result is a very highly conductive material with an unprecedented level of partial oxidation for a TSeT-based molecular conductor, accompanied by contraction in the interplanar spacing and increased interchain distances (decreased structural two-dimensionality). The use of F^- counterions in modifying the properties of other molecular metals is currently under investigation.

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Registry No. $(TSeT)F_{0.25}Cl_{0.50}$, 136283-11-9.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles for 1 (6 pages); table of and structure factors for 1 (3 pages). Ordering information is given on any current masthead page.

Articles

Synthesis of Stoichiometric Cadmium Selenide Films via Sequential Monolayer Electrodeposition

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A convenient procedure for synthesizing CdSe that may be generally applicable to binary materials is described. The method involves the electrodeposition of sequential layers of CdSe by sweeping the potential of Ti or Ni substrates continuously between −0.4 and −0.8 V vs SCE at a scan rate of 10 V s^{-1} in solutions containing between 0.1 and 0.3 M $CdCl_2$ or $CdSO_4$ and 0.3 mM SeO_2. The Se solution concentration is low enough that only submonolayer amounts of Se are reduced per cycle, while a large excess of Cd is deposited and subsequently stripped. The CdSe films that result are found by electron microprobe analysis to have 1:1 stoichiometry. By contrast, most conventionally electrodeposited CdSe films are either Cd- or Se-rich. Scanning electron microscopy indicates that the films consist of a dense layer of 100-nm grains beneath micron-size dendritic features, and X-ray powder diffraction confirms the existence of both cubic and hexagonal phases of CdSe.

Introduction

Thin films of many semiconductors can be conveniently and inexpensively synthesized by electrochemical deposition from aqueous or nonaqueous solutions of the appropriate soluble precursors.[1,2] For the II–VI semiconductors CdSe and CdTe, electrodeposition has been investigated as an inexpensive route into large area thin films for solar cell operation,[3-16] although electrodeposited materials are also of interest for their potential applications in microelectronic, photon detector, and quantum well technologies. For instance, electrodeposited films of CdS and CdSe have been generated with grain sizes small enough to show electronic quantum size effects.[14,17,18] Electroplating has the advantage of being a low-temperature method, so that in principle it can be utilized in systems where thermal diffusion or decomposition are barriers to obtaining the desired materials.

A major obstacle to forming high-quality films of binary materials electrochemically is that one of the constituent elements may plate out preferentially, leading to an excess of that element in the film. In the case of CdSe, Se tends to build up in the films, necessitating a subsequent heat

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treatment to drive off the excess and produce an acceptable quality semiconductor. Skyllas-Kazakos and Miller attributed the occurrence of excess Se to reaction of H_2Se in solution with H_2SeO_3 via reactions 1 and 2.[19] Elec-

$$H_2SeO_3 + 6H^+ + 6e^- \rightarrow H_2Se + 3H_2O \qquad (1)$$

$$2H_2Se + H_2SeO_3 \rightarrow 3Se + 3H_2O \qquad (2)$$

trodeposition of CdSe was postulated to occur via reaction of H_2Se with Cd^{2+} (reaction 3). Thus, deposition of CdSe

$$H_2Se + Cd^{2+} \rightarrow CdSe + 2H^+ \qquad (3)$$

is in competition with production of excess Se, and at low H_2SeO_3 concentrations, reaction 2 is expected to be suppressed. Skyllas-Kazakos and Miller observed rapid electrode passivation when H_2SeO_3 solution concentrations were above 2 mM, attributed to formation of an insulating Se layer.[19] Mishra and Rajeshwar have argued that the mechanism for CdSe deposition is a direct $6e^-$ reduction via eq 4,[20] although presumably reactions 1 and 2 operate

$$H_2SeO_3 + Cd^{2+} + 6e^- + 4H^+ \rightarrow CdSe + 3H_2O \qquad (4)$$

in competition with this process. For either possible mechanism, the net reaction is that represented by eq 4.

