Intrinsic and Doped Zinc Oxide Nanowires for Transparent Electrode Fabrication via Low-Temperature Solution Synthesis

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Undoped and doped zinc oxide (ZnO) nanowires were synthesized by decomposing metal salts in trioctylamine at 300°C. By adding metal salts during the formation of the wires, effective incorporation of Ga and Al up to 5% was achieved, as measured by energy-dispersive x-ray spectroscopy and Auger electron spectroscopy. No secondary phase was detected by high-resolution transmission electron microscopy and x-ray diffraction. The nanowires were single-crystalline with a wurtzite lattice structure. Films made with doped wires show a complex dependence of the sheet resistance on processing conditions and dopant concentration. Thermal annealing treatment reduced the sheet resistance to values of $10^3 \Omega/\text{square}$.

Key words: Zinc oxide, nanowire, transparent electrode, doping

INTRODUCTION

ZnO is proving to be an extremely versatile material with applications ranging from cosmetics and paints to high-power electronic devices. Some of the most compelling electronic devices that make use of ZnO include surface acoustic wave filters,¹ photonic crystals,² photodetectors,³ photodiodes,⁴ gas sensors,⁵ and photovoltaic cells.⁶ Recently, ZnO quantum dots and nanoparticles have been introduced in biomedical applications for targeted tumor imaging and treatment.^{7,8}

ZnO is a wide-bandgap, hence transparent, semiconductor ($E_g = 3.37 \text{ eV}$).⁹ It has been synthesized via various methods, such as physical and chemical vapor deposition,¹⁰ vapor-liquid-solid growth,¹¹ sputtering,¹² and solution chemistry techniques.¹³ The final microstructure of the reaction product is highly dependent on the method and synthesis conditions and can range from multicrystalline films to very well-defined isolated nanostructures, such as nanoparticles, nanorods, nanowires, nanobelts, and nanospirals.^{14,15} ZnO typically crystallizes

in a wurtzite lattice with lattice parameters of $a = 0.3296 \text{ nm}$ and $b = 0.5206 \text{ nm}$.¹⁶ The structure is composed of alternating planes of tetrahedrally coordinated O^{2-} and Zn^{2+} , which are stacked along the c -axis of the lattice. The polarity of the alternating Zn-rich and O-rich basal planes and the neutrality of the prismatic faces of the ZnO crystal create an anisotropy in surface-energy. Thus, the crystal grows preferentially along the c -axis of the wurtzite lattice, thereby facilitating the realization of one-dimensional nanostructures.^{13,16}

Highly doped ZnO has long been proposed as an alternative material to tin-doped indium oxide (ITO) as a transparent electronic conductor. For instance, ITO is currently used as a window electrode in thin-film solar cells.¹⁷ Thin-film solar cells offer the opportunity to dramatically lower the price of solar energy by using small amounts of materials and low-cost manufacturing technologies such as printing. There is widespread concern, however, that the natural abundance of indium may not be sufficient to support the expected expansion of the solar cell industry. Therefore, with current technologies and materials, the transparent electrode could become a critical barrier in the commercialization of low-cost thin film solar cells.

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Degeneratively doped solution-coated ZnO nanowires are a very attractive system to replace ITO as a transparent electrode material, being made with naturally abundant nontoxic elements and being compatible with high-throughput manufacturing methods such as printing. It has been found that doped ZnO films can indeed reach resistivities as low as $1.4 \times 10^{-4} \Omega \text{ cm}$ to $2 \times 10^{-4} \Omega \text{ cm}$.¹⁸

