CdSe-Coated ZnO Nanowires for Extremely Thin Absorber Solar Cells

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Solar cells can provide an abundant, clean, and sustainable source of electricity, but high costs have limited their implementation. Extremely thin absorber (ETA) cells are robust solid state cells that utilize low cost processing while promising potential efficiencies above 15%. However, the highest reported efficiency of ETA cells is only 2.5%. Improving this efficiency will require fundamental understanding and control of the charge transfer in materials and interfaces within the cell.

We report on materials synthesis and photovoltaic response of ETA cells consisting of a vertical array of $n$-type ZnO nanowires coated with CdSe absorber and with the pores between nanowires filled with $p$-type CuSCN. CdSe absorbs visible light and injects photoexcited electrons into the ZnO nanowires. The architecture of the ETA cell enables use of absorbers with smaller carrier lifetimes than those used in thicker planar films, and elimination of liquid electrolytes renders them more robust than conventional dye sensitized solar cells. However, CdSe deposition must be carefully controlled to obtain highly crystalline, uniform, and conformal coatings with an optimal thickness to achieve maximum light harvesting and charge injection efficiency.

We have deposited CdSe coatings at room temperature using electrodeposition with precise control over morphology and material properties. Detailed information about nucleation, crystal growth, and morphology of the coating on both planar ZnO films and ZnO nanowire arrays was obtained by electrochemical probes and electron microscopy at the early stages of deposition. Under potentiostatic deposition, applied potential of ~ -1.25 V resulted in instantaneous nucleation and high areal density of nuclei and, hence, conformal coatings. Smaller applied potentials ~-1.05 V resulted in sparse and progressive nucleation and non-uniform coatings. However, deposition at potentials larger than -1.6 V resulted in precipitation in electrolyte solution. After annealing, x-ray diffraction and transmission electron microscopy show nanocrystalline CdSe in both hexagonal and cubic phases. Using the optimal potential range determined from the potentiostatic studies, we investigated galvanostatic deposition of CdSe coatings on ZnO nanowire arrays. The thickness of CdSe coating is precisely controlled by electrodeposition charge density, and the deposition is conformal and uniform, which is ideal for ETA cells. UV-Vis transmission spectroscopy and photoelectrochemical solar cell measurements demonstrate that CdSe coatings effectively sensitize ZnO nanowires to visible light.
CdSe-Sensitized p-CuSCN/Nanowire n-ZnO Heterojunctions**

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Nanostructured semiconductors offer the opportunity to design new optoelectronic devices. In the field of photovoltaics, the dye-sensitized nanostructured titanium dioxide photoelectrochemical solar cell is the first and best-known example of a nanostructured cell.[1] The principle of that cell is to coat the wide-bandgap, transparent, porous titanium dioxide with a monolayer of a ruthenium dye, each layer playing the roles of an electron acceptor and light absorber, respectively. However, serious stability problems have inspired research toward solid-state variants, many of which suffer similar stability problems.[2-4] As a result, the concept of the extremely thin absorber (ETA) solar cell based on a semiconducting, extremely thin absorber sandwiched between two transparent, highly interpenetrated nanostructured semiconductors has been recently proposed.[5,6] In this paper we report preparation and characterization of a novel composite nanostructure ZnO/CdSe/CuSCN, based on free-standing ZnO nanowires, which can be considered the fully inorganic analogue of the dye-sensitized solar cell. The three layers of the nanostructure have been produced using easily accessible electrochemical- and solution-deposition techniques. The nanostructure exhibits an energy-conversion efficiency greater than 2%, demonstrating the validity of the ETA solar cell concept.

Figure 1 illustrates the basic design of an ETA solar cell. It consists of a nano- or microstructured layer of a wide-bandgap material ($E_g > 3$ eV) which also serves as a n-type window layer to the cell, an absorber with $1.1 < E_g < 1.8$ eV conformally coated on this window layer, and a void-filling p-type wide-bandgap material ($E_g > 3$ eV). When judiciously chosen in terms of their energy bands, the two transparent p- and n-type semiconductors develop a very high electrical field at their interface. A highly structured interface can substantially reduce the transport path for excited charge carriers in the absorber, and, at the same time, increase the optical path length for photon absorption.[1] Surface enlargement of the interface allows a reduction of the thickness of the absorber by an order-of-magnitude due to the area enlargement. This reduction in the absorber thickness significantly improves the probability of carrier collection owing to the shorter transport path length for the excited carriers, as the extremely thin absorber (tens of nanometers) is located within the electric field of the heterojunction. In addition, light scattering at the internal interfaces of the heterostructure will increase the optical path length through the sample, thereby enhancing the absorbance in a light-trapping effect. For light trapping, the substrate should have a structure with dimensions in the wavelength range of solar light, and in order to obtain a reduction of the electronic path, deep structuring on the 50–300 nm length scale is desirable. With these conditions, the optical and the electronic properties of the ETA solar cell are advantageous for photovoltaic applications. Several fundamental studies on nanostructured/porous n-type and absorber materials for ETA solar cells have been published.[8-11] Nevertheless, there are few published results of complete ETA solar cells. A TiO$_2$/Se/CuSCN heterostructure was reported in 1998 as a photovoltaic cell with an energy-conversion efficiency of ~0.13%. [12] Three years later, the TiO$_2$/CuInS$_2$/CuSCN heterostructure was proposed as an ETA solar cell, but no energy-conversion efficiency was reported.[13]

We choose to use n-type ZnO ($E_g = 3.3$ eV) and p-type CuSCN ($E_g = 3.4$ eV) as transparent semiconductors because the band alignment across the p-CuSCN/n-ZnO heterojunction is well adjusted to produce a high electric field at the interface.[14,15] As an absorber we selected CdSe, a 1.7 eV bandgap semiconductor, because its valence and conduction bands are in a good position for electron transfer with respect to the n- and p-type materials.[14,16] We have made several complete ETA solar cells using n-type ZnO nanowire films electrodeposited on conducting-glass substrates. Before electrodeposition ZnO nanowires, a thin continuous ZnO layer ~150 nm thick ($\text{ZnO}_{\text{np}}$) was deposited by spray pyrolysis on a transparent conducting ($10 \, \text{Ω square}^{-1}$) glass/SnO$_2$ substrate. The ZnO$_{\text{np}}$ layer was deposited in order to avoid contact and consequent short-circuiting, between the F-doped SnO$_2$ of the
conducting-glass substrate and the p-type material layer.\textsuperscript{17,18} The electrochemically deposited ZnO\textsuperscript{18} on the sprayed layer consisted of free-standing single-crystal nanowires oriented along the c-axis and was similar to that deposited directly on SnO\textsubscript{2}.\textsuperscript{8,10} The nanowires were ~100–150 nm across and had a length within the range of 1–2 μm (Fig. 2a). The surface area is calculated to have been larger by a factor of 10–20 over an unstructured layer. In addition to interesting geometrical properties favorable to light trapping, the n-type ZnO nanowire film exhibited unique electronic properties with electronic transport occurring only along the axis of the wires. Carrier concentration and electron mobility were found to be equal to 10\textsuperscript{20} cm\textsuperscript{-3} and 23 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1},\textsuperscript{8} respectively.

A conformal absorber layer of CdSe was galvanostatically deposited on the ZnO nanowires from an aqueous alkaline selenosulfate bath at room temperature.\textsuperscript{19–21} A CdSe layer with a thickness in the range of 30–40 nm has been estimated from a statistical evaluation of the nanowire diameters before and after CdSe deposition (Fig. 2b). The CdSe deposition was uniform over all parts of the nanowires (top and bottom), as can be seen in Figure 2c. X-ray diffraction shows the CdSe layer to be polycrystalline, with the cubic sphalerite phase.\textsuperscript{22} The samples were annealed in air for one hour at 350 °C before CuSCN deposition.