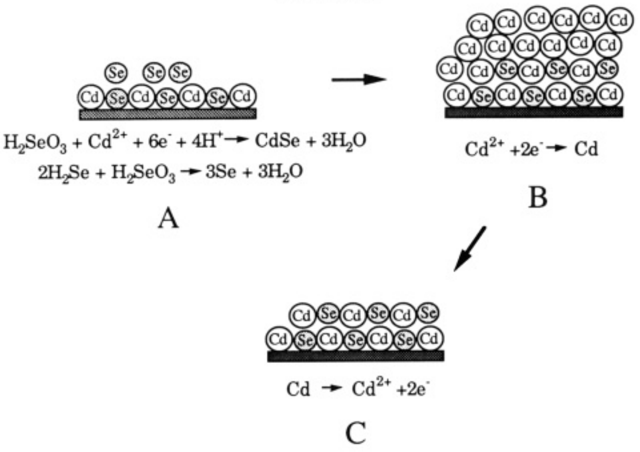
The procedure described in this work is an effort to eliminate the problem of bulk Se formation, using a cyclic deposition scheme that cathodically deposits submonolayer amounts of CdSe and a large stoichiometric excess of Cd. The excess Cd is then stripped off by sweeping the electrode to a positive potential (Cd is readily stripped close to its thermodynamic reduction potential[21]). Since the CdSe phase has a large negative free energy of formation ($\Delta G^\circ_{f,298K} = -141.5$ kJ mol^{-1}),[22] it was thought that any free Se that is deposited in this process will react with the excess Cd to form CdSe and not lead to large amounts of excess Se in the film. The net result is thus the sequential deposition of stoichiometric CdSe a monolayer (or less) at a time. Here we report that such a procedure leads to compositionally homogeneous, stoichiometric films and may be a general method to electrodeposit binary materials with large thermodynamic or kinetic stabilities.

Experimental Section

Materials. All solutions were made using 18-MΩ deionized water. Reagents were obtained from the following sources: ACS reagent grade $CdCl_2$ was purchased from Fischer Scientific; SeO_2 (99.999%) and $3CdSO_4{\cdot}8H_2O$ (98%) from Aldrich chemicals; ultrahigh-purity concentrated HCl and H_2SO_4 (Baker Ultrex II) from Baker Chemicals (*caution*: Se and Cd are highly toxic and should be handled with adequate precautions); Ti sheet (99.7%) and Ni sheet (99.5%) from Johnson Mathey Electronics; Ni rod (99.99%) from Aldrich chemicals. Wires were attached to the back of the Ti working electrodes with Ag paint, and the contacts were sealed in epoxy. The electrodes were ground smooth with sandpaper (#320) and then either etched in 10% (v/v) HF solution (referred to in the text as "unpolished"), or polished to a mirror finish with 0.05-μm Al_2O_3 on a polishing wheel (referred to in the text as "polished"). All electrodes were cleaned ultrasonically in trichloroethylene for 10 min immediately prior to use.

Preparation of CdSe Films. Films were deposited at room temperature with a conventional three-electrode setup, using a saturated calomel reference electrode (SCE) and a Pt flag counter electrode.[23] The Ti or Ni working electrode was oriented parallel to the counter electrode, at a spacing of ca. 1 cm. Typical plating solutions contained 0.1 M $CdCl_2$, 0.5 M HCl, and 0.3 mM SeO_2 or 0.3 M $CdSO_4$, 0.25 M H_2SO_4, and 0.3 mM SeO_2. The solution volume was large enough that the deposition reduced the Se solution concentration by less than 6%. For 0.2 cm^2 working electrodes the volume of solution was typically 75 mL. The RDE experiments were all performed with solution volumes of 200 mL and 0.20 cm^2 polished Ni electrodes. New solutions were used for each electrode, and all solutions were purged with Ar for ca. 20 min. prior to use.

Scheme I



A Bioanalytical Systems CV-27 potentiostat/coulometer was used, and the current–voltage traces for the fast scans were output to a Kikusui model 5020 oscilloscope. The potential was typically cycled between −0.4 and −0.8 V vs SCE at a scan rate of 10 V/s, and the coulometer was monitored until the desired amount of material had been deposited. A Pine Instruments Model ASR rotator and controller was used for the rotating disk experiments.

SEM Studies. Scanning electron micrographs were obtained with 20-keV electrons in the secondary electron imaging mode, using a Cambridge Model 360 electron microscope with a LINK analytical AN10 X-ray energy analyzer. Quantitative elemental analyses were performed on a JEOL 733 Superprobe WDS spectrometer operating at 10-kV accelerating voltage and a 35-nA beam current. The spot size ranged from 10 to 30 μm. The Kα lines of Ti and Cl and the Kβ lines of Cd and Se were used in the analysis. Triplicate measurements were made on each sample. The samples subjected to quantitative microprobe analysis had been deposited onto polished Ti or Ni substrates.