ZnO nanowires have been previously grown by vapor deposition,¹⁰ pulsed laser ablation techniques,¹⁹ and solution chemistry.¹³ Vapor-based synthesis produces high-quality nanowires with lengths of several microns owing to the high growth temperatures (450°C to 900°C). If synthesis and deposition are combined in a single step, however, vapor-grown nanowires do not offer any advantage compared with traditional thin-film deposition methods. It is thus advantageous to separate synthesis and deposition in order to decouple the thermal budget limitations of the substrate from those of the active materials and, for instance, allow deposition on low-temperature flexible substrates after a high-temperature synthesis step. Nanowires grown by vapor synthesis on a substrate could in principle be harvested, dispersed in a solvent, and redeposited. Because material growth occurs on a flat surface however, the yield of such a process is low. Solution-based methods to synthesize ZnO nanowires operate at much lower temperatures (50°C to 300°C) and reach higher materials production than gas-phase growth. These methods can be divided into two major families: (1) aqueous methods which rely on the hydrolysis of Zn salts in water and (2) decomposition of Zn salts in organic solvents with a high boiling point. Lower temperatures can be maintained using aqueous synthesis; however, effective incorporation of dopant atoms in the ZnO crystal structure becomes problematic. Most metal ions undergo efficient complexation reactions with water molecules, which prevent them from being assimilated into the lattice. It is thus challenging to produce highly doped nanowires by aqueous synthesis. This major drawback can be circumvented by using decomposition methods that operate in the absence of water at slightly higher temperatures, thereby increasing the chances of successful incorporation of the dopants.

In this work, ZnO nanowires were synthesized by thermal decomposition of zinc acetate in trioctylamine at 300°C. The influence of surfactants (oleic acid) on the growth of the nanowires was investigated. After successful synthesis of undoped wires, intentional doping with aluminum and gallium was achieved. The wire morphology was characterized by scanning electron microscopy (SEM) of films drop-cast from nanowire ethanol suspensions. Additional characterization was performed by transmission electron microscopy (TEM). Scanning energy-dispersive x-ray spectroscopy (s-EDS) and Auger electron spectroscopy (AES) were used to determine whether dopant incorporation occurred

in the wires. The sheet resistance of films produced from the different nanowire batches was measured by a standard four-probe technique. Finally, the effect of thermal annealing on the electrical and morphological properties of wire assemblies was investigated.

EXPERIMENTAL

Synthesis of ZnO Nanowires

10.4 mmol of zinc acetate [$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$, 99.99%, Sigma Aldrich] was added to 100 mL trioctylamine in a three-necked flask. In a standard synthesis run, the reaction mixture was kept under a continuous N_2 flow and refluxed at 300°C for 3 h. The effect of oleic acid, which acts as a surfactant, on wire morphology was studied by adding 0.15 mol equivalent to the reaction flask. Doped wires were synthesized by adding a desired amount of aluminum acetate [$\text{Al}(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)_2$, Sigma Aldrich] or gallium nitrate hydrate [$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.9%, Sigma Aldrich] to the reaction mixture before starting the reflux process. The dopant salt was added in quantities of 1 mol.% and 5 mol.% in the synthesis solution. A complete overview of the synthesized batches is given in Table I. After terminating the synthesis, the reaction mixture was divided into 50 mL batches and centrifuged at 6000 rpm. Subsequently, the supernatant was separated from the reaction product. The purified nanowires were resuspended in ethanol, filtered over a nylon membrane with a porosity of 100 μm , and precipitated out by a second centrifugation step. The last step was repeated, reducing the filter porosity to 40 μm . The final product was left to dry and placed into vials for subsequent characterization.

Structural and Chemical Characterization

Films were drop-cast on silicon substrates from ethanol solution and characterized by SEM (FEI XL30 Sirion) to get a first insight into the nanoscale morphology of the reaction products. For TEM characterization, samples were prepared by dispersing the powder into ethanol in a polyethylene (PE) cuvette. A small quantity of the powder was added to the cuvette, which was then topped off with anhydrous ethanol. The sample was shaken by

Table I. Overview of Materials Synthesized in This Work

Undoped	Al Doped	Ga Doped
With and without oleic acid	1% Al-acetate solution With and without oleic acid 5% Al-acetate solution With and without oleic acid	1% Ga-nitrate solution With and without oleic acid 5% Ga-nitrate solution With and without oleic acid

hand, and then sonicated for the minimum possible time to avoid damaging the nanowires. Several trials indicated that 3 s was sufficient for most samples; prolonged sonication was found to damage the wires, causing them to break into smaller pieces. The suspension was then loaded in a disposable PE capillary-tip pipette and dispensed dropwise onto a holey carbon-coated copper grid. The excess liquid was drawn through with a blotter. The samples were then dried in a desiccator overnight prior to microscopy.

