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Microstructural changes in CdSe-coated ZnO nanowires evaluated by \textit{in situ} annealing in transmission electron microscopy and x-ray diffraction

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Abstract

We report on the crystallite growth and phase change of electrodeposited CdSe coatings on ZnO nanowires during annealing. Both \textit{in situ} transmission electron microscopy (TEM) and x-ray diffraction (XRD) reveal that the nanocrystal size increases from $\sim 3$ to $\sim 10$ nm upon annealing at $350^\circ$C for 1 h and then to more than 30 nm during another 1 h at $400^\circ$C, exhibiting two distinct growth regimes. Nanocrystal growth occurs together with a structural change from zinc blende to wurtzite. The structural transition begins at $350^\circ$C, which results in the formation of stacking faults. Increased crystallite size, comparable to the coating thickness, can improve charge separation in extremely thin absorber solar cells. We demonstrate a nearly two-fold improvement in power conversion efficiency upon annealing.

(Some figures may appear in colour only in the online journal)

1. Introduction

CdSe is a II–VI semiconductor with a bandgap of 1.7 eV, making it nearly ideal for solar cell applications \cite{1}. Recently CdSe has been used as the absorber in extremely thin absorber (ETA) solar cells \cite{2,3}. In a typical ETA cell, an absorber is sandwiched between nanostructured, interpenetrating n-type and p-type semiconductors \cite{4,5}. The large surface area of the n-type semiconductor, provided in our case by ZnO nanowires \cite{3}, allows much thinner absorbers compared to planar photovoltaics \cite{6,7}. Absorbers thinner than the charge collection length reduce bulk recombination and enhance charge separation at the interface.

The charge collection length is determined by carrier mobility and lifetime, which are directly related to the microstructure of the absorber coating. Absorbers whose thickness is spanned by a single crystalline grain present the ideal landscape for charge separation, where photo-generated electrons and holes are easily transported to the interface with the n-type and p-type semiconductors, respectively. However, the time required for separation of photo-generated charges will increase if they must pass through multiple nanocrystals and cross multiple grain boundaries on their way to the interface \cite{8}. Additionally, internal interfaces and grain boundaries within the absorber present new opportunities for recombination. Slower charge transport and increased recombination results in lower efficiency of charge separation compared to a single-crystal absorber.

Ideally, a single crystallite will extend through the entire absorber thickness. Our previous work on electrodeposited CdSe on ZnO nanowires showed that applied current density does not drastically change the crystallite size \cite{3}. However, Tena-Zaera \textit{et al} showed that post-deposition thermal annealing increases CdSe nanocrystal size and consequently enhances the external quantum efficiency of the solar cell \cite{9}. Understanding the evolution of the microstructure and
morphology during heat treatment will enable determination of optimal annealing protocols. X-ray diffraction (XRD) and transmission electron microscopy (TEM) are complementary characterization techniques as the former provides a statistical average over a large sample, whereas the latter offers local information at high magnification [10]. XRD and TEM with in situ annealing are powerful tools to provide new insight into thermally induced changes in morphology and structure, as previously demonstrated for a variety of materials including silver, copper oxide, and iron oxide [11–13]. In situ annealing TEM takes advantage of maintaining sample position and orientation compared to an ex situ heating TEM. Hence, real-time observations of structural and morphological changes during annealing in in situ TEM provide answers to fundamental questions in crystal growth. In this paper, we report the use of in situ annealing in both TEM and XRD to uncover new details regarding the evolution of the microstructure and morphology of the CdSe coating. These techniques reveal different mechanisms for crystallite growth at 350 and 400 °C.

2. Experiments

2.1. Synthesis

CdSe coatings were electrodeposited onto an array of ZnO nanowires. The nanowires were grown on fluorine-doped tin oxide (FTO) substrates coated with 40 nm thick polycrystalline ZnO thin films having strong (0001) orientation [14]. The ZnO nanowires were grown by chemical bath deposition at 90 °C from an aqueous solution of 0.025 M zinc nitrate and 0.025 M hexamethylenetetramine in two 3 h cycles. The CdSe coatings were electrodeposited at 25 °C in a three-electrode electrochemical cell from an alkaline aqueous solution of 0.05 M cadmium acetate, 0.1 M nitrilotriacetic acid trisodium salt, and 0.05 M selenosulfate with excess sulfite. The pH of the electrolyte was adjusted to 8 by adding acetic acid. The galvanostatic current density was 1.78 mA cm⁻². The final charge density was fixed at 125 mC cm⁻² unless otherwise mentioned. Areas are referenced to the flat substrate area, rather than the nanowire area which is approximately ten times larger. Further details are reported elsewhere [3]. The CdSe-coated ZnO nanowires were annealed consecutively at 350 and 400 °C.

