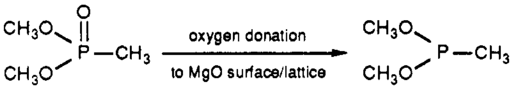
Table III. DMMP Decomposition (atom percent) over $Mg^{18}O$: Labeled Formic Acid Formed

	$Mg^{18}O(130)$		$Mg^{18}O(390)$	
sample	$HCOOH^a$	$HCO^{18}OH^a$	$HCOOH^a$	$HCO^{18}OH^a$
on $Mg^{18}O$ sample saturated at 500 °C	66	34	33	67
on $Mg^{18}O$ sample saturated at 700 °C	63	37	34	66

[a] Decomposition products.

MgO,[1-3] we have shown that formic acid is a major product of the destructive adsorption of $(CH_3O)_2P(O)CH_3$(DMMP) on MgO. A question arises as to where the oxygen comes from in order to oxidize adsorbed OCH_3 groups to formic acid.

At 500 and 700 °C the $Mg^{18}O(130)$ and $Mg^{18}O(390)$ were pulsed with 1-μL portions of DMMP, and the formic acid released was monitored by GC-MS. The formic acid was found to be partly labeled with ^{18}O (Table III). The ^{18}O label could only have come from the $Mg^{18}O$, since no $H_2{}^{18}O$ was added to the DMMP pulses. Therefore, large portions of surface/lattice ^{18}O were taken up to form formic acid. This oxygen was replaced, we believe, by oxygen donation from other molecules of DMMP, probably as follows:



$$(CH_3O)_2P(O)CH_3 \xrightarrow[\text{to MgO surface/lattice}]{\text{oxygen donation}} (CH_3O)_2P{-}CH_3$$

In general, our experiments suggest that surface/lattice oxide is likely to be involved in a wide variety of adsorption/decomposition processes.

Acknowledgment. The support of the Army Research Office is acknowledged with gratitude.

Registry No. DMMP, 756-79-6; HO, 7732-18-5; MgO, 1309-48-4; CaO, 1305-78-8; Fe_2O_3, 1309-37-1.

Preparation and Characterization of $Cd_{1-x}Hg_xSe$ Thin Films

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Received November 7, 1991. Revised Manuscript Received January 3, 1992

Thin-film $Cd_{1-x}Hg_xSe$ was deposited on indium/tin oxide coated glass (ITO) by electrochemical reduction of an aqueous solution containing Cd^{2+}, Hg^{2+}, and $SeSO_3{}^{2-}$. Deposition potential and Hg^{2+} concentration in the deposition solution affected the composition of the film. Proton-induced X-ray emission showed that x could be varied from 0.074 to 0.45 by adjusting the deposition potential. The Hg composition could also be altered by varying the Hg^{2+} concentration in the solution. The effect of composition on the bandgap of the film was determined by optical absorption spectra and was found to decrease as the Hg content increased. Annealing at 320 °C caused the bandgap to shift to higher energy; at this maximum temperature significant loss of Hg was observed. X-ray diffraction confirmed that the crystallite size increased significantly upon annealing the film, and scanning electron microscopy showed that these films were free of cracks and pinholes.

Introduction

CdSe is an n-type semiconductor with the minimum bandgap energy about 1.7 eV, which is suitable for solar cell applications.[1] HgSe alloy is a semimetal with the minimum bandgap energy that is essentially zero.[2] Consequently, the minimum bandgap energy of the $Cd_{1-x}Hg_xSe$ (CMS), in principle, can be varied between 0 and 1.7 eV by varing the Cd:Hg ratio.[3] This flexibility provides the possibility for various practical applications ranging from infrared detection to solar energy conversion. For solar cell applications the optimum bandgap energy is in the range 1.0–1.6 eV,[4] which can be achieved by adjusting the composition of CMS.

A few methods have been reported for preparing CMS. Single crystals of CMS were grown by the Bridgman method.[5] Recently, thin-film CMS has been grown epitaxially on CdSe substrates.[6] Nelson et al.[2] studied the electron mobility of the single-crystal compounds with the mole fraction of Hg ranging from 0.88 to 0.32 in the temperature range 4.2–300 K. They determined that the CMS semiconductor was n-type and that the electronic conduction was dominated by intrinsic and defect scattering mechanisms.

