Properties of Cadmium Telluride Containing Impurities Introduced during Spray Pyrolysis

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Received November 29, 1994. Revised Manuscript Received February 16, 1995®

Thin-film CdTe was prepared in three steps: spray pyrolysis to form CdO, conversion of CdO to CdS, and conversion of CdS to CdTe. It was also possible to prepare CdTe directly from CdO, but longer reaction times were required. Efficiencies of spray deposition were as high as 25%. The film thickness and uniformity were reproducible, and stoichiometric CdTe films were obtained. When As and P were incorporated into the films, the CdTe conductivity was increased from 3 to 5 orders of magnitude. The lowest resistivity value obtained for these films was 10^3 Ω cm, mobilities ranged up to 35 $cm^2 V^{-1} s^{-1}$. High concentrations of Ag and Cu were required to reduce the resistivity of the CdTe films. In these cases, the films may be composite materials with material segregation. The incorporation of Ga had no effect on the resisitivy. $CdCl_2$ treatment of CdTe lowered resistivity by 1 order of magnitude, and hole density increased.

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] metalorganic 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] In a number of cases, thin film CdTe prepared by these processes has been used in solar cells that gave power conversions efficiencies of 10% or more.[4,7-9,16,17,28] 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 CdS, CdTe, and doped CdTe using a process developed in our laboratory.[19] This procedure involves the conversion of either thin-film CdO or CdS to CdTe by reaction with Te vapor at atmospheric pressure. For this purpose, thin-film CdO was prepared by spray pyrolysis. The goal of the present study was to survey the scope of these two steps. In particular, we were interested in the efficiency of the spray pyrolysis step, the effect of additives on film density and morphology as well as other properties of the film, and the relation between solution composition and the composition of the oxide. In regard to the conversion process, we were interested in the effect of conversion conditions on film composition, carrier transport properties, volume change upon conversion, and the effects of additives (dopants) on film properties. Finally, we wished to determine if the incorporation of dopants in CdTe by this procedure was more successful in altering the conductivity than other procedures used for preparation and doping thin film CdTe.

Experimental Section

Cadmium Oxide. Thin-film CdO was prepared by spray pyrolysis as described earlier[20] using a solution of cadmium nitrate (Aldrich, 99.999%) in water that had been purified by reverse osmosis and subsequent deionization by the Millipore technique to give a resistivity of 18 MΩ. This solution was sprayed on to a Corning 7059 glass plate, which was maintained at 150 °C. The spray, which was developed by an ultrasonic nebulizer (Sunbeam), was directed toward the substrate through a glass nozzle using a regulated air flow. The spray assembly was mounted on a moving table, and the vapor was rastered across the substrate in the *x* and *y* directions.

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® Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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0897-4756/95/2807-0786$09.00/0

It is important to maximize the efficiency of film formation and, therefore, minimize material losses. For this reason, the effects of the following spray parameters were investigated: temperature of substrate, pressure inside spray chamber, raster rate, distance of the substrate from the spray nozzle, ultrasonic nebulizing rate, duration of spraying, and cadmium nitrate concentration. The efficiency of the spray was calculated as the ratio of the amount of Cd in the film to the amount of Cd sprayed on the surface. The mass of Cd in the film was obtained from ICP elemental analysis. The total mass of Cd that was sprayed was obtained from the sprayed volume of solution.

Cadmium Sulfide and Cadmium Telluride. Thin-film CdS was prepared by reacting sulfur vapor with thin-film CdO, using reactors described earlier.[19] In this process, the CdO films were heated in the presence of sulfur powder (Aldrich, 99.999%) in a nitrogen atmosphere in a closed glass vessel. The vessel was heated to temperatures ranging from 400 to 500 °C for 1 h. Similarly, CdS was converted to CdTe by exposing the CdS film to tellurium vapor obtained by heating tellurium powder (Aldrich, 99.999%) in a stainless steel (SS304) reactor under nitrogen. The vessel was heated at temperatures ranging from 550 to 600 °C for 1 h. The conversion reactions were optimized for temperature and time. Direct conversion of CdO to CdTe required substantially longer periods.

Impurities. Impurities were incorporated into CdTe by introducing the impurities at the spray pyrolysis stage. Theses impurities were added to the cadmium nitrate solution as salts or acids. Materials added to the cadmium nitrate solution included: gallium(III) nitrate hydrate (Aldrich, 99.999%), copper(II) nitrate (JM, 99.999%), silver nitrate (Engelhard, unknown purity), arsenic(III) oxide (Aldrich, 99.99%), and phosphoric acid (certified Fisher, 85.5%). In each case, the concentration of the additive was varied relative to the concentration of cadmium nitrate. The atomic percent of dopant in the spray solution was compared to the value in CdO and CdTe.

