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Preparation and Properties of Cadmium Telluride Prepared by a Three-Step Process

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Cadmium telluride has been prepared by a new process involving three steps: (a) spray pyrolysis to deposit thin film cadmium oxide, (b) reaction of cadmium oxide with sulfur vapor to form thin film cadmium sulfide quantitatively, and (c) the quantitative conversion of cadmium sulfide to cadmium telluride by reaction with tellurium vapor. X-ray diffraction (XRD) showed that the film was of the zincblende type with a slight preference toward the (111) orientation. Scanning electron microscopy (SEM) measurements indicated that the films prepared at 500 and 550 °C appeared to be dense and relatively compact whereas the 600 °C films had a much more open and porous morphology, perhaps due to evaporation. Composition studies by means of proton induced X-ray emission revealed that the reaction time required for the quantitative conversion of CdS to CdTe decreased as the temperature increased, and the minimum Cd/Te ratio was around 0.94, independent of temperature. The resistivity of the films prepared under various conditions was very large and very nearly the same (in the 10^6–10^7 Ω cm range). The carrier density as determined from the Hall voltage exhibited a similar reproducibility. Except for three of the samples, all films had carrier densities in the 10^{10}–10^{11} cm^{-3} range, and the mobilities were in the 10–20 cm^2/V s range.

Introduction

Thin film CdTe with a bandgap around 1.5 eV has been considered a good prospect as an absorber in solar cells for a number of years.[1] This material has been prepared by a number of methods, including electrodeposition,[2–5] evaporation of elemental cadmium and tellurium,[6] screen printing,[7–9] metallorganic chemical vapor deposition,[10,11] annealing elemental layers of cadmium and tellurium,[12] close spaced vapor transport,[13–15] and spray pyrolysis using undisclosed precursors.[16,17] In a number of cases, thin-film CdTe prepared by these processes has been used in solar cells that gave power conversion efficiencies of 10% or more.[4,7–9,16] Because the bandgap of CdTe is an optimum match for the solar spectrum, practical thin-film cells could potentially reach efficiencies as high as 18%.[18] For this reason, it is important to explore other inexpensive methods for the preparation of thin film CdTe. In the present paper, we report the preparation of thin-film CdTe by a new process, which involves three inexpensive steps: (a) spray pyrolysis to form CdO; (b) reaction of CdO with sulfur vapor to form CdS; and (c) reaction of CdS with tellurium vapor to quantitatively form CdTe. Determination of the composition and some of the physical and electrical properties of this material is also reported.

This preparative technique appears to be quite general. A number of other binary and ternary chalcogenides have already been prepared.[19–22] The advantage of this process is that any species added to the spray solution is incorporated in the oxide and remains in the chalcogenide film after conversion. Consequently, there is the possibility that the film can be doped uniformly and quantitatively.

Experimental Section

Cadmium Oxide. Thin film CdO was prepared by spray pyrolysis as previously described.[20] The aqueous spray solution contained 50 mM cadmium nitrate (Aldrich, 99.999% purity). The substrate (Corning 7059 glass) was maintained at 150 °C. With a spray rate of 8 mL/h, an oxide film about 0.5 μm thick was obtained in about 35 min.

Cadmium Sulfide. Thin-film CdS was prepared by reaction of sulfur vapor with thin-film CdO in a stainless steel reactor described previously.[23] The oxide film and a small glass boat

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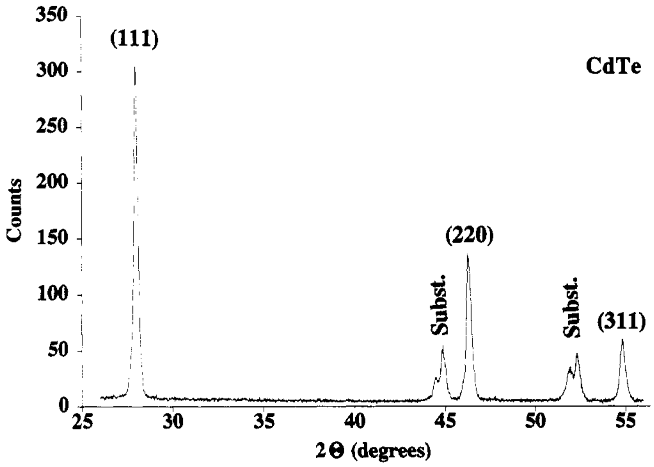

Figure 1. X-ray diffraction of a thin film of CdTe (sample υ) prepare by conversion of CdS that was exposed to Te vapor at 550 °C for 1 h.

containing sulfur powder (Aldrich, 99.999% purity) were sealed in a nitrogen ambient, and the reactor was kept at 400 °C for 1 h to quantitatively convert the oxide to the sulfide. After the conversion the sulfide film was thicker than the original oxide film by about 50%. The sulfide film appeared very smooth and was a very pale yellow in contrast to the darker yellow-brown color of the oxide. Adhesion was very good, and no pinholes were apparent.

