

Laser Ablation Synthesis and Electron Transport
Studies of Tin Oxide Nanowires**By Zuqin Liu, Daihua Zhang, Song Han, Chao Li, Tao Tang,
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One-dimensional metal oxide nanowires, such as In_2O_3 ,^[1] ZnO ,^[2] SnO_2 ,^[3] CdO ,^[4] and CuO ^[5] nanowires, have attracted a lot of attention because of their unique properties for applications ranging from nanoelectronic devices to gas sensors. Among them, SnO_2 is particularly interesting and has many important applications. For instance, SnO_2 is a very important n-type semiconductor with a large bandgap ($E_g = 3.6$ eV at 300 K^[6]), thus making it ideal to work as transparent conducting electrodes for organic light emitting diodes and solar cells.^[7–9] In addition, SnO_2 thin films have been extensively studied and used as chemical sensors for environmental and industrial applications.^[7–9] SnO_2 in the nanowire form has enormous potential to work as building blocks for nanoelectronics, and is also expected to offer superior chemical sensing performance due to the enhanced surface to volume ratio. Despite the utmost importance, only a relatively small effort has been directed toward the synthesis of SnO_2 whiskers, nanorods, and more recently nanobelts.^[3,10–12] Much is left to be explored, especially for the synthesis of high-quality, single-crystalline SnO_2 nanowires with precisely controlled diameters below 30 nm, as required for high-performance field-effect nanowire transistors. In this paper, we report an efficient and reliable laser-ablation approach for large-scale synthesis of SnO_2 nanowires. Precise control over the nanowire diameters has been achieved by using monodispersed gold clusters as the catalyst. Detailed material analysis, such as transmission electron microscopy (TEM) and X-ray diffraction (XRD), were used to confirm the single-crystalline nature of our nanowires. In addition, field effect transistors (FETs) have been constructed based on individual SnO_2 nanowires with on/off ratios up to 10^3 . These nanowire transistors were further demonstrated to work as sensitive UV and polarized UV detectors.

A quartz tube furnace was used for our SnO_2 synthesis, where a pure Sn target was placed at the upper-stream of the tube outside the hot zone of the furnace, and Si– SiO_2 substrates covered with 20 nm gold catalytic clusters were placed in the middle of the quartz tube. The tube was then purged with 0.02 % oxygen diluted in argon, followed by heating of

the furnace to 900 °C. The Sn target was then ablated with a Nd:YAG laser to supply Sn vapor, which was carried downstream by the oxygen–argon mixture. The chamber was maintained at 400 torr during the laser ablation, and the typical reaction time used was about 10–30 min. Our synthesis follows the well-known vapor–liquid–solid (VLS) growth mechanism, where the Sn vapor first diffuses into the gold catalytic particles, and grows out and reacts with O_2 to form SnO_2 once the Sn–Au alloy reaches supersaturation. Continued addition of Sn into the Sn–Au nanoparticle feeds the SnO_2 growth and eventually the diameter of the SnO_2 nanowire is directly linked to the catalytic particle size. After cooling down, the samples were characterized using scanning electron microscopy (SEM), TEM, selected area electron diffraction (SAED), and XRD. The nanowire diameters were usually determined from TEM and the lengths were measured from SEM images.

Figure 1a shows a typical SEM image of SnO_2 nanowires grown atop the Si– SiO_2 substrates decorated with gold clusters. Most of the nanowires have smooth sidewalls and appear

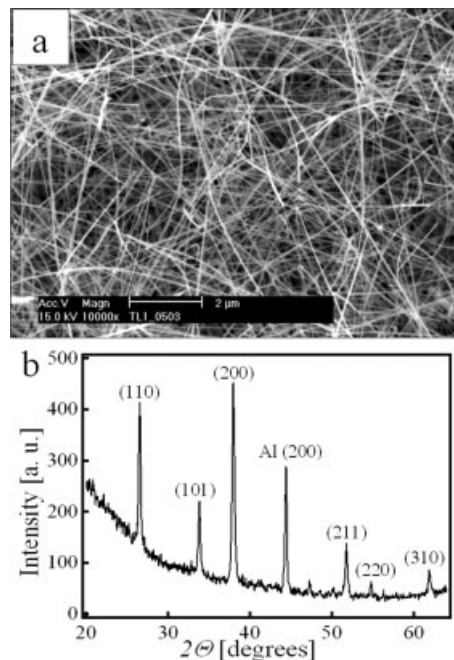


Fig. 1. a) SEM image of tin oxide nanowires grown on a Si– SiO_2 substrate. b) XRD pattern of SnO_2 nanowires obtained on Si– SiO_2 substrate.