CdCl$_2$ Annealing. A few drops of a saturated solution of CdCl$_2$ (JM, 99.998% purity) in methanol (Fisher, 99.9%) was spread over the CdTe films and allowed to dry after the excess was shaken off. The films were then heated to 400 °C for 15 min in a nitrogen atmosphere using a method similar to that reported by other workers.[21,22]

Characterization. Proton-induced X-ray emission (PIXE) spectroscopy was used to determine the composition of some CdTe films, in the manner described by Weng et al.[23] The PIXE data were analyzed using standard computer software developed by Professor J. S. Campbell (Department of Physics, University of Guelph) and provided elemental analysis. The PIXE microprobe records X-rays for approximately 4 min, and the variation in signal gives rise to an error of about 1%.

The composition of some films was analyzed by inductively coupled plasma (ICP) optical emissions spectroscopy using a LECO Plasmarray instrument and photodiode array. For this purpose, some films were dissolved in a nitric acid solution. The X-ray diffraction (XRD) analysis was made using a Rigaku Geigerflex D/Max II X-ray system using a 1.7889 Å Co $K\alpha_1$ radiation source. Data were collected over a 10 s count time for 2θ ranging from 26° to 56° with a step width of 0.02°. Surface morphology was determined using a Hitachi S570 scanning electron microscope (SEM) operating with an acceleration voltage of 10 kV. Thickness was determined using a Sloan Dektak surface profile measuring system. The accuracy depended on the surface morphology of the film. Smooth films gave a typical accuracy of 0.1 μm while rough films could be measured to within 0.2−0.4 μm because of the lower signal-to-noise ratio.

Conductivity and Hall effect measurements were made on a home-built apparatus described earlier.[24] Contacts were made using colloidal graphite 2-propanol-based paint at the end of each arm of a cross formed in the film as described previously.[22] The Hall effect measurements were performed at a magnetic field strength of 0.8 T.

Results and Discussion

Efficiency of Spray Pyrolysis. The efficiency of the spray deposition depends critically on a number of parameters associated with the spray system, and these parameters were found to depend on the spray characteristics through the nozzle. The results described below were obtained using a nozzle that provided a narrow conical spray. It was constructed from the tip of a pipet. The efficiency of deposition went through a maximum as the nozzle was moved toward the substrate, and the optimum distance was found to be 2.9 cm. The effect of the distance of the homemade nozzle on the efficiency varies from nozzle to nozzle because the divergence of the conical spray changes. Consequently, each spray tip must be calibrated. For this reason, a tabulation of efficiency as a function of distance is not very informative. The efficiency also went through a maximum as the temperature was decreased from 190 to 130 °C, with the optimum value at 150 °C. Below 130 °C, evaporation was not sufficiently rapid, and smooth uniform films were difficult to obtain. The spray rate depended on the power applied to the nebulizer and on the air flow through the nebulizing chamber. The air flow was regulated by controlling the air pressure, and the optimum value was found to be 12 cm of water at the nozzle, which combined with an applied power of 24 W gave a spray rate of 0.4 mL/min. Under these conditions for 0.1 M Cd(NO$_3$)$_2$, a spray duration of 15 min, and a scan rate of 1.5 cm/s gave a CdO thickness of 1.1 μm for a substrate surface of 2.5 × 5.0 cm and resulted in a deposition efficiency of 25%. Although many studies of spray pyrolysis deposition have been reported, few seem to address the issue of deposition efficiency. However, in one paper it was indicated that the deposition without corona discharge assistance usually had efficiencies of only a few percent.[25] Furthermore it was found that the deposition efficiency could be increased to <80% when the aerosol droplets were loaded in a corona discharge and transported to the substrate by an electric field. Although the efficiency of our procedure was not as high as the one for this more complicated approach, it compares favorably with the simpler methods.

Film Uniformity and Reproducibility. To determine the uniformity of the CdO film, its thickness at various points across the surface was measured for three separate CdO films having different thicknesses: 0.32, 0.62, and 0.77 μm. The length of the film was approximately 5 cm, and the thickness was measured at intervals of 0.5 cm starting at 1 cm from the edge. An absolute variation of 0.05 μm or less was achieved for each of the three films. This variation was smaller than the 0.1 μm accuracy of the measurement technique, indicating that the films were of uniform thickness within these limits.