Preliminary microscopy, for the measurement of nanowire dimensions and shapes, was conducted using a Hitachi H7600 TEM at 150 kV accelerating voltage. Elemental analysis was accomplished on a Hitachi HD2000 STEM operated at 200 kV, equipped with an Oxford INCA Energy 200 x-ray EDS system. The crystallinity of the wires was investigated with a 300-kV Hitachi H9500 high-resolution TEM (HRTEM) with a lattice resolution of 0.10 nm.

X-ray diffraction (XRD) measurements were obtained in a Bragg-Brentano geometry on an X'PERT-PRO diffractometer (PANalytical), with a tube voltage of 45 kV and a current of 40 mA. Cu-K α 1 emission was used for the XRD experiments.

AES (PHI 700 Scanning Auger Nanoprobe) measurements were performed on nanowire films on a silicon substrate. The instrument was operated at 25 keV accelerating voltage, maintaining the current at 20 nA, ensuring the highest possible resolution: 6 nm for the secondary electron image and 8 nm Auger resolution with high elemental sensitivity. The nature of the Auger surface analysis process is such that Auger electrons can only escape from the outer 5 Å to 50 Å of a solid surface at their characteristic energy. This effect makes AES extremely surface sensitive, which requires caution in the interpretation of recorded spectra.

Electrical Characterization

Nanowire films were prepared by drop-casting controlled amounts of nanowire suspensions in ethanol on a thermally oxidized Si wafer. All suspensions have the same mass concentration of ZnO; therefore the amount of ZnO is the same in all films. To determine the sheet resistance of the nanowire

films, four Al (80 nm) electrodes capped with a thin (20 nm) Pd layer to prevent oxidation were deposited by thermal evaporation through a shadow mask. The pads were contacted in a probe station and I - V curves were measured with a Keithley 2612 double source-measurement unit. The films were also thermally annealed in vacuum at 240°C, 400°C, and 600°C for 30 min.

RESULTS AND DISCUSSION

Structural and Chemical Characterization

The morphology of all nanowire batches was first characterized by SEM. The nanowire width and length varied somewhat from batch to batch and ranged from 20 nm to 80 nm in width, while lengths varied from 100 nm (rod-like morphology) up to a few microns. Overall, the wires can be classified into two categories: (1) wires attached in a group to a common base and (2) standalone wires with no connection to neighboring wires or nanoparticles. ZnO nanowires grown by colloidal chemistry in organic solvents start with the formation of a seed crystal. Subsequently, by preferential growth along the c -axis of the crystal structure, several nanowires branch out from the common base plate. During the synthesis, the nanowire length exceeds a certain threshold, depending on its width and on the size of the seed crystal, after which it breaks off and becomes a standalone wire. A detailed study of the initial growth stages of the nanowires by quenching the synthesis reaction at different stages is currently underway and will be the subject of a separate publication. The morphology is reproducible from batch to batch and a few representative examples are shown in Fig. 1. More in-depth structural characterization was previously reported.²⁰ Differences in the growth patterns of undoped and doped nanowires were nonetheless systematically observed.

Undoped ZnO Nanowires

The seed crystal of undoped nanowires was observed to be a hexagonal platelet with flat basal faces (Fig. 1b) in agreement with Yuhas et al.²¹ The seed platelet is likely a single crystal of ZnO that

Fig. 1. SEM micrographs of (a) drop-cast film of ZnO nanowires, 5% Ga, without oleic acid; (b) bundled wires with a common platelet crystal base, 1% Al, without oleic acid; (c) standalone wire, 5% Al, with oleic acid.