2.2. Material characterization

Scanning electron microscopy (SEM, Zeiss Supra 50 VP) was used to study the morphology of the coating. In situ annealing was carried out using both TEM and XRD. TEM annealing was done in vacuum and XRD annealing was done in ambient air. The TEM was a JEOL JEM2100 LaB6 instrument equipped with a Gatan 628 single-tilt heating holder. The XRD was a Philips/PANalytical X’Pert PRO equipped with an Anton Paar DHS900 heating stage and used Cu Kα radiation. The heating and cooling rates were 200 °C min⁻¹ and 60 °C min⁻¹ in TEM and XRD, respectively.

2.3. Solar cell fabrication

Solar cells with and without annealing treatment (sequential 350 and 400 °C in air for 1 h each) were compared to determine the effect of heat treatment on solar cell performance. FTO substrates with CdSe-coated ZnO nanowires were coupled with a bare FTO-glass counter electrode in a sandwich cell configuration. Substrates were separated with a 60 µm thick spacer, and the gap was infiltrated with aqueous electrolyte containing 200 mM K₂Fe(CN)₆, 20 mM K₃Fe(CN)₆, and 200 mM KCl. I–V characteristics were recorded under AM1.5 illumination with an intensity of 100 mW cm⁻² and a spot size of 0.25 cm². An ultrathin, ~3 nm, layer of CdS was deposited on the ZnO nanowires by successive ionic layer adsorption and reaction according to the method of Joo et al [15] before electrodeposition of CdSe in order to decrease recombination at the ZnO/CdSe interface. CdSe was electrodeposited as described in section 2.1 with a final charge density of 157 mC cm⁻², corresponding to a coating thickness of ~25 nm.

3. Results and discussion

3.1. Morphology of CdSe-coated ZnO nanowires

Electrodeposited CdSe coats ZnO nanowires conformally. SEM images of bare and coated nanowire arrays are shown in figure 1. Figure 1(a) shows that bare ZnO nanowires are densely packed and vertically well aligned. Individual nanowires are ~1 µm long with diameters of ~50 nm. Cross-sectional SEM of CdSe-coated ZnO nanowires reveals that a uniform CdSe shell coats the ZnO core from the base to the tip, figure 1(b). A uniform and conformal coating is essential for application in ETA cells. The CdSe coating is estimated to be ~40 nm thick by comparing top-view SEM images of bare and coated nanowires. The final charge density was 240 mC cm⁻².

3.2. In situ annealing TEM

Annealing increases the crystallite size and smoothness of the CdSe coating. Figure 2 shows TEM bright-field images of a 20 nm as-deposited CdSe coating on a ZnO nanowire. The CdSe-coated nanowires were scraped off the substrate and then dispersed on a lacey carbon grid. Real-time TEM observations show that rough edges in the as-deposited CdSe coating, figure 2(a), become smoother after annealing, figure 2(b). Figure 2(c) shows a representative high-resolution TEM (HRTEM) image of the as-deposited CdSe coating on the ZnO nanowire. The HRTEM micrographs illustrate that the as-grown, 15 nm thick CdSe coating is composed of many 2–6 nm CdSe crystallites that are randomly agglomerated. Upon heat treatment, multiple small crystals grow to form a single larger crystal until the crystallite size becomes equal to the film thickness, figure 2(d). Crystallite growth is likely driven by Ostwald ripening, where small nanocrystals dissolve and add to larger crystals to minimize the energy of surfaces and interfaces [16]. The large quantity of CdSe...
generally complicates interpretation of TEM micrographs due to the heavy projected overlap of CdSe particles, thus making it very difficult to further elucidate the mechanisms responsible for the increased crystallinity and smoothness of the coating.

**In situ** annealing reveals the increase in the crystallite size together with the crystal structure transition. Figure 3(a) shows a bright-field TEM image of a thin, discontinuous CdSe coating on a ZnO nanowire. ZnO nanowires with lower CdSe loading were scraped off the substrate, followed by sonication in isopropanol for 1 h. They were then dispersed on a 20 nm silicon nitride grid followed by plasma cleaning in oxygen for 2 min. The black arrows in figures 3(a)–(c) highlight that the connecting neck between two clusters decreases in size at 350°C and disappears at 400°C. The gradual disappearance of the narrower coating and the growth of neighboring crystallites, which increases the exposed area of ZnO, is attributed to Ostwald ripening.