Cadmium Telluride. Thin-film CdTe was prepared by reaction of tellurium vapor with thin-film CdS because the corresponding conversion using CdO did not occur as readily. The sulfide film and a glass boat containing tellurium powder (Aldrich, 99.999% purity) were sealed in a nitrogen ambient. The conversion was performed at various temperatures ranging from 500 to 600 °C for periods ranging from 5 min to 5 h. The degree of conversion depended on the temperature and the reaction period. The resulting CdTe films appeared smooth and adhesive, and no cracks or pinholes were apparent. The final thickness of the films was about 1 μm.

Characterization. Proton-induced X-ray emission (PIXE) spectroscopy was used to determine the composition of the CdTe films in the same manner as described for CdSe[19] and In_2Se_3.[20] The PIXE data were analyzed using standard computer software developed by Professor J. L. Campbell (Department of Physics, University of Guelph) and provided atomic abundances with an accuracy of about 1%. Powder XRD was determined using a Rigaku GeigerflexD/Max II X-ray system using a cobalt K α_1 radiation source as described previously.[19,20] Surface morphology of the films was determined using a Hitachi S570 scanning electron microscope (SEM) operating with an acceleration voltage of 10 kV. Optical absorption spectra between 300 and 1000 nm were measured using a Shimadzu visible/near IR spectrometer with a blank piece of 7059 glass in the reference beam. Conductivity and Hall effect measurements were made as described previously.[24]

Results and Discussion

Structure and Morphology. Figure 1 illustrates the XRD pattern obtained at room temperature for thin film CdTe (sample ν, prepared by reaction of CdS at 550 °C for 1 h). In addition to three peaks due to CdTe, there are four due to the substrate.[18-20] The interplanar spacings and the assignment of the CdTe peaks are given in Table I along with reference data. The good agreement with the reference data indicates that the structure of the film was of the zincblende type with a slight preference toward the (111) orientation.

Table I. Powder XRD Data for Thin-Film CdTe (Sample ν) Prepared by Reaction of Te with CdS at 550 °C for 1 h

Observed Data		XRD Powder Data File[a]		
d (A)	I/I_1	*d* (A)	I/I_1	*hkl*
3.71	100	3.74	100	111
2.37				substrate
2.35				substrate
2.28	28	2.29	60	220
2.04				substrate
2.03				substrate
1.94	22	1.95	30	311

[a] ASTM Special Technical Publication 48-J, card no. 15-770.

Film morphology as a function of conversion temperature was determined by SEM measurements. Figure 2 presents the SEM photographs at two magnifications for CdTe films prepared at 500, 550, and 600 °C with reaction times of 2.0, 1.0, and 1.0 h, respectively. Figure 2a–c, at lower magnification (a 10-μm mark is at the bottom), demonstrate that the film prepared at 600 °C had a rougher morphology than those prepared at 500 and 550 °C. Furthermore at higher magnification (Figures 2d–2f), it is clear the films prepared at 500 and 550 °C appear to be dense and relatively compact. On the other hand, the 600 °C film had a much more open and porous morphology, indicating that some of the CdTe may have evaporated at this temperature. Thus, conditions can be chosen to make either porous or nonporous films, and determination of the properties of each type will be interesting.

Composition and Bandgap. Composition studies indicated that the reaction time required for the quantitative conversion of CdS to CdTe decreased as the temperature increased, as might be expected. This conclusion is supported by the composition data presented in Table II for films prepared under a variety of conditions. The composition was determined by PIXE measurements. PIXE could quantitatively determine the sulfur, tellurium, and cadmium content, but it could not be used to determine the oxygen content. Nevertheless the oxygen content must be very low because the conversion of CdO to CdS gave Cd/S ratios of 1.0 for all films measured. Furthermore in the CdTe films, no sulfur was detected indicating that sulfur content was less than 1%. Comparison of samples m, s, and f illustrate that the Cd/Te ratios are 1.43, 1.76, and 2.68 for reaction times of 8, 5, and 60 min, respectively, indicating the conversion reaction was slowest at the lowest temperature. Quantitative conversion occurred in 30 minutes at 550 °C to give a Cd/Te atomic ratio of 0.94, which was very nearly the minimum value observed for samples prepared at any temperature. Thus, the reaction had reached completion when this value was attained. The fact that this value was observed at all temperatures indicated that the final ratio was independent of temperature in this temperature range. Consequently, the variation in temperature had no effect on the final composition but did affect the surface morphology.