Fig. 2. TEM micrographs of ZnO nanowires synthesized (a) without and (b) with oleic acid.

acts as an initiation point for the growth of undoped ZnO nanowires.²¹ We were however not able to verify this hypothesis. The effect of the presence of a surfactant during the synthesis process on the nanowire morphology was investigated as well²⁰ and is only summarized here. Nanowires synthesized for the same amount of time in the absence and in the presence (0.15 mol. equivalent) of oleic acid were characterized by TEM (Fig. 2). In both cases, smooth elongated particles are produced. The batch that was synthesized without oleic acid however was made of rather short nanorods (maximum length 300 nm), attached to the hexagonal base plate. The batch that was synthesized with oleic acid on the other hand was made of wires up to 1 μm in length. The surface-energy anisotropy of ZnO provides the initial driving force for the formation of high-aspect-ratio structures.^{13,16} The effect of oleic acid on the aspect ratio of the wires can be explained by a preferential physisorption of surfactant molecules on the prismatic faces of the nanowire, further

exacerbating the surface-energy anisotropy of the material and preventing fresh reagent from attaching to the sides of the wire. The composition of the nanowires was confirmed by XRD of a cast film (Fig. 3a): the diffraction pattern is in perfect agreement with that of bulk ZnO in the wurtzite structure. HRTEM further indicates that the nanowires are single crystals of ZnO oriented with the *c*-axis parallel to the length of the wire (Fig. 3b). The absence of the (002) peak in the XRD pattern is explained by the texture of the film, where most of the wires lie in the plane of the substrate.

Doped Nanowires

The initial nanowire seeding process might be different in doped nanowires compared with undoped ones. While nanowire bunches still seem to emerge from a common seed, the hexagonal platelet is not clearly observed anymore.²⁰ In some instances, s-EDS revealed that the seed crystal was

Fig. 3. (a) XRD pattern of an undoped ZnO nanowire film. (b) HRTEM micrograph of a ZnO nanowire.

Fig. 4. TEM micrographs of ZnO nanowires synthesized in 1 at.% Al solutions without (a) and with (b) oleic acid. SEM micrographs of ZnO nanowires synthesized in 5 at.% Al solutions without (c) and with (d) oleic acid.

enriched in dopant atom, although this observation was not always reproducible. Thus, it may be possible that in the synthesis of doped nanowires, seeding is provided by precipitation of excess dopant salt or other impurities. This hypothesis will be tested by introducing dopant at different times during the synthesis and characterizing the resulting morphology.

Oleic acid influences the wire morphology dramatically in the presence of dopants rather than just affecting their aspect ratio. In the case of Al-doped ZnO for instance (1 at.% in solution), adding oleic acid greatly increases the aspect ratio of the wires, similarly to what was observed in undoped wires (Fig. 4a and b). The effect of oleic acid is also visible on the wires formed in solutions containing 5 at.% Al (Fig. 4c and d). Overall, these nanowires are rougher compared with those synthesized in a 1 at.% Al solution. The roughness is greater in wires synthesized without oleic acid and, in this case, more particulate between the wires is observed as well. When performing HRTEM measurements on both materials, however, a distinct difference could be observed in the wire crystallinity depending on the presence of oleic acid in the synthesis bath. Lattice fringes perpendicular to the wire axis are clearly resolved in both cases and correspond to the *c*-axis of the crystal being parallel

to the nanowire axis. The wires grown without oleic acid, however, show the presence of a second, amorphous phase surrounding the crystalline core of the wire (Fig. 5a). Nanowires grown in the presence of oleic acid on the other hand are entirely crystalline (Fig. 5b). Because the amorphous shell is systematically present only in nanowires grown without surfactant it is not an artifact due to beam damage. The presence of an amorphous sheath surrounding the crystalline nanowire is expected to affect the electrical properties of nanowire assemblies significantly.

