Growth and Electrical Properties of Free-Standing Zinc Oxide Nanomembranes

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ABSTRACT: We report the synthesis of free-standing two-dimensional semiconductor zinc oxide (ZnO) nanomembranes (NMs) using a bottom-up approach, i.e., nanomembranes grown from the faceted sidewalls of horizontally oriented ZnO nanowires (NWs). The ZnO NMs were synthesized on r-plane sapphire substrates utilizing high purity ZnO powder and graphite mixture and oxygen as source materials and argon (Ar) as carrier gas. Material characterization confirms that the horizontally oriented ZnO NWs were guided grown via a vapor—liquid—solid growth mechanism using gold as catalyst. The ZnO NMs were nucleated from the coated gold catalysts on the sidewalls of NWs. The electrical properties of the ZnO NMs were characterized based on a back-gate field effect transistor. The estimated carrier mobility of the ZnO NM is ∼150 cm² V⁻¹ s⁻¹. The as-grown free-standing NMs can serve as the fundamental building blocks for a variety of applications in electronics and optoelectronics as well as sensing technologies. The unique bottom-up synthesis approach of the free-standing ZnO NMs is applicable for other material systems.

INTRODUCTION

Two-dimensional (2D) semiconductor nanomembranes (NMs) are generally referred to as monocrystalline structures with thicknesses of less than a few hundred nanometers and lateral dimensions at least 2 orders of magnitude larger than the thickness.1–3 Because of their unique geometrical shapes, semiconductor NMs exhibit a significantly reduced flexural rigidity as compared to their bulk counterpart and thus can be attached to curved, irregular, and stretched surfaces. In addition, their unique mechanical properties allow the use of strain to alter the interatomic bond length and thus engineer the physical properties of materials without prompting fracturing or buckling.2,4,5 NMs with appropriate thickness have quantum confinement characteristics in their electrical and photonic properties. NMs are also compatible with traditional top-down processing technologies, which provide a new route to address the current assembly and manufacturing challenges associated with 0D and 1D nanostructures. Thus, semiconductor NMs have significant potential to serve as important building blocks for future nanotechnology devices. Inorganic nanomembranes are attracting increasing interest recently in many applications ranging from electronics, catalysts, and energy devices, such as lithium-ion batteries, because of their unique mechanical properties that allow them to bend and wrinkle.6–7 As a result, they can buffer the strain of lithium ion insertion and extraction and can also delay the pulverization of the electrode materials for lithium ion batteries.

Current available methods to fabricate semiconductor NMs are essentially based on “top-down” approaches: (i) Chemical or mechanical exfoliation of NMs from solids that have naturally layered structures, such as graphite, semiconductor MoS₂, GeS, GeSe, and so forth.8–10 This exfoliation approach yields large numbers of NMs, but they only applicable for certain classes of materials, and yet, it is still difficult to control their dimensions and shapes. (ii) Release of NMs from bulk semiconductors by use of specialized anisotropic etching procedures. This method is applicable to specific materials that have anisotropic etching properties along different crystal orientations, such as Si.11,12 (iii) Release of NMs from epitaxially grown multilayer assemblies. For example, GaAs NMs can be released from GaAs/AlGaAs stacks by selective removal of AlGaAs with hydrofluoric acid.13,14 Recently, GaN NMs with a freestanding thickness between 90 and 300 nm were obtained using conductivity-selective electrochemical etching.15 These approaches require the stacks to be epitaxially compatible, and the sacrificial layer needs to be removed with high selectivity with respect to the functional membrane. In addition, these selective etching processes are required to create via-holes15 to allow the etching solutions to access the sacrificial layers. Each of the above methods is applicable to a certain category of materials that have very specific properties, enabling the release of NMs from bulks or stacks via selective etching processes. Nevertheless, there does not exist a general and controllable approach for direct synthesis of free-standing NMs from the “bottom-up”.

