mmol) of *N,N*-dimethylethylenediamine were used instead. Orange yellowish needles (0.15 g, 75%) resulted after etheral workup.

2((CH$_2$)$_2$N$^+$(Me)$_3$). The procedure for preparing 2(Py$^+$Me) was followed except that 20.9 mg (0.078 mmol) of ((CH$_2$)$_2$N(CH$_3$)$_2$) and 67 μL (0.78 mmol) of dimethyl sulfate were used. A pale white precipitate (52 mg, 80%) was collected. IR (KBr) 3080, 2949, 2820, 2770, 1702, 1657, 1582, 1455, 1350, 1245, 1160 cm^{-1}. ^{1}H NMR (D$_2$O) 8.73 (4 H, s), 4.64 (4 H, t, J = 7.7), 3.67 (10 H, m), 3.29 ppm (18 H, br s). FAB MS (MNBA matrix) calculated for $C_{24}H_{30}N_4O_4$ 438.2260, observed (M$^+$) 438.2257. HPLC retention time 3.53 min; flow rate 0.5 mL/min.

2((CH$_2$)$_3$N(CH$_3$)$_2$). The procedure for 2(Py) was used except that 0.101 g (0.38 mmol) of anhydride and 142 μL (1.13 mmol) of *N,N*-dimethylpropylenediamine were used instead. A bright yellowish powder (0.09 g, 54%) was isolated after workup.

2((CH$_2$)$_3$N$^+$(Me)$_3$). The procedure for preparing 2(Py$^+$CH$_3$) was followed except that 48.7 mg (0.1 mmol) of 2(CH$_2$)$_3$-N(CH$_3$)$_2$ and 106 μL (1.1 mmol) of dimethyl sulfate were used. A pale white precipitate (48 mg, 70%) was collected. IR (KBr) 2975, 2944, 2814, 2779, 2759, 1698, 1653, 1454, 1345, 1254, 1242, 1041 cm^{-1}. ^{1}H NMR (D$_2$O) 8.63 (4 H, s), 4.23 (4 H, t, J = 7.7), 3.68 (6 H, m), 3.51 (4 H, t, J = 7.7), 3.12 (18 H, br s), 2.26 (4 H, m). FAB MS (MNBA matrix) calculated for $C_{26}H_{34}N_4O_4$ 466.2572, observed (M$^+$) 466.2591. HPLC retention time 3.58 min; flow rate 0.5 mL/min.

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Thin-Film Indium Selenide Prepared by Reaction of Selenium Vapor with Indium Oxide

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A new process involving two steps has been developed to prepare thin-film In_2Se_3. The first step is formation of indium oxide by spray pyrolysis of an aqueous solution of indium nitrate, and the second is reaction of this oxide with selenium vapor in nitrogen at atmospheric pressure to form In_2Se_3. Shorter exposure time was needed for complete conversion as the temperature was increased from 400 to 500 °C. Auger depth profiling of the composition of a partially converted film indicated that the conversion process appears to involve three steps: (a) reaction between selenium vapor and the oxide at the surface; (b) subsequent diffusion of selenium into the film until much of the oxide was converted to InSe; (c) further reaction involving selenium vapor and InSe to form In_2Se_3. It was possible to convert In_2Se_3 into InSe by reacting it with indium vapor, and it was also possible to incorporate cadmium. p-type In_2Se_3 and n-type InSe were prepared by this relatively inexpensive process. Resistance and Hall effect measurements gave a variety of resistivity and carrier density values, depending on the preparation conditions. X-ray diffraction indicated that the In_2Se_3 film may consist of several crystalline phases, and optical absorption spectra indicated a direct bandgap of 1.84 eV. A direct bandgap of 3.64 eV was found for In_2O_3, which was n-type and had a very low resistivity and high electron density.