X-ray Powder Diffraction. Powder patterns were obtained on spinning samples using a Scintag PAD V diffractometer and data acquisition system with Ni-filtered Cu Kα radiation. The samples were not removed from the Ti substrates, and diffraction peaks associated with Ti were observed in all of the spectra. Annealed samples were prepared as follows: All epoxy was removed from the unpolished Ti electrodes, and they were placed in Ni boats and then heated under an Ar atmosphere at 650 °C for 15 min. The samples were removed after the furnace had cooled (ca. 1 h).

Results and Discussion

Cyclic Voltammetric Deposition of CdSe at Fast Scan Rates at Ni RDE. The method described in this work is an attempt to form homogeneous, stoichiometric films of a binary compound. A diagram of the rationale behind the process is given in Scheme I. In part A, corresponding to the potential region labeled A in Figure 1, CdSe along with excess Se are deposited onto the substrate at a rate less than or equal to the diffusion-controlled rate. The SeO_2 concentration is chosen such that the diffusion-limited H_2SeO_3 reduction current (see below) is on the order of 1–5 mA/cm^2, which corresponds to a CdSe

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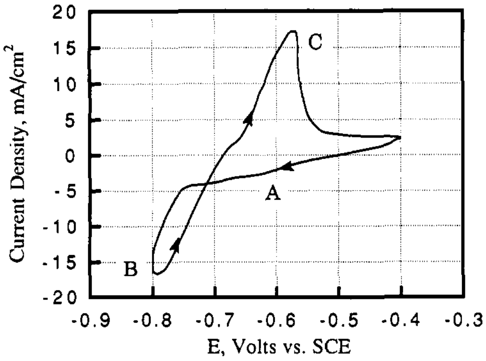

Figure 1. Current–voltage trace obtained during cyclic electrodeposition of CdSe onto a Ni rotating disk electrode (1000 rpm): (A) potential region where Se and CdSe are deposited; (B) deposition of bulk Cd; (C) stripping wave of excess Cd. Voltage scale is referenced to SCE. Negative potentials are to the left; cathodic (negative) currents are in the downward direction. Scan rate is 10 V/s.

deposition rate of about 2 × 10^{-9} mol cm^{-2} s^{-1}, or 7 Å/s. Thus at a scan rate of 10 V/s, a submonolayer amount of CdSe (and far less elemental Se) is expected to be deposited in the time it takes to reach the deposition potential for bulk Cd, part B. The high concentration of Cd^{2+} in solution results in deposition of excess Cd in this region (on the order of 5 atoms of Cd/atom of Se under our conditions). During the anodic half of the scan, part C, the excess Cd is stripped back off,[24] leaving behind a small amount of CdSe. Provided the CdSe is thermodynamically or kinetically stable enough, it will not be stripped in the process. The deposition sequence is then repeated, building layer upon layer of CdSe on the electrode surface.

Assuming CdSe deposition is limited by diffusion of the Se-containing species to the electrode, an upper limit on the amount of CdSe that can be deposited per potential cycle can be calculated from the Levich equation (eq 5).

$$I_{\text{lim}} = 0.62nFAD^{2/3}\nu^{-1/6}C_0{}^*\omega^{1/2} \qquad (5)$$

For a solution concentration of 0.4 mM H_2SeO_3, a diffusion coefficient of 7.0 × 10^{-6} cm^2/s (see below), an RDE spin rate of 1000 rpm, and a scan rate of 10 V/s over the potential range −0.4 to −0.8 V vs SCE, a maximum of 1.6 × 10^{-10} mol/cm^2, or 0.17 monolayers, will be deposited per cycle. Because CdSe is not deposited at the diffusion-limited rate at all times in the potential range −0.4 to −0.8 V vs SCE (see below), this calculation gives an upper limit for the rate of CdSe deposition. In contrast, integration of the Cd stripping wave from Figure 1 indicates that during the same scan, 7.0 × 10^{-10} mol/cm^2 of Cd is deposited and subsequently stripped. Thus at least a 4-fold excess of Cd is deposited and stripped during CdSe deposition.