The present report describes an electrochemical reduction method for making CMS semiconducting thin films. The approach is similar to the one used in our laboratory to make polycrystalline thin-film CdSe.[7] One of the goals of this work was to ascertain if solution composition and/or deposition potential could be employed to control the Hg content in the CMS film and also determine if the film was a uniform alloy or a composite of CdSe and HgSe crystals. Another goal was to determine the effect of annealing temperature on the composition and bandgap of the film. In addition we wished to explore the effect of heat treatment on crystal structure and surface morphology of the film and obtain some preliminary information about the conductivity of this material.

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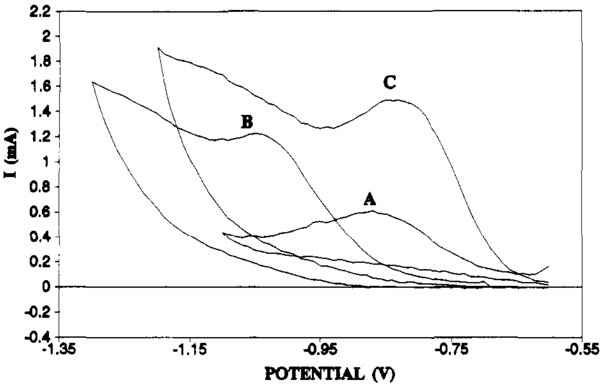

Figure 1. CVs of three deposition solutions for the preparation of (a) HgSe, (b) CdSe, and (c) $Cd_{1-x}Hg_xSe$. The substrate used was ITO-coated glass having approximately the same area. The scanning rate was 100 mV/s, and the forward scan was initiated at –0.6 V with the reduction wave occurring on the first half of the cycle.

Experimental Section

Solution. The Se powder (Aldrich) was first dissolved in a solution containing 0.62 M $(NH_4)_2SO_3$ and 0.13 M Na_2SO_3 to make a 0.042 M $SeSO_3^{2-}$ solution using millipore water with pH between 9 and 10. To this solution were added 0.040 M $CdCl_2$ (Fischer) and 0.045 M sodium ethylenediaminetetraacetate (NaEDTA, Aldrich) and mercuric acetate (Aldrich) whose concentration was varied from 0 to 0.75 mM. In place of sodium nitriloacetate used in the CdSe study, EDTA was used to make a more stable complex with Hg^{2+} and slow down its chemical reaction with $SeSO_3^{2-}$ to form HgSe. Under these conditions the solution was stable for 1 or 2 days so long as the Hg concentration remained less than 1 mM.

Electrodeposition. Depositions were carried out potentiostatically at the cathode in a three-electrode cell containing a carbon anode and a calomel reference electrode. The cathode was glass coated with a thin layer of tin-doped indium oxide (Donnelly Corp., Holland, MI). Prior to electrodeposition, ITO was cleaned ultrasonically in a solution of 5% Extran (BDH) and then rinsed with water and isopropyl alcohol before drying. Electrodeposition of CMS was performed in air at room temperature using potentials ranging from –0.78 to –1.05 V. The resultant films were annealed in a Lindberg tube furnace at temperatures upto 320 °C.

Chemical and Physical Characterization. Chemical composition was analyzed by proton-induced X-ray emission (PIXE) using a Van de Graaff accelerator that provided a 0.75-MeV proton beam having a 0.4 × 0.4 mm spot size. The PIXE data were analyzed using standard computer software developed by Campbell and provided information about the relative quantities of each element in the films.[8] Samples were annealed according to the following procedure: the temperature was increased at the rate of 5 °C/min and then kept at the desired temperature for 20 min, whereupon it was cooled at a rate of 1 °C/min. This slow cooling rate was used to avoid possible cracks in the film after heat treatment.

