Improvements in the Structure and Adhesion of Electrodeposited Thin Film CdSe

Henry Wynands and Michael Cocivera*

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Received July 11, 1990. Revised Manuscript Received October 1, 1990

CdSe was electrodeposited onto treated and untreated indium–tin oxide coated glass substrates (ITO). CdSe deposited onto untreated ITO was smooth and featureless on the micron scale but was cracked after deposition and frequently flaked off the substrate after an annealing treatment. Adherent and crack-free CdSe films were deposited onto modified ITO substrates. Two types of substrate treatments were used prior to CdSe deposition: (1) thermal treatment of ITO with an elemental vapor of Se, Cd, or In; (2) electrochemical reduction to form Se, Cd, or In on the surface. Scanning electron microscopy and X-ray diffraction were used to study the surface and structure of both the modified substrates and the electrodeposited CdSe films. After removal from the conductive substrate, the resistivity of thin film CdSe was measured as a function of temperature. The morphology and electrical properties of the CdSe were shown to be dependent on the type of substrate treatment used.

Introduction

The electrical and optical properties of CdSe make it a suitable material for a wide range of applications. CdSe has been studied as a photoconductor[1-3] and in both solid-state[4] and photoelectrochemical[5] photovoltaic solar cells. The high electron mobility of CdSe makes it is suitable for the use in thin-film transistors.[6,7] As part of a focus on the development and characterization of electrochemical processes for the deposition of chalcogenide thin films in this lab,[8-12] the present study has concentrated on improving the properties of CdSe electrodeposited onto conducting glass substrates.

The materials chosen for application in an electronic device must exhibit specific electrical or optical properties. However a more obvious, though often unstated requirement, is that the thin film remain adherent to the substrate and retain its structural integrity throughout the deposition process and subsequent treatments. This requirement is not a trivial one for electrodeposited CdSe. Several researchers have reported the cracking and peeling of CdSe thin films from conductive substrates,[9,13] particularly upon thermal treatment.

Our approach to improving the adhesion and structure of CdSe was to modify the chemical and physical structure of the interface between the semiconductor and substrate. Prior to electrodeposition of CdSe, the substrates were treated thermally or electrochemically to produce a thin interfacial layer that was rich in Se, Cd, or In. Although the chemical and physical effects are not separable, they serve different purposes. Physical modification of the interfacial structure presumably affected the microcrystallization of the CdSe during the electrochemical deposition. Chemically the effects were 2-fold. First, the bonding between the CdSe and substrate was altered by the thin interfacial layer and the adhesion of the thin film was improved. Second, the electrical properties of the CdSe were influenced. In some cases dopants were incorporated into the CdSe by diffusion from constituents of the interfacial layer during an annealing cycle. Using treated substrates for CdSe electrodeposition resulted in CdSe thin films that were successfully annealed to 500 °C while remaining adherent, pinhole-free, and crack-free.

Experimental Section

Indium–tin oxide coated borosilicate glass substrates (ITO), which were doped with approximately 10% tin oxide, were purchased from Donnelly Corp.of Holland, MI. Two general methods were employed to produce the interfacial layers on the ITO: (a) thermal and (b) electrochemical treatments. Thermal treatments involved exposing the ITO to an elemental vapor within a stainless steel reactor[14] in a tube furnace. Substrates were loaded into the reactor with approximately 0.5 g of elemental powder. After the exclusion of oxygen, the temperature was raised to 500 °C for a set reaction time (Se, 40 min; In, 180 min; Cd, 180 min). Electrochemical treatments of the substrates involved galvanostatic or potentiostatic reduction in a solution containing the appropriate ion. Se was deposited potentiostatically from aqueous solutions of either 0.05 M selenous acid or 0.035 M sodium selenosulfate. Cd was reduced at −0.95 V SCE from an aqueous solution containing 0.05 M cadmium chloride, 2 M acetic acid, and 2 M sodium acetate. A propylene carbonate solution containing 0.1 M lithium perchlorate and 0.02 M indium(III) chloride was used to deposit In at 1–2 mA/cm^2.

The CdSe was electrodeposited from an aqueous solution containing 0.0211 M cadmium chloride, 0.0300 M of trisodium nitrilotriacetate, 0.0368 M sodium selenosulfate, and 0.540 M sodium sulfite.[5,9] Depositions were carried out on a 2-cm^2 area for 40 min at −1.0 V SCE. The films were rinsed with ultrapure water and were dried with a nitrogen stream. A common annealing treatment was used for all CdSe samples. A nitrogen atmosphere was maintained while the temperature was ramped to 200 °C and held for 30 min, ramped to 500 °C and held for 10 min, and then cooled to room temperature. For one sample the electromigration of copper was attempted by applying a 0.1 mA/cm^2 cathodic

---

* Address all correspondence to this author.

[1] Hyugaji, M.; Miura, T. *Jpn. J. Appl. Phys.* **1985**, *24*, 1575.
[2] Hyugaji, M.; Miura, T. *Jpn. J. Appl. Phys.* **1985**, *24*, 950.
[3] Buragohain, M.; Barua, K. *Indian J. Phys.* **1987**, *61A*, 559.
[4] Richter, H.; Hewig, G. H. *European Communities Solar Energy Conference, 7th Proceedings of International Conference*; Seville, 1986; p 470.
[5] Szabo, J.; Cocivera, M.; *J. Electrochem. Soc.* **1986**, *133*, 1247.
[6] Van Calster, A.; Vervaet, A.; De Rycke, I.; De Baets, J.; Vanfleteren, J. *J. Cryst. Growth* **1988**, *86*, 924.
[7] Vanfleteren, J.; Van Calster, A. *IEEE Electron Device Lett.* **1985**, *EDL-6*, 11.
[8] von Windheim, J.; Darkowski, A.; Cocivera, M. *Can. J. Phys.* **1987**, *65*, 1053.
[9] Szabo, J.; Cocivera, M. *Can. J. Chem.* **1988**, *66*, 1065.
[10] Sanders, B. W.; Cocivera, M. *J. Electrochem. Soc.* **1987**, *134*, 1075.
[11] Preusser, S.; Cocivera, M. *Solar Energy Mater.* **1990**, *20*, 1.
[12] Wynands, H.; Cocivera, M. *Solar Energy Mater.* **1988**, *17*, 185.
[13] Fantini, M. C. A.; Moro, J. R.; Decker, F. *Solar Energy Mater.* **1988**, *17*, 247.
[14] von Windheim, J.; Cocivera, M. *J. Appl. Phys.* **1990**, *67*, 4167.