Wide band gap materials, such as III-nitride,16 SiC17 and Ga₂O₃18 have been studied for applications in optoelectronic and electronic devices. ZnO with a wide direct bandgap (3.37...
eV) and a large exciton binding energy (60 meV)\textsuperscript{19} represents one of the most attractive wide bandgap semiconducting materials for applications related to ultraviolet (UV) optical devices,\textsuperscript{20} solar cells,\textsuperscript{21} sensors,\textsuperscript{22} photocatalysis,\textsuperscript{23} transparent field effect transistors,\textsuperscript{24} and acoustic wave devices.\textsuperscript{25} In addition, ZnO has been applied for mechanical energy-harvesting devices due to its outstanding piezoelectric property.\textsuperscript{26} ZnO-based nanostructures,\textsuperscript{27} such as nanowires, nanobelts, nanowalls, hierarchical nanostructures, nanobridges, and nanonails, have been extensively explored. However, it is still challenging to grow these ZnO nanomaterials (except ZnO NWs) on a large scale and with good uniformity for device applications.

In this paper, we present a new approach to synthesize free-standing ZnO NMs from the bottom-up by growing the NMs from the sidewalls of the horizontally oriented NWs on r-plane sapphire substrates. The small lattice mismatch of 1.53% between two parallel planes of ZnO (11−20) and sapphire (01−12) led to the horizontal ZnO NW growth on r-plane sapphire substrate\textsuperscript{33,34} and simultaneous NM growth from NW sidewalls with proper growth conditions. The ZnO NM growth mechanism was investigated. The electrical properties of the ZnO NMs were characterized based on a back-gate field effect transistor (FET).

\section*{EXPERIMENTAL SECTION}

\textbf{Growth of ZnO NMs.} We used a single zone tube furnace for the synthesis of the ZnO NMs by the carbothermal reduction process. R-plane sapphires were used as the substrates for the growth. Prior to the chemical vapor deposition (CVD) growth, the substrates were cleaned with acetone and isopropanol, rinsed with deionized water, and dried with nitrogen flow. Au films with different thicknesses (0.5−5 nm) were deposited on top of the substrates via thermal evaporation. A mixture of equal amounts (by weight) of ZnO powder (Alfa Aesar, 99.99%) and graphite (Alfa Aesar,200 mesh, 99.9995%) were used as the source materials. The mixture was put in an alumina crucible and placed at the center of a quartz tube of diameter 1 in. The substrates were placed horizontally downstream of the tube separated from the source by 6 in. Then, the chamber was pumped down to a base pressure of approximately 1 mTorr. Prior to heating the chamber to the desired growth temperature, the chamber was purged with argon (200 sccm) for 30 min. The chamber was then heated to 915 °C under argon flow. Upon reaching the desired temperature, the growth was carried out under the flow of 10 sccm of oxygen and 200 sccm of argon. The growth pressure was maintained at around 1 Torr during the growth.

\textbf{Fabrication of ZnO NM-Based FETs.} The free-standing ZnO NMs can readily be transfer-printed onto desirable substrates to fabricate FETs. Using thermal release tape, ZnO NMs were transferred onto p-type doped Si (100) substrates coated with 300 nm thermal silicon dioxide. Ti/Ni (100 nm/50 nm) contacts were deposited via electron beam evaporation.

\textbf{Characterization of ZnO NMs.} The crystal structure and morphology of the ZnO NMs were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The XRD pattern was collected on a Bruker Discover D8 with Co Kα radiation (1.79026 Å). The X-ray beam diameter is 500 μm. FESEM images were taken with Helios 650. High resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) were taken with FEI Tecnai F30 at 300 kV. The Raman spectrum was taken at room temperature using a linearly polarized laser beam of 532 nm. The beam was focused on the sample using a 100× objective. The laser power and the beam diameter were ~200 μW and ~1 μm, respectively. Transistor measurements were performed with a probe station for contacting the electrodes and with high-precision source measurement units in Keithley 4200 SCS for applying voltage and measuring current. All current−voltage traces were taken from positive to negative $V_D$ or $V_G$.

\section*{RESULTS AND DISCUSSIONS}

Figure 1 shows the as-grown ZnO NMs on an r-plane sapphire substrate with a 0.5 in wafer scale. Au film with a thickness of 0.5 nm was deposited on the substrate as the catalyst. The sample was uniformly covered with ZnO NMs, which were grown at a tilted angle with respect to the substrate surface. As observed from Figure 1, the NMs are tapered as they extend away from the horizontal nanowires, having a wider width at the bottom close to the nanowire where it started to first grow and a narrower width at the tip. For the sample shown in Figure 1, the lateral dimension at the bottom of the NMs range between 1.5 to 3 μm. The thickness of the NMs ranges between 50 and 70 nm.

