Probing the electrical properties of highly-doped Al:ZnO nanowire ensembles

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The analysis of transparent conducting oxide nanostructures suffers from a lack of high throughput yet quantitatively sensitive set of analytical techniques that can properly assess their electrical properties and serve both as characterization and diagnosis tools. This is addressed by applying a comprehensive set of characterization techniques to study the electrical properties of solution-grown Al-doped ZnO nanowires as a function of composition from 0 to 4 at. % Al:Zn. Carrier mobility and charge density extracted from sensitive optical absorption measurements are in agreement with those extracted from single-wire field-effect transistor devices. The mobility in undoped nanowires is $28 \text{ cm}^2/\text{V s}$ and decreases to $\sim 14 \text{ cm}^2/\text{V s}$ at the highest doping density, though the carrier density remains approximately constant ($10^{20} \text{ cm}^{-3}$) due to limited dopant activation or the creation of charge-compensating defects. Additionally, the local geometry of the Al dopant is studied by nuclear magnetic resonance, showing the occupation of a variety of dopant sites. © 2010 American Institute of Physics. [doi:10.1063/1.3360930]

I. INTRODUCTION

Transparent conducting oxides (TCO) have been the focus of intense research in recent years, due to their applications in electronics and photovoltaics. These wide-bandgap materials have been used as the active channel material for field-effect transistors, as the electron-accepting material in dye-sensitized solar cells, and, when doped, as transparent electrodes for transistors, organic light emitting diodes, solar cells, and electrochromic windows. The most widely used TCO is indium-tin oxide (ITO). However, due to high processing costs and indium scarcity there has been a field-wide push to find a suitable alternative. Zinc oxide (ZnO) is an extensively studied material and well-suited to replace ITO, due to its low cost and marginal toxicity combined with its competitive electrical and optical properties. Without any intentional doping, ZnO is naturally n-type and can be extrinsically doped by introducing heteroatoms (such as Al, Ga, In, B, or Sn) into the ZnO crystal lattice, reaching carrier concentrations as high as $1.5 \times 10^{21} \text{ cm}^{-3}$. Electron mobility in ZnO can reach values of $200 \text{ cm}^2/\text{V s}$ for ZnO single crystals at low doping levels, with mobility generally decreasing at higher doping levels. However, for heavily doped ZnO films obtained with techniques such as magnetron sputtering, pulsed laser deposition, and metal-organic chemical vapor deposition, the mobility varies between 10 cm$^2$ V$^{-1}$s$^{-1}$ and 60 cm$^2$ V$^{-1}$s$^{-1}$ depending on the microstructure of the material. The lowest resistivity achieved in ZnO is on the order of $10^{-4} \Omega \text{ cm}$, comparable to ITO. Recent research has focused on tailoring the properties of these materials by modifying their morphology at the nanoscale. ZnO has a wurtzite crystal structure comprised of a series of alternating planes of tetrahedrally coordinated O$^{2-}$ and Zn$^{2+}$ ions stacked along the c-axis, with characteristic polar surfaces that give rise to a number of different nanostructures including rods, wires, belts, springs, and tubes.

The key qualities of TCOs are their optical transmission in the visible and near-IR and their electrical conductivity. Films made of networks of doped ZnO nanowires have been shown to have potential to be used as a TCO in photovoltaics; as long as the sheet resistance value can be decreased to compete with other transparent electrode materials, while maintaining a high transparency. Doped ZnO nanowire mats can exhibit currently a sheet resistance of $10^{3} \Omega/\square$ combined with 80%–85% transmission.

For flexible substrates, the benchmark values of sheet resistance and light transmission for non-ITO materials have been set by carbon nanotube networks (200 $\Omega/\square$ and 85%, respectively), and silver nanowire meshes (10 $\Omega/\square$ and 80%). Conduction through networks of quasi-one-dimensional (1D) structures depends on charge transport through each element and on charge transfer from one element to the next; at this point we will focus on the conduction within individual doped ZnO nanowires.

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In n-ZnO, the conductivity is approximated as \( \sigma = e\mu N_e \) where \( e \) is the elementary charge; \( \mu \) and \( N_e \) are the electron mobility and concentration, respectively. Accordingly, proper characterization of a TCO’s conductivity requires quantitative determination of the density and mobility of the charge carriers. The carrier concentration and mobility in semiconducting thin films are typically obtained using Hall effect measurements, whose application is problematic for extracting electrical characteristics from quasi-1D structures such as nanowires. As an alternative, single-wire field effect transistors (SWFET) have been used to measure carrier mobility.\(^2\)\(^\text{12–19} \) In this technique, only a single device (i.e., a single wire) can be measured at a time, making the collection of data from a set of nanowires a labor-intensive and time-consuming process. This technique is also hindered by additional issues associated with the deposition of electrical contacts on nanomaterials, including the effects of contact resistance and the alteration of the material’s properties (such as unintentional doping and/or damage caused by the ion or electron beam) that must be taken into account during measurement interpretation.