0897-4756/91/2803-0143$02.50/0

current in an aqueous solution of 0.05 M copper(II) chloride.

The temperature dependence of CdSe resistivity was measured by using previously reported techniques and apparatus.[14] Because the substrates were conductive, it was necessary to remove the CdSe before resistance measurements were performed. This was accomplished by applying a nonshrink epoxy and thermal shock. The CdSe adhered to the nonconductive epoxy, and resistivity measurements could be performed without current flow through the substrate. After defining a sample geometry, electrical contacts were made to the CdSe with indium gallium eutectic. Two strip measurements were made by applying contacts along the longer sides of a sample rectangle (in the range of 5–10 mm long and 1–3 mm wide). For four-probe van der Pauw measurements[15] small area contacts were made to the corners of a square, typically 1 mm to a side.

Because of the high resistivity of the samples, special precautions were taken in performing measurements. High-input impedance electronics and careful shielding were necessary to avoid leakage current and reduce noise. A guarded differential electrometer amplifier[14] was used in conjunction with a Keithley Model 220 current source. Two-strip measurements were also performed with a Keithley 614 electrometer. Resistivity measurements were made under dynamic vacuum in a cell constructed in-house. The sample temperature was controlled by the flow of temperature controlled gaseous nitrogen through an electrically insulated copper stage in thermal contact with the sample. A Eurotherm 808 temperature controller, interfaced to an XT clone computer, was used to monitor and control the cell temperature.

The structure and morphology of the treated substrates and the CdSe thin films were characterized primarily by scanning electron microscopy (SEM) using a Hitachi S-570 microscope. Energy-dispersive X-ray spectroscopy (EDS) was performed to test the elemental composition of the residue left on the substrate after CdSe film removal. A 35-kV accelerating voltage was used in a Tracor Northern TN 5500 instrument. Several samples were analyzed by powder X-ray diffraction, for the range of 2-θ from 20 to 45°, using a Rigaku Geiger Flex DMax-2 instrument employing a Co $K\alpha_1$ beam.

Results and Discussion

CdSe films electrodeposited onto untreated ITO substrates contained cracks immediately after deposition. Upon annealing, the film flaked and peeled from the untreated ITO substrates. When the ITO substrates were subjected to either thermal or electrochemical treatment prior to electrodeposition, the CdSe thin films were generally both crack-free and adherent. Both the physical nature and chemical composition of the interface were modified by the treatments used. The creation of surface texture or roughness of the treated ITO substrate was an important aspect of the surface treatments. The nature of the effects are discussed first for Se and then for Cd and In. In regard to the thermal treatments, sulfur and tellurium vapours were also found to react with ITO, but the study of these treatments was not pursued.

Selenium Treatments. The interaction of Se vapor[16,17] with ITO substrates was studied more exhaustively than the interaction of other elements. Evidence indicates that at a suitable temperature a chemical reaction resulted from this interaction. One possible reaction is the replacement of oxygen in indium–tin oxide by Se:

$$In_2O_3/SnO_2(s) + {}^5\!/_2Se_2(g) \leftrightarrow In_2Se_3/SnSe_2(s) + {}^5\!/_2O_2(g) \quad (1)$$

A second possible reaction, involving the partial reduction of the oxide coating and the oxidation of Se vapor is shown in

$$In_2O_3/SnO_2(s) + {}^1\!/_2Se_2(g) \leftrightarrow In_2O_{3-x}/SnO_{2-x}(s)/xSeO_2(s) \quad (2)$$

The evidence presented below appears to support reaction 1. In the discussion below, the ITO substrates reacted with Se vapor will be referred to as Se/ITO.

Formation of an adsorbed Se layer or a SeO_2 layer on ITO (reaction 2) is considered less likely than reaction 1 for the following reasons: first the selenium vapor preferentially interacted with the ITO coating, not the uncoated glass, although Se was not completely absent from glass. Second, the appearance of the coating changed dramatically after a lengthy reaction. Untreated ITO is essentially colorless and is very smooth; after 15 h of reaction the Se/ITO was an opaque, grey-blue, textured layer. Third, the coating of the same completely reacted Se/ITO substrate was found to dissolve so completely in a 1 M/1 M/1 M $S^{-2}/S/OH^-$ electrolyte solution that no ITO or Se/ITO was left on the glass after 5 min. Since untreated ITO was not affected by immersion in this electrolyte for 90 min, the Se treatment of ITO must have chemically altered the entire layer of ITO.

It is interesting that the high-temperature treatment of a Se/ITO sample in air resulted in a reoxidation of the surface. The completely reacted Se/ITO was a textured grey-blue opaque coating with a resistance of 1.5×10^{11} Ω across a 4-mm sample. After air annealing the layer was transformed into a textured, translucent, faint yellow coating with a resistance of 1.5×10^3 Ω across 4 mm. By comparison the untreated ITO was smooth and featureless, and a 4-mm sample had a resistance of 28 Ω. In the reoxidation of Se/ITO, the Se was subsequently vaporized since it was not detected in the EDS spectra of this oxidized sample.