Introduction

There has been a recent interest in the growth of thin films of In_2Se_3 for a variety of applications.[1-3] The complex hexagonal layered structure of this material makes it possible for ions to diffuse in and alter the physical properties without changing the structure.[4,5] This behavior permits the use of this material as a cathode in microbatteries and as solid solution electrodes in microcapacitors.[6] The bandgap and other properties of this material also make it attractive for solar energy conversion.[7-11] Various methods have been used to prepare thin-film indium selenide including elemental evaporation,[12,13] molecular beam epitaxial growth,[14] electrodeposition,[15] and evaporation of indium selenide powder.[16] In the present paper, we report a new process for preparing indium selenide, which employs two steps that do not require the use of expensive equipment. The first step involves the use of spray pyrolysis to prepare thin-film In_2O_3, and the second step involves the formation of In_2Se_3 by reaction of elemental selenium vapor with the indium oxide film at atmospheric pressure in a nitrogen ambient. Some of the preparation parameters are explored to determine the effects on film composition and the extent of the conversion. In addition preliminary results are presented for the structural, electrical and optical properties

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Table I. Chemical Composition and Electrical Properties of Indium Selenide and Indium Oxide Thin Films

sample[a]	Se treat[b]	annealing[c]	Se/In[d]	ρ, Ω cm	n, cm^{-3}	μ, $cm^2\ V^{-1}\ s^{-1}$
A	5 min, 400 °C	no	1/1.0			
B	20 min, 400 °C	no	2/1.6			
C	1 h, 400 °C	no	3/2.0			
D	5 min, 450 °C	no	1/1.0			
E	10 min, 450 °C	no	3/1.8	9.3×10^5	3.7×10^{12}	2.0
F	20 min, 450 °C	no	3/1.9			
G	5 min, 500 °C	no	3/1.8			
H	15 min, 500 °C	no	3/2.1			
I	1 h, 500 °C	no	3/1.8	1.7×10^4	8.8×10^{14}	0.4
J	1 h, 500 °C	no	3/2.0			
K	1 h, 500 °C	20 min (500 °C), N_2	3/1.9	4.7×10^4	1.1×10^{14}	1.2
L	1 h, 500 °C	20 min (500 °C), In	1/1.0	4.3×10^{-1}	7.8×10^{18}	1.9
M	1 h, 500 °C	30 min (500 °C), Cd	1/0.38/0.87[e]	3.4×10^{-2}	7.8×10^{19}	2.4
N	In_2O_3[f]	no		2.6×10^1	1.7×10^{17}	1.5
O	In_2O_3[f]	60 min (500 °C), air		3.1×10^0	7.9×10^{17}	2.6

[a] Samples N and O are In_2O_3 and all others are indium selenide films. [b] Se treatments were made for various lengths of time (minutes) and temperatures under N_2 ambient and 1 atm. [c] Subsequent heat treatment in minutes under different conditions of temperature and ambient. [d] Ratio of atomic compositions determined by PIXE. [e] Ratio of atomic composition for Se/In/Cd. [f] Substrate temperature, 200 °C.

of films prepared under a variety of conditions.

Experimental Section

Indium Oxide. Thin-film In_2O_3 was prepared by spray pyrolysis using a solution of 50 mM indium nitrate (Aldrich) in water that had been purified by reverse osmosis and subsequent deionization by the Millipore technique. The deposition rate depended on the spray rate. Thus, a spray rate of 6 mL/h gave film thicknesses around 0.5 μm after 0.5 h. The substrate was Corning 7059 glass plate, which was maintained at about 200 °C. The temperature was monitored with a chromel–alumel thermocouple, which was mounted on the substrate. The spray, which was developed by an ultrasonic nebulizer (Sunbeam), was directed to the substrate through a glass nozzle using a regulated flow of air. The spray assembly sat on a moving table so that the spray could be rastered over the substrate, and pinhole-free films were obtained.

Indium Selenide. Thin-film In_2Se_3 was prepared from thin-film In_2O_3 using a conversion reaction involving selenium vapor. The plates coated with In_2O_3 and a small boat of metallic selenium pellets (Aldrich) were placed in a cylindrical, stainless steel reaction chamber described previously.[17] This chamber was heated in a Lindberg tube furnace at temperatures ranging from 400 to 500 °C for durations ranging from 1 to 60 min. An ambient of nitrogen gas was maintained at 1 atm. The composition of the resultant film was determined by proton-induced X-ray emission (PIXE) using a Van de Graaf accelerator that provided a 0.75-MeV proton beam having a 0.4 by 0.4 mm spot size. The PIXE data were analyzed using standard computer software developed by Professor J. L. Campbell (Department of Physics, University of Guelph) and provided information about the relative quantities of each element in the films.[18] In addition the composition of two films of partly converted indium oxide was analyzed by Auger profiling at Surface Science Western at the University of Western Ontario to determine the composition of the In_2O_3/In_2Se_3 interface. This analysis was performed using a Perkin-Elmer Physical Electronics Model 600 scanning Auger microprobe with an electron beam energy of 5 kV and current about 100 nA rastered over a 100 μm^2 area. Depth profiling involved a 3-kV argon ion beam rastered over a 1 by 1 mm area.