The absorption spectrum has been measured, and a plot of $(\alpha h\nu)^2$ as a function of photon energy is given in Figure 3. The linear relation at the absorption edge indicates a direct transition, and extrapolation to the energy coordinate gave a bandgap of 1.47 eV, which is very similar to the values reported in a number of studies[1] and close to the value accepted for single-crystal CdTe.

Resistivity. Except in two cases, the resistivity of the films prepared under the various conditions was very large

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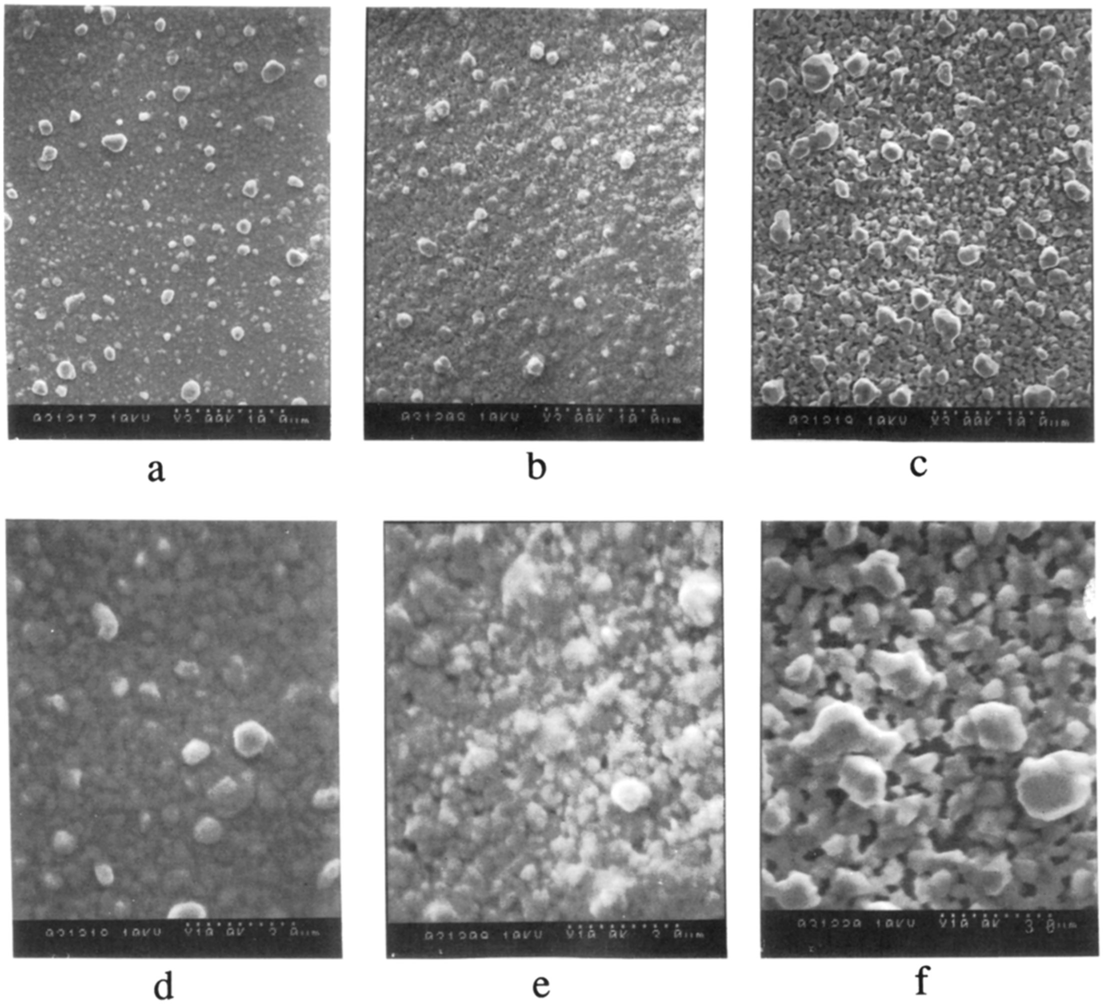

Figure 2. SEM pictures of thin films of CdTe prepared by conversion of CdS at various temperatures. Parts a, b, and c were obtained at a magnification of 3000. Pictures d, e, and f were obtained a magnification of 10 000. Conditions: (a) and (d), 2 h at 500 °C; (b) and (e), 1 h at 550 °C; and (c) and (f), 1 h at 600 °C.