To investigate the growth mechanisms of the ZnO NMs, we designed a series of growths with various growth times. Figure 2 illustrates the ZnO NWs and NMs at different stages and confirms that the ZnO NMs were nucleated and grew from the sidewalls of the horizontally oriented NWs. Here, the growth process is composed of two parts: (i) the growth of horizontal NWs along the substrate surface via a vapor−liquid−solid (VLS) growth mechanism, and (ii) the growth of NMs from the sidewalls of NWs with the assistance of the Au catalyst on the sidewalls. The Au catalyst deposited on the substrate acts as the nucleation site for the horizontal ZnO NW growth on appropriate substrates. It is well-known that the Au catalysts provide suitable sites for precursor deposition.\textsuperscript{19} Because of the selective wetting of Zn on Au, Zn vapor produced from the source was absorbed on the Au clusters. Thus, Au/Zn alloy droplets were formed through diffusion of the Zn atoms into the Au clusters.\textsuperscript{19} The continuous supply of the Zn flux further supersaturated the alloy droplets, and nucleation of the Zn phase started. The Zn atoms that precipitated out of the alloy droplets then reacted with the oxygen atoms and led to the formation of ZnO nanowires. For enabling the horizontal ZnO NW growth, an r-plane sapphire substrate was used. The small lattice mismatch of 1.53% between two parallel planes of ZnO (11-20) and sapphire (01-12) along the growth direction led to the horizontal nanowire growth. The horizontal nanowires are enclosed by {10-10} side planes. As the growth of the NWs...
proceeded, the Au catalysts migrated from the tips to the sidewalls of the NWs. Such phenomena have been observed previously for the growth of silicon and ZnO nanowires using Au and Sn as catalysts, respectively. We believe that the diffusion of the Au catalysts to the sidewalls of the nanowires and the growth of the lateral nanowires occurred simultaneously. These migrated Au catalysts acted as the new nucleation centers for the formation of ZnO NMs. There was no intentional change of growth conditions when the growth transited from nanowire to nanomembrane. However, it is possible that a perturbation of local energy may trigger the start of NM growth. The local energy perturbation leads to the transferring of the catalyst for NW growth to NM growth. Thus, the NW growth was terminated when the NM started to appear. To support our hypothesis, top view FESEM images of ZnO NWs and NMs grown at different stages are shown in Figure 2.

Figure 2. (A–D) Schematic illustration of the growth mechanism of free-standing ZnO NMs. (E–H) Top view FESEM images of the as-grown ZnO NMs grown on an r-plane sapphire substrate using a Au film as catalyst.

Figure 3. (A) Schematic of the signal detection for the tilted FESEM image of ZnO NMs, (B) 30° tilted FESEM image of ZnO NMs showing the NMs forming an angle of 60° with the substrate, (C) high magnification top view FESEM image of the ZnO NMs intersecting each other with extended growth time, and (D) 60° tilted FESEM image of ZnO NMs.
Figures 2E–H. The SEM images were selected from a series of experiments that were designed to illustrate the growth mechanisms of the ZnO NMs. Note that these SEM images do not represent different growth stages for the same sample. Figure 2E shows the supersaturation of the Au catalysts and nucleation of lateral ZnO NWs. Panels F–H in Figure 2 represent the nucleation and evolution of ZnO NM morphology. The tapered shape of the ZnO NMs can be clearly seen from the images. Three possible reasons may contribute to the tapering of the NMs during the growth: (i) the reduction in the volume of the Au catalysts due to the evaporation, (ii) the migration of the Au catalysts from the tips to the surfaces and sidewalls of the NMs, which results in reduction of the Au catalyst volumes on the NM tips, and (iii) the lateral growth of the NMs due to VLS or vapor–solid (VS) growth mechanisms. From the high-resolution SEM images, it is clearly visible that the Au catalysts at the tips of the NMs became smaller as the growth proceeded.