Characterization. Structural analysis of the as-deposited In_2O_3 and both the as-prepared and annealed In_2Se_3 films was determined by XRD on a Rigaku Geigerflex D/Max II X-ray 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 25° to 50° with a step width of 0.02°. Optical absorption spectra between 200 and 1100 nm were obtained with a Shimadzu spectrometer Model UV160U using a blank piece of 7059 glass in the reference beam. For conductivity and Hall effect measurements, a cross was formed in the film, and contacts were made with colloidal graphite isopropyl alcohol based paint; the apparatus was fabricated in-house, and the measurement details have been described previously.[19] Surface morphology of the indium oxide and selenide films before and after heat treatment was determined using a Hitachi S570 scanning electron microscope (SEM) operating with an acceleration voltage of 10 kV. One of the In_2O_3 films was annealed at 500 °C in air, and one In_2Se_3 film was annealed in nitrogen to determine if the crystallite size could be increased. In addition two indium selenide films were treated with either indium vapor or cadmium vapor at 500 °C and atmospheric pressure in a nitrogen ambient to change the film composition and electrical properties.

Results and Discussion

Composition. Table I gives the composition of indium selenide films prepared under a variety of conditions. The error in the PIXE measurement for each element is 10%. In general when the reaction between In_2O_3 and selenium vapor is allowed to go to completion, the Se/In atomic ratio is close to 3/2, as can be seen for samples C and E–J. A measure of the relative rates of reaction at various temperatures can be ascertained by comparison of Se/In atomic ratios at various times for each temperature. Thus at 500 and 450 °C, conversion to the selenide is complete in as little as 5 and 10 minutes (samples G and E, respectively). Extending the selenium exposure to longer times does not alter the ratio at either temperature, indicating that the conversion of oxide to selenide is complete. At 400 °C, the reaction is not complete after 20 min (sample B) but gives the limiting ratio after 1 h (sample C). These results indicate that temperature can be used to fine tune the reaction and perhaps control the crystal size of the films. Furthermore, the relatively low temperatures required for conversion and the use of atmospheric pressure mean that these reactions can be carried out with inexpensive equipment. It was also found that the process could be reversed. For example, indium selenide reverted back to indium oxide when it was heated in air above 400 °C.

This type of reaction, involving a metal oxide and elemental chalcogen, seems fairly general. It has been used

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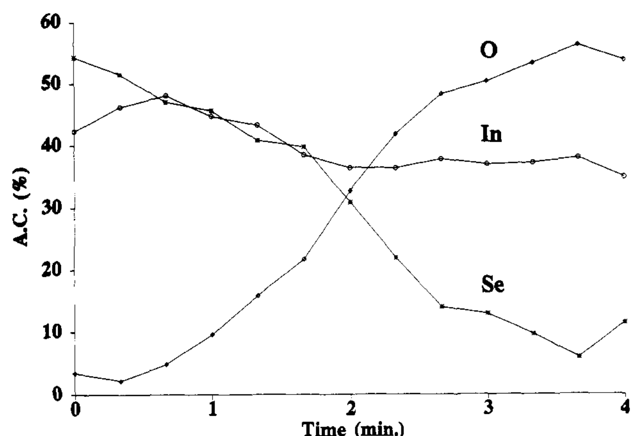
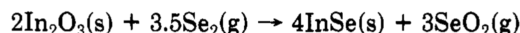


Figure 1. Auger composition profile using a sputter rate of about 71 nm/min. This sample was made from a In_2O_3 thin film exposed to Se vapor for about 1 min at 500 °C.

to prepare CdSe,[20] and pyrite was formed using a similar reaction with sulfur vapor.[21] The preparation of a variety of tellurides, selenides, and sulfides has been explored in our laboratory. This approach offers the possibility of fine tuning the electrical properties of the films because a variety of dopants can be introduced at the oxide formation stage. The undoped film can be prepared with a minimum of impurities because purified nitrate salts can be dissolved in highly purified water for the spray pyrolysis step, and highly purified chalcogen can be used for the conversion step.