The effect of the surfactant is different in Ga-doped nanowires. Here oleic acid influences the nanoscale morphology of the wires. Ga-doped ZnO nanowires grown without oleic acid show a succession of ~5 nm protrusions along the edges of the wire (Fig. 6a). It should be noted that the lattice fringes are undisturbed going from the nanowire to the protrusion. Therefore, the protrusions are not due to additional nucleation sites but rather to surface instabilities during the growth of the nanowire and are coherent with the rest of the crystal. Wires with extremely smooth edges on the other hand are observed when oleic acid is used in the synthesis process (Fig. 6b). We can speculate that the surface-energy anisotropy that gives rise to steady nanowire growth is greatly stabilized by the

Fig. 5. HRTEM micrographs of ZnO nanowires synthesized in 1 at.% Al solutions without (a) and with (b) oleic acid. The amorphous edges are indicated with arrows.

Fig. 6. HRTEM micrographs of ZnO nanowires synthesized in 5 at.% Ga solutions without (a) and with (b) oleic acid.

presence of the surfactant. Surprisingly, the aspect ratio of the Ga-doped ZnO nanowires is not much affected by the presence of oleic acid: in both cases nanowires with a high aspect ratio between 30 and 40 are obtained (length $\sim 4\ \mu\text{m}$, width $\sim 60\ \text{nm}$ to $100\ \text{nm}$).

In order to determine whether the dopant was incorporated in the wires, s-EDS and AES were performed on selected nanowire samples. In the 5% Al-doped nanowires, the dopant is incorporated in the wires in nearly the same composition as it is found in the synthesis bath. Indeed, compositional analysis by s-EDS on different locations of a nanowire film reveals that the Al/Zn ratio varies between 4% and 6%. Interestingly, the composition in the irregular particles found on the substrate surface is significantly more Al rich (up to 30%). This result suggests that 5% may be close to an upper limit for the solubility of the Al dopant. In

5% Ga-doped ZnO on the other hand, the dopant concentration determined by s-EDS is closer to 1% (Fig. 7). This concentration is close to the sensitivity limit of the instrument, therefore s-EDS could not detect Ga in ZnO nanowires grown in 1 at.% Ga solutions where the Ga concentration is presumably $< 1\%$.

The s-EDS measurements were complemented by scanning Auger spectra. With this technique, the elemental composition of thin films can be analyzed with high resolution, in a pointwise manner, across a line of a specific sample area or within a specific area of the film. The intensity of the Auger signal attributed to elements of interest (Zn, O, Al or Ga) and on two different locations within the SEM analysis area are shown in Fig. 8 for ZnO nanowires doped with 5% Al and Ga, respectively. Elemental mapping points out that for both cases the dopant is indeed located on the

Fig. 7. Scanning EDS analysis of a ZnO nanowire synthesized in a 5% Ga solution: (a) TEM micrograph, (b) oxygen signal, (c) Zn signal, and (d) Ga signal.

Fig. 8. AES spectra of ZnO nanowires synthesized in 5 at.% Al solutions (left) and 5 at.% Ga solutions (right). The dopant percentages in two different sample locations are indicated as insets in the respective graphs.

ZnO nanowire (Fig. 9), confirming its incorporation into the material from solution during growth. The composition is in general agreement with the s-EDS results: dopants are incorporated in a concentration range of a few percent. The dopant signal intensity measured by AES is not very uniform across a single sample. At this stage, it is not clear whether this lack of uniformity is due to nonuniform dopant distribution or rather to an experimental artifact due to multiple scattering of the electrons by overlapping nanowires. X-ray photoelectron spectroscopy was also attempted in an effort to quantitatively determine the average dopant concentration in nanowire films (data not

shown). The results are in general agreement with s-EDS and AES. Even though the exact Al and Ga concentration could not be determined in all films, dopant concentrations of the order of a few percent were always measured, thus confirming the extremely high dopant incorporation rate.

XRD on the doped ZnO nanowires was performed to detect whether secondary phases are formed (Fig. 10). No secondary phases (Al_2O_3 , Ga_2O_3 , or unreacted Ga or Al salts) were detected. Within this series of experiments, no systematic correlation between doping level and lattice parameters was detected to indicate whether the dopant atoms are interstitial or substitutional.