Reaction time for the interaction of Se vapor and ITO was a significant variable. The untreated ITO has a very smooth and featureless surface. The SEMs shown in Figures 1A and 2A demonstrate the dramatic change in the substrate surface upon Se treatment for different periods of time. The hexagons, or partial hexagons, on the surface shown in Figure 1A illustrate the quite dense structure resultant from a 40-min reaction. The very dense texture of a completely reacted surface (15-h reaction time) is shown in Figure 2A. The color of the coating changed from a transparent and virtually colorless ITO, to a translucent, faint reddish brown Se/ITO after the intermediate reaction time (40 min), to an opaque grey-blue Se/ITO coating after the long reaction time (>4 h).

CdSe electrodeposited onto thermally prepared Se/ITO substrates reflected the typical surface features of the substrates. The Se/ITO was smooth after a reaction for 10 min, and the structure of the CdSe electrodeposited onto this substrate appeared similarly smooth, very fine grained, and lacking any large surface features. Likewise, the hexagonal surface features of Se/ITO reacted for 40 min (Figure 1A), typical of intermediate reaction times, are shown covered with electrodeposited CdSe (Figure 1B). The surface texture of Se/ITO after 15 h of reaction (Figure 2A) is reflected by the CdSe thin film electrodeposited onto it (Figure 2B).

The effect of the morphology of the Se-treated surface is illustrated by comparison of Se/ITO substrates prepared thermally and electrochemically. Smooth featureless Se- or Se-rich layers on ITO were produced by electrochemical reduction. The morphology of the CdSe on these surfaces was similarly smooth and featureless, like CdSe deposited

---

[15] Runyan, W. R. *Semiconductor Measurements and Instrumentation*; McGraw-Hill: New York, 1975; p 73.

[16] Glang, R. Vacuum Evaporation. In *Handbook of Thin Film Technology*; Maissel, L. I., Glang, R., Eds.; McGraw-Hill: New York, 1970; pp 1–38.

[17] Se vapor species may be polyatomic (Se_n, n = 1–8); we denote these as Se_2.

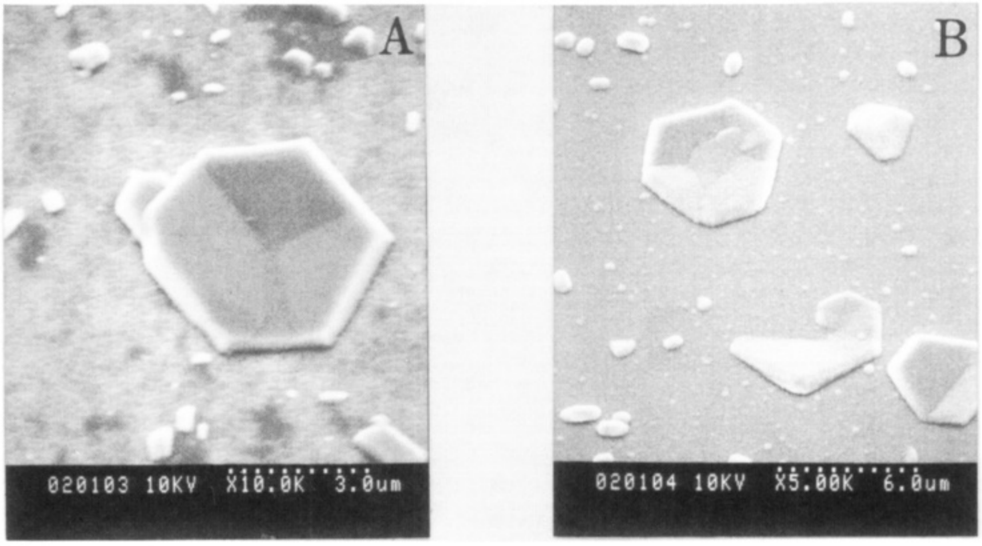

Figure 1. (A) SEM photo of a Se/ITO substrate prepared by a 40-min interaction of Se vapor with ITO. (B) SEM photo of CdSe electrodeposited and annealed on the Se/ITO substrate shown in Figure 1A.

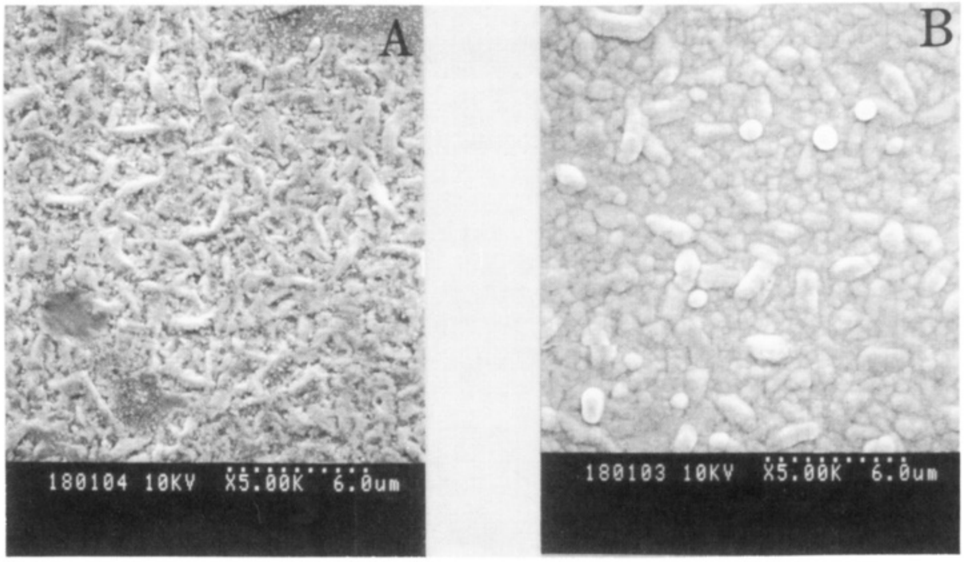

Figure 2. (A) SEM photo of a completely reacted Se/ITO substrate prepared by a 15-h interaction of Se vapor with ITO. (B) SEM photo of CdSe electrodeposited and annealed on the Se/ITO substrate shown in Figure 2A.

on untreated ITO. Regardless of the method of surface treatment, CdSe films were adherent to the substrates when a Se-rich interface was prepared. However, crack-free CdSe films were obtained when thermally treated substrates were used. Smooth electrochemically prepared Se/ITO did not prevent the cracking of CdSe films.