The growth of films in the experiments utilizing the cyclic potential sweep deposition technique was monitored coulometrically, and the deposition current was determined from plots of net charge passed (Q) vs time. Figure 2 shows a plot of deposition current vs time for the potential sweep and for a conventional potentiostatic deposition. These data were taken at a H_2SeO_3 solution concentration of 3 mM, for which electrode passivation via Se formation has previously been noted.[19] Consistent with prior observations, the cathodic current for the potentiostatic deposition drops significantly within an hour. By contrast, the cathodic current for deposition using a cyclic potential scan is relatively constant over the same time period. Compositional analysis of the two films shows that the potentiostatically deposited film contains excess Se (Se:Cd ratio = 2.57), while the film deposited with the cyclic potential scan is stoichiometric (Se:Cd = 1.03). In addition, Figure 2 shows the current–time behavior of an electrode that was cycled between −0.4 and −0.76 V vs SCE. The lower limit in this scan is positive of the bulk CD deposition wave; hence this experiment did not incorporate the sequential deposition and stripping of excess Cd. The data also show the drop in current characteristic of excess Se formation, confirmed by microprobe analysis (Se:Cd = 1.33). Thus the sequential deposition and stripping of excess Cd is required to obtain stoichiometric films under these conditions.

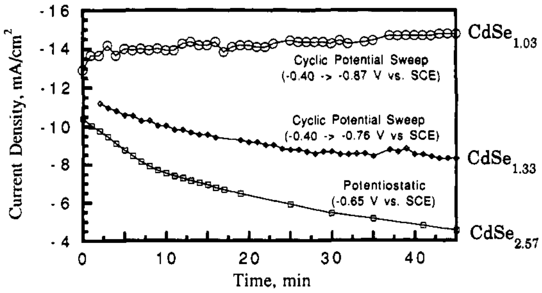

Figure 2. Current density versus deposition time for three different CdSe deposition techniques, showing electrode passivation. All runs used identical solution composition and volumes (0.3 M $CdSO_4$, 0.25 M H_2SO_4, 3.0 mM SeO_2, 100 mL) and identical electrode arrangements (Ni RDE, 2000 rpm). The top curve represents the sequential monolayer deposition scheme used in the present work. Conditions are identical to those used in Figure 1 except that [SeO_2] = 3 mM. Note that no electrode passivation is observed. The middle curve represents a fast scan cyclic voltammetric deposition that does not scan negative enough to include the deposition/stripping wave of excess Cd. The lower curve shows the current density-time trace for a potentiostatically deposited CdSe film, showing significant electrode passivation. The compositions indicated to the right of each curve were determined by postdeposition electron microprobe analyses.

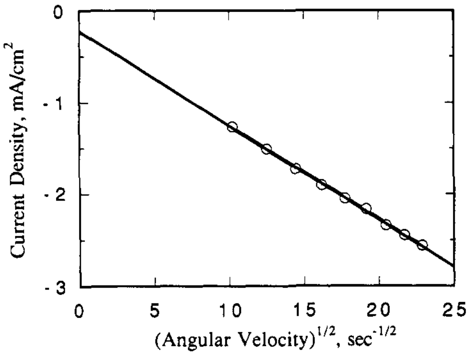

Figure 3. Levich plot for CdSe deposition rate under sequential monolayer deposition conditions. CdSe was deposited onto a Ni RDE (area = 0.20 cm^2). Current densities were determined from plots of net cathodic charge passed versus time.

A Levich plot of the CdSe growth rate under rapid potential scanning conditions is shown in Figure 3. The diffusion coefficient calculated from this data (assuming a $6e^-$ reduction) is (6.1 ± 0.3) × 10^{-6} cm^2/s (average of six Levich plots). These data agree well with the measured diffusion constant of H_2SeO_3, indicating that film growth is controlled by diffusion of H_2SeO_3. In addition, the cathodic current at the Ni RDE scales linearly with H_2SeO_3 concentration (Figure 4), as expected for a mechanism dependent on diffusion of H_2SeO_3 to the substrate. The diffusion coefficient derived from Figure 4 is 7.6 × 10^{-6} cm^2/s. Levich plots with slopes corresponding to smaller

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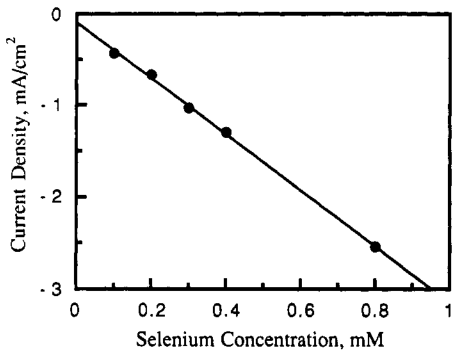

Figure 4. Dependence of the CdSe deposition rate on Se solution concentration. CdSe was deposited onto a Ni RDE (spin rate = 1000 rpm, area = 0.20 cm^2) using the sequential monolayer deposition technique described in the text. Current densities were determined from plots of net cathodic charge passed versus time.

diffusion constants were obtained when the positive scan limit set more positive than ca. −0.3 V vs SCE. Presumably under these conditions the electrode potential is not negative enough to reduce H_2SeO_3 at a constant diffusion-controlled rate, resulting in a slower film deposition rate and smaller "apparent" diffusion coefficients.