Fig. 9. AES analysis of ZnO nanowires synthesized in 5% Al solutions: (a) SEM micrograph, (b) Zn Auger electron map, and (c) Al electron map; and in 5% Ga solutions: (d) SEM micrograph, (e) Zn Auger electron map, and (f) Ga electron map.

Fig. 10. XRD spectra of all the synthesized nanowire batches.

Electrical Characterization and Optical Characterization

Because the synthesis is carried out at 300°C, dopant incorporated in the ZnO nanowires may already be partially electrically active immediately after the synthesis. The conductivity of nanowire mats deposited from solution in the same conditions for all samples was measured by the four-point method. The film roughness prevented an exact film thickness measurement. The film thickness was estimated to be a few microns for all films. The sheet resistance measurements thus include effects of single wire resistance and film microstructure. Moreover, we investigated the effect of thermal annealing up to 600°C (240°C, 400°C, and 600°C) on the sheet resistance of a ZnO nanowire film.

Films made with undoped ZnO are virtually insulating, as expected for an intrinsic wide-band-gap semiconductor at room temperature (Fig. 11).

Fig. 11. Sheet resistance of nanowire films formed from different batches and annealing conditions.

In the Al-doped materials family, only the films made with nanowires grown in a 1 at.% Al synthesis solution have a lower sheet resistance than that of the undoped ZnO nanowires. The effect is particularly significant in the wires synthesized in the presence of oleic acid, which have a sheet resistance over three orders of magnitude lower than that of the undoped wires. In the films made from wires synthesized in a 5 at.% Al solution, the sheet resistance prior to annealing is equal to or higher

than that of undoped films. Furthermore, Al-doped wires synthesized in the presence of oleic acid always outperform those synthesized without oleic acid. The presence of the amorphous shell around the nanowires in the latter case is the likely cause of this observation. Moreover, the morphology of wires synthesized in a 5 at.% Al solution is more irregular than that of wires synthesized in a 1 at.% Al solution. Thus, even though more Al may be incorporated into the wires synthesized in a 5 at.% Al solution, the sheet resistance of such a nanowire film is higher. Thermal annealing always decreases the sheet resistance of the nanowire films. This effect is large, with resistance decreases exceeding five orders of magnitude in two cases. Because a large drop in sheet resistance is not observed in films made with undoped wires, the effect of annealing is most probably due to dopant activation and not sintering of the nanowire crossing points or other microstructural effects. Indeed, SEM characterization of annealed films did not show any morphological indication of melting or sintering. Differential scanning calorimetry of nanowire powder samples (not shown here) confirms that no phase transformation or decomposition takes place up to 600°C. Within the Al-doped materials, the lowest sheet resistance was measured in films made with wires synthesized in a 1 at.% Al solution in the presence of oleic acid (~ 10 k Ω /square after annealing). While this value is still two to three orders of magnitudes too high to be competitive with current technologies, it is encouraging since no materials or film optimization was undertaken here.

Ga behaves quite differently from Al. All films made with Ga-doped nanowires exhibit significant sheet resistance decreases compared with the undoped materials even before annealing. In the case of the film made with wires synthesized in a 5 at.% Ga solution without oleic acid, this effect is particularly large (six orders of magnitude). Thus, the electrical activation during synthesis is more efficient with Ga than with Al. Ga may be more easily incorporated into the ZnO lattice than Al because its atomic radius (1.3 Å) is very similar to that of Zn (1.35 Å) while Al is a substantially smaller atom (1.25 Å). Contrary to the case of Al, Ga-doped nanowires synthesized without oleic acid systematically produce films with a lower sheet resistance than those made with nanowires synthesized in the presence of oleic acid by a factor of 20 to 100. Since in the case of Ga doping the crystallinity of the wires was not affected by the oleic acid, the increased resistance may be due to the presence of adsorbed insulating oleic acid molecules along the nanowires. This hypothesis is corroborated by the observation that, after annealing at 600°C, which burns off the oleic acid, the sheet resistance of both types of films becomes similar. Among the Ga-doped materials, the lowest sheet resistance was measured in films made with wires synthesized in a 5 at.% Ga solution without oleic acid (~ 1 k Ω /square, one order of