Cadmium and Indium Treatments. Treatment of ITO substrates by Cd or In was employed for comparison to Se/ITO. For both of these elements, electrochemical and thermal treatments of the ITO were successful. As was the case for Se modified substrates, the surface texture created by Cd or In treatment of ITO provided a surface on which electrodeposited CdSe remained crack-free and adherent both before and after heat treatment. SEM was used to investigate the structure and morphology of (a) treated substrates, (b) CdSe on the substrates, and (c) CdSe removed from the substrates.

The surface of Cd/ITO substrates, prepared by thermal reaction, differed from Se/ITO substrates in that the large features of the Cd/ITO surface were round lumps rather than distinct hexagons. CdSe electrodeposited onto Cd/ITO covered the surface, including the large features, and had a morphology similar to that of the substrate (Figure 3A). No changes were observed in the surface after annealing, and each of the several samples made remained completely adherent and crack-free over the entire area except the bottom 1 mm. In/ITO substrates, prepared by thermal reaction, had a very fine-grained surface with micron-sized features that were similar in appearance to, but at a lower density than, the Cd/ITO surface features. A similar fine-grained morphology, with sparse surface features, was exhibited by the CdSe electrodeposited onto In/ITO. Again it was evident that the surface features remained after annealing, that each of the CdSe films made were completely adherent, and that the CdSe was crackfree in greater than 90% of the area; again, the few cracks occurred at the bottom edge.

Upon removal of the CdSe from either of the Cd/ITO or In/ITO substrates, an interesting feature was highlighted. The surface of CdSe, removed from the Cd/ITO substrate and shown in Figure 3B, was smooth but had many shallow depressions. Comparing this to Feature 3A, the micrograph of CdSe on Cd/ITO substrates, it is clear that the surface lumps of films on the substrate correlate in size, general shape, and density with the surface depressions of CdSe removed from the substrate. Similar characteristics were exhibited by CdSe films removed from In/ITO substrates. The CdSe films electrodeposited onto

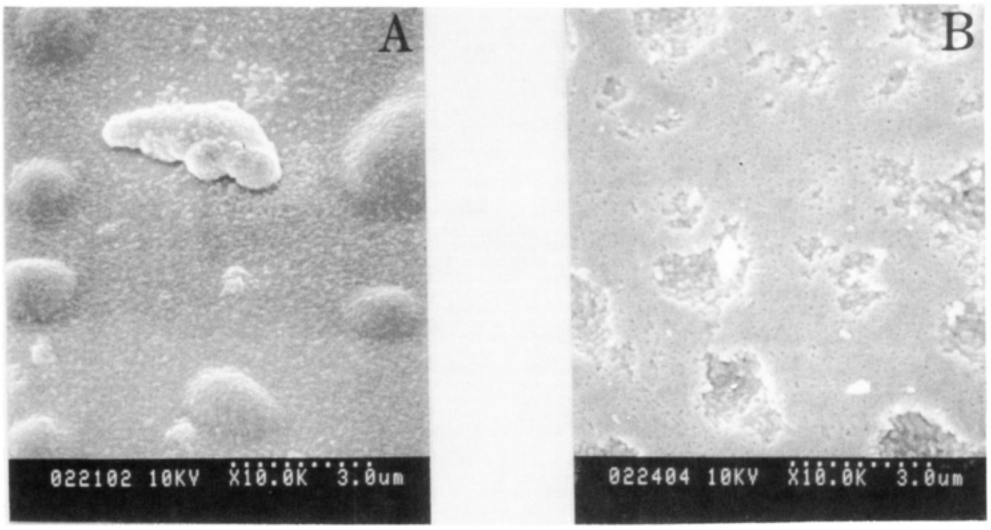

Figure 3. (A) SEM photo of CdSe electrodeposited and annealed on a thermally prepared Cd/ITO substrate. (B) SEM photo of the CdSe film shown in Figure 3A, prepared on Cd/ITO, but removed from the substrate. Before removal from the substrate, the pictured CdSe surface was at the interface between the CdSe and the substrate.

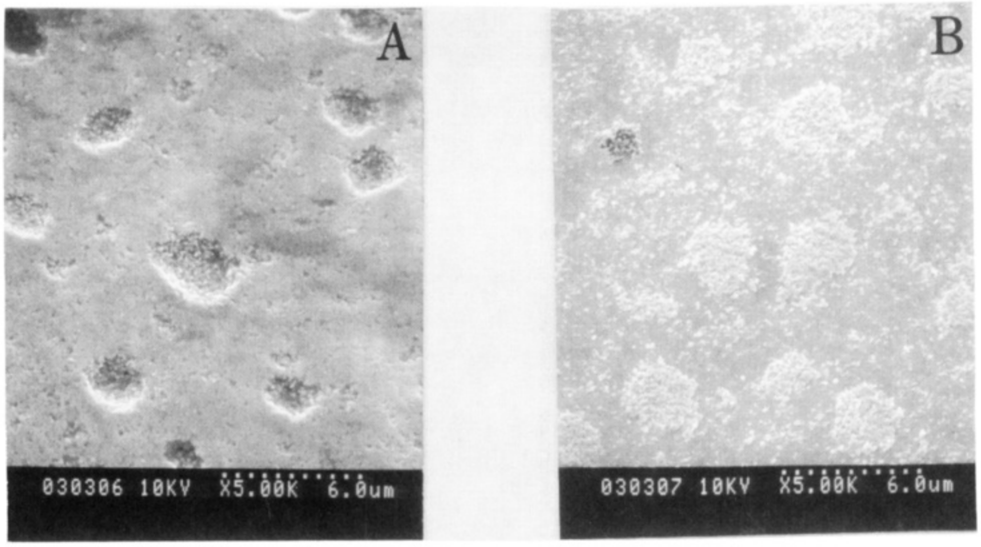

Figure 4. (A) SEM photo CdSe electrodeposited, annealed, and removed from a thermally prepared In/ITO substrate. The illustrated surface was at the substrate interface before removal. (B) SEM photo of the In/ITO substrate surface after removal of the CdSe.