All of the Levich data obtained using the rapid potential scanning technique displayed negative intercepts on the current axis, of the order 0.1–0.2 mA/cm^2. This is attributed to solvent reduction occurring at the negative end of the potential scans. Cathodic currents obtained in the absence of added H_2SeO_3 at CdSe-covered Ni electrodes (either in the presence or absence of Cd^{2+}) were also on the order of 0.1–0.2 mA/cm^2 and did not scale appreciably with spin rate, indicative of a solvent background. Background currents observed on CdSe-covered Ni electrodes in the absence of H_2SeO_3 were unstable and tended to increase with time, presumably due to gradual disruption of the CdSe overlayer and exposure of the underlying Ni substrate, which displays a much larger H_2 evolution background under the deposition conditions used in this work. However, in solutions containing Cd^{2+} and between 0.1 and 3 mM H_2SeO_3, cathodic currents were constant and stable for the duration of the deposition experiments. At the H_2SeO_3 concentrations used to deposit CdSe films (typically 0.3 mM), the background current accounts for ca. 10% of the total current. The Coulombic efficiency for the overall process is between 70 and 100%, determined by weighing films peeled from unpolished Ti substrates with tape. The amount of material recovered from polished electrodes is substantially less, corresponding to only 20% of the total charge passed. Presumably this is due to loss of CdSe dendrites that grow on the surface of a much denser film (see below).

Diffusion Coefficient of H_2SeO_3. To ensure that CdSe deposition was restricted to submonolayer amounts per cycle, the diffusion-limited rate of H_2SeO_3 reduction was determined from a Levich plot of rotating disk electrode data. The determination of the H_2SeO_3 diffusion coefficient in 0.5 M H_2SO_4 was hampered by electrode passivation, due to formation of an insulating Se layer.[19] Thus Levich data for H_2SeO_3 reduction were obtained in solutions containing 0.1–0.3 M $CdSO_4$ and low H_2SeO_3 concentrations, for which stable limiting currents could be obtained (Figure 5). Under these conditions, primarily CdSe formed at the working electrode, and for either mechanism represented by eqs 1 or 4, the limiting current represents diffusion-limited 6e$^-$ reduction of a Se species at the RDE. The Levich plot for this system is given in Figure 6. The diffusion coefficient calculated from three separate experiments is (7 ± 1) × 10^{-6} cm^2/s.

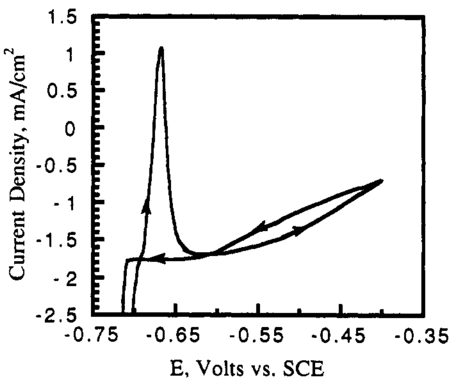

Figure 5. Current–voltage trace (slow scan) obtained on a Ni rotating disk electrode (spinning at 2000 rpm) in a solution containing 0.4 mM H_2SeO_3, 0.3 M $CdSO_4$, and 0.25 M H_2SO_4. Potential was scanned at 2 mV/s. Voltage scale is referenced to SCE.

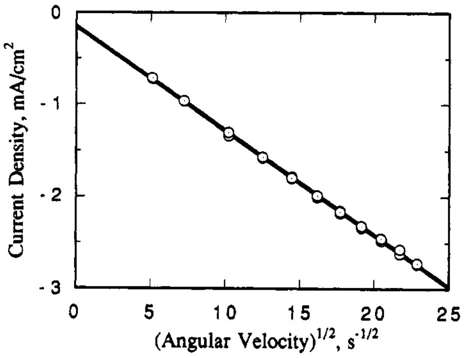

Figure 6. Levich plot of H_2SeO_3 reduction used to determine H_2SeO_3 diffusion coefficient. Experiment performed at a Ni RDE in 0.4 mM H_2SeO_3, 0.3 M $CdSO_4$, and 0.25 M H_2SO_4. Potential was held at −0.63 V vs. SCE. Temperature was 21 ± 1 °C.

