ZnO Nanowire and WS_2 Nanotube Electronics

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Abstract—**In this paper, we report on the synthesis and applications of semiconducting nanostructures. Nanostructures of interest were zinc oxide (ZnO) nanowires and tungsten disulfide (WS_2) nanotubes where transistors/phototransistors and photovoltaic (PV) energy conversion cells have been fabricated. ZnO nanowires were grown with both high- and low-temperature approaches, depending on the application. Individual ZnO nanowire side-gated transistors revealed excellent performance with a field-effect mobility of 928 $\mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$. ZnO networks were proposed for large-area macroelectronic devices as a less lithographically intense alternative to individual nanowire transistors where mobility values in excess of 20 $\mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$ have been achieved. Flexible PV devices utilizing ZnO nanowires as electron acceptors and for photoinduced charge separation and transport have been presented. Phototransistors were fabricated using individual WS_2 nanotubes, where clear sensitivity to visible light has been observed. The results presented here simply reveal the potential use of inorganic nanowires/tubes for various optoelectronic devices.**

Index Terms—**Nanotubes, nanowires, solar cells, transistors, tungsten disulfide, zinc oxide.**

I. Introduction

Due to their unique structural one dimensionality, semiconducting nanotubes and nanowires exhibit novel electronic and optical properties. These one dimensional (1-D) semiconductor nanostructures, with a broad selection of chemistries and band structures, are the essential components in a wide range of novel nanoscale device applications [1]–[11]. Current research is directed toward the exploration of new synthesis methods, characterization tools for exploiting novel properties, controlled assembly, and fabricating devices utilizing these nanostructures [12]–[17]. This paper focuses on the synthesis and applications of ZnO nanowires and WS_2 multiwalled nanotubes in particular and highlights recent developments on these nanostructures through work carried internationally in collaboration between a number of laboratories.

An overarching theme in the work reported is the exploration of electronics on flexible substrates through the use of nanowires. Unlike thin films where the formation of the active semiconducting film occurs directly on the substrate on which the device/circuit is formed, nanowire synthesis can take place externally on substrates under optimum growth conditions. Given the nanoscale nature of the synthesized semiconducting structures, they can then be dispersed, for example, by using techniques such as spin coating, stamping, or printing, at low temperatures onto virtually any substrate. The performance of the resulting devices is then governed by the "ensemble" behavior of the semiconducting nanowires/tubes. Compared to the alternative of using organic films which are deposited from a liquid state and then solidified for flexible substrate electronics, inorganic nanowires have the advantage of not being as sensitive to the environment and being able to operate without the need for hermetic sealing.

One of the particularly exciting application areas where nanowires enable electronics on flexible substrates is clothing. The emerging vision of that is having clothing with integrated electronic circuits which allow sensing of the environment and body functions on clothing, with low-bandwidth communications as in RFID. In this paper, we show results from the application of ZnO and WS_2 nanowires/tubes to some basic elements which would be required to realize such a system. These include transistors, PV energy conversion cells, and visible-light sensing.

This paper describes our efforts toward nanowire/nanotube electronics. In particular, we have utilized ZnO nanowires and WS_2 nanotubes for the fabrication of devices. Towards this end, in the first part, synthesis methods for these nanostructures are

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described. We have utilized both high-temperature chemical vapor deposition (CVD) method and low-temperature hydrothermal method for the synthesis of ZnO nanowires. We have developed a technique in which commercially available microwave oven is used for the rapid synthesis of ZnO nanowires at low temperatures on various substrates. It is then followed by the WS_2 nanotube synthesis. In the second part, we describe our work on PV devices and transistors utilizing nanowires and nanotubes. ZnO nanowires were used to fabricate organic PV (OPV) devices and photoelectrochemical devices. ZnO nanowires grown at lower temperatures directly on single-walled carbon nanotube (SWNT) networks were used for the fabrication of flexible OPV devices, whereas ZnO nanowires grown at higher temperatures directly on carbon fibers were used for the fabrication of photoelectrochemical devices. ZnO nanowire/carbon fiber composite was found to be a promising anode material for the fabrication of flexible dye-sensitized solar cells (DSSCs). Individual field-effect transistors (FETs) with ZnO nanowires are also presented in the second part. We then report a new class of material, ZnO nanowire networks, for the fabrication of macroelectronic devices which could bring the interesting properties of ZnO nanowires and the fabrication ease of various optoelectronic devices. Finally, we present phototransistors with individual WS_2 nanowires where clear response to visible light has been detected.

II. MATERIAL GROWTH AND CHARACTERIZATION

A. Microwave Growth of ZnO Nanowires

Among semiconducting oxide nanowires, ZnO is one of the most promising materials with its direct wide bandgap ($E_g =$ 3.37 eV at 300 K) and relatively large exciton binding energy (~60 meV). The field of ZnO nanowire research is reaching maturity through the demonstration of various electronic and optoelectronic devices such as UV nanolasers, FETs, solar cell electrodes, and nanogenerators [18]–[21]. ZnO nanowires are synthesized by the following two primary methods: gas condensation using catalytic reactions [22]–[24] and hydrothermal method [25], [26]. It is possible to produce ZnO nanowires at low temperatures and atmospheric pressure over large areas on any type of substrate by using the hydrothermal method. Due to its versatility and simplicity, the hydrothermal ZnO nanowire synthesis method has been engineered by many researchers. It has been shown that ZnO nanowires can be aligned [27] and patterned [28] and that their growth direction can be controlled [29] using the hydrothermal method. A major problem associated with the hydrothermal synthesis is the time required for the synthesis of nanowires spanning from several hours to days which necessitate the development of a rapid technique for large-area growth of ZnO nanowires.

We have reported on the use of microwave heating for the rapid hydrothermal synthesis of aligned ZnO nanowires on various substrates where the average growth rate of nanowires is determined to be as high as 100 nm/min [30]. ZnO nanowires were hydrothermally grown based on the method developed by Greene *et al.* [25], [26]. Specifically, a 10-mM solution of zinc acetate dihydrate (98%, Aldrich) and 1-propanol (spectroscopic grade) was prepared. The solution was then spin coated on n-type silicon [(100), $R = 0.015$–$0.025\ \Omega \cdot \mathrm{cm}$], glass, and poly(ethylene terephthalate) (PET) substrates at 2000 r/min for 30 s. The substrates were annealed at 100 °C for 1 min after each spin coating to enhance adhesion. A uniform seed layer was obtained after three layers of spin coating. Vertical ZnO nanowires were then grown by dipping the substrates in a mixture of equimolar 25-mM zinc nitrate hexahydrate ($\mathrm{Zn(NO_3)_2 \cdot 6H_2O}$, Sigma Aldrich) and hexamethylenetetramine (HMTA, Sigma Aldrich) solution in deionized (DI) water (resistivity of 16 $\mathrm{M\Omega \cdot cm}$) and heating with a commercially available microwave oven (2.45 GHz) at different power settings (120, 385, and 700 W) at atmospheric pressure for 1–30 min. A turntable inside the microwave revolved at 4 r/min to ensure homogeneous heating of the solution. For comparison purposes, several samples were grown at 90 °C using a furnace. At the end of the growth, substrates were removed from the growth solution, rinsed with DI water, and dried under nitrogen flow.