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Table 1. Chemical Composition of Undoped CdS and CdTe Films Determined by PIXE

film	Cd atomic %	S atomic %	Te atomic %	thickness μm
CdS 10	45.8 ± 0.2	54.2 ± 0.1	0.0[a]	
CdS 11	46.3 ± 0.2	53.7 ± 0.1	0.0[a]	
CdS 12	46.1 ± 0.2	53.8 ± 0.1	0.0[a]	
CdTe 10[b]	49.9 ± 0.3	0.3 ± 0.1	49.9 ± 0.5	0.65
CdTe 11[b]	49.2 ± 0.3	0.2 ± 0.1	50.6 ± 0.5	1.00
CdTe 12[b]	49.9 ± 0.2	0.1 ± 0.1	50.0 ± 0.4	0.56

[a] Less than 0.1%. [b] Prepared from the corresponding CdS film.

Table 2. Effect of Postconversion Annealing on the Composition Determined by PIXE

film[a]	Cd atomic %	S atomic %	Te atomic %
CdTe 13[b]	50.9 ± 1.3	26.4 ± 0.05	22.7 ± 0.5
CdTe 13A[c]	49.0 ± 0.4	2.9 ± 0.02	48.1 ± 0.7
CdTe 14[b]	47.7 ± 0.3	4.1 ± 0.02	48.1 ± 0.6
CdTe 14A[c]	53.2 ± 0.4	0.5 ± 0.02	46.4 ± 0.6

[a] The conversion of CdO to CdS was done for 1 h at 400 °C. [b] The conversion of CdS to CdTe was done at 550 °C for 1 h. [c] The annealing was done at 550 °C under nitrogen, for 1 h.

Similarly, the reproducibility in film thickness from sample to sample was tested by preparing a series of films having the same spray parameters, which were 150 °C, 0.100 M $Cd(NO_3)_2$, 60 min spray time with the nozzle 2.2 cm from the substrate, which is shorter than the optimum distance. For 6 films, the average thickness was 0.56 μm with a standard deviation of 0.11 μm. This standard deviation is close to the 0.1 μm accuracy of the thickness measurement; nevertheless, this variation may be real. It is difficult to attribute this variation to any one factor. The thickness of the film can be greatly influenced by changes in any of the spray parameters, such as temperature of the substrate, distance from the nozzle to the substrate, density of nebulized cadmium nitrate aerosol relative to the airflow rate, the transfer of power to the solution, and the decrease in power output of the nebulizer as it ages. As will be noted below, the presence of other metal ion additives in the solution can also affect the deposition rate. Consequently, to obtain films of desired thickness, calibration of the system is necessary not only for the spray system but also for the nature of the film, and periodic recalibration is necessary. It should be noted that the thickness increases by about a factor of 2 upon conversion from CdO to CdTe. Consequently the variation in thickness of CdTe from film to film will be double the value observed for CdO.

Composition. Elemental analysis using PIXE indicates that the conversion of CdO to CdTe by way of CdS yielded stoichiometric films, with only residual amounts of sulfur remaining in the films. Table 1 shows a series of three films that were first converted from CdO to CdS and then from CdS to CdTe. The sulfide and telluride conversions were performed at 400 and 550 °C, respectively, for 1 h. The CdTe films had a Cd:Te ratio of 1:1. The thickness of the films range from 0.6 to 1.0 μm. It is possible that no sulfur remained because the sulfur content is very close to the limit of detection of 0.1%.

The reaction period required for complete conversion of CdS to CdTe increases as the film thickness increases. Table 2 presents the composition of two films having different thicknesses 0.4 and 0.7 μm obtained by treatment for CdS to tellurium vapors for 1 h. As can be seen, the thicker film exhibited a substantially larger sulfur content, indicating that exposure to Te vapor for 1 h was inadequate. A longer exposure period of about 2 h was required to reduce the sulfur composition to 0.2%. By increasing the treatment temperature from 550 to 600 °C, it was also possible to increase the degree of conversion and reduce the sulfur content to 0.2%. These results are consistent with a mechanism in which diffusion of Te into the films is required. As mentioned above, the volume increases by about a factor of 2 upon conversion from CdO to CdTe.

