁷ Clearly, NCs with ternary, quaternary, quinary compositions and beyond can in principle be obtained by adding more sources.

Manipulating the condensation process is key to synthesizing NCs with different sizes, phases, and oxidation states. Several parameters can be adjusted to fine-tune the NC condensation, including (Ar) gas flow rate, aggregation length (AL, defined as the distance between the targets and the exit aperture), and cooling temperature of the condensation zone. Ar flow rate and aggregation length are the two most important variables, which work together to change the dwell time and, thus, the NC size distribution.^{2,8,34} Illustrated in Figure 1.2c, for a fixed Ar flow rate, a longer AL promotes a longer dwell time, resulting in a bigger NC mode size and a wider size distribution.³⁹ Figure 1.2b also shows that, under the same aggregation length, increasing the Ar flow rate produces more sputtering, more seed formation, and shorter dwell time, which results in a narrower NC size distribution and a smaller mode size. Tuning the NC size distribution is especially important because it also maximizes the deposition efficiency when the NC beam passes through the mass filter. Cooling temperature of the condensation zone is more difficult to manipulate than the other two parameters, even though the cooling rate could strongly affect the lattice structure. While water or liquid nitrogen has been used to cool the condensation chamber wall,³² there are some others report the use of cold fingers attached to

the substrate to cool down the deposited NCs.⁴⁰ Simultaneously introducing some reactive gases, such as O₂ and H₂O, into the condensation chamber can alter the oxidation state or aggregation status of the NCs. Indeed, introducing oxygen with a leak valve is a commonly used method to modify the oxidation state of transition metal oxide NCs, such as TiO_x.⁴¹ Zhao *et al.* demonstrated that introducing water vapor into the condensation germs acted as an adhesive component to form core-satellite Au NC complexes.⁴² Alternatively, introducing He as another inert carrier gas could significantly increase the gas flow speed inside the aggregation chamber, resulting in a narrower NC size distribution with a smaller mode size. However, too much He may prevent seed formation and could result in the loss of sputtering atoms and low NC beam current.¹⁸

As demonstrated in Figure 1.3, when combined with ultra-high vacuum (UHV) techniques, various in-flight modifications can be incorporated alongside mass-filtering. For instance, positioning an additional magnetron sputtering source adjacent to the NC beam allows for additional coating on the as-synthesized NCs, thereby enabling the realization of core-shell or even core-shell-shell structures within the NCs.⁴³ Other in-situ characterizations, such as time-resolved UV-Vis spectroscopy (Figure 1.3b)³³ or small-angle X-ray scattering measurement (Figure 1.3c),⁴⁴ can also be conducted. To facilitate these analyses, a window is incorporated near the sputtering source in the condensation chamber, in order to facilitate the transmission of ultraviolet and visible light or X-ray. These *in-situ* measurements provide insights into cluster growth and material transport. Furthermore, the application of substrate bias can alter the kinetic energy upon which the NCs land on the substrate, which is a particularly effective parameter given the inherent charge of the NCs. This variation in the landing energy strongly affects the ultimate morphology of the NCs deposited on the substrate.⁴⁵ This is supported by Langevin molecular dynamics simulation, which shows that upon reaching the substrate with distinct kinetic energies, the ensuing impact energy elevates the NC temperature significantly, reaching thousands of Kelvin.⁴⁶ Consequently, contingent on the substrate bias, the NCs could undergo structural deformation and re-crystallization. Under either a negligible bias or a low bias condition, specifically with values lower than 0.1 eV/atom, the scenario can be construed as one of soft landing, where the NCs experience no deformation upon impact, consequently generating a loosely packed porous film. On the other hand, as the bias is increased above this soft-landing threshold, the NCs experience a more forceful collision with the substrate, culminating in the creation of a relatively dense film.⁴⁷

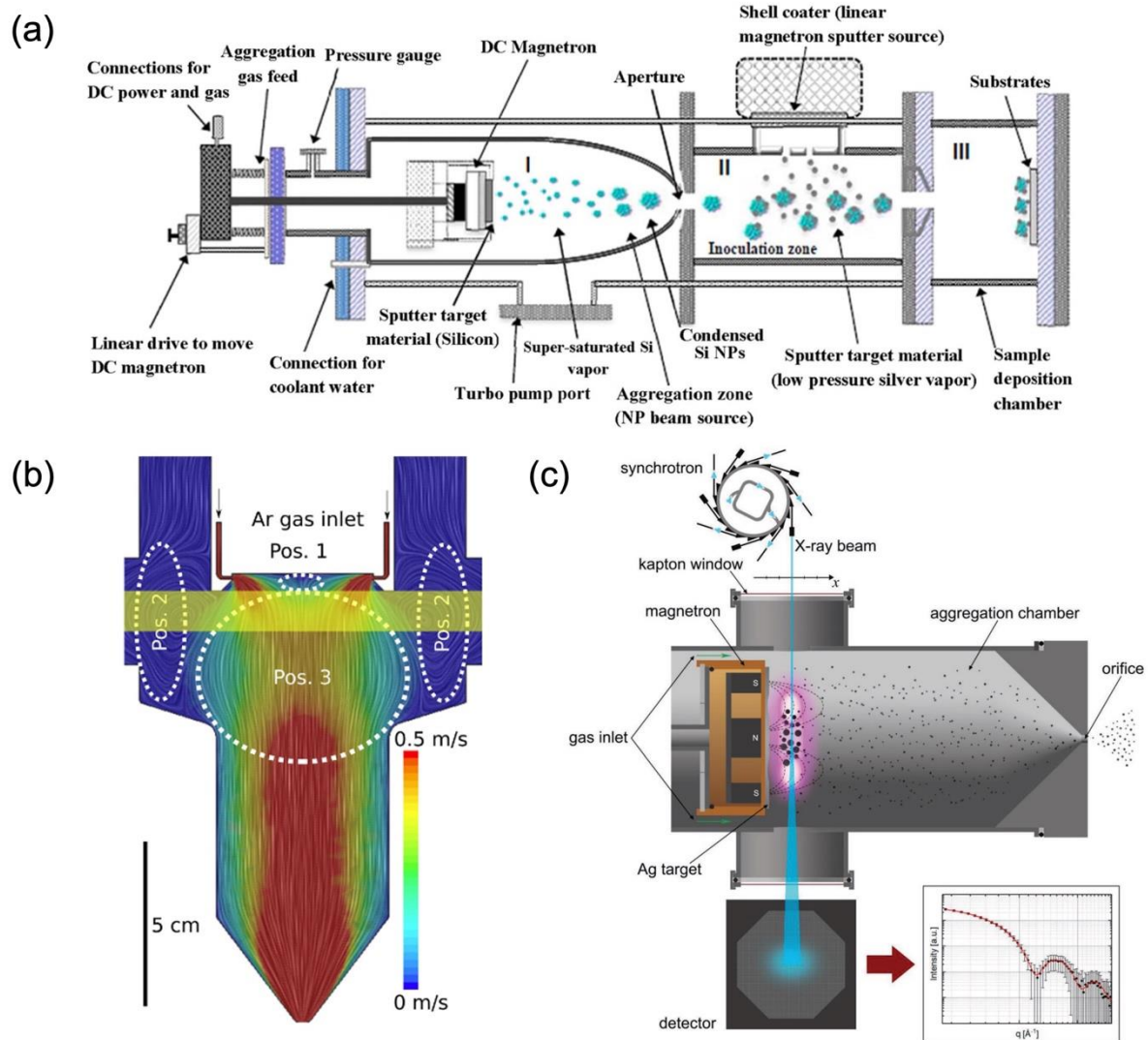


Figure 1.3 (a) An additional magnetron sputtering is equipped to provide a shell coating of the NCs passing through, as an example of Ag coated Si nanoclusters.[†] (b) An example of a computational fluid dynamics velocity distribution is shown, and the yellow region corresponds to the UV-Vis beam path to provide *in-situ* UV-Vis characterization of the assembling NCs. Positions 1 and 2 correspond

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to the loss regions and Position 3 corresponds to the trapping region.[‡] (c) In-situ small-angle X-ray scattering characterization of the NCs to reconstruct the scattering intensity as a function of the magnitude of the wave vector q in order to obtain the NC size distribution and relative volume fraction by fitting these curves. In (b) and (c), the position of the magnetron sputtering source is movable so that the nucleation and growth of the NCs at different distance from the source can be studied.[§]

1.1.3 Advantages, Limitations and Improvements of the Gas-phase Condensation Technique

Gas-phase condensation offers several advantages over traditional NC synthesis methods. It provides high flexibility in material selection and the ability to simultaneously incorporate multiple targets in one condensation chamber. With the help of a DC or RF magnetron sputtering source, it can generate NCs with most solid metals and metal oxides, particularly those with high melting point targets.^{29,36,38} More importantly, this technique is capable of synthesizing NCs without using any solvents, ligands, or linkers and therefore free of any contaminant. Compared to the wet chemistry or hydrothermal method, it allows for more precise tuning for both size and composition of the resulting NCs without involving complicated operation and procedures. In-flight modifications, coatings, and characterization can also be easily achieved, allowing for precise control over the properties of the NCs.⁴³ Moreover, the technique can be used with any type of substrate that can withstand low-vacuum conditions, and the substrate preparation is relatively less time-consuming. Overall, gas-phase condensation is a highly versatile method for producing NCs with tailored functionalities for diverse applications.

[‡] Reprinted with permission from Drewes, J.; Ali-Ogly, S.; Strunskus, T.; Polonskyi, O.; Biederman, H.; Faupel, F.; Vahl, A. Impact of Argon Flow and Pressure on the Trapping Behavior of Nanoparticles inside a Gas Aggregation Source. *Plasma Processes and Polymers* **2022**, 19 (1), 1–11. Copyright 2021 by John Wiley and Sons.

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Despite these advantages in gas-phase condensation technique, there are several limitations that could still impede the broader industrial utilization of NCs. Among these, a prominent issue is the low NC beam current.^{17,36} This predicament arises from the geometry of the magnetron and the buffer gas inlet, which results in a significant proportion of the sputtered atoms undergoing re-deposition onto the central target area post-collision with the buffer gas. Consequently, a phenomenon known as a "racetrack" can manifest. The appearance of this racetrack on the target surface greatly diminishes the sputtering yield, thereby inducing inconsistency in NC production. Given that only a small fraction (~1%) of NCs manages to escape from the plasma region, the dominant factor contributing to the NC loss is caused by diffusion onto the chamber wall.³² This is supported by an additional computational fluid dynamics simulation that confirms the presence of three distinct areas where the NCs could become ensnared or lost due to the influence of vortexes and drag forces, as shown in Figure 1.3b.³³ The exceedingly low NC beam current necessitates extensive hours of sputtering to generate a compact NC film, thereby exacerbating the erosion issue encountered by the sputtering target and further reducing the NC beam intensity.

Considerable advancements have been made in the last decade in enhancing the sputtering yield and ensuring the consistency of the NC beam quality from its source. Augmenting sputtering yield represents a direct approach to elevate the atom density of the target within the condensation chamber. Departing from the conventional planar magnetron sputtering sources, a novel hollow cathode sputtering source with a tube target has been devised.⁴⁸ This tube-integrated sputtering engenders self-sustained sputtering devoid of magnetic field assistance, thereby conferring substantial advantages in terms of sputtering yield and target utilization (Figure 1.4a). Alternatively, the development of the full-face erosion (FFE) magnetron seeks to enhance target utilization by employing moving magnets to sweep across the entire target surface (Figure 1.4c).¹⁷ This approach mitigates the low sputtering yield linked to the challenge of "racetrack" formation on planar sputtering targets. Conversely, the employment of high-power impulse magnetron sputtering (HiPIMS) enables heightened energy levels compared to conventional DC sputtering. This engenders not only an augmented influx of gas-phase atoms but also a denser plasma for seed formation, thereby amplifying the NC yield (Figure 1.4b).³⁸ Interestingly, HiPIMS exhibits differential effects on the degree of ionization of the sputtered material, thereby influencing the final NC structure, particularly in the case of bimetallic NCs. Furthermore, an innovative cluster source called the Matrix Assembly Cluster Source (MACS) that uses an innovative operating principle has been pioneered by Palmer *et*

al. (Figure 1.4d).⁴⁹ This involves the utilization of a cold finger mesh to condense a blend of metal atoms and buffer gas atoms into a solid germ. Cold NCs materialize after the condensed matrix is sputtered by an additional buffer gas (Ar^+) beam and subsequently deposited onto the substrate. More significantly, the MACS maintains a robust potential to scale up cluster beam current to the milliamperere level in comparison to the nanoampere level achieved through the traditional gas-phase condensation technique.

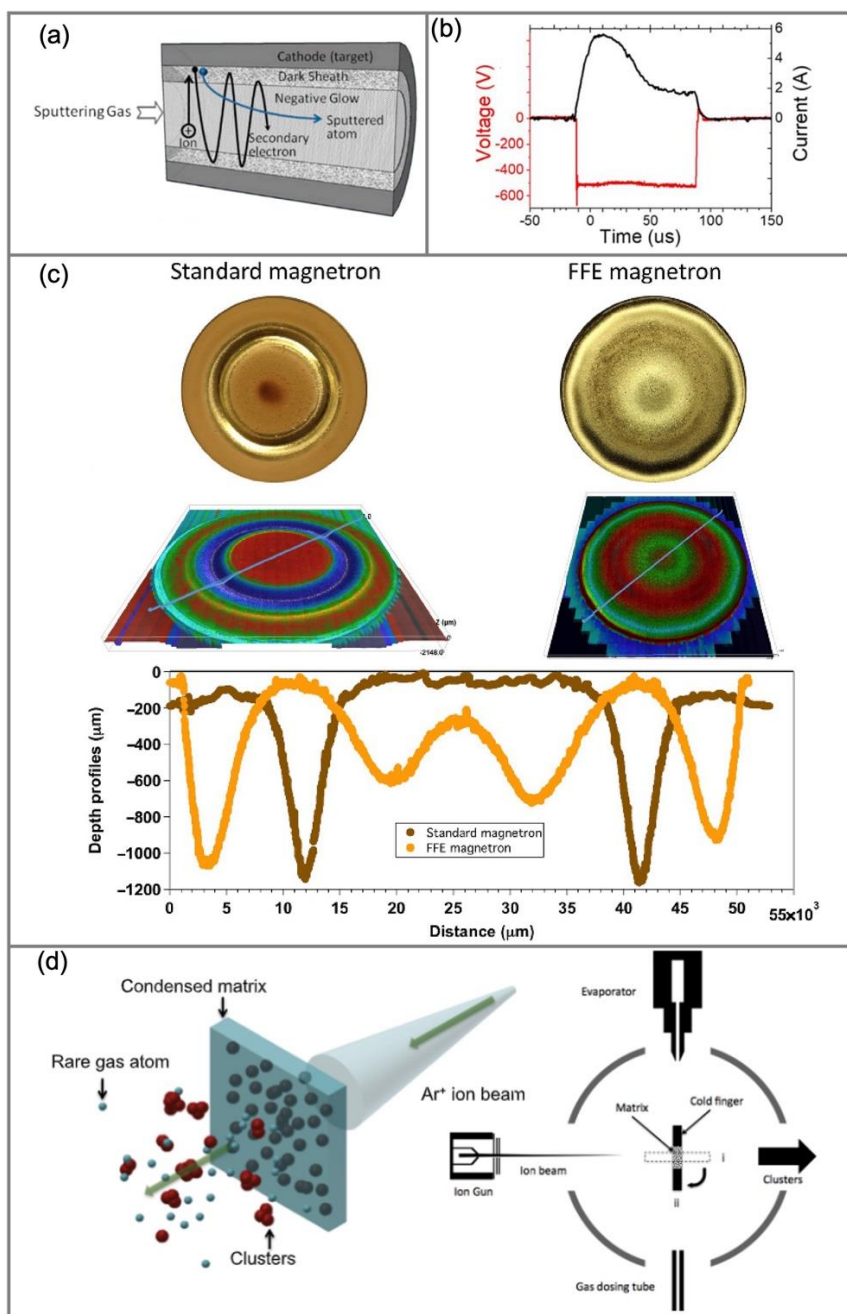


Figure 1.4 (a) A schematic representation of a magnetron sputtering source using a self-sustained hollow cathode sputtering source. ** (b) Representative temporal shape of the HiPIMS pulse with the

** Reprinted with permission from Liu, J.; He, S. H.; Wang, J. P. High-Yield Gas-Phase Condensation Synthesis of Nanoparticles to Enable a Wide Array of Applications. *ACS Appl Nano Mater* **2020**, 3 (8), 7942–7949. Copyright 2020 American Chemical Society.

voltage labelled in red and the current labelled in black.^{††} (c) Surface images (top), light microscope images (middle) and depth profiles (bottom) of a standard magnetron sputtering target (left) compared to a Full-Face Erosion magnetron (right).^{‡‡} (d) Schematic diagram of the concept of Matrix Assembly Cluster Source (MACS) and the apparatus. The matrix is formed by condensing the evaporated target atoms and buffer gas atoms simultaneously onto the matrix support grid (held at below 15 K by a rotatable cold finger). The deposition is then triggered by high energy Ar⁺ beam (1 keV).^{§§}

1.1.4 “Size-dependent” Properties of Nanoclusters

The size-dependent properties of nanoclusters constitute a compelling area of investigation that profoundly influences their performance in potential applications. As outlined in the preceding section, the method of nanocluster synthesis significantly governs their size, structure, and composition. Table 1.1 summarizes the metal targets used in most of the popular NCs synthesized by the magnetron sputtering based gas-phase condensation technique (with a comprehensive table and its own bibliography given in Appendix A). Building upon this foundation, the subsequent analysis delves into how these size variations intricately shape the distinctive characteristics and performance of NCs. Unraveling the intricacies of size-dependent behavior is of paramount importance, as it empowers researchers to engineer nanoclusters tailored precisely for a wide range of specific applications, from catalysis to electronics to biology, and to energy conversion. In this section, we embark on a comprehensive exploration of the captivating realm of the size-dependent structure-property-performance relation in nanoclusters and its far-reaching implications across diverse realms of scientific inquiry and technological advancement.

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^{§§} Reprinted with permission from Palmer, R. E.; Cao, L.; Yin, F. Note: Proof of Principle of a New Type of Cluster Beam Source with Potential for Scale-Up. *Review of Scientific Instruments* **2016**, 87 (4), 046103. Copyright 2016 by AIP Publishing.

Table 1.1 The target material that has been synthesized into nanoclusters using the magnetron sputtering gas-phase condensation technique.

[illegible]

Controlling the dwell time of collisions among gas-phase atoms and aggregates during the gas-phase condensation stage can effectively produce different size distributions of synthesized NCs while simultaneously modifying their crystallinity and morphology. For example, ultra-small size-selected ZrO_2 NCs synthesized through Zr metal NC formation followed by natural oxidation in the ambient environment exhibit an amorphous structure at 3 nm (diameter in size) and start to form crystalline structures at 5 nm.² In contrast, TiO_2 NCs from the same Group IV-B show a crystalline core surrounded by an amorphous shell when their size is larger than 6 nm.⁸ On the other hand, HfO_2 in the amorphous form is only observable in NCs below 10 nm due to surface energy relaxation. These findings suggest that small grain size thermodynamically favors the formation of the amorphous phase.⁵⁰ Furthermore, Pearmain *et al.* demonstrated that Pd NCs showed a notable deviation from a spherical shape with increasing cluster size from 887 to 10,000 atoms.⁵¹ This is due to different relaxation between cluster-cluster collisions in the aggregation chamber. These novel structures and morphologies that are markedly different from their bulk forms could lead to the

emergence of new properties not found in their bulk phases and to potentially improved performance in relevant applications.

In catalysis work, NCs emerge with their distinct advantages arising from their high surface area-to-volume ratio that has led to more active sites and enhanced surface reactivity. In addition, the size-dependent morphology, lattice structure and chemical states could also significantly affect the catalytic performance of the NCs. Conventionally, a substrate is required not only for retaining the NCs into a certain region, but also for enhancing the charge transfer process resulting in better performance. Since the gas-phase condensation is a physical vapour deposition technique that do not depend on the nature of the substrate, many different substrates have been reported and they include Si, MgO (powder), FTO, and STO (SrTiO₃).^{8,22,52,53}

In the field of photoelectrochemical water splitting chemistry, NCs have been extensively studied and employed for both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), showcasing their broad functionality and versatility. NCs of transition metals and their oxides have been mostly used in the OER work, while noble metal NCs are used as photocathodes. Strong size-dependent performance has been observed in such catalysis work, where NCs with smaller sizes exhibit higher catalytic activities. For example, Yang *et al.* found that the sputtering power significantly affects the morphology and size of Co:Sm NCs, and the NCs with the smallest size and highest Co concentration exhibit the highest electrocatalytic properties in the OER.²⁰ Additionally, Srivastava *et al.* showed that size-selected TiO₂ NCs with sizes smaller than 6 nm exhibit higher photoelectrochemical catalytic activity, shown in Figures 1.5a and 1.5b,⁸ while Khojasteh *et al.* demonstrated that size-selected MnO NCs synthesized by gas-phase condensation with sizes of 4, 6, and 8 nm exhibit enhanced catalytic activities with decreasing size.⁵² In the HER work, the size-selected Pt_n/STO electrode exhibits enhanced electrochemical HER activity, with the maximum performance found for n = 30 in the range of n = 1-45 between -1.35 V and -1.5 V vs Ag/AgCl, as demonstrated in Figure 1.5c.⁵³ Anion photoelectron spectroscopy also showed a shift in the LUMO level of the Pt NCs as a function of size. Interestingly, Pt NCs and nanostructures are so versatile that they can be used not only as a photocathode for HER but also as a promoter to improve the performance of other semiconductor NC photoanodes. Srivastava *et al.* also demonstrated that introducing Pt NC promoters could significantly reduce the electron-hole pairs generated in the semiconductor TaO_x during the OER and efficiently enhance photoconversion.⁹

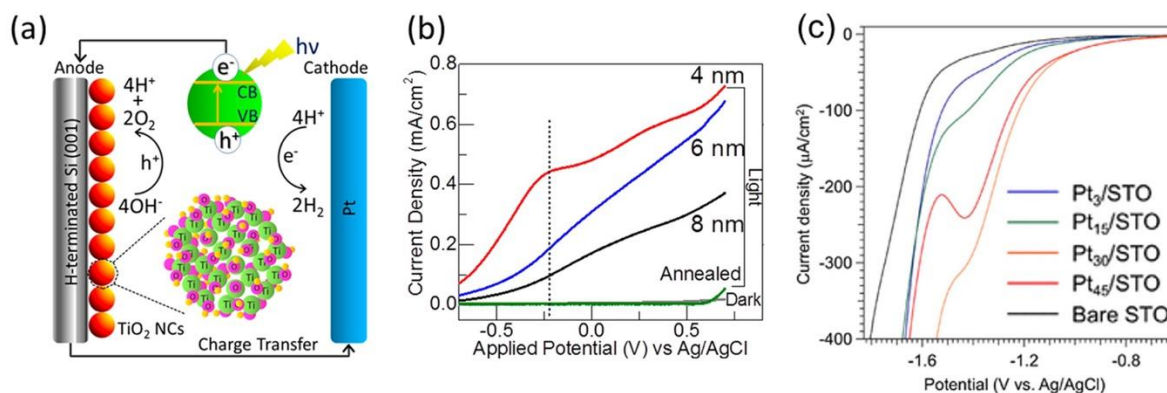


Figure 1.5 (a) Schematic diagram of the mechanism of a photoelectrochemical water splitting reaction. An expanded view of a TiO₂ nanocluster (NC, red sphere), consisting of Ti (green spheres), O (pink spheres), and H atoms (brown spheres), is shown as the lower inset. The upper inset shows the electron-hole pair generation in TiO₂ upon UV-vis light illumination, which supplies holes (h⁺) for the oxidation of OH⁻ leading to O₂ evolution at the photoanode and electrons (e⁻), upon traveling to the counter electrode through an external circuit, for reduction leading to H₂ generation. (b) Photocurrent densities as a function of applied potential obtained in a photoelectrochemical water splitting reaction in a 5 M KOH electrolyte using TiO₂ nanoclusters of different sizes (4, 6 and 8 nm) and the post-annealed TiO₂ NCs (6 nm). *** (c) Linear-sweep voltammograms curves for electrocatalytic HER with STO and the Pt_n/STO electrodes in a 0.1 M aqueous solution of Na₂SO₄ under Ar from + 0.5 V to -1.8 V.†††

Two main characteristics have been identified to account for the size-dependent photocatalytic performance of NCs. The first one is attributed to the "geometric size effect".⁵⁴ Since photocatalysis is primarily related to reactions occurring on the surface, smaller NCs with a higher specific surface area provide more reactive sites per unit area than larger NCs when they form a monolayer on the substrate. The second feature involves changes in the lattice structures and electronic states that could

*** Reprinted with permission from Srivastava, S.; Thomas, J. P.; Rahman, M. A.; Heinig, N. F.; Leung, K. T. Size-Selected TiO₂ Nanocluster Catalysts for Efficient Photoelectrochemical Water Splitting. *ACS Nano* **2014**, 8 (11), 11891–11898. Copyright 2014 American Chemical Society.

††† Reprinted with permission from Tsunoyama, H.; Yamano, Y.; Zhang, C.; Komori, M.; Eguchi, T.; Nakajima, A. Size-Effect on Electrochemical Hydrogen Evolution Reaction by Single-Size Platinum Nanocluster Catalysts Immobilized on Strontium Titanate. *Top Catal* **2018**, 61, 126–135. Copyright 2018 by Springer Nature.

occur with the NC size. In perfect nanocrystalline NCs, the band gap inherently increases as the NC size decreases, which could limit photon absorption. However, NCs are more likely to possess higher defect concentrations compared to bulk materials. These defects introduce midgap states, consequently increasing photon absorption and enhancing the overall photocatalytic efficiency.⁵⁵

In addition to the photoelectrochemical water splitting reaction, NCs also provide catalytic activities for other diverse reactions. The influence of both size and composition on selectivity and efficiency is especially important to atom-atom synergies. For instance, Cai *et al.* utilized a dual target gas-phase condensation technique to synthesize Au-rich, Cu-rich, and Au/Cu-equal (with 1:1 composition) bimetallic NCs on agitated MgO powder.²² Although the total sputtering powers are consistent for all the NCs, the Au/Cu-equal NCs (~ 4.6 nm) are larger than both Au-rich and Cu-rich NCs (~ 3.6 nm) due to surface agglomeration. Their study revealed that the Au/Cu-equal bimetallic NCs provide more active sites for oxygen group formation, leading to the highest catalytic reduction of 4-nitrophenol by NaBH₄. Furthermore, 5 nm PdTi NCs show excellent selectivity and efficiency for 3-hexen-1-ol hydrogenation.⁵⁶ The NCs produced using the gas-phase condensation technique exhibit superior performance in hydrogenation experiments compared to materials synthesized through traditional wet chemistry method.

The NCs with varying sizes give rise to novel structures and different levels of defects could also have a significant impact on the spin alignment within the NCs, particularly in the context of defects resulting from surface oxidation in transition metal oxide NCs. Early density functional theory (DFT) studies have shown that oxygen vacancy defects in ZrO₂ NCs are more likely to form at low coordination locations such as corners and edges.⁵⁷ Therefore, the number and type of oxygen vacancy defects could vary depending on the size of the ZrO₂ NCs. These defects also stabilize the tetragonal structure of ZrO₂ NCs at room temperature, while the most stable structure for bulk ZrO₂ is monoclinic.^{2,58} As illustrated in Figure 1.6b, in tetragonal ZrO₂ NCs, a single oxygen atom can trigger the reduction of four nearby Zr⁴⁺ ions into Zr³⁺ ions, forming a resonance structure. The electron hopping between the Zr³⁺ ion and the single-charged oxygen vacancy favors spin splitting and ferromagnetic alignment, in marked contrast to bulk ZrO₂, which is diamagnetic. This work also shows that the ferromagnetism in the ZrO₂ NCs is size-dependent (Figure 1.6a), which is also related to the surface defect concentration. This behavior promotes another way of manipulating the magnetic performance by size control. Similarly, the NCs of HfO₂, another Group IV-B metal oxide, obtained by gas-phase condensation are also reported to have a mixture of tetragonal and monoclinic

structures that exhibit paramagnetism.⁵⁹ These dopant-free, ligand-free transition metal oxide NCs could become strong material candidates for the next generation of spintronics.⁶⁰

Other remarkable performance in biology, energy storage, electrical device applications have also been demonstrated for the NCs obtained by the gas-phase condensation technique without delving too much about their size-dependency. Mery *et al.* demonstrate that there is a significant change in both density and morphologic effect for cell spreading onto sterile glass covers decorated with Ag NCs. The cells change from their typically expanded morphology to a spherical one. Surprisingly, no toxicity has been found for those Ag NCs.⁶¹ In the field of energy storage, the efficiency of H₂ storage in Mg films can be significantly enhanced by depositing Pd NCs onto a Mg thin film.⁶² The DFT study also reveals that the transformation of cubic Pd into a hexagonal structure near the interface is governed by the interfacial strain. Furthermore, the study indicates that prior hydrogen saturation of the Pd NCs enhances their nanoportal efficiency. Another area of applications for NCs is memristors, which are two-terminal non-volatile memory devices that can maintain their resistance states based on the bias and current passing through them.^{63,64} Their memory capabilities, low power consumption, and scalability make them attractive for a variety of applications, including artificial intelligence and neuromorphic computing, data storage, and energy-efficient electronics. Since they hold the key to the next evolution of storage devices, there is a strong interest to fabricate them at the nanoscale.⁶⁵ Vahl *et al.* successfully used the gas-phase condensation technique to embed 11 nm AgAu or 9 nm AgPt NCs into a SiO₂ dielectric matrix, forming a vertical sandwich two-terminal device, shown in Figure 1.6c.⁶⁶ The device exhibits a reliable pinched current-voltage hysteresis loop at the level of individual NCs, without requiring any additional electroforming steps. These studies utilizing these ultra-small NCs illustrate their immense potential for revolutionary applications spanning catalysis, electronics, medicine, and beyond. Leveraging the inherent advantage of precise size manipulation facilitated by the cluster beam technique, their performance can be optimized to its zenith through meticulous size-dependent investigations.

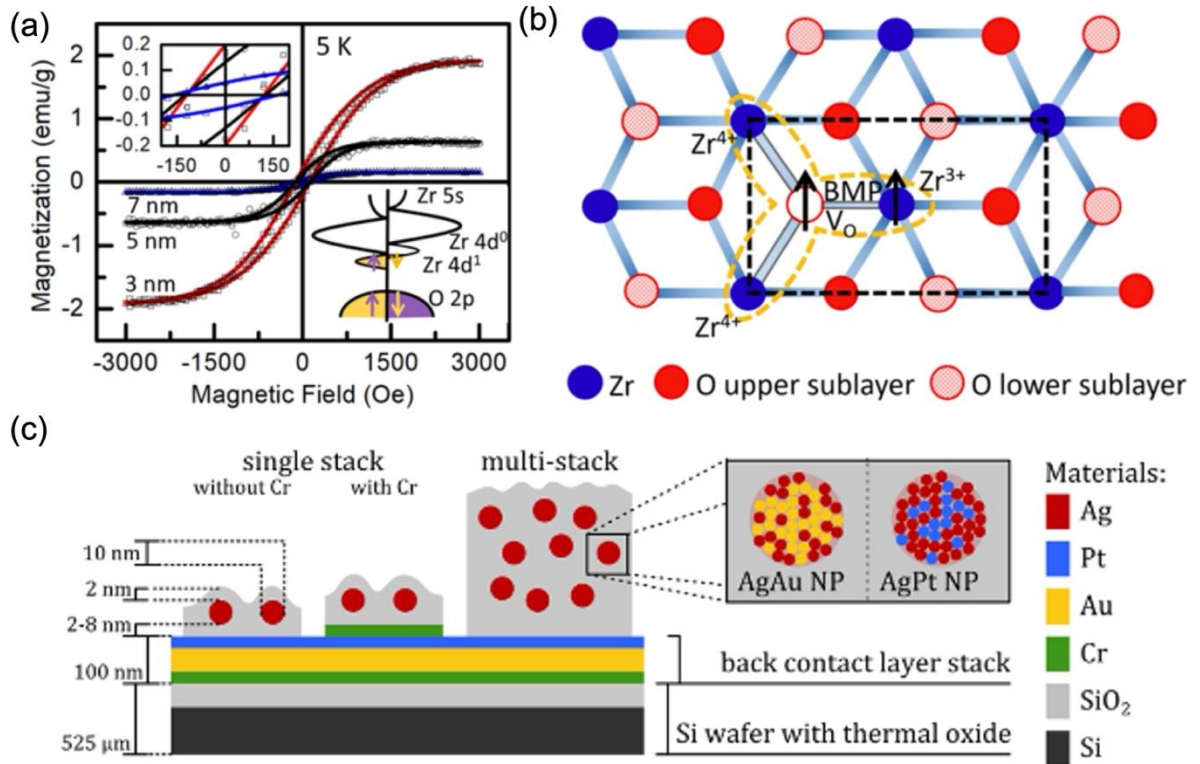


Figure 1.6 (a) Measured (symbols) and fitted ferromagnetic hysteresis loops (solid lines) of as-grown ZrO₂ NCs of different sizes obtained at 5 K. The right bottom insert presents the band-splitting leading to ferromagnetism generation: an impurity band contributed by Zr 4d₁ (Zr³⁺) is generated by the oxygen vacancy defects. This impurity band could merge and hybridize with the conduction band, which triggers band-splitting into spin-up and spin-down states. (b) Schematic presentation of the formation of magnetic polarons in an unreconstructed ZrO₂ (1 0 1) surface. The missing oxygen vacancy (V_O) in the lower sublayer triggers four nearby Zr ions (the one below V_O is not shown) with two excess electrons. The electron trapping in the oxygen vacancy could couple with the other electron located in Zr³⁺ via exchange interaction, generating the magnetic polaron. (c) Schematic depiction of the typical setup of NC-based memristor. For a detailed assessment of memristive

behaviour of single NCs, single stack SiO₂/NC/SiO₂ devices (with and without an additional Cr wetting layer) are characterized by C-AFM.^{†††}

1.2 Magnetic Semiconductors

1.2.1 From Dilute Magnetic Semiconductors to Dopant-Free Magnetic Semiconductors

In the realm of solid-state physics, the manipulation of electron spin significantly enhance the traditional charge-based functionalities, paving the way for a novel paradigm in device applications.^{67,68} The advent of the giant magnetoresistance (GMR) effect has heralded an era wherein the intrinsic spin of electrons is not merely a passive attribute but an actively coupled and transportable entity in electronic devices.⁶⁹ In the context of semiconductors, specific compounds such as EuO and EuS, illustrated in Figure 1.7a, encompass periodic magnetic elements within the lattice.⁷⁰ These materials have engendered significant scholarly attention, underscored by phenomena such as the spin filtering effect and spin magneto-optical effect.⁷¹ However, it is imperative to underscore that the majority of semiconductors remain devoid of magnetic ions, culminating in their intrinsically non-magnetic nature, typified as either paramagnetic or diamagnetic, as shown in Figure 1.7c. Additionally, the crystallographic attributes of these europium chalcogenides are markedly distinct from canonical semiconductors such as Si and GaAs.⁷⁰ To confer magnetic attributes upon quintessential non-magnetic semiconductors like GaAs and ZnO, strategic doping with magnetic elements is employed, culminating in the formation of diluted magnetic semiconductors (DMSs), depicted in Figure 1.7b.^{72,73}

^{†††} Reprinted with permission from Vahl, A.; Carstens, N.; Strunskus, T.; Faupel, F.; Hassanien, A. Diffusive Memristive Switching on the Nanoscale, from Individual Nanoparticles towards Scalable Nanocomposite Devices. *Sci Rep* **2019**, 9, 17367. Copyright 2019 by Springer Nature

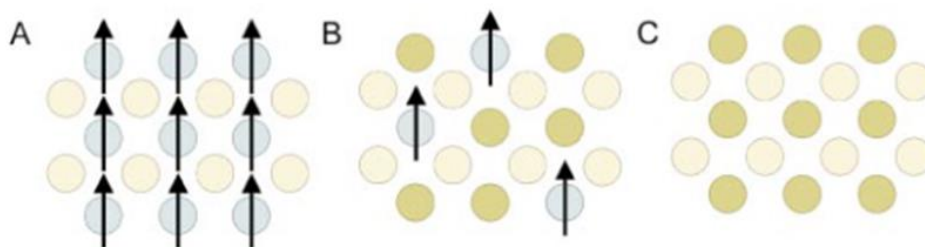


Figure 1.7 Illustration of three distinct semiconductor categories: (A) a magnetic semiconductor composed of magnetic elements; (B) a diluted magnetic semiconductor; and (C) a nonmagnetic semiconductor without any intrinsic or doped magnetic ions.^{§§§}