In/ITO substrates were fine grained, they covered the micron-sized surface features on the substrate, and they were adherent upon annealing. Figure 4 clearly illustrates the correspondence of the features of the CdSe, removed from In/ITO substrates, and the substrate surface after CdSe removal. The surface of CdSe on the epoxy (Figure 4A) appears to be the inverse of the substrate surface (Figure 4B); the size, shape, and density of features all correlate well. The parallel of thermally prepared Cd/ITO and In/ITO substrates is striking.

The interfacial material of the Cd/ITO substrates greatly improved the adherence and morphology of the CdSe film. From the resistivity measurements reported below, it is not clear if any Cd diffused from the interface into the CdSe during the annealing treatment. Likewise, the interfacial material on the surface of In/ITO substrates remained adherent to the substrate and was not removed with the CdSe. Surface depressions were, therefore, left in the CdSe upon removal. The lower resistivity values of CdSe samples deposited on In/ITO indicate that some of the In diffused into the CdSe during heat treatment.

Additional information concerning the nature of the material left on the substrate, after CdSe removal, was obtained by using energy-dispersive X-ray spectroscopy (EDS). Se and In were detected on the surface of In/ITO substrates, but Cd was not. Indium was a constituent of the ITO coating and of the surface layer of In/ITO. The only source of either Cd or Se, for this type of sample, was the electrodeposition solution. A form of indium selenide was produced by reaction, chemically or electrochemically, of the selenosulfate solution with the In at the substrate surface. A precise composition was not obtainable because the EDS spectra were collected qualitatively without the use of standards. It was clear, however, that both In and Se were present in significant concentrations. Since Cd was not present at levels above the background (Bremstrahlung) spectra, CdSe was not a major constituent of the material remaining on the surface. Cd was detected in the spectra of a region where CdSe remained on the substrate.

ITO substrates were also modified with Cd or In layers made by electrochemical reduction. In general the In or Cd layers deposited electrochemically were less consistent across the surface of the substrate than thermally treated samples. Consequently, the CdSe films also exhibited more variation of surface structure for the electrochemically treated substrates than for thermally treated ones. The Cd or In layers still provided enough surface structure

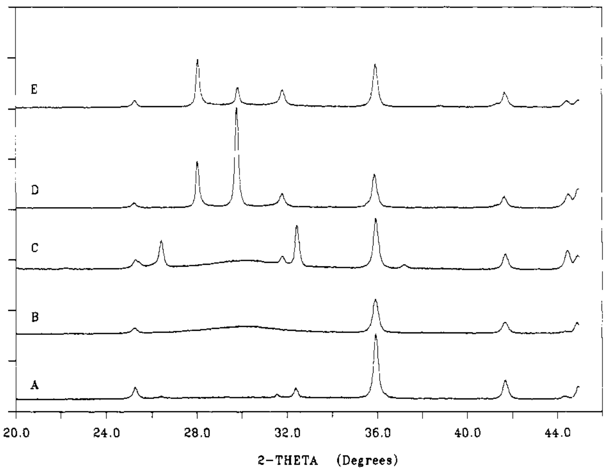

Figure 5. X-ray powder diffraction patterns for (A) Se/ITO substrate, (B) CdSe as deposited on untreated ITO, (C) CdSe as deposited on thermally prepared Se/ITO, (D) the same CdSe sample as Figure 5C, but annealed for 16 h at 500 °C, (E) CdSe deposited on thermally prepared Cd/ITO and annealed for 10 min at 500 °C.

and improved interfacial bonding to prevent cracks and improve the adhesion of the CdSe. These crack-free CdSe samples had features similar to those of CdSe on thermally prepared In/ITO substrates. Micron-sized surface features were sparsely distributed on a fine-grained background. When removed from the substrate, the CdSe had shallow depressions in the surface, similar to the films prepared on thermally treated substrates.

The current–time profiles for the electrodeposition of CdSe were recorded for depositions on many different types of substrates. With the exception of In/ITO, the current maximum occurred after 5–10 min. The current then decreased for the next 10 min to the final current, which was constant for the remainder of the deposition. Maximum currents were different for various substrates, but the final current density was approximately 250 μA/cm^2 for all samples. For the In/ITO samples the maximum current occurred immediately (within 2 s). The remainder of the current–time profile was similar to other samples. The fine-grained surface of In/ITO substrates provided a higher density of nucleation sites for CdSe growth than did other substrates. During the initial stages of film deposition CdSe is expected to grow radially from each nucleation site; the reduction current rose continually during this radial growth. As the CdSe nuclei coalesced, radial growth was no longer possible and the current decreased. The final phase of planar film growth gave a relatively constant deposition current. The short rise time of the current–time profile for electrodeposition on In/ITO is consistent with the fine-grained structure of this substrate and the subsequently deposited CdSe.

