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Rolf Könenkamp
Portland State University, rkoe@pdx.edu

Robert Campbell Word
Portland State University

Athavan Nadarajah

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Nanostructured semiconductor heterojunctions from quantum dot layers

R. Könenkamp,[a)] A. Nadarajah, and Robert C. Word

Department of Physics, Portland State University, 1719 SW 10th Avenue, Portland, Oregon 97201, USA

We report the deposition of conformal thin layers of 10–50 nm thickness from II-VI quantum dot suspensions on ZnO nanowire substrates. Smooth polycrystalline films of high electronic quality can be obtained from CdSe quantum dots after annealing at moderate temperatures. The electronic properties are adequate for detector and solar cell applications. The growth and annealing temperatures permit deposition on light-weight and flexible substrates. Some elemental diffusion of Se across the CdSe/ZnO interface occurs in the film formation. A comparison with CdS/ZnO junctions indicates that the low Se diffusion rates are essential for efficient charge transfer. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3193531]

Thin layer deposition on deeply structured substrates and templates has become a serious challenge for a variety of nanodevice applications such as light-emitting diodes, solar cells, transistors, and sensors. Solar cells in particular have recently been prepared on the basis of nanostructured II-VI heterojunctions involving porous films as well as nanowire films.[1–5] The main promise in this approach to photovoltaics is the high light trapping capability of random-structured thin films and the short transport distances in nonplanar absorber layers.[6] In the past decade, various techniques, such as atomic layer deposition,[7] ion layer gas reaction,[8] and successive ionic layer adsorption and reaction,[9] have been applied. However, long deposition times, high processing temperatures, and small crystallite sizes have limited the applicability of some of these methods.

In this letter, we report results of the deposition of thin polycrystalline layers from quantum dots on nanowire films. The nanowire films consist of near vertically aligned ZnO wires of ~ 100 nm diameter and 2 μm length. Ligand-terminated CdSe and CdS quantum dots are deposited on the nanowires by applying simple solution-based techniques such as spraying, spin coating, and droplet deposition. Typically these techniques produce layers of 5–50 nm thickness, which consist of loosely packed quantum dots. The initial layers are not very conformal. Upon annealing in appropriate flux agents the quantum dots are freed from their ligands and fused to compact and polycrystalline films with grain sizes of 20–100 nm. These films have much improved conformality and exhibit good electronic transport properties after moderate annealing. The annealing process is completely compatible with some polymers, such as kapton, whose glass transition temperature is 380 °C and higher.

Apart from the low temperature processing that can be achieved in these deposition techniques, we consider the avoidance of interface strain as another important advantage. When ligand-terminated quantum dots are deposited on a substrate, the force transfer between substrate and deposit is comparably small. This is quite different to many conventional deposition methods in which a thin wetting layer is formed in intimate contact with the substrate. This often accommodates considerable lattice and orientation mismatch between substrate and deposit. The resulting strain and dis-

location defects usually have a strong negative effect on the electronic properties near the interface. In nanostructured devices, a "soft" method to prepare interfaces is particularly advantageous, as interface areas are inherently larger than in planar configurations, and surface orientation and polarity add more strains. By carefully choosing the suspending solvent with respect to surface tension, polar strength, and redox energy, the growth interface in the present method can be further optimized to accommodate these strains. It thus appears that quantum dot layer deposition may open new ways in interface engineering.

Vertically oriented single-crystalline ZnO nanowires were monolithically grown in electrodeposition on F-doped SnO_2 covered glass substrates using a standard three-electrode electrochemical setup with a saturated Ag/AgCl reference electrode and a Pt foil as a counter electrode.[10] The deposition was carried out at 80 °C in an aqueous electrolyte containing 3 mM $ZnCl_2$, 5 μM $AlCl_3$ and 0.1*M* KCl. Oxygen bubbling and magnetic stirring were provided to produce an oxygen-saturated electrolyte solution. Deposition potentials were -1.0 V versus Ag/AgCl. Addition of $AlCl_3$ to the electrolyte had previously been found to improve the conductivity of the nanowires.[10] After deposition the ZnO nanowire films were annealed in air at 380 °C for 2 h.

CdSe quantum dots of 8 nm average diameter, terminated with octadecylamine ligands, and suspended in toluene were obtained commercially from NN-Laboratories, Arkansas. For deposition, these dispersions were diluted to concentrations of 2 g/l, and the deposition was carried out with micro-pipettes at a temperature of 60 °C. Spray deposition at 120 °C in a chemical hood vented with laboratory air at ambient conditions, spin coating in N_2 ambient, and dip coating at ~ 40 °C, gave very similar results. The quantum dot layers were annealed at 380 °C for 2–24 h in $CdCl_2$/air ambient.

Simple photodetector structures were prepared by spin coating a thin *p*-type polymer on the CdSe-coated nanowire-film and subsequent evaporation of 100 nm thick Au dots with ~ 7 mm^2 area on top of the polymer film. Spectral photocurrent measurements were carried out on these diode structures at typical photon densities of 10^{13} photons/(cm^2 s) and at short-circuit conditions.