Early research in this field made significant progress by introducing Mn into GaAs. The (Ga,Mn)As thin film is grown using low-temperature molecular beam epitaxy (MBE) to prevent phase segregation.⁷⁰ In comparison to other doped II-VI compound semiconductors, such as Mn-CdTe, which has a Curie temperature of $< 4\text{ K}$, (Ga,Mn)As presents a notably elevated Curie temperature, reaching 110 K . Subsequent research indicates that post-synthesis treatments including annealing processes can significantly increase the transition temperature to proximally 200 K .⁷⁴ However, such a temperature remains unpractical for device operations within ambient conditions. Transparent conductive oxides (TCOs), characterized by their wide bandgap ($> 3\text{ eV}$) that enables light transmission up to the UV region, have garnered increased attention due to their availability, biocompatibility, and enhanced performance.⁷⁵ In response to this growing interest, extensive studies have been directed towards doping TCOs with magnetic elements, giving rise to what is termed as dilute magnetic oxide (DMO) or dilute magnetic semiconductor oxide (DMSO). In the 2000s, room-temperature DMSs (RT-DMSs) were reported, specifically in Mn:ZnO and Co:TiO₂.^{76,77} Subsequent research has broadened the scope of dopants from magnetic elements to non-magnetic transition metals like V and Cu. As those non-magnetic transition metals do not require any external spin from the dopants, the doped lattice structure as well as the defects created from the dopant must play an important role in ferromagnetism. Leveraging the capability to manipulate spin and charge

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independently, RT-DMSs offer a wide range of potential applications, spanning from spintronics and optoelectronics to magnetoelectronic devices.^{78,79}

With advances in nanotechnology and the synthesis of new TCO nanomaterials, the observation of unanticipated room-temperature ferromagnetism in these nanomaterials has been striking, especially given that their bulk counterparts remain non-magnetic in the absence of dopants. Notably, among these dopant-free ferromagnetic TCOs, oxides of all metal elements in the IV-B group, including TiO_2 , ZrO_2 , and HfO_2 , exhibit ferromagnetic properties in their nanostructured forms.^{2,80–82} The manifestation of this ferromagnetism is significantly influenced by the specific nanostructure. Figure 1.8 highlights the ferromagnetic attributes across various ZrO_2 nanostructures.⁸¹ Further characterization reveals that these nanomaterials possess a substantial concentration of oxygen vacancy defects, and some even stabilize unique phases at room temperature. It has been suggested that the pronounced surface area-to-volume ratio inherent to these nanostructures may be instrumental in stabilizing defects and thereby inducing their ferromagnetic behavior.^{2,81} These dopant-free magnetic semiconductors offer superior benefits, notably without any dopant segregation.^{83,84} Gaining a comprehensive understanding and mastering control over magnetic interactions within DMS materials are crucial for the continued development of spintronic devices.^{79,85}

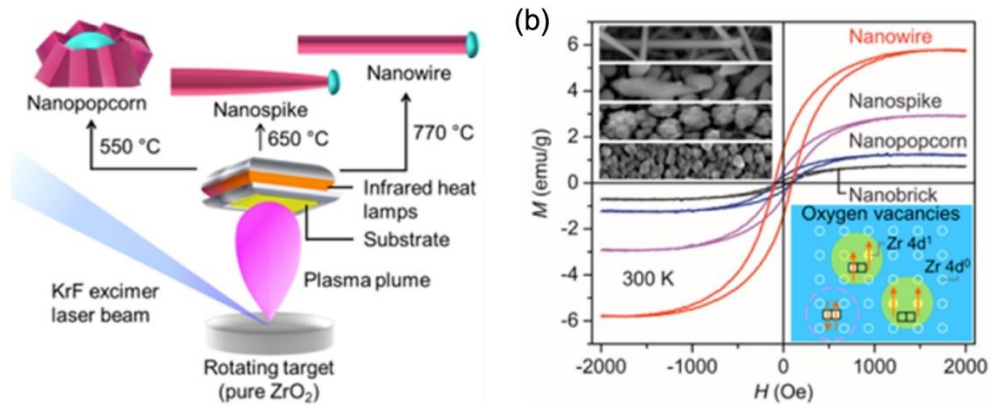


Figure 1.8 (a) A schematic representation of the growing mechanism of defect-rich ZrO_2 nanostructures on Au islands coated oxidized Si templates. (b) The hysteresis loops between magnetization (M) of as-grown ZrO_2 nanostructured films and external magnetic field (H) under room temperature. The top left inset shows the SEM images of the corresponding nanostructures (from top to bottom): nanowires, nanospikes, nanopopcorns, and nanobricks. The bottom right inset presents a schematic model of the formation of bound magnetic polarons (green circles) by singly and doubly

charged oxygen vacancies (squares), where the Zr^{4+} ions are marked by open white circles and the Zr^{3+} ions are shown as solid white circles.****

1.2.2 Existing Models of Dilute Magnetic Semiconductors

The phenomenon of ferromagnetism in dilute magnetic semiconductors has been a focal point of research since its initial discovery. Over the years, researchers have put forward various models attempting to elucidate the underpinnings of this intriguing behavior. However, despite these endeavors, the precise nature and mechanisms of magnetic interactions within DMS are yet to be fully understood.^{81,85} The landscape of this study becomes even more complex with the subsequent revelations of ferromagnetism in dopant-free TCO nanomaterials, including a range of structures from nanofilms and 2D materials to 1D nanostructures and to 0D nanoclusters, which adds layers of complexity to the existing narrative.^{2,55,58,82} Consequently, the true origin and mechanisms driving ferromagnetism in these various systems remain subjects of active investigation and debate in the academic community.

In the early stages of research, the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction was a dominant theory. Rooted in the realm of impurity metals, this interaction offers an account of the indirect exchange process mediated by conduction electrons.⁸⁶ It provides insights into how magnetic impurities interact over extended distances within a metallic host, shaping the ferromagnetic properties. However, the RKKY interaction is characterized by its oscillatory behavior as a function of distance, which means the spin parallel (ferromagnetic) and anti-parallel (antiferromagnetic) can change depending on their separation.⁸⁵ Therefore, the RKKY model is limited and it can complicate the understanding of magnetic ordering when it is applied into the field of semiconductors, especially in materials with varying magnetic impurity concentrations.

In the field of DMS, the Zener model has shown to be increasingly relevant. This model pivots on the p-d exchange mechanism, highlighting the interplay between the localized d-electron magnetic moments, typically introduced by transition metal ions, and the valence band holes.⁸⁷ The Zener

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model underscores the carrier-mediated nature of ferromagnetism in DMS and points towards the profound influence of doping and carrier concentration on the magnetic properties of the material. Recognizing the need for a more generalized and quantitative approach to analyze the complexities of these interactions, the mean-field Zener model was formulated. By adopting the spin-orbital coupling and the carrier-mediated exchange interaction, this model distills the essence of interactions into an "average" behavior instead of just considering individual interactions.^{88,89} As a result, it can be used to explain long-range interactions and predict critical parameters, such as the Curie temperature.

With the discovery of more non-magnetic transition metal-doped DMS materials, such as Cu-doped ZnO, there arose a need for a new theoretical framework to elucidate the origin of the observed ferromagnetism.⁹⁰ The bound magnetic polaron (BMP) model has been introduced to address this, emphasizing the exchange interaction between the spin polarization of the dopant and adjacent localized holes, as shown in Figure 1.9.⁹¹ Concurrently, oxygen vacancy defects are perceived as localized holes, facilitating the formation of magnetic polarons. As the dopant concentration increases, the prevalence of oxygen vacancies rises along with the magnetic polarons. These magnetic polarons may eventually overlap, bolstering the long-range ferromagnetic order. Additionally, this model postulates that the spins of oxygen vacancies could also establish exchange interaction and form polarons to enhance ferromagnetism in the absence of dopants.⁵⁷ Although the BMP model has become popular for explaining both transition metal doped and dopant-free magnetic semiconductors, there is a large number of unaccounted for non-magnetic TCO materials with a large fraction of oxygen vacancy defects.⁶⁷

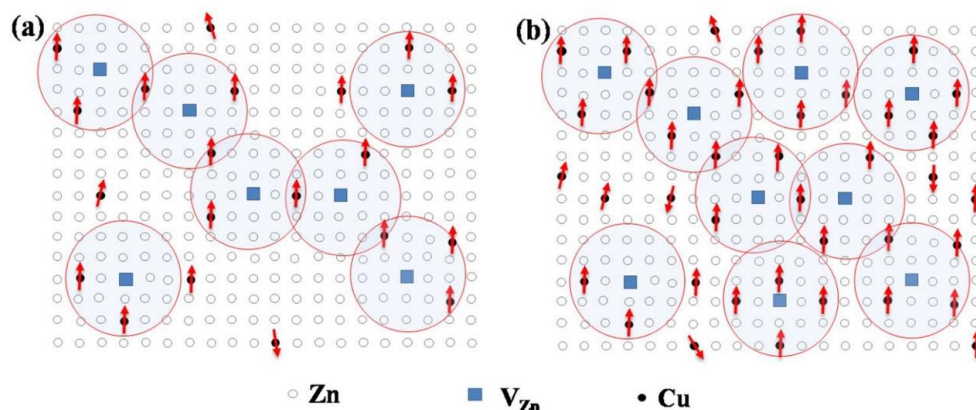


Figure 1.9 Schematic illustrations of the long-range ferromagnetic ordering in Cu-doped ZnO via bound magnetic polarons at (a) a low doping level of 0.05% and (b) a high doping concentration of 2% Cu-doped ZnO.^{††††}

The charge-transfer ferromagnetism model has been proposed to elucidate the behavior of defect-rich transition metal doped DMSs, as illustrated in Figure 1.10.⁹² Given that most transition metal dopants possess multiple valence states, they can function as charge reservoirs, facilitating electron hopping into oxygen vacancy defects.⁹³ This electron injection elevates the Fermi level within the local density of states, subsequently leading to the formation of an impurity band and causing Stoner splitting.^{57,81} However, the applicability of this model is constrained by the multivalence states of the dopants. Consequently, there remains a need for an alternative model to comprehensively explain dopant-free magnetic semiconductors.

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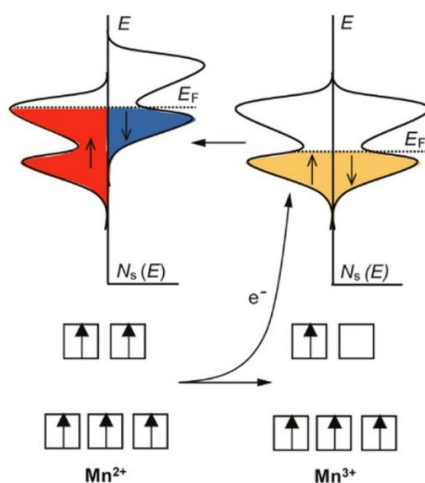


Figure 1.10 Schematic representation of the charge-transfer ferromagnetism in defect-rich transition metal doped DMSs. This mechanism involves electron transfer from Mn^{2+} to the local density of states ($N_s(E)$) associated with the interfacial structural defects, raising the Fermi level to a peak in $N_s(E)$ and causing Stoner splitting of the defect band (indicated with red and blue colors).^{††††}

1.2.3 The “Twin Oxide”: ZrO_2 and HfO_2

ZrO_2 and HfO_2 emerge as recently identified TCOs with robust research potential following the exhaustive study of TiO_2 . Despite all are originated from the IV-B group in the periodic table, ZrO_2 and HfO_2 exhibit greater similarity to each other in comparison to TiO_2 . Owing to the lanthanide contraction, Hf, encompassing more protons and orbitals, parallels Zr in radius, culminating in a plethora of analogous physical and chemical properties between these two oxides.⁹⁴ Both oxides are characterized by relatively high bandgaps (5.8 eV for ZrO_2 and 6.0 eV for HfO_2) and dielectric constants (4.8 and 4.0, respectively).⁹⁵ Their bulk forms demonstrate stability in a monoclinic structure at ambient temperature. With the escalation of temperature, a transformation to a tetragonal structure is observed, and a further increase in temperature yields a cubic phase. Notably, ZrO_2 and HfO_2 both share the monoclinic, tetragonal and cubic phases, with the monoclinic phase being the

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most stable phase at room temperature. The monoclinic phase is transformed at higher temperature to the tetragonal phase (ZrO_2 at 1170°C , HfO_2 at 1720°C) and the cubic phase (ZrO_2 at 2370°C , HfO_2 at 2600°C).⁹⁶ Concomitant lattice constants for each phase are similarly observed from previous DFT studies.⁹⁷ Furthermore, their low thermal conductivity and elevated mechanical strength make them prime material candidates for diverse applications.⁹⁶ These multifarious similarities lead to their common characterization as “twin oxides”.

These twin oxides exhibit parallel applications based on thin films and nanostructures. Their thin films are employed in optical coatings, waveguides, gas sensors, and gate dielectrics. Intrinsically, both ZrO_2 and HfO_2 in their bulk forms are diamagnetic. However, they are also being explored as DMS materials, such as Fe, Co, and Ni-doped ZrO_2 and Sc, Ti, Ta-doped HfO_2 .^{98,99} As these compounds are synthesized into various nanostructures from nano-thin films to nanowires and nanoclusters, they begin to demonstrate unique ferromagnetic properties without any dopants.^{2,80,81} Notably, these nanomaterials exhibit a plethora of defects that are not typically observed in their bulk counterparts. Furthermore, owing to the comparable lattice spacings of these two oxides, they demonstrate enhanced mutual solubility. Some research suggests that by combining these two oxides into a solid solution (as in HfZrO_2), a distinct orthorhombic structure could emerge.¹⁰⁰ This unique lattice bonding mechanism may induce internal polarization, potentially leading to concurrent ferroelectric and ferromagnetic properties.^{101,102}

The study of ZrO_2 , HfO_2 , and their mixtures is of paramount importance to contemporary materials science research. The analysis of defects, especially in the nanocluster, provides invaluable insights into the intrinsic properties of these materials and their behavior under various conditions. Such defects often play a pivotal role in influencing electrical and magnetic properties, which can be harnessed for technological applications. Furthermore, the ability to tune the composition of these materials opens a plethora of opportunities to optimize their properties for specific applications. Figure 1.11 demonstrates the thickness and composition dependence of the ferroelectric performance of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ film prepared by atomic layer deposition. By carefully tuning the composition of ZrO_2 and HfO_2 , researchers can tailor the characteristics of the material to meet the desired criteria. Considering their promising attributes, ZrO_2 and HfO_2 , both individually and in combination, stand out as new material candidates in the future development of electronic devices.^{103–105} Their versatility and adaptability make them strong contenders in the evolving landscape of modern electronics.

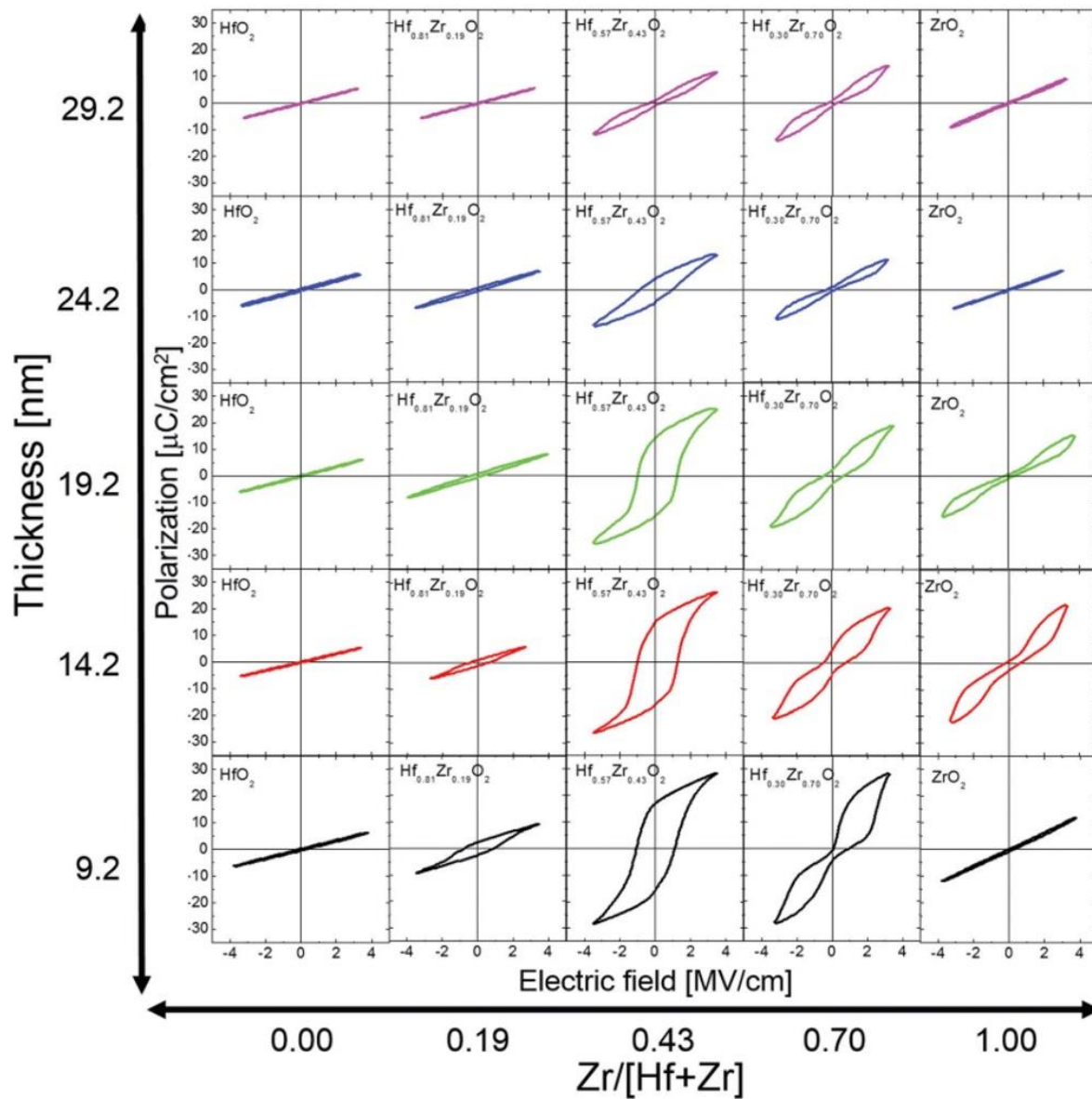


Figure 1.11 Polarization versus electric field graphs of $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films prepared by atomic layer deposition as functions of composition (x values of 0.00, 0.19, 0.43, 0.70, 1.00) and film thickness (approximately 9.2, 14.2, 19.2, 24.2, and 29.2 nm).^{§§§§}

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1.3 Interdigital Electrodes and Nanogap Devices

1.3.1 Interdigital Electrodes

One of the great challenges in studying nanoclusters is the development of appropriate nanoscale device dies to capture and secure these nanoclusters for measurements. Interdigital Electrodes (IDEs) represent a specialized class of device structures composed of tightly spaced metal or semiconductor fingers, resembling the interlocking teeth of a comb.¹⁰⁶ This unique configuration that defines the IDEs underlies their broad range of applications across diverse fields. IDEs typically consist of two sets of parallel fingers, with each set linked to a separate electrode. The critical feature of this design is the close proximity of the fingers, which maximizes the available electrode length for interactions with specific substances that are targeted to be captured and secured. Consequently, these structures result in a substantial enhancement in signal detection and sensitivity, positioning IDEs as a pivotal device structure not only for nano-object characterization but indeed for advanced sensing system and electronics.^{107–109}

Sensing plays a crucial role not only in industrial processes but also in daily life, ranging from humidity measurement to toxic gas detection.^{107,109,110} As electronic devices evolve to become more sophisticated, there is an increasing demand for sensors that are compact, quick in response, and energy-efficient.¹⁰⁸ In this context, IDEs emerge as an ideal device architecture for such applications. By incorporating specific active sensing materials between the electrode fingers, a variety of sensors can be fabricated. These sensors can detect various targets, including water (for relative humidity measurement) and inorganic hazards such as CO, SO₂, and NO.^{111–113} During a typical sensing operation, the chemical signal from the targeted gas modifies the electronic state of the active sensing material. This, in turn, affects the electrical signal between the electrodes. The variations in this electrical signal can manifest as changes in capacitance, resistance, or impedance.¹⁰⁷ The same working mechanism can be extended to biosensing applications. When integrated with the IDE platform, a diverse array of biosensor systems can be developed, encompassing applications such as antigen and biomarker detection.^{114,115} Furthermore, lab-on-chip designs that leverage the IDE platform pave the way for advanced detection methods and dielectrophoretic transport within microfluidics, a capability rooted in the uniformly distributed electric field across the IDE fingers.¹¹⁶ Beyond the traditional parallel straight-fingered configurations, V-shaped interdigital electrodes have been specifically engineered to enhance the efficiency of blood cell separation in microfluidic chips,

notably for PSA (prostate specific antigen) detection.¹¹⁵ Moreover, by coating the Pt electrodes with an Al₂O₃ protective layer, nano-thick IDEs can be adapted for use in langasite-based high-temperature surface acoustic wave sensing devices.¹¹⁷

Beyond their applications in sensing, IDEs are also integral to advancement in electronics. Their compact nature and precisely defined geometry make them essential in the fabrication of electronic components in micro to nanoscale. Innovative energy storage devices such as supercapacitors bridge the gap between traditional capacitors and batteries, positioning them as prime candidates for powering compact portable electronic devices.^{109,118} Leveraging the extended electrode length per unit area, IDEs combined with electrolytes can be fashioned into micro-supercapacitors. The interlocking finger design of IDEs not only minimizes current leakage but also facilitates easy integration into miniaturized devices, offering a clear advantage over traditional vertical metal-electrolyte-metal sandwich structures. Furthermore, the energy density of these micro-supercapacitors can be augmented by reducing the electrode width and interspacing, while ensuring operational stability.¹⁰⁹ Concurrently, Ding *et al.* have demonstrated that by vertically aligning the lower p-type electrodes with higher n-type electrodes, such as GaN, as the IDE architecture, photodiodes can be created.¹¹⁹

Recently, Zhang *et al.* present another intriguing nanoenergy harvesting device by incorporating Poly(vinylidene fluoride-trifluoroethylene) copolymer (P(VDF-TrFE)) nanofibers into IDEs.¹²⁰ As illustrated in Figure 1.12, the P(VDF-TrFE) nanofibers function as electrospun materials separated by the electrodes. When the IDE is compressed, the uneven distribution of the nanofibers results in the generation of an output potential. The device demonstrates an output voltage of 0.14 V and a current output of 0.59 nA. In a short, devices crafted with the aid of IDEs provide improved performance, energy efficiency, and miniaturization, underscoring their significance in the advances of modern electronics.

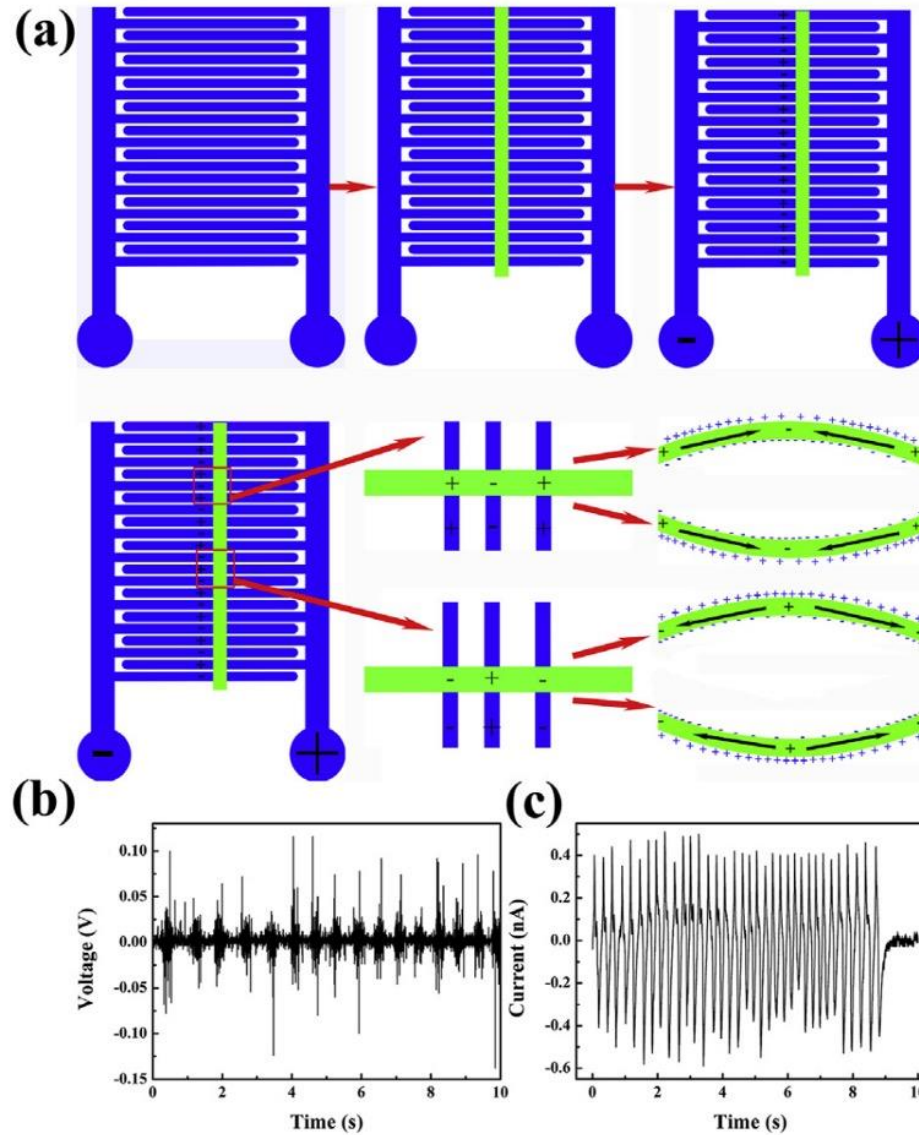


Figure 1.12 (a) Operational principle of the nano energy harvesting device using interdigital electrodes and P(VDF-TrFE) nanofibers. Output signals of the same device showing (b) voltage versus time curve; (c) current versus time curve. *****

***** Reprinted with permission from Zhuang, Y.; Han, S.; Liu, W.; Wei, X.; Xu, Z. An Interdigital Electrode Type Sensor Based on P(VDF-TrFE) Nanofibers. *J Alloys Compd* **2020**, 831, 154657. Copyright 2020 by Elsevier.

1.3.2 Nanogap Devices

Characterized by their extremely small separations on the nanometer scale, nanogap devices have become a focal point of modern research in the realms of nanoscience and nanotechnology. These nanogap devices, with a typical width less than several tens of nanometers, are intriguing not just as fundamental circuit building blocks but also as an important platform for trapping and characterizing material at the nanoscale. Their inherently small dimensions make them ideal platforms for exploring quantum phenomena, particularly quantum tunnelling effects, and for facilitating the study of electron transport across individual molecules.¹²¹ Moreover, in the burgeoning field of plasmonics, nanogaps play an indispensable role, allowing for the confinement and enhancement of electromagnetic fields, thus leading to applications in advanced sensing, site-selective chemical reactions and plasmon-based optical trapping.¹²² Given the myriad of applications, the effort in fabricating and studying nanogap devices has intensified, as the insights derived from such studies can profoundly impact areas ranging from biosensing to molecular electronics, extending Moore's law with future nanoscale technologies.^{123,124}

Over the years, a plethora of methods have been developed and refined to fabricate nanogaps with high precision and reproducibility. Broadly, these methods can be categorized into top-down and bottom-up approaches. Top-down methodologies, including electron beam lithography, focused ion beam milling and mechanical controllable break junction, are driven by external tools and instruments to carve out structures with the desired nanogaps on substrates.^{124–126} These approaches offer the advantage of direct-write patterning with reasonable control over the gap dimensions. On the other hand, bottom-up strategies, such as electrochemical plating and electro migration,^{127,128} leverage the intrinsic properties of materials and molecules to autonomously assemble or grow structures that define the nanogap. Each of the techniques has demonstrated promising outcomes and is characterized by its unique attributes, and multiple methods can be synergistically employed to achieve the desired configuration.¹²⁹

1.4 Scope of the Thesis

Our primary focus is to investigate the formation and induced properties provided by oxygen vacancy defects within size-selected group IV-B transition metal oxide NCs. In particular, we aim to discern the relationship between these defects and the unique properties of the nanoclusters. Our ultimate goal is to harness and control these defects to optimize the performance of NCs for selected applications.

Our approach involves: (a) Creating and fine-tuning size-selected defect-rich NCs via a gas-phase condensation technique, using mono-metal TCO ZrO_2 and bimetallic or hybrid $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ as examples; (b) Conducting a detailed analysis of these NCs, focusing on their morphologies, lattice structures, and oxidation states; (c) Exploring possible applications generated by these defects and their size-dependent properties. To deepen our understanding of the electrical characteristics of these defects for potential electronic applications, we develop nanoelectrodes, specifically interdigital electrodes and nanogap devices, utilizing a diverse set of lithography methods. In this chapter (Chapter 1), we provide an extensive review of NCs generated by the gas-phase condensation technique, elaborating on their formation, size-dependent properties, and multifaceted applications, along with a detailed table and its own bibliography. After emphasizing the importance of NCs, this chapter also briefly discusses dilute magnetic semiconductors, and brings attention to the origin of the ferromagnetism in dopant-free magnetic semiconductors. Finally, we provide an overview of recent progress in crafting interdigital electrodes and nanogap devices for varied applications. Chapter 2 gives an introduction to the gas-phase condensation technique used here for producing defect-rich size-selected nanoclusters, and briefly discusses the tuning parameters. This will be followed by a brief overview of the characterization methods used to examine the morphologies, physical and electronic structures (including chemical state compositions) of NCs, along with a description of magnetometry used to study the magnetic properties of these NCs. We also present details about the clean room facilities and lithography methods, including the advanced ion beam lithography technique, used for device fabrication.

Our data are presented in Chapters 3-5. In Chapter 3, we employ a straightforward DC magnetron-sputtering-based gas-phase condensation system to synthesize defect-rich ZrO_2 NCs with selected sizes of 3 nm, 5 nm, 7 nm, and 9 nm. Subsequent size selection is achieved using a quadrupole mass filter. The as-deposited ZrO_2 NCs display a unique tetragonal structure, a form typically obtained at extremely high temperature in their bulk phase. Additionally, these NCs exhibit sub-oxidization photoemission features for the metal ions that vary according to their size, which can be attributed to distinct oxygen vacancy defects. Most notably, the pristine ZrO_2 NCs exhibit size-dependent ferromagnetism, with enhanced solubility and magnetic uniformity in comparison to conventional magnetic semiconductors. A model centered on defect-band hybridization is proposed to elucidate this observed size-related ferromagnetism. This study highlights a new approach to

modulating magnetization via size control and suggests potential spin-based nanotechnology applications for these size-selected NCs.

In Chapter 4, we expand our exploration of ZrO_2 NCs by introducing its “twin oxide”, HfO_2 , to craft hybrid $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($x < 1$) NCs. These hybrid nanoclusters, with sizes ranging from 5 nm to 14 nm, are synthesized using a one-step gas-phase condensation technique. Their sizes and compositions can be precisely adjusted, as evidenced by thorough morphological and chemical analysis. The crystalline nature of these NCs is dependent on the conditions of deposition. In particular, these NCs manifest as amorphous structures for sizes < 6 nm, adopt a single crystalline form between 6-10 nm, and evolve into a core-shell structure with a predominant Hf content or assume a polycrystalline state with a higher Zr concentration for sizes > 10 nm. Interestingly, a unique orthorhombic structure is found in the single-crystalline $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs, analogous to the HfZrO_2 film. Their bandgaps exhibit sensitivity to both size and composition. XPS evaluation further pinpoints distinct chemical state deviations, predominantly within the Zr 3d region, attributable to oxygen vacancy defects and alloy interactions. We propose a model emphasizing Hf-induced polarons to elucidate the distinct properties of these NCs. This investigation not only provides a blueprint for the fabrication of other hybrid semiconductor NCs but also underscores the potential of these specific $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs in advancing the capabilities of new single-cluster non-volatile memory devices.

In Chapter 5, we delve deeper into the electrical analysis of these novel NCs by conducting a comprehensive study on the fabrication of nano-electrodes. This includes the development of nanoscale interdigital electrodes (nano-IDEs) and nanogap devices, achieved through selected lithographic techniques for precision patterning. We perform a comparison of maskless optical lithography, electron beam lithography, and ion beam lithography for IDE fabrication. Of these, ion beam lithography offers superior flexibility, while maskless optical lithography excels in patterning interconnections. The nano-IDEs we produce are subsequently used for cross-array memristor applications. We enhance the refinement of the nano-IDEs and nanogap devices by utilizing the direct-write capability of ion beam lithography, which allows for meticulous control of the gap spacing based on the exposure dose. By depositing the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs into the nanogap, we successfully construct a single-cluster device, setting the stage for future electrical evaluation of the NCs.

In Chapter 6, we summarize our findings from the current research and offer some suggestions for future work.

Chapter 2

Experimental Techniques

This chapter provides an overview of the methodologies used for the synthesis and characterization of nanoclusters (NCs). It also illustrates the fabrication techniques employed for the nanoelectrodes that are vital for the nanocluster-based device applications.

2.1 High Vacuum Nanocluster Source

In the present work, the metal/metal oxide nanoclusters are synthesized by using a magnetron sputtering based gas-phase condensation cluster source, followed by in-flight size-selection up to 2% accuracy using a quadrupole mass filter. The entire Nanogen 500 system (Mantis Deposition Ltd) is housed in the QPrep 500 Modular Sputtering System (Mantis Deposition Ltd) with a base pressure of 5×10^{-9} mbar, shown in Figure 2.1.^{130,131} The Nanogen system is equipped with a trio DC magnetron sputtering source, with the power individually controlled to each of the three sputtering heads (for sputtering target size of 25 mm dia and 3 mm thick). This provides a huge advantage in synthesizing multi-composition NCs with up to three material components in a combinatorial fashion. The trio sputtering source can also be positioned at a range of distance from the exit aperture of the Nanogen chamber, which defines the aggregation length. Moreover, the Nanogen system is equipped with a quadrupole mass filter for size selection with a current to monitor of the NC beam flux. In addition to the Nanogen system, the QPrep ultrahigh vacuum system also contains 2 DC and 2 RF magnetron sputtering sources, and a quartz crystal microbalance that can be used to measure the deposition rate in real time. These four sources can be used to deposit high purity thin films of a wide range of materials including metals and oxides, and to enable co-deposition with the Nanogen cluster beam to produce exotic nanostructures. There are several key parameters for tuning the Nanogen source to optimize the deposition, including sputtering power, carrier gas flow rate (Ar or He), aggregation length, AC/DC voltage ratio of the quadrupole mass filter, deposition temperature and substrate bias (Chapter 1). In our work, we have successfully optimized the cluster beam to achieve cluster size ranging from 2 nm to 20 nm.