magnitude better than the best Al-doped films), eight orders of magnitude more conductive than the initial undoped films. For the same reasons as for the Al-doped films, the decrease in sheet resistance upon annealing is attributed to dopant activation rather than microstructural effects such as nanowire fusion. Future experiments to determine the coordination of dopant elements by x-ray spectroscopy will be performed.

CONCLUSIONS

ZnO nanowires were synthesized by thermal decomposition of Zn salts in high-boiling-point organic solvents. The incorporation of electrically active dopants (Al and Ga) in the ZnO nanowires in high concentrations (order of 1% or more) was demonstrated as well, without the formation of secondary phases. The dopant concentration inside the nanowires is of the same order as the dopant concentration in the synthesis solution, suggesting a very efficient incorporation process. A suite of techniques was used to study the morphological, chemical, and electrical properties of the ZnO nanowires. TEM and XRD analysis confirmed the synthesis of single-crystalline ZnO wires with a wurtzite lattice structure. The aspect ratio and the morphology of the nanowires depend on the presence of a surfactant (oleic acid) during the synthesis; for instance, an amorphous shell was formed around the crystalline core of Al-doped nanowires synthesized without surfactant, which negatively affects the electrical conductivity of the wires. Moreover, a high ($> \sim 2$ mmol/L) Al concentration in the solution disturbs nanowire growth. In the Ga-doped nanowires, synthesis without surfactant led to nanosized protrusions along the length of the wires. Adding a surfactant, however, produced nanowires with a very smooth morphology up to $\sim 1\%$ Ga doping in the wires. Scanning TEM and AES measurements unambiguously proved that dopant atoms are incorporated into the nanowires. Depth profiling measurements will be performed to get more insight into the radial composition of the wires. Electrical measurements show that incorporation of the dopant has an effect on the conductivity of the wires, which is further increased by thermally annealing the thin films. Thermal annealing activates the dopant but does not otherwise affect the structure of the nanowires. Minimum sheet resistance values as low as 10^3 Ω /square are obtained after annealing the films at 600°C, a decrease of eight orders of magnitude compared with undoped materials.

These results are extremely encouraging toward the realization of a solution-processable replacement for ITO in solar cell windows. In order to improve the performance of the films, however, more fundamental understanding of the materials must be gained. The nanowire nucleation and growth mechanisms, for instance, are still poorly

understood, as is the role of the surfactant. Furthermore, the amount of dopant activation and the carrier density and mobility need to be determined as a function of processing conditions. Moreover, electron trapping is always a concern with ZnO-based conductors. Further work is also needed to determine whether the annealing step can be done *ex situ* prior to the deposition of the nanowires, which would make the materials truly compatible with roll-to-roll low-temperature processing.