Film Morphology. The sequential deposition of CdSe onto polished electrodes produces shiny films that adhere well to Ni but are readily removed from Ti substrates. Scanning electron microscopy reveals that the films consist of scattered 0.5–1-μm nodules uniformly covering a smooth dense film (Figure 7). The underlying film appears to be made up of tightly packed 100-nm-size beads, and cross-sectional SEM measurements indicate that this dense film corresponds to 20% of the cathodic charge passed (thickness of a 0.6 cm^2 film after −4.22 C was 900 ± 100 nm). Deposition onto unpolished electrodes produces qualitatively similar films that adhere better to Ti and contain a higher density of the overlying nodules. Accordingly, the films on unpolished substrates are matte black in appearance. Qualitative X-ray analysis (EDS) of all samples indicates the presence of Cd and Se in both the nodules and the underlying layer. CdSe films deposited in conventional potentiostatted experiments typically display a heterogeneous "cauliflower" morphology,[6,7,10,24] although electrodeposited materials more similar in appearance to those of the present study have also been previously observed.[3,7,10,11,15] Thus the morphology of the films produced in the present study does not differ significantly from earlier work.

Film Composition and Structure. Electron microprobe analyses confirmed the Cd:Se ratio in the films to be close to 1:1, within the error limits of the measurement. For films deposited from $CdCl_2$-containing solutions, the Cd:Se ratio was 1.02 ± 0.06 (95% confidence interval based on three measurements each on four samples), and for films deposited from $CdSO_4$ baths, Cd:Se was 1.03 ± 0.1 (for three measurements each on three samples). The Kα line from the underlying Ti substrate was also observed

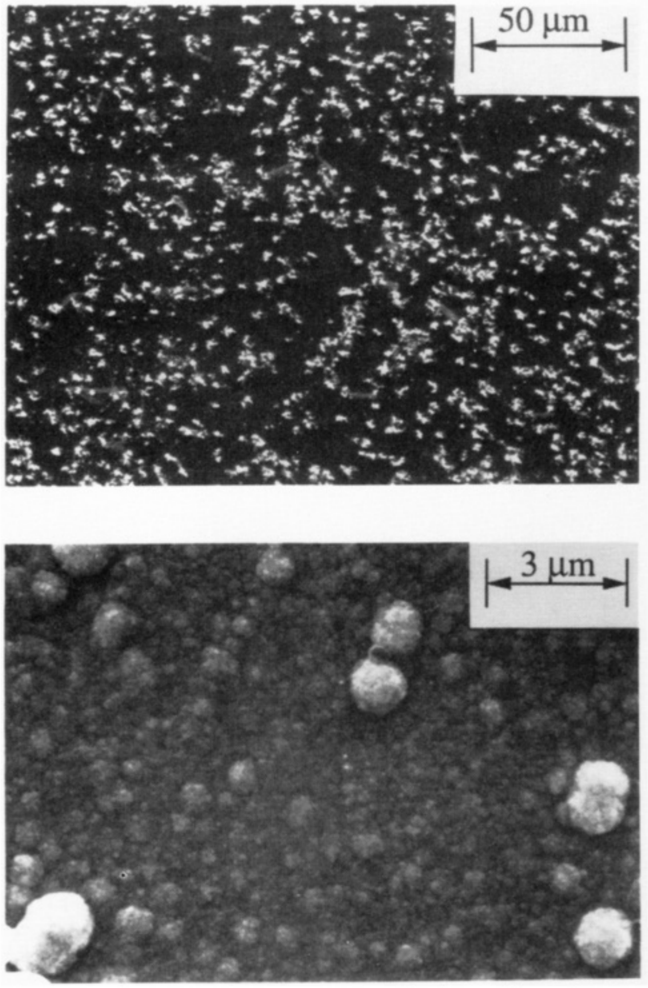

Figure 7. Scanning electron micrographs (secondary electron images, 20 keV) of (top) ca. 100-nm-thick CdSe film electrodeposited with a fast cyclic scan (10 V s^{-1}) on a polished Ni RDE (spin rate = 1000 rpm); (bottom) close-up view of the dense film underlying the dendritic features.