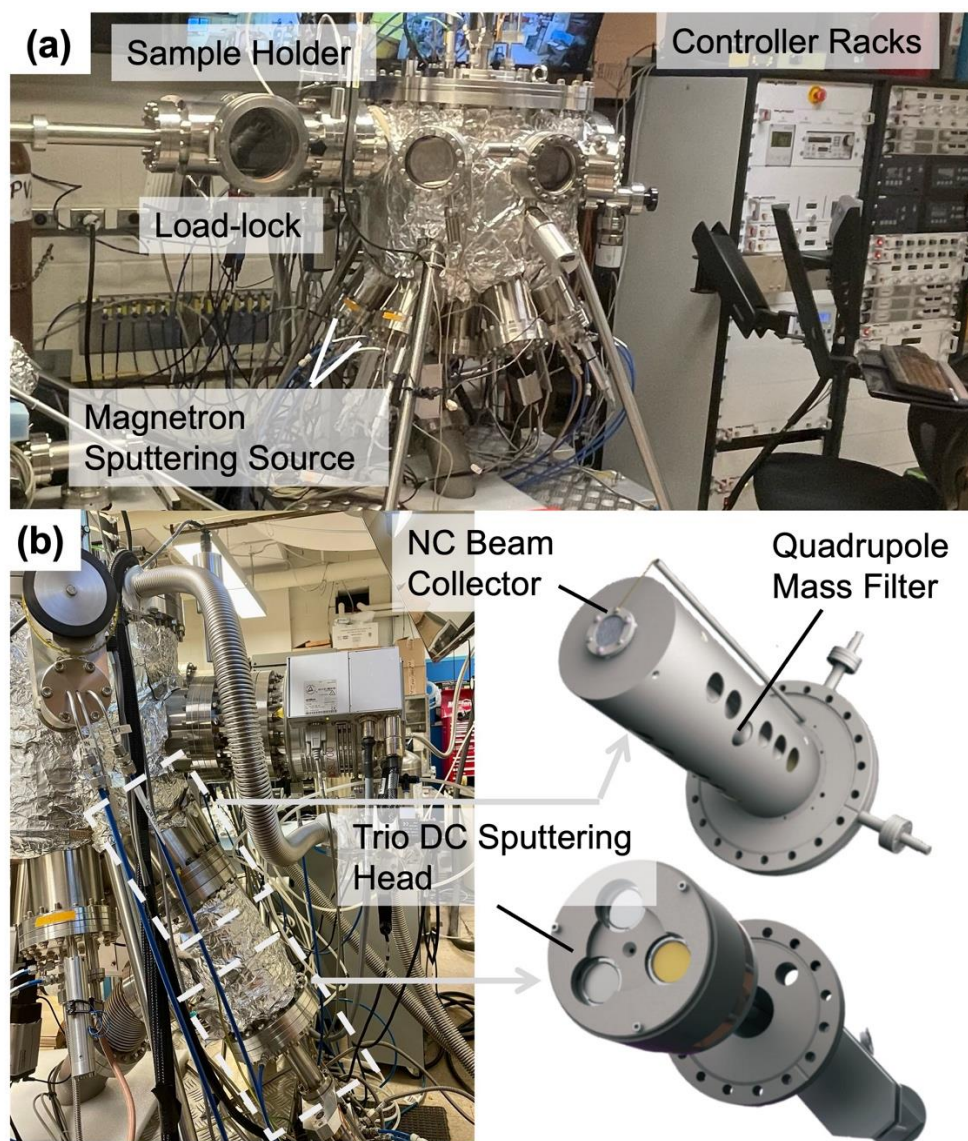


Figure 2.1 Photographs of (a) QPrep 500 Modular Sputtering System (Mantis Deposition Ltd) equipped with a load-lock sample transfer system, two DC and AC magnetron sputtering sources and a Nanogen cluster source, along with sample heating facility and a quartz crystal microbalance and (b) the side view of the deposition system, showing the Nanogen nanocluster source at the back. The Nanogen source is composed of a trio DC magnetron sputtering head (lower right) and the size-selection chamber containing a quadrupole mass filter and cluster beam collector (upper right).^{†††††}

^{†††††} Copyright 2013 by MANTIS Deposition Ltd.

2.2 Clean-Room Facility

2.2.1 Pattern Generation by Direct-write Maskless Optical Lithography

Optical lithography is widely used in almost all industrial device fabrication processes due to its fast speed and no vacuum requirement, even though the wavelength of the photon limits its spatial resolution in defining the ultimate minimal feature size. Furthermore, making the appropriate mask for optical exposure could be tedious and rather time-consuming. In this work, we employ a novel maskless optical lithography system (SF-100 XPRESS, Intelligent Micro Patterning Ltd) to directly write the pattern in the device fabrication process, shown in Figure 2.2.¹³² The system uses a proprietary matrix of mirrors to represent each pixel of the pattern created in bitmap (.bmp) format by using the Microsoft Paint software. The mirror matrix is mount on the light path of a 365 nm UV light from the filtered poly-chromatic light source using an Ushio™ bulb. By controlling ON and OFF of individual mirrors, the system can conveniently write the pattern without any mask. Before the exposure, a high-performance positive photoresist Shipley S1805 (Microchem Corp.) is coated onto a Si substrate using a spin coater (Laurell Tech. Corp.) at 4500 rpm for 40 s followed by baking on a hot plate at 120° C for 60 s. Once the pattern writing step is completed, the sample is developed in the MF-24 developer (Microchem Corp.) for 30 s to dissolve the UV exposed area. The developed part of the pattern is then removed by rinsing with filtered high-resistivity water (18.2 MΩ·cm) and the resulting patterned substrate is ready for the metal deposition and lift-off processes.

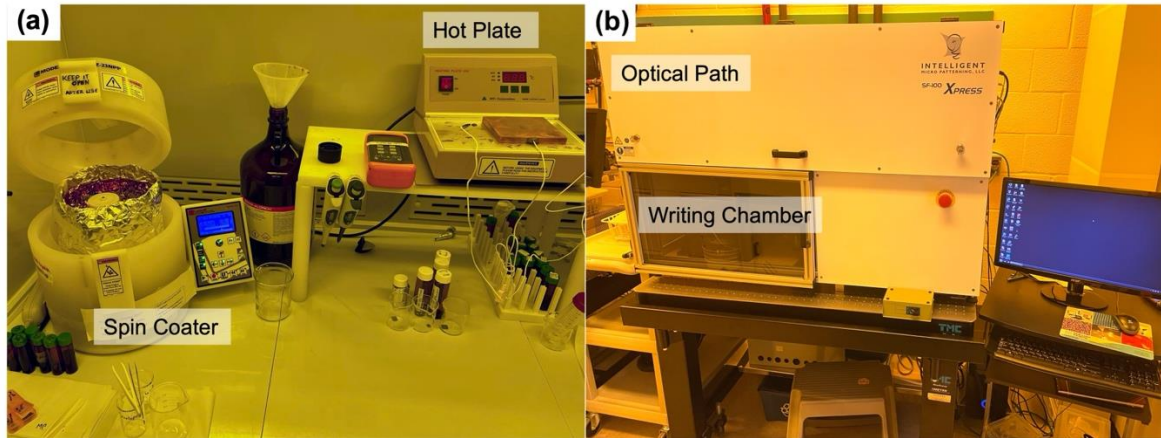


Figure 2.2 Photograph of the clean room facility, composed of (a) a clean room fume hood with a spin coater and hot plates for substrate preparation before lithography exposure, and (b) an Intelligent Micro Patterning SF-100 Xpress maskless optical lithography.

2.2.2 Metallization by Magnetron Sputtering and Lift-off

In the next fabrication step, the patterned substrate is subjected to a metal deposition process by using a Leica EM ACE600 tabletop DC magnetron sputtering system, as shown in Figure 2.3. This system is equipped with two DC magnetron sputtering heads, allowing for the alternating deposition of two different materials. It is also fitted with a quartz crystal microbalance to facilitate real-time monitoring of the film thickness during deposition. This system offers rapid vacuum pump-down, user-friendly operation, and flexible deposition of high-purity metal films. During the deposition, the metal film will bond to the bare substrate areas not covered by photoresist. After deposition, the substrates undergo a lift-off process to remove the photoresist, leaving behind the metal film in the desired patterns. To finalize the electrode fabrication process, the substrate is rinsed with high-resistivity water and dried with nitrogen. This protocol enables us to fabricate a pattern of metal electrodes on the Si substrates with high productivity and reproducibility.

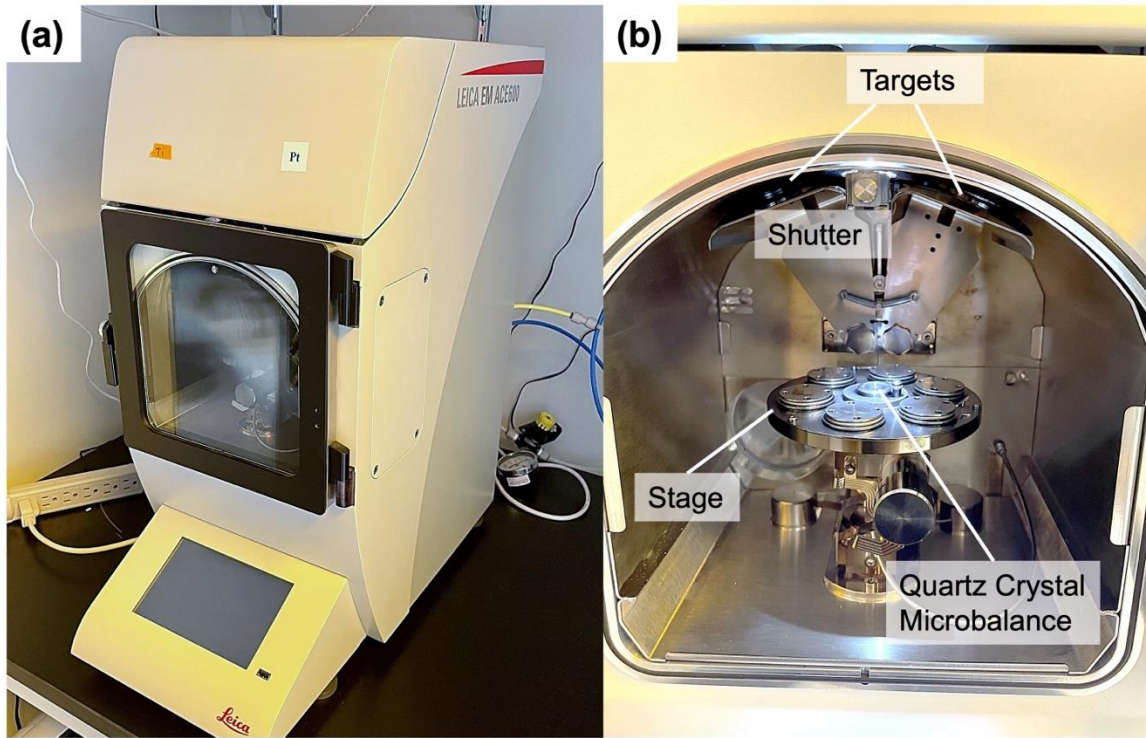


Figure 2.3 Photographs of (a) the full view and (b) the functional components of Leica EM ACE600 tabletop DC magnetron sputtering system.

2.3 Electron Beam Lithography and Ion Beam Lithography

2.3.1 Scanning Electron Microscopy and Electron Beam Lithography

Scanning electron microscopy (SEM) is one of the most essential characterization techniques for nanomaterials and nanodevices. Equipped with a field-emission electron source, the Merlin SEM microscope (Carl Zeiss, SMT, Figure 2.4) employs the advanced Gemini-II electron optics column, which can accelerate the electron from 100 V up to 30 kV to meet the most demanding imaging requirements at both low beam energy for fragile and low-conductivity materials and high beam energy for high resolution morphology studies. During the operation, the SEM directs a focused electron beam using electromagnetic lenses. As the electrons penetrate and interact with the sample, they produce different types of signals, including secondary electrons (SE) and backscattered electrons (BSE), which are collected by specialized detectors. In particular, secondary electron detectors capture signals responsible for revealing surface topography, while backscattered electron detectors provide contrasts based on elemental compositions in the specimen.¹³³ To achieve clear and undistorted images, the sample must be either inherently conductive or coated with a conductive layer (such as gold) to prevent electron accumulation and charging. Furthermore, the SEM chamber maintains a high vacuum environment, ensuring that the electron beam remains uninterrupted and the sample uncontaminated upon interaction with the electron beam. In our projects, the Merlin SEM is used not only for imaging studies of the distribution and surface morphology of the deposited NCs and of the quality of the fabricated nanodevices, but also for electron beam lithography (EBL) used for patterning in fabrication of the nanoelectrodes. To activate the advanced lithographic capability, a Nano-Patterning and Visualization Engine (NPVE) from Fibics, Inc. and a proprietary fast beam blanker from Spellman are used.

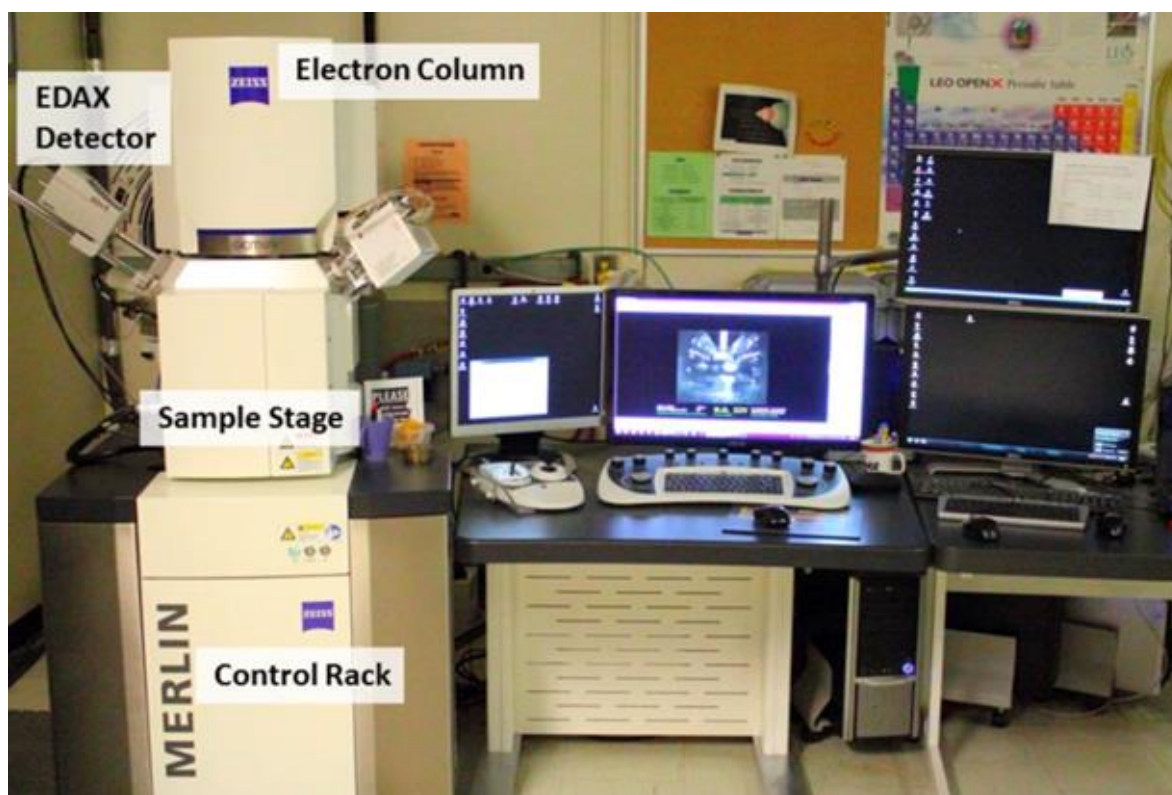


Figure 2.4 Photograph of the Zeiss Merlin field-emission SEM used for advanced imaging and EBL. This instrument is equipped with both in-lens and out-of-lens (SE2) secondary electron detectors, an in-column four-sector backscattered electron detector (BSD), and an integrated energy-dispersive X-ray spectrometer system from Octane, EDAX Inc.

2.3.2 High Performance Ion Beam Lithography

A Raith IONLine high performance ion beam lithography (IBL) system is used in this work for creating ultra-small features in our nanodevices (Figure 2.5).¹³⁴ A SiAu liquid metal alloy ion source is used to produce Si^+ , Si^{++} , Au^+ , and Au^{++} ions for patterning with an ion beam energy up to 45 kV, The choice of the ions can be made by simply adjusting the E×B mass filter. The laser-interferometer stage in this system significantly improves the alignment for both lateral write field and overlayer. By either patterning on a photoresist or direct-write without any photoresist by using the ion beam for ion-milling and/or machining on the substrate, IBL provides a state-of-the-art technique in nanodevice fabrication and nanomachining. The system is also equipped with a gas injection source

system for metal deposition by ion-induced chemistry with appropriate organometallic materials and with dual nanomanipulators for *in-situ* electrical characterization. This novel IBL system is the only one in Canada and one of just five in the world, with two each in the United States and European Union. PMMA A2 (MicroChem Corp.) is used as the positive photoresist for ion beam lithography and also for the electron beam lithography. The photoresist is spin-coated at 4000 rpm for 35 s on the Si substrate followed by baking at 180 °C for 90 s on a hot plate. After the ion (or electron) beam exposure, the predefined patterns are developed using MIBK/IPA (MicroChem Corp.) in a 1:3 ratio for PMMA, then rinsed in IPA to remove the residual PMMA and developer and finally dried with clean nitrogen.

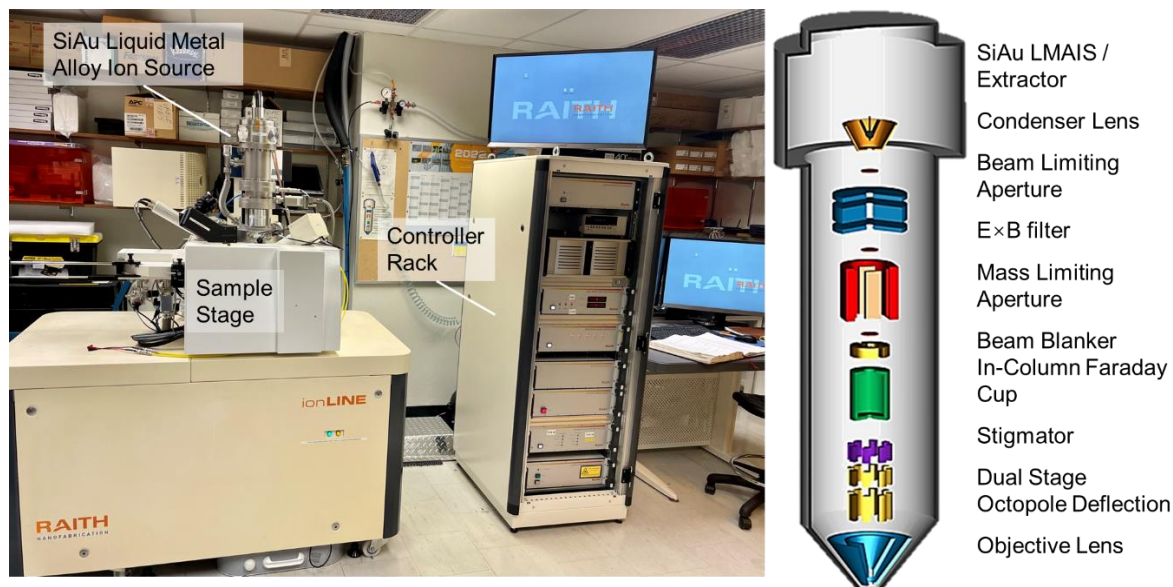


Figure 2.5 Photograph of Raith IONLine high performance ion beam lithography system to generate nanopatterns by either patterning on a photoresist or direct-write ion milling on the substrate. This system is equipped with a SiAu liquid metal alloy ion source, a laser interferometer stage, a gas injection source and dual nano-manipulators. The right inset shows the schematic diagram of the advanced ion optics column. ****

2.3.3 Helium Ion Microscopy and Helium Ion Beam Lithography

The Orion plus helium ion microscope (HIM), from Carl Zeiss SMT Inc., is similar to a scanning electron microscope (SEM), except that it uses a helium ion beam for illumination instead of an electron beam (Figure 2.6).¹³⁵ Its standard operating procedure includes setting the extractor to an optimal imaging voltage, typically between 35 to 40 kV, at which the most luminous trimer produced by the gas-phase field-ionization ion source is achieved. The setup also includes a 10 μm beam-limiting aperture, a 5 mm working distance, and a helium gas pressure of 2×10^{-6} mbar. With these conditions, the beam current is approximately 1 pA, and the spot size is ~ 0.5 nm, considerably smaller than the few nanometers spot size achievable with the best SEM like the Merlin. Images are collected by using an external Everhart–Thornley secondary electron detector.^{136,137}

The relatively massive helium ions have a much shorter de Broglie wavelength than electrons with the same energy, which reduces diffraction around the aperture and maintains a small focusing spot. The smaller energy and radial dispersions of the helium ions alleviate chromatic and spherical aberrations, respectively, further improving the focusing spot. As a result, an ultimate focusing spot on the sample surface has been predicted to be as small as 0.25 nm.¹³⁸ Furthermore, due to the less scattering of the He ions with the substrate surface, the He ions interact with a substrate in a much more localized and confined manner when compared to the electrons, which provides a much higher resolution (typically 0.3 nm) and a considerably greater depth of view compared to even the best SEM like the Merlin (typically 0.8 nm).

Additionally, the Orion plus HIM is also integrated with the NPVE system from Fibics Inc. (same as that used in the Merlin SEM), allowing for nanopatterning and nanomachining at high spatial resolution as well as precise helium beam control to achieve preset doses in the designated direct-write field. In the present work, this HIM has been employed to pattern the crossed-finger electrodes for the nano-interdigital electrodes application.



Figure 2.6 Photograph of the Orion plus helium ion microscope. Equipped with the integrated Nano-patterning and Visualization Engine (NPVE) by Fibics Inc., this HIM can also be used to perform helium ion beam lithography for nanodevice fabrication.

2.4 Surface Morphology, Lattice Structure and Chemical State Composition Characterization

2.4.1 Atomic Force Microscopy

Atomic force microscopy (AFM) is a powerful nanoscale imaging technique that is based on the interaction between a sharp probe, typically a silicon nitride (Si_3N_4) tip as used in our work, and the surface of the sample.¹³⁹ As the tip is moved or "scanned" across the sample surface, it responds to minute force interactions, either through deflection or oscillation changes. These changes can be registered by the movement of a laser beam deflected from the back of the tip onto a photodetector, which is then translated into topographical or other property related images that offer detailed views of the sample at the nanoscale level. In our study, AFM is conducted by using the Dimension 3100

Nanoman Nanoscope IV from Digital Instruments (Figure 2.7). During the analysis, the samples are meticulously scanned in the tapping mode with the silicon nitride tip. Although AFM boasts impressive precision, its lateral resolution is typically limited by the size of the tip, which can be larger than some of our observed nanoclusters. To navigate this challenge and obtain accurate measurements, we focus on the vertical height profile. This method capitalizes on the exceptional height resolution of a few angstroms ($\text{\AA}$), enabling the AFM for precise measurement of the size distribution of the nanoclusters and the thickness of the nanocluster thin film.

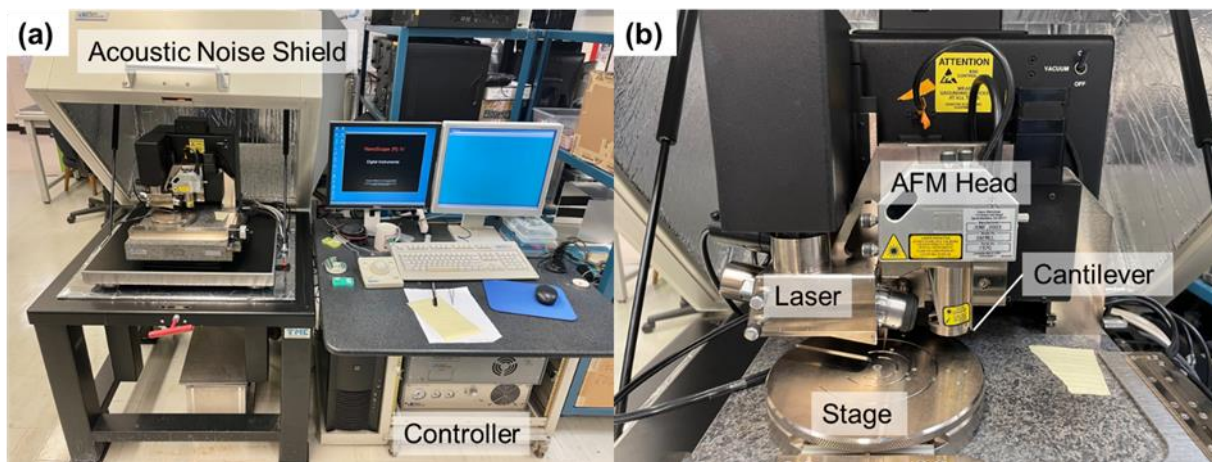


Figure 2.7 Photographs of (a) Digital Instrument Dimension 3100 atomic force microscope and (b) its key components.

2.4.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a powerful imaging technique that relies on the transmission of a high-energy electron beam (typically 200 kV) through an ultra-thin sample (< 100 nm thick). As these electrons pass through the sample, they interact with the columns of atoms in the sample. The resulting diffraction and interference patterns provide invaluable information about the sample structure on an atomic scale.¹⁴⁰ In our studies, a Zeiss Libra 200 MC microscope (Figure 2.8), operated at an electron acceleration voltage of 200 kV, is used for TEM measurements. With the corrected omega energy filter, this tool offers excellent imaging capabilities, providing detailed insights into the crystalline structure of materials and enabling precise identification of crystal planes in an individual nanocluster. The TEM sample is prepared by directly depositing the NCs onto a lacey

carbon-coated copper grid in the Mantis QPrep system. Furthermore, this TEM is also equipped with a high-angle annular dark field (HAADF) detector and an energy dispersive spectroscopy (EDS) system. The HAADF detector provides detailed insights into the morphology of the NC in the STEM (Scanning TEM) mode, while the EDS system is used for determining the elemental composition of individual NCs based on their characteristic electron-induced X-ray emission lines.

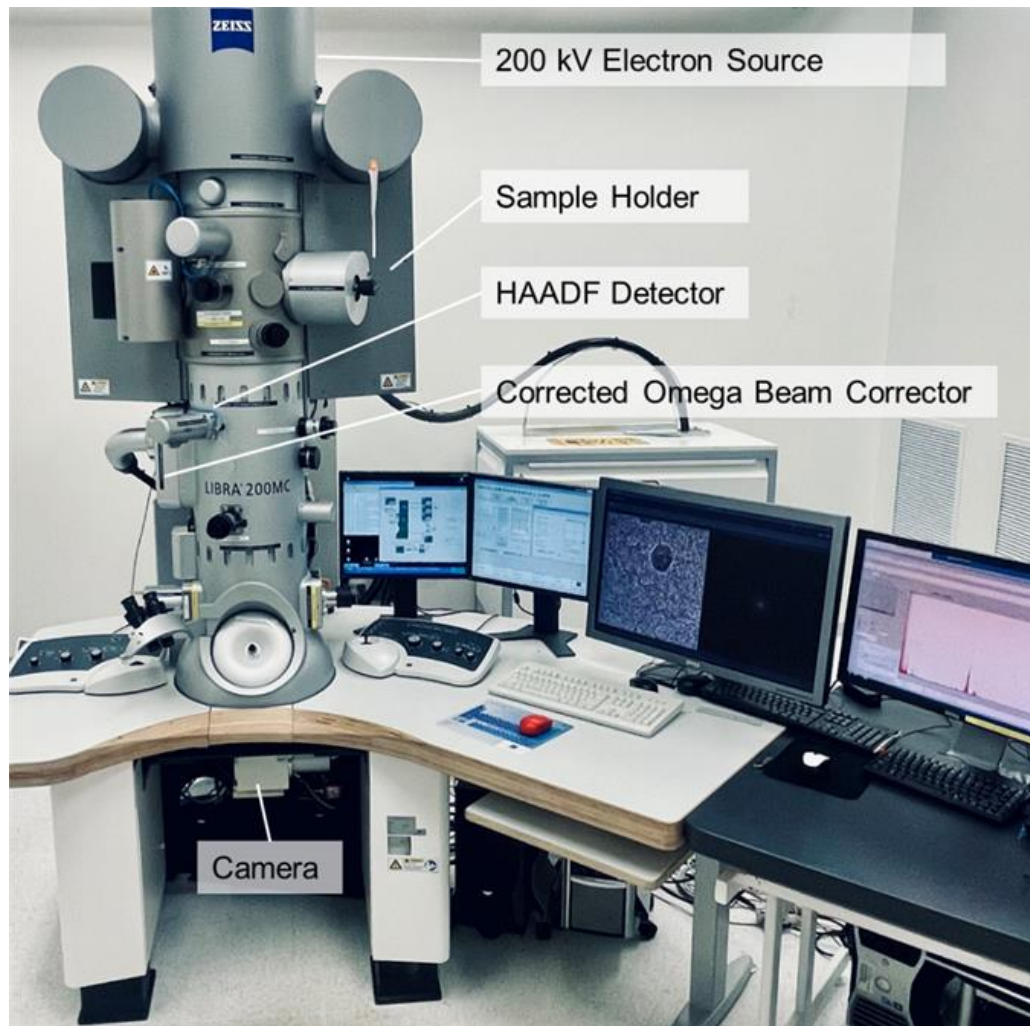


Figure 2.8 Photograph of the Zeiss Libra 200 MC transmission electron microscope, operating at 200 kV.

2.4.3 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is a powerful and non-destructive analytical technique primarily used to identify and quantify the crystalline phases in a material and to study its structural properties. When a monochromatic X-ray beam strikes the atoms inside a crystalline sample, the X-ray undergoes diffraction in specific directions with varying intensities. Each crystalline phase produces a unique diffraction pattern that acts as its “fingerprint”, allowing for its structural identification according to Bragg’s law.¹⁴¹ A PANalytical MRD X’Pert diffractometer equipped with a Cu-K α source (Figure 2.9) is employed in a glancing incidence setup in the present work. Glancing-incidence XRD is a specialized setup that is particularly useful for examining thin films and surface layers. In this technique, the X-ray beam is directed and paralleled, by using a Cu X-ray mirror, at a very shallow incidence angle to the sample surface (0.3° for our NC samples), thus enhancing the sensitivity to the surface and near-surface regions. The diffracted beams are collected in a parallel beam optical setup that incorporates a parallel-plate collimator.

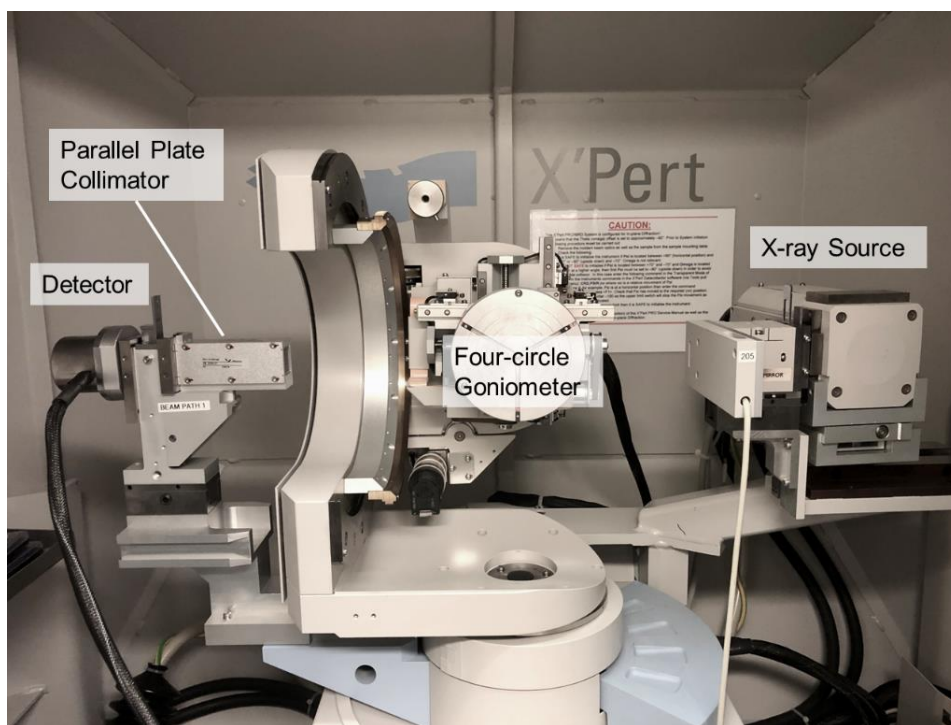


Figure 2.9 Photograph of the Panalytical MRD X’pert Pro X-ray diffractometer. Equipped with a four-circle goniometer, the system is set up in a parallel beam configuration, utilizing an X-ray mirror for the incident beam optics and a parallel plate collimator for the diffracted beam optics.

2.4.4 X-ray Photoelectron Spectroscopy (XPS)

The chemical composition and electronic states of the NCs are characterized by X-ray photoelectron spectroscopy (XPS) using a Thermo-VG Scientific ESCALab 250 Microprobe and also a recently installed Thermo Scientific Nexsa G2 surface analysis system. When the sample is irradiated with a monochromatic X-ray beam, electrons from the surface region of the sample are ejected. These emitted photoelectrons predominantly come from the topmost 1-10 nm, making XPS a highly surface-sensitive technique for identifying surface components via their characteristic chemical states.¹⁴² A hemispherical electron energy analyzer is used to determine the kinetic energy of these photoelectrons, which is then used to calculate the binding energy of the chemical state using the Einstein equation.

$$E_B = E_{h\nu} - (E_K + \phi)$$

where E_B is the binding energy of the chemical state, $E_{h\nu}$ is the X-ray photon energy (1486.8 eV for Al K α in the ESCALab 250 and Nexsa G2), h is the Planck constant and ν is the light frequency), E_K is the kinetic energy of the photoelectron measured by the analyzer, and ϕ is the work function dependent on both the spectrometer and the material. The resulting binding energy spectrum reveals details about the chemical states and their compositions, and the electronic structure of the sample surface. Furthermore, binding energy features with special chemical shifts (or changes in the binding energy associated with local chemical environments) found for the metal ions in the NCs can be associated with oxygen vacancy defects. XPS therefore offers insights into the presence, concentration, and nature of these defects, making it invaluable for studying materials where oxygen vacancies play a critical role in determining their properties.

The Nexsa G2 surface analysis system is also equipped with a helium UV light source, enabling analysis by ultra-violet photoelectron spectroscopy (UPS). This UPS technique is instrumental in determining the work function of the sample. Additionally, the electron flood gun in this system serves a dual purpose. While its primary function is used to neutralize any charge on the sample surface, which is especially important for a non-conducting sample, it can also be used as a 1 kV electron source to facilitate reflection electron energy loss spectroscopy (REELS) study. REELS operates by directing a primary electron beam onto a specimen, and then measuring the distribution of secularly reflected electrons as a function of the energy loss suffered by the primary electron beam.¹⁴³ The bandgap of the specimen can be calculated from the energy loss distribution curve.

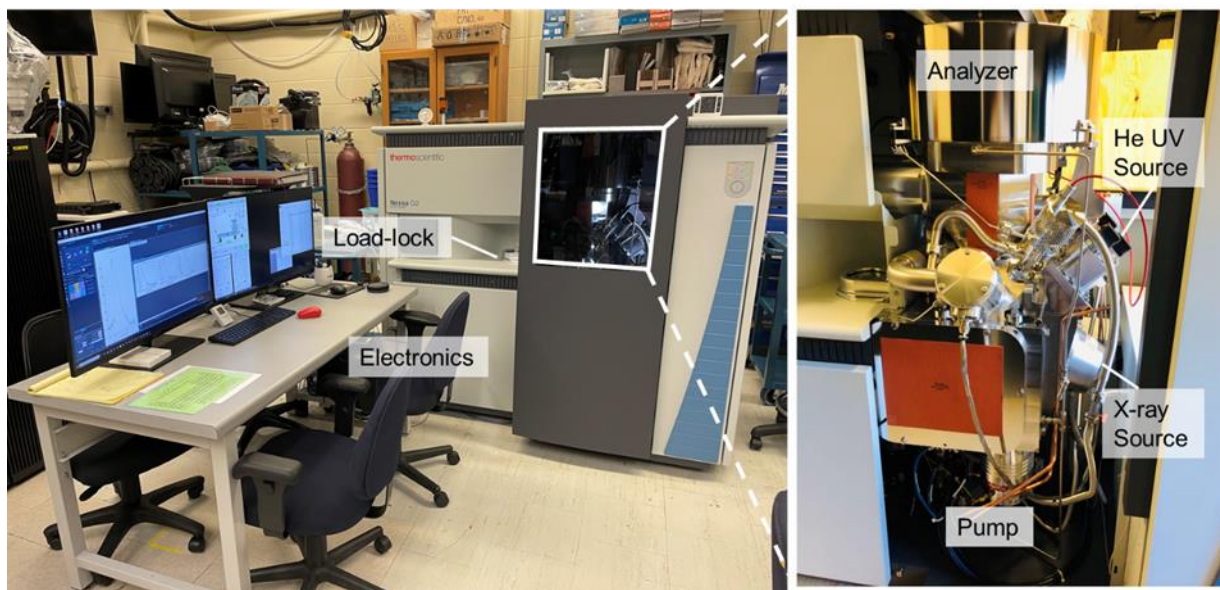


Figure 2.10 Photograph of the Thermo Scientific Nexsa G2 surface analysis system. This highly compact system is capable of multiple techniques including XPS, UPS, REELS and ISS (Ion Scattering Spectroscopy).