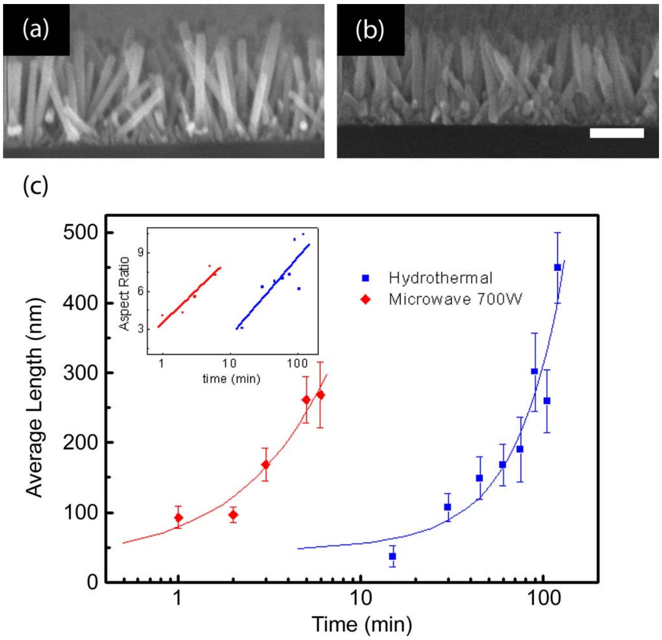

Fig. 1. SEM images of ZnO nanowire arrays grown in (a) furnace for 90 min and (b) microwave at 700 W for 6 min. Scale mark: 200 nm. (c) Axial growth rates of samples grown with microwave heating as compared to hydrothermal growth with standard deviation. Polynomial fits were shown for visualization. The inset shows the aspect ratio of the same samples.

Microwave heating was found to shorten the growth time without altering the structure and optical properties of the nanowires. The cross-sectional scanning electron microscopy (SEM) images of the ZnO nanowire arrays with the same length that are grown in the furnace for 90 min and at 700 W for 6 min are shown in Fig. 1(a) and (b), respectively. The effect of microwave heating and power on enhancing the aspect ratio can be clearly seen. The axial (length) growth rates of the samples are shown in Fig. 1(c).

The aspect ratios of the ZnO nanowires are shown in the inset. As with furnace heating, microwave heating was found to enhance both the axial and lateral growth rates of the nanowires, where the former was found to be a lot quicker than the latter. The effect of microwave growth can be observed as compared

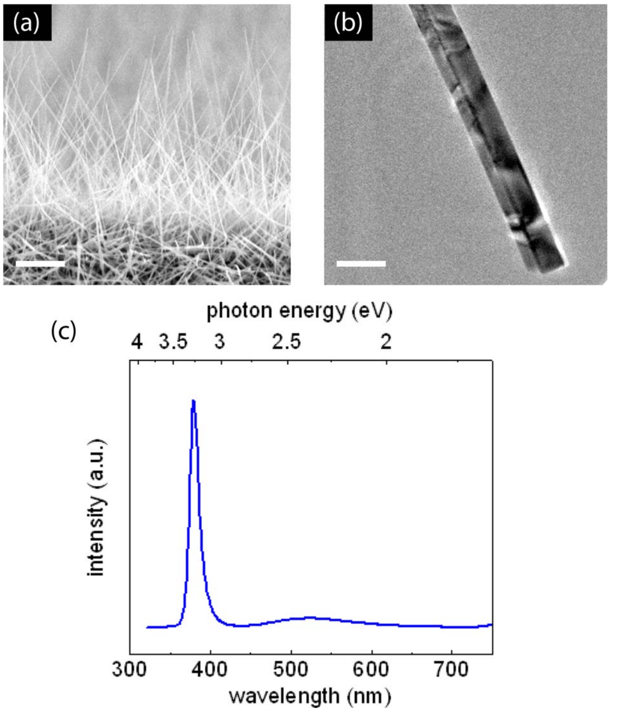

Fig. 2. SEM image of the CVD-grown ZnO nanowires on silicon substrates. The scale bar corresponds to 4 μm. (b) TEM image of the nanowires. The scale bar corresponds to 100 nm. (c) PL spectra of the CVD-grown nanowires.

to furnace heating. This can be attributed to the rapid heating of the reaction precursors to the crystallization temperature, and the shorter crystallization times associated with the rapid dissolution of precipitated hydroxides by microwave heating. Samples grown at high microwave powers (700 W) revealed growth rates 15 times faster than the hydrothermal growth rates in our experiments. It has also been shown that it is possible to grow patterned ZnO nanowires over large areas by using this simple and rapid microwave heating method which could be easily applied to other nanomaterials synthesis processes.

B. Chemical Vapor Deposition Growth of ZnO Nanowires

ZnO nanowires were synthesized by the CVD method via carbothermal reduction of ZnO nanopowders at 860 °C on gold-deposited silicon substrates [31]. Typical growth pressure and time were 3 mbar and 30 min, respectively. Fig. 2(a) shows the SEM image of the as-grown ZnO nanowires which are 5–7 μm long and 40–60 nm in diameter. Detailed transmission electron microscope (TEM) analysis [Fig. 2(b)] revealed the defect-free nature of the ZnO nanowires. Fig. 2(c) shows the photoluminescence (PL) spectra taken from ZnO nanowires grown on silicon samples. The PL spectra showed a strong UV peak with a full-width-at-half-maximum value of 13 nm. Defect-related broad green peak, with an intensity smaller than that of hydrothermally grown ZnO nanowires, was also observed.