Structural analysis of as-deposited and annealed CMS films was carried out on a Rigaku Geigerflex D/Max II X-ray diffraction system using a cobalt $K\alpha_1$ radiation source (λ = 1.7889 Å). Data were collected over a 10-s count time for 2θ from 27° to 55° with a step width of 0.02°. Optical absorption experiments were made with a Shimadzu Model UV160U spectrometer. Spectra were recorded between 200 and 1100 nm with the film on the ITO substrate and an uncoated piece of ITO in the reference beam. For the conductivity measurement, a CMS film was peeled from ITO using Torr Seal epoxy, and ohmic contacts to the film were made with colloidal graphite isopropyl alcohol based paint. The home-built conductivity apparatus has been described previously.[9] Surface morphology of the film before and after heat treatment was determined using a Hitachi S-570 scanning electron microscope operating with an accelerating voltage of 10 kV.

Table I. Mercury Content in the CMS Film Relative to the Electrodeposition Conditions

$[Hg^{2+}]$,[a] mM	potential,[b] V	film no.[c]	x[d]
0.23	–1.05	1	0.076
0.50	–1.05	1	0.145
		4	0.117
		7	0.098
		9	0.074
0.50	–0.95	1	0.145
	–0.87	1	0.267
	–0.78	1	0.456
0.75	–1.05	1	0.162

[a] For concentrations of other species, see the Experimental Section. [b] Relative to calomel reference electrode. [c] Position of the film in a sequence of films deposited from a given solution. [d] Mercury content in the film.

Results and Discussion

Cyclic Voltammetry. Figure 1 illustrates cyclic voltammograms (CV) at a scanning rate of 100 mV/s for three solutions containing the following active components: (a) Hg^{2+} and $SeSO_3^{2-}$; (b) Cd^{2+} and $SeSO_3^{2-}$; (c) Cd^{2+}, Hg^{2+}, and $SeSO_3^{2-}$. These CVs were recorded after the fifth scan to allow a uniform film to coat the electrode and, therefore, pertain to electrochemical reduction at coated rather than uncoated ITO. The lack of an anodic wave on the positive scan indicated that the film was not oxidized in the potential range employed. Solutions (a) and (b) each exhibited one reduction peak at –0.87 and –1.02 V, respectively, and the CV of solution (c) appeared to be a superposition of these two waves with the first wave at a slightly more positive value of –0.82 V due to overlap with the second wave. Reduction of solution (b) gave CdSe and involves the reduction of $SeSO_3^{2-}$ at –1.05 V with a subsequent reaction of Se^{2-} with Cd^{2+} to form CdSe.[10] The reduction of solution (a) gave HgSe and is indicative of reduction of Hg^{2+} at –0.87 V and subsequent reaction with $SeSO_3^{2-}$ to form HgSe; however, a detailed kinetic study will be required to confirm this tentative description. At any rate it is clear that reduction of solution (c) will result in a film that is rich in Hg unless the rate of reduction of Hg^{2+} is made slower than that of $SeSO_3^{2-}$. This was accomplished for the film preparation described below by keeping the concentration of Hg^{2+} low relative to the other ions.

Composition. As the Hg^{2+} concentration in the deposition solution was increased the mercury content of the film increased. Thus for 0.23, 0.50, and 0.75 mM mercuric acetate, x was 0.076, 0.145, and 0.162, respectively, for a deposition potential of –1.05 V (Table I). Because of the low concentration of Hg^{2+} in the solution, the mercury content was monitored in each of a series of 11 CMS films grown from the same solution to determine the effect of depletion of Hg^{2+} from the solution. The electrodeposition conditions were 0.5 mM mercuric acetate and a potential of –1.05 V (vs calomel) with the concentrations of the other species given in the Experimental Section. The deposition time of 1 h resulted in films that were about 2 μm thick. Table I illustrates the gradual decrease in the mercury content over the sequence of nine films in the series. Analysis of all 11 films was not possible due to heavy demand for the PIXE apparatus. Nevertheless these four films are more than sufficient to illustrate the gradual decrease in mercury as the film number increased. The