2.5 Magnetic Characterization and Electrical Measurement

2.5.1 SQUID Magnetometry

The magnetic properties of ZrO_2 and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs are examined by using a 7-Tesla Quantum Design EverCool Magnetic Property Measurement System (MPMS) that operates based on the Superconducting Quantum Interference Device (SQUID) Vibrating Sample Magnetometry (VSM) technology (Figure 2.11). This advanced technology harnesses the principles of superconductivity and the quantized magnetic flux in the Josephson junctions, which are thin insulating barriers between two superconductors. When a magnetic field is applied, the resulting magnetic flux alters the current-voltage characteristics of these junctions, allowing for highly sensitive magnetic property measurements.¹⁴⁴

The magnetic moment of a sample is measured as a function of temperature from 1.8 K to 400 K with a remarkable sensitivity of 1×10^{-8} emu. To maintain superconductivity, both the SQUID and the encompassing magnet require cooling with liquid helium. An integrated pulse-tube cryocooler-dewar

system provides this essential cooling medium. Furthermore, liquid helium ensures that the sample chamber remains at the optimal low temperature. For effective measurement, the sample must not exceed a dimension of $5 \times 5 \text{ mm}^2$ to fit within the bore of the magnet. Proper positioning ensures the vibrational motion of the sample occurs within the uniform field region of the magnet. Due to the high-sensitivity of SQUID-VSM technique, only plastic tweezers and quartz sample holders are used during sample preparation and magnetization measurement, in order to prevent any accidental magnetic contamination.

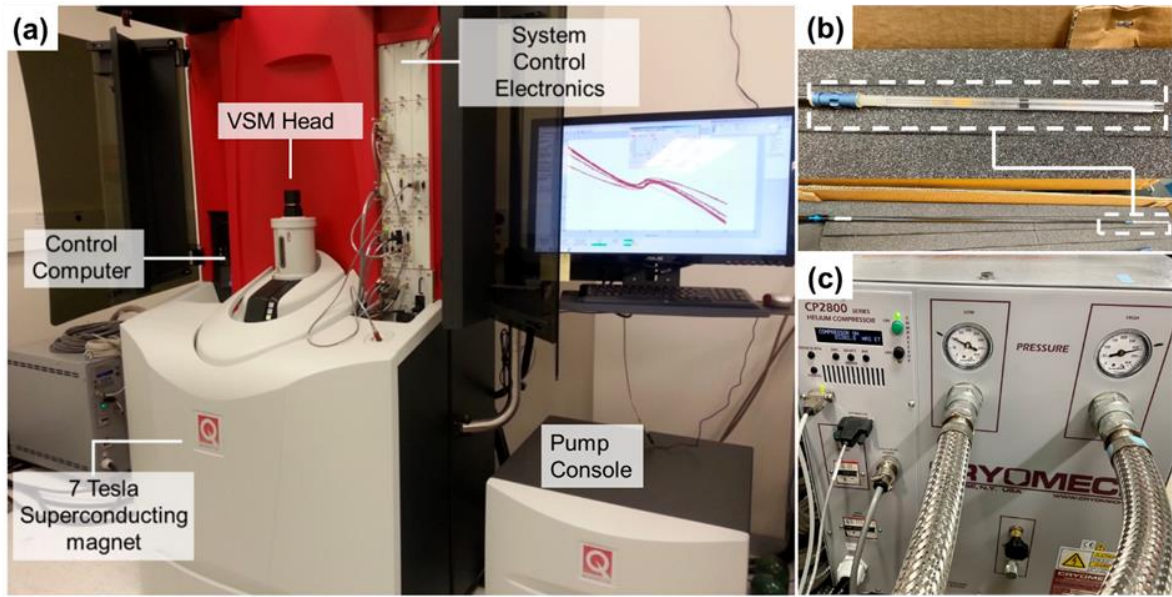


Figure 2.11 Photograph of (a) the Quantum Design EverCool Magnetic Property Measurement System (MPMS) Vibrating Sample Magnetometer (VSM) that operates based on the Superconducting Quantum Interference Device (SQUID) technology, (b) the VSM sample rod and quartz sample holder for a $5 \text{ mm} \times 5 \text{ mm}$ sample and (c) the Cryomech compressor to cool the helium gas to the liquid phase.

2.5.2 Probe-station with B1500 Semiconductor Characterization Platform

Each fabricated device is tested using a semiconductor device analyzer from Agilent Technologies B1500, paired with a Signatone S1160A probe station, as illustrated in Figure 2.12. During the tests, tungsten probes with a $2 \text{ }\mu\text{m}$ tip width establish contact with the device, and the assessments are

consistently carried out at room temperature. The prevalent testing approach employs a dual-probe method. For DC measurements, one probe is energized with a voltage, while the other is grounded, enabling the measurement of the current between the electrodes. Additionally, this semiconductor measurement system is equipped with a four-channel AC measurement module, ranging from 1 Hz to 5 MHz. This feature is crucial for capacitance measurements, especially when characterizing IDE-based nanodevices.

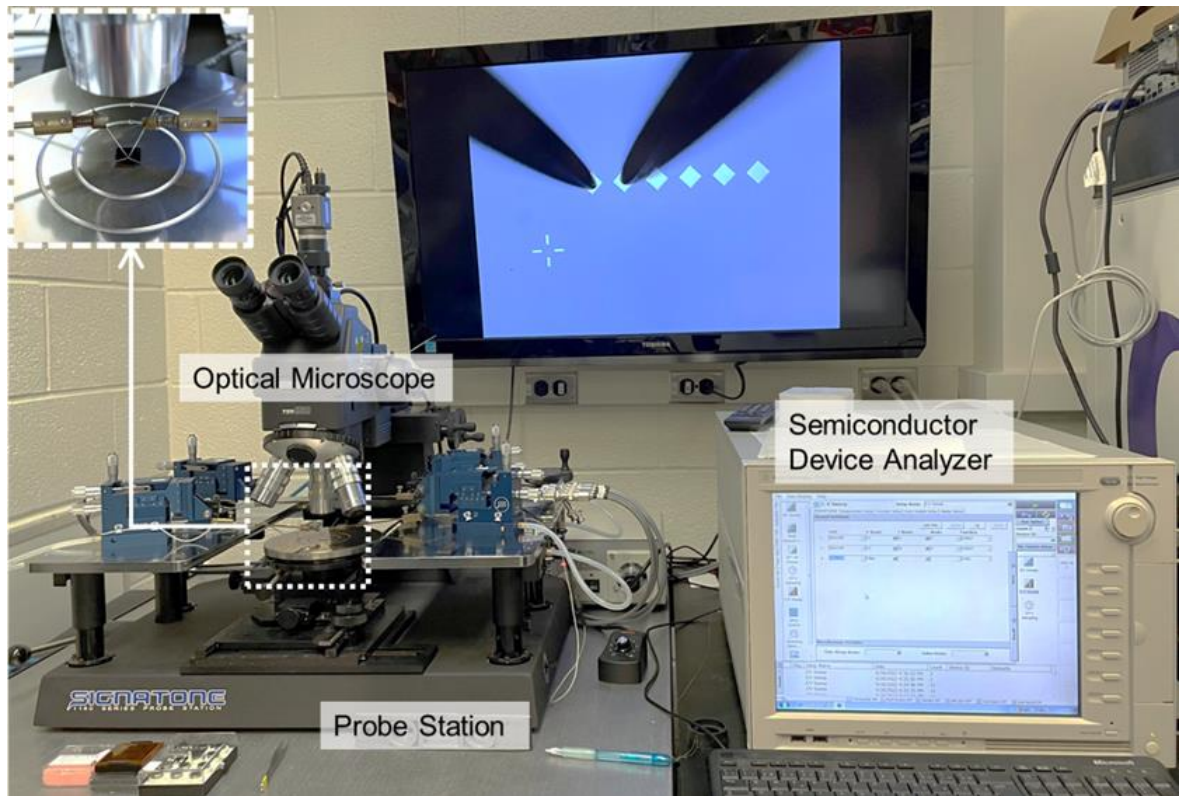


Figure 2.12 Photograph of the DC measurement setup for the nanogap electrodes. The device is connected by using the Singatone S1160A probe station to the Agilent B1500 semiconductor device analyzer. The top-left inset gives a close-up view of the electrical measurement setup where two probes are connected to the two contact pads of the device.

Chapter 3

Defect-Rich Dopant-Free ZrO₂ Nanoclusters and Their Size-Dependent Ferromagnetism^{§§§§§}

3.1 Introduction

Nanoclusters (NCs) are defined as small aggregations of atoms or molecules generally less than 10 nm in size,^{3,9,145} and they are considered to be the link between free atoms or molecules and the bulk. In this interesting size regime, individual states in the electronic structure have not fully merged into bands and remain intact as multiple distinct states. NCs can also be regarded as giant molecules, and they hold the key to understanding the evolution of electronic structures and other properties from single atoms or molecules to the bulk phase with increasing size of the NCs. Because of a significantly higher surface area-to-volume ratio (or specific surface area) compared to their bulk phase, NCs have also attracted a lot of attention in surface-driven research.¹⁴⁶ The high air stability of noble metals such as Au, Ag, and Pt makes their NCs especially attractive to such applications as catalysis,⁹ fuel cells,¹⁴⁷ and biosensing.^{5,6} The study of transition-metal/ metal oxide NCs has also become popular in the past two decades. In addition to the different band structures from the bulk phase, these NCs exhibit notable defects in various oxidation states, which could become dominant and lead to mid-gap states.^{8,9,148} These semiconducting oxide NCs with mid-gap states and structures consisting of different ordered arrays and assemblies are strong candidates for applications in light illumination⁴ and magnetic sensors.¹⁴⁹ Just as important is the band gap manipulation in Si for microelectronics and in GaAs for photonics, the understanding and control of defects with size-specific NCs over a wide size range are essential to achieve viable applications based on these novel monosized semiconducting oxide NCs.⁷⁹

To date, there are a number of methods to synthesize transition-metal NCs, which include hydrothermal method,¹⁵⁰ self-assembly,⁴ and gas-phase condensation.^{8,9,151} With a better understanding and continued advancement of the cluster beam technique,¹⁵² gas-phase condensation along with size-selective mass filtering technique has become one of the most promising methods to synthesize NCs. Based on a well-developed magnetron sputtering system with an adjustable

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condensation zone, this technique enables fine-tuning of the cluster size with highly reproducible results. By coupling with a quadrupole mass filter, the system can produce a broad monosized NC beam over a large deposition area.^{8,9,153,154} As multiple targets can be placed into the magnetron sputtering system to generate plasma from these targets simultaneously or combinatorically, it is also possible to synthesize a variety of alloy NCs for a wide range of research and technological applications.²⁴

Recently, ZrO₂ has become an attractive material alternative to TiO₂ for applications such as photoelectrochemical water splitting⁵⁵ and fuel cells.¹⁵⁰ Bulk ZrO₂ does not have any magnetic states, whereas an undoped ZrO₂ film obtained by pulsed electron beam deposition in a partial oxygen environment has been found to have a tetragonal structure, showing ferromagnetic properties at room temperature.⁵⁸ Similarly, other undoped transition-metal oxides (TiO₂¹⁵⁵ and HfO₂⁸⁰) with surprising ferromagnetic properties have also been reported. Recently, we showed that dopant-free, defect-rich ZrO₂ nanowire and nanobrick films exhibit strong ferromagnetic properties at room temperature.⁸¹ Unlike the conventional dilute magnetic semiconductors (DMSs) such as Mn-doped GaAs or InAs, these undoped ferromagnetic transition metal oxide nanostructured films have a significantly higher Curie temperature (T_C) than those of conventional DMSs with $T_C < 200$ K.⁷⁸ For materials with promising magnetic applications at room temperature, their Curie temperature should be greater than 500 K.¹⁵⁶ Although some transparent oxide DMSs, such as Cr-doped In₂O₃ films¹⁵⁷ and Co-doped TiO₂ film,¹⁵⁸ have generally high T_C and could therefore serve as a viable material alternative for room temperature spin-based electronic applications, the solubility of the dopants remains one of the biggest challenges that limit their potential application. Furthermore, the nonuniform distribution of the dopants caused by their natural tendency to form aggregates leads to inhomogeneous magnetism within the material.^{159,160} As defects in crystalline structures appear to play an important role in dopant-free ferromagnetic oxides,^{58,81} these oxides could have the advantage of uniform magnetization. With the origin of these ferromagnetic properties remaining under debate, the study of defects and the important role that they play in these oxides is therefore fundamentally important to the development of future magnetic devices and spin-based electronics.

Here, we produce size-specific ZrO₂ NCs over the 2–16 nm size regime. Size-tuning is achieved in the gas-phase condensation technique by using a magnetron sputtering source coupled to a quadrupole mass filter, and the NCs so produced can be deposited uniformly over a large area (2 in. dia.). The as-deposited monosized ZrO₂ NCs (3, 5, 7, and 9 nm in diameter) are oxygen-deficient, and

these oxygen-vacancy defects introduce strongly size-dependent ferromagnetic hysteresis. To account for the origin of this ferromagnetism, we propose an improved magnetic polaron generation model involving defect-band hybridization. In addition to this size dependent ferromagnetism, the high dielectric constant of ZrO_2 also attracts a lot of interest for use as a gate oxide in high electron mobility transistors.^{161,162} Biocompatibility and excellent surface charge properties further make ZrO_2 NCs a strong material candidate for nanobiosensors.¹⁶³

3.2 Experimental Details

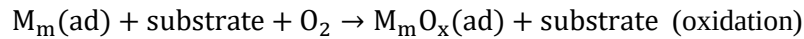
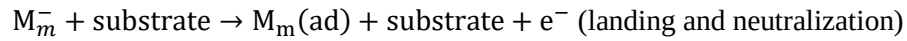
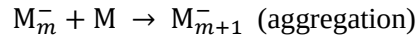
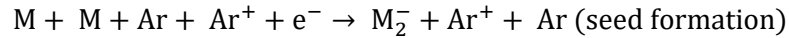
ZrO_2 NCs are directly deposited on hydrogen-terminated Si(100) substrates by using a magnetron-sputterer-based NC generation system (Nanogen 50, Mantis Deposition Ltd.).^{8,9} The silicon substrates are cleaned by high-performance liquid chromatography grade acetone and isopropyl alcohol, each with 10 min of ultrasonication, followed by 5 min of etching in hydrofluoric acid (2 vol %) to remove the native oxide layer, thoroughly rinsed in filtered ultrapure high-resistivity water after each step, and finally dried under a nitrogen stream. The resulting H-terminated Si (H-Si) substrates are then transferred to a high vacuum chamber with a base pressure of 1.5×10^{-8} mbar. The Nanogen source is equipped with three 1 in. dia. DC magnetron sputtering heads, the power output of which can be individually controlled. The zirconium targets (99.9% purity, ACI Alloys) are sputtered by Ar plasma. The sputtered atoms enter a condensation zone (equipped with a cooling jacket), where the atoms collide with one another and condense into clusters.¹⁶⁴ The NCs can be transported by diffusion or carried forward by the Ar buffer gas.¹⁵² As the broad beam containing NCs with a large size distribution is collimated through the condensation aperture, it undergoes mass selection in the quadrupole mass filter region. An appropriate set of AC and DC voltages is applied to the quadrupole mass filter to allow the passage of NCs with the preselected mass-to-charge ratio. The size selection process produces a monosized NC beam up to 10^6 amu with a 2% deviation.⁸ As no bias is applied on the substrate, the clusters are deposited on the substrate under soft-landing condition. In the present work, we focus on clusters smaller than 10 nm and investigate the nano size dependency of their magnetic properties.

The surface morphology of the deposited NC film is characterized by field emission scanning electron microscopy (SEM) with a Zeiss Merlin microscope and by atomic force microscopy (AFM) using a Digital Instruments Dimension 3100 Nanoman Nanoscope operating in tapping mode. The crystalline structure of individual clusters is determined by transmission electron microscopy (TEM)

with a Zeiss Libra 200 MC microscope with a corrected Omega filter operated at 200 kV. The TEM specimen is prepared by depositing the clusters directly on a 300-mesh copper grid with a lacey carbon film using the Nanogen source. The crystal structure of the NC film deposited on a Si substrate is measured by glancing-incidence X-ray diffraction in a PANalytical MRD X'pert Pro diffractometer equipped with a Cu K α source and a parallel X-ray beam setup operated at an incident angle of $\omega = 0.3^\circ$ over the selected 2θ range. The chemical state composition of the NC film is characterized by X-ray photoelectron spectroscopy (XPS) using a Thermo-VG Scientific ESCALab 250 Microprobe with a monochromatic Al K α X-ray source (1486.6 eV). The XPS features are fitted by using the CasaXPS software after appropriately removing the Shirley background. To characterize the magnetic properties at different temperatures, the ZrO₂ NCs are deposited onto a $5 \times 5 \text{ mm}^2$ Si substrate to allow the sample to be mounted on a quartz sample holder for superconducting quantum interference device (SQUID) magnetometry in a Quantum Design MPMS SQUID-VSM. After appropriately removing the diamagnetic contribution from the Si substrate and the sample holder to the signal, the magnetization of the ZrO₂ NC film is normalized by mass, as converted by volume estimation using AFM data (without considering the filling factor, shown in Figure S4) and a bulk density of 5.68 g/cm^3 . Care is taken to prevent magnetic cross-contamination by using only plastic tweezers and quartz sample holders in all our sample preparation and data collection processes.

3.3 Results and Discussion

The formation and growth of ZrO₂ NCs, obtained by using a magnetron sputterer-based source and a condensation chamber, involve the following mechanism:



where Ar is the buffer gas, Mm ($m = 2, 3, \dots, n$) is a free metal cluster species, $M_m(\text{ad})$ is a metal cluster adspecies on the substrate, and $M_mO_x(\text{ad})$ is an oxidized cluster adspecies on the substrate. As the free Zr atoms start to form nucleation seeds upon collision with one another and with the buffer gas within a restricted region from the sputter target, the seeds grow into bigger and bigger clusters as more free atoms become attached to the seed surface.¹⁵⁴ Both the aggregation length (AL), defined as

the separation between the top of the sputter target and the exit aperture (Figure 3.1a), and the Ar gas flow could critically affect this cluster formation process. Figure 3.1b shows that increasing the Ar flow at a fixed AL promotes the growth of clusters with a smaller size. The buffer gas is therefore not only important for generating plasma to sputter the Zr target and for carrying the clusters forward to the deposition chamber and onto the substrate but also crucial for facilitating the seed formation that leads to the cluster beam becoming negatively charged.^{9,164} A higher Ar flow rate promotes the formation of a larger amount of seeds and causes a smaller dwell time for the seeds to pass through the aggregation chamber and therefore reduces the extent of the NC growth for a fixed AL, both of which effectively reduce the overall size of the NCs. On the other hand, increasing the AL for a selected Ar flow would increase the dwell time of the NCs passing through the chamber, therefore promoting a larger mode cluster size and a broader near-Gaussian size distribution (Figure 3.1c). Figure 3.1b also shows that increasing the Ar flow from 40 to 80 sccm reduces the cluster diameter at a greater rate for a larger AL than a smaller AL. As a smaller AL has already limited the dwell time for nucleation, the effect of the Ar flow becomes less prominent. In contrast, the Ar flow for a larger AL appears more effective in changing the dwell time. By optimizing both the Ar flow and the AL, the desired size of the NCs can be tuned from 2 to 10 nm (in diameter), and the smallest NC (of 3 nm in mode size) is obtained for an AL of 10 mm at an Ar flow of 80 sccm. By either passing O₂ into the deposition chamber or exposure to the ambient air atmosphere, the Zr NCs could be easily oxidized during the deposition process or upon removal from the chamber.¹⁶⁵ Further details of tuning the dimensions of the clusters with various parameters are discussed elsewhere.^{8,9,24,153,154,164,165}

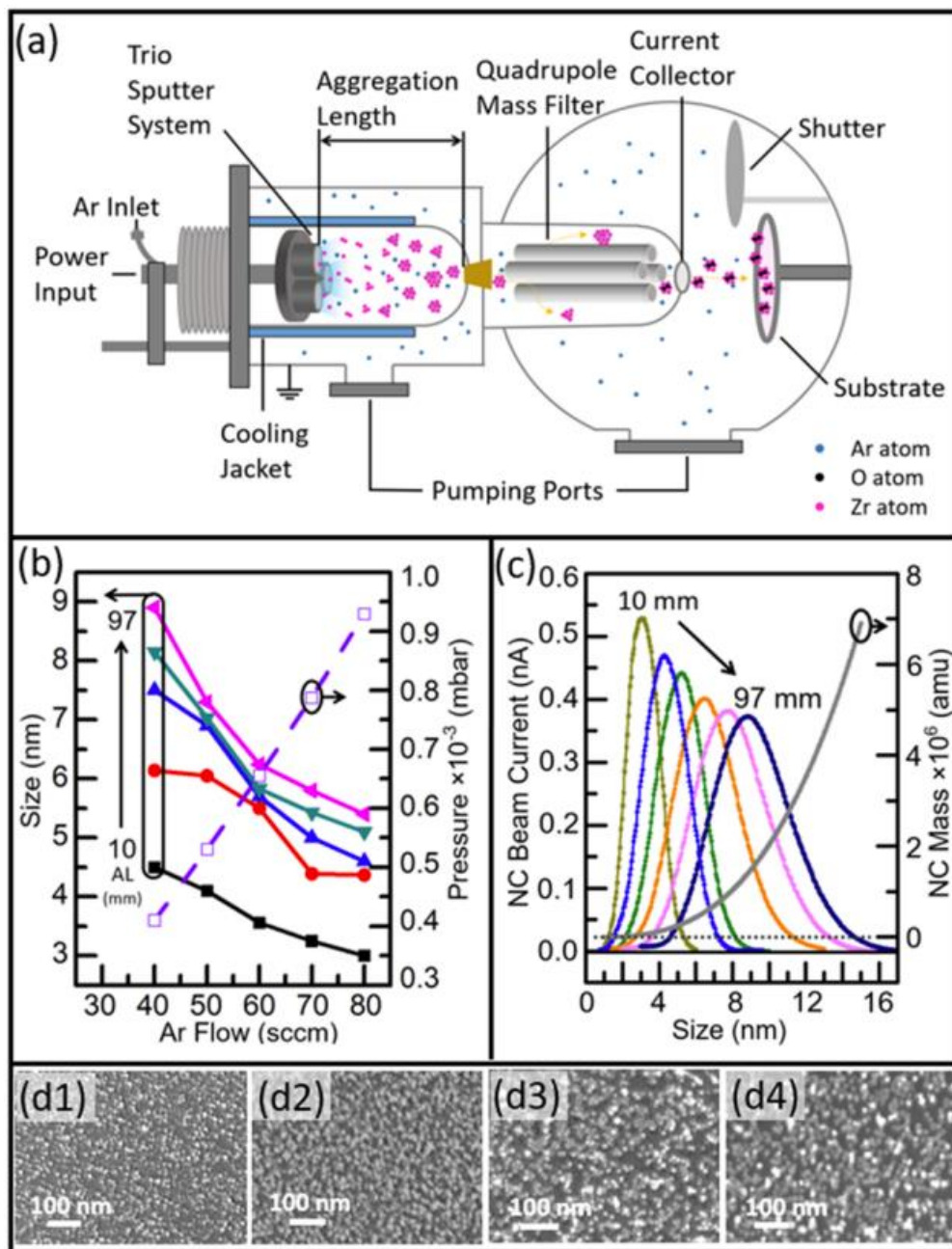


Figure 3.1 (a) Schematic representation of the Nanogen NC deposition system for producing a size-selected NC beam, which involves (i) generation of free atoms by DC magnetron sputtering, (ii) seed formation by collision and atom aggregation into bigger clusters, and (iii) beam collimation via a 3 mm diameter entrance aperture and size selection of the NCs by a quadrupole mass filter. (b) Mode cluster size (in diameter, left axis) and the deposition chamber pressure (right axis) as a function of Ar

flow rate (from 40 to 80 sccm in steps of 10 sccm) for different ALs (10, 30, 50, 70, and 97 mm). The mode cluster size corresponds to the size (diameter) of the maximum in the cluster size distribution. (c) Cluster size distribution, as reflected by the beam current obtained at the collector of the quadrupole mass filter, for a fixed Ar flow rate (50 sccm) and different ALs (10, 30, 50, 70, 90, and 97 mm), along with the mass of Zr NCs (right axis) for different NC sizes. SEM images of ZrO₂ NCs with selected sizes of (d1) 3, (d2) 5, (d3) 7, and (d4) 9 nm as-deposited on H-Si substrates for 60 min by using appropriately optimized deposition parameters and quadrupole mass filter operating voltages.

Figure 3.1d1–d4 shows the SEM images of the surface morphology of size-selected ZrO₂ NC films. The NCs are directly deposited on H-Si substrates for 60 min with appropriately optimized deposition parameters (AL and Ar flow) and with the quadrupole set to filter the selected mass (i.e., the peak position of each size distribution curve). Evidently, the as-deposited NCs are dispersed on the substrate into groups or islands of clusters, and these islands of clusters are spread over the substrate producing a NC film with increasing deposition time. The NCs are found to have a near-spherical shape, and they also appear very similar to one another in size, which confirms that the quadrupole mass filter provides good size selection with a narrow size distribution.

Figure 3.2 shows the low-magnification TEM images of groups of ZrO₂ NCs (with different mode sizes as set by the Nanogen). The center insets depict the narrow size distributions of the NCs produced by the Nanogen, thus demonstrating its excellent size selection. The near-spherical shape of the NCs also indicates that there is no discernible deformation of the ZrO₂ NCs deposited under the soft-landing condition.^{8,9} From the high-resolution phase contrast TEM images (Figure 3.2, top right insets), the ZrO₂ NCs show well-defined crystallinity for the NC size of 5 nm or above. The interplanar spacings of the 5 nm (and 9 nm) and 7 nm NCs are found to be 2.95 and 2.59 Å, respectively, which are in good accord with those of the (1 0 1) and (0 0 2) planes of the tetragonal ZrO₂ lattice. The degree of crystallinity of the tetragonal ZrO₂ NC film is also confirmed by our XRD profiles (Figure S1). On the other hand, the 3 nm NCs appear to be amorphous, likely due to the short dwell time available for the crystalline growth. This is also supported by the corresponding fast Fourier transform (FFT) patterns of the TEM images of individual NCs (Figure 3.2, bottom right insets), which show a notable contrast between the spot pattern of the crystalline 5 nm NC (Figure

3.2b) and the ring pattern of the amorphous 3 nm NC (Figure 3.2a). These amorphous NCs with ultrasmall size could contain a higher density of defects that would likely give rise to stronger magnetic properties.^{8,9} It is of interest to note that for bulk ZrO_2 the most stable phase is the monoclinic phase, followed by the tetragonal and cubic phases. Because of the difference in the surface free energy of the nanostructure within the sub-10 nm size regime, the tetragonal ZrO_2 NCs can be formed and become stable at room temperature.^{58,166}

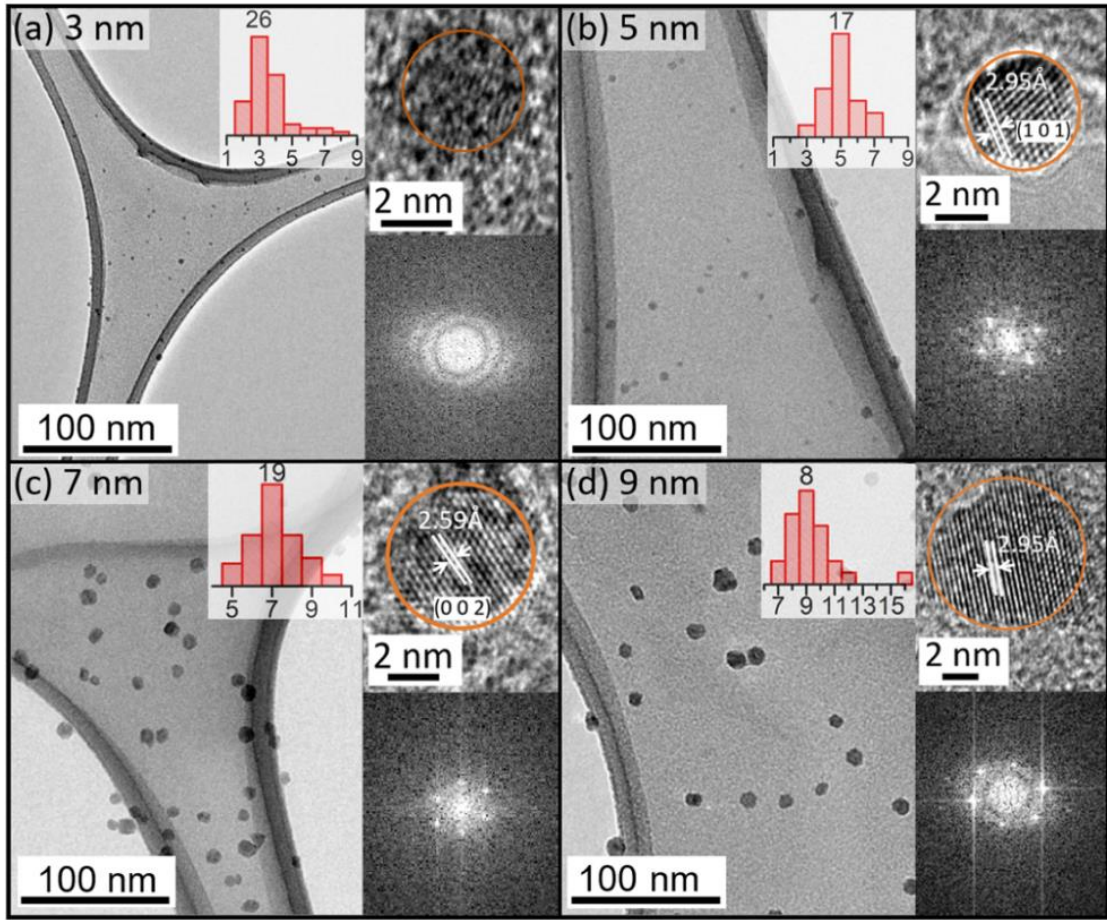


Figure 3.2 TEM images of a group of ZrO_2 NCs deposited on a TEM copper grid with a lacey carbon film obtained at low magnification with mode sizes of (a) 3, (b) 5, (c) 7, and (d) 9 nm, along with the individual NC of each size obtained at high resolution (top right insets) and the corresponding simulated diffraction patterns generated by FFT (bottom right insets). The NCs so obtained exhibit a very narrow size distribution, as shown in the respective center insets (where the bar label shows the

number of NCs with the corresponding mode size in the TEM image), as selected by the quadrupole mass filter in the Nanogen source.

Figure 3.3 shows the XPS spectra of the Zr 3d and O 1s regions of the as-deposited ZrO₂ NC films. The survey spectra (Figure S2) indicate the presence of Zr, O, C, and Si. It should be noted that the presence of a minute amount of carbon in the form of a carbonaceous layer is often found on samples due to normal handling in air. Evidently, there are no features corresponding to Mn 2p at 638.3 eV, Fe 2p at 706.8 eV, Co 2p at 779.4 eV, and Ni 2p at 852.6 eV, which confirms that the ferromagnetic signals are generated by the ZrO₂ NCs and not any magnetic impurities. The predominant Zr 3d_{5/2} feature at 183.4 eV and the prominent O 1s feature at 531 eV (Figure 3.3) correspond to the Zr⁴⁺ cation in stoichiometric ZrO₂. The residual intensities between the Zr⁴⁺ and metallic Zr₀ peaks can be attributed to oxygen-deficient ZrO_x (Table 3.1). Evidently, the residual band corresponding to ZrO_x shifts from 181 eV to the binding energy position of metallic Zr (at 178.9 eV) with decreasing intensity as the NC size increases from 5 nm to 9 nm. Based on the binding energies of Zr¹⁺ (179.8 eV), Zr²⁺ (180.9 eV), and Zr³⁺ (182.1 eV), we attribute the ZrO_x band to a combination of these oxidation states, which are used in the fitting (Figure 3.3).¹⁶⁷ More details of the composition of the residual features are given in Table S1 (Supporting Information). For the 3 and 5 nm NCs, the ZrO_x features consist largely of Zr³⁺ and Zr²⁺ contributions. For the larger 7 and 9 nm NCs, the respective Zr³⁺ residual intensities have become extremely low, and the predominant contributions are Zr²⁺ and Zr¹⁺. For the O 1s spectra, after removing the SiO₂ feature at 532.9 eV, the remaining feature at 533.5 eV can be attributed to oxygen-deficient ZrO_x. As the deposition is performed in a low vacuum condition, the aggregated Zr NCs are oxidized in ambient conditions, which could produce nonstoichiometric oxide states.⁹ While the surface-to-volume ratio increases with decreasing NC size from 9 to 3 nm for an individual NC, the total specific surface area increases with decreasing NC size. As the formation of ZrO_x could be caused by the presence of oxygen vacancies at locations with low coordination (i.e., in the near-surface region) in the NCs, the smaller NCs are more favorable to introduce oxygen vacancies. As the surface of the NC becomes oxidized with various states, more discernible ferromagnetic properties are expected if the surface is populated with oxygen-deficient sites.

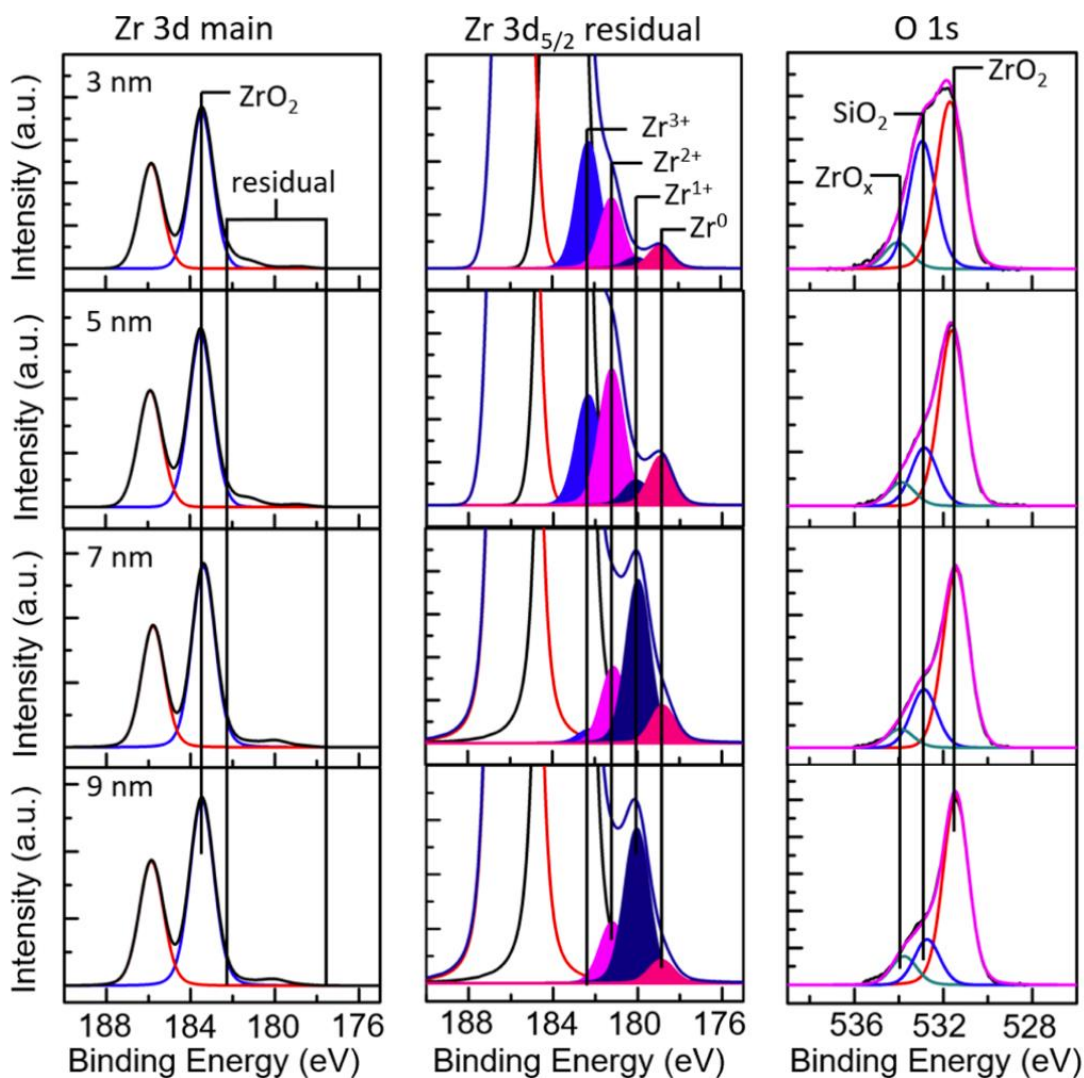


Figure 3.3 XPS spectra of the Zr 3d region (left column), along with the expanded view of the fitted residual intensities of the Zr 3d_{5/2} region (middle column), and the O 1s region (right column) of ZrO₂ NCs of different sizes (3, 5, 7, and 9 nm) as-deposited on H-Si substrates.