Table II. Composition and Electrical Properties of Thin-Film CdTe Prepared under Various Conditions

sample	Te Cond[a] (°C, min)	anneal[b] (°C, min)	Cd/Te ratio	ρ^c (Ω cm)	μ^d(cm^2/V s)	carrier density[e]
g	500, 120		0.92	1.7×10^6	2.3	1.7×10^{12}
		450,60		1.4×10^7	17	2.6×10^{10}
h	500, 300		1.00	1.0×10^7	16	4.0×10^{10}
i	550, 120		0.95	8.2×10^6	21	3.5×10^{10}
j	550, 120		0.94	4.8×10^3		
		450,60		2.7×10^6	18	1.6×10^{11}
e	550, 60		0.95	8.2×10^6	11	7.2×10^{10}
t	550, 60		0.96	2.1×10^7	22	1.3×10^{10}
υ	550, 60		0.96	3.4×10^4	0.1	1.4×10^{14}
		500,60		4.6×10^6	19	7.2×10^{10}
r	550, 30		0.94	4.0×10^6	2	7.4×10^{11}
		500,60		2.5×10^7	10	2.8×10^{10}
l	600, 30		0.95	6.1×10^6	27	3.8×10^{10}
q	600, 60		0.95			
k	600, 60		0.94			
m	600, 8		1.43			
d	550, 60		0.91			
u	550, 30		0.94			
s	550, 5		1.76			
f	550, 60		2.68			

[a] The temperature and duration in minutes for the tellurium treatment to convert thin-film CdS to CdTe. [b] The temperature and duration in minutes of CdTe films that were heat treated in nitrogen ambient at 1 atm. [c] Resistivity of the CdTe films. [d] Mobility of the CdTe films. [e] Carrier density in cm^{-3}. All films exhibited p-type conductivity except sample *υ*. However, it was converted to p-type upon annealing.

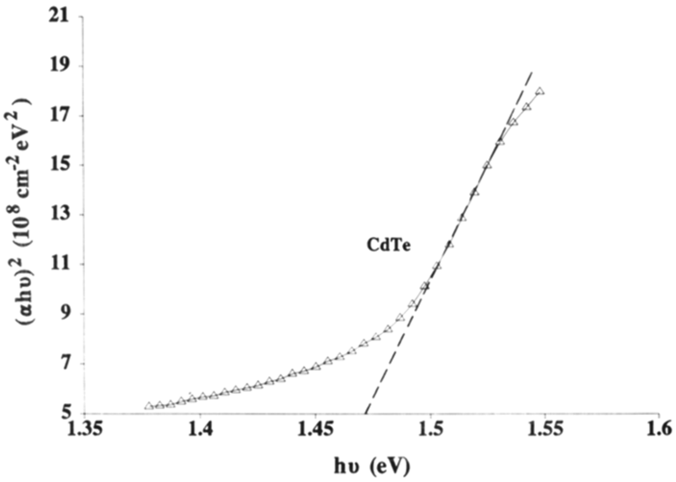

Figure 3. Plot of $(\alpha h\nu)^2$ as a function of photon energy for thin-film CdTe prepared under the conditions described in Figure 1.

and very nearly the same (in the 10^6–10^7 Ω cm range). The only exceptions were samples *j* and ν, which had values in the 10^3–10^4 Ω cm range even though the Cd/Te ratios were the same as those of the other high resistivity samples. However, upon annealing in nitrogen at 450 or 500 °C for 1 h, the resistivities of these samples moved up to the 10^6 Ω cm range. Presumably, the heat treatment reduced the density of the defects that contributed to the lower resistivity. The change in the carrier density upon annealing the film, as described below, is consistent with this conclusion.

Part of the reason for these fluctuations may rest with the reactor used for these conversions. This reactor exhibited a temperature gradient and, presumably, caused a density gradient in the Te vapor during the reaction. This gradient was not necessarily reproducible. A new reactor that is currently being fabricated has been designed to markedly reduce or completely remove the temperature gradient. Nevertheless, the fact that only two out of nine samples deviated from the norm indicated that even with this crude reactor the reaction was fairly reproducible. Furthermore when a deviation occurred, it could be corrected by an annealing step.