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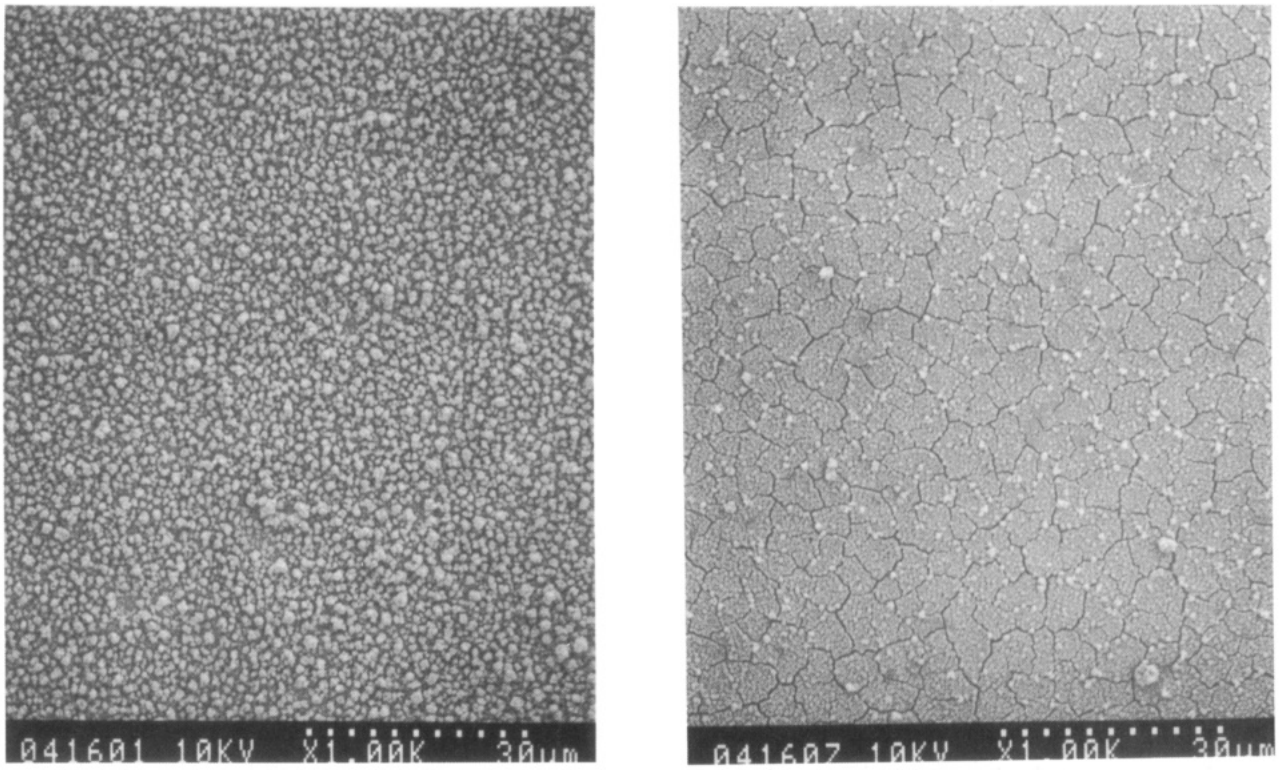

<A> <B>

Figure 2. SEM of two $Cd_{1-x}Hg_xSe$ films annealed at 200 °C after deposition from the same solution at the following potentials: (A) −0.95 V; (B) −1.05 V.

PIXE error is 5% of the measured value for each element. This error is a statistical one based on cross sections and X-ray yields for each element. A data base, which has been obtained experimentally, is available for a large number of elements. Measurements were made at different spots on each film. Consequently, the difference in composition between the first and the fourth films was slightly greater than experimental error. By the ninth film the trend toward lower mercury content seems clear. In contrast a sequence of CdSe films grown from the same solution showed very little variation in composition. For $Cd_{1-x}Hg_xSe$ it will be necessary to maintain a nearly constant Hg^{2+} concentration either by periodic addition of more mercuric acetate or by use of a mercury pool anode in combination with the carbon one.

A series of four films were prepared at different potentials ranging from −0.78 to −1.05 V (Table I). Each film was prepared using a fresh solution containing 0.50 mM Hg^{2+} with the concentrations of the other species the same as described above. The results are consistent with the CV data (Figure 1). Thus, the more positive reduction potentials promote a higher Hg content. The relatively small change in Hg content for the change in potential from −0.95 to −1.05 V probably indicates that reduction of $SeSO_3^{2-}$ is approaching the diffusion control limit around −1.05 V, in agreement with the CV data. Consequently, control of the Hg content in CMS is possible by choice of either potential and/or solution composition. However, the most negative potential will be limited by the tendency of the film to crack at higher deposition currents (Figure 2b). Thus, good adhesion was obtained so long as the potential was −0.95 V or more positive for the solution compositions employed.