As the substrate has significantly greater mass than the deposited NCs, the main contribution to the sample (NCs + substrate) during the SQUID magnetometer measurement is expected to be dominated by the silicon substrate. After subtracting the diamagnetic signals from the silicon substrate and quartz sample holder (Figure S3a), we observe a hysteresis loop in the respective magnetization curves of the NC films. In order to perform quantitative analysis of the loop, we

minimize the effect of noise by employing a curve-fitting procedure developed by von Döbeneck *et al.*^{168,169} This procedure is based on the symmetry of the loop and the use of hyperbolic functions, the details of which are provided in the Supporting Information (Figure S3). The magnetization is normalized by the mass of the NC film, which is estimated from the volume of the NC film (Table 3.1) obtained from the NC film thickness measurements (Figure S4).

Table 3.1 Comparison of ZrO_x Chemical-State Content, Saturated Magnetization (M_s), Remanence (M_r), and Coercivity (H_c) Measured at 5 and 300 K for ZrO₂ NC Films of Different NC Sizes.

NC size (dia.)		3 nm	5 nm	7 nm	9 nm
Number of Zr atoms		606	2809	7696	16383
Mass (×10 ³ amu)		55.3	256	702	1490
Surface to volume ratio (nm ⁻¹)		2.00	1.20	0.86	0.67
NC film thickness (nm)		4.9	6.1	35.2	34.6
Sample volume (×10 ⁻⁷ cm ³)		1.20	1.49	8.62	8.48
Sample mass (μg)		0.68	0.85	4.90	4.82
Relative residual intensity in Zr 3d content		10.6%	8.6%	5.7%	4.5%
5 K	M _s (emu/g)	1.91	0.54	0.16	NA
	M _r (emu/g)	0.20	0.11	0.05	NA
	H _c (Oe)	120	125	162	NA
300 K	M _s (emu/g)	1.80	0.46	0.13	NA
	M _r (emu/g)	0.12	0.07	0.02	NA
	H _c (Oe)	77	79	94	NA

Figure 3.4a and b show magnetization as a function of magnetic field (the M–H curves) of the monosized ZrO₂ NC films, with the three smallest NC sizes (3, 5, and 7 nm), obtained at 5 K and room temperature. Evidently, all the NC films start to reach saturation at 2000 Oe. Although the magnetization curves measured at room temperature appear noisier than those at 5 K, they clearly follow the characteristic ferromagnetic profile (after the respective contributions from the substrate and the sample holder have been appropriately removed). The magnetic saturation (M_s), remanence (M_r), and coercivity (H_c) are calculated from the corresponding fitted M–H curves and are summarized in Table 1.1. Among the monosized NCs, the 3 nm ZrO₂ NCs exhibit the strongest M_s and M_r , both at 5 K and 300 K. The M_s value for the 5 nm NCs (0.54 emu/g at 5 K) is found to decrease significantly to 28% of that of the 3 nm NCs (1.91 emu/g at 5 K), and M_s continues to decrease as the NC size increases to 7 nm (0.16 emu/g at 5 K). However, the 9 nm NCs start to show bulk-like properties without any ferromagnetism (Figure S3d). The changes in magnetization are likely due to the changes in the defect concentration and in the NC packing density on the substrate. As the NCs are deposited on the substrate under soft-landing condition, they are expected to be loosely packed and stacked on the substrate without deformation. There is therefore more space among the larger NCs, which reduces their material density. On the other hand, H_c is found to increase slightly from the 3 nm ZrO₂ NCs (120 Oe at 5 K) to 5 nm (125 Oe) and to 7 nm NCs (162 Oe). For the 9 nm NCs, the nearly linear and noisy magnetization curve (Figure S3d) suggests that these larger NCs start to essentially follow the bulk (paramagnetic) profile. Except for the smaller corresponding values, the trends in M_s and H_c observed for the magnetization curves measured at 300 K generally follow those at 5 K with respect to the changes in the NC size, which suggests that there is no phase change between 5 and 300 K. Furthermore, it should be noted that we have also performed post annealing of the as-grown ZrO_x NCs in O₂ in order to “heal” (or reduce the amount of) the oxygen vacancy defects. These post annealed samples do not exhibit any ferromagnetism, which confirms that the observed ferromagnetism comes from the oxygen vacancies.

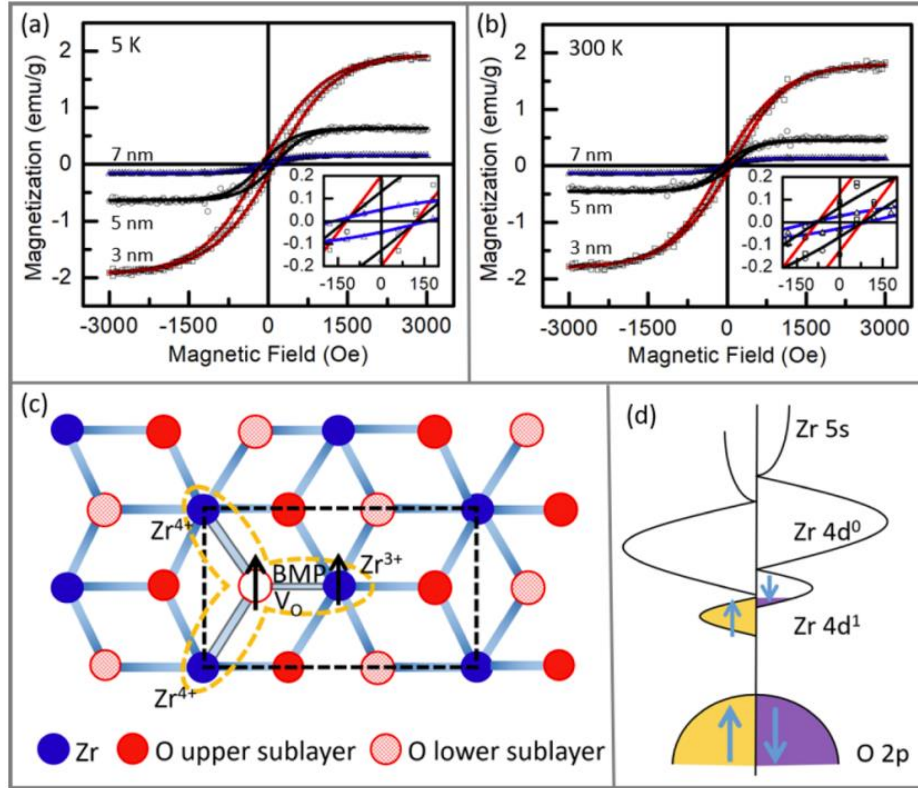


Figure 3.4 Measured (symbols) and fitted ferromagnetic hysteresis loops (solid lines) of as-grown ZrO₂ NCs of different sizes obtained at (a) 5 and (b) 300 K. (c) Schematic presentation of the formation of magnetic polarons in an unreconstructed ZrO₂ (1 0 1) surface. The missing oxygen vacancy (V_O) in the lower sublayer triggers four nearby Zr ions (the one below V_O is not shown) with two excess electrons. The electron trapping in the oxygen vacancy could couple with the other electron located in Zr³⁺ via exchange interaction, generating magnetic polaron. (d) Schematic diagram of band-splitting leading to ferromagnetism generation: an impurity band contributed by Zr 4d¹ (Zr³⁺) is generated by the oxygen vacancy defects. This impurity band could merge and hybridize with the conduction band, which triggers band-splitting into spin-up and spin-down states.

To date, there are only a few theoretical studies on magnetic ordering and the origin of magnetic semiconductor oxides. In the bound magnetic polaron (BMP) model, which is highly applicable to materials with transition-metal dopants, magnetic coupling is generated via exchange interaction between the donors and local magnetic ions, resulting in a cloud of polarized spins and the so-called

ferromagnetic alignment.¹⁷⁰ In a dopant-free semiconductor oxide material, the grain boundary defects that are proposed to correspond to oxygen vacancies have strong effects on their interactions. The magnetic exchange interaction is enhanced by a high concentration of the oxygen vacancy defects overlapping among the BMPs. However, this model could not explain how this ferromagnetism could exist at room temperature or in some other nonferromagnetic materials with a high concentration of oxygen vacancies.^{57,81} In the charge-transfer ferromagnetism (CTF) model, developed as an extension of the BMP model, the high defect concentration contributes to an impurity band. Electron hopping between the impurity band and the charge reservoir created by the dopants leads to splitting of the spin states.^{93,156,157} As the ZrO₂ NCs obtained in the present work do not have any dopant, the observed ferromagnetism for the clusters of different sizes is therefore related to oxygen vacancy defects. The presence of oxygen vacancy defects is in good accord with the XPS residual intensities of the Zr 3d feature between 179 and 182 eV and the O 1s feature between 532 and 536 eV attributed to ZrO_x (Figure 3.3).

Based on the previous theoretical studies involving the BMP and CTF models and our XPS analysis, we propose a band hybridization model to explain the size-dependent ferromagnetism of the ZrO₂ NCs. Unlike Ti in TiO₂ and Zn in ZnO, the Zr atoms in the ZrO₂ bulk are not easily reduced from Zr⁴⁺ to a lower oxidation state (i.e., Zr³⁺, Zr²⁺, or Zr¹⁺).¹⁴⁸ However, in the presence of a high electric field or a surface, it is possible for Zr⁴⁺ to be reduced to a lower oxidation state.^{57,167} In a recent density functional theory study,^{57,148,166} oxygen vacancies are found to have a lower formation energy in a ZrO₂ NC than the bulk ZrO₂, which makes the ZrO₂ NC more favorable to host oxygen-reducible structures. Because of the presence of these oxygen vacancy defects, the ZrO₂ tetragonal phase could become stabilized at room temperature. The oxygen vacancies are more easily formed in a lower-dimensional structure such as the surface of the clusters. There is therefore a higher relative concentration of oxygen vacancy defects (i.e., ZrO_x) in the NC film with smaller NCs because of their higher surface-to-volume ratio (when compared to a uniform film or powders). In the tetragonal ZrO₂ structure, one missing oxygen atom (i.e., an oxygen vacancy defect) could trigger the reduction of one of the nearby Zr⁴⁺ ions to Zr³⁺, leaving a resonance structure that contains a singly charged oxygen vacancy and a Zr³⁺ ion. The excess 4d electron in the lattice starts to form a magnetic polaron due to the exchange interaction (Figure 3.4c). As the Zr³⁺ ions become the charge reservoirs as a result of this defect formation, an impurity band arises between the conduction band and valence band. Hybridization between the impurity band and the conduction band causes band-splitting that leads to

spin-up and spin-down states, which favors the ferromagnetic ordering (Figure 3.4d).^{57,81} As the size of NC increases and approaches the bulk, there are more nearby missing oxygen atoms (i.e., >2 atoms/unit cell), and more Zr^{2+} , Zr^{1+} , or even Zr^0 (metallic) states are introduced. Although there is a higher concentration of defects along with more unpaired d-shell electrons, too close overlapping of the electron wave functions (leading to exchange interaction) could induce antiparallel alignment and therefore give rise to antiferromagnetism. In addition, the excess electrons in Zr^{1+} and Zr^0 occupying the orbitals individually may lead to paramagnetic property as well. Hence, when the NC size increases from 3 to 9 nm, the concentration of Zr^{3+} decreases (as revealed by the XPS spectra in Figure 3.3) and less magnetic polarons are produced, which in turn leads to weaker magnetic saturation. The present model is found to be consistent with the recently reported first-principle calculations on even smaller clusters (< 3 nm).⁵⁷

Our ferromagnetic NCs are novel and unique because they represent one of the rare dopant-free DMS materials. Our ZrO_2 NCs only require less than 2000 Oe external field to reach saturation. The sensitivity and saturation (1.8 emu/g) are much higher than most of the magnetic transparent oxide materials, including undoped ZrO_2 film (0.18 emu/g),¹⁷¹ Mn-doped ZrO_2 thin film (0.02 emu/g),¹⁷² and Cu-doped ZnO nanowire film (0.2 emu/g).¹⁷³ In addition to presenting further insights of the ferromagnetic property of these NCs, our magnetic ZrO_2 NCs also promise some potential technological applications. In cancer theragnostic, these ultrasmall NCs combined with designer surface chemistries are highly appealing to diagnostic assays and MRI contrast agents.¹⁴⁹ Furthermore, as the ferromagnetism of ZrO_2 NCs are strongly size-dependent, the magnetization can be manipulated by controlling the size. These magnetic NCs with a high dielectric constant could potentially serve as tunnel junctions in future nanoscale spintronic devices.⁶⁰

3.4 Conclusion

In summary, we have successfully synthesized and deposited dopant-free size-selected ZrO_2 NCs of 3, 5, 7, and 9 nm in size on silicon substrates. These monosized NCs exhibit strong size-dependent ferromagnetism. Together with the nature of the nanostructures, the built-in oxygen vacancy defects near the surface of the NCs are found to be responsible for the magnetic properties. Our XPS study further shows that there is a correlation between the magnetization and Zr^{3+} content of the NCs. The present study establishes a strong link between the proposed mechanism involving defect-induced band hybridization and the observed magnetization properties. This work also demonstrates a novel

approach to synthesize dopant-free magnetic semiconductors and to manipulate the magnetization by size control. The simplicity of the technique and the room-temperature deposition promise high reproducibility and a wide substrate choice that are attractive to a broad range of applications, such as tunneling junctions and future spintronics.

Chapter 4

Hf_xZr_{1-x}O₂ Solid Solution Nanoclusters with Tunable Size and Composition

4.1 Introduction

Zirconia (ZrO₂) and hafnia (HfO₂) have been regarded as new technological materials with unique physical and chemical properties. They are both group IV-B metal oxides. Both ZrO₂ and HfO₂ have relatively large bandgaps (5.8 eV and 6.0 eV, respectively) and high κ -dielectric constants (4.8 and 4.0, respectively). They have therefore been used as an emerging class of gate electrode materials.⁹⁵ Bulk ZrO₂ and HfO₂ are very stable in the monoclinic phase at room temperature. The monoclinic phase is transformed at higher temperature to the tetragonal phase (ZrO₂ at 1170 °C, HfO₂ at 1720 °C) and the cubic phase (ZrO₂ at 2370 °C, HfO₂ at 2600 °C).⁹⁶ Both zirconia and hafnia are also very similar in other properties such as relatively high stiffness, low thermal conductivity, and biocompatibility, making them known as “twin oxides”.^{2,96,174}

Recently, creating nanostructures of ZrO₂ and HfO₂ has attracted a lot of attention. This is because not only these nanostructures provide a high specific surface area with a rich variety and a large number of active sites for catalysis and sensing applications, but they could also contain stabilized higher-temperature tetragonal and cubic phases as well as the metastable orthorhombic phase, in addition to the monoclinic phase found at room temperature.^{58,174} Furthermore, these nanostructures could support the existence of oxygen vacancy defects. With a high concentration of oxygen vacancy defects, there could be a large number of defect states arising between the conduction band and valence band.^{2,81,175} These so-called mid-gap states in the novel phases could promote photoabsorption when the material is working as a photocatalyst, or enhanced spin-splitting that favors ferromagnetic alignment. The oxygen-deficient ZrO₂ and HfO₂ are also strong candidates for use as the active components in the next-generation non-volatile memories (i.e., RRAM).^{103–105}

Nanoclusters (NCs) are one of the most fundamental nanostructures with the highest surface-to-volume ratio. The number of defects that often affects the performance of the material in a selected application can be controlled by size manipulation.^{2,8} The most common method to synthesize NCs is self-assembly in the liquid or gas phase. Gas-phase condensation is a well-developed technique for NC generation. The target material is vaporized into the gas phase and carried into a cooled

condensation chamber by a buffer gas, where the gaseous atoms/molecules of the target collide with one another, losing thermal energy and condensing into clusters. To generate a mono-sized cluster beam, a quadrupole mass selector is employed at the exit aperture of the condensation chamber. This technique provides the flexibility of the choice of the target material and offers the tuning of cluster size and composition.^{176–178} There are many gaseous species generation techniques that can be used in a gas-phase condensation NC source, including e-beam evaporation, ultra-sonication, and magnetron sputtering. In the present work, we use DC magnetron sputtering to produce Zr and Hf atoms for cluster synthesis because of its easy sample preparation and precise control.

To date, there have only been a few studies in combining these twin oxides into a homogeneous film, less than 10 nm thick. The HZO film has attracted great interest because it exhibits ferroelectric behavior with ultralow power dissipation.^{179–182} The great solubility and homogeneity of these “twin oxides” in the film lead to a great advantage compared to traditional doping. In the present work, we produce, for the first time, oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($x < 1$) hybrid NCs by using a gas-phase condensation technique with specific size and composition control. We provide detailed characterization of their crystalline structures and chemical states as well as their bandgaps and propose a model to explain the novel structure of these solid-solution NCs.

4.2 Experimental Details

The $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs are synthesized using a novel NC generator based on a DC magnetron-sputter coupled to a quadrupole mass selector (Nanogen 50, Mantis Deposition Ltd.). With a base pressure of 4.3×10^{-9} mbar, the system operates at a deposition pressure from 2.4×10^{-4} mbar to 4.9×10^{-4} mbar depending on the selected argon flow rate. The zirconium and hafnium metal targets (99.9% purity, ACI Alloys) are mounted on separate 1 inch diameter magnetron sputtering heads, each of which can be individually controlled to obtain different sputtering power. In this work, the Zr and Hf targets are sputtered simultaneously with independent control to provide alloy clusters in various relative compositions. The quadrupole mass filter coupled to the NC beam path provides a precise *in-situ* mass selection with a 2% accuracy up to 10^6 amu. To determine the surface morphology and the crystalline structure of the as-deposited clusters, a Zeiss Libra 200 MC transmission electron microscope (TEM) is employed. This omega-filter-corrected TEM can be operated at 200 kV in both STEM (Scanning TEM) and HRTEM (High-resolution TEM) modes, providing detailed morphological and structural analysis. The TEM is also equipped with an energy-dispersive X-ray

spectrometer (EDS), which, in STEM mode, can provide elemental analysis of an individual NC to determine the alloy oxide composition. The TEM specimen is prepared by depositing the clusters directly on a 300-mesh copper grid with a holey carbon film in the Nanogen source.

To determine the Zr and Hf composition and their oxidation states, we perform an X-ray photoelectron spectroscopy (XPS) study using a Thermo-VG Scientific ESCALab 250 microprobe with a monochromatic Al K α X-ray source (1486.6 eV). The Hf_xZr_{1-x}O₂ NCs are directly deposited on hydrogen-terminated Si(100) substrates (H-Si) for XPS measurements. Before transferring into the Mantis high vacuum deposition chamber, the Si substrates are precut into 5 mm $\times$ 10 mm pieces, and then cleaned with 10-min ultrasonication in high-performance liquid chromatography (HPLC) grade acetone and isopropyl alcohol, followed by a 5-min etch in hydrofluoric acid (2 vol %) to remove the native oxide layer. Filtered ultrapure high-resistivity (18.2 $\Omega\cdot\text{cm}$) water is used to thoroughly rinse the substrates between each preparation step. All the XPS features are analyzed by using the CasaXPS software after appropriately removing the Shirley background. Moreover, reflection electron energy loss spectra (REELS) are also taken to measure the bandgaps of these hybrid NCs in a Thermo Nexsa G2 surface analysis system with an electron beam of 1000 eV incident energy.

4.3 Results and Discussion

The size-selected Hf_xZr_{1-x}O₂ hybrid NCs have been synthesized using the gas-phase condensation technique, shown schematically in Figure 4.1a. Argon gas is injected from behind the sputtering targets and activated into a plasma, which is then used to sputter the Zr and Hf targets into gaseous atoms. The Ar ions in the plasma not only sputter the targets, but also serve as seeds to initiate cluster formation.² As the seeds propagate through the water-cooled aggregation chamber, they collide with other free sputtered atoms and Ar atoms, losing thermal energy and coalescing into clusters. These clusters then pass through a 4-mm dia. exit aperture into the deposition chamber, following the pressure gradient. The Ar gas also serves as the carrier gas for deposition, providing the momentum for the NCs to travel at $\sim$ 200 m/s through the quadrupole mass filter for *in-situ* size-selection. Since there is no bias applied on the sample holder, the NCs undergo soft-landing on the substrate without any structural deformation.^{2,8,9}

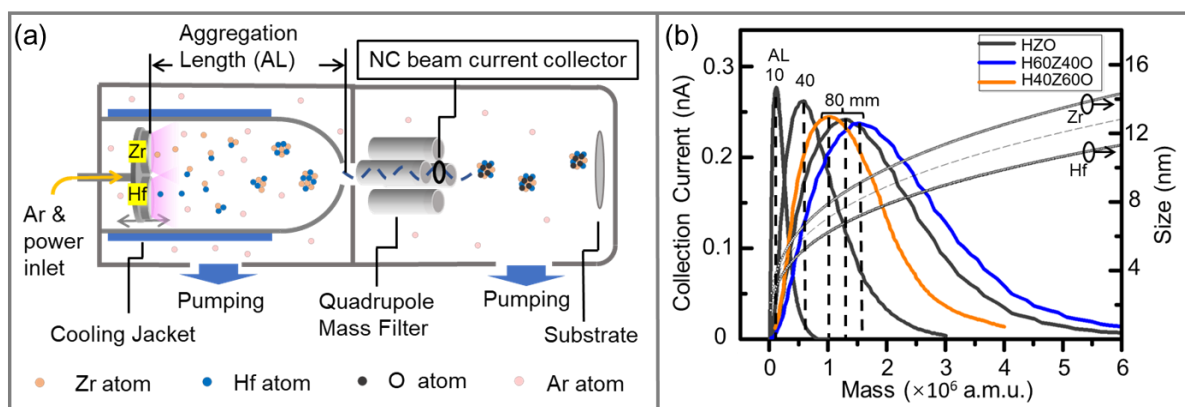


Figure 4.1 Schematic representation of synthesis of Hf-Zr hybrid oxide NCs by gas-phase condensation technique, which involves magnetron sputtering of both Zr and Hf metal targets simultaneously under different sputtering conditions, and the resulting gaseous species then aggregate in the gas phase over an aggregation length (AL) to form clusters with a size distribution. The as-formed clusters then undergo size selection in a quadrupole mass filter before soft-landing onto the substrate. (b) Mass distributions of the as-formed clusters passing through the quadrupole mass filter (as reflected by the collection current) at selected aggregation lengths (10, 40, 80 mm) and an Ar flow rate of 30 sccm. The grey lines indicate the corresponding estimated sizes of the pure Zr or Hf NCs of each mass (right axis), where the grey dash line gives the mass-to-size relationship of the HfZr alloy hybrid NCs with a 1:1 Hf-to-Zr ratio (i.e., HZO). The mass distributions obtained with an 80 mm aggregation length are also shown for NCs with other relative compositions of 60% Hf and 40% Zr (blue) and 40% Hf and 60% Zr (orange), indicated as H60Z40O and H40Z60O respectively.

By modifying the cluster dwell time in the aggregation chamber, the size of the NCs can be optimized for precise size-selection by using the quadrupole mass filter. The cluster dwell time is mainly controlled by the Ar flow rate and the aggregation length (AL), the latter of which is defined as the distance between the movable sputtering targets and the exit aperture of the aggregation chamber. The mass distributions of selected HfZr alloy NCs in this work as scanned by the quadrupole mass filter are shown in Figure 4.1b, while those of other alloy NCs can be found in Figure S5 (Supporting Information). Figure 4.1b and Figure S5 also show that the combination of a high Ar flow rate and a short AL generally leads to smaller NCs. Conversely, the combination of a low Ar flow rate and a longer AL leads to bigger NCs. It should be noted that the AL provides the

most effective control of the NC size, while the Ar flow rate is a secondary parameter more effective in maximizing the NC beam current for optimal productivity. The NCs so synthesized could therefore be finely tuned and appropriately selected from 1×10^5 amu to 6×10^6 amu, which corresponds to 8 to 14 nm for Zr NCs, 6 to 11 nm for Hf NCs and 7 to 13 nm for $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ NCs. Both Zr and Hf targets are sputtered simultaneously, with the sputtering power for each target controlled independently. Since the Zr and Hf have similar sputter yields,¹⁸³ three different sputtering current combinations of 120 mA/80 mA, 100 mA/100 mA and 80 mA/120 mA for Hf/Zr targets are applied to achieve different Hf and Zr compositions in the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs, which we denote respectively as H60Z40O, HZO, and H40Z60O (with H for Hf, Z for Zr and O for oxide (O_2) and the digits 40 and 60 correspond to the approximate atomic percentage to indicate the relative composition of Hf and Zr). Table 4.1 summarizes the different sputtering conditions (including sputtering power, aggregation length and Ar flow rate) used to obtain $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs with selected sizes and relative compositions. We also provide a simple notation to identify these NC samples along with their properties obtained from TEM and XPS discussed below. More details about tuning the size of the NCs are given elsewhere.^{2,8,21,24,184,185}

Table 4.1 Summary of deposition conditions used to obtain $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs and their typical physical and chemical-state properties.

Nanocluster Sample ID*****	H40Z60 O-10	HZO-10	H60Z40 O-10	H40Z60 O-40	HZO-40	H60Z40 O-40	H40Z60 O-80	HZO-80	H60Z40 O-80
Zr sputtering current (mA)	120	100	80	120	100	80	120	100	80
Hf sputtering current (mA)	80	100	120	80	100	120	80	100	120
AL (mm)	10			40			80		
Ar flow rate (sccm)	45			30			30		

***** In our sample ID notation, H, Z and O represent Hf, Zr and O respectively. The two digits after H (or Hf) and Z (or Zr) represent the atomic percentages of the respective metals in the oxide and the two digits after the hyphen correspond to the aggregation length (AL) in unit of mm. The Ar flow rate is used as a secondary control parameter to primarily optimize the cluster beam current. As it has a minor effect on the target cluster size, it is not included in the sample ID.

Alloy NC mode mass (amu)		0.95×10^5	1.19×10^5	1.42×10^5	4.23×10^5	5.78×10^5	8.06×10^5	1.02×10^6	1.30×10^6	1.54×10^6
Approximate NC mode size (nm)		4			8			14		
NC crystallinity		Amorphous			Single crystal	Crystalline core with thin amorphous shell		Poly-morph	Crystalline core with amorphous shell	
Zr ⁴⁺	Binding Energy (eV)	184.3	184.7	184.3	183.6	183.4	183.5	183.5	183.4	183.6
	Content	58.1%	43.4%	59.2%	55.9%	60.5%	64.2%	69.3%	65.5%	50.6%
Zr ^{x1a} / Zr ^{x1b}	Binding Energy (eV)	187.3	187.5	187.7	188.3/186.1	187.9/185.7	187.6/185.7	187.0/185.5	187.7/185.7	188.1/185.9
	Content	19.6 %	14.8%	19.0%	10.0%/19.9%	10.6%/19.1%	8.1%/16.7%	5.4%/10.2%	9.3%/14.8%	9.8%/24.9%
Zr ^{x2/} Zr ⁰	Binding Energy (eV)	182.0	183.0	182.1	180.9	181.1	181.2	181.5/179.8	181.0/179.3	181.1
	Content	22.4%	48.8%	21.9%	14.3%	9.9%	11.1%	7.1%/8.1%	7.7%/2.8%	14.8%
Band Gap (eV)		3.92	3.98	4.04	4.08	4.20	4.31	4.49	4.53	4.59

Figure 4.2 shows the STEM images of the Hf_xZr_{1-x}O₂ NCs as-deposited directly on the holey carbon TEM grids. All the NCs appear to be evenly distributed on the TEM grids and each individual NC shows a spherical shape. The NC samples deposited under different selected conditions all follow a near-Gaussian size distribution, which closely resembles the corresponding NC beam current curve collected by the quadrupole mass filter (Figure 4.1b). As expected, the NCs appear slightly larger when compared to the mass profiles obtained from scanning the quadrupole mass filter because they become oxidized in the ambient environment.

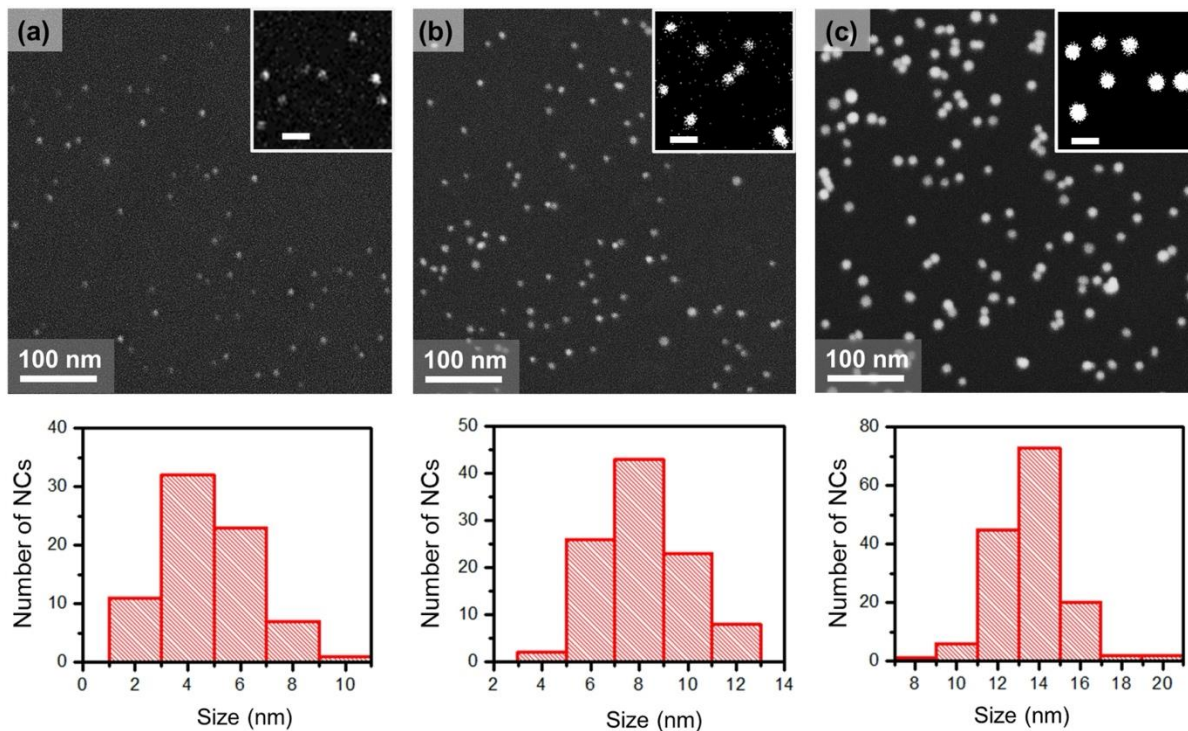


Figure 4.2 STEM images of as-deposited (a) HZO-10, (b) HZO-40 and (c) HZO-80 NCs on the holey carbon TEM grids with the corresponding size distribution profiles shown in lower panels. The NC size corresponds to the diameter of the near-spherical NC. The insets provide images at a higher magnification to show the near-spherical shape for each NC, with 20-nm scale bars.

Figure 4.3 shows the HRTEM images of the as-deposited NCs of selected sizes and compositions to illustrate their crystalline structures. Under the soft-landing condition, there is no discernible deformation for the NCs. The NCs obtained with 10 mm AL and 45 sccm Ar flow appear amorphous, which is likely due to the extremely short dwell time in the aggregation (growth) process (Figure S6). As the AL is increased to 40 mm, the NCs become larger and apparently more crystalline. Interestingly, the simulated diffraction patterns generated by FFT match with the space group $Pca2_1$ (orthorhombic),^{186,187} which is not one of the three normal stable phases (i.e., monoclinic, tetragonal, and cubic) of ZrO_2 and HfO_2 . It should also be noted that the NCs with the highest Zr content are found to have the highest crystallinity. As the Hf content increases, the NCs start to convert into a structure of a crystalline core with an amorphous shell, where the core still maintains the

orthorhombic structure. Even though the twin oxides (ZrO_2 and HfO_2) have very similar lattice parameters, the orthorhombic HfO_2 has a smaller unit-cell size than the orthorhombic ZrO_2 (Table S2).⁹⁷ As the deposition condition changes to 80 mm AL, the hybrid NCs grow beyond 10 nm and start to become polycrystalline. The emergence of polycrystallinity suggests that the NCs are evolving from a “giant molecule” to bulk, with each grain still maintaining the novel orthorhombic phase. We therefore estimate the critical size for a single crystalline $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NC to be ~ 10 nm. The HRTEM images for those hybrid NCs obtained under other synthesis conditions are also shown in Figure S6.

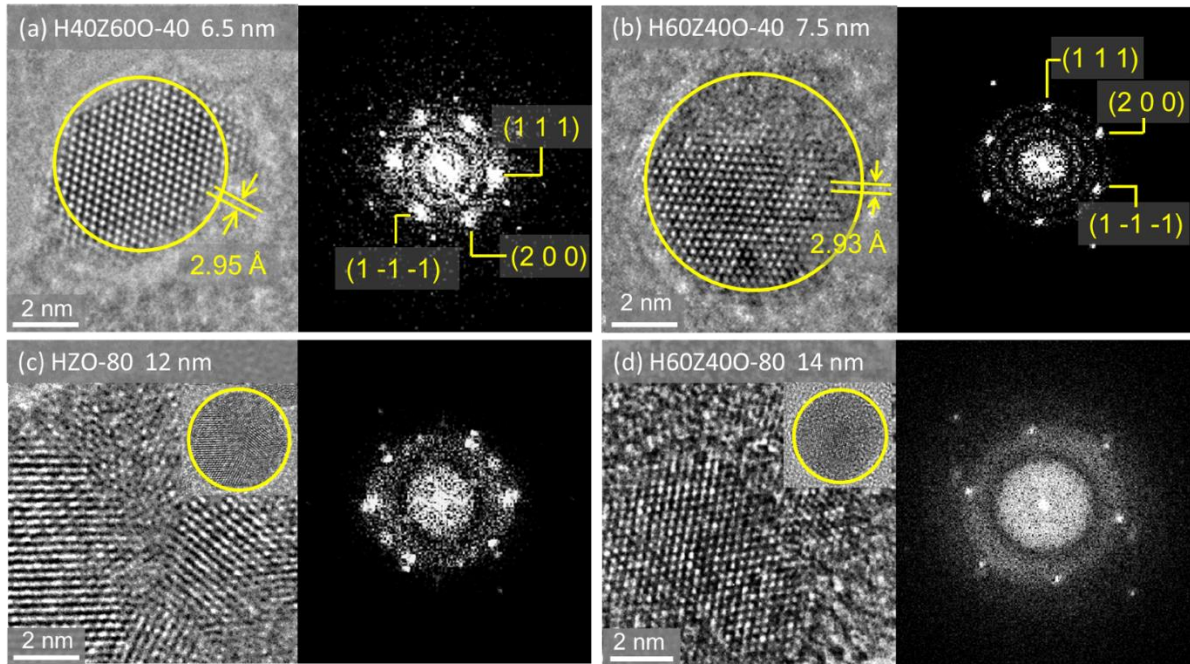


Figure 4.3 High-resolution TEM images of as-deposited $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs obtained with 40 mm AL for samples (a) H40Z60O-40 ($\text{Hf}_{0.4}\text{Zr}_{0.6}\text{O}_2$) and (b) H60Z40O-40 ($\text{Hf}_{0.6}\text{Zr}_{0.4}\text{O}_2$), and with 80 mm AL for samples (c) HZO-80 ($\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$) and (d) H60Z40O-80 ($\text{Hf}_{0.6}\text{Zr}_{0.4}\text{O}_2$), along with the corresponding FFT patterns (right panels) to illustrate the different crystalline features. The right insets in (c) and (d) provide images of the entire NCs, with their corresponding sizes (12 nm and 14 nm dia.) marked by circles.