The changes observed in the selected area diffraction patterns (SADPs) in figures 3(d)–(f) indicate a structural transformation from zinc blende to wurtzite. Figure 3(d) shows the SADP from the as-coated nanowire. The rectangular array of reflections arises from the ZnO nanowire. The arrow shows the [0001] growth direction of the bare ZnO nanowire. The broad, diffuse ring is created by diffraction from the randomly oriented sub-5 nm CdSe nanocrystallites. The intensity maximum of this ring was 3.5 Å, as determined using a circular Hough transform (CHT) algorithm [17]. Both zinc blende {111} and wurtzite {0002} planes have d-spacings of ~3.5 Å; however, the HRTEM images confirmed that as-grown CdSe nanocrystals are zinc blende. After annealing, the broad ring transforms into two separate rings, figure 3(f). Sharp diffraction spots within those rings are visible, consistent with the increase in crystallite size. The inner ring measures 3.74 Å, which unambiguously belongs to {10\bar{1}0} wurtzite planes that have spacings of 3.72 Å.

Considering the small quantity of CdSe and the small crystallite size at 350°C, the diffraction pattern alone is not sufficient to determine when the phase change starts. However, complementary TEM images show stacking faults start to appear at 350°C. Figure 4(a) shows a TEM image of a CdSe-coated ZnO nanowire annealed in situ at 350°C for 5 min. After 30 min of annealing, the morphology of the coating has not changed, figure 4(b). However, stacking faults are formed during this time, as highlighted by the circles in figure 4. Stacking faults are often associated with a structural transition from zinc blende to wurtzite [18]. Hence,
the formation of stacking faults implies that the phase change happens during the early stages of annealing at 350 °C. In addition to Ostwald ripening, the formation of stacking faults can be a pathway for matter diffusion, resulting in a larger crystallite size [19].

We note that lacey carbon or SiN TEM grids were used in this work to avoid excessive contact of CdSe with carbon during annealing. Amorphous carbon from carbon film grids graphitizes during annealing at 350 °C in the presence of CdSe. Many-layered graphitic carbon completely encapsulated the CdSe-coated nanowires (and also free-standing CdSe particles on carbon films in a different experiment), thus interfering with surface-related matter transport during the annealing process. The formation of graphite at low temperatures (350–400 °C) is likely to be catalyzed by CdSe, similar to metal-induced crystallization of amorphous carbon [20]. No graphitization was observed in any of the TEM images shown here because either the selected area was in vacuum far from the lacey carbon support or the nanowire was on carbon-free SiN. Additionally, during the in situ annealing experiments, the electron beam was blocked when not needed for data collection in order to inhibit beam-induced crystal growth or structural changes.

3.3. In situ annealing in XRD

XRD results confirm the increase in crystallite size and phase transformation. Figure 5(a) shows XRD scans of CdSe-coated ZnO nanowires before and after in situ sequential annealing in air at 350 °C and then 400 °C. The intense (0002) peak at 34.6° shows well-aligned ZnO nanowires. Both ZnO and FTO peaks remain unchanged during annealing. Broad CdSe peaks at 25.5° and 42.1° could contain both zinc blende and wurtzite reflections, which have indistinguishable lattice spacings, but HRTEM indicates a zinc blende structure before annealing. Real-time scans in figures 5(b) and (c) show the evolution of the peaks at 25.5° and 42.1°. These peaks become more intense and narrower, indicating the increase in crystallite size. Additionally, after 55 min annealing at 350 °C, a shoulder is formed in the peak at 25.5°. This shoulder then becomes a distinct peak at 24.1° after annealing at 400 °C for 1 h. The new peak at 24.1° is unambiguously assigned to the wurtzite (1010) plane. The appearance of the wurtzite (1010) peak after annealing, which was also observed in the TEM diffraction pattern, confirms the transition of the CdSe crystal structure from zinc blende to wurtzite [21].
Figure 5. (a) XRD scans of CdSe-coated ZnO nanowire arrays on FTO substrates before and after in situ sequential annealing at 350 °C and 400 °C for 1 h each. Real-time XRD scans showing the evolution of the CdSe peak at (b) 24.1° and 25.5°, and (c) 42.1°.