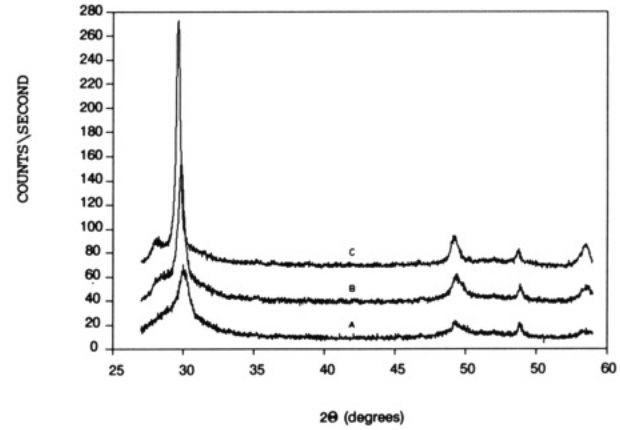

Figure 3. X-ray diffraction profiles of $Cd_{1-x}Hg_xSe$ films annealed at the following tempertures: (A) as-deposited; (B) 200 °C; (C) 320 °C. The deposition occurred at a potential of −870 mV from a solution containing 0.50 mM mercuric acetate. The concentrations of the other species are given in the Experimental Section.

Heat Treatment. The composition of the film was not affected by heat treatment provided the annealing temperature did not exceed 200 °C. Thus the Hg content (x) of a film was 0.27, 0.26, and 0.16 for the as-deposited film, one annealed to 200 °C, and another at 320 °C, respectively, indicating that a 200 °C treatment did not cause loss of Hg. Although these three films were deposited consecutively, the study presented in the previous section indicated that their as-deposited compositions should exhibit little difference.

The X-ray diffraction data presented in Figure 3 indicate that the crystalline structure of the films was altered after heat treatment. Although the X-ray data were obtained for CMS films on ITO, Figure 3 illustrates only the lines due to CMS for clarity. In ascending order the three plots are due the as-deposited film and films annealed at 200 and 320 °C for 20 min, respectively. Diffraction peaks

Table II. Powder X-ray Data for CdSe and Data for CMS Films Annealed at Various Temperatures in Air

CMS thin films								
as deposited		200 °C		320 °C		CdSe[a]		
d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*hkl*
		3.68	20	3.70	10	3.72	100	100
3.46	100	3.48	100	3.51	100	3.51	70	002
						3.29	75	101
						2.55	35	102
2.15	22	2.14	19	2.15	12	2.15	85	110
1.98	18	1.98	12	1.98	6	1.98	70	103
						1.86	12	200
1.83	12	1.83	11	1.83	8	1.83	50	112
						1.80	12	201
						1.46	20	203
						1.31	14	105
						1.25	10	300

[a] Reference 11.

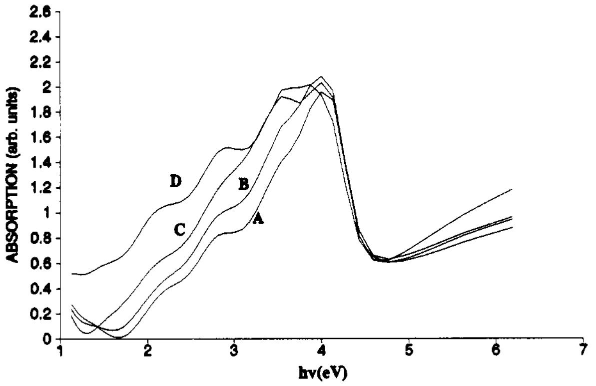

Figure 4. Optical absorption spectra of CdHgSe films deposited at −1.05 V from solutions containing the concentrations given in the Experimental Section plus the following Hg^{2+} concentrations: (A) 0.0 ; (B) 0.25; (C) 0.50; (D) 0.75 mM.