To get better understanding of the compositions that lead to the hybrid NC structures, we perform a detailed XPS study of the hybrid NCs to characterize their chemical states. Figure 4.4 confirms the

presence of Zr and Hf features in the XPS spectra of all the NCs obtained with different sizes and compositions. This is in agreement with the TEM-EDS measurements (Figure S7) of individual NCs, which verify the integration of Zr and Hf within the hybrid NCs. Since the Hf 4s spectra have direct overlap with the O 1s features, the O 1s spectra are not used to analyse the oxidation states. Among the NCs reported here, the most prominent Hf 4f_{7/2} feature at 17.8 eV corresponds to Hf⁴⁺ (HfO₂)¹⁸⁸ and it becomes more intense with increasing AL (from Figure 4.4d to Figure 4.4e to Figure 4.4f), which suggests that the Hf atoms tend to integrate more readily into larger clusters. On the other hand, the Zr components in the hybrid NCs appear much more active and they exhibit a large variation in oxidation states (Figure 4.4a-Figure 4.4c), with the most prominent Zr 3d_{5/2} peaks at 184.0 eV corresponding to Zr⁴⁺ (ZrO₂).^{2,81} For NCs obtained with 10 mm AL, two more components can be fitted, Zr^{x1} (x1 > 4+) and Zr^{x2} (0 < x2 ≤ 3+) on the respective higher and lower binding energy sides of the Zr⁴⁺ feature. The Zr^{x2} feature can be attributed to oxygen-deficient states based on our previous study.² As the Zr^{x2} feature appears to become more intense and shift to a higher binding energy from H40Z60O-10 to HZO-10, there are more singly charged oxygen vacancy defects (Zr³⁺) in the integrated hybrid NCs. For the Zr^{x1} features that have discernibly higher binding energies than Zr⁴⁺ first observed here, they provide evidence for the presence of possible solid solution in NCs due to the interaction between Zr and Hf, which will be discussed later. While there are some reports about the higher binding energy shifts for Zr alloys in the XPS studies,^{189,190} none of these reported shifts are as large as the one shown here.

As the size of the hybrid NCs obtained with 40 mm AL increases, the width of the Zr 3d features (Figure 4.4b) becomes notably smaller than the smaller NCs obtained with 10 mm AL, indicating a more homogeneous chemical environment around the Zr atoms, while the Zr⁴⁺ features remain the most dominant. With the narrower widths, the Zr^{x1} component in the higher binding energy range could be easily fitted with two peaks, Zr^{x1a} and Zr^{x1b}. These two peaks could likely be attributed to two different and more well-defined Zr bonding sites in the Hf_xZr_{1-x}O₂ orthorhombic structure when compared with the amorphous NC structure obtained with 10 mm AL. There is also a small oxygen-deficient Zr^{x2} feature in the NCs obtained with 40 mm AL (Figure. 4.4b), which has a lower intensity relative to Zr⁴⁺ than the NCs obtained with 10 mm AL (Figure 4.4a).

Most of the characteristics found in the Zr features are carried over for the larger NCs obtained with 80 mm AL as the intensity in the higher binding energy region above Zr⁴⁺ can also be easily fitted with two peaks corresponding to Zr^{x1a} and Zr^{x1b}. The relative intensities of these Zr^{x1a} and Zr^{x1b}

features evidently increase with decreasing Zr (or increasing Hf) content. Interestingly, there is a Zr metallic state (Zr^0) emerging in addition to the Zr^{x2} features (residual component in the lower binding energy region) for H40Z60O-80 and HZO-80 NCs. As the H40Z60O-80 hybrid NCs are the largest NCs studied here, it is more difficult for oxygen to penetrate the entire cluster and fully oxidize the metal deposit, thereby leaving more oxygen-deficient sites and a stronger metallic state. The binding energy positions and relative concentrations of all the Zr features are also summarized in Table 4.1.

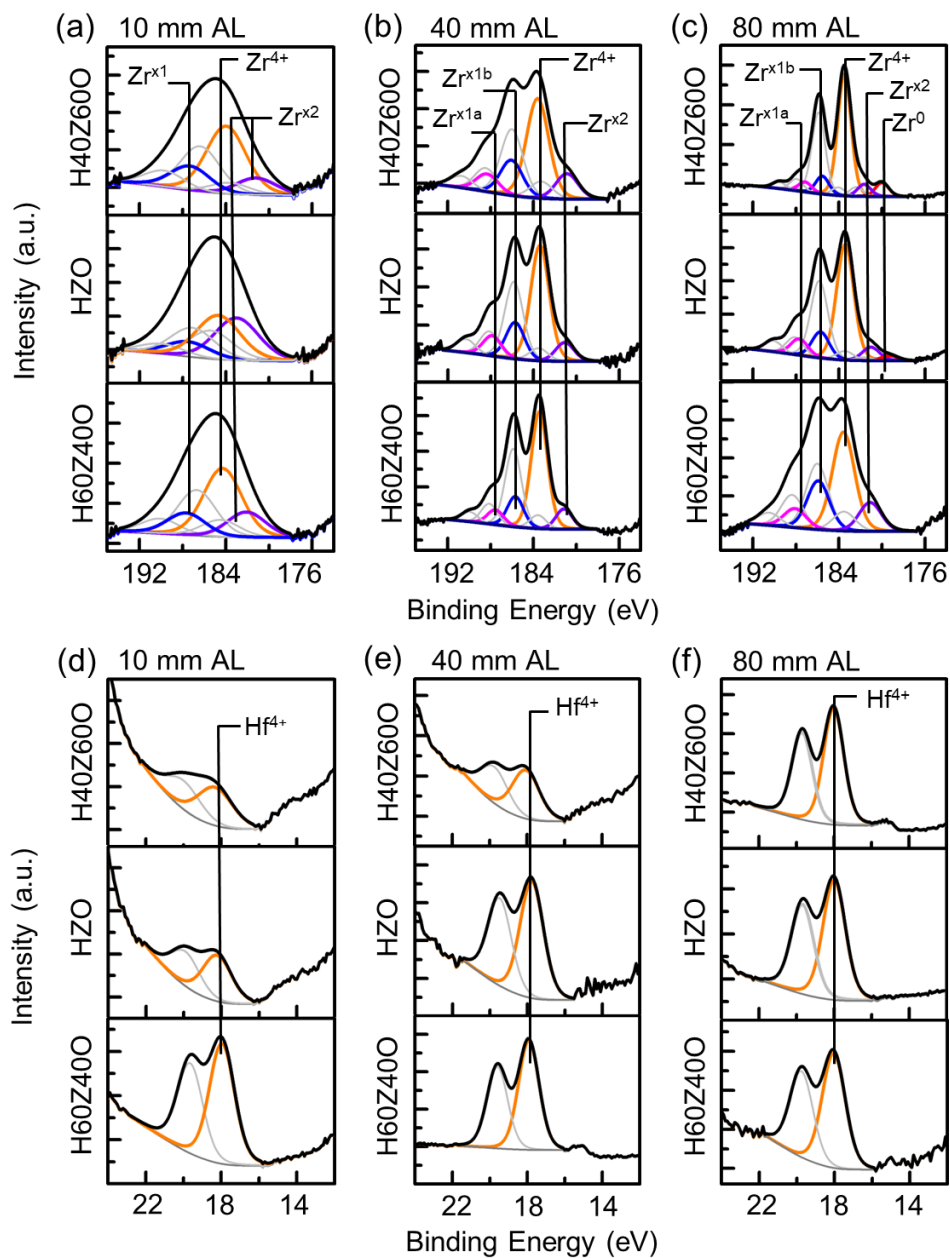


Figure 4.4 XPS spectra of (a, b, c) Zr 3d_{5/2} and (d, e, f) Hf 4f_{7/2} regions of the as-deposited Hf_xZr_{1-x}O₂ NC samples obtained with different aggregation lengths (ALs) and compositions on H-Si substrates. Only the Zr 3d_{5/2} and Hf 4f_{7/2} features are used to identify the oxidation states. The NC cluster size generally increases with increasing AL (i.e., from left panel to right panel) while the relative Hf content generally increases from top to bottom within an individual panel.

As the ultra-small and transparent nature of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs are beyond the detection scope of traditional UV-Vis spectroscopy, we use reflection electron energy loss spectroscopy (REELS) to characterize, for the first time, the bandgaps of these novel NCs, shown in Figure S8. Figure 4.5 summarizes the measured bandgaps as functions of the NC size, obtained with different AL, and of relative Hf compositions. Evidently, the bandgap is found to follow the unexpected increasing trend with increasing NC size, in contrast to the bandgap of nanomaterials generally becoming larger with decreasing size.¹⁹¹ We believe that the crystallinity and the defects in these NCs are playing an important role in controlling their bandgaps. For the smaller NCs obtained with 10 mm AL, lattice structures cannot be formed due to the short dwell time. These amorphous NCs therefore exhibit the smallest bandgap of about 4.0 ± 0.1 eV. As the NCs start to become crystalline for 40 mm AL, their bandgap increases slightly due to the crystalline structure and then further increases to about 4.5 ± 0.1 eV for the NCs grown with 80 mm AL. The XPS results show that the NCs obtained with 40 mm AL also have more relative Zr^{x2} than NCs obtained with 80 mm AL for H40Z60O and HZO NCs, which indicates the presence of more oxygen vacancy defects, and therefore the smaller bandgaps are likely due to the midgap defect states. Furthermore, Figure 4.5 also shows that the bandgap follows the increasing trend with increasing Hf content for NCs obtained with the same AL, which is consistent with the larger bandgap for HfO_2 than ZrO_2 .⁹⁵ Interestingly, all the NCs are found to have smaller bandgaps than both bulk ZrO_2 and bulk HfO_2 (5.8 eV and 6.0 eV, respectively). This observation can be attributed to the substantial concentration of defects introduced within the NCs resulting from the intermixture of Zr and Hf.

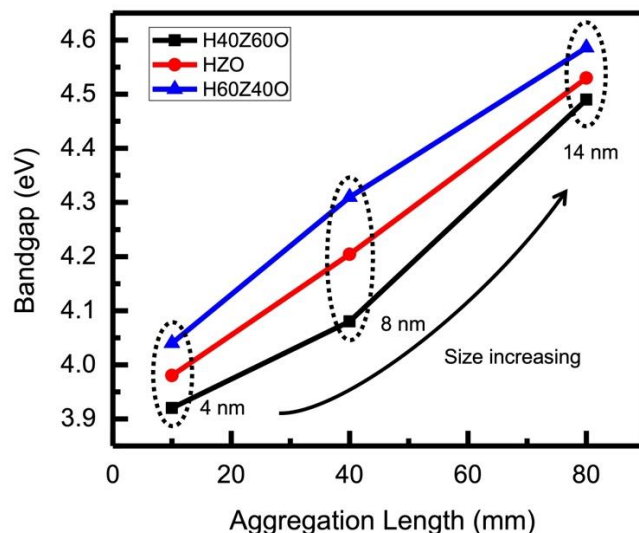


Figure 4.5 Bandgaps of NCs obtained with ALs of 10 mm, 40 mm, and 80 mm (corresponding to NC sizes of 4 nm, 8 nm, and 14 nm, respectively) and three different relative compositions. These values are summarized in Table 4.1.

Orthorhombic ZrO_2 and HfO_2 (both space group $Pca2_1$) have attracted early studies over three decades ago. These “rare” orthorhombic bulk structures are usually developed under extremely high temperature and pressure.^{192,193} A schematic representation of the $Pca2_1$ orthorhombic structure is shown in Figure 4.6a.¹⁹⁴ In an orthorhombic ZrO_2 or HfO_2 structure, an individual Zr or Hf atom is bonded with seven neighboring O atoms, in contrast to the structures of the normal phases (i.e., monoclinic, tetragonal, and cubic phases), in which a metal atom is bonded to eight O nearest neighbours. Accordingly, there are two types of oxygen sites with different coordination in the lattice structure. The O atoms in the first type of sites are bonded to four nearby metal (Zr or Hf) atoms, forming a distorted tetrahedron. The O atoms in the second type of sites are bonded to three nearby metal atoms, forming a trigonal planar geometry. An early theoretical study has shown that this special bonding arrangement has introduced possible strain and stress in this orthorhombic phase, leading to instability in the bulk.⁹⁷ The reported calculation also showed that a critical grain size is needed to obtain a stable orthorhombic structure at room temperature. The presence of defects or

reconstructions between the grain boundaries is therefore expected to alleviate the strains and to sustain the orthorhombic structure.

Based on the previous studies^{2,81} and our characterization data, we propose a new model to account for the structure of this novel solid nano-solution. While atomic layer deposition by cyclically producing HfO₂ and ZrO₂ layers alternately followed by annealing has been used to form a HZO thin film,^{102,181} no nanostructures of ZrHf alloy have ever been reported. Here, we synthesize ZrHf alloy NCs for the first time and with size and composition control by using a magnetron-sputtering gas-phase condensation technique. The alloy NCs are very reactive due to their high specific surface area, and they become oxidized upon soft-landing on the substrate and upon subsequent exposure to the ambient environment, which lead to the observed orthorhombic structure. Although the twin oxides have very similar lattice structures, which facilitates superior solubility into each other, their formation energies are different.¹⁹⁵ As the seeds are negatively charged in the condensation chamber during cluster growth, the Zr atoms with their higher electron affinity than Hf atoms would be more likely to condense during free collision.² Hence, the sputtered Hf are less favorable to condense in a short dwell time (i.e. under a low AL condition). Meanwhile, the HfO₂ are relatively less conducive to defect formation than ZrO₂, as all the Hf in the NCs maintain Hf⁴⁺ states. At a low Hf concentration, the Hf atoms can be regarded as a dopant in the orthorhombic ZrO₂ lattice structure. Although the Zr⁴⁺ and Hf⁴⁺ ions have a very similar atomic radius due to the lanthanide contraction,⁹⁴ the Hf⁴⁺ ion with much more protons than the Zr⁴⁺ ion has a higher electric field that could cause stronger attraction from electrons from nearby O²⁻ ions and even Zr⁴⁺ ions. As the Hf⁴⁺ atoms are evenly distributed within the entire NC due to the superior solubility, this “polaron effect” (i.e., the dipole moment within a polaron) cancels out each other within the lattice under the periodic boundary condition. Once the “polarons” are close to the NC surface, this causes the chemical shifts of Zr⁴⁺ that we identify as Zr^{x1} (Figure 4.6c). Meanwhile, with the presence of the Hf⁴⁺ ions, the surface may attract more oxygen atoms, which might lead to different surface reconstruction. Those oxygen atoms could attract electrons from the Zr⁴⁺ ions, also resulting in the chemical shifts of Zr^{x1}. The direct attraction from Hf⁴⁺ and induced attraction from oxygen are illustrated in Figure 4.6c and Figure 4.6d. As the NCs have a high specific surface area, the Zr^{x1} features become observable. Our TEM study also shows that the NC slowly transforms from being entirely crystalline to a crystalline core with an amorphous shell, as the Hf content is increased for NCs obtained with AL 10 nm to 40 nm.

However, as the Zr^{x1} intensity appears to decrease with increasing Hf content, we therefore expect that the amorphous shell could introduce more surface relaxation.

Since the Hf^{4+} ions have much stronger bonds with O^{2-} ions than Zr^{4+} , the oxygen vacancies are more likely to form in regions of the NC containing no Hf dopants (i.e., the oxygen site that attaches to all Zr neighbours). In Figure 4.6b, the oxygen vacancy defects at two different sites are illustrated on an orthorhombic (1 0 0) plane. Each oxygen vacancy defects could introduce a resonance structure with three or four nearby Zr^{4+} ions and cause a reduction of Zr^{4+} ions into lower oxidation states, which leads to the appearance of the low binding energy components in the Zr $3d_{5/2}$ feature that we denote as Zr^{x2} .² As the NCs obtained with 80 mm AL become larger, a polycrystalline structure begins to emerge, which is consistent with the evolution of the NC to bulk HZO material. Since the previous study has shown that the oxygen vacancies in ZrO_2 are more favourable to form at the lower coordination sites (i.e., surfaces, edges, and grain boundaries),⁵⁷ there could be more defects locating not only at the NC surface, but also in the grain boundary region. Therefore, the new Zr^0 features emerging for samples H40Z60O-80 and HZO-80, in addition to the Zr^{x2} features within the polycrystalline NC obtained with 80 mm AL, are related to the metallic states and they serve as an interconnecting component between the grains. Compared to our previous study on defect-rich ZrO_2 NCs,² introducing Hf does create a higher content of oxygen vacancy defects (Zr^{x2}). The defects in these NCs are highly probable in generating spin polarization that favors ferromagnetic alignment. On the other hand, the Hf atoms have a greater tendency to form Hf^{4+} ions under such a high AL, so there could be more Hf^{4+} ions within the clusters. As a result, the higher the Hf content the stronger becomes the Zr^{x1} component. With increasing Hf content, more Hf atoms are substituting Zr atoms in the lattice. As the Hf content change continues, the NC crystal structure eventually transforms into orthorhombic- HfO_2 from orthorhombic- ZrO_2 with reduced lattice parameters, which also strengthen the bonding between electrons and holes and therefore increase the bandgap.¹⁰⁰ The O^{2-} ions in the site with four neighbouring metal ions (site 1) are more affected by Hf^{4+} than those with three neighbouring metal ions (site 2), which are more likely related to Zr^{x1a} . However, it could also be possible that the Zr^{x1a} features are reflecting the closest Zr^{4+} ions near the Hf^{4+} polaron while the Zr^{x1b} features correspond to Zr^{4+} ions in the outer shell region of the polaron (Figure 4.6d), since most of the Zr^{x1a} peaks are ~ 2 eV higher in binding energy than Zr^{x1b} but are considerably reduced (approximately half) in intensity. Further study including DFT calculations could provide deeper understanding of this novel $Hf_xZr_{1-x}O_2$ hybrid solid nano-solution.

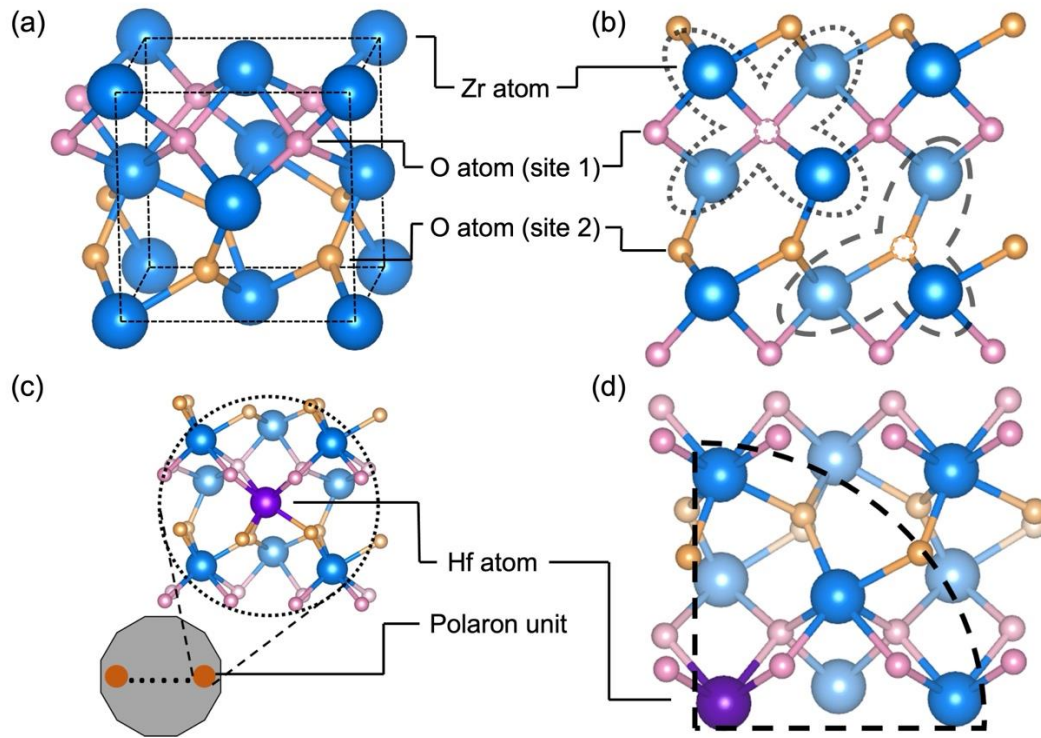


Figure 4.6 (a) A schematic representation of *Pca2₁* orthorhombic structure of ZrO₂ (HfO₂), showing two different oxygen bonding sites within the lattice. (b) An orthorhombic ZrO₂ (1 0 0) plane depicting oxygen vacancy defects from site 1 (missing O atom at the centre of the dotted area) and site 2 (missing O atom at the centre of the dashed area). The light-colored atoms correspond to the second front-most metal layer. Each oxygen vacancy could induce a resonance structure, leading the reduction of Zr⁴⁺ to Zr^{x2} states ($0 < x2 \leq 3$). (c) A schematic diagram of the polaron model to explain the NC structure and the chemical shift of Zr^{x1}. The Hf atom (purple sphere at the centre) in effect becomes a dopant atom in the orthorhombic ZrO₂ structure, creating a Hf_xZr_{1-x}O₂ solution. (d) An expanded view of a polaron on a Hf_xZr_{1-x}O₂ (1 0 0) plane. The Hf⁴⁺ ion could attract the electrons from either the neighbouring Zr⁴⁺ ions or the directly attached oxygen, which would affect the electron distribution of the Zr-O bonds. The shift of the entire electron distribution gives rise to the formation of the polaron and causes the chemical shift of Zr^{x1}. The closest Zr⁴⁺ ions nearby Hf⁴⁺ could have more attraction than those from the outer shell, which leads to the Zr^{x1a} and Zr^{x1b} residuals.

4.4 Conclusion

In this work, we have successfully synthesized $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ hybrid NCs with both size selection and tunable composition at the same time. As these nanoclusters become more crystalline with sufficient dwell time during growth, the presence of Hf induces, for the first time, the novel orthorhombic structure in the NC. This is in marked contrast to the nominally tetragonal structure for ZrO_2 reported in our previous study. We also find that the condensation of Hf trending over a longer dwell time during growth (i.e., a larger AL) has a significant impact on the NC structure. Indeed, the Hf content could greatly affect the structure of the NC, from an entirely amorphous structure for small NCs (< 6 nm), to core-shell structures for the mid-size NCs (6 to 10 nm), and to polycrystalline structures for the near-particle size NCs (> 10 nm, beyond the giant molecule regime). Introducing Hf into the NC not only brings along a higher fraction of defect states than that found in our previous ZrO_2 NC study, but also leads to new Zr 3d features with higher binding energy shifts and to “unconventional” bandgap changes observed for the first time. We propose a new model for the structure of these defect-rich solid-solution NCs. This model offers a starting point for future theoretical study and/or other experimental work on hybrid ultra-small solid solution nano-objects. Since the defects could play an important role in HfO_2 based ferroelectric material,¹⁹⁶ we believe that our NCs with a high specific surface area may provide not only such novel properties as ferroelectricity like the bulk HZO material, but also other composition-specific characteristics that promise new applications in this special quantum size regime.

Chapter 5

Fabrication of Nano-Interdigital Electrodes and Nanogap Devices by Optical, Electron-beam, and Ion-beam Lithographies and Their Memristor Applications

5.1 Introduction

Interdigital Electrodes (IDEs) serve as a foundational electronic component for a diverse range of applications, from the basic parallel electronic capacitors and diodes^{119,197,198} to delicatied sensors,^{110,120,199} and surface acoustic devices.¹¹⁷ Moreover, when integrated with lab-on-chip platforms, IDEs enhance electrochemical sensing capabilities due to their increased surface area and optimized electric field distribution. As a result, there is a significant demand to fabricate these IDEs with specific materials, finger widths, and gap spacings. To date, several techniques are used for the fabrication of IDEs, including optical lithography, laser scribing, inkjet printing, 3D printing, and screen printing.^{109,118} With typical gap spacings in the micrometer range,^{109,110,116,120,199} these approaches seek to strike a balance between size precision and cost-effectiveness. Among these, laser scribing is noted for its relative simplicity and speed,²⁰⁰ while its efficacy is predominantly contingent upon the substrate, thus limiting its broader application. Both inkjet and 3D printing methods are recognized for their optimal material efficiency and compatibility with flexible substrates.^{201,202} However, they often present limitations in achieving high resolution, especially in the case of 3D printing. Screen printing, albeit analogous to lithography, operates on a macro scale.²⁰³ While this technique offers advantages in terms of simplicity, cost, and expediency, its resolution, typically in the millimeter range, diminishes its competitiveness in the realm of advanced micro/nano device fabrication.

Lithography is the art and science of patterning structures on substrates with remarkably high precision. Serving as a fundamental nanofabrication technique, lithography has a wide range of applications across multiple industries, from semiconductor manufacturing to optics and biotechnology.^{204–206} By harnessing the principles of light, electron beam or ion beam exposure, lithography enables the creation of intricate patterns on substrates, offering unparalleled control over feature sizes and shapes.^{207,208} In nanomaterial research, IDEs play an indispensable role as conduits connecting nanomaterials with precision testing instruments, and therefore the fabrication of IDEs at

the nanoscale is crucial. The shift to nanoscale fabrication for the IDEs (or nano-IDEs) offers several distinct advantages. First, it results in a significant reduction in size, paving the way for more compact electronic devices with a higher device density. Moreover, nanoscale IDEs boast an increased surface area, a feature that potentially enhances their sensing capabilities.¹⁰⁶ This becomes especially significant in areas such as healthcare and environmental monitoring, where the detection of trace amounts of specific substances is vital.²⁰⁹ In summary, lithography serves as the vehicle that connects the broader realm of precision nanofabrication with the specific demand for nano-IDEs, which drive technological advances across multiple disciplines.

Reducing the gap spacing of IDEs can also markedly increase the density of the electrodes and the total length of all the electrodes, and thereby increasing the capture efficiency of the nanomaterials. Conversely, simultaneously decreasing both the gap spacing and the electrode length can reduce capture of undesirable materials (e.g., those that are not compatible with the dimension of the nanogaps). A nanogap device is an “empty” structure, characterized by spatial dimensions in the nanometer range, that is formed devoid of material by two or more electrodes or other material components that are closely spaced.^{129,210,211} Unlike conventional designs aimed at maximizing surface area and contact points, nanogap devices are specifically engineered to limit the number of conductive pathways and electron hopping events. As the dimension of the nanogap approaches the quantum scale, the manifestation of quantum phenomena such as tunneling becomes critical in the operation of nanoelectronic devices.^{122,212} Both nanogap devices and nano-IDEs are regarded as primary platforms to capture materials in complementary ways. As foundational elements in nanodevice fabrication, both necessitate intricate patterning using advanced lithographic methods. Various lithography techniques, such as optical lithography, electron beam lithography, and ion beam lithography, can be employed to transfer the intricate designs onto substrates.^{136,207} Each of these methods offers its own set of advantages and limitations, with ion beam lithography standing out due to its unique capabilities inherent to fast moving ions.

As IDE and nanogap devices are important templates in nanofabrication, the fabrication and study of those elements can not only advance the understanding of nanoscale phenomena, but also promote innovations in diverse fields ranging from electronics to biotechnology to quantum computing.^{115,119,212,213} In this chapter, we begin with a comparative study of the main lithography techniques: optical lithography, electron beam lithography, ion beam lithography with a helium gas field ionization source (He ion beam lithography) and with a liquid alloy metal ion source (SiAu ion

beam lithography), to evaluate their respective patterning capabilities. Leveraging insights obtained from this comparative analysis, we then employ state-of-the-art ion beam lithography to fabricate micro/nano-IDEs and nanogap devices and investigate their potential applications in cross-array memristors and single nanocluster devices.

5.2 Experimental Details

The IDE fabrication process is carried out on p-type Si (1 0 0) substrates, after cleaning by ultrasonication, each for 10 minutes, in acetone, isopropanol and filtered high-resistivity (18.2 M Ω ·cm) water. Both acetone and isopropanol are high-performance liquid chromatography (HPLC) grade. The cleaned Si substrates are then annealed at 900 °C for 90 minutes in atmosphere to build up a relatively thick oxide layer to isolate the IDEs (to be made) from the substrates. A photoresist solution is spin-coated onto the Si-SiO₂ substrates before the lithography exposure. The photoresist used for the maskless optical lithography is Shipley 1805, which is spin-coated on the Si substrate at 4500 rpm for 40 seconds to form a 500 nm thick film followed by baking at 120 °C for 60 seconds on a hot plate. For all other exposures used for e-beam lithography and ion beam lithography, PMMA A2 (MicroChem Corp.) is employed as the photoresist, which is spin-coated at 4000 rpm for 35 second on the Si substrate followed by baking at 180 °C for 90 seconds on a hot plate. The optical lithography exposure is performed on the SF-100 Xpress maskless optical lithography system from the Intelligent Micro Patterning, LLC equipped with a 4X objective lens and a 365 nm mercury light source. The electron beam exposure is performed in a Zeiss Merlin scanning electron microscopy (SEM) system, while the helium ion exposure is performed in a Zeiss Orion Plus helium ion microscope. Both microscopes employ integrated Nano-patterning and Visualization Engine (NPVE) provided by Fibics Inc. for pattern generation and transfer. Furthermore, a Raith IonLine ion beam lithography system is used for the exposure of the Si⁺⁺ or Au⁺⁺ ion beam using Raith's own proprietary IONLine pattern generator (NANOSUIT Software release 6 SP 9.0). After the exposure, the predefined patterns are developed for 30 seconds using the corresponding developers: MF-24A (MicroChem) for Shipley 1805 and MIBK/IPA (MicroChem) in a 1:3 ratio for PMMA. This is followed by a rinse with filtered high-resistivity water, metal or metal oxide layer deposition using a DC magnetron sputtering system (Leica EM ACE600), and the lift-off process in acetone.²¹⁴ For specialized fabrications, such as those for memristors and nanojunctions, the aforementioned exposure protocols are repeated with meticulous feature alignment. The surface morphology of the

fabricated device is also characterized by using the Zeiss Merlin SEM, and the electrical measurements are carried out on a Signatone Series 1160 probe station coupled with an Agilent B1500 semiconductor device parameter analyzer.

5.3 Results and Discussion

5.3.1 Nano-IDEs Patterning by Various Lithography Techniques

The SEM image of a reference pattern shown in Figure 1a illustrates the capabilities of the maskless optical lithography.¹³² Rather than relying on exposure through a mask, this system employs a digital pixel mirror to selectively reflect UV light onto the substrate, thereby greatly enhancing convenience and turnaround time in the pattern design and avoiding the potential difficulties in making the shadow mask. Utilizing a 4X lens and an exposure wavelength of 365 nm, this system can produce both straight and curved elements on the photoresist-covered substrate with a resolution of 3 μm as represented by each pixel. However, in the case of small curved elements, the pixel traces may become noticeable, resulting in less than perfectly smooth edges. Figures 1b and 1c display SEM images of Ag nanowires drop-casted onto platinum-based IDEs fabricated using maskless optical lithography with gap spacings of 5.1 μm and 2.2 μm , respectively. Each finger is designed to be 100 μm in length, and all the fabricated IDEs exhibit uniformly distributed fingers with consistent pitch spacing. It is important to note that all the patterns, including the electronic characterization interface (Figure 5.1 (a) to (c)), have been exposed to UV light for under 1.5 seconds. This short exposure time represents a significant advantage for the iterative device design optimization process and for large-scale production.

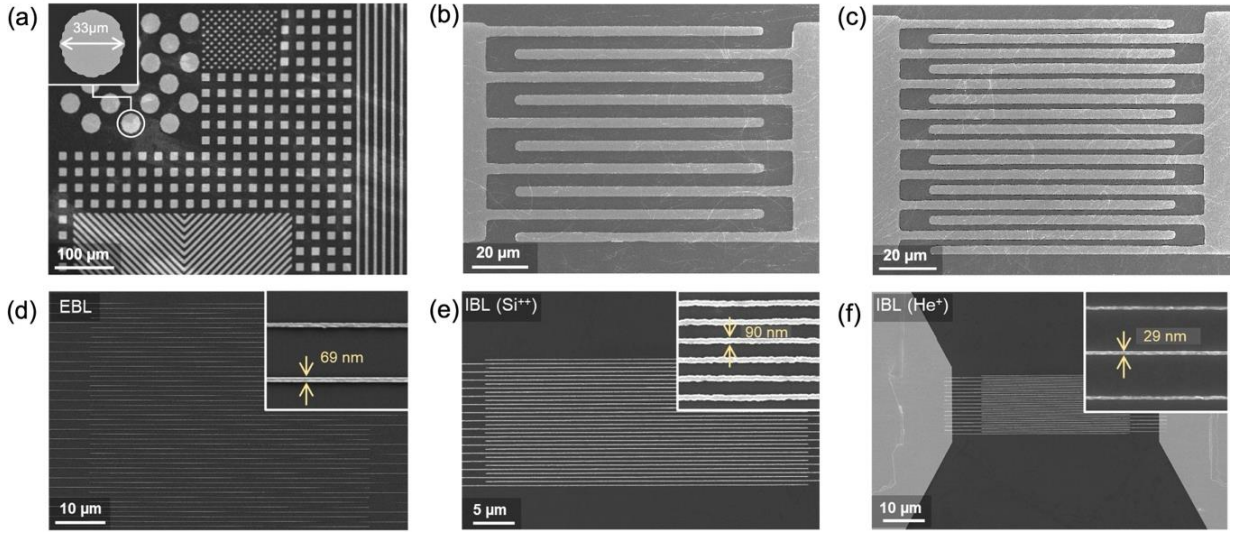


Figure 5.1 (a) SEM images of a reference pattern to illustrate the feature resolution of maskless optical lithography achieved with the SF100 Xpress system, and of IDE patterns obtained by maskless optical lithography with respective finger width and gap spacing of (b) 5.5 μm and 5.1 μm , (c) 3.3 μm and 2.2 μm . SEM images of nano-IDE fabricated by (d) electron beam lithography operated at 20 kV, and ion beam lithography with (e) a Si^{++} ion beam operated under 35 kV and (g) a He^+ ion beam operated at 35 kV. The insets show expanded views to illustrate the resolution of the feature size at a higher magnification. All the patterns are deposited with a 20 nm thick Pt metallization layer followed by the lift-off process.

Both high-energy electron beams and ion beams possess substantially smaller de Broglie wavelengths compared to the 365 nm photons used in optical lithography (used here). Consequently, when employing electron beam lithography (EBL) and ion beam lithography (IBL) patterning not restricted by the optical limit can be achieved and the resulting IDEs can be precisely generated with closely spaced lines with minimal gaps in between. This substantial increase in electrode density augments the effective total electrode length, greatly enhancing the target capture capability and response characteristic.^{215,216} Figure 5.1 also shows the IDEs patterned by particle-beam lithography with an electron beam (Figure 5.1d), Si^{++} beam (Figure 5.1e) and He^+ beam (Figure 5.1f). All three particle-beam lithography techniques demonstrate great resolutions achievable for patterning the IDE fingers on a 70 nm thick PMMA film, as long straight lines under sub-100 nm width with clean gaps

in between. The EBL exhibits slightly superior focusing capabilities compared to the Si^{++} based IBL, resulting in a marginally narrower line width. However, it should be noted that ions with heavier masses have much greater kinetic energy than electrons, making them more effective in breaking down PMMA into smaller fragments during the exposure process. Additionally, ion beams have the potential to generate a higher number of secondary electrons, thereby greatly enhancing the exposure process.²¹⁷ Consequently, IBL with a SiAu liquid metal alloy ion source (LMAIS) has a significant advantage in terms of patterning time, particularly for a relatively large write field. IBL with a He^+ gas field ionization ion source (GFIS) provides the best resolution with a remarkable 29 nm line width. Since IBL holds a natural advantage of proximity effect compared to EBL, it becomes feasible to fabricate these electrodes with a small gap spacing.²¹⁸ This increase in electrode density enables IDEs to excel in capturing and detecting nanoscale entities, making IBL with a GFIS or LMAIS an invaluable tool for advanced sensor technology.¹⁰⁶

With their substantial mass and momentum, ions not only can be used for patterning on a photoresist akin to EBL but also interact directly with the metal layer on the substrate (without the photoresist patterning step) by direct-write exposure. Consequently, direct-write ion beam-induced chemistry and ion milling provide additional techniques to construct nanoscale patterns. Furthermore, each ion type possesses distinct characteristics in its interactions with the metal layer or the substrate. In the case of high-energy He^+ ions, owing to their relatively low mass and small size, they tend to implant themselves into the substrate.¹³⁷ Zhang *et al.* successfully employed He^+ ions on silicon substrates to create diverse 3D features, including cones and pyramids. On the other hand, Ga^+ ions, due to their considerable mass, are widely used for milling and micromachining. Because of their relatively low melting point, Ga^+ has become the most popular, easily accessible liquid metal ion source for focussed ion beam microscopy. With the objective to achieve narrower gap spacings in the fabrication of IDEs, we can construct the entire electrode as a single die by using Si^{++} ions or Au^{++} ions to machine out the individual fingers on the metallization layer, as illustrated in Figure 5.2a. As Au^{++} , with a larger mass, exhibits the best milling yield (among the available ions in the IBL tool), it only requires 50 nC/cm to mill out the 20 nm thick Pt film (the metallization layer) into IDE fingers with 43 nm gap spacing. As the dose increases to 0.3 $\mu\text{C}/\text{cm}$ (Figure 5.2b), the milling process is so quick that the milling is easily extended to reach the substrate. Consequently, sputtered atoms are highly likely to redeposit onto the finger electrode surfaces, resulting in uneven surfaces and edges. As further increasing the dose to 0.5 $\mu\text{C}/\text{cm}$ is obtained by extending the dwell time at each spot, this

longer exposure leads to collisions between the high-energy incident ions and the sputtered atoms from the film, causing localized temperature surges. Consequently, the electrodes appear to have more “burnt” edges, as shown in Figure 5.2c. Meanwhile, Si^{++} ions with varying doses are also employed to study their direct-write capability in the IDE fabrication. Due to their lower mass, Si^{++} ions have a lower sputtering power than Au^{++} ions, necessitating a higher dose to achieve the desired gap spacing. In Figure 5.2d, it shows remnants of the incompletely milled out Pt film within the gap spacing, even with a dose as high as $0.3 \mu\text{C}/\text{cm}$. It takes a dose of $0.5 \mu\text{C}/\text{cm}$ to eventually generate a completely milled out 80 nm gap (Figure 5.2e).