Some of the details of the conversion step had been explored using Auger profiling of the composition of two oxide films that have been partially converted to selenide (conditions: 500 °C for 1 min). For one film, composition profiling was obtained at three different spots; for the other, at two different spots. All showed similar trends, and a typical composition profile as a function of sputter time is given in Figure 1. The sputter rate was 71 nm/min. There were surface contaminants such as carbon and chlorine. As can be seen in the figure, selenium occurred throughout the film, although the amount decreased as the depth increased. In the region near the surface, the selenium content was highest, but the Se/In atomic ratio did not approach 3/2. Instead it remained at about 1 to a depth of about 140 nm, beyond which it decreased to a nonzero value. Thus, selenium penetrated well into the oxide film after only a 1-min exposure. The oxygen composition profile was the converse; it was low at the surface and increased as the depth increased. These results indicate that the oxide was initially converted to InSe and that conversion to In_2Se_3 occurred subsequently. The fact that the selenium content was high in the surface region but, nevertheless, extended well into the film indicates that the oxide-to-selenide conversion reaction occurred at the surface after which the selenium diffused into the film while oxygen diffused out to the surface. This conclusion is supported by the presence of oxygen in the surface region. Consequently we conclude that the conversion process occurred in at least two steps: (a) chemical reaction at the surface of the film to form indium selenide; (b) diffusion of selenium into the film. Furthermore the diffusion occurred mainly at the stage when the oxide was being converted to InSe. Presumably, In_2Se_3 formation becomes important when the Se concentration gradient in the solid is sufficiently shallow to allow the InSe-to-In_2Se_3 conversion rate to compete with the diffusion rate. It seems unlikely that the InSe formation involves a direct substitution of selenium for oxygen. Consequently one possible reaction sequences that seems reasonable is



$$2In_2O_3(s) + 3.5Se_2(g) \rightarrow 4InSe(s) + 3SeO_2(g)$$

$$2InSe(s) + 0.5Se_2(g) \rightarrow In_2Se_3(s)$$

Electrical Properties. Table I also presents the resistivity, carrier density, and Hall mobility for a variety of undoped and doped In_2Se_3 as well as In_2O_3. The undoped In_2O_3, which was n-type, had a low resistivity and a large conduction electron density. When indium oxide was annealed in air for 1 h at 500 °C, the conductivity type remained unchanged, but the resistivity decreased by about a factor of 9 while the electron density and mobility increased. Because oxygen is an acceptor, the increase in electron density cannot be explained by the doping effect of oxygen. On the other hand, this effect is consistent with the grain boundary model for carrier transport in polycrystalline semiconductor films.[22,23] Thus during the air anneal, the oxygen might be reducing the density of subbandgap states at the grain boundaries. According to the model, a reduction in the density of these states would increase the effective carrier density and mobility. Incorporation of dopants can lower the resistivity even more. Substantially lower resistivities and higher electron densities were obtained when n-In_2O_3 was doped with tin during reactive sputtering of indium in the presence of oxygen. In this case the resistivity increased as the oxygen pressure was increased, indicating oxygen vacancies.[24]

The undoped In_2Se_3 films (samples E, I and K) were p-type. Of the two samples prepared at 500 °C, the unannealed sample I had a slightly lower resistivity and hole mobility but a larger hole density than sample K, which was annealed at 500 °C for 20 min in nitrogen. A decision on whether these changes are meaningful will require a more detailed study of annealing effects. On the other hand, there appears to be a clear difference between the films prepared at 500 and 450 °C. Thus, sample E had a resistivity at least an order of magnitude larger than that for the samples prepared at 500 °C, and the hole density was about 2 orders of magnitude smaller. Direct comparisons with previous work are not possible because the phases and/or carrier type were different.[12,13]