The mobility \( (\mu) \) and free carrier density \( (N_e) \) in aluminum-doped ZnO (AZO) films can also be measured using polarized light ellipsometry.\(^2\)\(^\text{20,21} \) Ellipsometry experiments have the advantage of being a noncontact technique, therefore, avoiding the unintentional modification of the sample. However, values extracted from ellipsometry depend on the accurate measurement of the change in the polarization state of light reflected from the sample surface. Because nanowire films are rough and scatter light effectively, the validity of ellipsometry experiments is compromised.

Fourier-transform infrared spectroscopy (FTIR) (Refs. \(22\) and \(23\)\)\) or attenuated total reflection FTIR (Ref. \(24\)\) have also been used to analyze the free carrier absorption in ZnO films. For highly scattering films, however, the detected signal attenuation is not necessarily correlated with the absorption of the sample alone.

These issues pose a need for a better way to measure the electrical properties of an ensemble of nanowires, which we address by applying a comprehensive set of spectroscopic techniques to the characterization of highly Al-doped ZnO nanowires obtained with a solution-based low-temperature process.\(^8\)\(^\text{25} \)

II. EXPERIMENTS

Previous studies of these nanowires using spatially-resolved analytical techniques such as Auger electron spectroscopy and energy-dispersive x-ray spectroscopy confirmed that the aluminum dopant is incorporated into the nanowires. High-resolution transmission electron microscopy was used to show that the as-synthesized nanowires are highly crystalline with the growth axis being the c-axis of the ZnO wurtzite crystal [Fig. 1(c)].\(^8\)\(^\text{25} \) Typical dimensions for the nanowires are diameters in the 20–80 nm range, and lengths of up to a few microns [Fig. 1(d)].\(^8\)\(^\text{25} \)

The Al:Zn ratio in the product material is determined using an inductively-coupled plasma atomic emission spectrometer (ICP-AES). Films of AZO nanowires were prepared on quartz substrates by drop-casting from an ethanol suspension. The electrical properties of nanowire ensembles were obtained by applying the Drude model\(^2\)\(^6 \) for metals to the absorption spectrum of these films measured using photothermal deflection spectroscopy (PDS) (Refs. \(27\) and \(28\)\) and subsequently compared to SWFET measurements. Finally, the coordination environment of dopant atoms was investigated using \(^2\)\(^7\)Al solid-state nuclear magnetic resonance (NMR).

A. Synthesis process

0.104 M solutions of zinc acetate [Zn(CH₃CO₂)₂, Sigma Aldrich] in trioctylamine ([CH₃(CH₂)₇]₃N, Sigma Aldrich) with varying amounts of basic aluminum diacetate [Al(OH)(C₂H₅O₂)₂, Sigma Aldrich] were prepared in a three-necked flask. The reaction mixture was kept under a continuous N₂ flow and refluxed at 300 °C for 3 h. The synthesis products were centrifuged at 6000 rpm. Subsequently, the supernatant was discarded and the precipitates were resuspended in ethanol, filtered over nylon membranes with porosities of 100 and 40 \( \mu \)m, and precipitated out by additional centrifugation steps. The final product was left to dry and placed into vials for subsequent characterization.\(^8\)\(^\text{25} \)

Low-temperature solution-based synthesis processes are attractive due to their relative simplicity, low cost, and scalability but they also have significant drawbacks, particularly...
a higher inhomogeneity in morphology and doping when compared to more strictly controlled processes (i.e., chemical vapor deposition).

B. ICP-AES

A small portion of each powdered sample was dissolved in a 2% HCl aqueous solution, and the detected intensities of the spectral lines were calibrated with standards of Al and Zn, also in a 2% HCl aqueous solution.

C. PDS

PDS relies on the complete or fractional conversion of absorbed electromagnetic radiation by the material of interest into heat via nonradiative de-excitation processes. This conversion process causes a temperature rise in the material itself and its surroundings. The temperature rise leads to a localized change in the index of refraction in the surrounding deflection medium, which is measured and correlated with the absorption coefficient of the material of interest. During a measurement, a modulated monochromatic pump beam (arranged perpendicular to the plane of the substrate) is absorbed by the sample. A second (transverse) probe laser beam is deflected by the localized change in the refractive index of the surrounding deflection medium, and a position sensitive detector records the periodic deflection by a lock-in technique. The measured deflection is proportional to the absorption coefficient of the measured thin film.