By combining the advantages of fast patterning speed from optical lithography and of dual capabilities of fine feature writing on photoresist and direct write on metal film from ion beam lithography, we demonstrate the complete IDE fabrication workflow in Figure 5.2a, where the peripheral interconnection electrode pads (with the larger feature size) are patterned by maskless optical lithography. The extended electrode pads make the device easy to connect with other characterization instruments. Table 5.1 summarizes and compares different lithographic techniques used in this IDE fabrication study. The utilization of various lithographic techniques in IDE fabrication provides a versatile toolbox for controlling electrode dimensions and spacing. This flexibility in lithographic methods contributes to improved feature resolution and quality, device miniaturization, and enhanced performance across a wide spectrum of applications.^{136,205,207,219} Tailoring the choice of lithographic technique to specific requirements plays a pivotal role in addressing the evolving demands of nanoscale sensor technologies and nanoelectronic devices.

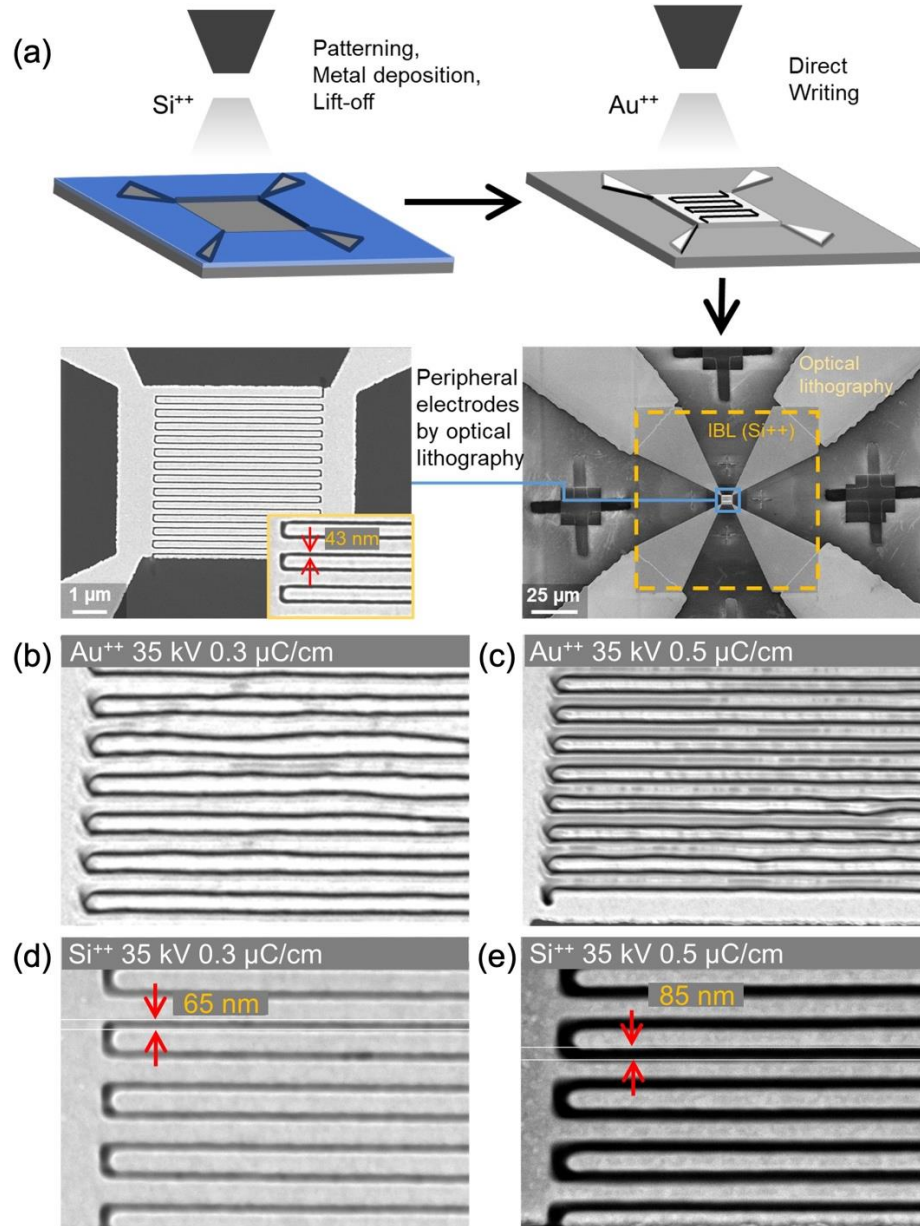


Figure 5.2 (a) A schematic representation of the nano-IDE fabrication workflow by utilizing the SiAu liquid metal alloy ion source in ion beam lithography, which starts with the fabrication of a one-piece central electrode and then followed by direct-write milling using the Au^{++} ions. The nano-IDE pattern is then connected with the peripheral electrode pads pre-patterned by maskless optical lithography. SEM images of the IDEs obtained at different ion and dose combinations: (b) Au^{++} 0.3 $\mu\text{C}/\text{cm}$, (c) Au^{++} 0.5 $\mu\text{C}/\text{cm}$, (d) Si^{++} 0.3 $\mu\text{C}/\text{cm}$ and (e) Si^{++} 0.5 $\mu\text{C}/\text{cm}$.

Table 5.1 Lateral comparison of the lithography techniques used in the IDE fabrication.

	Maskless Optical Lithography	EBL	IBL (He⁺)	IBL (Si⁺⁺, Au⁺⁺)
Source	UV Photon	Electrons	He ⁺	Si ⁺ , Si ⁺⁺ , Au ⁺ , Au ⁺⁺
Particle Energy	362 nm wavelength	20 kV	37 kV	35 kV
Source Type	UV light bulb	Field emission	Gas field ionization ion source	Liquid metal alloy ion source
Source Lifetime	~ 1200 hours	>12 months	6-12 months, with each trimer requires regeneration every 10 days	6-12 months
Patterning Environment	Ambient Environment	High Vacuum	High Vacuum	High Vacuum
Patterning Speed (for a write-field of 100 × 100 μm²)	Highest throughput, especially for very large areas (1.4 sec for 500 × 500 μm ²)	Very slow (16 min) [♦]	Very slow (~ 1h) [♦]	High throughput (~ 7 sec)
Resolution	Low (microscale)	High	Highest	High, especially for closely packed features
Limitation	Microscale features patterning	Proximity effect, large area patterning	High precision overlayer alignment	Unwanted ion sputtering
Interaction with the Substrate	Photon exposure	Electromagnetic interaction without significant physical damage	He implantation	More milling than implantation

♦ The EBL and IBL (He⁺) have similar exposure dosage on a 70-nm PMMA photoresist film. The actual patterning time depends on the beam current which is limited by different apertures for different feature resolutions. The numbers listed are using a small aperture, assuming patterning fine features in the 100 × 100 μm² area.

5.3.2 Cross-array Memristor Fabrication Using IBL

The memristor is the fourth basic circuit element, in addition to the resistor, capacitor and inductor, which is theoretically proposed by Leo Chua in 1971³⁶ and experimentally demonstrated by Williams' group in 2008.^{63,64} As a two-terminal circuit element, the memristor is one of the advanced devices that could benefit from the IDEs platform. Some study has already demonstrated the transformation of IDEs into memristors by filling the electrode with active material such as CQDs-

PEG1500_N (Carbon Quantum Dot with oligomeric poly (ethylene glycol) diamine),²⁸ Squaraine nanowires³⁸ and PCL-MWCNT/C60.^{213,220,221} Indeed, by taking the advantage of the two-terminal devices, the IDEs offer a powerful platform to fabricate the memristor into a cross-array device by stacking the active material vertically into the IDEs.²²² Their unique interlocking finger structure maximizes the available device positions in a 3D approach. In this work, we further utilize the nano-IDEs fabrication protocol in building the cross-array memristors at the nanoscale. These nano-cross-array devices not only significantly improve the component density as an integrated electronic storage device, but also provide a unique opportunity to mimic and understand complex neural network behaviors, allowing researchers to explore fundamental principles of brain function.^{223,224} Their potential for emulating synaptic plasticity, learning, and memory processes is particularly relevant to neuroscience, where unravelling the intricacies of the functioning of the human brain remains a paramount challenge.

Expanding upon the rapid patterning capabilities across a large write area, we leverage the precise alignment of overlayers using the Raith ionLine IBL system equipped with a laser interferometer stage in the fabrication of high-density cross-array memristors with IDEs, as demonstrated in Figure 5.3a. Figures 5.3b and 5.3d show the 1×4 linear-array memristor devices with dimensions of $500 \text{ nm} \times 500 \text{ nm}$ and $200 \text{ nm} \times 200 \text{ nm}$, respectively. A 30 nm TaO_x film is used as the active switching matrix between top and bottom electrodes of a memristor device based on our previous study.²²⁵ The corresponding I-V curves for each device size are presented in Figures 5.3c and 5.3e, respectively. The pinched hysteresis loops clearly indicate memristive phenomena, representing discernible high and low resistance states.²²⁶ Both devices exhibit stable switching behavior well over 300 and 50 cycles respectively. Interestingly, the device with the smaller dimensions of $200 \text{ nm} \times 200 \text{ nm}$ demonstrates both lower switching voltage and current, indicating reduced operating power consumption and enhanced efficiency.

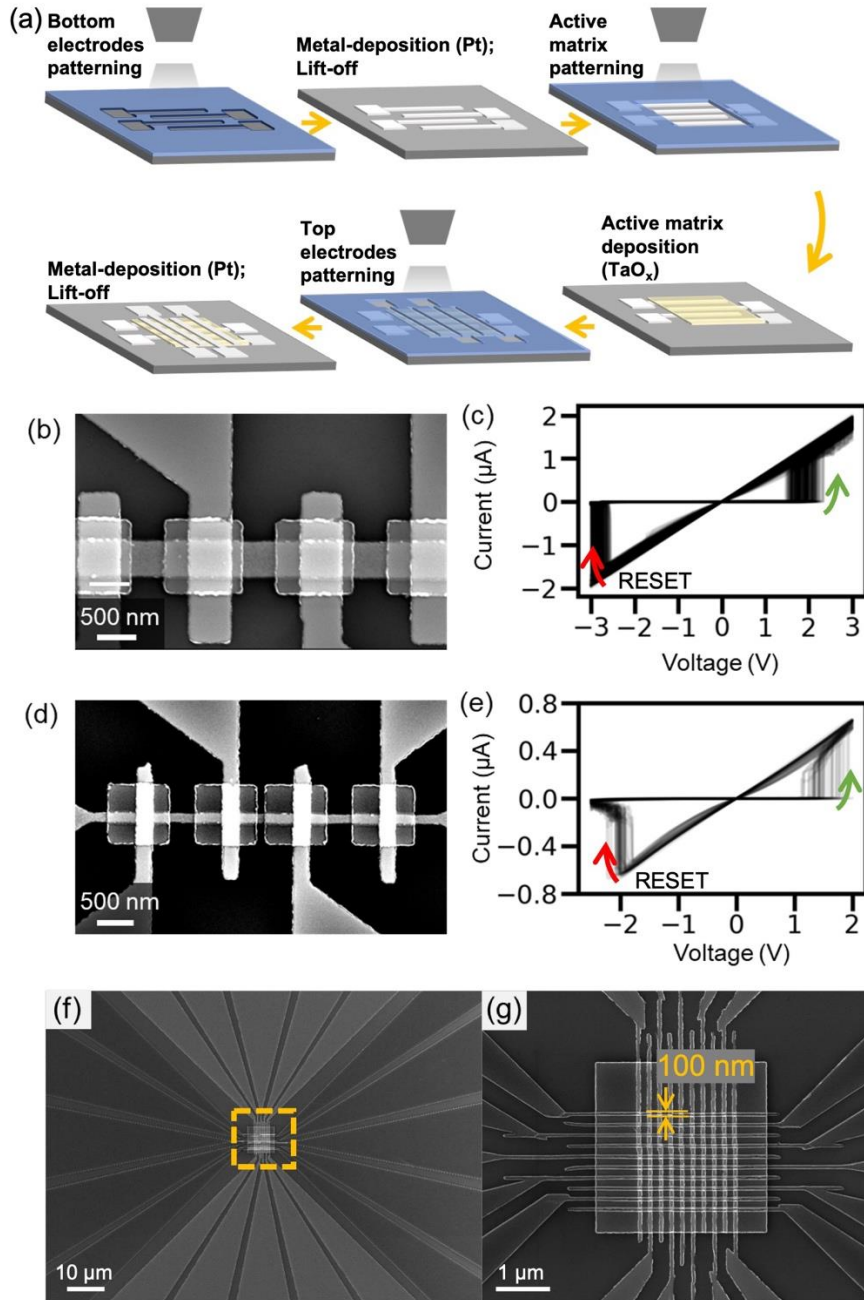


Figure 5.3 (a) A schematic representation of cross-array memristor device fabrication workflow. This three-layer device architecture is fabricated by layer-by-layer patterning, metal/metal oxide deposition followed by lift-off process with high-precision alignment. SEM images of 1×4 cross array memristors with active device areas of (b) $500 \text{ nm} \times 500 \text{ nm}$ and (d) $200 \text{ nm} \times 200 \text{ nm}$ and the corresponding I-V curves (c) for the device in (b) with 300 switching cycles and (e) for the device in

(d) with 50 switching cycles. SEM images of (f) an overview of a 10×10 cross-array memristor device and (g) expanded view depicting the individual $100 \text{ nm} \times 100 \text{ nm}$ active switching areas. The device contains a 30 nm thick TaO_x active switching matrix and it is patterned by Si^{++} ion beam lithography.

As the smaller device has demonstrated lower switching power and improved space efficiency, it becomes imperative to further pursue devices of reduced size. However, the increasing complexity of this endeavor has become apparent, presenting formidable challenges that must be addressed when delving into the intricacies of crafting these advanced devices. Scaling down the device size introduces a direct challenge in the manipulation of nanomaterials, particularly concerning the densely packed top and bottom IDEs. With an increased number of contact points on a single arm of the electrode, there is a compelling need for uniformity and continuity in both the top and bottom electrodes. Moreover, the precise control of active film thickness and gap spacing between electrodes assumes critical importance in mitigating cross-talk, which could cause inconsistent switching behavior and unwanted false device activation.²²⁷ Building upon these fundamental considerations, we have embarked on the endeavor to extend our device to a 10×10 cross-array configuration within a $2 \mu\text{m} \times 2 \mu\text{m}$ area by using Si^{++} ion beam lithography as shown in Figures 5.3f and 5.3g. This design incorporates cross-finger IDEs as both the top and bottom electrodes to increase the electrode density. The 30 nm thick TaO_x thin film serves as the active matrix material due to its consistent switching behavior in the previous 1×4 device. This incorporation of IDEs fabrication into memristor research not only facilitates the creation of precise and scalable memristor-based devices but also plays a pivotal role in unravelling the intricate mechanisms governing memristive phenomena. By employing IDEs in memristor studies, we unlock pathways to innovative technologies and gain new insights into the development of cross-array memristor devices for next-generation computing and memory storage applications.^{114,223,224,228}

5.3.3 Nanogap Device Fabrication by IBL

Since the IBL with the liquid metal alloy ion source technology holds distinct advantages in patterning flexibility and reduced proximity effect when compared to EBL, it stands out to become the primary technique for our single-cluster nanojunction device fabrication. Beyond the traditional photoresist patterning strategy for making nanogap (open nanojunction) devices, we harness the

direct-write milling power of the ion beam to create a nanogap device by simply carving out a patterned nanowire. Our previous study has shown that although Au^{++} has more sputtering yield than Si^{++} , the Si^{++} beam has a narrower interaction volume. Therefore, the Si^{++} beam is selected to “break” the circuit by cutting across a pre-deposited metalized nanowire, as depicted in Figure 5.4a. The interaction between the high-energy incident beam and the nanowire results in terminals with sharp tip features. In contrast to a directly patterned nanojunction with round terminals on both sides, the tip terminals exhibit a cleaner and more orderly appearance. Compared to nanojunctions produced through nanoimprint lithography, this direct-write nanomachining methodology offers a notable advantage in achieving pristine and precisely defined gaps with a contactless sputtering process (without risk of contamination due to contact with a shadow mask). This gap spacing in the sculpted open nanojunctions can be fine-tuned by controlling the milling dose. Figure 5.4b shows the correlation between the gap spacing of the nanojunction and the milling dose. Evidently, control of the gap spacing is more sensitive to the dose at lower doses (< 400 nC/cm), with a steeper slope. From 400 nC/cm to 1000 nC/cm, the gap spacing exhibits a nearly linear dependence on the sputtering dose. Since the interaction volume is fixed between the incident beam and the substrate, the gap spacing is expected to eventually reach a maximum value. Using this nanomachining technique, it is possible to create a gap spacing as small as 13 nm.

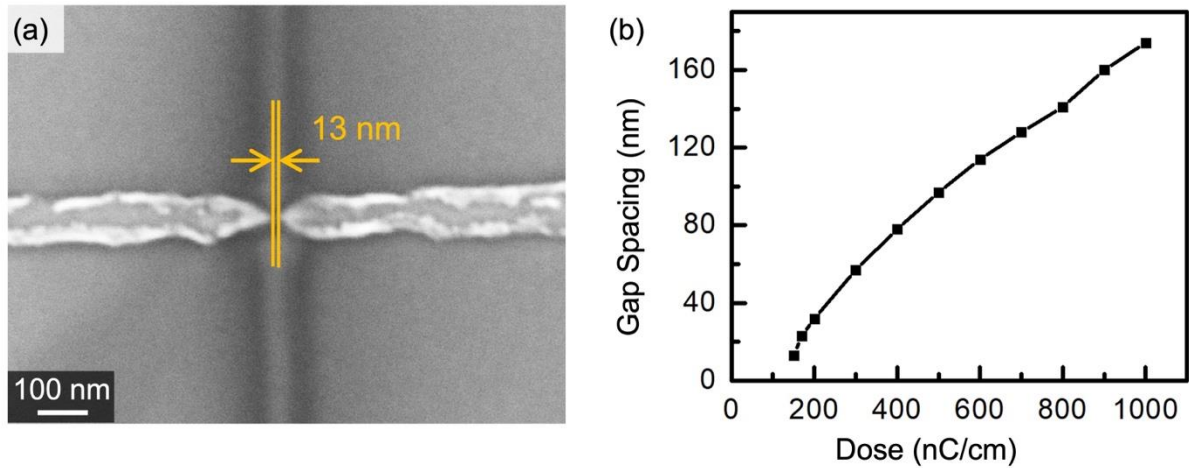


Figure 5.4 (a) SEM image of a cleanly sculpted nanogap with a 13 nm spacing in a nanowire by Si^{++} nanomachining with the IBL tool. (b) The relationship between the gap spacing within the open nanojunction and the Si^{++} ion dose.

The fabrication of nanogap devices assumes a pivotal role, notably in the field of nanomaterial trapping, where meticulous control and precision at the nanoscale are imperative. These devices have become one of the basic components in various scientific and technological applications. Given its ultrasmall dimensions, our nanogap devices promise new applications in nano- and quantum electronics. As the synthesized nanoclusters are found to exhibit unique structural characteristics and chemical states, the nanogap devices can be used to construct novel single-cluster nanojunction devices by capturing these nanoclusters into the gaps of the devices. Figures 5.5a and 5.5b demonstrate the creation of a single-nanocluster nanojunction device achieved by depositing $\text{Zr}_{0.4}\text{Hf}_{0.6}\text{O}_2$ nanoclusters onto the nanogap device. A direct-write nanojunction nanowire is employed to enhance the likelihood of trapping the nanoclusters, the target size of which is well defined by the gap spacing, shown in Figures 5.5c and 5.5d.

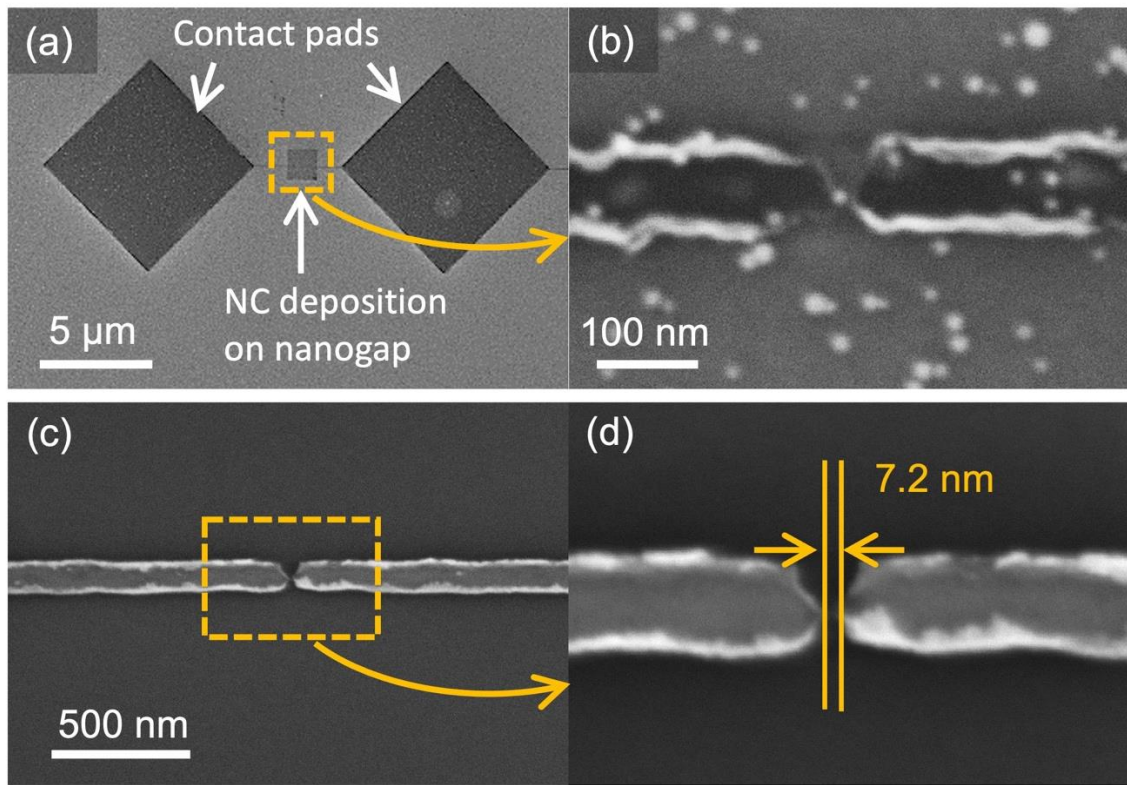


Figure 5.5 SEM images of (a) a single-cluster nanojunction device fabricated by depositing nanoclusters into an open nanojunction, (b) the center of the device at a higher magnification, (c) an empty nanojunction device obtained by direct-write nanomachining before nanocluster trapping and (d) at a higher magnification, depicting a record gap spacing of 7.2 nm.

The fabrication of a single-cluster nanojunction device, achieved by depositing sub-10 nm nanoclusters into an open nanojunction (a nanogap device), therefore represents a significant milestone in the field of nanoelectronics and materials science. This intricate and precise engineering endeavor carries profound implications for our understanding of nanoscale phenomena and the development of advanced technologies. By successfully creating and studying these single-cluster devices, we bridge the gap between fundamental materials research and practical applications. These single-cluster devices hold the potential to revolutionize data storage, computing, and sensing technologies, offering improved performance and efficiency. Furthermore, they provide a powerful platform to explore the fascinating quantum world. As we continue to refine our skills in building these single-cluster devices, we pave the way for groundbreaking innovations that will shape the future of electronics and materials science.

5.4 Conclusion and Outlook

In this study, we conduct a detailed study of the advantages and limitations associated with optical lithography, electron beam lithography, and ion beam lithography utilizing He^+ , Si^{++} , and Au^{++} ions, with focus particularly on IDEs fabrication. Through the synergistic integration of the capabilities of these techniques, IDEs can be fabricated with optimal efficiency tailored to the specific size requirement. Furthermore, we harness the unique direct-write nanomachining capabilities of ion beam lithography to enhance IDEs fabrication by achieving smaller gap spacings, a strategy that can be extrapolated to the fabrication of nanojunction devices. Indeed, we have successfully incorporated these IDEs and nanogap devices in the creation of cross-array memristor devices and single-cluster devices (involving size-selected $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoclusters). These latter devices promise, for the first time, detailed characterization of the electrical properties of these nanoclusters and in future other physical and chemical properties as well. These devices provide the tools to uncover novel nanoscale phenomena, including the behavior of oxygen defects in nanocrystalline structures and electron hopping in the quantum regime.

Chapter 6

Concluding Remarks and Outlook

6.1 Summary of Contributions

The objective of the present work is to understand the behavior of defects in transparent conductive oxide nanoclusters of group IV-B transition metal elements, specifically ZrO_2 and HfO_2 . We have developed the necessary protocols for the synthesis and characterization of these size-selected transition metal oxide nanoclusters, and examined the effects of defects within these NCs. In the first part of our research, we synthesize monosized ZrO_2 nanoclusters over large deposition areas by using gas-phase condensation with *in-situ* size selection by using a quadrupole mass filter. Interestingly, the as-deposited ZrO_2 nanoclusters are found to exhibit a novel tetragonal structure at room temperature, a phase typically stable only at extremely high temperature. Furthermore, these size-specific nanoclusters reveal sub-oxide photoemission features that correlate with the cluster size, which can be attributed to their unique oxygen vacancy defect states. More importantly, we observe an unexpected size-dependent ferromagnetism at room temperature. When compared with conventional dilute magnetic semiconductors, these dopant-free ferromagnetic ZrO_2 nanoclusters promise new opportunities for manipulating magnetization based on size, eliminating notable concerns about dopant solubility and homogeneity.

To understand the mechanism behind this size-dependent ferromagnetism, we propose a defect-band hybridization-induced magnetic polaron model. In this framework, an oxygen vacancy defect formed at a lower coordination site (such as corners and edges) of the nanoclusters prompts one of the adjacent four Zr^{4+} ions to reduce to a Zr^{3+} ion. This results in a resonant structure comprising a singly charged oxygen vacancy and a Zr^{3+} ion. The excess 4d electrons in the lattice begin to form a magnetic polaron due to the exchange interaction. Given that the Zr^{3+} ions act as charge reservoirs arising from this defect creation, an impurity band emerges between the conduction and valence bands. The hybridization of the impurity band with the conduction band results in band-splitting, producing spin-up and spin-down states, thereby favoring ferromagnetic ordering.

Expanding on this, we synthesize size-specific hybrid $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoclusters, for the first time, by co-sputtering Zr and Hf within the aggregation chamber. In this setting, the sputtering power for each target is independently controlled and appropriately adjusted. Through the optimization of gas

flow and aggregation length, the nanocluster beam can be refined for precise size selection. The dimensions of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoclusters can be meticulously controlled from 4 to 14 nm, while modulating the Zr and Hf relative compositions. The crystalline structure of the resulting $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ solid solution nanoclusters is found to be size-dependent and contingent on the deposition conditions. Specifically, nanoclusters smaller than 6 nm exhibit an amorphous character. In contrast, those sized between 6 and 10 nm present a single crystalline structure, and those with a pronounced Hf concentration manifest a core-shell configuration. Additionally, nanoclusters exceeding 10 nm in size with a dominant Zr concentration adopt a polycrystalline structure. Using reflection electron energy loss spectroscopy, we measure the bandgaps of these size-specific nanoclusters. The measured bandgaps are found to follow an unexpected trend that increases with increasing nanocluster size. Our XPS analysis highlights distinct chemical shifts found predominantly in the Zr 3d region that are likely caused by oxygen vacancy defects and the alloying effect.

We introduce an Hf-induced polaron model to interpret the structures and chemical states of these size-specific hybrid nanoclusters. In this model, Hf ions are treated as dopants integrated into the orthorhombic lattice structure of ZrO_2 . Owing to coulomb interactions, the Hf ions, despite having a similar radius but possessing more protons than Zr ions, draw adjacent electrons from the neighboring O and Zr ions. This electron relocation from the O ions further leads to a secondary electron shift in the nearby Zr ions. Our $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ solid nano solution is the first reported hybrid dual transition metal oxide nanoclusters with tunable compositions. We expect that the synthesis and characterization methodology presented in this study will pave the way for further investigations into other hybrid transparent conductor oxide nanoclusters. Indeed, the HZO nanoclusters that we have synthesized possess a unique orthorhombic configuration and a substantial defect density, positioning them as potential candidates for nanodevices and dopant-free ferromagnetic semiconductor applications.

The final stage of the present study pivots to laying the groundwork to understand electron behaviors caused by the interesting defects in an individual size-specific nanocluster, with a particular focus on their electrical properties. This has led us to work out the mechanics and workflow needed for nano-electrode fabrication, where we employ several lithographic techniques, including maskless optical lithography, electron beam lithography, helium ion beam lithography and silicon/gold ion beam lithography. For patterning of nano-interdigital electrodes (IDEs), helium ion beam lithography emerges as the frontrunner in achieving the smallest minimal feature size, while silicon ion beam lithography excels in patterning speed. The SiAu ion beam lithography has also provided a new

direct-write nanomachining capability for device fabrication. A nano-IDEs with a 43-nm gap spacing has been successfully fabricated by such a method using an Au^{++} ion beam on a Pt thin film. We validate the superior performance of the ion beam lithography tool for nanogap device fabrication. These ion beam-sculpted nanogaps present sharp termination, which offers great advantage for studies involving tunneling or electron hopping phenomena. Furthermore, the gap spacing can be carefully adjusted by using the ion beam exposure. As a final proof-of-principle demonstration of our present approach, we have also successfully deposited a single $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanocluster into the nanogap and turned it into a single-cluster device. These nano-electrodes and nanogap devices not only offer a powerful platform for characterizing the electric properties of individual nanoclusters, but also promise novel applications based on single-cluster quantum science.

6.2 Future Work

The present work offers foundational insights into the characteristics and potential applications of ZrO_2 nanoclusters and $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoclusters, underscoring the multifaceted nature of the present work and the plethora of avenues it opens for future exploration. We offer three general examples below.

In Chapter 4, we study the impact of the Hf content on the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanocluster structure. Specifically, introducing more Hf content causes the hybrid nanoclusters to possess a less crystalline structure especially on the shell region when compared to the ZrO_2 nanoclusters, which could lead to complete diminution of ferromagnetism in the as-deposited nanoclusters. To further investigate the contribution of oxygen vacancy defects in the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ lattice structure, our experiments involving post-annealing with 3% H_2 in pure Ar at 400 °C for 3 hours show the hidden magnetization potential of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoclusters. Remarkably, all the nanoclusters synthesized under 10 nm aggregation length exhibit superior ferromagnetism at both room temperature and 5 K, and this behavior reveals a distinct dependency on their composition. Furthermore, XPS spectra display narrower peaks for the Zr 3d components, and the corresponding REELS measurements suggest a larger bandgap for the NCs after post-annealing. However, other hybrid nanoclusters, despite their defect content, do not display any ferromagnetic properties upon H_2/Ar post-annealing. These contradicting results demand a deeper investigation to understand the causes, particularly the exchange interaction, underlying the defects for the dopant-free dilute ferromagnetic semiconductor nanoclusters, and these preliminary findings require further morphological characterization and modeling studies.

Chapter 5 demonstrates the fabrication of various nano-devices with innovative designs that represent the frontier of this research area. The nanogaps could be used to demonstrate Fowler-Nordheim tunneling under extreme external electric fields. Potential Coulomb blockage has also been observed in the single-cluster device and this remains a hot topic that is of great significance. To eliminate the effects of ambient electromagnetic fields and acoustic noise, one strategy to enhance our analysis is to take advantage of our state-of-the-art Physical Property Measurement System (PPMS) from Quantum Design. By deploying nanoclusters with specific sizes and compositions into the nanogap devices, we could investigate in detail not only the nanocluster size dependence but also the defect composition effect on several fundamental properties, including resistivity, heat capacity, and thermal conductivity. Understanding these changes could elucidate the intricacies of charge and spin behaviors introduced by the oxygen vacancy defects, which promise to revolutionize future quantum electronics.

Another intriguing study involves incorporating the defect-rich, size-selected nanoclusters (Chapters 3 and 4) into nano-IDEs (Chapter 5) to construct a mixed array of nanocluster-based devices. By taking advantage of the distinct length of the parallel electrodes from the IDEs design, these arrays of nano-devices have potential for cutting-edge applications including nano-supercapacitors, nano-sensors, and even nano-memristors. These novel nanoclusters trapped between the nanoelectrodes could be ultimately modified by injecting appropriate ions by using the ion beam lithography tool to create point-defects that can be used as new quantum materials platform for quantum technologies. The small fraction of doped ions could further introduce defects with unexpected phenomena.

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Chapter:
Chapter 3 Production of Nanoparticles on Supports Using Gas-Phase Deposition and MBE
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Author: Xiaoyi Guan, Saurabh Srivastava, Joseph Palathinkal Thomas, et al

Publication: Applied Materials

Publisher: American Chemical Society

Date: Oct 1, 2020

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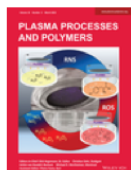
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Impact of argon flow and pressure on the trapping behavior of nanoparticles inside a gas aggregation source

Author: Alexander Vahl, Franz Faupel, Hynek Biederman, et al

Publication: Plasma Processes and Polymers

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Author: Artem Shelemin, Pavel Pleskunov, Jaroslav Kousal, et al

Publication: Particle & Particle Systems Characterization

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Size-Selected TiO₂ Nanocluster Catalysts for Efficient Photoelectrochemical Water Splitting

Author: Saurabh Srivastava, Joseph Palathinkal Thomas, Md. Anisur Rahman, et al

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SPRINGER NATURE

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Publication: Topics in Catalysis

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Evidence of Charge-Transfer Ferromagnetism in Transparent Diluted Magnetic Oxide Nanocrystals: Switching the Mechanism of Magnetic Interactions

Author: Shokouh S. Farvid, Tahereh Sabergharesou, Lisa N. Hutfluss, et al

Publication: Journal of the American Chemical Society

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Date: May 1, 2014

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An interdigital electrode type sensor based on P(VDF-TrFE) nanofibers

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Appendix A

This appendix summarizes the metal nanoclusters studies reported to date (1992-2023), with their literature references given in the bibliography. Only nanoclusters generated by using magnetron-sputtering based gas-phase condensation technique are included here. The records are arranged alphabetically according to the metal element symbol.