The CuSCN layer was deposited from a saturated solution of CuSCN in propyl sulfide\textsuperscript{23} onto glass/SnO\textsubscript{2}/F/ZnO\textsubscript{aq}/ZnO\textsubscript{aq}/CdSe samples preheated to ~80 °C. The CuSCN layer filled the nanowire structure as shown in Figure 2d. It was crystalline, hexagonal β-CuSCN highly oriented along the [0001] direction.\textsuperscript{24} Figure 3 shows optical transmittance and reflectance spectra of the transparent conducting substrate, and the successively built-up layers. The disappearance of optical interferences in the ZnO\textsubscript{aq} layer indicates the loss of the flat morphology in the sample. An energy gap (E\textsubscript{g}) close to 3.31 eV for ZnO and 1.68 eV for CdSe has been estimated from these spectra using the relation for a direct transition,\textsuperscript{25} in good correlation with reported values.\textsuperscript{15,26–27} The optical bandgap of the CuSCN layer in the cell could not be measured because it was deposited on CdSe; however, for the ETA-solar-cell device, the optical transmission in the range of interest did not show a significant change after CuSCN deposition.

The reflectance spectra clarify and permit comparison of the optical role of each material. The composite ZnO/CdSe film shows a low reflectivity due to a strong light-trapping effect. Two relevant parameters for solar cells are the effective reflectance (R\textsubscript{E}) and effective absorption (A\textsubscript{E}) in the 400–800 nm range of the solar spectrum (air mass, AM 1.5).\textsuperscript{10} The ZnO/CdSe/CuSCN nanostructure showed efficient light trapping with R\textsubscript{E} ~ 8 % and A\textsubscript{E} ~ 89 %. The high A\textsubscript{E} value obtained with less than 40 nm of CdSe thickness is similar to that obtained in crystalline Si with a thickness of ~100 μm.\textsuperscript{29}

The flat surface morphology of CuSCN favors the deposition of an efficient metallic contact, and gold was deposited by vacuum evaporation. Current-density–voltage (J–V) measurements were made on the ETA-solar-cell layers as they were built up. The SnO\textsubscript{2}/F/ZnO junction was an ohmic contact, and subsequent junctions (ZnO/CdSe, ZnO/CuSCN, and CdSe/CuSCN) were rectifying. J–V curves measured for several samples from the front contact, SnO\textsubscript{2}, to the back contact, evaporated Au on CuSCN, were rectifying. Our best ZnO/CdSe/CuSCN ETA solar cell showed an open-circuit voltage of ~500 mV, a short-circuit current density close to 4 mA cm\textsuperscript{-2}, and an overall energy-conversion efficiency of 2.3 % under 360 W m\textsuperscript{-2} (~1/3 sun) (Fig. 4). Other cells showed efficiencies greater than 1.5 %. The electron lifetime, measured from transient photovoltage decay under bias light of 1 sun, was 14 μs. The decay time of the transient photocurrent at short circuit was also 14 μs, implying that recombination was limiting charge collection in these devices.\textsuperscript{29} This in turn implies that reducing recombination would give significant increases in photocurrent.

The 2.3 % energy-conversion efficiency is the highest reported for this kind of solar cell. It is similar to that attained by solid-state solar cells with a dye as absorber material,\textsuperscript{24} which are known to show serious degradation problems.\textsuperscript{14} The melting points of CdSe and CuSCN are well over 1000 °C, while those of or-

Figure 2. Scanning electron microscopy (SEM) images. a) Cross-section of glass/SnO\textsubscript{2}/F/ZnO\textsubscript{aq}/ZnO\textsubscript{aq} sample; b) top view of the ZnO nanowires covered by CdSe; c) detail of (b); d) top view of CuSCN layer covering the ZnO/CdSe nanowires.
Nanowires. The zinc oxide “bumpiness” bounces photons within the light-absorbing layer, increasing the chance for light absorption. Meanwhile, the thinness of the cadmium selenium layer facilitates transfer of photogenerated electrons to ZnO. This nanostructure creates an output current that is up to 50 times greater than in a solar cell made of flat, dense substrate material. The device, made of small quantities of average quality, inexpensive semiconductor materials using low-cost techniques, could provide a cheaper alternative to existing solar cells.

**Experimental**

*Heterojunction Synthesis:* Commercial conducting (10Ω square–1) glass/SnO2:F substrates from Solems SA were covered by a thin continuous layer of ZnO by spray pyrolysis at 400 °C. The spray solution was 0.1 M zinc acetate dihydrate (Zn(CH3COO)2·2H2O) and 0.2 M acetic acid (CH3COOH) in a 25:75 (v/v) water/ethanol mixture [17]. ZnO nanowires were electrodeposited on the SnO2/ZnO substrates at −1 V versus standard calomel electrode (SCE) from an aqueous solution of 5 × 10−5 M ZnCl2 and 0.1 M KCl supporting electrolyte in ultrapure water (18 MΩ·cm), saturated with bubbling oxygen at 80 °C [10,30]. The counter electrode was Pt. ZnO nanowire films were electrodeposited according to the reaction Zn2+ + 1/2O2 + 2e− → ZnO. CdSe was deposited electrochemically from an aqueous alkaline selenoluate solution at room temperature (0.05 M cadmium acetate, 0.1 M nitritriacetic acid trisodium salt, and 0.005 M selenolate, with excess sultite). The pH was adjusted to pH 8. CdSe was deposited galvanostatically in a two-electrode electrochemical cell with the glass/SnO2:F/ZnO/SnO2 sample as the cathode and a Pt counter electrode. The current density of deposition was 0.67 mA cm−2. CdSe electrodeposited according to the overall reaction Cd2+ + Se + 2e− → CdSe. The amount of charge passed in the ZnO and CdSe electrodeposition processes were 20 C cm−2 and 0.25 C cm−2, respectively. The CuSCN layer was deposited from a saturated solution of CuSCN in propyl sulfide [23] onto pre-heated –80 °C glass/SnO2:F/ZnO/SnO2 sample as the cathode. The amount of solution used in the CuSCN deposition process was 0.1 mL cm−2. The samples were annealed in air for 1 h at 350 °C before CuSCN deposition. A gold electrical contact was vacuum-evaporated on the CuSCN layer.

The morphology and crystalline structure of the various layers of the cells were analyzed using a Leica Stereoscan 440 scanning electron microscope and a Philips PW1710 powder X-ray diffractometer. The optical properties (transmission and reflectivity) were measured at room temperature with a Hitachi UV-VIS-NIR 4001 spectrophotometer fitted with an integrating sphere from 300 to 1200 nm. Photoconversion was measured by taking current–voltage (i–V) curves in the dark and under illumination. The electrical contacts were made on the conducting glass/SnO2:F substrates and on the gold evaporated on CuSCN. Samples were illuminated using a halogen lamp directed through a fiber-optic bundle. The fiber optic was used to minimize heating of the substrate by the light source. 360 W m−2 was the maximum illumination possible with this source. The power output of the light source was measured using an Eplab Spectral Pyranometer from Eppley Laboratory.

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Aerogels with a Microporous Crystalline Host Phase**

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Aerogels are a unique class of materials characterized by a highly porous network, and are attractive for many applications, such as thermal and acoustic insulation, and catalysis. Since the invention of aerogels by Kistler in 1931,[1] many papers focusing on the fabrication and characterization of aerogel materials have been published.[2] Although their preparation methods have been marked by several breakthroughs since the 1930s, all aerogels produced so far are characterized by chemically bonded three-dimensional networks.