Carrier Density. The carrier density, as determined from the Hall voltage, exhibited a similar reproducibility. Except for three of the samples, all films had carrier densities in the 10^{10}–10^{11} cm^{-3} range. Samples *g* and *ν* deviated from this range, and the Hall voltage for *j* was too small to measure. In fact, sample *ν* exhibited n-type conductivity even though it was prepared under the same conditions as a number of films that exhibited p-type conductivity. Annealing sample *ν* in nitrogen converted it to p-type conductivity. Furthermore, the carrier densities of all three samples could be brought into this range by annealing in nitrogen at either 450 or 500 °C. As discussed above, the heat treatment presumably removed defects that were responsible for the higher carrier density. Like the resistivity, the carrier density did not depend on the reaction temperature or duration for those films that had reached the minimum Cd/Te ratio. The three exceptions (samples *g*, *j*, and *ν*) appeared to be random since they were made at two different temperatures and various tellurium exposure times. These results indicated that the variations were not inherent in the process but were probably due to the temperature gradient in the reactor.

As might be expected, the mobility, which was calculated from the resistivity and carrier density, exhibited a similar behavior. After annealing the samples that deviated from the norm, all of the samples had mobilities in the range 10–20 cm^2/Vs. Consequently, CdTe films prepared by this process in the temperature range between 500 and 600 °C exhibited uniform carrier transport properties, although the surface morphology of the films prepared at 600 °C was different from that of films prepared at the lower temperatures.

A brief survey of the carrier transport properties of thin film CdTe prepared by various techniques indicated that a wide variation was possible. Thus, films grown by metalorganic chemical vapor deposition had low resistivities with carrier densities around 10^{15} cm^{-3}, which was fairly independent of the ratio of dimethylcadmium and diethyltellurium employed. Furthermore, doping with arsenic caused an increase by a factor of 10 with hole mobilities as high as 75 cm^2/V s.[11] On the other hand, using diisopropyltellurium and hydrogen resulted in high resistivities (between 10^7 and 10^8 Ω cm) with very little dependence on the ratio of precursors.[10] Screen printing gave films with carrier densities in the 10^{15} cm^{-3} range with resistivities around 10^5 Ω cm.[9] Electrodeposited films had resistivities around 10^7 Ω cm and carrier concentrations in the 10^9–10^{10} cm^{-3} range.[24] Films prepared by direct combination of elemental Cd and Te exhibited carrier densities around 10^{16} cm^{-3}, which was independent of the Cd/Te vapor ratio, and the conductivity type depended on the substrate temperature.[25] Coevaporation of CdTe and Te gave thin film CdTe, which had resistivities ranging from greater than 10^6 to less than 50 Ω cm and carrier densities around 10^{18} cm^{-3}, depending on the Te content of vapor.[26] Using a similar method other workers found[27] that the resistivities of the films depended on the substrate temperature. Thus, the films had resistivities ranging from 100 to less than 1.0 Ω cm, while the carrier density remained relatively constant around 10^{18} cm^{-3}. It is interesting that coevaporation of CdTe and Te could give such a wide range of resistivities by controlling the Te content in the vapor.[26] In contrast, increasing the Te vapor content seemed to have no effect when CdTe was prepared by CVD of elemental Cd and Te.[27] Similarly in this approach, increasing the Te pressure by increasing the temperature had no effect on the resistivity or the carrier density. Consequently, a wide variation in Cd and Te content occurred even when the same preparation technique is employed, and it is clear that the details of the conditions are very important.

Reaction Stoichiometry. The nature of the conversion reactions has not been studied at present time. However, it seems thermodynamically unlikely that a simple exchange occurs in either case. One possible reaction sequence is

$$^2/_3x\mathrm{CdO(s)} + \mathrm{S}_x\mathrm{(g)} \rightarrow {}^2/_3x\mathrm{CdS(s)} + {}^1/_3x\mathrm{SO_2(g)}$$

$$\mathrm{CdS(s)} + \mathrm{Te_2(g)} \rightarrow \mathrm{CdTe(s)} + \mathrm{TeS(g)}$$

In other words the conversion of CdO to CdS can occur readily because there is a sufficient excess of sulfur to combine with the oxygen to drive the reaction to the right. Similarly, there is a sufficient excess of tellurium to combine with the sulfur and drive the reaction completely to the right. Analogous reactions have been suggested for the conversion of cadmium oxide and indium oxide into cadmium selenide[19] and indium selenide.[20]

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