Ref.	Metal Composition	Size (nm)	Structure	Substrate	Comments	Year
[1]	Ag	1-10		Graphite	Size-selection; He carrier gas; immobilization of protein molecules	2003
[2]	Ag	5-15		TEM grid	Investigating the influence of the experimental parameters on the NC size distribution	2012
[3]	Ag	3-15 atoms		TiO ₂	Atomically precise synthesis and mass filtering (Liquid-Nitrogen cooled condensation chamber)	2014
[4]	Ag	4-8		SiO ₂	Biological response	2018
[5]	Ag	12-20		glass	Kinetic Monte Carlo (KMC) simulations of the growth of NCs	2018
[6]	Ag	6-12	crystalline	ZnO:Ag	Volatile organic compounds (VOC) sensor	2019
[7]	Ag	24.7	crystalline	Si-glass	Plasmonic efficiency enhancement in a-Si solar cell	2019
[8]	Ag	5-30		Si	Charging state investigation using electrostatic quadrupole mass selection (EQMS)	2019
[9]	Ag	50-100		Si	Time-resolve small angle X-ray scattering (SAXS)	2020
[10]	Ag	5	single crystalline	glass/FTO/TiO ₂ -MgO	Ag embedded MgO, Perovskite solar cell	2021
[11]	Ag	15-35		Si	In-situ UV-vis analysis	2022
[12]	Ag			Au/Pt electrode	Memristor application	2022

[13]	Ag, AgCu	2-1000 atoms		TEM grid	Hollow cylindrical magnetron sputtering to enhance NC yield	2014
[14]	Ag/Au	4-9	single element Au NCs, AuAg alloy NCs, Ag core-Au shell NCs	Si, TEM grid	Adjustable multi-sputtering source; Full-face erosion (FFE) magnetron sputtering	2018
[15]	Ag/Au, Ag/Pt	11, 9 respectively		SiO ₂ matrix	Memristor Application	2019
[16]	Ag/plasma polymer	75-175		Si	Localized surface plasma resonance (LSPR)	2020
[17]	Ag/Pt	Ag ₉ Pt ₂ , Ag ₉ Pt ₁₃		α -Al ₂ O ₃	CO oxidation catalysis	2017
[18]	AgAu	2-30		quartz	Composition control by operando optical emission spectroscopy	2020
[19]	AgAu, AgPt	3-18	crystalline	ZnO:Ag	H ₂ and VOC sensor	2020
[20]	Ag-Cu	3-9	Janus or Ag@Cu core/shell	undoped Si, Si ₃ N ₄ TEM grid	Bi-metallic coalescence nanoparticle synthesis and characterization with molecule dynamics and Monte Carlo simulation	2016
[21]	Au	923	crystalline with different geometries	TEM grid	Atomic structural control	2014
[22]	Au	561 - 742 atoms	crystalline with different geometries	TEM grid	Molecule dynamics (MD) simulation study	2015
[23]	Au	2.5	crystalline	ZnO NW	Biosensor for DNA and streptavidin, using a DNA aptamer	2019
[24]	Au	2-8	core-satellite crystalline	TEM grid	Introduce H ₂ O to produce core-satellite NCs, modeling the kinetic formation of these complex structures	2020
[25]	Au	2.5		Graphene device	DNA and streptavidin using a liquid gate measurement	2020
[26]	Au	10-1000 atoms		QCM	Gas-dynamics; Computational fluid dynamics (CFD) simulation	2021
[27]	Au/Au/Pd	4-8	multi-crystalline	Si	Bimetallic (AgAu) and trimetallic (AuAuPd) adjustable size and stoichiometry	2012

[28]	Au/Cu	2-8	multi-crystalline	MgO powder	4-Nitrophenol reduction	2018
[29]	Au@Co	7.5-8	Co core with Au shell	TEM grid	Icosahedron Co core by face center cubic Au facets	2015
[30]	AuFe	4.7-7.9	Nonequilibrium chemically ordered L1 ₂ and L1 ₀ phase	Si, TEM grid	Structure dependent magnetic ordering	2014
[31]	AuPd	5 nm	core-shell	TEM grid	In-flight annealing	2010
[32]	AuPtPd	2.3-5.9	crystalline	Silicon nitride (Si ₃ N ₄), TEM grid	MD simulation of NC growth and investigate the parameter governing the nucleation and growth	2019
[33]	CoHf, CoZr	~7.7	crystalline	Si, TEM grid	Rare-earth-free permanent magnets	2014
[34]	Co/Au	2-8		Si	Magnetic	2019
[35]	Co/Au/Ag	3-9		TEM grid	Single-element Co, Au, Ag NCs, bi-metallic AuCo, AgCo and AgAu NCs, ternary AgAuCo NC with different core shell structure	2014
[36]	Cr	5		PET	Strain-sensor (100 G.F.)	2014
[37]	Cu	5-10		Si	Size-controlled formation of Cu nanoclusters in pulsed magnetron sputtering system	2011
[38]	Cu	10-40		Ti-Si	High yield hollow cathode	2013
[39]	Cu	4-10	polycrystalline	glass, Si	controlled Cu, CuO through Cu ₂ O and their mixture	2018
[40]	Cu	10-40		Si	<i>In-situ</i> SAXS	2018
[41]	Cu	5	crystalline	CVD graphene	Glucose biosensor	2018
[42]	Cu	Cu ₄		Al-Si	CO ₂ conversion into C1 fuels	2019
[43]	Cu	10-150	polycrystalline, spherical, cubic	Si	The effect magnetic field of the sputtering source on the NC formation	2019
[44]	Cu			SLG on FTO	Glucose biosensor	2020
[45]	Cu	3-12 atoms		ZrO _x	CO ₂ hydrogenation	2021
[46]	Cu	10-27		Si	Post cylindrical Cu magnetron and rotating magnetic circuit to increase the NC yield	2021

[47]	Cu	15-33		QCM	A mechanical time-of-flight filter intended for measurement of velocities of nanoparticles exiting a gas aggregation source	2021
[48]	Cu	1-7 atoms		TiO ₂ , SnO ₂ , Al ₂ O ₃ , SiO ₂	Selective oxidative dehydrogenation of cyclohexane	2022
[49]	Cu	10-40		QCM	High resolution nanoparticle velocity measurement outside of gas aggregation source.	2022
[50]	Cu	5-25		Si, Al ₂ O ₃	Solar radiation absorbance	2022
[51]	Cu	3-7		Silica	Modeling of NC nucleation and growth based on classical nucleation theory	2010
[52]	Cu, Ag	2-7, 5-9	crystalline	FET based on graphite-oxide	Non-enzymatic glucose sensor application	2017
[53]	Fe	20	body center cubic	polyethylene glycol (PEG) precoated glass slides, TEM grid	DNA immobilization	2013
[54]	Fe	10-20	different crystalline with different shape	SiN	MD and KMC simulation	2016
[55]	Fe, Fe-Au	7.1-27.5,	crystalline	PVP on glass, TEM grid	NO ₂ detection; magnetron-plasmonic properties	2017
[56]	Fe/Ag-Si	core<10, overall 15 - 45	multi FeAg core by Si shell	PVP on glass	Single-step co-sputter gas-phase condensation	2014
[57]	Fe/Al/O	10.8	Fe core Al-O shell	Si, TEM grid	Single-step synthesis of soft magnetic alloy NCs	2014
[58]	Fe/Co	4-12	Good crystallinity with various phase	TEM grid	High-yield hollow cathode dc sputtering-based GPC system	2020
[59]	Fe/Fe oxide	20	core-shell	TEM grid	The reaction of metallic Fe NC between atmosphere	2014
[60]	Fe/Fe ₃ O ₄	5-20	core-shell	TEM grid	Morphology and oxide shell structure study	2007

[61]	FeAu	5-15	various crystalline core-shell	TEM grid	MD+MMC simulations, selective wetting of specific sites on Fe NCs by Au	2019
[62]	FeCo	10-18	body center cubic	Polyethylene glycol (PEG) pre-coated glass slide	Protein immobilization	2014
[63]	FeCo-Au/Ag	10-20	FeCo core with Ag or Au shell	Au coated glass	High magnetic moment	2005
[64]	FePd	9	single crystalline	SnO ₂ NW,	CO sensing	2017
[65]	FePt	2-10	L1 ₀ order	Si	Tunable ferromagnetic hysteresis loop	2005
[66]	FePt	5.6 - 6.7	L1 ₀ , or FCC	TEM grid	Quantitative structure analysis of L1 ₀ -ordered FePt NCs	2007
[67]	FePt	~ 6.5	single crystal L1 ₀	Si, Au grid	Magnetic	2012
[68]	Ge	7.1-14.7	single crystalline	TEM grid, Au-Si	Size-dependent optical properties	2020
[69]	GeSb	8	amorphous to crystalline	Au electrodes	Phase-change memory application	2012
[70]	GeSbTe	8-17	Ge ₂ Sb ₂ Te ₅	TEM grid	Size-dependent crystallization temperature	2016
[71]	HfO ₂	7-12		Si	Paramagnetic	2013
[72]	HfO ₂			YCBO	Integrated pulsed laser deposited YBCO multilayer to form biaxially BaHfO ₃ , enhancing the pinning force density	2017
[73]	IrTaO	1.1-6.4		polycrystalline Au support	High oxygen evolution reaction (OER) performance with long term stability	2022
[74]	MgTi, MgNi, MgCu		Multi-core-shell	TEM grid	High thermal stability during production and hydrogenation	2014
[75]	MgTi, MgC, MgPd	12-35	TiC core-Mg shell, tetragonal MgPd	TEM grid	Introduce H ₂ /CH ₄ as a reactive/nucleating gas; Introduce self-nucleating Pd to provide nucleation of MgPd NCs	2017
[76]	Mn ₅ Si ₃	~8.6	hexagonal	Si, TEM grid	Novel ferromagnetism	2016
[77]	MnO	4-8		Si	OER	2018
[78]	Mo	2.9		polished Cu substrate	Combining a magnetron sputter discharge with a gas aggregation source	1992

[79]	MoCu	5-60	various core-shell	silicon-nitride membranes	Tuning structural motifs and alloying of bulk immiscible Mo–Cu NCs	2013
[80]	MoS ₂	2-10	crystalline	TEM grid	Lateral time-of-flight (TOF) mass filter for size-selection	2017
[81]	Ni@Cu	18-24	polycrystalline core	TEM grid, Si	Analytical model describing the deposition of Cu shell on top of existing Ni core	2014
[82]	Ni@Ti	4-30	core-shell	Si, TEM grid	In-flight shell deposition onto the Ni shell	2017
[83]	Ni-Co-Cr	3-6		glass	Multicore-shell, magnetic	2021
[84]	Ni-Cr	4-7	core-satellite	Si	Magnetic NCs	2017
[85]	NiFeO _x H _y	3.9-8.4	polycrystalline with defects	TEM grid, Au sheet	High performance OER	2018
[86]	Pd	55- 400 atoms	crystalline	Graphite tape, TEM grid	1-pentyne hydrogenation reaction	2012
[87]	Pd				Size-dependent morphology	2015
[88]	Pd	10	crystalline	Si with Au electrodes	H ₂ sensor	2017
[89]	Pd	5	crystalline	MgO	H ₂ storage	2018
[90]	Pd	7.9-8.2		PET	Strain-sensor (1000 G.F.)	2018
[91]	Pd	7.5		PET + Ag IDE	Flexible H ₂ gas sensor	2018
[92]	Pd	3, 5	single crystalline	Mg/MgO	OER	2019
[93]	Pd	5	bulk Pd FCC	PET	H ₂ detector	2019
[94]	Pd	16		PET	Pressure-sensor/Barometer (0.13 Pa ⁻¹)	2019
[95]	Pd/Ti	~5		Alumina powder	(1-pentyne) selective hydrogenation	2016
[96]	Pt	4.5		Si	Strain-sensor (75 G.F.)	2012
[97]	Pt	2-12		Si with Au electrodes	Gas sensors	2012
[98]	Pt	4-6		Si with Au electrodes	DNA biosensor	2016
[99]	Pt	5		Si with Au electrodes	Lead (Pb ²⁺) detection	2017
[100]	Pt	1		STO	electrochemical HER	2018

[101]	Pt	2-4		Si	Strain-sensor (45 G.F.)	2018
[102]	Pt	4-6		Si with Au electrodes	Acetamiprid and atrazine detection	2018
[103]	Pt	3		Si with Au electrodes	Pesticide detection	2018
[104]	Pt	1-5	single crystalline	SnO ₂ , Si, TEM grid	CO sensing	2020
[105]	Pt	4.5		Au/Ti IDEs on Polyimide substrate	Strain-sensor	2020
[106]	Pt	5		Si with Au electrodes	Chloract and Relative Humidity (R.H.) sensing	2020
[107]	Pt			TEM grid	Tuning, size-shape control	2021
[108]	Pt-TiO ₂	2-5	multi core-shell	Glassy carbon electrode, TEM grid	Size-dependent multi-core (55000 Daltons)	2015
[109]	Pt _x Y	4-9	polycrystalline	glassy carbon substrate	High OER performance	2014
[110]	Ru	2.8	icosahedral and HCP	CuO NW	Ru to RuO _x transformation during bias, interfacial charge transfer study	2019
[111]	Si-Ag			Si	Ag shell coating	2013
[112]	SmCo	~7	annealing dependent	Si, TEM grid	<i>In-situ</i> annealing, temperature dependent coercivity	2003
[113]	SmCo	4.2-7	single crystalline	Si, Au grids	Ferromagnetic to superparamagnetic	2011
[114]	SmCo	~ 39.2	crystalline	TEM grid	Hexagonal disk shape with its easy axis perpendicular to the disk plane	2013
[115]	SmCo	2-20		carbon cloth	OER	2023
[116]	SmCoNi, SmCoCu	5-15	amorphous as-deposit	Si, TEM grid	In-flight annealing; ferromagnetic	2019
[117]	Ta	3	single crystalline	embedded a-Si on Cu foam	Li-ion battery	2017

[118]	Ta	3	single crystalline	Si amorphous film	Li-ion battery	2021
[119]	TaO _x + Pt	4-5	amorphous Ta, crystalline Pt	Si	OER	2017
[120]	Ti, Co				Influence of reactive gases on the formation of NCs	2012
[121]	Ti-Cu	5-10 (8)		Si	Modeling of NC growth, Ti-Cu alloy cluster	2018
[122]	TiO ₂	4-8	amorphous till 8 nm	Si	Size-selected, OER	2014
[123]	TiO _x	10-30		Si	Role of oxygen admixture in stabilizing TiO _x nanoparticle deposition	2013
[124]	TiO _x @Au	5.5-6.5	crystalline Au core with amorphous TiO _x shell	TEM grid, Si	multi-magnetron source, single step formation, Ti shell get oxide in flight	2017
[125]	V	4		TEM grid, glassy carbon substrate	Controlled size, composition and morphology	2015
	Pt/Ti	8				
	Ti	7				
	V/Ti	5				
	Mo	5				
	V	8				
	Pt/V	7				
[126]	W/WO ₃	3 - 5.5		Si	Introduce O ₂ into aggregation chamber to produce oxide cluster	2015
[127]	Y/Co	8-10			Magnetic	2011
[128]	ZrO ₂	3-9	crystalline	Si	Ferromagnetism	2020

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Appendix B

Supporting Information

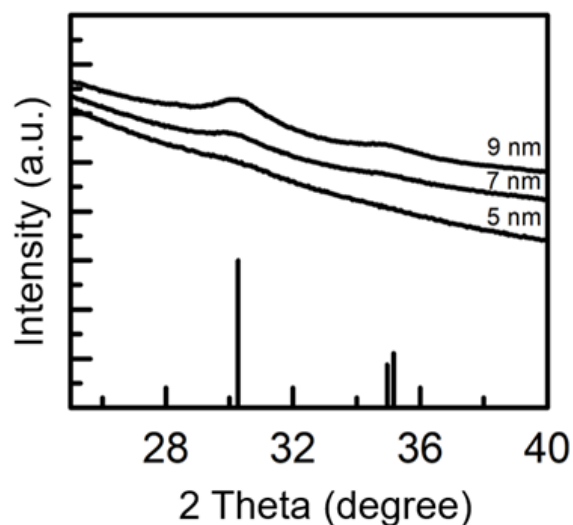


Figure S 1: Glancing-incidence XRD patterns of as-grown nanoclusters with selected sizes (5 nm, 7 nm, 9 nm) obtained at an incidence angle of 0.3° . The PDF2 reference pattern of the ZrO_2 tetragonal phase (#01-080-2155) is shown as the bottom bar graph. The most prominent peak for all three monosized clusters corresponds to the (1 0 1) plane at 30.27° , while the weaker features correspond to the (0 0 2) plane at 34.96° and (1 1 0) plane at 35.16° for the 7-nm and 9-nm nanocluster samples. As the cluster size is reduced from 9 nm to 5 nm, the peaks appear broader, which is consistent with the grain (or nanocrystallite) size becoming smaller.

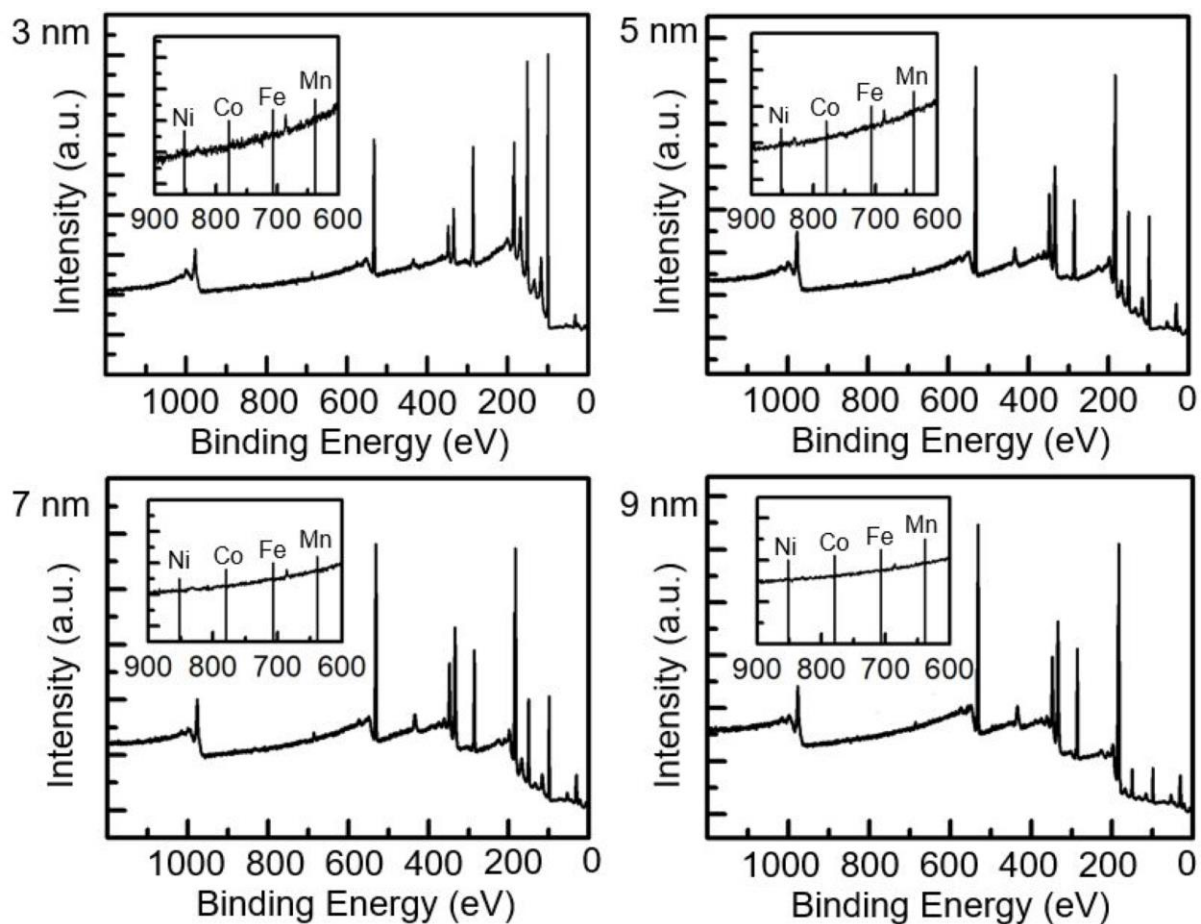


Figure S 2: The survey spectra of as-deposited ZrO_2 nanocluster films with different cluster sizes on the Si substrates. Locations of possible magnetic components are marked to indicate their absence in the insets.

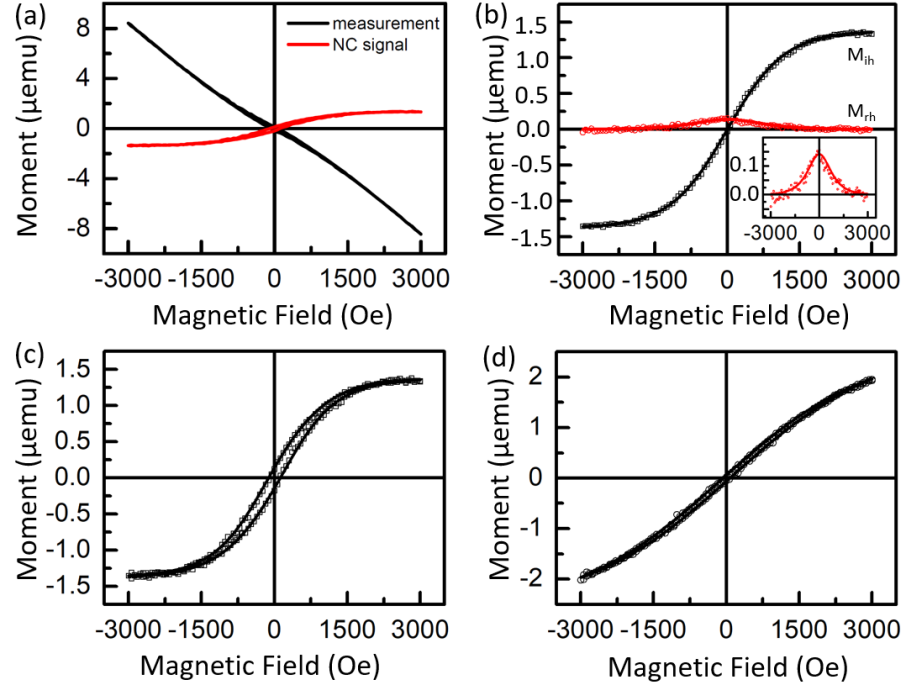


Figure S 3: Quantitative analysis of the magnetization curve of the 3-nm ZrO₂ nanocluster film sample used as an example. (a) The hysteresis loop of the nanocluster film is obtained by subtracting the background from the Si substrate and the quartz sample holder. (b) The hysteresis loop can be regarded as a combination of an odd function, M_{ih} (induced-hysteretic magnetization), and an even function, M_{rh} (remanent-hysteretic magnetization):

$$M_{ih} = \frac{M^+(H) + M^-(H)}{2} \quad \text{Eq. (1)}$$

$$M_{rh} = \frac{M^+(H) - M^-(H)}{2} \quad \text{Eq. (2)}$$

$$M_{ih} = a \times \tan(b \times H) \quad \text{Eq. (3)}$$

$$M_{rh} = \frac{a}{\cosh(b \times H)} \quad \text{Eq. (4)}$$

where $M^+(H)$ and $M^-(H)$ correspond to the upper branch and the lower branch of the hysteresis loop. The M_{ih} curve is fitted by Eq. (3) and the M_{rh} curve is fitted by Eq. (4) with appropriate fitting parameters a and b , and the fitted curves are shown as solid lines in (b). (c) The entire fitted loop is then generated by using the fitted M_{ih} and M_{rh} curves. (d) The fitting analysis applied to the 9-nm ZrO₂ nanocluster film, which shows the absence of any magnetic character.

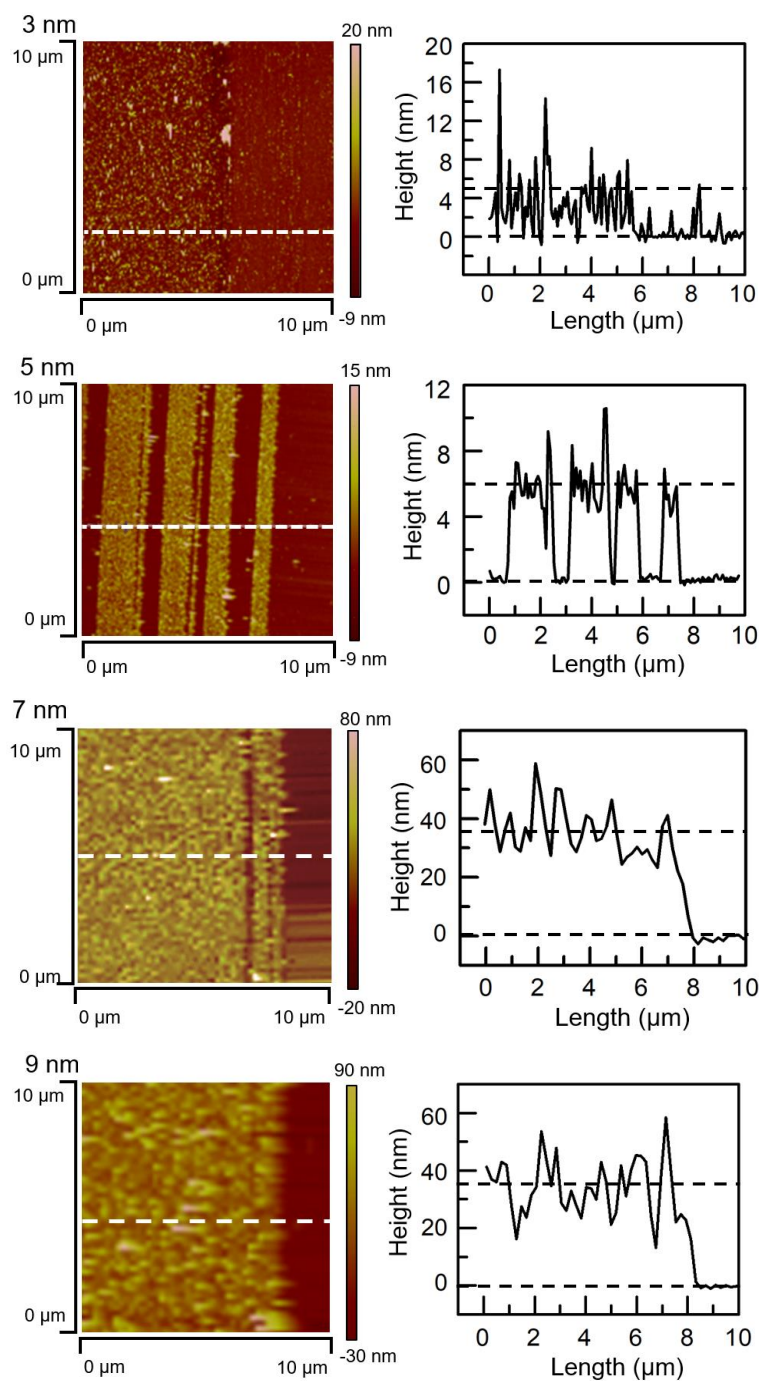


Figure S 4: (Left) AFM apparent height images of as-deposited nanocluster films of different cluster sizes. (Right) Height profiles of the cross-sections of the respective nanocluster films along the white dash lines in the left height images. The nanocluster films have been scratched appropriately to reveal the thicknesses of the films.

Table S1: Relative compositions of Zr 3d oxidation states (Zr^{4+} , Zr^{3+} , Zr^{2+} , Zr^{1+} and Zr^0) obtained from the respective Zr 3d XPS spectra for the 3 nm, 5 nm, 7 nm and 9 nm ZrO_2 nanocluster films. The fitted values for the binding energies of the respective Zr^{n+} features are essentially the same for the nanocluster films, i.e., to within the experimental accuracy (0.1 eV) provided by the XPS system.

	3 nm		5 nm		7 nm		9 nm	
	Binding Energy (eV)	Content	Binding Energy (eV)	Content	Binding Energy (eV)	Content	Binding Energy (eV)	Content
Zr^{4+}	183.45	89.36%	183.49	91.38%	183.38	94.33%	183.46	95.47%
Zr^{3+}	182.29	5.80%	182.34	2.92%	182.23	0.27%	182.31	0.00%
Zr^{2+}	181.19	3.29%	181.23	3.70%	181.26	1.46%	181.20	1.13%
Zr^{1+}	180.03	0.48%	180.07	0.67%	179.96	3.21%	180.04	2.95%
Zr^0	178.86	1.07%	178.90	1.33%	178.79	0.74%	178.87	0.44%

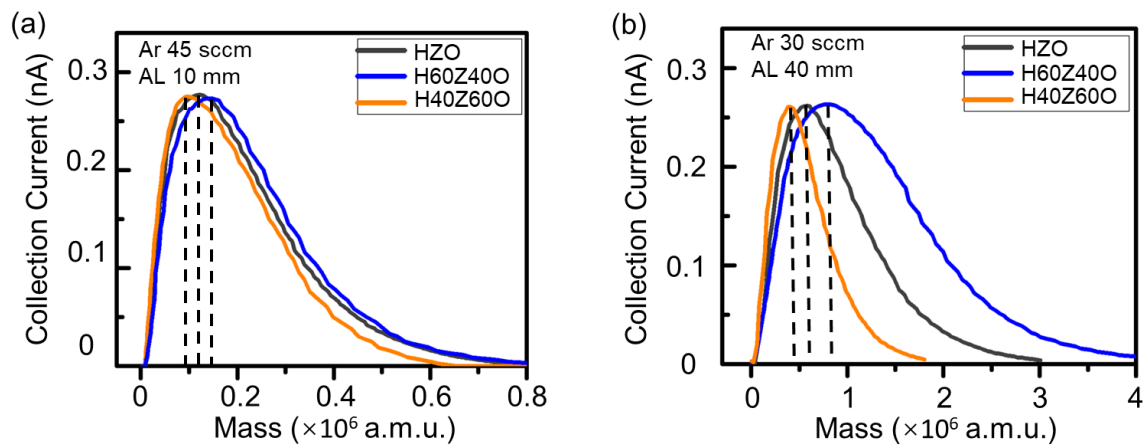


Figure S 5: Mass distributions of as-formed $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoclusters with different compositions passing through the quadrupole mass filter (as reflected by the collection current) at (a) 10 mm and (b) 40 nm aggregation length, and with the Ar flow rate appropriately optimized.

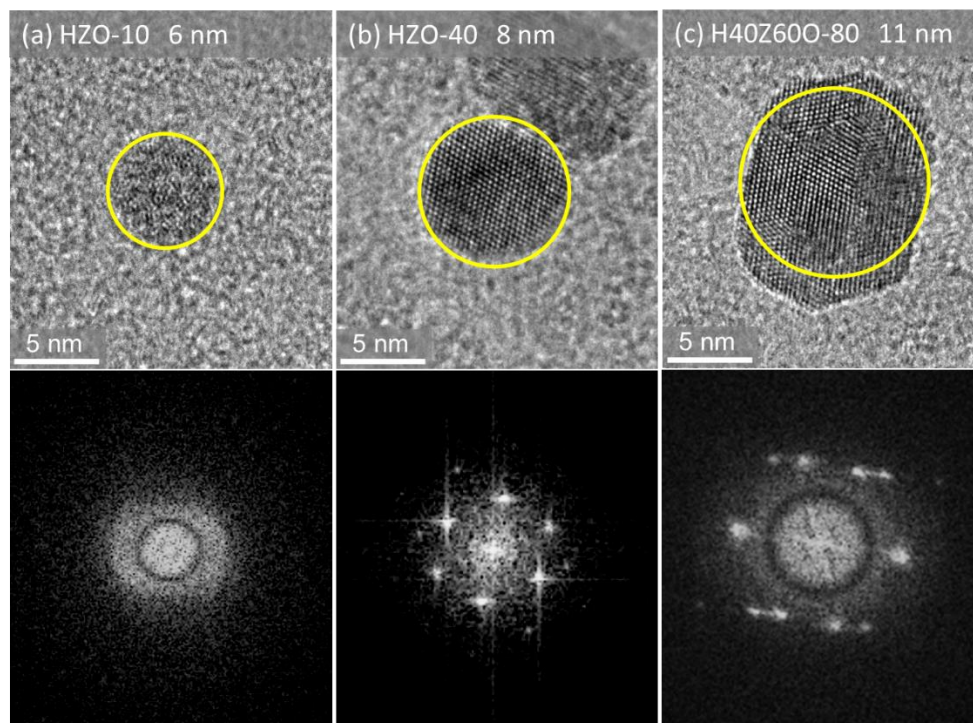


Figure S 6: High resolution TEM image of as-deposited $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ NCs, demonstrating different crystal structures for different NC sizes: (a) HZO NC as an example of an amorphous structure obtained with 10 mm AL, (b) single crystalline HZO NC obtained with 40 mm AL, and (c) polycrystalline $\text{H}_{0.4}\text{Z}_{0.6}\text{O}_2$ NC obtained with 80 mm AL. The corresponding representation of diffraction pattern by FFT is shown in the lower panel of the respective image.

Table S2. Lattice parameters of $Pca2_1$ orthorhombic ZrO_2 and HfO_2 , reported by Materlik *et al.*⁹⁷

	O-ZrO ₂	O-HfO ₂
a (Å)	5.04	5.01
b (Å)	5.09	5.06
c (Å)	5.26	5.23
V(Å³)	134.9	132.6
$\alpha = \beta = \gamma = 90^\circ$		

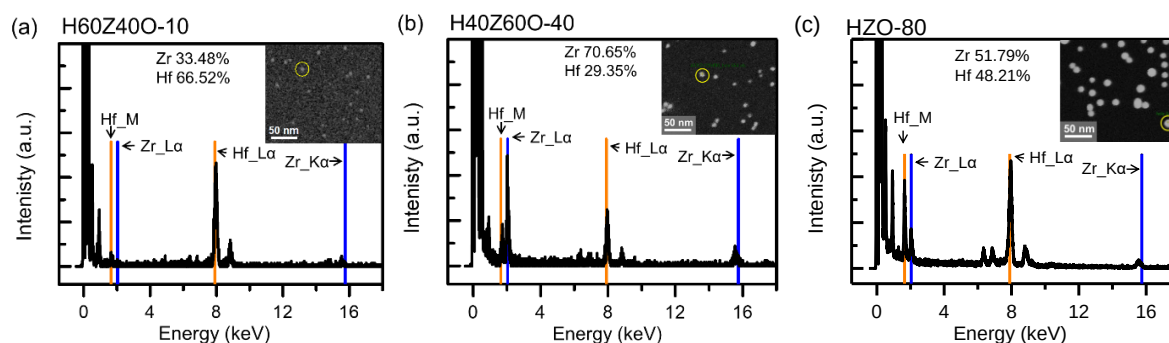


Figure S 7: TEM EDS spectra of a single $Hf_xZr_{1-x}O_2$ NC for (a) H60Z40O-10, (b) H40Z60O-40, and (c) HZO-80. The individual NC used for the EDS analysis is marked by the yellow circle in the STEM image shown in the inset. Only the Zr $K\alpha$ and Hf $L\alpha$ features are used for elemental analysis. The respective spectrum shows that the NC has both Zr and Hf content, in nearly the same relative composition, demonstrating a true mixture of the twin oxide for all three NC samples. The intense O $K\alpha$ feature at 0.525 keV is off scale and therefore not shown completely here. It should be noted that the relative content of the Zr and Hf obtained with different AL is also proportional to the sputtering power.

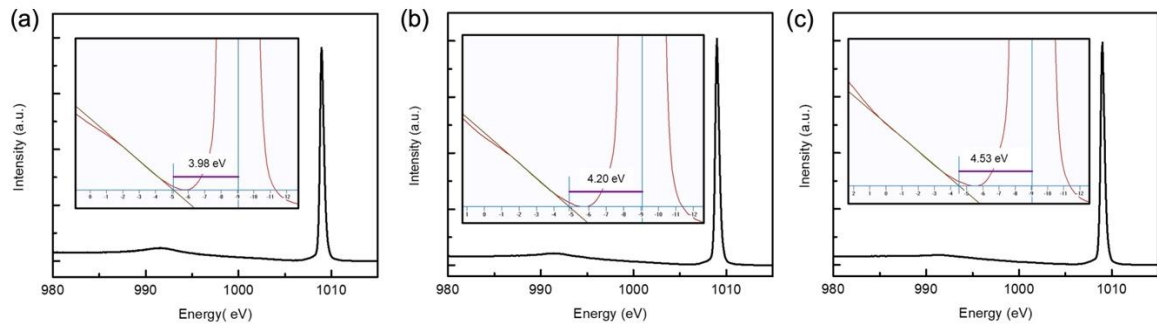


Figure S 8: Reflection electron energy loss spectra (REELS) of (a) HZO-10, (b) HZO-40 and (c) HZO-80 to demonstrate the bandgap determination of Hf_xZr_{1-x}O₂ NCs.