Diameter-Controlled Growth of Single-Crystalline In$_2$O$_3$ Nanowires and Their Electronic Properties

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One-dimensional nanostructured systems have recently attracted much attention due to their novel properties and potential applications in numerous areas such as nanoscale electronics and photonics.[1–7] Nanowires of various compositions have been synthesized using a wide variety of methods including chemical vapor deposition (CVD),[1–4] laser ablation,[5–7] and electrochemical deposition.[8] These efforts have led to the successful growth of many semiconducting nanowires including Ge,[1] ZnO,[8,9] Si,[10] GaN,[11] and GaAs[10] which were then employed to construct such exciting systems as nanowire integrated systems[12] and nanolasers.[12]

Parallel to the success with group IV and III–V compound semiconductor nanowires, semiconducting oxide nanowires such as ZnO,[2] CdO, and In$_2$O$_3$ are becoming increasingly important. Among them, In$_2$O$_3$ is a wide-bandgap transparent semiconductor (with a direct bandgap around 3.6 eV and an indirect bandgap around 2.5 eV), and In$_2$O$_3$ in the bulk form has been widely used in solar cells and organic light-emitting diodes.[13–14] More importantly, In$_2$O$_3$ films have been demonstrated to work as ultra-sensitive toxic-gas detectors,[15] with detection levels down to 5 ppm for NO$_2$, due to the surface interaction and electron transfer between NO$_2$ molecules and In$_2$O$_3$ surface. In$_2$O$_3$ in the nanowire form is expected to offer enhanced sensitivity and also improved response time due to the enhanced surface-to-volume ratio. It is therefore important to be able to synthesize In$_2$O$_3$ nanowires with highly uniform geometries, preferentially in the single-crystalline form, for electronic properties studies and potential sensor applications. Several methods were developed in the past to grow In$_2$O$_3$ nanowires. For example, polycrystalline In$_2$O$_3$ nanowires were grown by electrodeposition indium into an anodized alumina template and subsequent oxidation.[16] More recently, single-crystalline In$_2$O$_3$ nanowires were grown by a rapid heating process from indium grains in a mixture of Ar and O$_2$,[16] however, this method yields nanowires with a wide diameter distribution due to the lack of a diameter-control mechanism. The same is also true for semiconductive oxide nanobelts reported recently.[17] This drawback can be overcome by using the vapor–liquid–solid (VLS) growth approach,[5] where the nanowire diameters can be controlled by the catalyst nanoparticle size.[18] Here, we report an efficient route for the synthesis of single-crystalline In$_2$O$_3$ nanowires via the VLS mechanism, where the In vapor was generated by laser ablation of an indium-containing target. While catalysts made of a thin gold film produced In$_2$O$_3$ nanowire with a broad diameter distribution, excellent diameter control was achieved by using monodispersed gold clusters as the catalyst. Detailed transmission electron microscopy (TEM) examination confirmed the composition of our nanowires and reveals our nanowires exhibit narrow diameter distributions peaked at 10, 20, and 30 nm, respectively. In$_2$O$_3$ nanowire field-effect transistors were also made for the first time with on/off ratios up to 1000.

First, In$_2$O$_3$ nanowires were grown using Si/SiO$_2$ substrates covered with 20 Å gold films as the catalyst. The substrates were placed into a quartz tube at the downstream end of a furnace, while an InAs target was placed at the upper stream of the furnace and later on ablated to supply the In vapor. During the laser ablation, the chamber was maintained at 220 torr, 770°C with a constant flow of 150 standard cubic centimeters per minute (sccm) of Ar mixed with 0.02% O$_2$. The typical reaction time used was about 35 minutes. After cooling down, the samples were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and X-ray diffraction (XRD). The nanowire diameters were usually determined using TEM and the lengths were measured from SEM images.

Figure 1a shows a typical SEM image of In$_2$O$_3$ nanowires grown on the Si/SiO$_2$ substrate with evaporated Au catalysts. These nanowires covered the whole substrates and appeared to be straight. Detailed TEM and SEM examination show that these nanowires have diameters in the range of 30–50 nm and lengths exceeding 3 μm, indicating an aspect ratio of more than 100:1. XRD patterns of such nanowire samples were utilized to examine the crystal structure of the nanowires. All samples showed similar XRD patterns, indicating the nanowires’ high crystallinity. There are three major diffraction peaks, as showed in Figure 1b. They can be indexed to the (222), (440), and (400) crystal planes of a cubic structure of[...]

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bulk In$_2$O$_3$ with a cell constant of $a = 1.01$ nm. Two gold peaks from the Au catalysts can also be identified; however, no diffraction peaks from InAs can be found in any of our samples. Although this laser ablation process generated both In and As vapors, we believe O$_2$ is more reactive than As, and hence In$_2$O$_3$ instead of InAs was found to be the final product. Energy-dispersive X-ray spectroscopy (EDS) was also performed to analyze the composition of our nanowires and no peaks corresponding to As were detected down to the limit of our equipment.