Figure 3A shows a schematic of the signal detection for tilted FESEM imaging for ZnO NMs. A thirty degree tilted FESEM image of ZnO NMs grown on an r-plane sapphire substrate is clearly visible that the Au catalysts at the tips of the NMs are not representative of the NMs grown from the two directions. The crystal structure of the as-grown ZnO NMs was characterized with transmission electron microscopy (TEM) as shown in Figure 5. Figure 5A shows the bright field TEM image of ZnO NW with ZnO NM originating from the sidewall of the nanowire. The nanowire has a uniform diameter of 75 nm. The thickness of the NM is 20 nm. Figure 5B shows the high resolution transmission electron microscopy (HRTEM) image of the interface between the NW and the NM. The uniform lattice fringes across the interface between the NW and the NM are clearly visible. The individual HRTEM images of the NW and NM are shown in Figure 5C and D, respectively. The insets show the corresponding selected-area electron diffraction (SAED) patterns for both the NW and NM. The diffraction patterns were taken along the [01-10] zone axis. The SAED patterns confirm that the synthesized NMs and NWs are single crystalline wurtzite ZnO having the same crystal orientation. From Figure 5C, the interplanar spacing for the nanowire NW is 0.52 nm, which corresponds to the distance of wurtzite ZnO (0001) plane. The (0001) plane is perpendicular to the NW growth direction, which indicates that the NW grew along the <0001> polar c-plane direction. The NM growth directions can be both perpendicular and parallel to the nanowire growth direction.

A room temperature Raman spectrum of ZnO NMs taken with a linearly polarized laser beam of 532 nm wavelength is shown in Figure 6. ZnO with wurtzite crystal structure belongs to the space group C\(\text{6}_{\text{v}}\). The optical phonon modes predicted by group theory for ZnO are \(A_{1g} + 2B_{1g} + E_{1g} + 2E_{2g}\). Among them, \(A_{1g}\) and \(E_{1g}\) modes are polar and both Raman and infrared active. They split into transverse optical (TO) and longitudinal optical (LO) phonons. \(E_{2g}\) modes are nonpolar but Raman active, whereas \(B_{1g}\) modes are Raman inactive. The phonon mode at 326.5 cm\(^{-1}\) is a second order feature originating from the zone-boundary phonons of 2\(-E_{2g}(M)\) for ZnO.\(^{39}\) The mode at 438 cm\(^{-1}\) with the highest intensity is assigned to \(E_{1g}\)(high) phonon mode.\(^{38–41}\) This mode is a typical characteristic feature of wurtzite lattice and is used to understand the stress-induced phenomena in a wurtzite crystal structure. For free-standing ZnO, this peak is located at 437 cm\(^{-1}\). A small increase of 1 cm\(^{-1}\) in the \(E_{1g}\)(high) phonon frequency of the ZnO NMs with respect to free-standing ZnO is within the measurement tolerance limit and indicates that the ZnO NMs are not obviously under stress. The other first-order Raman peak at 376.8 cm\(^{-1}\) corresponds to \(A_{1g}(TO)\) mode.\(^{42}\) The absence of peaks from impurity in the spectrum indicates that the synthesized materials are phase pure and perfectly crystallized.

Figure 7 demonstrates the mechanical property of the as-grown ZnO NM with significantly reduced flexural rigidity. By applying strain via a tungsten probe, the ZnO NM does bend, which indicates the NM has flexural rigidity that is significantly reduced as compared to its bulk counterpart. After removing the probe, the NM returns to its original flat morphology. The flexural rigidity is proportional to \(\sim Eh^3/12\), where \(E\) is the elastic modulus and \(h\) is the thickness.\(^{43}\) Thus, the thinnest ZnO nanomembrane (thickness \(\sim 20\) nm) that we have synthesized is expected to have flexural rigidity 12 orders of magnitude smaller than the bulk ZnO.
magnitude smaller than that of the bulk ZnO wafer (thickness \(\sim 200 \mu m\)). With such small flexural rigidity, the behavior of semiconductor NMs can resemble that of a soft material, which previously belonged exclusively to organic materials. The demonstration of a significantly reduced flexural rigidity of the synthesized ZnO NMs provides an opportunity to apply them for flexible electronic and optoelectronic devices, which are of great scientific importance as they can be bent or stretched, and their properties can be manipulated.44