Table I. *d* Spacings from X-ray Powder Diffraction Data for Electrodeposited CdSe[a]

annealed sample	cadmoselite (wurtzite)[b]	as-deposited sample	CdSe (zincblende)[b]	Ti metal[b]
		4.62 (4)		
3.72 (100)	3.72 (100)	3.67 (31)		
3.50 (50)	3.51 (70)	3.49 (100)	3.51 (100)	
3.29 (64)	3.29 (75)	3.26 (16)		
2.55 (24)	2.554 (35)			2.557 (30)
2.34 (38)		2.34 (37)		2.342 (26)
2.24 (28)		2.24 (28)		2.244 (100)
2.14 (54)	2.151 (85)	2.13 (29)	2.149 (55)	
1.975 (47)	1.98 (70)	1.988 (7)		
1.947 (1)		1.963 (9)		
1.861 (8)	1.863 (12)	1.857 (9)		
1.830 (35)	1.834 (50)	1.823 (16)	1.833 (25)	
1.796 (7)	1.8 (12)			
1.726 (8)		1.726 (12)		1.726 (19)
1.643 (4)	1.645 (8)			
1.474 (1)				1.475 (17)
1.454 (11)	1.456 (20)			
1.403 (4)	1.407 (8)			

[a] Numbers in parentheses are relative intensities. Error in *d* spacings reported is ±5 in the last digit. [b] Data from JCPDS powder diffraction file.[27]

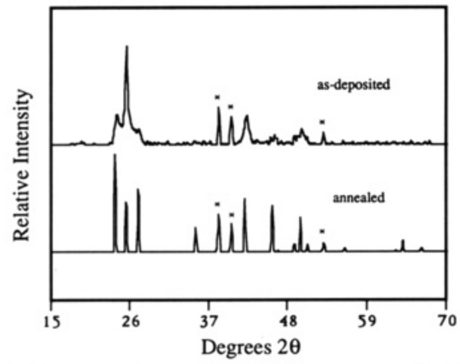

Figure 8. X-ray powder patterns of an as-deposited CdSe film (top) and a CdSe film that was annealed at 650 °C under an Ar atmosphere for 15 min (bottom). Both films were deposited via cyclic electrodeposition within the potential window 0.0 to −0.90 V vs SCE at a scan rate of 10 V/s. Film thicknesses are approximately 0.5 µm. The *d* spacing and relative intensity data are listed in Table I. Peaks from the Ti substrate are marked with an asterisk.

in the analyses, being more pronounced for the thinner samples. In the samples synthesized from Cl^--containing solutions, around 3–4 wt % of Cl was detected as the only major impurity. Such low levels of Cl have previously been observed in CdTe films electrodeposited from chloride ion-containing solutions.[15] For the CdSe films deposited from SO_4^{2-}-containing solutions, small (0.04–0.8 wt %) amounts of S were detected as the only impurity. Microanalysis results from three different spots on each sample typically did not deviate by more than 5% from each other, with the rougher samples showing the largest deviations. This is in line with the qualitative EDS measurements and indicates that these materials are compositionally homogeneous within the error limits of the measurement. Traditionally electrodeposited films generally show marked variations in composition within a sample.[11,15,24]

X-ray powder diffraction data were collected on annealed and as-deposited samples and are presented in Table I and Figure 8. As previously observed for electrodeposited CdSe, the as-deposited films display broad peaks associated with the cubic zincblende structure of CdSe.[8,18] The broadness of the X-ray lines observed in the as-deposited films is attributed to the small crystallite size. Peaks assignable to the hexagonal wurtzite structure of CdSe are also observed in the diffraction patterns, indicating the presence of this phase as well. Trace amounts of the hexagonal phase have been previously observed in electrochemically deposited CdSe films.[8] On annealing at 650 °C, films of the sequentially electrodeposited CdSe display sharp diffraction patterns corresponding to the hexagonal wurtzite structure. The annealing process apparently results in complete conversion to the wurtzite form along with a significant increase in crystallite size, consistent with prior results on conventionally electrodeposited (potentiostatic or galvanostatic) CdSe films.[8,18] The X-ray data confirm that the compound deposited in the cyclic electrodeposition process is CdSe.