Almost complete removal of sulfur from the partially converted films was achieved by annealing. The composition of films 13A and 14A in Table 2 shows that annealing in a nitrogen atmosphere at 550 °C for 1 h removed most of the sulfur. Presumably CdS evaporated because the films tended toward stoichiometric CdTe upon annealing. Furthermore, XRD analysis indicated that film 14A peaks at *d* spacings of 3.675, 2.259, and 1.927 Å, which agreed with literature values of 3.675, 2.259, and 1.95 Å for CdTe.[26] No peaks were observed for CdS or Cd. These results are consistent with those from PIXE analysis, which indicated that the sulfur content was near the detection limit and, therefore, almost completely removed.

Impurities. The incorporation of a variety of impurities was studied to explore the scope of the spray technique for doping thin-film CdTe and to ascertain how effective these additives were in altering the carrier transport properties of the film. Any impurity added to the spray solution was incorporated into the CdO film and, subsequently, into the final CdTe film. Determining the extent of incorporation was one of the goals of the study. Due to the insensitivity of the analytical techniques available to us, it was necessary to incorporate relatively large amounts of impurity in the film to determine the relation between solution composition and resultant film composition. As a result, when the impurities were present in large amounts, they were no longer acting merely as dopants and were altering the nature of the film. Nevertheless, these composition levels were useful for the determination of the efficiency with which the impurity in the solution was incorporated into the film. The impurities such as Ga, Cu, Ag, and As could be incorporated into CdO in appreciable quantities. Although P could not be detected by our analytical techniques, its presence was confirmed by alterations in the carrier transport properties described below. On the other hand Sb and Au were not detected analytically and did not alter the carrier transport properties, probably due to poor solubility of the precursors used.

One interesting consequence of introducing additives in the spray solution was that the thickness of the resultant CdO film increased as a function of additive concentration, for similar spraying parameters. The effect of various compositions of Cu, Ag, As, and P on film thickness is illustrated in Table 3. As can be seen, the increase in thickness with additive concentration was significant for all species; however, the extent of the increase depended on the nature of the additive. It ranged from a 3-fold increase for Cu up to a 7-fold increase for P when the solution composition was increased from 0.01% to 10.0% for the additive relative to the Cd composition. In the case of Cu and Ag, some

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(26) Mineral Powder Diffraction File, Data Book, International Center for Diffraction Data.

Table 3. Dependence of the Thickness of CdO Films on the Composition of Various Impurities in the Spray Solution

	CdO film thickness[a]			
dopant atomic %[b]	As_2O_3	$Cu(NO_3)_2$	H_3PO_4	$AgNO_3$
0.01%	0.33	1.05	0.57[c]	0.49[d]
0.1%	0.48	1.29	1.33	
1.0%	0.66	2.30	0.99	0.85
5.0%	1.29	2.37[e]	1.78	1.67
10.0%	1.39	2.96[e]	4.06	1.91[f]

[a] Thickness in micrometers. The films were sprayed for 120 min unless specified otherwise. [b] Atomic percent of impurity in solution relative to the cadmium content. [c] This film was sprayed for 150 min but corrected for 120 min. [d] The silver series became so thick in 120 min that reduced times had to be used to spray. The reported thickness are corrected for 60 min. [e] These films were sprayed for 90 min but corrected for 120 min. [f] The film was sprayed for 40 min but corrected for 60 min.

of this increase can be attributed to their incorporation into the film in large amounts at the highest solution compositions (see below). However, up to a solution composition of 1.0%, they were present in the film at a composition of less than 5% of the Cd content while the film thickness increased by a factor of 2. For As, the maximum film composition was only about 1% while the film thickness increased 4-fold. Unfortunately the ICP equipment was not effective in providing quantitative information about the phosphorus content, probably due to interference of other lines. Nevertheless, the film thickness increased up to a factor of 7. This increase also cannot be attributed to a decrease in density of the film as the solution content of the additive increased. In all cases, the density of the film either remained nearly the same or increased slightly with solution composition. Consequently, it is clear that the presence of small amounts of these additives are effective in increasing the efficiency of the spray process. Any explanation for this effect would be speculative at this time.