X-ray Diffraction. Several interesting features were revealed by the XRD patterns. It was evident again that the structure of the CdSe films was dependent on the type of substrate used. This is revealed by the XRD patterns recorded for CdSe electrodeposited onto the three following types of substrates: (a) untreated ITO, (b) Se/ITO, and (c) Cd/ITO. These patterns are shown in Figure 5 as patterns B, C, and E, respectively. The pattern for a Se/ITO substrate, pattern A, is shown for comparison. The four peaks in pattern B are assigned to the indium oxide substrate. The published peaks of CdSe[18] were not resolved in the samples of CdSe deposited onto either untreated ITO or Se/ITO, indicating that the CdSe was amorphous. A second XRD pattern (not shown) was recorded for the sample on Se/ITO after it was subjected to the standard annealing treatment at 500 °C for 10 min. No change in the crystallinity was noted as the pattern was identical with the as-deposited sample; the CdSe remained amorphous. However, the CdSe peaks are resolved for a sample deposited onto Cd/ITO and annealed under standard conditions (pattern E). Either this sample was more polycrystalline upon deposition, or the transformation from an amorphous to a polycrystalline structure was much more facile for CdSe on the Cd/ITO than on the Se/ITO substrate. The CdSe on Se/ITO sample that exhibited pattern C was further annealed in a nitrogen ambient for 16 h at 500 °C. The resolved CdSe peaks in the range 28–32°, shown in Figure 5D, indicate that the CdSe film was polycrystalline after this treatment.

Table I. CdSe Activation Energy and Resistivity as a Function of Substrate Pretreatment

sample	substrate treatment	E_a, eV	resistivity, Ω cm	light response
1	Se, thermal	0.37	1.7×10^5	4000
2a[a]	Se, thermal	0.43[b]	2.2×10^6	1000
2b	Se, thermal	0.38	7.4×10^5	2500
3a[a]	Se, thermal	0.39	2.0×10^6	900
3b	Se, thermal	0.37	6.6×10^6	2500
4[c]	Se, thermal	0.15	3.8×10^4	<2
5	Cd, electrochemical	0.28	1.8×10^4	1900
6a	Cd, thermal	0.34	1.1×10^6	2500
6b	Cd, thermal	0.33	3.0×10^6	1780
7	In, electrochemical	0.21	4.1×10^3	10
8	In, electrochemical	0.15	9.0×10^4	4500
9	In, thermal	0.19	7.1×10^4	20
10	In, thermal	0.33	9.3×10^5	2350

[a] Repeat measurement, after storage with atmospheric exposure. [b] Average of two measurements. [c] Sample was electromigrated with copper.

CdSe Resistivity and Activation Energy Measurements. The electrical properties of CdSe were also affected by the materials used to modify the substrates. The electrical resistivity of CdSe thin films electrodeposited on treated ITO was measured as a function of temperature. The effect of the diffusion of Se, Cd, or In into the CdSe during the heat treatment was monitored by measurement of the activation energy and resistivity for each type of sample.

The resistivity measurements reinforced the conclusions drawn from the SEM study. It was necessary to control the interface between the CdSe and ITO in order to produce an adherent and crack-free CdSe film. Films deposited on untreated ITO substrates were consistently cracked immediately after deposition and often flaked off after annealing. Measurements of the resistivity of samples having even very minute cracks were not meaningful. Either the data were very scattered, or the plot of the natural log of the resistivity versus $1/T$ showed substantial curvature. Not surprisingly the measured resistivity was 2–3 orders of magnitude larger for cracked samples than for crack-free samples.

Resistivity results are presented in Table I for CdSe films deposited on and subsequently removed from the three types of substrates used: Se/ITO, Cd/ITO, and In/ITO. The activation energy (E_a) is the slope of ln (resistivity) versus $1/T$ plot. The room-temperature resistivity is the value for 25 °C, as calculated from the plot. Light response is the ratio between the dark resistivity and the resistivity measured, at 25 °C, under 100 mW/cm^2 incident light intensity.

Samples 1–3 in Table I represent crack-free CdSe removed from Se/ITO substrates. When more than one

---

(18) ASTM powder diffraction file, card number 8-459.

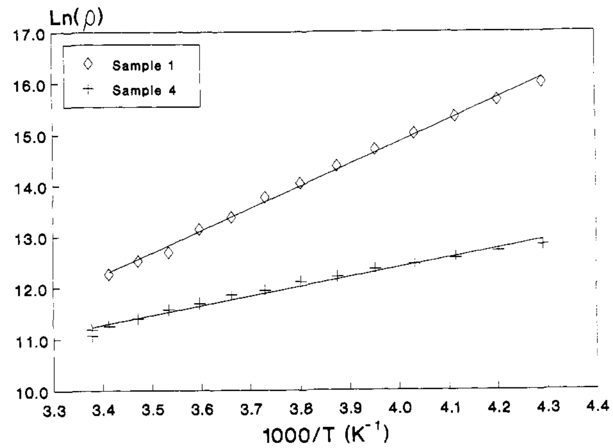

Figure 6. Natural log of the resistivity versus 1000/*T*, for sample 1, CdSe deposited on Se/ITO, and sample 4, an identical sample that was subsequently treated by copper electromigration.

resistivity sample was prepared from the same film, the sample number in the table is followed by a letter (e.g., 2a and 2b). The activation energy values were consistently 0.38 eV, aside from sample 2a, while the resistivity values of these samples were in the range 2×10^5–6×10^6 Ω cm. The resistivity was reduced by a factor of 1000–4000 under 100 mW/cm^2 illumination. A representative plot of data obtained for sample 1 is shown in Figure 6. Copper, like In and Cd, is expected to be an electron donor in CdSe and therefore to reduce the resistivity. The effect of Cu on CdSe, introduced by electromigration into CdSe on Se/ITO, is demonstrated by the data for sample 4. Although the sample had minute cracks, as evidenced by SEM and the curvature in the ln (resistivity) versus 1/*T* plot (Figure 6), semiquantitative data could be obtained. Thus, in comparison to samples 1–3, the resistivity was lowered to 4×10^4 Ω cm, the activation energy to 0.15 eV, and the light response to less than a factor of 2.