C. WS_2 Nanotube Growth

Fullerene and cylindrical structures occur not only in carbon but also in a variety of inorganic compounds [32]. WS_2 nanotubes were the first among the inorganic nanotubes that came to light, which were synthesized by Tenne *et al.* in 1992 [33]. WS_2 nanotubes are quite similar to carbon nanotubes. They are formed up by a rolled up 2-D layered WS_2 sheet, consisting of one or more sets of triple layers including a layer of tungsten atoms sandwiched between two layers of sulfur atoms. These triple layers are stacked together by van der Waals interactions with an interlayer spacing of 6.18 Å [34]. According to the rolling direction of these layered sheets, WS_2 nanotubes present certain chiralities which can be described by two integer indices (n, m). However, unlike carbon nanotubes, they are all semiconducting as the bulk WS_2 material, with direct and indirect band transitions, and their bandgaps vary with the tubes' chirality and diameter $(E_g = 1.8\text{–}2.2\ \mathrm{V})$ [34]. The WS_2 nanotubes used in this paper were synthesized as described in [35]. The TEM analysis revealing their multiwall structure is shown in Fig. 3(a). Fig. 3(b) shows an SEM image of a WS_2 nanotube on the substrate prior to the e-beam lithography step to define the device structure. Fig. 3(c) shows the device prototype.

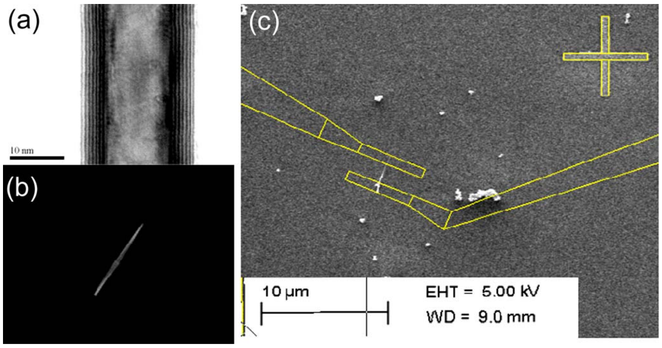

Fig. 3. (a) TEM image of a WS_2 nanotube. (b) SEM image of an individual WS_2 nanotube. (c) SEM image of a WS_2 nanotube FET structure prior to the formation of contacts by e-beam lithography, metal sputtering, and lift-off.

III. ZnO NANOWIRE AND WS_2 NANOTUBE DEVICES

A. OPVs With ZnO Nanowires

1-D inorganic nanotubes and nanowires have been commonly blended with polymers, and devices have been fabricated by solution casting the blend [36]–[39]. 1-D nanostructures not only enhance the exciton dissociation area but also provide direct and efficient electron transport to the respective electrodes. However, problems associated with disordered nanostructures are yet to be solved. Morphological control via ordered microstructures has been proposed, where dimensions of both phases can be controlled to minimize recombination rate and to increase mobility by improving conjugated polymer chain stacking [40]. Recently, it has been shown that hydrothermally grown ZnO nanowires can be used as electron-acceptor molecules in OPVs without the need for the [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) molecule in a nonflexible configuration [41]. We have utilized nanoscale heterojunctions of ZnO nanowires and SWNT thin films as electron-acceptor molecules and transparent conductors, respectively, and poly(3-hexylthiophene) (P3HT) as electron-donor molecules for fabricating flexible OPVs.

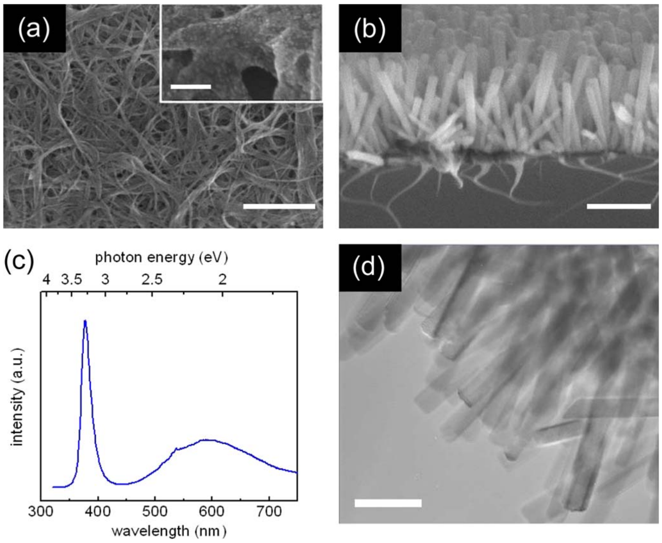

Fig. 4. SEM image of (a) an SWNT thin film. The scale bar is 500 nm. The inset shows the ZnO nanoparticles attached to the SWNT thin films. The scale bar is 100 nm. (b) ZnO nanowires grown hydrothermally on functionalized SWNT thin films. The scale bar is 200 nm. (c) PL spectra. (d) TEM image of the hydrothermal nanowires. The scale bar corresponds to 100 nm.

We have investigated the growth of ZnO nanowires on top of SWNT thin films via hydrothermal method. SWNT thin films are transparent and flexible conductors with tailorable optoelectronic properties [42], and they are potential candidates for indium tin oxide [43] replacement. First, SWNT thin films were transferred onto PET substrates as described in detail elsewhere [44]. In particular, SWNT thin films with optical transparency and sheet resistance of 65% and 320 $\Omega/\square$, respectively, were used for the experiments. Samples were then functionalized by azeotropic nitric acid (69.7% HNO_3) for 3 h and dried with gentle nitrogen flow. Following functionalization, the sheet resistance of the SWNT thin films was found to decrease to 250 $\Omega/\square$. ZnO seed particles were then formed on SWNT thin films by spin coating the aforementioned zinc acetate solution. In this particular case, the spin coating process was repeated ten times, while annealing the substrates at 100 °C for 1 min, after each spin coating step. The SEM image of the SWNT thin film is shown in Fig. 4(a), where uniform coverage of the surface of the PET substrate can be seen. The inset shows high-resolution SEM image of the ZnO nanoparticles, with an average diameter of ~10 nm, attached to the SWNTs. Nitric acid treatment was found to be crucial for uniform attachment of ZnO nanoparticles which led to homogeneous nanowire growth on SWNT thin films. ZnO nanowires were then hydrothermally grown on SWNT thin films using the previously mentioned chemistry in a furnace at 90 °C for 1 h. Fig. 4(b) shows the SEM cross section of the nanoscale heterojunctions of ZnO nanowires grown on SWNT thin films. Fig. 4(c) shows the PL spectra taken from hydrothermally grown ZnO nanowires. The PL spectra showed a strong luminescence peak at 378 nm, corresponding to the near-bandgap emission responsible for the recombination of free excitons in ZnO. Defect-related broad green peak was also observed. The TEM image for the hydrothermally grown ZnO nanowires is shown in Fig. 4(d).