In this contribution, we present the first examples of physically bonded aerogels, for which the three-dimensional connectedness is provided by intermolecular physical bonding at crystalline junction zones. These semicrystalline aerogels are obtained by supercritical CO2 extraction from syndiotactic polystyrene (sPS) physical gels.[3] This communication shows, in addition, that the crystalline phase of these semicrystalline aerogels can also be δ type.[4–7] This is relevant since, in general, δ-form sPS samples have been proposed as helpful molecular tools suitable for the purification[8] and sensing[7] of volatile organic compounds, both in air and water. In fact, the δ-phase is characterized by two identical micropores, with a maximum extension of about 0.8 nm and a volume of nearly 120 Å³ (and eight styrene monomeric units) per unit cell,[16] which can host generally isolated volatile organic molecules, being absorbed from water and air even when present at very low concentrations.[5]

It is well known that sPS can easily form physical gels with several organic solvents, and a large body of work has been devoted to sPS gelation.[3] Depending on the type of solvent and/or thermal treatment, the polymer-rich phase of the gels

[29] B. O’Regan, personal communication.

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Raman Effect in Zinc Oxide

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The Raman effect in zinc oxide has been measured using the continuous helium-neon and ionized argon lasers as sources. The frequency and symmetry character of the fundamental modes have been determined. The results are: two $E_2$ vibrations at 101 and 437 cm$^{-1}$; one transverse $A_1$ at 381 cm$^{-1}$ and one transverse $E_1$ at 407 cm$^{-1}$; one longitudinal $A_1$ at 574 cm$^{-1}$ and one longitudinal $E_1$ at 583 cm$^{-1}$.

INTRODUCTION

The optical-phonon spectra of solids have been studied mainly by neutron-diffraction, Raman effect, infrared-absorption, and reflectivity techniques. The role of the Raman effect as a tool for these determinations of optical-phonon spectra, particularly of semiconductors, has been limited because of the difficulties associated with crystal size and the relatively low flux density associated with the classical Raman light sources. This has often led to the inability to obtain good angular-dependence and polarization measurements, so that much of the information that would allow unequivocal identification of symmetry character of these vibrations is lost.

The laser—in particular, the visible continuous gas laser—is able to overcome these disadvantages associated with the Raman observations in solids. The advantages of the laser are high-power density, monochromaticity, parallelism, and linear polarization.

In the case of liquids or gases, where there is random orientation of the molecules, one has to average the Raman process over all molecular orientations with respect to the incident electric field. This averaging process smear out many of the properties of the polarizability tensor associated with the molecules of the liquid or gas.

In the case of a single crystal, where this averaging process is not needed, the polarization measurement of a certain Raman line will be a direct indication of which of the components of the polarizability tensor change during the vibration. The angular dependence will allow us to study the influence of the conservation of momentum of the phonon on the frequency and selection rules of the Raman effect.

For ZnO, the phonon spectrum has been studied by both Raman and infrared techniques. Infrared-absorption data have been mostly connected with multiphonon processes, with phonons having wave vectors in the vicinity of the Brillouin zone edge. Those multiphonon spectra are, in our opinion, not well resolved and difficult to interpret. The infrared-reflection data yield the infrared active transverse optical phonons near the zone center. Finally, preliminary Raman measurements reported on ZnO lack polarization data, and therefore cannot unambiguously designate symmetry. In view of the present interest in the wurzite piezoelectric semiconductors, it was felt that a verification of the selection rules would be of value.

However, our interpretation is in almost complete disagreement with the work of Mitra and Bryant, and there also appears to be some discrepancy with respect to the reflection work of Collins and Kleinman.

EXPERIMENTAL

The experimental setup is similar to the one used for Raman effect of liquids. It consists of a gas-laser source focused into the crystal, an oriented crystal sample, a light-collector lens, a polarizer, a spectrometer, a photomultiplier, and a lock-in amplification and recording system.

The exciting wavelengths used were 6328 Å from an He-Ne laser and 4880 or 5145 Å from a continuous A$^+$ laser with average powers of around 50 mW. (No significant shift in phonon frequencies was observed for different laser frequencies.) The laser light was chopped at 400 cps and scattered light observed at 90° from incidence, after a single pass of the laser light through the crystal; this technique yields less direct scattering and cases interpretation of results in terms of the crystal symmetry. The spectrometer used is a "tandem" grating spectrometer consisting of two identical $f$:6.8 grating spectrometers driven by the same shaft. In this spectrometer stray light and grating ghosts are strongly suppressed and the background light at 15 cm$^{-1}$ from the laser frequency is down by $10^4$. The slit widths used were of the order of 8 cm$^{-1}$.

Final data was taken on two ZnO crystals. One of the crystals was cut so that the $z$ or optical axis was parallel to a sample edge (designated the $z$-cut crystal), and the other was cut so that the $z$ direction was parallel to a sample face and at 45° to the sample edges (designated 45° crystal). Both crystals were approximately cubic with the $z$-cut crystal having a linear dimension of about 6 mm and the 45° crystal about 3 mm. All data were

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ZnO has wurtzite symmetry with $C_{6v}$ or 6 mm symmetry. There are 4 atoms per unit cell leading to 12 phonon branches, 9 optical and 3 acoustic. Group theory predicts, near the center of the Brillouin zone, that there is an $A_1$ branch, a doubly degenerate $E_1$ branch, two doubly degenerate $E_2$ branches, and two $B$ branches.\(^6\) The $A_1$ and $E_1$ branches are both Raman- and infrared-active, the $E_2$ branches are Raman-active only, while the $B$ branches are inactive. Group theory, however, does not take into account the macroscopic electric field associated with the infrared-active longitudinal optical mode, and the interpretation of the $A_1$ and $E_1$ branches must be modified.\(^6,8\) This is discussed below.

The scattering intensity of a Stokes-Raman transition, if a harmonic-oscillator approximation is assumed, can be written

$$I = C
\left(\frac{n_p + 1}{n_p}\right)\left(e_p^*\alpha_{pe}\epsilon_{pe}\right)^2,$$

where $C$ is a constant, $\nu_s$ is the Stokes-shifted Raman frequency, $\nu_p$ is the vibrational frequency of the oscillator, $n_p$ is the occupation number of the initial vibrational state, $e_p^*$ is the $\rho$th component of the unit polarization vector of the incident light, $\epsilon_{pe}$ is the $\sigma$th component of the scattered light, and $\alpha_{pe}$ is the change of the polarizability tensor component $\alpha_{pe}$ during the vibration having normal coordinate $q_a$:

$$\alpha_{pe}(q_a) = (\partial \alpha_{pe}/\partial q_a).$$

For each normal mode, only certain polarizability components change during the vibration: For the $C_{6v}$ point group these tensors are given by\(^6\)

$$\alpha'(A_1(x)) = \begin{bmatrix} \alpha_{11}' & 0 \\ 0 & \alpha_{11}' \end{bmatrix},$$

$$\alpha'(E_1(-x)) = \begin{bmatrix} 0 & 0 & -\alpha_{13}' \\ 0 & 0 & 0 \\ -\alpha_{13}' & 0 & 0 \end{bmatrix},$$

$$\alpha'(E_1(y)) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{13}' \\ 0 & \alpha_{13}' & 0 \end{bmatrix},$$

$$\alpha'(E_2) = \begin{bmatrix} 0 & \alpha_{13}' & 0 \\ \alpha_{13}' & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \alpha'(E_2) = \begin{bmatrix} \alpha_{11}' & 0 & 0 \\ 0 & -\alpha_{11}' & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

For the infrared- and Raman-active $A_1$ and $E_1$ modes the coordinate in parenthesis designates the direction of phonon polarization. That is, an $A_1$ phonon is polarized parallel to the $z$ axis, while the $E_1$ phonons are polarized in the $xy$ plane.