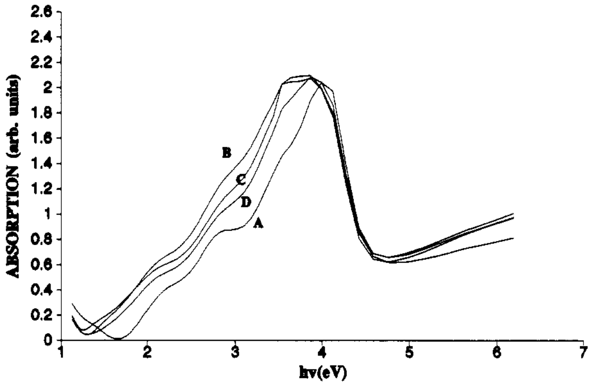

Figure 5. Optical absorption spectra of CdSe and Cd$_{1-x}$Hg$_x$Se films deposited at −0.87 V and annealed at the following temperatures: (A) as-deposited (0.0 mM Hg); (B) as-deposited (0.50 mM mercuric acetate); (C) 200 °C; (D) 320 °C.

corresponding to the as deposited film are broad and those corresponding to the film annealed at 320 °C are sharp while those to the film annealed at 200 °C are in between. Thus the crystallite size increased as annealing temperature increased. The (100) peak at the lowest diffraction angle become observable after the film was annealed at 200 °C and became more prominant after annealing at 320 °C. The position of the (002) peak at the second lowest diffraction angle shifted slightly toward lower angle as the annealing temperature increased.

The basic crystal structure of CMS is very similar to that of CdSe since the observed peak positions were very close to those reported for CdSe.[10] In Table II the data for CMS are compared with those of CdSe. The crystal structure of HgSe shows X-ray diffraction peaks[11] that are close to those of CdSe solid. Hence the X-ray data cannot be used to determine if the CMS film is either a true alloy or a mixture of HgSe and CdSe crystals. On the other hand, the shift in bandgap with composition provides evidence for alloy formation.

Figure 4 shows the results of optical absorption measurements. For comparison, the absorption spectra of four as-deposited films are presented. The films were grown at −1.05 V (vs calomel) from four solutions that had mercuric acetate concentrations of 0, 0.23, 0.50, and 0.75 mM. On the basis of the data in Table I, the Hg content (x) of these films was 0, 0.076, 0.145, and 0.162, respectively. The absorption curve shifted correspondingly as th Hg content increased, and the calculated bandgap decreased from 1.7 to 1.3 eV as the Hg content increased from zero to 0.162. Using the data in Figures 4 and 5, a plot of $(\alpha h\nu)^2$ as a function of $h\nu$ resulted in a straight line, indicating a direct electronic transition,[12] and the intercept provided the bandgap E_g. A direct comparison of single-crystal data is not possible; however, a value of 1.25 eV is obtained for $1 - x = 0.84$ by linear extrapolation of data for single-crystal CMS alloy having $0.3 < 1 - x < 0.69$.[13] This value agrees very well with 1.3 eV obtained for thin film CMS in the present study. These results support the conclusion that CMS is a uniform mixture of cadmium, mercury, and selenide ions, and demonstrates that the bandgap can be controlled by the Hg content in the film. Absorption in the lower energy region distinctively increased as the Hg concentration increase. The onset of absorption below the bandgap is probably due to transitions from subband gap states.

The effect of annealing temperature on the optical absorption spectrum is illustrated in Figure 5. For comparison the spectrum of as-deposited CdSe and the one for as-deposited CMS are presented also. The CMS film was grown at −0.87 V from a solution containing 0.50 mM mercuric acetate. As can be seen, the absorption edge for as-deposited CMS and the film annealed at 200 °C is very nearly the same. On the other hand, the absorption edge of the film annealed at 320 °C has moved back toward higher energy. This increase in bandgap is consistent with the loss of Hg from the film upon annealing at 320 °C as

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(11) *X-ray Powder Data File*; ASTM Special Technical Publication 48-j, card no. 8-459; American Society for Testing and Materials: Philadelphia, 1960.