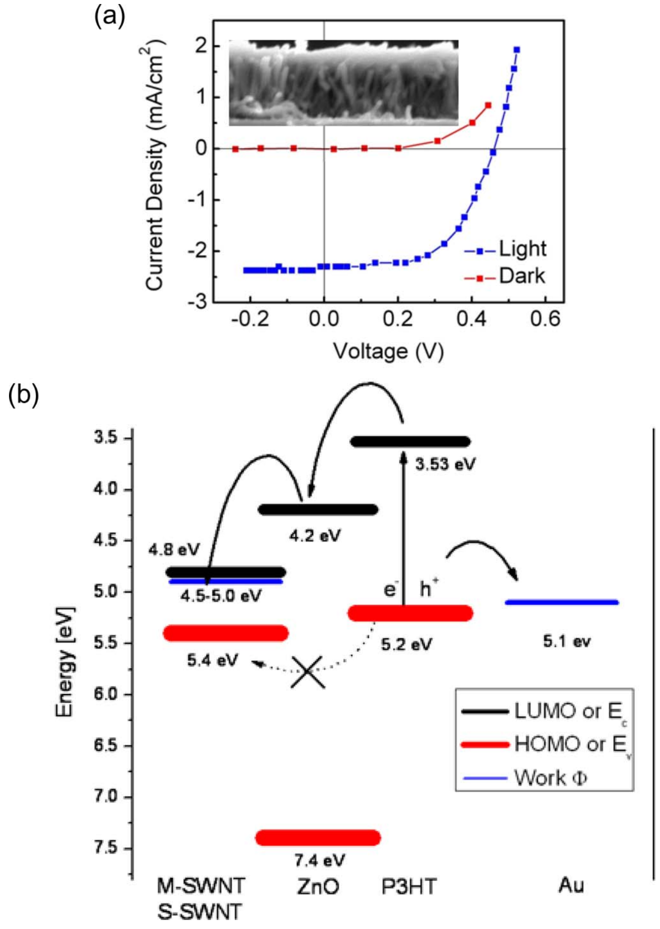

Fig. 5. (a) Energy-level diagram with respect to the vacuum level for the PET-SWNT/ZnO nanowire/P3HT/Au device. The arrows indicate hole and electron flows. m-SWNTs and s-SWNTs refer to metallic and semiconducting SWNTs, respectively. (b) Current density versus voltage curve for the PET-SWNT/ZnO nanowire/P3HT/Au device at AM 1.5 light at 100 mW/cm^2 and in the dark. The inset shows the cross section of the nanowires/P3HT interface. This result is repeated in [45].

For the fabrication of OPVs, P3HT was spin coated on ZnO nanowires grown on SWNT thin films. Regioregular P3HT (Rieke Metals, Inc.) was spin coated at 1000 r/min from a 25-mg/mL chloroform solution, followed by annealing at 120 °C for 10 min under argon atmosphere. The Fig. 5(a) inset shows the SEM cross section of the nanowire/P3HT interface. OPVs were completed by the deposition of 100-nm gold electrode by thermal evaporation. The PV characteristics were evaluated using the PET-SWNT/ZnO nanowire/P3HT/Au device configuration with an AM 1.5 light source (100 mW/cm^2) and compared with the diode characteristics in the dark. The light source intensity was calibrated in milliwatts per square centimeter with a reference Si solar cell. Fig. 5(a) shows the current density versus voltage (J–V) curves for our device which exhibited a photocurrent (J_{sc}) of 2.3 mA/cm^2, an open-circuit voltage (V_{oc}) of 460 mV, and a fill factor (FF) of 0.6 with a conversion efficiency of 0.65%. Results from this paper suggested that ZnO–SWNT heterojunctions can be used in flexible OPVs with their easy fabrication method that is compatible with roll-to-roll processing. In addition, the use of ZnO nanowires instead of functionalized fullerenes (i.e., PCBM) can provide a cost-effective alternative for OPVs. Another advantage of using the wide-bandgap ZnO nanowire as an electron acceptor is that it also acts as a large barrier to holes, as shown in the energy-level diagram in Fig. 5(b). This result is repeated in [45]. This allows, in principle, for effective electron–hole separation and enhanced PV current.

B. Dye-Sensitized ZnO Nanowires Grown on Carbon Fibers for a Photoelectrochemical Cell

DSSCs are promising candidates for replacing commercial silicon-based solar cells [46]–[50]. They provide advantages such as low cost, high efficiency, and low angle dependency on the incident light. The conversion efficiency of liquid-electrolyte DSSCs utilizing fluorine-doped-tin-oxide-coated glass substrates as anode materials has been currently improved to above 11% [51]. Efficiency values for flexible DSSCs, however, are limited. One of the reasons for poor performance is the sintering temperature for the nanoparticles where dye molecules are attached. This imposes a temperature limit on the type of the substrate that could be used for the fabrication. Examples for flexible anode materials include stainless steel sheets, wires, and meshes [52]–[54].

In a DSSC, following the absorption of photons by the dye molecules, excitons are created where they rapidly split to electrons and holes at the nanoparticle interface. Electrons are injected to the nanoparticles where holes travel to the cathode through redox species in an electrolyte. Commonly used anode materials for DSSCs include nanoparticles or thin films of titanium dioxide (TiO_2), tin dioxide (SnO_2), and ZnO that are deposited as a paste and then sintered for electrical continuity. ZnO nanowires as a scaffold for dye molecules in the fabrication of DSSCs recently received a lot of attention, where nanowires provide larger surface areas for higher dye loading [20], [55]–[57].

ZnO nanowires were conformably grown on highly conducting and flexible carbon fibers [58]. Sheet resistance value for the carbon fiber used in the experiments was 1.75 S/cm with a thickness of 80 μm. ZnO nanowire synthesis followed the previously described CVD method without the need of gold catalyst. The SEM image of the ZnO nanowire–carbon fiber composite is shown in Fig. 6(a). Nanowires were approximately 5 μm long. Carbon fibers retained their flexibility and conductivity after the growth of ZnO nanowires. We then demonstrated the implementation of this composite in a photoelectrochemical cell, where ZnO nanowires and carbon fibers were used for photoinduced charge separation/charge transport and current collection, respectively.

Photoelectrochemical measurements were conducted under ambient conditions using a platinum foil as a counter electrode. Pt foil was placed 1 cm away from the composite. Before the measurements, nanowire fiber composite was immersed into an ethanol solution of "black dye" overnight for the attachment of dye molecules [59]. Black dye has a visible absorption extending into the near-IR region up to 920 nm, and its chemical structure is shown in Fig. 6(b). Acetonitrile solution containing 0.1-M LiI and 0.05-M I_2 was used as the electrolyte. Fig. 6(c) shows the J–V curves for the composite obtained in photoelectrochemical measurements. Measurements were made under 100-mW/cm^2 (AM 1.5) illumination and in the dark. The measured open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and FF were 350 mV, 11.2 mA/cm^2, and 0.28, respectively.