\(^7\) See, for example, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956), p. 82 ff.
Sachs-Teller relationship:
\[ \nu_{l}^{\text{ST}} = \nu_{l}^{\text{P}} \left( \frac{\varepsilon_{0}}{\varepsilon_{\infty}} \right)^{1/2} \] and
\[ \nu_{l}^{\text{S}} = \nu_{l}^{\text{P}} \left( \frac{\varepsilon_{0}}{\varepsilon_{\infty}} \right)^{1/2}, \]
where \( \varepsilon_{0} \) is the static dielectric constant and \( \varepsilon_{\infty} \) is the high-frequency dielectric constant.

Furthermore, the change in the polarizability for a transverse component need not be equal to that for a longitudinal component. This difference arises from the nature of the electron-phonon coupling. For transverse waves, there is only deformation-potential coupling, while for longitudinal waves there is also electrostatic coupling. Since both contributions are of the same order of magnitude and can be additive or subtractive,\(^{10}\) the polarizability change and the resulting Raman intensities due to the longitudinal and transverse phonons can be considerably different.

Figure 1 (A–F) shows for the \( z \)-cut crystal the spectra for 90° Raman scattering at room temperature, when the polarization of the incident and scattered light are monitored and the exciting wavelength is 4880 Å. Each spectrum is designated by its incident and scattered polarization and propagation directions and by the normal mode expected to be active under these conditions. The “fundamentals” are designated by arrows and their frequencies in wave numbers (cm\(^{-1}\)) are given directly alongside. In the figure are also shown the frequencies for other prominent peaks. We estimate that the fundamental frequencies are reliable to \( \pm 3 \) cm\(^{-1}\).

In addition to magnitude and symmetry considerations, we have eliminated lines as “fundamentals” by virtue of their temperature dependence. For example, a

\[^{9}\] The reflection data of Collins and Kleinman (Ref. 2) led us to believe that this limit (electrostatic effects much larger than anisotropy effects) would be well satisfied. Their results are two transverse optical modes both at 414 cm\(^{-1}\) and a longitudinal optical mode at 591 cm\(^{-1}\) with no measurable anisotropy. We find that this limit is still satisfied, but there is a definite and striking anisotropy.

preliminary study of the temperature dependence has led us to eliminate the line at 334 cm\(^{-1}\) [Figs. 1(A) and 1(B)] from being a fundamental. A fundamental Stokes line has temperature dependence \(n+1\) where \(n = 1/(\varepsilon n k T - 1)\) is the thermal occupation number for a phonon of energy \(\varepsilon n k T\). This would lead, for the 334 cm\(^{-1}\) line, to an intensity decrease of around 25% from room temperature to liquid-nitrogen temperature. The observed decrease was at least a factor of 5, i.e., a factor of 20 too large.

We now give the detailed interpretation, based on Poulet\(^4\) and Loudon\(^3\) of Figs. 1 and 2 by the use of the vector diagrams given in Fig. 3. In Fig. 3(a), the incident light is propagating in the \(x\) direction and polarized along \(z\), and the scattered light along \(y\) and analyzed along \(z\) or \(x\). The phonon must conserve energy and momentum given by \(\nu_p = \nu_i - \nu_s\) and \(\mathbf{k}_p = \mathbf{k}_i - \mathbf{k}_s\). The first case (\(z\) polarization) is designated as \(x(ay)z\) [Fig. 1(B)] and has \(A_1\) character. Since the phonon propagates in the \(xy\) plane and is polarized along \(z\), it is pure transverse and is the \(A_1\) transverse phonon \(\nu_i^{(1)}\) at 380 cm\(^{-1}\). The second case (scattered light with \(x\) polarization) has \(E_1\) character and is shown in Fig. 1(F). For this \(x(ay)z\) arrangement, phonons will be excited having polarization along the \(x\) and \(y\) axis. These are decomposed into vibrations parallel and perpendicular (in the \(xy\) plane) to the phonon-propagation direction, and give rise to the \(E_1\) transverse phonon \(\nu_i^{(1)}\) and the \(E_1\) longitudinal phonon \(\nu_i^{(3)}\) with \(\nu_i^{(1)} = 407\) cm\(^{-1}\) and \(\nu_i^{(3)} = 583\) cm\(^{-1}\).

Similarly, in Fig. 3(b) for the incident and scattered light in the \(xz\) plane the \(x(ay)z\) arrangement [Fig. 1(D)] gives the \(E_1\) transverse phonon \(\nu_i^{(1)}\). In Fig. 1(A), \(x(yy)z\), and Fig. 1(C), \(x(ay)z\), the phonons have “quasitransverse” and “quasilongitudinal” components and mixed character for which the \(A_1\) character is observed in 1(A) and the \(E_1\) in 1(C). The transverse-phonon frequency is given, for \(\theta = 45^\circ\), by

\[
\nu_i^{(1)} = z(\nu_i^{(1)})^2 + (\nu_i^{(3)})^2,
\]

so that \(\nu_i = 395\) cm\(^{-1}\) for \(\nu_i^{(1)} = 380\) cm\(^{-1}\) and \(\nu_i^{(3)} = 407\) cm\(^{-1}\). Only the \(E_1\) character of the “quasi-longitudinal” phonon at 581 cm\(^{-1}\) can be seen, and because of its weak intensity and poor line shape, no conclusive frequency shift can be determined from the \(E_1\) longitudinal phonon \(\nu_i^{(3)}\).

However, as seen in Fig. 4, the 45°-cut crystal permits right-angle Raman scattering while requiring the phonon to propagate along either the \(x\) or the \(z\) axis by simply reversing the propagation direction of the incident light. This was done specifically to observe the \(A_1\) longitudinal phonon, since in none of the above cases was it possible for the longitudinal phonon to be polarized along the \(z\) axis.

Since the incoming and scattered light propagate and are polarized in the \(xz\) plane, the \(E_1\) longitudinal should be observed for phonon propagation along the \(x\) axis and the \(A_1\) longitudinal along the \(z\) axis. Because of the relatively weak \(E_1\) component and the smaller crystal size as compared to the \(z\)-cut crystal, the \(E_1\) longitudinal phonon was not observed here. The \(A_1\) longitudinal is, however, well resolved with frequency \(\nu_i^{(3)} = 574\) cm\(^{-1}\) and is seen in Fig. 2. [This is probably due to the \(s_{xx}\) component, since the \(s_{11}\) was shown to be small in Fig. 1(A).] There is thus a definite anisotropy of the longitudinal phonon, although it is smaller than we would have expected from the modified Lyddane-Sachs-Teller relationship.

Lastly, with regard to the \(E_2\) vibrations, two lines are found at 101 and 437 cm\(^{-1}\) which unambiguously have \(E_2\) character as can be seen in Figs. 1 and 2. That is, they appear with large intensities in \((syy)z\) [Fig. 1(A)] and \((syy)p\) [Fig. 1(E)] directions and are missing in all \((sz)\) and \((zx)\) directions. There is no measurable frequency shift in these lines.

Our interpretation can be compared to the results of Mitra and Bryant.\(^3\) They find a transverse \(E_1\) at 438 cm\(^{-1}\), a transverse \(A_1\) at 420 cm\(^{-1}\), two \(E_2\) vibrations at 180 and 383 cm\(^{-1}\), and two phonons of unspecified symmetry at 538 and 588 cm\(^{-1}\).