Despite the above-mentioned success, direct and precise control over the In$_2$O$_3$ nanowire diameter is still highly desired. Furthermore, nanowires with diameters below 30 nm are also necessary in order to make nanowire-based field effect transistors because of the finite depth a gate electric field can penetrate. This was achieved by using monodispersed gold clusters instead of the evaporated gold film as the catalysts. The idea is based on the VLS growth mechanism, where the In vapor first diffuses into the gold catalytic particles, and grows out and reacts with O$_2$ to form In$_2$O$_3$, once the In/Au alloy reaches supersaturation. Continued addition of In into the In/Au nanoparticle feeds the In$_2$O$_3$ growth and eventually the diameter of the In$_2$O$_3$ nanowire is directly linked to the catalytic particle size. This diameter-control feature is rather unique to the VLS mechanism, in contrast to the lack of control with the rapid heating process. Three types of clusters were used, with diameters around 10, 20, and 30 nm, respectively. These nanoclusters were dispersed onto a Si/ SiO$_2$ substrate following previously published work and atomic force microscopy (AFM) was performed to confirm these nanoclusters distributed uniformly across the surface. Abundant In$_2$O$_3$ nanowires were produced all over the substrate following the same laser ablation conditions described above. Figure 2a is a detailed TEM examination of a single In$_2$O$_3$ nanowire made from 10 nm Au cluster. The Au/In alloy particle, with a diameter around 10 nm, can be clearly seen at the very tip of the nanowire. The electron scattering cross section of the gold atom is larger than that of In$_2$O$_3$, and hence the Au/In alloy nanoparticle appears darker than the In$_2$O$_3$ nanowire in Figure 2a. The In$_2$O$_3$ appears rather homogeneous without any domain boundaries, indicating the single-crystalline nature of our material, as expected from the VLS growth mechanism. The nanowire diameter (~10 nm) is apparently consistent with the diameter of the catalytic particle. The highly crystalline nature of our In$_2$O$_3$ nanowires was further confirmed by selective-area electron diffraction. Figure 2b shows an SAED pattern, recorded perpendicular to a nanowire long axis. By analysis the SAED pattern, we can estimate the nanowire takes a cubic crystal structure with a lattice constant of 1.03 nm, also consistent with that of the bulk In$_2$O$_3$ ($a = 1.01$ nm). In addition, indexing the pattern demonstrates that the [110] direction is the nanowire growth direction. We performed TEM examination and SAED over many nanowires made from both Au film and cluster samples and also at different location along each nanowire. Similar diffraction pattern have always been observed.

The above-mentioned growth and characterization method allowed us to convincingly establish the diameter-controlled growth of In$_2$O$_3$ nanowires by using three kinds (10±1.5 nm, 20±2.0 nm, 30±3.0 nm) of Au clusters as the catalytic parti-
cles. Figures 3a, c, and e are typical TEM images of In$_2$O$_3$ nanowires grown from these clusters. A direct connection between the catalytic particle size and the nanowire diameter is clearly visible. TEM inspection was performed over fifty nanowires for each kind of gold clusters to generate the wire diameter distribution shown in Figures 3b, d, and f. The mean nanowire diameters are $10.9 \pm 1.1$ nm, $20.6 \pm 2.5$ nm, $30.1 \pm 2.4$ nm, respectively. From these histograms, we can see the width of the nanowires mirrors the colloid catalyst particle size very well.