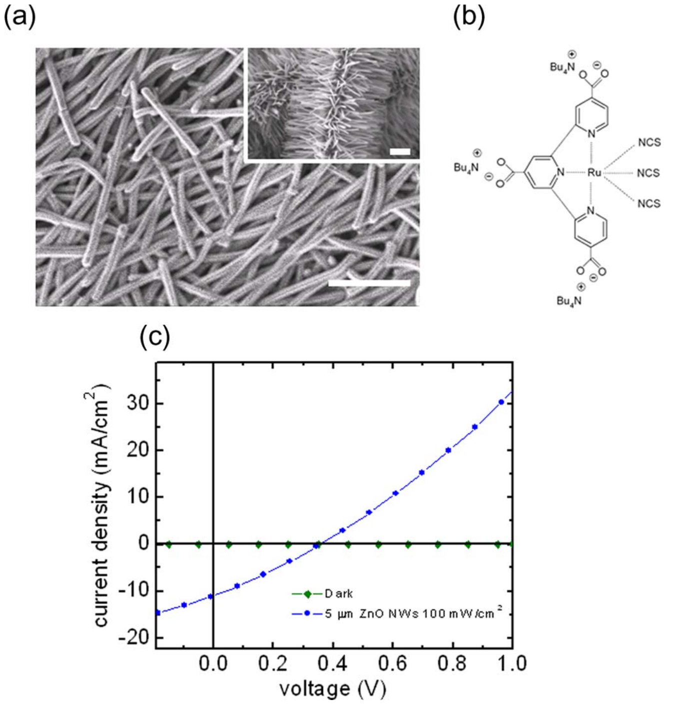

Fig. 6. (a) SEM image of the ZnO nanowire–carbon fiber composite. The scale bar corresponds to 100 μm. The inset shows a high-resolution image. The scale bar is 2 μm. (b) Chemical structure of the black dye molecule that was attached to the ZnO nanowires. (c) J–V characteristics under no illumination and under one sun (100 mW/cm^2) obtained during photoelectrochemical measurements.

Each ZnO nanowire is in direct contact with the conducting carbon fiber for improved charge transfer. Electron transfer in these highly crystalline nanowires is expected to be faster than the percolation through conventionally used TiO_2 particles in DSSCs. In addition, this composite material combines the flexibility of the fibers with the lightweight nature of the carbon. This dense and flexible 3-D nanowire network would enable high dye loading which leads to efficient exciton generation under illumination, making it a promising flexible anode material for DSSCs.

C. Individual ZnO Nanowire FETs

For the replacement of conventional silicon complementary metal–oxide–semiconductors, SWNTs are promising candidates for p-type FETs [60]–[62]. ZnO, on the other hand, unless SWNTs are functionalized or asymmetric contacts are used [63], is one of the strongest candidates for n-type FETs [64], [65]. ZnO nanowires are intrinsically n-type and are always semiconducting. This brings stability and reproducibility to ZnO FET devices as compared to SWNT FETs.

We have fabricated high-performance FETs with self-aligned gate and nanosized air-gap capacitors as the dielectric layer [66]. Following growth, ZnO nanowires were scraped off the growth substrates and dispersed in isopropanol through sonication. Nanowire dispersion was then used to spin coat on n-type silicon substrates with a thermally grown oxide layer of 1-μm thickness. Si/SiO_2 substrates had an 80-nm aluminum

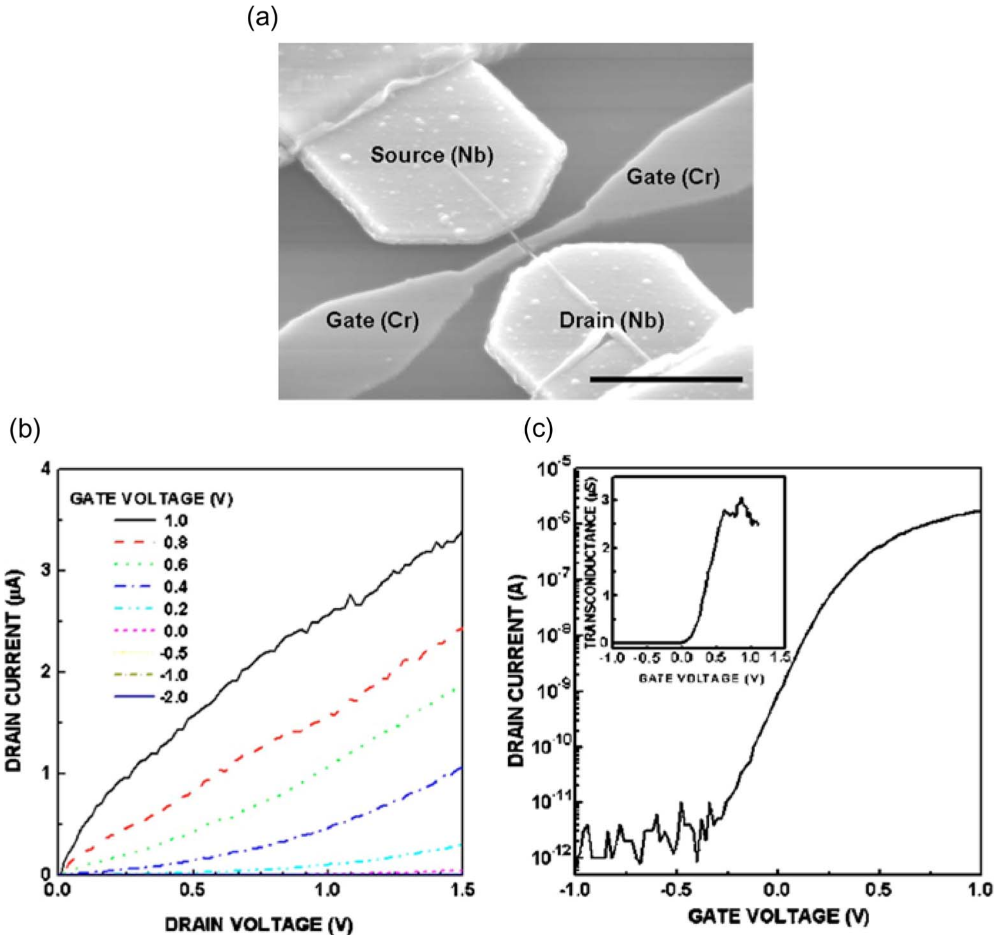

Fig. 7. (a) SEM image of the fabricated 5MAS-FET device. The scale bar is 2.5 μm. (b) Output characteristics of the ZnO MAS-FET. The gate voltage was varied from -2 to 1 V. (c) Transfer characteristics of the device with 0.8 V of source–drain voltage. The inset shows the transconductance curve of the device [66].