Films were deposited from ethanol-based solutions of the nanowire powders onto quartz substrates and immersed in a cuvette filled with Fluorinert™ (3M). The pump beam was obtained from either a halogen or xenon lamp (for different energy ranges), then monochromated and focused onto the sample. The probe beam is a commercial He:Ne laser, and the deflection signal is measured with a position sensitive detector.

D. Single-nanowire FETs

SWFETs were fabricated by dispersing AZO nanowires onto heavily doped, thermally oxidized silicon substrates (with the substrate serving as the gate and the 200 nm thick SiO₂ as the gate dielectric) and preparing source/drain contacts on the wires by electron-beam lithography, metal evaporation, and lift-off.

E. NMR

Spectra were obtained from powder samples using a 14.1 T magnet with magic angle spinning (MAS) to reduce peak broadening, with sample spinning rates of 20 kHz, rf tip angle (solids) of about 30° (0.2 µs pulse), pulse delay of 0.1 s, and referenced to a 0.1 M Al(NO₃)₃ standard. The ZnAl₂O₄ spinel sample was synthesized by heating reagent grade Al(OH)₃ and ZnO at 1400 °C in air for 24 h. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSIONS

To investigate the effect of dopant concentration, ZnO nanowires with varying aluminum content were synthesized from solutions containing dopant amounts of 1, 3, 5, and 7 at. %. The average incorporation rate (at. % in the nanowires versus at. % in the synthesis solution) is 60%, and the dopant content in the nanowires ranges from 0.7 to 4 at. %. This confirms that the materials are heavily doped and the dopant incorporation rate is very high, which is remarkable given the low synthesis temperature (300 °C). In addition, undoped nanowires were also synthesized without adding dopant atoms into the synthesis bath in order to confirm that the observed improvement in conductivity is caused by the inclusion of aluminum atoms in the ZnO.

The solubility limit of aluminum in the ZnO wurtzite lattice is still somewhat controversial, with reported values on the order of 1 at. %, corresponding to a carrier concentration of 4.1 × 10¹⁰ cm⁻³ for singly-ionized impurities, or 25% of the maximum reported concentration in thin films. It should be noted that different synthesis techniques work at different points in the phase diagram, and the maximum attainable doping level therefore depends on the specific growth process. Moreover, the thermodynamic solubility limit can be exceeded in nonequilibrium situations. In addition, as reported by Minami et al., the high carrier concentrations in AZO films are not always due only to impurities but also to intrinsic donor states.

A. Drude metal model

Such large free-carrier concentrations make AZO behave like a Drude metal, making it possible to determine crucial properties such as free charge concentration and mobility using optical spectroscopic techniques. The Drude model predicts that the free charge density of a metal determines a cut-off frequency, the plasma frequency ωₚ, such that for ω > ωₚ the material is practically transparent, and for radiation with ω < ωₚ the absorption coefficient and the reflectivity of the material are very high. There are two key parameters in this model: the plasma frequency and carrier scattering time

\[ \omega_p = \sqrt{\frac{N_e \epsilon_0}{m_e^* e}}, \quad \tau = \frac{\mu e_m^*}{e}, \]

where \( m_e^* \) is the effective electron mass at the bottom of the conduction band, and \( \epsilon_0 \) is the permittivity of vacuum. For ZnO with 1 at. % of active dopants and an electron effective mass of \( m_e^* = 0.27m_e \) (where \( m_e \) is the electron’s rest mass), the plasma frequency is close to \( \nu_p = \omega_p / 2\pi = 3.5 \times 10^{14} \) Hz, corresponding to a wavelength of \( \lambda_p = 860 \) nm. Further refinement of this model can account for variability within each sample, assuming that the population of measured wires follows a Gaussian distribution for the mobility and free electron concentration. In this case, the measured (effective) absorption spectra \( \alpha_{eff} \) will be a weighed superposition as follows

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incorporation of Al into the lattice of ZnO

device simulation variables.

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material. Region 2 illustrates defect-related absorption
efficient in the IR is due to free charge carriers present in the
region 2–3 eV, see Fig. 2 inset
samples are mostly transparent
of dopant in the nanowires is significant, a third approach
considering the nonparabolicity of the conduction band
was used as well but showed no significant difference with
the results presented here and was therefore not included.