The trends are less clear for CdSe samples removed from Cd/ITO and In/ITO substrates (samples 5–6 and 7–10, respectively). Both the activation energy and resistivity values were typically lower than for samples prepared on Se/ITO substates, although most samples retained a high light response. The CdSe samples prepared from electrochemically treated Cd/ITO substrates were initially measured by using colloidal graphite contacts, and high resistivity values were measured. When sample 5 was remeasured by using indium gallium eutectic contacts, the measured resistivity value was 3 order of magnitude lower. The high resistance of the graphite contacts contributed to a large series resistance. Samples 6a and 6b, prepared on thermally treated Cd/ITO substrates, showed slightly larger activation energy values than sample 5, but lower than Se/ITO samples. Samples 7–10, prepared on In/ITO, also exhibited values lower than Se/ITO for both activation energy and resistivity. Plots of the data for samples 6b, 7, and 10 are shown in Figure 7. Although the measured properties of CdSe prepared on Cd/ITO and In/ITO substrates clearly differed from those of CdSe on Se/ITO, a more definitive investigation is needed to understand the effect of the diffusion of any of these elements on the conduction mechanisms in electrodeposited CdSe thin films.

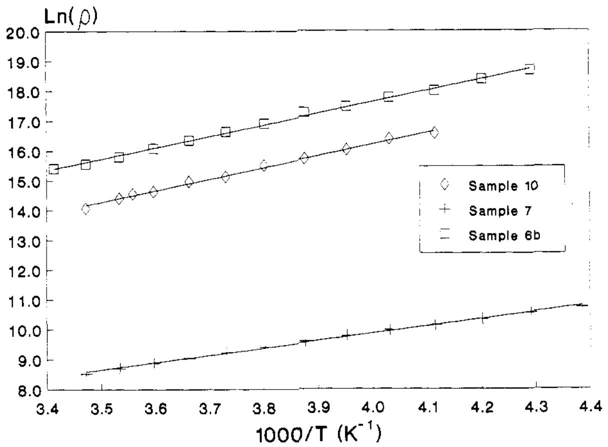

Figure 7. Natural log of the resistivity versus 1000/*T*, for samples 6b, 7, and 10. Sample 6b was CdSe deposited on thermally prepared Cd/ITO. Sample 7 was CdSe deposited on electrochemically prepared In/ITO. Sample 10 was CdSe deposited on thermally prepared In/ITO.

An aging effect was noted for CdSe samples removed from Se/ITO substrates. The values of the activation energy were consistent with other similar samples only if the sample was measured several days or more after the removal of the CdSe from the substrate. Thus consistent values were obtained for the activation energy (0.38 eV) and light response (2500–4000) of samples 1, 2b, and 3b, which were measured 9 days or more after removal from the substrate. On the other hand, the first measurements of samples 2a and 3a, made within 24 h of removal of the CdSe from the substrate, resulted in significantly higher activation energy values (0.53 and 0.43 eV) and a low light response (150). Measurements of samples 2a and 3a were repeated 60 days later. Sample 3a had an activation energy of 0.39 eV and a light response of 900 times. Sample 2a was remeasured twice; values of 0.41 and 0.46 eV were obtained for the activation energy and a value of 1000 for the light response.

It seems clear that the CdSe, when measured immediately after removal from the Se/ITO substrate, exhibited different properties from aged samples. This effect was only monitored for CdSe samples removed from Se/ITO substrates, but it cannot be ruled out for CdSe removed from other types of samples. This aging effect may be explained by oxygen adsorption at the grain boundaries or surface of the CdSe films because the samples were exposed to air during storage. Oxygen effects on the properties of CdSe have been reported for both polycrystalline thin films[19-21] and single crystals.[22] In a temperature-programmed desorption study on evaporated thin film CdSe, a 2 order of magnitude increase has been reported in the resistance of CdSe after a 2-min oxygen adsorption at 406 K.[19] Increases in the resistivity were also noted for our samples. Oxygen effects on the conductivity of and electron lifetime of single-crystal CdSe have also been reported.[22] The minority carrier diffusion length and the donor density of thin film CdSe have been shown be irreversibly affected by an annealing treatment in an oxygen-containing ambient.[23]

Summary

The interaction of ITO with various elements was reported. The changed physical structure and chemical composition of the ITO coating altered the structure and improved the adhesion of CdSe layers that were electrodeposited onto the modified surfaces. The textured in-

---

(19) Chan, D. S. H.; Hill, A. E. *Thin Solid Films* **1976**, *38*, 163.
(20) Brodie, D. E.; LaCombe, J. *Can. J. Phys.* **1967**, *45*, 1353.
(21) Wilson, H. L.; Gutierrez, W. A. *J. Electrochem. Soc.* **1965**, *112*, 85.
(22) Bube, R. H. *J. Electrochem. Soc.* **1966**, *113*, 793.
(23) Szabo, J.; Cocivera, M. *J. Appl. Phys.* **1987**, *61*, 4820.

terface resulted in CdSe thin films that remained crack-free during the deposition and annealing treatments. The surface structure of the treated substrates and the electrodeposited CdSe was clearly documented by SEM. The CdSe film morphology and structure was dependent on the method and conditions of the substrate preparation. The entire surface, inclusive of large features, was consistently covered by the CdSe, and no pinholes were evident. Upon annealing, no changes were evident in the structure or morphology of the CdSe. When removed from the substrate, the CdSe film remained crack-free. The CdSe surface, upon removal from the In/ITO or Cd/ITO substrates, showed shallow depressions where a portion of the interfacial material remained adherent to the substrate.