The extent to which the impurities were incorporated into the film depended on their nature. The behavior ranged from a very low degree of incorporation to preferential incorporation. For As, P, and Ga, the atomic percent in the film was very low despite a content as high as 10% in the spray solution. In fact, the content of As and Ga was near or below the limit of detection of the PIXE technique in the CdTe film. Thus, the maximum content of As and Ga was 0.5 and 2%, respectively, of the total film content. Consequently, although there may be a trend toward higher content as the solution content increased, the PIXE analysis is not sufficiently accurate to be reliable. On the other hand, the data clearly indicate that a major portion of the As and Ga in the solution failed to be incorporated. In other words, the efficiency of spray deposition of the oxides of these elements was less than that for cadmium oxide. Phosphorus also appeared to exhibit a low degree of incorporation, although the ICP analysis for this element was erratic due to interference from other lines. On the other hand, the conductivity data given below indicates that the phosphorus content of the film probably varies with the solution content. Consequently, a more sensitive analytical technique is required to demonstrate this variation. At any rate, these analytical techniques are sufficient to indicate that the extent of incorporation of these three elements into CdO films by spray pyrolysis was low relative to the solution content.

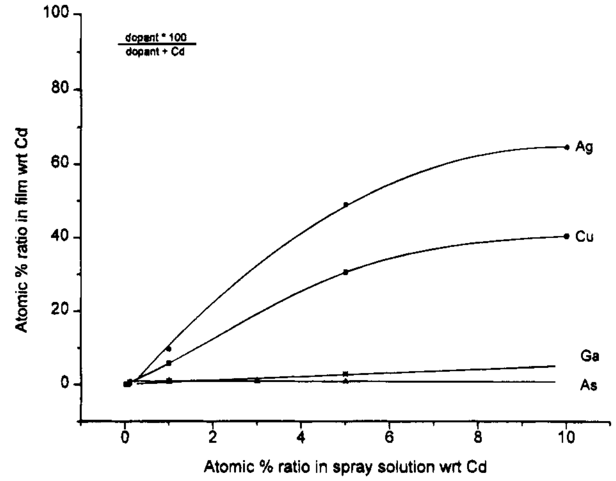

Figure 1. Impurity content in CdTe films in relation to the impurity content in the spray pyrolysis solution. The films were all deposited under the same spray pyrolysis conditions; see text. The content is reported as a percentage of the cadmium content.

It was interesting to note that conversion from oxide to telluride caused a measurable increase in the Ga content (3.0 to 4.6% with respect to cadmium) and a decrease in the As content (1.0 to 0.3% with respect to cadmium). In other words, during the tellurium reaction, the gallium was less volatile than the cadmium and arsenic.

Preferential incorporation was observed for Ag and Cu, indicating that the spray deposition of their oxides was more efficient in comparison to cadmium oxide. These results can be seen in Figure 1 along with those for As and Ga. In this figure, the composition is presented as a percentage of the total metal content in both the film and the solution. As can be seen, the deposition of the oxide of silver is more efficient than that of the copper. It should be noted that the telluride film containing the largest amount of silver was not completely converted to the telluride. However, the conclusion concerning the efficiency of deposition is still valid.

Higher concentrations of silver in the spray solution produced films with nodules which may be localized concentration of Ag_2Te. These nodules were visible in the scanning electron micrographs of these films (Figure 2) as well as in a stereo microscope. They occurred with some regularity on the films and were approximately 30 μm in diameter. X-ray diffraction analysis of the film containing 5% Ag in the initial spray solution showed characteristic Ag_2Te peaks at d spacings of 2.146, 2.325, and 2.887 Å (literature value at 2.141, 2.323, and 2.880 Å).[26] A large peak at 3.855 Å may be due to CdTe (3.74 Å). Nodule formation was observed when the concentration of silver in the initial spray solution was greater than 1% of the cadmium content. Nodule formation also occurred for copper at approximately the same solution concentration.

$CdCl_2$ Annealing. Heat treatment of the CdTe film with a thin coating of $CdCl_2$ is known to increase the efficiency of the solar cells. Although the mechanism is not fully understood, it is believed to cause grain growth, reduced leakage current and cause a change in carrier transport mechanism.[22] Two sets of films were