rather straight. Detailed TEM and SEM examinations show that these nanowires have diameters around 20 nm and lengths on the order of 10 μm , indicating an aspect ratio of $\sim 500:1$. Further analysis by XRD is depicted in Figure 1b. Six of the diffraction peaks can be indexed to the (110), (101), (200), (211), (220), and (310) crystal planes of the rutile structure of bulk SnO_2 with lattice constants $a = b = 4.750$ Å, and $c = 3.198$ Å. One peak corresponding to Al (200) can also be identified and is attributed to the aluminum sample holder used in our XRD system. All of our SnO_2 nanowire samples showed similar XRD patterns, indicating high crystallinity of the nanowires.

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TEM examination was carried out to further determine the nanowire crystal structure and confirm the VLS growth mechanism. The nanowires were sonicated into a suspension in isopropanol and then deposited onto a TEM grid. Figure 2 shows a TEM image of a thin nanowire of 16 nm in diameter. An Au–Sn alloy can be clearly identified at the tip of the nano-

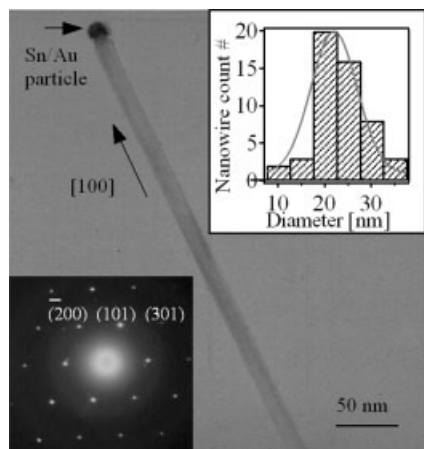


Fig. 2. TEM image of a SnO₂ nanowire with a catalyst at the tip. Lower inset: SAED pattern taken perpendicular to the nanowire long axis. Upper inset: Histograms of the nanowire diameter distributions. The solid line is a Gaussian fit.

wire, thus confirming our synthesis followed the VLS approach. Such alloy tips were consistently observed with all SnO₂ nanowires. The nanowire appeared homogeneous and free of domain boundaries under TEM observation even with the sample tilted, indicating the single-crystalline nature of our nanowires. This is further confirmed by the sharp SAED pattern (Fig. 2 lower inset) recorded perpendicular to the nanowires' long axis. Analysis of the SAED pattern revealed that the nanowires have the rutile crystal structure with lattice constants $a = b = 4.740 \text{ \AA}$ and $c = 3.196 \text{ \AA}$, consistent with the values for bulk SnO₂. In addition, indexing the pattern demonstrates that our SnO₂ nanowires grow along the [200] crystal direction. We performed TEM examination and SAED of many nanowires and also at different locations along each nanowire. Similar diffraction patterns have always been observed. Furthermore, we have used TEM to determine the diameter of an ensemble of 53 nanowires, and a histogram of the diameter distribution is shown in the upper inset of Figure 2. The majority of the nanowires have diameters between 15 nm and 25 nm, and the distribution can be well fitted with a Gaussian curve peaked at 19.4 nm. This convincingly demonstrates the precise control over the nanowire diameter we can achieve by using monodispersed gold clusters, an important advantage of the VLS approach.