The mean values for the mobility (free charge density) dis-
tributions (Fig. 3) are in the range 27–14 cm2 V−1 s−1
(8.8–11.6 × 1019 cm−3), with standard deviations close to
2 cm2 V−1 s−1 and 3 × 1019 cm−3, with the exception of the
1.58 at. % Al:Zn sample (6.7 cm2 V−1 s−1 and 5.5
× 1019 cm−3) which can be explained by a larger degree of
variability in the synthesis products compared to other (and
better optimized) synthesis runs.

B. PDS

In order to overcome problems associated with many
traditional methods for measuring electrical properties in
ZnO nanowire thin films, we have used transverse PDS.27,28
PDS has the advantages of being a noncontact and nonde-
structive technique that enables the measurement of the op-
tical properties of an entire ensemble of nanowires in a single
experiment. It should be noted that when the free charges
absorb the incoming light from the PDS pump beam, their
oscillation amplitude is well inside a single nanowire, so
the properties we obtain from these measurements correspond to
an average over an ensemble of single AZO nanowires.

The measured spectra can be divided into three distinct
regions (Fig. 2). The first region corresponds to free carrier
absorption (ℏω< 2 eV). Here, the increase in absorption co-
efficient in the IR is due to free charge carriers present in the
material. Region 2 illustrates defect-related absorption (ℏω
∼ 2–3 eV, see Fig. 2 inset). Samples are mostly transparent
in the visible region but a pronounced absorption band
∼ 2.5 eV (500 nm) can be observed, most likely due to the
incorporation of Al into the lattice of ZnO (such a band is

Fig. 2. (Color online) PDS spectra of ZnO nanowire films (● undoped, ○
0.68 at. % Al, □ 1.58 at. % Al, ○ 2.34 at. % Al, △ 3.98 at. % Al) and the
corresponding Drude model fits (solid lines). Inset: absorption coefficient vs
photon energy in the band edge and sub-bandgap regions.

\[ \alpha_{\text{eff}}(\lambda) = \frac{1}{2\pi\sigma_{\mu}\sigma_{N}} \int_{0}^{\infty} \int_{0}^{\infty} \exp(-1/2(v - \mu)^2\sigma_{\mu}^2 + (\eta - N)^2\sigma_{N}^2) \alpha_{\text{Drude}}(\lambda, \mu, \eta) d\mu d\eta, \]  

(2)

where \( \mu \), \( N \), and \( \sigma_\mu \), \( \sigma_N \) are the average value and standard deviation for the mobility (free charge density) distribution, and \( \alpha_{\text{Drude}}(\lambda, \mu, N) \) is the Drude model free carrier absorption at a wavelength \( \lambda \) for a material with a mobility (free electron density) of \( \mu \) \( N \); \( \mu \) and \( \eta \) are dummy integration variables.

The oscillation amplitude is well inside a single nanowire, so the
tical properties of an entire ensemble of nanowires in a single
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in the visible region but a pronounced absorption band
∼ 2.5 eV (500 nm) can be observed, most likely due to the
incorporation of Al into the lattice of ZnO (such a band is

absent in the undoped ZnO nanowires). Further study is nec-
essary to clarify the exact origin of the defect-related absorption
phenomena in these materials and their dependence on
dopant inclusion. Region 3 corresponds to the absorption
edge (ℏω> 3 eV).

The low-energy region of each absorption spectrum was
fitted using the Drude model as described above, with the
fitting parameters being the average values and standard dev-
iations \( \mu, N, \sigma_\mu, \) and \( \sigma_N \). A similar approach was used to measure the interfacial charge in transparent, nonscattering
ZnO field-effect transistors by Kim et al.23 Since the amount
of dopant in the nanowires is significant, a third approach
considering the nonparabolicity of the conduction band

was used as well but showed no significant difference with
the results presented here and was therefore not included.

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× 1019 cm−3) which can be explained by a larger degree of
variability in the synthesis products compared to other (and
better optimized) synthesis runs.