**Table I. Frequency and symmetry of the fundamental optical modes in ZnO.**

<table>
<thead>
<tr>
<th>Symmetry character</th>
<th>Frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_2)</td>
<td>101</td>
</tr>
<tr>
<td>(E_2)</td>
<td>437</td>
</tr>
<tr>
<td>(E_1) (transverse)</td>
<td>407</td>
</tr>
<tr>
<td>(A_1) (transverse)</td>
<td>380</td>
</tr>
<tr>
<td>(E_1) (longitudinal)</td>
<td>583</td>
</tr>
<tr>
<td>(A_1) (longitudinal)</td>
<td>574</td>
</tr>
</tbody>
</table>
CONCLUSIONS

We have made a careful polarization study of the 90° scattering for the fundamental Raman-active phonons in ZnO. We have found two $E_2$ phonons, and one transverse $E_1$ phonon and one transverse $A_1$ phonon with a definite anisotropy shift. The "quasitransverse" phonon of "impure" symmetry has the expected frequency. The $A_1$ and $E_1$ longitudinal phonons have also been found, and an anisotropy, although small, has been determined. We cannot, however, say anything conclusive concerning the "quasilongitudinal" phonon. There are also several prominent peaks which are attributed to multiphonon processes.

ACKNOWLEDGMENTS

The paper has greatly benefited from a critical reading by D. A. Kleinman. We are also indebted to him for, hopefully, clarifying our notation. We wish to thank R. J. Martin for sample preparation.

In Table I are listed the frequencies and symmetries of the fundamental optical phonons in ZnO.

In Table II are listed the most prominent multiphonon processes. These processes presumably occur for phonon wave vectors considerably removed from the center of the Brillouin zone, and we have not seriously attempted an interpretation. Such an interpretation would require a knowledge of critical points and selection rules for various points in the zone, and may soon become available.\textsuperscript{11}

Synchrotron x-ray scattering of ZnO nanorods: Periodic ordering and lattice size

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We demonstrate that synchrotron x-ray powder diffraction (XRD) is a powerful technique for studying the structure and self-organization of zinc-oxide nanostructures. Zinc-oxide nanorods were prepared by a solution-growth method that resulted in uniform nanorods with 2-nm diameter and lengths in the range 10–50 nm. These nanorods were structurally characterized by a combination of small-angle and wide-angle synchrotron XRD and transmission electron microscopy (TEM). Small-angle XRD and TEM were used to investigate nanorod self-assembly and the influence of surfactant/precursor ratio on self-assembly. Wide-angle XRD was used to study the evolution of nanorod growth as a function of synthesis time and surfactant/precursor ratio.

I. INTRODUCTION

One-dimensional (1D) nanostructures such as nanotubes, nanowires, and nanorods exhibit novel electronic and optical properties associated with their low dimensionality and quantum confinement.1–6 They have been proposed as interconnects and functional components in nanoscale electronic, optoelectronic, and electrochemical devices. Among the many techniques used to fabricate 1D nanostructures, colloidal growth is a particularly attractive synthetic technique since it is convenient and capable of producing large material quantities. This solution-phase method has been used extensively in the production of many 1D nanomaterials including metals,7 semiconductors,8–10 and oxides.11

There continue to be major challenges in this field. For example, one is the development of new synthetic methodologies, which enable shape- and size-controlled uniform 1D nanostructures. To use these methods effectively, for example, one wishes to understand the trade-offs in size and its dispersion with solution constituents or composition. A second challenge is to grow ordered assemblies of 1D nanostructures into well-defined two- and three-dimensional (2D and 3D) superstructures. The assembly of rod-shaped 1D nanostructures has generally been less explored than that of nanoparticles. Thus only a few examples of 3D spontaneous superlattice formation, e.g., Ag,12 Au,13 Te,14 BaCrO₄,15 FeOOH,16 and CdSe,17 nanorods have been reported. To investigate these structural questions, it is necessary to use probes with high spatial resolution. In this regard, x-ray diffraction (XRD) and transmission electron microscopy (TEM) are two key techniques used for structural studies of nanostructures. Synchrotron-radiation x-ray diffraction has high sensitivity and angle resolution and is suitable for both wide- and small-angle x-ray diffraction/scattering. These techniques not only measure the nanostructure size and lattice parameters, but they can also accurately probe structural periodicity, also at the nanoscale. Despite its capability, small-angle scattering has so far been used to only a limited extent, such as in probing the assembly of certain nanoparticles systems.17–20

ZnO has been the subject of several recent studies of nanoparticle growth. The material is of interest because of its many practical applications such as light-emitting diodes for ultraviolet/blue wavelengths, piezoelectric
devices, acousto-optical devices, and chemical sensors.\(^{21}\) It is a semiconductor with a direct band-gap of 3.37 eV at room temperature and an exciton binding energy ~60 meV. This large exciton binding energy makes the material an attractive candidate for room-temperature ultraviolet (UV) lasing; low-dimensional ZnO nanostructures may further improve lasing conditions due to quantum-confinement.\(^{22}\)

Many solution-phase methods have been used to synthesize 1D ZnO nanostructures; however, thusfar, these have generally failed to produce small-diameter (<50 nm) ZnO nanorods.\(^{23}\) Recently, Yin et al. developed a new synthetic approach for ZnO nanorods based on thermal decomposition of zinc acetate in organic solvents using oleic acid as a capping agent.\(^{24}\) This method produces relatively monodisperse ZnO nanorods with extremely small diameters (~2 nm). This diameter range is an order of magnitude smaller than previously reported for ZnO nanorods using other preparation methods, and as a result, strong quantum confinement was observed for ZnO rods prepared in this manner.\(^{24}\)

Here we report on the use of synchrotron x-ray powder diffraction as a powerful technique to study the structure and self-assembly of zinc-oxide nanostructures. Zinc-oxide nanorods were prepared by a solution growth method\(^{24}\) that resulted in uniform nanorods with diameters of 2 nm and lengths in the range of 10–50 nm. These nanorods were deposited onto substrates and structurally characterized by a combination of small- and wide-angle synchrotron XRD and transmission electron microscopy (TEM). In particular, we used small-angle x-ray diffraction (SAXRD) to observe ordering of the nanorods into periodic structures and wide-angle XRD to study systematically the influence of various growth parameters on the size and lattice constants of the ZnO rods.

II. EXPERIMENTAL

A. Nanorod synthesis

ZnO nanorods were prepared by thermal decomposition of zinc acetate in organic solvents in the presence of oleic acid, which produces relatively monodisperse ZnO nanorods (ZnO quantum rods) as reported previously.\(^{24}\) In a typical reaction, 4 mmol dry zinc acetate [Zn\((\text{CO}_2\text{CH}_3)\)_2, Aldrich, St. Louis, MO] is added to a mixture containing 15 ml trioctylamine and 3 g of oleic acid (12 mmol) at room temperature. The solution is heated to 180 °C under vacuum for one hour; the temperature is then rapidly raised to 286 °C. After about an hour, the solution turns from a clear yellow to cloudy color, indicating the formation of the rods. In the timed-growth experiment, timing started from the point when the solution turned cloudy. The nanorods are precipitated by adding ethanol after cooling the reaction mixture to room temperature and are separated and cleaned by repeated precipitation of the hexane solution with ethanol. The final products are then re-dispersed in hexane without further size selection. In our experiments, the growth conditions (heating times and surfactant/precursor ratio) were varied to investigate the effects of these parameters on synthesis dynamics.

B. Characterization

Our ZnO nanorods were characterized with TEM and XRD. The XRD measurements were taken on a Beamline X18A at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory. The incident x-ray beam was focused by a bent cylindrical, platinum-coated aluminum mirror and “slitted” to dimensions of 0.5 mm vertical and 1 mm horizontal. The wavelength was selected to be 1.2915 Å (corresponding to a photon energy of 9.6 KeV) by a double, flat, crystal Si (111) monochromator. The samples were mounted onto a Huber four-circle diffractometer. The XRD powder diffraction measurements were performed using a standard θ-2θ scan, in which, when the Si wafer sample is tilted by angle θ, the detector simultaneously moves by angle 2θ (see inserts in our figures below). During this variation, the ϕ and ψ angles of the four-circle diffractometer were set at zero. The incident x-ray beam and diffracted beam were in a plane with the silicon-wafer surface normal. An avalanche photodiode detector was used to collect the scattered beam. XRD samples were prepared by drying the hexane nanorod dispersions on the silicon wafer sample (1 × 1 cm). The instrument width of the XRD peak in our experiments was determined by measurement of a characteristic diffraction peak for large powder particles; any increased broadening due to the finite size of the nanoparticles could then be determined by deconvolution of the instrument width. In general, deconvolution introduced only a small correction to the measured width.