The ability to produce SnO₂ nanowires of small and uniform diameters paved the way for using them as building blocks for nanoelectronics. SnO₂ is known to be a non-stoichiometric n-type semiconductor in the bulk form due to the O₂ deficiency.^[6] We have made SnO₂ nanowire FETs based on our successful synthesis. A degenerately doped silicon wafer covered with 500 nm SiO₂ was used as the substrate, on

which SnO₂ nanowires of 20 nm in diameter were deposited. Photolithography was performed, followed by evaporating Ti–Au to contact both ends of the nanowires.^[13] A typical SEM image of our device is shown in Figure 3a inset, indicating a channel length of 3 μm between the source and drain electrodes. The silicon substrate was used as a back gate. Fig-

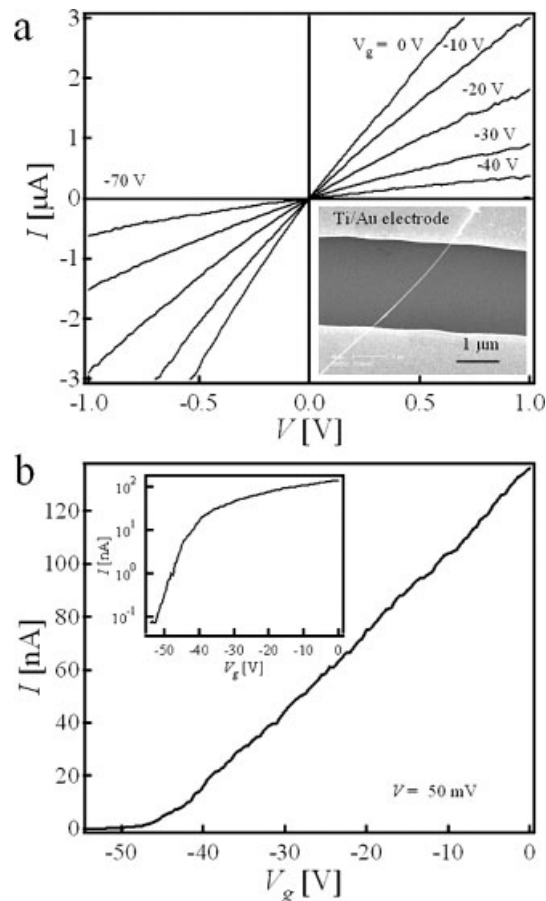


Fig. 3. Electrical transport of SnO₂ nanowires. a) Gate-dependent I – V curves recorded at room temperature. Inset: SEM image of a SnO₂ nanowire between two Au–Ti electrodes. b) I – V_g curve recorded at $V = 50 \text{ mV}$. Inset: Semi-log plot of the I – V_g curve showing an on/off ratio of ~ 1000 .

ure 3a displays six current–voltage (I – V) curves of the device recorded in vacuum under gate bias $V_g = 0, -10, -20, -30, -40, -70 \text{ V}$, respectively. An almost linear I – V curve was observed under $V_g = 0 \text{ V}$, with a zero-bias conductance of $4.4 \times 10^{-6} \text{ S}$ (227 k Ω), indicating ohmic contacts were achieved. With negatively increasing gate voltage ($0 \text{ V} \rightarrow -70 \text{ V}$), the conductance of the device was gradually suppressed, as expected for n-type nanowire transistors. More information regarding the gate dependence can be obtained by sweeping the gate voltage with a fixed drain-source bias of 50 mV, as shown in Figure 3b. The current decreased dramatically from 120 nA at $V_g = 0 \text{ V}$ to 80 pA at $V_g = -52 \text{ V}$, indicating an on/off ratio exceeding 10^3 , as evident in the semi-log plot of I – V_g in Figure 3b inset. The one-dimensional doping concentration of the nanowire can be estimated as $n = CV_T/eL$, where V_T is the threshold voltage (-45 V for the device in Fig. 3), e is the

electron charge, L is the nanowire channel length, and C is the nanowire capacitance estimated to 1.4×10^{-18} F.^[14,15] This leads to a doping concentration of 1.5×10^8 cm⁻³. In addition, the mobility of the electrons can be deduced from the transconductance of the FET. In the linear regime, it is given by $dI/dV_g = \mu(C/L^2)V$. From Figure 3b, we get $dI/dV_g = 3.1 \times 10^{-9}$ A V⁻¹ at $V = 50$ mV, corresponding to an electron mobility of 40 cm² V⁻¹ s⁻¹.