Treatment of In_2Se_3 with either indium or cadmium vapor at 500 °C caused a marked change in the composition of the film. Thus, treatment with indium converted In_2Se_3 to InSe (sample L), which had n-type conductivity. Furthermore, the resistivity of this sample was lower than that for the untreated samples of In_2Se_3 by about 5 orders of magnitude, while the carrier density was correspondingly larger. Treatment with cadmium vapor converted the film to a cadmium rich one that was n-type with very low resistivity and very large electron density. Although the conversion clearly went too far, it demonstrates the range of possibilities and shows that it will be possible to fine tune the temperature and time of exposure to prepare films

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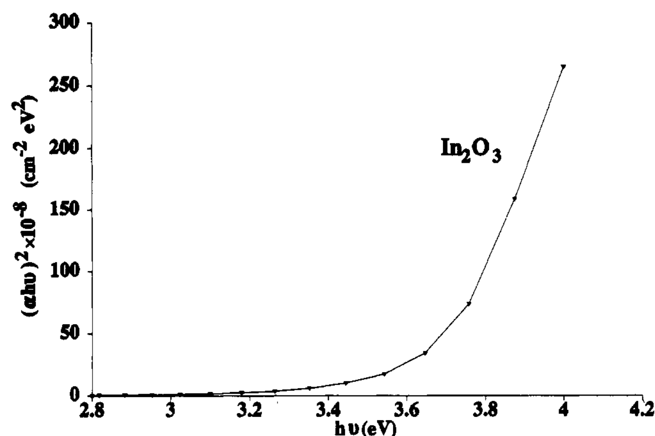

Figure 2. Energy dependence of α for thin film In_2O_3, which was prepared by spraying a solution of 50 mM $In(NO_3)_3$ on to Corning 7059 glass held at about 200 °C for 30 min.

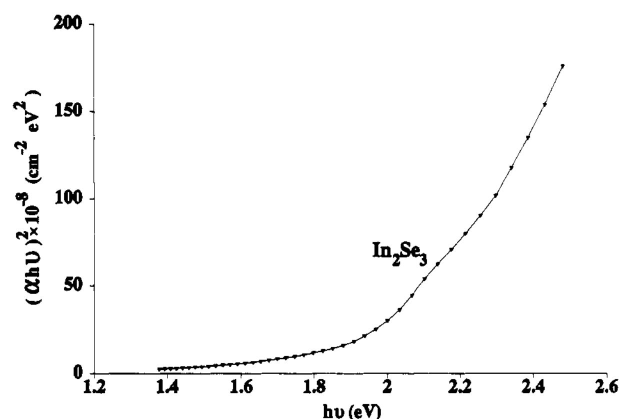

Figure 3. Energy dependence of α for thin film In_2Se_3 (sample G), which was prepared from an In_2O_3 thin film exposed to Se vapor at 500 °C for about 5 min.

having a range of composition, resistivity, and carrier density.

Optical Absorption. Absorption spectra were obtained for In_2O_3 films. Using thickness data, the absorption coefficient was determined as a function of photon energy. A plot of $(\alpha h\nu)^2$ as a function of $h\nu$ is linear (Figure 2), indicating a direct bandgap.[25,26] The intercept gives a band gap of 3.4 eV. These results agree with earlier studies that indicated In_2O_3 is an n-type semiconductor having a direct bandgap of 3.6 eV.[27] For In_2Se_3 a similar analysis of samples F–H (Figure 3 for sample G) indicates a direct bandgap of 1.84 eV, which agrees well with the value of 1.81 eV measured for polycrystalline In_2Se_3 films prepared by vacuum evaporation.[28] This particular comparison seems germane to the present work because in both cases the films appear to be a mixture of crystal phases (see X-ray data below). Other values ranging from 1.22 to 2.0 eV have been reported for either the amorphous film or polycrystalline films having specific crystalline phases.[1,12,13,16,29–31]