(Al) layer to act as a sacrificial layer. After mapping the ZnO nanowires through SEM imaging, electron beam lithography (EBL) was performed to deposit source and drain electrodes. Niobium (Nb) was chosen for the source and drain electrodes because its work function (4.30 eV) is well matched to the electron affinity of the ZnO channel (4.35 eV). Nb deposition was followed by the removal of the sacrificial Al layer. A second EBL step was carried out for determining the self-aligned in plane gate electrodes oriented normal to the ZnO nanowire. The final step in the fabrication of FETs is the evaporation of chromium (Cr) for gate electrodes and the consequent lift-off process. During evaporation, the ZnO nanowire was used as a shadow mask, forming nanosized gaps on both sides of the nanowire. Fig. 7(a) shows the SEM image of the metal–air-gap semiconductor FET (MAS-FET) consisting of an individual ZnO nanowire and two self-aligned gate electrodes. That particular device had a measured channel length of 968 nm, dielectric thickness (air gap) of 26 nm, channel width (nanowire diameter) of 60 nm, and gate width of 360 nm.

Fig. 7(b) shows the output characteristics (I_{ds}–V_{ds}) of the MAS-FET device as a function of gate voltage. Output characteristics indicate the operation mode of the MAS-FET as n-channel enhancement mode. The transfer characteristics of the same device at a V_{ds} of 0.8 V are shown in Fig. 7(c). An on/off ratio of 10^6 was obtained with a subthreshold slope of 129 mV/decade and a threshold voltage (V_{th}) of 0.4 V. The transconductance (g_m) of the device is shown in the inset of Fig. 7(c). Transconductance and normalized transconductance are 3.06 μS and 51.2 $\mu\mathrm{S}/\mu\mathrm{m}$, respectively. The field-effect mobility (μ) of the ZnO MAS-FET was derived using the following relationship:

$$\mu = L/(W \times C_i \times V_{\mathrm{ds}}) \times g_m \tag{1}$$

where L is the channel length, W is the channel width of the device, and C_i represents the capacitance per unit area of gate dielectric. C_i is calculated using the 3-D finite-element method, taking into account the FET structure and the space around it. The entire suspended nanowire between source and drain electrodes was considered to be the semiconducting channel, and the field-effect mobility was then estimated to be 928 $\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$. The electrical characteristics are the best obtained characteristics to date for a ZnO transistor, and this MAS-FET structure opens up the possibility of using ZnO as the n-type FET, with SWNT as the p-type FET, in the fabrication of nanoscale complementary logic circuits.

D. ZnO Nanowire Network Transistors

A major drawback of using individual nanowires in nano- or microelectronic applications is the lack of a manufacturable process to precisely assemble nanowires into small devices. The use of ZnO networks avoids this issue for relatively large-area macroelectronic devices since the devices exhibit the average properties of a large number of random individual nanowires. Although the mobility of the ZnO networks is lower than that of individual nanowires, they provide a less lithographically intensive alternative to the individual nanowire devices and offer advantages like high transparency and flexibility. Networks of ZnO nanowires that are grown at low temperatures through hydrothermal routes have already been presented with promising thin-film transistor (TFT) characteristics [67], [68]. High operating voltages have been reported for both cases with no information on the transparency of the devices.

We have prepared ZnO networks by a simple stamping method at ambient conditions on functionalized substrates [15]. The room-temperature deposition of ZnO networks rules out the constraints on the type of the substrates that can be used and provides potential for the realization of cheap, flexible, and transparent electronics. In this paper, ZnO nanowires grown on Si substrates, as previously mentioned, were transferred through mechanical means onto poly-L-lysine functionalized Si/SiO_2 substrates. The nanowires were not dispersed in polymer to form a composite, as reported in a companion paper in this issue [Hsieh *et al.*]. As such, the transistor characteristics obtained are due only to the action of a ZnO nanowire network channel. A thermally grown 200-nm-thick oxide layer was used as a dielectric in these experiments. Nb electrodes were then sputtered onto Si/SiO_2 substrates to form metallic electrodes and define transistors with channel lengths of 5–50 μm. The SEM images of the channel region of the 5- and 50-μm devices are shown in Fig. 8(a) and (b), respectively. For all devices fabricated in this paper, nanowire density was above the percolation threshold. ZnO nanowires were stamped on quartz disks for optical measurements. The normal incidence transmittance of our ZnO networks in the 1.5–3-eV photon energy range is shown in Fig. 8(c). The transmittance of the nanowire network is larger than 95% due to the large bandgap of the ZnO nanowires.

The gate transfer and output characteristics of a 20-μm-channel-length ZnO network TFT are shown in Fig. 9(a) and (b), respectively. The ON-state current of the device at ambient conditions and under a source–drain voltage of $V_{\mathrm{DS}} = 4$ V equals to $I_{\mathrm{ON}} = 4.5 \times 10^{-7}$ A with an OFF-state current of $I_{\mathrm{OFF}} = 8.5 \times 10^{-11}$ A. This yields an on/off ratio of about 10^4 with a threshold voltage of $V_{\mathrm{th}} = -10$ V. The field-effect mobility was estimated using (1) to be $\mu_{\mathrm{eff}} = 7.4\ \mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$, taking into account the effective channel width. The effective width of the channel is estimated by multiplying the nanowire diameter by the number of nanowires in the channel area. For comparison, the mobility for the 20-μm-channel-length ZnO network TFT was $0.59\ \mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$ when the full-width of the channel was taken into account. The effects of different channel lengths on the ON/OFF ratio and mobility of TFT devices were investigated. The ON-current was found to increase more dramatically than the OFF-current, leading to an increase in the ON/OFF ratio with a decrease in channel length. The increase in the ON-current can be attributed to the formation of more conductive channels between source and drain electrodes with the decrease of channel length. It was found that mobility behaves similarly with the ON/OFF ratio, increasing with the decrease of channel length which could also be attributed to the formation of extra conductive channels with the decrease of channel length. Fig. 9(c) shows the effect of channel length on the mobility and ON/OFF ratio of TFT devices. Smallest channel-length devices (5 μm) consist of arrays of nanowires bridging the source–drain electrodes and exhibited an ON/OFF ratio of $\sim 10^6$ with a field-effect mobility of $\sim 25\ \mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$. Largest channel-length devices (50 μm) yielded an ON/OFF ratio of $\sim 10^2$ with a mobility of $\sim 0.25\ \mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$. It is worth emphasizing that the mobilities of our ZnO nanowire TFTs are significantly larger than or comparable to those of organic and a-Si TFTs $(< 1\ \mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s})$ even at very large channel lengths, and our approach opens up new opportunities for fabricating high-performance TFTs based on transparent and semiconducting nanomaterials for applications requiring low-cost low-temperature manufacturing on large-area and flexible substrates.