Theoretical calculations based on first principle density functional theory (DFT) have shown strain effects on structural transformations, electronic structure, and electron effective mass of wurtzite ZnO.45−47 Effects of bending and stretching on the electronic transport properties of ZnO-based devices have been experimentally studied previously.48−52 The change in piezoelectric potential due to bending and stretching-induced strain may shift the local Fermi level and modify the local band structure. These changes in turn can affect the charge transport process due to modified effective mass of the charge carriers.

For investigation of the electrical properties of the as-grown ZnO NMs, back-gate FETs based on ZnO NMs were fabricated. Figure 8A shows a schematic illustration of the ZnO NM-based FET device structure. Figure 8B shows a top view SEM image of the fabricated ZnO NM FET with a channel length of 7.5 \(\mu m\) and thickness of \(\sim 60 \text{ nm}\). All transistors were measured in the dark under ambient conditions. For all of the measurements, the gate voltage was applied directly to the back of the Si substrate. A current−voltage plot in Figure 9A shows typical accumulation-mode n-type transistor behavior. In general, \(I_{DS} vs \ V_{DS}\) curves are linear up to 5 V, suggesting that the electrodes on ZnO NMs are
Ohmic contacts. As $V_{DS}$ increases further, the current becomes saturated with positive bias and eventually breakdown occurs at $V_{DS} \sim 58$ V. A representative transconductance measurement ($I_{DS}$ vs $V_G$) was obtained at $V_{DS} = 0.1$ V, as shown in Figure 9B, exhibiting n-type transistor behavior. By plotting the current on a logarithmic scale (Figure 9B inset), we obtained an on–off current ratio ($I_{ON}/I_{OFF}$) of $\sim 10^6$. From the transconductance plots, the mobility of ZnO NM FETs can be estimated by the relation of 53,54

$$\mu = \frac{I_{DS}}{V_{DS}^2} \frac{L}{2 \mu C V_{DS}}$$

where $\mu$ is the carrier mobility and $L$ is the length of the active ZnO NM channel. The capacitance is given by

$$C = \epsilon_{SiO_2} A \frac{h}{h}$$

where $\epsilon_{SiO_2}$ is the dielectric constant of the gate SiO$_2$ and $h$ is its thickness. $A$ is the parallel area of ZnO NM crossing the channel. The carrier concentration ($n_e$) is estimated by

$$n_e = \frac{V_{NM}}{q V_{NM}}$$

where $V_{NM}$ is the volume of ZnO NMs crossing the channel. From Figure 9, the mobility of the ZnO NM FET was estimated to be $157$ cm$^2$ V$^{-1}$ s$^{-1}$, and the estimated carrier concentration was $3.6 \times 10^{16}$ cm$^{-3}$ by using the equations listed above. The carrier mobility of the as-grown ZnO NMs from this study is higher than that of the previously reported ZnO NWs (5–100 cm$^2$ V$^{-1}$ s$^{-1}$)55,56 or ZnO thin films ($\sim 40$ cm$^2$ V$^{-1}$ s$^{-1}$).57,58

### CONCLUSIONS

In summary, we have performed the synthesis of free-standing semiconductor ZnO NMs using a bottom-up approach, i.e., NMs grown from the sidewalls of horizontally oriented ZnO NWs. HRTEM demonstrated atomic uniformity at the junction between the lateral ZnO NW and the ZnO NM. A mechanical stressor applied on the NM indicates a significantly reduced flexural rigidity as compared to that of the bulk counterpart. The electrical measurements on the as-grown ZnO NM-based FETs revealed a high carrier mobility of $157$ cm$^2$ V$^{-1}$ s$^{-1}$. Because of their significantly reduced flexural rigidity, semi-
conductor ZnO NM with high material quality is a promising candidate for flexible, bendable, and stretchable devices. Moreover, the presented synthesis approach and proposed growth mechanism of ZnO NMs is applicable to other material systems.

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**Notes**

The authors declare no competing financial interest.

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