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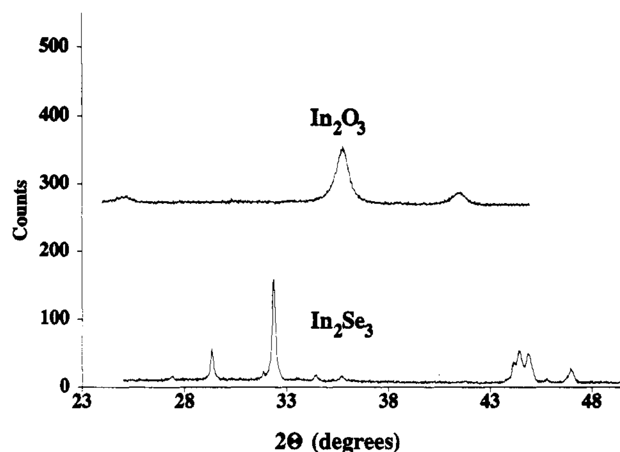

Figure 4. X-ray diffractograms of In_2O_3 and In_2Se_3 (sample G) thin films prepared under the conditions indicated in Figures 2 and 3.

Table II. X-ray Diffraction Peaks

obsd		rep[b]		assignment
d (Å)	*I*[a]	*d* (Å)	*I*	*hkl*
		(1) In_2O_3		
4.11	w	4.12	14	211
2.91	s	2.921	100	222
2.53	w	2.529	30	400
		(2) In_2Se_3[c]		
3.81	vw	?		
3.55	m	3.54 (β)	85	
3.23	s	3.23 (γ)	35	
		3.18 (β)	85	
		3.27 (α)	80	
3.11	vw	3.11 (β)	15	
		3.10 (α)	40	
3.03	w	3.01 (γ)	35	
		3.05 (InSe)	40	
2.92	w	2.908 (β)	45	
2.38	m	2.369 (β)	70	
		2.38 (InSe)	40	
2.37	m	from substrate		
2.34	m	2.361 (α)	40	
2.30	vw	2.296 (β)	45	
		2.291 (α)	40	
2.24	m	2.245 (β)	70	

[a] Peak intensities are defined as follows: s, strong, m, medium; w, weak; vw, very weak. [b] X-ray Powder Data File, ASTM Special Technical Publication 48-j, card no. 6-0416 and 17-356 to 359, respectively. [c] Phase transitions: α to β (190–200 °C); β to γ (650 °C).

For comparison, the absorption spectrum of the InSe film (sample L, Table I) was measured, also. This film was found to have a direct bandgap of 1.8 eV in exact agreement with the value reported for an electrodeposited film that was annealed at 400 °C[15] and, therefore, should have a similar polycrystalline phase. As was the case for In_2Se_3, there was a variation in values reported for the InSe bandgap, ranging from 1.03 for the amorphous film[16] up to 1.8 eV for the polycrystalline film.

Structure and Morphology. The X-ray diffraction results are presented in Figure 4 for In_2O_3 and In_2Se_3. For the oxide, which was grown at 200 °C, there are three peaks that are relatively broad. The X-ray diffractogram given for In_2Se_3 in Figure 4 was measured for sample G for which the bandgap was determined as described above. Comparison of the measured and reported *d* values given in Table II indicates that a number of the peaks cannot be assigned exclusively to one crystalline phase. Consequently, it would appear that the film may consist of at least three crystalline phases of In_2Se_3. Furthermore a