Inspired by the excellent photoconduction and light-enhanced chemical sensing properties of SnO₂ bulk materials,^[6] we have further studied the UV response of our SnO₂ nanowire transistors described above, and a strong modulation of the conductance by UV illumination was observed. Our experiment involved a UV lamp of 254 nm in wavelength fixed at a distance of approximately 2 cm away from the nanowire transistor, which was kept under practical conditions, i.e., in air, at room temperature, and under indoor incandescent light during the measurements. Figure 4a shows the current measured over time at constant $V = 50$ mV and $V_g = -10$ V, and

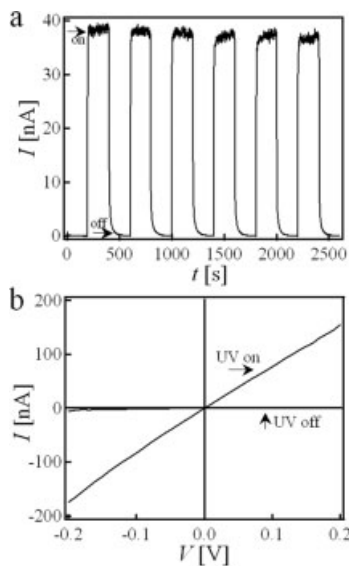


Fig. 4. UV response of a SnO₂ nanowire transistor. a) Current versus time recorded with the UV illumination turned on and off repeatedly. b) I - V curves taken with the UV illumination on and off.

the conduction modulation was induced by turning a shutter for the UV lamp on and off six times. The current was observed to increase dramatically and stabilize at a high-conductivity “on” state upon UV exposure, whereas it decreased quickly and landed at a low-conductivity “off” state after the UV light was blocked, leading to an on/off ratio as high as 10^3 . The response time of the device, defined as the time duration for the conductance to change by one order of magnitude,^[16] is less than 0.1 s. Figure 4b displays two I - V curves taken with the device in the “on” and “off” states, respectively. The device in the “on” state exhibited a linear I - V curve and a high conductance ~ 760 nS, whereas the device in the “off” state exhibited a minimal conduction of 0.66 nS. Two major mechanisms may account for the UV response of our SnO₂ nanowires. First of all, for UV light of 254 nm in wavelength, each

photon has the energy of 4.9 eV, which is sufficiently large to excite electrons directly from the valence band into the conduction band. This subsequently leads to enhanced carrier concentrations and significantly more conduction. The second mechanism is related to the desorption of oxygen and moisture species off the nanowire surface through reactions like $h^+ + O_2^- \rightarrow O_2$.^[17] This process serves to cleanse the adsorbed oxidative species and also result in enhanced conduction. Overall our results indicate that SnO₂ nanowires are highly sensitive to UV light and the observed high on/off ratios may bode well for SnO₂ nanowires to work as UV detectors.

Besides working as photodetectors, semiconducting nanowires are also expected to discriminate different polarization states of the incident radiation due to their one-dimensional nature.^[18,19] Early studies have focused on GaAs–AlAs or InAs–InP nanowires fabricated by the cleaved edge overgrowth method for polarized infrared radiation.^[18] Similar structures for polarized UV detection will likely require cleaved edge overgrowth of nitride (InGaN–AlN) nanowires, which have not been reported so far presumably due to the apparent difficulty involved. SnO₂ nanowires possess both one-dimensional structures and a bandgap in the UV regime, and thus present an excellent opportunity for polarized UV studies. The “polarization detection” measurements were carried out with the experimental setup shown in Figure 5a, where a rotating polarizer was mounted in front of the nano-

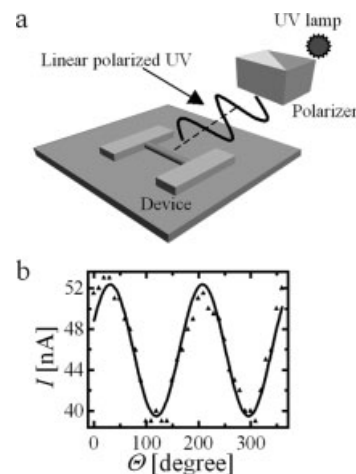


Fig. 5. a) Schematic depicting of the experimental setup for polarized UV detection. b) Current versus the angle of the polarizer. Discrete symbols are experimental data points, and the solid line shows a fit to $I_0 + I_1 \cos^2 \theta$.