(12) Dwight, K.; Wold, A. In *Photoeffects at Semiconductor–Electrolyte Interfaces*, Nozik, A. J., Ed.; American Chemical Society: Washington DC, 1981; p 210.

(13) Summers, C. J.; Broerman, J. G. *Phys. Rev. B* **1980**, *21*, 559.

described above.

Heat treatment at 200 °C did not cause any cracks or pinholes in the film provided the film was deposited at −0.95 V or a more positive voltage. Figure 2 illustrates the SEM of two CMS films annealed at 200 °C in air for about 20 min. The SEM of the film grown at −0.95 V (Figure 2A) shows no cracks or pinholes, whereas the one grown at −1.05 V (Figure 2B) exhibits a number of fine cracks. Most likely these cracks developed because the more negative potential resulted in a deposition rate (current) that was sufficiently high to cause occlusion of solvent and other impurities. The deposition time for these films was about 1 h, with the area typically 1.5 cm^2, and film thickness was estimated to be about 2 μm.

A CMS film deposited at −0.87 V from a solution containing 0.50 mM mercuric acetate and annealed at 200 °C in air for 20 min had a measured room-temperature resistivity of 4×10^6 Ω cm. This value is close to that obtained for CdSe thin films prepared under similar conditions.[14] Consequently incorporation of Hg into CdSe by this technique does not appear to cause a decrease in resistivity of the film. Nevertheless the decrease in bandgap of CMS films relative to CdSe indicates that a more detailed study of their electrical and photophysical properties is warranted.

Summary

Thin-film $Cd_{1-x}Hg_xSe$ was prepared by an electrochemical reduction method similar to that used to prepare CdSe. Because of the more positive reduction potential of Hg^{2+}, the Hg content of the film was controlled by using millimolar concentrations of mercuric acetate and substantially larger concentrations of Cd^{2+} and $SeSO_3^{2-}$ ions. Furthermore, the Hg content of the film could be controlled by adjusting the applied potential. A more negative potential resulted in lower Hg content provide the Hg^{2+} concentration was kept low. Annealing the film increased the crystallite size without affecting composition provided the temprature did not exceed 200 °C. This temperature did not have an appreciable effect on the bandgap of the film, which was close to that of the as-deposited film. Annealing at 320 °C caused the bandgap to shift to higher energy, and this shift is consistent with the substantial loss of Hg from the film found by PIXE measurements. The bandgap of the as-deposited film was found to decrease as the Hg content of the film increased. Consequently, this procedure shows promise for providing variable-bandgap materials that may be useful for a variety of applications. The resistivity of CMS is comparable to that of CdSe, and additional studies of techniques to control this and other properties are planned.

Acknowledgment. This work was supported in part by a grant to M.C. from the Natural Science and Engineering Research Council of Canada. We are indebted to Sandy Smith for her SEM instruction, to Bill Teesdale for PIXE analyses, and to Glen Wilson for X-ray diffraction analyses. Thanks to Professor Robert J. Balahura for the generous use of his spectrophotometer and to Henry Wynands and Christa L. Colyer for helpful discussions.

Registry No. $Cd_{0.92}Hg_{0.08}Se$, 141017-14-3; $Cd_{0.86}Hg_{0.14}Se$, 114823-95-9; $Cd_{0.88}Hg_{0.12}Se$, 141017-15-4; $Cd_{0.9}Hg_{0.1}Se$, 107372-10-1; $Cd_{0.93}Hg_{0.07}Se$, 141017-16-5; $Cd_{0.86}Hg_{0.14}Se$, 114823-95-9; $Cd_{0,73}Hg_{0,27}Se$, 141017-17-6; $Cd_{0.54}Hg_{0.46}Se$, 141017-18-7; $Cd_{0.84}Hg_{0.16}Se$, 141017-19-8; $Cd_{0.54-0.93}Hg_{0.07-0.46}Se$, 141017-20-1; $SeSO_3^{2-}$, 16450-48-9; Sn, 7440-31-5; Se, 7782-49-2; $(NH_4)_2SO_3$, 10196-04-0; Na_2SO_3, 7757-83-7; NaEDTA, 64-02-8; indium oxide, 1312-43-2.

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