Figure 1(a) shows a transmission electron micrograph of the as-deposited quantum dot film. The as-deposited layers
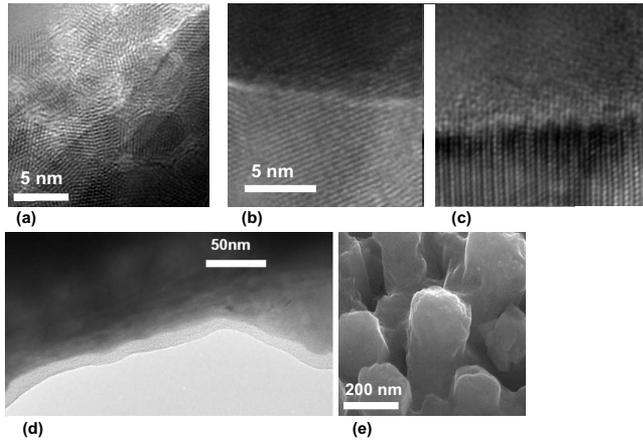
a)Electronic mail: rkoe@pdx.edu.

FIG. 1. (a) HRTEM micrograph of the as-deposited quantum dot film on a ZnO nanowire. Individual quantum dots are single-crystalline and clearly discernible. (b) Same sample after annealing for 24 h at 380 °C. The average crystallite size has grown to ~20–50 nm. (c) TEM micrograph of the ZnO/CdSe interface. (d) SEM micrograph showing that the film has been compacted to ~15 nm thickness and exhibits excellent conformality. (e) SEM micrograph showing the nanowire film with CdSe coverage after annealing.

FIG. 2. (Color online) TEM-EDX linescans across the CdSe-coated ZnO nanowires: (a) in the as-deposited state, (b) after a 24 h anneal at 380 °C, (c) CdS quantum dot layer on ZnO after 2 h anneal at 380 °C.

are typically comprised of several quantum dot monolayers. The quantum dots are loosely packed and the individual 8 nm particles are clearly discernible in the micrographs. Part (b) of the figure shows the same film after annealing in air/$CdCl_2$ at 380 °C for 24 h. A compact polycrystalline film with a grain size of 20–50 nm has been formed, which covers the nanowire substrate conformally. Selected area electron diffraction shows the expected diffraction pattern for the CdSe wurtzite structure. As shown in Fig. 1(c), the interface between substrate and coverage remains smooth on the atomic level. These results indicate that the annealing process is effective in removing the organic ligands from the quantum dots. It is well known that $CdCl_2$ vapor acts as a flux agent in transition metal chalcogenide compounds and strongly promotes grain growth[11] and surface smoothing. Figures 1(d) and 1(e) show the conformality of the films annealed in air and $CdCl_2$ vapor. Without the addition of $CdCl_2$ the coverage is less smooth.

For device applications, the integrity of the CdSe/ZnO interface will be of considerable importance. Even though the ZnO nanowires are single crystalline, it is clear from high-resolution transmission electron microscopy and x-ray diffraction work that the wires have comparably large dislocation densities.[12] High diffusion rates from materials adjacent to the ZnO may therefore be expected. We studied the element distributions at the CdSe/ZnO interface using high resolution energy dispersive x-ray spectroscopy (EDX). Typical results are shown in Fig. 2. For clarity the EDX count rates have been normalized with respect to their maximum value. For a cross-sectional scan through a coated wire, the element profile is expected to start out with counts only for the coating material. At later stages in the scan, the wire core material and the coating material are probed, and the signal for the coating material decreases. Figure 2(a), obtained before annealing, shows that the stoichiometry between Cd and Se is accurately maintained, and the shape of profile is consistent with a ~25 nm thick quantum dot coating before compaction and a ~120 nm wire core radius.
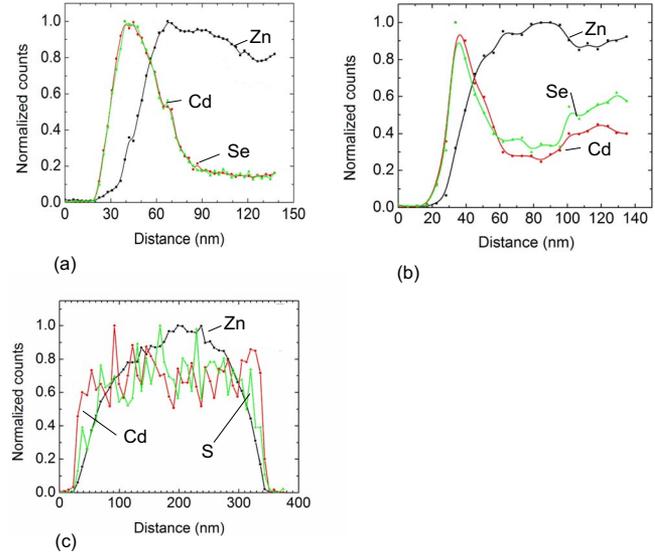
After annealing at 380 °C, the EDX profile in Fig. 2(b) indicates slight indiffusion of Cd and Se into the ZnO wire core. As expected, Se appears to be the faster diffuser in that process, its count rate in the core region being somewhat higher than the Cd count rate. It is likely that the chalcogen diffusion is coupled to a chalcogen/oxygen ion exchange in the ZnO core. Such an ion exchange has been observed by us earlier in a different application.[13] The EDX profile also shows a reduced coating layer thickness after the annealing process consistent with the conversion of the quantum dot assembly into a continuous polycrystalline film. Figure 2(c) shows equivalent results for a CdS quantum dot film on the same ZnO nanowires. In this case, after annealing, both the Cd and the S are distributed homogeneously across the nanowire cross section. It is clear that a substantially stronger indiffusion has occurred in the presence of S, likely caused by the larger mobility and reactivity of sulfur ions.