Optical Properties. An optical absorption spectrum of an as-deposited CdSe film is shown in Figure 9. The film was prepared on a Ti substrate and removed with Scotch tape. A plot of (absorbance × energy)^2 vs photon energy (inset of Figure 9) yields an intercept of 1.6 eV for the bandgap of this material, based on the assumption that it is a direct gap semiconductor.[25] The value is comparable to that previously observed for electrodeposited CdSe.[18,26] The break in the absorption spectrum characteristic of the

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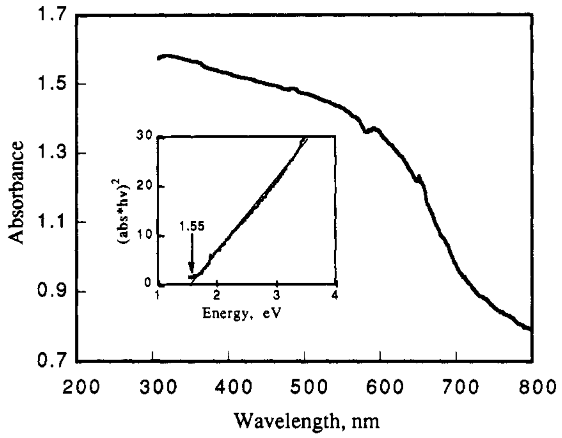

Figure 9. Absorption spectrum of CdSe film as deposited on Ti and removed with Scotch tape. The inset shows a plot of (absorbance × $h\nu$)^2 vs $h\nu$ for the same sample.

band edge was not as obvious in all films analyzed, indicating that the electronic properties of this material vary somewhat from sample to sample. Presumably this arises from the very fine grain structure in these films. Deviations from the expected bulk properties of CdSe films have previously been attributed to quantum confinement effects arising from the very small crystallite size obtained with electrodeposited films.[14,17,18] Hot-probe measurement of the as-deposited CdSe films indicated that the material in n-type.

Conclusions

The cyclic electrodeposition technique used in the present study produces homogeneous films of CdSe that are close to 1:1 atomic ratio of Cd to Se. The scan parameters are designed to lay down sequential monolayers of CdSe in order to avoid the accumulation of excess Se in the material. For the purpose of producing stoichiometric semiconductor films, this is an improvement over previous potentiostatic or galvanostatic electrochemical techniques, which tend to produce films containing excess Se. The key feature in this process appears to be the continuous deposition and stripping of excess Cd, which is proposed to react with any excess Se that may deposit. The material produced by sequential monolayer electrodeposition contains 3–4% by weight Cl as the major impurity when $CdCl_2$ is used as the Cd source. The films produced using the present technique consist of a dense layer underneath scattered dendrites, similar to CdSe films electrodeposited by other routes. In addition, the optical properties of these films are similar to those of previously studied films. Thus, although the present technique provides an improvement in the stoichiometry of electrodeposited films, in other respects the films do not significantly differ from those made by previous routes. Current work is directed at elucidating the mechanism of CdSe growth, characterizing the electronic properties of these films, and extending the procedure to other semiconductor systems.

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Registry No. CdSe, 1306-24-7; Ti, 7440-32-6; Ni, 7440-02-0; $CdCl_2$, 10108-64-2; $CdSO_4$, 10124-36-4; SeO_2, 7446-08-4; H_2SeO_3, 7783-00-8.

Redox Photochromism in Films of Viologens and Related Compounds Bearing Long-Chain Alkyl Groups

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1,1′-Bis(benzyl or *p*-methylbenzyl)-4,4′-bipyridinium and *trans*-4,4′-vinylenebis(1-benzylpyridinium) bis-(*p*-alkylbenzenesulfonate)s bearing long-chain alkyl groups (viologen Ia,b), prepared from their respective dichlorides by the anion-exchange reaction, were sandwiched between two glass plates by melting to afford thin transparent and mainly isotropic films. These almost colorless or pale yellow films developed intense visible colors by near-UV irradiation, which bleached upon heating (photochromism). This behavior is considered to be due to reversible redox reactions consisting of the one-electron transfer to viologen Ia,b dication from the counteranion by the photon mode (color development) and vice versa by the heat mode (bleaching).

Introduction

It has been widely known that some 1,1′-disubstituted bipyridinium, i.e., viologens, and related salts reversibly develop intense colors with visible lifetimes when exposed to radiation of the solar level in solutions in the presence of reductants,[1] in activating matrix polymer films,[2] and in the crystalline state.[3]

We report here reversible photoreductions accompanied by visible color developments (photochromism), which have been found for thin isotropic films made of the viologens bearing long-chain alkyl groups without any

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