In the case of SAXRD, large surface concentrations of nanorods were deposited on the substrates (>10 drops of hexane solution of rods). In the case of wide-angle XRD, a much smaller surface concentration was needed; typically 1 or 2 drops of hexane solution of rods were used. The TEM experiments were performed on a JEOL 100cx instrument with an accelerating voltage of 100 kV (JEOL, Inc., Peabody, MA). The TEM samples were prepared by drying a drop of the hexane solution of nanorods deposited on a copper grid backed with Formvar.

III. RESULTS AND DISCUSSION

A. Determination of inter-rod spacing in self-assembled arrays by SAXRD

Small-angle synchrotron diffraction is a well-established technique for measuring the periodicity in
structures for which the length scale of the periodicity is orders of magnitude greater than the crystal-lattice spacing. Here, we used SAXRD to examine periodic ordering within solvent-evaporated films of nanorods on Si substrates and to thus infer the degree of self-assembly during deposition. Figure 1 shows a series of SAXRD patterns, which were observed at angles \(2\theta > 1^\circ\), from ZnO nanorods synthesized with different molar ratios of oleic acid to zinc acetate. The peaks in each curve can be fitted to a sequence of Bragg-diffraction orders resulting from long-length scale periodic structures. In particular, comparison of the \(d\)-spacing using Bragg’s law \((2d\sin\theta = n\lambda)\) shows that diffraction peaks for each SAXRD curve originated from different orders of the same Bragg condition. These well-defined SAXRD peaks must originate from periodic structure along the normal of the Si substrates formed as a consequence of self-assembly within the nanorod film.

To understand the nature of this periodicity, TEM measurements were taken of a dried, deposited layer of nanorods on a TEM copper grid. Figure 2 shows a typical TEM image of these layers. The measurement of individual rods using either somewhat higher resolution micrographs or magnified images showed an average diameter of 2 nm and average length of 45 nm. A previous study\(^{24}\) by some of the authors of the present paper also found the same characteristic 2-nm diameters. Figure 2 shows that the nanorods self-assemble into close-packed “stacking” arrays, in which the rods align themselves parallel to each other with respect to the long axis of the rod. Recent studies have also shown that rod-shaped metallic and semiconductors nanocrystals self-assemble into ordered 2D/3D superstructures after solvent evaporation or Langmuir–Blodgett-film preparation.\(^{9,12–16,25–27}\) In the case of solvent evaporation, the final arrangement of self-assembled nanorods was attributed to a balance of intra-nano-object and thin-film forces (surface tension, van der Waals forces, and capillary forces).\(^{13,14}\) Furthermore, surfactants in the nanorod-growth solution were shown to be of key importance in controlling self-assembly. In our work, the center-to-center distances between adjacent rods in nanorods stacks were observed to be \(-4.5\) nm, which is nearly equal to the sum of the length of extended molecule length (2.3 nm) of oleic acid and the diameter of nanorods (2 nm). This spacing suggests interdigitation between oleic-acid chains.

Based on the scattering geometry we used, our small-angle x-ray scattering can measure any periodicity in the nanorod sample, which is perpendicular to the sample surface, i.e., to the substrate surface. Further, in these SAXRD experiments we used higher coverage of nanorods, as measured approximately by drops applied per area, than for our TEM samples. Thus, any layered arrangement of these nanorod bundles (or arrays) would cause constructive interference of x-rays scattered from vertically aligned periodic arrays of these ZnO nanorods and produce diffraction peaks at small angles. The dimensions obtained from the major small-angle diffraction peaks in Fig. 1 should be approximately the same as the inter-rod space in nanorod bundles (or arrays) shown in Fig. 2. In fact, the values of \(d\) obtained from the SAXRD pattern in Fig. 1 using the Bragg equation are \(-3.5–4.4\) nm; this value is the periodicity of nanorods bundles. Specifically, this range is consistent with the center-to-center distance between neighboring nanorods.
of ~4.5 nm observed in our TEM images (see above). Furthermore, the average number of ZnO nanorods in the “vertical direction” within the deposited film—that is, the average coverage, i.e., monolayers along the “substrate surface normal,”—can be estimated by the width of the maximum in our periodic diffraction pattern and through the Scherrer equation, $L = 0.94\lambda/B_{1st}\cos\theta_{1st}$, where $B_{1st}$ and $\theta_{1st}$ are the full width at half-maximum (FWHM) width and peak position of first-order diffraction peaks, respectively, which are obtained by fitting these peaks to a Lorentz function. This is analogous to the well-known behavior of a wide-angle XRD system, for which the XRD peak width is inversely related to the number of scattering centers in a periodic array, whereas in SAXRD, each nanorod acts as a scattering center. In fact, based on our calculation using the Scherrer equation, we estimate 5–10 monolayers of ZnO rods are formed on our Si substrates.

This same nanorod coverage dependence is seen in the variation in peak width of the 5 data plots shown in Fig. 1. In this case, the peak width of SAXRD patterns becomes broader with decreasing surfactant/precursor ratio. This behavior is explained by a decrease in coverage, i.e., monolayer thickness of ZnO nanorods, with decreasing surfactant/precursor ratio. This result suggests that the surfactant ligands, attached to the nanorod surface, are important in controlling self-assembly. In addition, Fig. 1 also shows that the periodicity of nanorod arrays becomes slightly larger with increasing the surfactant/precursor ratio. Thus as the ratio increases, more organic ligands attach to the surface of nanorods, resulting in the increase of the separation of the adjacent nanorods. In general, various forms of self-assembly have been seen via small-angle x-ray scattering/diffraction; however, the sharp interference seen in our experiments has not been as clearly observed. The sharp periodicity seen here may be attributed to the high crystallinity and uniformity of our as-synthesized ZnO nanorods.

### B. Influence of synthetic parameters on the size and lattice of rods

#### 1. Overview

XRD spectra at or near wide angles were examined to determine the crystal structure of the as-synthesized ZnO nanorods. Figure 3 shows a comparison of the XRD pattern for our synthesized ZnO nanorods with that of high-purity ZnO powder (Alfa Aesar, Ward Hill, MA). The XRD pattern of the nanorods shows a high degree of crystallinity; the diffraction peaks can be indexed to the hexagonal wurtzite structure of bulk ZnO with lattice constants of $a = 3.2514 \text{ Å}$ and $c = 5.2133 \text{ Å}$. This uniform crystallinity is in agreement with a previous study using high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED). In that work, it was also found that the preferential growth direction of the ZnO nanorods is along the $c$ axis. Note that the somewhat larger peak broadening for the nanorods is due to the finite-size effect (see discussion below in this section). Note also in our case that other, much smaller, diffraction peaks are observed, each with a width approximately that of the $c$-axis (002) peak. We attribute these smaller peaks to a small amount of generally spherical-shaped precipitates present in each solution sample.

In many cases, properties of nanomaterials are sensitive to their near-atomic dimensions; as a result, precise control over their size is critical. In the following, we present XRD measurements near wide angles for ZnO nanorods synthesized with different synthesis times and surfactant/precursor ratios. In general, these two growth parameters are two of the most fundamental factors in affecting the size of the nanocrystal during colloidal-solution growth. As mentioned above, the changes in the length of ZnO nanorods and corresponding changes in lattice constants, due to lattice relaxation, can be measured through the XRD peak broadening and position, respectively.