wire FET to linearly polarize the incoming UV light. Figure 5b shows a plot of the current of the SnO₂ nanowire ($V = 50$ mV, $V_g = 0$ V) as a function of the angle θ of the polarizer. The current exhibited significant cyclic behavior and can be fitted well to the function of $I_0 + I_1 \cos^2 \theta$ with $I_0 = 39.5$ nA and $I_1 = 12.8$ nA, respectively, as can be seen from the solid curve in Figure 5b. The maximum (minimum) current was obtained when the UV light was polarized parallel (perpendicular) to the nanowire long axis. This is consistent with previous experiments using carbon nanotubes^[19] and

InP nanowires^[20] for polarized light detection, and is attributed to the polarization-dependent light absorption due to the dielectric contrast between the nanowire and its surroundings. Because of the confinement in the nanowire radial direction, where the nanowire diameter is far smaller than the incident wavelength, an incident electric field that is perpendicular to the nanowire would be effectively attenuated compared to the electric field parallel to the nanowire, therefore leading the observed polarization-dependent photocurrent.^[20] The current ratio for parallel and perpendicular excitation is around 4:3, comparable to the ratio obtained with single-walled carbon nanotube polarization infrared detectors.^[19] The non-zero current measured with the UV radiation polarized perpendicular to the nanowire is likely caused by depolarization of light when scattered by the nearby metal electrodes. Theoretical simulations are currently underway for a better understanding. We stress that our results represent a significant step toward using nanowires as polarized UV detectors and further optimization will lead to even better performance.

In summary, high-quality and large-quantity tin oxide nanowires were synthesized using a laser ablation technique and their composition and single crystalline structures were confirmed using XRD, TEM, and SAED. The growth mechanism was confirmed to follow the vapor–liquid–solid model. Precise control over the nanowire diameter was achieved by using mono-dispersed gold clusters as the catalyst. Field-effect transistors were made based on our SnO₂ nanowires, and excellent n-type transistor characteristics have been observed with threshold voltages ~ -50 V and on/off ratios of $\sim 10^3$ at room temperature. Photoconduction properties of SnO₂ nanowires were also studied based on our devices, where a strong modulation of the conductance by UV illumination was observed. Typical devices showed substantial increases in conductance up to four orders of magnitude upon UV illumination. SnO₂ nanowire transistors have furthermore been found to work as polarized UV detectors.

Experimental

Tin oxide nanowires were prepared using a pulsed Nd:YAG laser with a repetition rate of 10 Hz and a pulse power of 1.0 W. A pure Sn (Alfa Aesar, 99.995 %) target was mounted at the upper-stream of a quartz tube furnace and then ablated to supply the vapor, which was carried downstream by diluted oxygen in argon. SiO₂-Si substrates coated with Au nanoparticles were placed at the downstream of the tube furnace with the Au particles serving as the catalyst for growth. The reaction was typically carried out around 900 °C for 10–30 min with 100 standard cubic centimeters per minute Ar–O₂ mixture flowing. The chamber pressure was controlled at 400 torr during the growth.

The as-synthesized nanowires were characterized and identified using XRD (Rigaku RV-120 apparatus, Cu K α = 1.5418 Å radiation), SEM (Philips XL30 apparatus operated at 15 keV), and TEM (Phillips 420 apparatus operated at 120 keV).

SnO₂ nanowires field effect transistors were made by first depositing the nanowires onto Si–SiO₂ substrates, followed by photolithography and successive deposition of 4 nm Ti and 50 nm Au to work as the source and drain electrodes. *I*–*V* measurements were performed by applying a bias to the drain electrode and using the silicon substrate as a back gate. Photoconduction properties of SnO₂ nanowires were also studied based on our devices by using a UV lamp of 256 nm in wavelength with a power density of 3 mW cm⁻². All the electrical

measurements were carried out using a semiconductor parameter analyzer (Agilent 4156B apparatus).

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Exfoliation of Single-Walled Carbon Nanotubes by Electrochemical Treatment in a Nitric Acid**

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Single-walled carbon nanotubes (SWNTs) usually exist in the form of bundles due to the strong van der Waals interactions between the long tube walls. However, applications of SWNTs to electronic and energy storage devices often require an individual nanotube or at least well-dispersed nanotubes. Simple sonication of SWNTs in distilled water with small addition of surfactant often damages the nanotube walls.^[1] Stirring SWNTs in a H₂SO₄/HNO₃ (3:1) solution creates defects

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