The average crystal size increases from 3 to ∼10 nm upon annealing at 350 °C, and then to over 30 nm after 1 h at 400 °C, figure 6. This evolution of the crystal size is consistent with TEM observations. Doubling the CdSe coating thickness did not change the evolution of the crystallite size. The crystallite size was calculated using the diffracting plane at 42.1°, figure 5(c), by applying the Scherrer equation at each annealing time [22]. A Lorentzian fit was used along with the Cauchy–Cauchy relationship to calculate the intrinsic broadening in the Scherrer equation. The FWHM of the ZnO(0002) peak was used for instrumental broadening. Evolution of the average crystallite size shows that the growth rate is much faster at 400 °C than at 350 °C, indicating two different growth regimes. The change in growth rate occurs because of the existence of a second activated process. This conclusion arises from comparison of growth rates at these two temperatures at 250 °C from Tena-Zaera et al [9], which cannot all be consistent with a single growth mechanism with a single activation energy.

The in situ TEM and XRD results show two major changes to the CdSe nanocrystals during the 350 °C annealing step. First, the average size of the CdSe crystals increases from a range of 2–6 nm to ∼10 nm in diameter. Second, the crystals begin to transform from cubic to hexagonal symmetry. The increase in crystallite size is driven by Ostwald ripening during this initial regime. Presumably the ripening process is dominated by surface diffusion, as the large surface area of the CdSe clusters provides ample pathways for the smaller CdSe crystallites to diffuse to the larger clusters. Figure 6 shows that this initial coarsening occurs within the first minutes of the annealing process, and the crystallite size continues to increase very slowly, reaching ∼10 nm after 60 min.

When the annealing temperature is increased to 400 °C, the crystallite diameter increases approximately linearly in time to ∼30 nm. While coarsening due to surface diffusion continues, the clear difference in crystallite growth rates indicates that 400 °C is sufficient to overcome the activation energy for another mechanism of matter transport. For example, growth could also occur by grain-rotation-induced grain coalescence [23], solid-state sintering of CdSe crystals [24], or melting and recrystallization. The melting temperature drops dramatically for very small crystal size [25]. CdSe nanocrystals can melt at 400 °C, well below
the bulk melting point of 1240 °C. Our initial annealing step is performed at 350 °C to avoid significant melting while crystallites are very small, but some melting of small crystallites could still occur. Sintering generates a definitive grain boundary, which itself is a transport path of matter. Additionally, the phase transformation from zinc blende to wurtzite generates many stacking faults which can act as pathways for diffusion, further driving an increase in crystallite size [18]. Further work is required to identify the dominant mechanism.

3.4. Improvement in solar cell performance due to annealing

Annealing CdSe-coated ZnO nanowire arrays improves their performance in ETA solar cells. Figure 7 shows the $I$–$V$ characteristics of representative ETA cells with and without annealing after CdSe deposition. The ETA cells with CdSe that underwent heat treatment are clearly superior, showing improvement in photocurrent, fill factor, and efficiency. The power conversion efficiency of the annealed cell is nearly double the efficiency of the cell whose CdSe was not annealed, 2.1% compared to 1.1%. As stated earlier, annealing drastically increases crystallite size from <5 nm to ~30 nm. Increased crystallite size reduces the density of grain boundaries, likely leading to both increased lifetime of photoexcited carriers and increased carrier mobility. Annealing may also reduce the density of point defects that can act as mid-gap recombination centers, although this was not investigated directly. In any case, the increased lifetime–mobility product achieved by annealing improves the collection of photoexcited carriers, as evidenced by the increased short circuit current and the reduction in the voltage-dependence of charge collection [26]. Further details on charge separation and transport in ETA solar cells will be published separately.

4. Conclusions

The influence of thermal annealing on the crystal structure and morphology of the CdSe coatings on ZnO nanowires was investigated using in situ TEM and XRD. Crystal size studies assist in determining the optimum annealing conditions required to achieve a conformal and uniform coating that is single crystalline across the thickness. The initial increase in crystallite size from ~3 to ~10 nm at 350 °C is likely to be driven by Ostwald ripening. Annealing at 400 °C further increases the crystallite size to ~30 nm and smoothes the surface of the coating. Crystallite growth is faster due to additional mechanisms of matter transport. Understanding and controlling the morphology and microstructure of CdSe coatings is essential for applications such as ETA solar cells, which benefit from conformal and uniform coatings with a grain size comparable to the coating thickness.

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