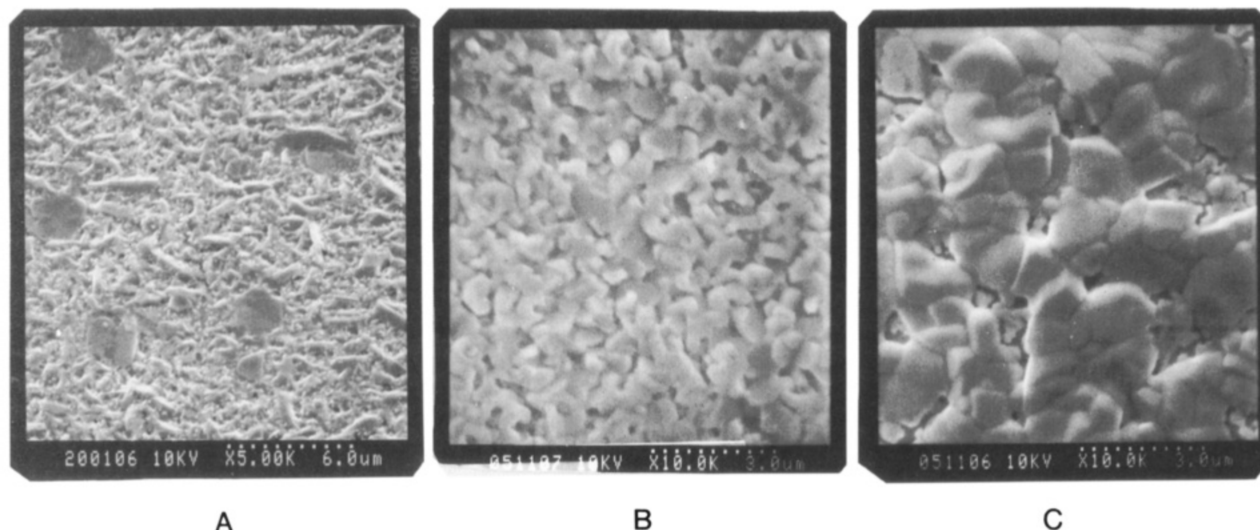

Figure 5. Scanning electron micrographs for thin films of In_2Se_3: (A) film prepared by exposure of ITO to Se vapor for 2 h at 500 °C; (B) and (C) were films prepared from In_2O_3, which was made as indicated in Figure 2 and subsequently exposed to Se vapor at 500 °C for about 5 min and 1 h, respectively.

contribution from a small amount of InSe cannot be ruled out. Earlier work found that a transition from the α to the β phase occurred at 200 °C and that the β phase was stable up to 650 °C.[32,33] In addition it has been reported that the β phase was unstable at room temperature.[34,35] For sample G, the absorption spectrum and the X-ray diffraction were measured approximately 1 month after the film had been prepared. Consequently the presence of two peaks that can be assigned exclusively to the β phase indicates that this phase has not disappeared completely. This result, therefore, indicates that the lifetime for this phase is not as short as that suggested by the conductivity measurement.[35]

The morphology of the In_2Se_3 film depended on that of the In_2O_3 percursor. The indium oxide film commercially prepared by Donnelly, Inc. (ITO) was very smooth and featureless; the films prepared by our spray process were not quite as smooth but still gave relatively featureless SEMs. This lack of surface features of the indium oxide is in contrast with the substantially larger crystallites found for cadmium oxide prepared by a similar method.[20] The selenide films prepared from the ITO films were rather small grained in comparison with those prepared from our In_2O_3. Thus, Figure 5a illustrates the morphology of the selenide prepared by treatment of ITO with selenium vapor at 500 °C for 2 h, whereas Figure 5b shows the larger crystallites obtained after only a 5-min exposure of an oxide prepared by our spray procedure. The crystallite size could be increased by longer exposure of the film to the selenium vapor. After exposure for 1 h, the crystallites were appreciably larger, with some approaching 2.5 μm (Figure 5c).

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Summary

Thin-film In_2Se_3 was prepared by a new process involving two steps: (a) formation of indium oxide by spray pyrolysis of an aqueous solution of indium nitrate; (b) reaction of this oxide with selenium vapor to form In_2Se_3. The rate of reaction for step (b) increased as the temperature was increased from 400 to 500 °C. Auger depth profiling of the composition of a partially converted film indicated that this conversion process appears to involve three steps: (a) reaction between selenium vapor and the oxide at the surface; (b) subsequent diffusion of selenium into the film until much of the oxide was converted to InSe; (c) further reaction involving selenium vapor and InSe to form In_2Se_3. It was possible to convert In_2Se_3 into InSe by reacting it with indium vapor, and it was also possible to incorporate cadmium. p-type In_2Se_3 and n-type InSe were prepared by this relatively inexpensive process, and preparation of these materials with a variety of dopants will be possible by incorporation of the dopants during the spray pyrolysis step. Furthermore this process is fairly general because preliminary work indicates that a wide variety of metal oxides can be converted to sulfides, selenides, and tellurides.

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