C. FET measurements

Because undoped ZnO does not display free carrier ab-
sorption, the value of the carrier mobility in undoped ZnO
nanowires was measured using a SWFET device. The pos-
sible presence of unknown amounts of trapped charge at the
nanowire/dielectric interface prevented us from estimating
the residual free carrier density using SWFET measurements.
Also, the calculation of the true gate capacitance is particu-
larly important since it directly affects the calculated mobil-
ity value. However, the capacitance can be estimated by ei-
ther using a finite-element model to calculate the gate
Fig. 3. Analysis of the transfer curves (Fig. 4) indicates
that the device has an on/off ratio of ~ 106, with a mobility
close to 28 cm2 V−1 s−1, and an off-current on the order of
10−13 A. Comparing these results to similar devices previ-
ously reported,13,14,16 which were synthesized by chemical
vapor deposition methods at higher temperatures
(700–950 °C), our on/off ratio is two to three orders of
magnitude higher, with comparable mobilities. The low off-
current of our device suggests that the synthesized wires are highly crystalline and have a low density of defects as these would typically lead to residual conductivity. ZnO SWFETs with various device structures reported elsewhere\(^3,12–19\) have on/off ratios in the range \(10^3–10^8\), with the higher end being for devices employing an ozone post-treatment with a self-assembled superlattice as the dielectric.\(^18\) The dimensions of the channels are comparable in all devices. SWFET devices with doped nanowires were also fabricated to confirm that the inclusion of Al in the material leads to increased conductivity. The minimum resistivity of our material measured optically was \(2.6 \times 10^{-3}\) \(\Omega\) cm for wires with 0.68 at. % Al, which agrees with previous reports.\(^6\)

Due to the short length of our nanowires (1–5 \(\mu\)m), it is difficult to fabricate multicontact SWFET devices to account for contact resistance. This prevents us from accurately determining the nanowire resistivity and mobility (and thus, free charge concentration). When comparing the mobility values obtained from PDS to those of SWFETs, it should be noted that contact resistance in FET devices results in an underestimation of the field effect mobility.\(^39\) Two different SWFET devices are shown to demonstrate their variability, and the discrepancy with the values fitted using the Drude model (by a factor of 1.4–2.2) is explained by the fact that they are not corrected for contact resistance effects. In general, extracting materials properties from device measurements introduces issues associated with spurious nonideal effects. Given these considerations, the values obtained with the available measurements can be considered in agreement with the values extracted from the optical data (Fig. 3), showing that the electron mobility in the AZO nanowires is lowered by the presence of dopant levels. Also, the observed carrier density in all the samples is lower than expected if all the aluminum present in the nanowires was in zinc substitutional sites (\(Al_{Zn}\)), which would add one electron to the conduction band per each aluminum atom.

**D. NMR**

The oxidation state of Al, hence its electrical activity, is determined by its position in the lattice. The carrier concentration data suggest that not all Al atoms occupy donor sites within the lattice, with the remaining (inactive) Al creating defects that do not contribute to the free electron density and instead hinder charge transport by acting as scattering centers. In order to study the local environment of the Al atoms, we used \(^{27}\)Al NMR. Historically, the active sites are thought to be substitutional in tetrahedrally coordinated zinc sites but solid state \(^{27}\)Al NMR data indicates a far richer solid state chemistry that warrants further investigation.

\(^{27}\)Al MAS NMR spectra of all samples are dominated by three partially overlapping components (Fig. 5). The peak at about 10 ppm corresponds to Al sites with six oxygen neighbors (\(^{\text{VI}}\)Al), and is mainly comprised of a narrower peak with the same position and width as that of ZnAl\(_2\)O\(_4\) spinel,\(^{29}\) suggesting that this phase may be present. The amount of this secondary phase, however, must be lower than the detection limit of other analytical techniques that were used to...
properties of the obtained materials have been measured. The electron mobility in the highly doped Al:ZnO nanowires decreases noticeably with increasing Al concentration, due to the Al acting as scattering centers. The free charge carrier density, however, shows no significant dependence on the Al:Zn ratio, which suggests either a limited activation of the dopant in the ZnO lattice or the appearance of compensating defects. NMR spectroscopy shows that aluminum can occupy a rich variety of sites and suggests that not all are electrically active. The measured properties (\(\mu_e, \rho\)) of these solution-grown nanostructured materials are comparable to ZnO single crystals grown by high-temperature vapor-phase or hydrothermal methods, doped either during synthesis or with ion diffusion into intrinsic ZnO crystals. Improved dopant activation without a further decrease in mobility in these AZO nanowires would result in conductivities rivaling those of ITO and AZO thin films (~\(10^{-4}\) \(\Omega\) cm).

The results obtained point out the need to understand the dopant incorporation and activation mechanisms as well as the charge transport process in nanostructured ZnO, and establish a combination of techniques that allows the effective, reliable, and comprehensive characterization of an ensemble of nanowires.

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**Figure 5.** (Color online) \(^{27}\)Al MAS NMR spectra for Al-doped ZnO (at. % Al:Zn as labeled), collected at 14.1 T (156.5 MHz), with sample spinning rates of 20 kHz, rf tip angle (solids) of about 30° (0.2 \(\mu\) s pulse), pulse delay of 0.1 s, and referenced to 0.1 M Al(NO\(_3\))\(_3\). The only prominent spinning sideband (spin echo) in the range plotted, identified by varying the spinning rate, is marked by “ssb.”

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