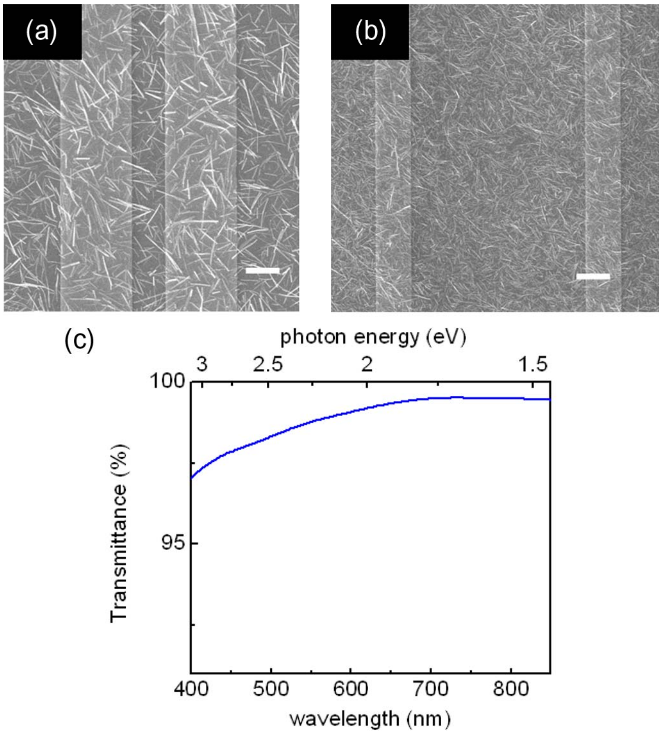

Fig. 8. SEM image of the ZnO nanowire network TFTs with different channel lengths. The scale bars correspond to (a) 5 μm and (b) 10 μm. (c) Optical transmittance of the ZnO network as a function of wavelength.

E. Photosensitive Transistors With WS_2 Nanotubes

Phototransistors are solid-state light detectors that are more sensitive than photodiodes and can be used to provide either analog or digital signals. Recently, photoinduced conductivity has been shown in various novel nanomaterials, such as semiconducting SWNTs when illuminated with infrared laser illumination [69], ZnO nanowires when illuminated both with UV light in the range near 365 nm ascribed to near-band-edge excitation, and longer wavelengths (400–740 nm) caused by defect levels within the bandgap such as ionized oxygen

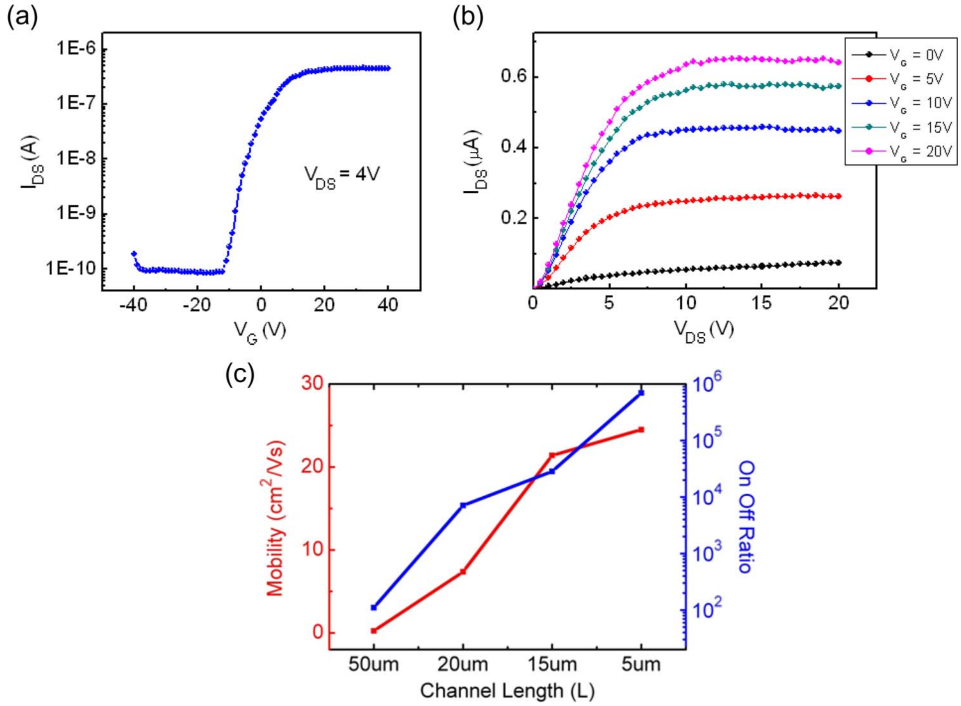

Fig. 9. Transfer (a) and output (b) characteristics of 20-μm-channel-length ZnO nanowire TFTs. (c) Effect of channel length on the mobility and on/off ratio of the ZnO nanowire TFTs.

vacancies [70], and GaN nanowires, again when illuminated with UV light due to their primary bandgap of 3.4 eV [71]. However, none of these nanomaterials possesses an intrinsic sensitivity to the light of visible wavelength. Transistors capable of detecting visible light, on the other hand, would have a wide range of applications in consumer and medical electronics.

Since photosensitivity of WS_2 thin films to visible light yielded promising results [72], we have investigated the optoelectronic properties of WS_2 multiwall nanotubes by fabricating photosensitive FETs using individual nanotubes. For the fabrication of photosensitive FET devices, the tubes were first dispersed in isopropanol by sonication and spin coated onto highly doped silicon substrates with a 200-nm-thick SiO_2 layer. Molybdenum electrodes were then defined as source and drain contacts on individual WS_2 nanotubes by electron beam lithography (EBL, Nanobeam I) and sputtering, followed by a standard lift-off process.