Note here that since the lattice parameter $c$ depends on the nanorod length, the experimentally measured XRD peak broadening includes not only the contribution from the finite length of nanorods but also a contribution from the associated variation of the lattice parameter due to a distribution in nanorod length. Therefore, some minimal degree of monodispersity in nanorod length is necessary to determine accurately the average length of nanorods from the XRD peak width. In fact, in our experiments, the dispersion appears to be relatively small. In particular, in our TEM measurements, it is found the size...
distribution in our nanorod length is typically \(-10\text{--}15\%\). This suggests that the as-synthesized nanorods were relative monodispersed, considering that there is no further size selection made during the preparation of our nanorods.

In addition, it is possible to roughly estimate the broadening of the XRD peak \(B_{ld}\) due to the variation of the lattice parameter \(c\) with length coupled with a distribution of nanorod lengths. In particular, if this broadening \(B_{ld}\) is much smaller than that due to the finite length of nanorods \(B_{fl}\), the contribution of this nanorod-length distribution to the XRD peak broadening can be neglected in the first approximation. To estimate \(B_{ld}\), we can use Bragg’s law along with the Scherrer equation

\[
B_{ld} = 2\Delta \theta = -2 \times (\Delta d/d) \times \tan \theta ,
\]

and

\[
B_{fl} = 0.94\lambda/L \cos \theta ,
\]

where \(L\) represents the average length of nanorods, \(d\) is the spacing of the Bragg diffraction planes for the (002) diffraction peak, and \(\Delta d\) is the average variation in \(d\) (related to the variation of the lattice parameter) due to the average variation in nanorod length. Combining these two equations we obtain

\[
B_{ld}/B_{fl} = -1.06 \times \frac{\Delta d}{d} \times \frac{L}{d} .
\]

We can estimate the value of \(\Delta d/d\), from our measured data shown in Fig. 5(b) in the next section. In particular, using our measured variation of lattice parameter, \(\Delta 2d = 0.04\ \text{Å}\) for \(L = 10\ \text{nm}\), we obtain \(B_{ld}/B_{fl} \approx 31\%\), a relatively modest value. This result indicates that the contribution of the nanorod length distribution on XRD peak broadening is small to negligible compared with that due to finite-length broadening. We were unable to find other values relating nanotube lattice parameters to their length. However, for additional comparison, we use typical values found for other forms of nano-objects found in the literature. For example, Perebeinos et al. report that \(\Delta d/d\) can be written as \(\Delta d/d = \alpha/L\) where \(\alpha\) is a constant.\(^{28}\) Perebeinos et al. obtained an experimental value of \(\alpha = 0.37\ \text{Å}\) for CeO\(_2\) nanoparticles; using this value one finds \(B_{ld}/B_{fl} \approx 15\%\). Obviously some variation in these values should be seen since other effects than size may play a role in determining \(d\), including surface defects, capping agents, and adsorbed species on nanocrystals. Nonetheless, the estimated values suggest that \(B_{fl}\) is the dominant effect for our samples; thus we assume that this is the case in our discussions below.

Finally, one additional comment can be made based on the above analysis; namely, the above equations suggest that the ratio \(B_{ld}/B_{fl} \equiv \alpha/d\) is independent of nanorod length. This linear dependence is reasonable because the physical effects, which lead to the change in \(d\) with \(L\), will decrease with increasing nanorod length. The length independence suggests that a relative comparison of nanorod lengths would be expected to be accurate, even if the nanorod length calculated from XRD peak broadening has a small systematic error due to a contribution from a length distribution of nanorods.

2. Synthesis time

The effect of synthesis time on the size of ZnO nanorods was investigated using XRD and TEM. In TEM measurements, we observed that the diameter of nanorods remains nearly unchanged with time and surfactant/precursor ratio. Since the growth axis of the as-synthesized nanorods is overwhelmingly along \(c\) axis, we focused on the (002) diffraction peaks in the following XRD measurements. Figure 4 shows XRD spectra of the (002) peak from nanorods prepared with different synthesis time along with that from a commercial powder sample. The XRD peaks shown in Fig. 4 were normalized by comparison to their respective (002) diffraction peak intensity. Note that the XRD curves shown in Fig. 4 are raw data without any post-data processing, e.g., smoothing. In this connection, the XRD profiles in Fig. 4 have different signal backgrounds or signal/noise ratios.

![FIG. 4. XRD spectra of the (002) peak from ZnO nanorods prepared using different synthesis times. The inset shows a descriptive sketch of the scattering geometry for wide-angle XRD.](image-url)
This is because the counting times used for data collection were not always same for different samples when the XRD measurements were made due to the order of the measurements. As shown in Fig. 4, with increased synthesis time, the (002) peak gradually sharpens, and the peak position shifts toward larger angles in accord with increased rod length, resulting from growth along the longitudinal direction (c axis). In general, our TEM measurements show this same trend, i.e., the average length of the nanorod increasing with time while the diameter remains essentially constant. However, the absolute nanorod length determined by XRD tended to be smaller than that from TEM. Differences between TEM and XRD particles lengths have been noted before.29 In part, this difference is attributable to the fact that the XRD measurements average numbers of particles orders-of-magnitude larger than the TEM measurements do and thus are less sensitive to local fluctuation in particle size. In addition, any local variation in the lattice parameter due to surfaces and ligand binding would contribute to lattice broadening to the diffraction width, as mentioned above.

Figure 5(a) shows the temporal evolution of the nanorod length, determined using the Scherrer equation. Note that the data in Fig. 5(a) appear not to follow the same process of Ostwald-ripening growth kinetics that has been found in many spherical-nanoparticle colloidal systems. In solution-phase synthesis, nanoparticles are formed through the general sequence of nucleation, growth, (Ostwald) ripening, and aggregation/coalescence. In our case, nucleation and growth may not be sufficiently fast to be completed within the time range investigated here; thus, any solution supersaturation will not be depleted. As a result, coarsening and aggregation do not dominate the time evolution of the particle size. In fact, recently it has been proposed that in chemical-solution synthesis, a relative high-chemical-potential environment (very high monomer concentrations) is required for the growth of one-dimensional nanocrystals.30 For example, for wurtzite CdSe nanocrystals, one-dimensional growth occurs at very high monomer concentrations while Ostwald-ripening occurs in an interparticle manner at low monomer concentration.30 1D to 2D intraparticle ripening usually happens within the range of intermediate monomer concentration.

Generally speaking, the formation of nanorods requires anisotropic crystal growth, which is usually realized when the surface free energies of the various crystallographic planes differ significantly.11 To realize this anisotropic growth, e.g., of nanorods, a technique of using the selective binding of different surface ligands to different surface planes has been extensively used. Recently, it has been demonstrated that the formation of rod-shaped nanocrystals does not require either coordinating solvents or two ligands with distinguishable binding abilities.30 For example, the work of Cozzoli et al. on the synthesis of TiO2 nanorods showed that only one surfactant is needed to achieve anisotropic growth;11 this approach was used in our work. In Ref. 11, the authors suggested that the formation of TiO2 nanorods might arise from two intrinsic reaction conditions including anisotropic reactivity of the precursor (titanium oxocarboxylalkoxide) and inhibition by oleic acid of the growth rate along certain crystallographic directions. Recently it has been found that under hydrothermal conditions, the growth of ZnO nanorods along the c axis is related to the differential growth rate of various crystal faces, as controlled by either internal structurally related or external factors.23 In our case, since the diameters of ZnO nanorods remain nearly unchanged during the observation period, we suggest that the growth rate of the ZnO {011} planes; i.e. parallel to the long axis, have completely
been stopped or at least heavily retarded. This most probably is due to the choice of our adsorbing-chelating ligand, namely, that the oleic acid is more intrinsically prone to attaching to the \{0110\} planes than the \{0001\} plane, subsequently greatly inhibiting the growth rate of the \{0110\} directions. This result is similar to the case of Te nanorods, in which it was suggested that the sidewalls (four \{100\} and two \{110\} planes) of nanorods were completely passivated by surfactant while the axial growth planes \{001\} were partially passivated by surfactants. A second possibility is that the zinc-complex species in solution maybe also more attracted to adsorption sites with high surface energy [i.e., the \{0002\} plane of ZnO].