Preliminary resistivity measurements of CdSe showed that the substrate treatments not only affected the structure and adhesion of CdSe, but also the electrical properties. The CdSe samples from Se/ITO, after atmospheric exposure, gave consistent results. A more complete investigation of the effects of oxygen on the electrical properties of CdSe, and a more comprehensive study of the effects of Se, Cd, In, and other elements on the properties of CdSe are in progress.

Registry No. ITO, 50926-11-9; CdSe, 1306-24-7; Se, 7782-49-2; Cd, 7440-43-9; In, 7440-74-6.

Formation of Quantum-Size Semiconductor Particles in a Layered Metal Phosphonate Host Lattice

Guang Cao, L. K. Rabenberg,[†] Christine M. Nunn,[‡] and Thomas E. Mallouk*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712-1167

Received July 25, 1990

Quantum-size ZnSe, PbS, CdS, and CdSe particles 30–50 Å in diameter were grown in the interlamellar region of the layered host material $Zr(O_3PCH_2CH_2CO_2H)_2$ by reaction of H_2S or H_2Se with $M^{II}[Zr(O_3PCH_2CH_2CO_2)_2]$. Diffraction from the PbS particles indicated the rocksalt structure, whereas CdSe adopts the zincblende structure and grows with the [111] zone axis parallel to the host layering direction. CdSe crystallites within a single host platelet are oriented relative to each other, even though the crystallinity of the host is destroyed during particle growth. Little or no reaction was found under similar conditions with $M^{II}[Zr(PO_4)_2]$. It is postulated that $M^{II}[Zr(O_3PCH_2CH_2CO_2)_2]$, prepared by dehydration of $M^{II}[Zr(O_3PCH_2CH_2CO_2)_2]\cdot xH_2O$ ($x \approx 1.4$) has an open structure that allows for interlamellar diffusion of H_2S and H_2Se. Contraction of the layer axis upon dehydration is significantly smaller for $M^{II}[Zr(O_3PCH_2CH_2CO_2)_2]\cdot xH_2O$ than for $M^{II}[Zr(PO_4)_2]\cdot yH_2O$. For comparison, an analogously layered compound, $Zn[Zn(O_3PCH_2CH_2CO_2)]_2\cdot 3H_2O$, was prepared and structurally characterized. This compound crystallizes in orthorhombic space group *Pbcn* (No. 60) with $a = 5.126$ (1), $b = 10.837$ (2), $c = 28.596$ (9) Å, $V = 1588.5$ Å^3, $Z = 4$, $R = 0.028$, $R_w = 0.033$ for 1567 unique reflections with $F_o > 3\sigma(F_o)$. The structure contains one set of zinc atoms four-coordinated by oxygen atoms of the phosphonate groups and another set five-coordinated by oxygen atoms of the carboxyl groups and lattice water molecules. The repeating unit is $Zn/O_3PCH_2CH_2CO_2/Zn(H_2O)_3/O_2CCH_2CH_2PO_3/Zn...$ along the layering (*c* axis) direction. Complete dehydration of this compound causes a relatively small decrease in the layer spacing, from 28.6 to 28.0 Å.

Introduction

There has been intense research activity in recent years on the subject of semiconductor crystallites that are so small (less than 100 Å in diameter) that they exhibit quantum size effects.[1] The interest in semiconductor particles in this size domain stems both from a desire to understand, at a fundamental level, the transition from molecular to bulk electronic properties and from the prospects of practical applications of these particles as nonlinear optical materials[2] and photocatalysts.[3]

Crystallites of nanometer sizes are inherently unstable due to their high surface tensions. Under conventional nucleation/growth conditions, crystallites tend to grow larger than the quantum size domain. Therefore without the use of stabilizing reagents and/or reactions, the preparation of small particles must take place under kinetically controlled conditions. In addition, even if crystallites of nanometer sizes are formed, they tend to aggregate or undergo Ostwald ripening to minimize their surface tension. In view of the factors affecting the size of crystallites it is not surprising to find that successful methods for the synthesis of nanoclusters always involve

---

[†] Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX 78712-1167.

[‡] Present address: University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

(1) For recent review articles, see: (a) Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Mater. Sci.* **1989**, *19*, 471. (b) Henglein, A. *Top. Curr. Chem.* **1988**, *143*, 113. (c) Stucky, G. D.; Mac Dougall, J. E. *Science* **1990**, *247*, 669–678.

(2) (a) Wang, Y.; Suna, A.; Mahler, W. *Mater. Res. Soc. Symp. Proc.* **1988**, *109*, 187. (2) Wang, Y.; Mahler, W. *Opt. Commun.* **1987**, *61*, 233.

(3) (a) Youn, H.-C.; Tricot, Y.-M.; Fendler, J. H. *J. Phys. Chem.* **1987**, *91*, 581. (b) Kamat, P. V.; Dimitrijevic, N. M.; Fessenden, R. W. *J. Phys. Chem.* **1987**, *91*, 396. (c) White, J.-R.; Bard, A. J. *J. Phys. Chem.* **1985**, *89*, 1947. (d) Fojtic, A.; Weller, H.; Henglein, A. *Chem. Phys. Lett.* **1985**, *120*, 552. (e) Weller, H.; Fojtik, A.; Henglein, A. *Chem. Phys. Lett.* **1985**, *117*, 485.

(4) (a) Brus, L. *J. Phys. Chem.* **1986**, *90*, 2555. (b) Brus, L. E. *J. Chem. Phys.* **1984**, *80*(9), 4403. (c) Brus, L. E. *J. Chem. Phys.* **1983**, *79*(11), 5566.

(5) (a) Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 5566. (b) Weller, H.; Schmidt, H. M.; Koch, U.; Fojtic, A.; Baral, S.; Henglein, A.; Kunath, W.; Weiss, K.; Dieman, E. *Chem. Phys. Lett.* **1986**, *124*, 557.

0897-4756/91/2803-0149$02.50/0