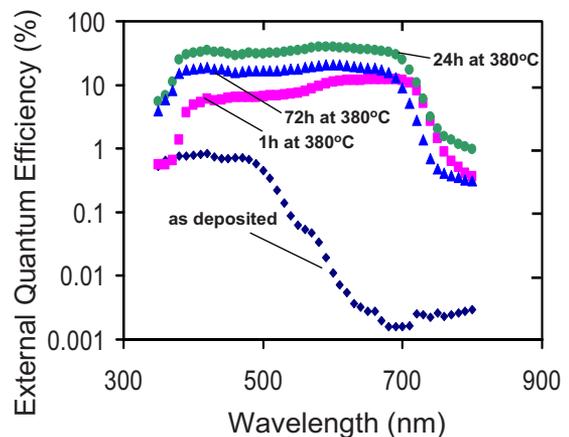In Fig. 3 we evaluate the electronic properties of the

FIG. 3. (Color online) External quantum efficiency vs wavelength for a photodetector incorporating the CdSe/ZnO nanowire structure. Various times of thermal anneal in $CdCl_2$/air at 380 °C are shown. In the as-deposited state the photocarrier collection efficiency is very low and the photocurrent onset is blueshifted due to electron confinement effects. After annealing the photocurrent onset occurs at the wavelength expected for bulk CdSe and the electronic transport across the layer obtains high efficiency.

CdSe/ZnO heterojunction using quantum efficiency measurements in a simple photodetector with the layer sequence glass/SnO$_2$/nanowire-ZnO/CdSe/poly[2-methoxy-5(2-ethylhexyloxy)-p-phenylene vinylene]/Au. This structure is the simplest approach to a solar cell or photodetector configuration.[3] As the polymer/Au deposition involves temperatures below 120 °C, it can be assumed that the CdSe/ZnO heterojunction remains largely unaffected by the additional processes used to assemble this structure. Figure 3 shows a dramatic increase in the quantum efficiency as the quantum dot layer converts to a polycrystalline film. In the as-prepared structure the quantum efficiency is below 1% and the photocurrent onset occurs at ~650 nm. Both results are well explained by assuming loosely connected quantum dots. The photocurrent onset at 650 nm coincides with theoretical estimates for 8 nm diameter CdSe quantum dots, and the onset wavelength coincides with the measured absorption edge of the quantum dots in solution. It is thus clear that there is considerable electron confinement in the as-prepared films. The low collection efficiency is a direct consequence of this carrier confinement and the inter-particle separation in the as-deposited layer. After annealing the photocurrent onset moves to the expected value for bulk CdSe. As the grain size increases with duration of the annealing process, the transport also improves. In optimized conditions we obtain external quantum efficiencies above 65%. These quantum efficiencies are obtained in short-circuit conditions, i.e., without external bias potential. Subtracting optical losses due to reflection and transmission, we estimate that the *internal* quantum efficiencies are close to 80% at a wavelength of 500 nm.

This strong electronic improvement upon annealing is not found for CdS/ZnO heterojunctions. We tentatively attribute this finding to the much enhanced interdiffusion, discussed in the context of Fig. 2(c).

When operated as solar cells under 85 mW/cm^2 white light illumination the annealed heterojunction devices typically produce open-circuit voltages of 0.4–0.5 V, short circuit currents of 8–10 mA/cm^2 and fill factors of ~50%.

In conclusion, we have shown that quantum dot suspensions can be used as precursor materials for polycrystalline thin semiconductor films with a typical thickness of 10–50 nm. In the as-deposited state, the films exhibit quantum confinement properties such as a blueshift of the absorption edge and marginal electronic transport. With moderate annealing and with the support of flux agents, structurally compact films with excellent conformality and crystallite sizes in the 50nm range can be obtained on deep nanostructured substrates. The electronic transport in these films is much improved and external photocarrier collection efficiencies of ~65% can be obtained. Our results indicate that these films may have interesting applications in photovoltaic devices.[1,6]

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