Finally, the measured dependence of the lattice constant $c$ of ZnO nanorods on synthesis time is displayed in Fig. 5(b), which shows that the lattice constant decreases with increasing synthesis time. The decrease in lattice parameter is most probably due to the elongation of nanorods with time. Similar size-related lattice relaxation of lattice parameters has been observed in other nanomaterials, e.g., cerium oxide. In this work, it was suggested that the surface Coulomb energy of nanocrystal decreases with the increase in the diameter of nanocrystal resulting in the decrease of the lattice constant. Note that this data in Fig. 5(b) can be explained by a variety of effects other than size effects, including surface defects, capping agents, and adsorbed species on nanocrystals, which would also affect surface energy leading to the change in lattice parameter. For example, Perebeinos et al. suggest that the point defects on nanoparticle surface might contribute 40% of the lattice parameter expansions experimentally measured. Therefore our explanation of the measured lattice expansion as shown in Fig. 5(b) should be considered only tentative as this point. As a result, we explore the effects of surface ligands and adsorbed species on nanorod lattice parameter in the following section.

3. Surfactant/precursor ratio

In our study, ZnO nanorods were synthesized by thermal decomposition of zinc acetate in organic solvents in the presence of oleic-acid surfactant. Oleic acid has been widely used in the synthesis of other nanocrystals such iron oxide and titanium oxide. Recently Yin et al. systematically investigated the influence of the more general class of carboxylic acids, i.e., those having variable alkyl carbon chain length, on the synthesis of $\gamma$-Fe$_2$O$_3$ nanoparticles. They found that this surfactant class not only gives rise to a steric barrier to aggregation through binding to the surfaces of nanoparticles but also influences the decomposition temperature of the precursor (iron pentacarbonyl). The authors found that the regularity of nanoparticle shape and size was optimized when oleic acid was used as surfactant. They also found, in agreement with Ref. 33, that the particle size climbs with the increase of the surfactant-to-precursor [oleic acid to Fe(CO)$_5$] ratio.

To understand the role of the surfactant-to-precursor ratio in the growth ZnO nanorods, we systematically increased the molar ratio of oleic acid to zinc acetate while keeping all other preparative parameters constant. The ZnO nanorods were then characterized by XRD. The nanorod lengths, calculated using the Scherrer equation, are plotted in Fig. 6 as a function of oleic acid/zinc acetate ratio. Note that the nanorod length is dependent on both synthesis time and surfactant ratio. Due to limited experimental time, we chose to make measurement such that the nanorods were prepared with different oleic acid/zinc acetate ratio while the synthesis time were kept same and relative short (~15 min). As a result for our measured data, shown in Fig. 6, the length of synthesized nanorods were in the lower range (10–20 nm) of those seen elsewhere in our measurements. The figure shows that the length of nanorods slightly decreases as this ratio increases. This result indicates that the longitudinal growth of nanorods, i.e., along [0001], is suppressed with increasing surfactant/precursor ratio. This result is different for the growth of metal oxide nanoparticles using similar chemical-synthetic methods. For example, in the case of iron oxide $\gamma$-Fe$_2$O$_3$ nanoparticles, it was found that the particle size increases with an increase in surfactant-to-precursor, i.e., oleic acid-to-Fe(CO)$_5$, ratio. This difference may originate from the specific role that oleic acid plays in the synthesis of these two materials. For the case of $\gamma$-Fe$_2$O$_3$ nanoparticles, increasing the concentration of oleic acid is thought to facilitate the decomposition of iron pentacarbonyl, resulting in an increase of particle size. Although oleic acid also serves as

![FIG. 6. Nanorod length versus molar ratio of oleic acid to zinc acetate. Nanorod length was determined using the Scherrer equation.](image-url)
an adsorbing-chelating ligand, inhibiting the growth of Fe₂O₃ particles in the aqueous solution, this effect is not dominant until very high surfactant/precursor ratio (5:1).³² For the case of ZnO nanorods, the decomposition of zinc acetate is most probably not affected by the oleic acid. Instead, increasing the surfactant/precursor ratio increases ligand passivation of the (0002) surfaces of nanorod. Steric effects from the surfactant are then predominant, thus inhibiting the growth rate along [0001] direction.

Changes in the lattice constant of a nano-object from that of the bulk crystal have been widely studied and reported. Our lattice constants c are plotted in Fig. 7 as a function of surfactant/precursor ratio with and without post-deposition heating. We observe that with increasing surfactant/precursor ratio and without heating, the lattice constant c decreases. Further, after the nanorods were heated at ~80–100 °C, it was found that the lattice constants for the nanorods with postdeposition heating were larger than those for the nanorods without post-heating and remained nearly unchanged with increasing the oleic acid/zinc acetate ratio. Over the nanorod-length range corresponding to the data in Fig. 7, size-dependent changes alone should cause a slight increase in the lattice constant; instead our data show a significant decrease in apparent lattice constant. Thus, our results suggest that other, e.g., surface-dependent, changes may contribute appreciably to our measured changes in lattice constant.

In particular, our results suggest that external factors such as the binding of surface ligands and adsorbed species, e.g., water, acetone, and hexane, on nanorods may vary with the change of surfactant/precursor ratio and subsequently could affect their surface energy leading to the abnormal dependence of the lattice constant on the oleic acid/zinc acetate ratio. Our results are consistent with a decrease of lattice parameter with increasing oleic acid/zinc acetate ratio due merely to a change in surface binding of capping agent and adsorbed species on nanorods. In fact, the ZnO (0001) surfaces (two cleavage sides of nanorods) are known to be reactive toward many species such as water, acetone, ethanol, and acetic acid.²⁹,³⁴ For example, it was recently reported that water and carbon dioxide are able to adsorb on ZnO nanoparticles from ambient air during the storage.²⁹ In the present work, we examined relatively low temperatures for post-growth heating; it will be of interest in future work to examine the effects of more severe heating and, thus, examine chemical effects such as complete removal or reaction of surface ligands.

IV. CONCLUSIONS

Synchrotron x-ray powder diffraction has been shown to be a powerful technique to study the growth and self-assembly of ultrathin ZnO nanorods. Measurements using SAXRD revealed that these rods self-assemble into periodic superstructures and that the surfactant ligands, attached to the nanorod surface, are important in controlling self-assembly. In particular, the nanorod-array periodicity can be controlled by variation of the surfactant/precursor ratio. In addition, measurements using wide-angle XRD enabled investigation of the effects of growth chemistry and physical parameters on the nanorod size and lattice constants. These results suggest that surface-dependent changes, such as the binding of surface ligands or other adsorbed species, may dominate the changes in nanorod lattice constants compared to the size-related lattice relaxation effect.

From a greater perspective, our results also indicate that synchrotron methods can be used in several new areas of nanoscience synthesis. For example, polarized x-ray diffraction of anisotropic nano-objects, such as rods, can be used to observe time- or solution-dependent changes in particle orientation on a nearby substrate. X-ray probes can also be used to probe, in situ, solution-phase time-dependent changes in nanoparticle properties such as ripening or assembly. Indeed in our experiments, changes were noted in the particle diffractive peaks when the liquid sample was subject to major changes in temperature. In effect, synchrotron XRD may be an effective in situ monitor of the complete nanoparticle synthesis process including nucleation, growth, and self-assembly, as well as particle structural changes.

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