The electrical and photoconductivity measurements were carried out using an Agilent low-noise-level precision semiconductor parameter analyzer in a vacuum chamber, with a linear polarizer and a halogen lamp. The photoconductivity of WS_2 nanotubes, working as the device channel, at different illumination power densities with a floating-gate bias is shown in Fig. 10(a). The conductivity is enhanced with increasing light intensity for $V_{\mathrm{ds}} > 0.75$ V, with a tendency for the photocurrent to saturate at higher intensities. The polarization anisotropy of the photocurrent further confirmed the photosensitivity of the 1-D nanotube channel, as shown in Fig. 10(b). The photocurrent exhibits a clear periodic dependence $(\cos 2\theta)$ on the polarization angle of the incident light. At a fixed source–drain bias, the drain current reaches a maximum when the light is polarized parallel to the nanotube axis, and reaches a minimum when the light is perpendicular to the nanotube axis. The photocurrent ratio upon polarization, $\rho = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, is calculated to be around 0.6. The carrier mobility of the device, extracted from the transconductance curves [Fig. 10(c)], shows an increase from about $4.1 \times 10^{-4}\ \mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$ without illumination to $1.3 \times 10^{-3}\ \mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$ with illumination, at $V_{\mathrm{ds}} = 3$ V. The carrier concentration (normalized by tube cross section) is calculated to be $1.54 \times 10^6\ \mathrm{cm}^{-1}$ in the dark and $> 2.57 \times 10^7\ \mathrm{cm}^{-1}$ in the light. This photosensitivity is ascribed to the absorption of visible photons from the halogen lamp across the WS_2 nanotube bandgap to create electron–hole pairs. The electrical measurements of the devices at temperatures ranging from 220 K to 300 K (not shown here) revealed typical semiconductor characteristics where channel conductivity is increased with temperature.

Transistors capable of detecting visible light would have a wide range of applications in consumer and medical electronics. Our results reveal promising device characteristics with clear photosensitivity to visible light. WS_2 nanotubes, either individually or in network form as described for ZnO nanowires, could form the basis for photosensitive devices on a variety of flexible substrates including fabrics for clothing.

IV. SUMMARY

We report here a "snapshot" of ongoing research in the use of inorganic nanowires for electronics. It is shown that nanowires can be used as active elements in transistors, PV cells, and photosensors. Characterization of individual nanowires is helpful in identifying the synthesis conditions for optimally performing nanowires, for example, we show that mobilities in

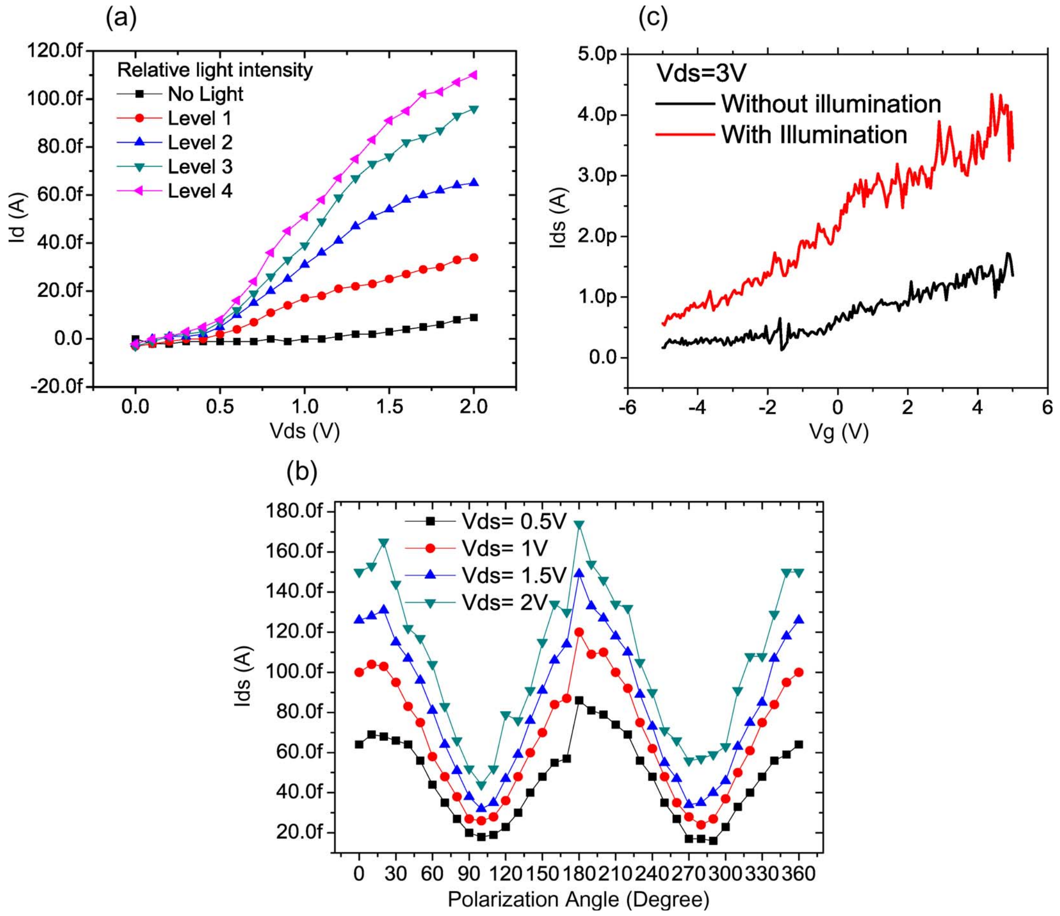

Fig. 10. (a) Photoconductivity versus relative illumination intensity. (b) Polarization anisotropy (I_{ds} in femtoampere unit). (c) Transconductance characteristics of the WS_2 nanotube FET at $V_{\mathrm{ds}} = 3$ V (I_{ds} in picoampere unit).

excess of 900 $\mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$ can be obtained from an individual ZnO nanowire. The approach taken here is to use the optimal synthesis conditions to obtain nanowires which are then transferable to a flexible substrate through a process such as printing or stamping. Alternatively, it is shown that ZnO nanowires can be grown directly at low temperature on flexible carbon electrodes. These, in turn, can be attached onto flexible substrates such as cloth via a process such as gluing.

We believe that the use of inorganic semiconductor nanowires in "ensemble" will enable a whole new class of electronics for applications such as functional and intelligent clothing. In addition, our results also show that ZnO network transistors can achieve mobilities in excess of 20 $\mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$. *Ex situ* nanowire synthesis and transfer method onto a large-area substrate therefore also holds promise for obtaining higher performance transistors which are suitable for applications such as matrix addressing in displays.

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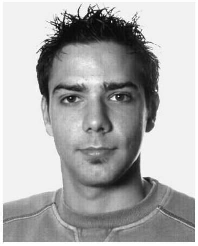

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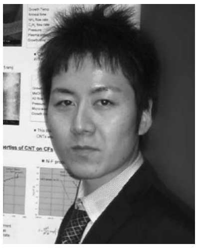

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