REFERENCES

1. W. Water, Y.S. Yan, and T.H. Meena, *Sens. Actuators A* 144, 105 (2008). doi:[10.1016/j.sna.2007.12.007](https://doi.org/10.1016/j.sna.2007.12.007).
2. S.Y. Yang, P.H. Yang, C.D. Liao, J.J. Chieh, Y.P. Chen, H.E. Hornga, C.Y. Hong, and H.C. Yang, *Appl. Phys. Lett.* 89, 231108 (2006). doi:[10.1063/1.2402876](https://doi.org/10.1063/1.2402876).
3. Y. Jin, J. Wang, B. Sun, J.C. Blakesley, and N.C. Greenham, *Nano Lett.* 8, 1649 (2008). doi:[10.1021/nl0803702](https://doi.org/10.1021/nl0803702).
4. D. Lin, H. Wu, and W. Pan, *Adv. Mater.* 19, 3968 (2007). doi:[10.1002/adma.200602802](https://doi.org/10.1002/adma.200602802).
5. J.B.K. Law and J.T.L. Thong, *Nanotechnology* 19, 205502 (2008). doi:[10.1088/0957-4484/19/20/205502](https://doi.org/10.1088/0957-4484/19/20/205502).
6. D.C. Olson, Y.J. Lee, M.S. White, N. Kopidakis, S.E. Shaheen, D.S. Ginley, J.A. Voigt, and J.W.P. Hsu, *J. Phys. Chem. C* 111, 16640 (2007). doi:[10.1021/jp0757816](https://doi.org/10.1021/jp0757816).
7. K. Byrappa, S. Ohara, and T. Adschiri, *Adv. Drug Deliv. Rev.* 60, 299 (2008). doi:[10.1016/j.addr.2007.09.001](https://doi.org/10.1016/j.addr.2007.09.001).
8. Y. Liu, Y. Zhang, S. Wang, C. Pope, and W. Chen, *Appl. Phys. Lett.* 92, 143901 (2008). doi:[10.1063/1.2908211](https://doi.org/10.1063/1.2908211).
9. D.C. Reynolds, D.C. Look, B. Jogai, C.W. Litton, T.C. Collins, W. Harsch, and G. Cantwell, *Phys. Rev. B* 57, 12151 (1998). doi:[10.1103/PhysRevB.57.12151](https://doi.org/10.1103/PhysRevB.57.12151).
10. Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.J. Cho, and H. Morkoç, *J. Appl. Phys.* 98, 041301 (2005). doi:[10.1063/1.1992666](https://doi.org/10.1063/1.1992666).
11. W. Lu and C.M. Lieber, *J. Phys. D: Appl. Phys.* 39, R387 (2006). doi:[10.1088/0022-3727/39/21/R01](https://doi.org/10.1088/0022-3727/39/21/R01).
12. K. Ellmer, *J. Phys. D: Appl. Phys.* 33, R17 (2000). doi:[10.1088/0022-3727/33/4/201](https://doi.org/10.1088/0022-3727/33/4/201).
13. L.E. Greene, B.D. Yuhas, M. Law, D. Zitoun, and P. Yang, *Inorg. Chem.* 45, 7535 (2006). doi:[10.1021/ic0601900](https://doi.org/10.1021/ic0601900).
14. Z.L. Wang, *Mater. Today* 7, 26 (2004). doi:[10.1016/S1369-7021\(04\)00286-X](https://doi.org/10.1016/S1369-7021(04)00286-X).
15. L. Schmidt-Mende and J.L. Macmanus-Driscoll, *Mater. Today* 10, 40 (2007). doi:[10.1016/S1369-7021\(07\)70078-0](https://doi.org/10.1016/S1369-7021(07)70078-0).
16. Z.L. Wang, *J. Phys. Condens. Matter* 16, R829 (2004). doi:[10.1088/0953-8984/16/25/R01](https://doi.org/10.1088/0953-8984/16/25/R01).
17. C.G. Granqvist, *Sol. Energy Mater. Sol. Cells* 91, 1529 (2007). doi:[10.1016/j.solmat.2007.04.031](https://doi.org/10.1016/j.solmat.2007.04.031).
18. K. Ellmer, *J. Phys. D: Appl. Phys.* 34, 3097 (2001).
19. Y. Sun, G.M. Fuge, and M.N.R. Ashfold, *Chem. Phys. Lett.* 396, 21 (2004). doi:[10.1016/j.cplett.2004.07.110](https://doi.org/10.1016/j.cplett.2004.07.110).
20. G.J. Kusinski, J.R. Jokisaari, R. Noriega, L. Goris, M. Donovan, and A. Salleo, *J. Electron Microsc.* (in print).
21. B.D. Yuhas, D.O. Zitoun, P.J. Pauzauskie, R. He, and P. Yang, *Angew. Chem. Int. Ed.* 45, 420 (2006). doi:[10.1002/anie.200503172](https://doi.org/10.1002/anie.200503172).