The ability to produce nanowires of small and uniform diameters is especially important for fundamental studies such as their electronic properties. In$_2$O$_3$ is known to be non-stoichiometric n-type semiconductor in the bulk form due to the O$_2$ deficiency.$^{[15]}$ To our best knowledge, we have made the first In$_2$O$_3$ nanowire field-effect transistors (FETs). A degenerately doped silicon wafer covered with 500 nm SiO$_2$ was used as the substrate, on which In$_2$O$_3$ nanowires of 10 nm in diameter were deposited. Photolithography was performed, followed by evaporating Ti/Au to contact both ends of the nanowires. A typical SEM image of our device is shown in Figure 4b inset, indicating a channel length of 3 μm between the source and drain electrodes. The silicon substrate was used as a back gate. Figure 4a shows a family of current–voltage ($I-V_{ds}$) curves of an In$_2$O$_3$ FET under various gate biases ($V_g$). The $I-V_{ds}$ curve for $V_g=0$ V displays a linear resistance of 70 MΩ with enhanced conductance at higher bias, indicating the electrical contacts are not completely ohmic. However, a positive gate bias of 5 V led to substantially enhance conduction (~6 MΩ) and also a linear $I-V$ curve, indicating n-type semiconductor behavior. This is further confirmed as a negatively increasing gate bias gradually reduced the conduction. With $V_g=-25$ V, the conduction was almost completely suppressed between $V_{ds}=-1.0$ V and $V_{ds}=0.8$ V. Figure 4b shows an $I-V_g$ curve measured at $V_{ds}=10$ mV, where $V_g$ was swept from ~30 V to 30 V. We can see the nanowire was conductive at $V_g=0$ V, but can be depleted with a $V_g$ below ~4 V. Current saturation was observed for $V_g>10$ V, as the conduction in this regime was limited by the contact resistance between the nanowire and the electrodes. A slight decrease in the current was further observed for $V_g>15$ V. This is likely due to a slight degradation of the carrier mobility under high gate bias, which brought electrons closer to the nanowire/SiO$_2$ interface and therefore led to enhanced electron scattering with the boundary of the nanowire and interface traps. Similar phenomena were observed with nanotubes transistors before.$^{[20]}$ The on/off ratio of our device can reach as high as 1000. From these data, it is possible to estimate the electron concentration and the mobility.$^{[21,22]}$ The total charge on the nanowire is $Q=C \cdot V_{g,\text{th}}$, where $C$ is the nanowire capacitance and $V_{g,\text{th}}$ the threshold voltage necessary to completely deplete the wire. The capacitance of nanowire is given by $C \approx \frac{2\pi \varepsilon \varepsilon_0 L}{\ln(2h/r)}$, where $\varepsilon$ is the dielectric constant, $h$ is the thickness of the silicon oxide layer, and $r$ and $L$ are the radius and length of the In$_2$O$_3$ nanowire. Using $L=3$ μm, $r=5$ nm, $h=500$ nm, and $\varepsilon=3.9$, we deduce a one-dimensional electron density of $n \approx \frac{Q}{eL} \approx 1.02 \times 10^7$ cm$^{-1}$ from...
Experimental

Si/SiO₂ substrates were cleaned in acetone and isopropanol. For growth with thin gold films as the catalyst, the substrates were coated with 20 Å Au using a Temescal e-beam evaporator, followed by baking in Ar atmosphere for half an hour to break the Au films into nanoparticles. For growth with nanoclusters as the catalyst, the substrates were coated with a layer of gold clusters (Ted Pella). Three kinds of clusters with diameters of 10 ± 1.5 nm, 20 ± 2.0 nm, 30 ± 3.0 nm were used, and atomic force microscopy (Digital Instruments Dimension 3100) was performed to confirm these nanoclusters distributed uniformly across the surface. The substrates were loaded into a quartz tube at the downstream end of a furnace, and an InAs (Alfa Aesar, 99.999 %) target was placed at the upper stream of the furnace. The system was first pumped to a base pressure below 1 mTorr, and then Ar mixed with 0.02 % O₂ was flown through the system at a rate of 150 sccm, while the InAs target was ablated to supply the indium vapor. During the laser ablation process, the chamber was maintained at 220 torr, 770 °C. A pulsed Nd:YAG laser (Continuum) (L = 532 nm) with repetition rate of 10 Hz, and a pulse power of 1.0 W was used. The typical reaction time used was about 35 min. After the furnace cooled down to room temperature, light gray materials were found on the surface of the substrate.

The crystal structure of the nanowires was characterized using XRD (Rigaku RV - 200) and SAED (Phillips, 420 operated at 120 KeV). The nanowire diameters were usually determined from TEM (Phillips, 420 operated at 120 KeV) and the lengths were measured from SEM (Phillips XL30 operated at 15 KeV) images.

For electronic transport studies In₂O₃ nanowires of 10 nm in diameter were sonicated in 1 h in isopropanol, and then several drops were deposited onto a degenerately doped silicon wafer covered with 500 nm SiO₂. Photolithography was performed, followed by evaporating Ti/Au to connect both ends of the nanowires. Devices with a single In₂O₃ nanowire between the source and drain electrodes were chosen for further studies after a thorough SEM inspection. The electrical measurements were carried out using a semiconductor parameter analyzer (Agilent 4156B).

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An Unusual Electrochromic Device Based on a New Low-Bandgap Conjugated Polymer**

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Over the past few years, electrochromic devices (ECDs) using electrochemically active conjugated polymers have been widely investigated. Interest in these materials is due to their advantageous properties such as low fabrication cost, processability, and dynamic, color-tunable “smart windows”, [1-2] Conjugated polyheterocyclic polymers, such as polyanilines, polypyridines, polypyrroles, poliothiophenes, and in particular, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have been studied as electrochromic materials. [3,4] These materials provide color changes within the visible spectrum, and some exhibit electrochromism, changing from a transparent doped state to a colored neutral state. As a decrease of absorption in the transparent doped state is accompanied by an increase of absorption in the infrared region, the application of a conducting-polymer-based “smart window” can be extended to infrared ranges. Infrared modulation devices show great potential in devices such as a vari-

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引起的电荷迁移率。它的功能性还可以通过在导电层下方添加的涂敷层来改善，以提高其在红外区域的应用。电致色变导电-聚合物基“智能窗口”可以扩展到红外范围。红外调制设备具有巨大潜力，因为它们能够在多种条件下工作，例如在温度变化时。