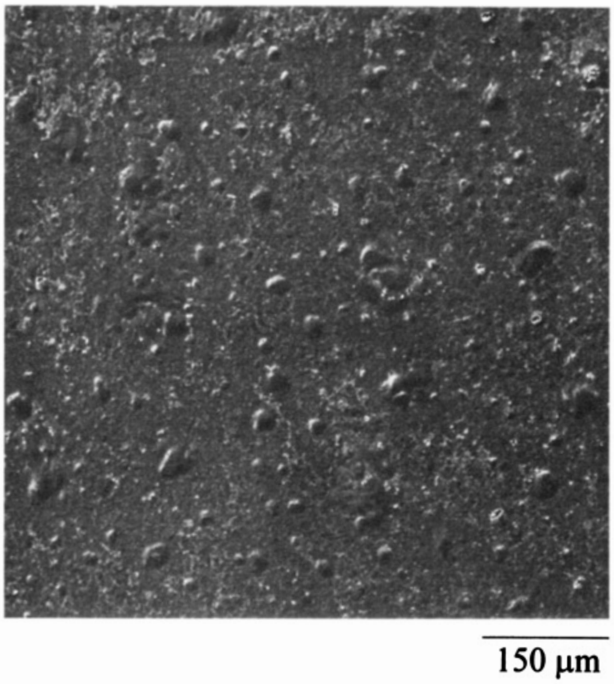

Figure 2. SEM picture of CdTe film prepared from a spray solution containing 5% $AgNO_3$ relative to $Cd(NO_3)_2$. The scale is indicated below the picture, and nodules approximately 30 μm in diameter are apparent.

annealed using $CdCl_2$ according to the method described by other workers.[21,22] One set was undoped CdTe, and the other was doped with 0.01% copper. Scanning electron microscope analysis was used to monitor any differences in the morphology of the CdTe films before and after annealing. Prior to annealing, the films contained a mixture of very small crystals and larger crystals of about 1 μm. Upon annealing, the smaller crystals appeared to coalesce into larger groupings of approximately 1 μm diameter. Consequently, treatment with $CdCl_2$ increased the size of the small crystals or incorporated the smaller crystals into adjoining crystals but did not affect the size of the larger ones appreciably.

Carrier Transport Properties. Generally, it is difficult to control the conductivity of p-type thin-film CdTe by intentional doping because of the formation of compensating complexes. Nevetheless, doping by means of the spray pyrolysis technique was explored to determine its effectiveness in altering the carrier-transport properties of thin-film CdTe. For this purpose, Hall effect and resistivity measurements were carried out on undoped, doped, and annealed CdTe films. It was not always possible to measure the Hall effect because some of the films had very low carrier mobility due to impurity scattering. In all cases where the majority carrier type could be determined, the undoped and doped films were p-type films. This included acceptor dopants such As, P, Au, Cu and Ag, and was consistent with previous work.[27-38]

Undoped CdTe prepared by our method had resistivity values that were typically 10^7-10^8 Ω cm, but in some cases the value was as low as 10^3 Ω cm. Films exhibiting lower resistivity probably contained excess Te because annealing them raised the value to 10^7-10^8 Ω cm instead of causing the expected decrease due to increased crystallite size. A similar effect of heat treatment on the resistivity of CdTe films was attributed to removal of excess Te.[19] The effect of Te on resistivity varies with the method of incorporation. When Te was incorporated by coevaporation of CdTe and Te, variation of the Te vapor content was found to lower the resistivity from 10^6 to <50 Ω cm.[39] Similarly, a change from 100 to less than 1.0 Ω cm was caused by varying the substrate temperature using this method.[40] On the other hand, the same approach showed no effect on resistivity, which remained constant at about 5×10^6 Ω cm over a range of Te vapor content.[36] It is interesting that coevaporation of CdTe and Te could give such a wide range of resistivities by controlling the Te content of the vapor. In contrast, increasing the Te vapor content seemed to have no effect on the resistivity when CdTe was prepared by CVD of elemental Cd and Te.[6] Other workers achieved CdTe resistivities of 10^2-10^4 Ω cm using excess Te.[36,41] Consequently, the nature of the effect of excess Te on resistivity varied even when the same preparation technique was employed. Likewise, it seems unlikely that doping with Te by our method would be effecive because reproducibility is difficult to achieve.

The effect of adding As and P to the CdTe film is illustrated in Figure 3. The resistivity of As- and P-doped CdTe were both lowered to a minimum resistivity value of 10^3 Ω cm for a solution composition of 0.01% dopant. The resistivity then increased at higher dopant content to a level similar to undoped CdTe. Alnajjar et al.[34] obtained films with resistivities of 2 Ω cm after an 8 day treatment of CdTe single crystals with H_3PO_4 vapor at temperatures ranging between 400 and 550° C. Even lower values could be obtained in an open furnace; however, this effect appeared to be due to impurities in the furnace. There appear to be no reports of P-doped thin-film CdTe.

Chu et al.[30] found only a 10-fold reduction in the resistivity of CdTe films when they were doped with As during film formation by means of metalorganic chemical vapor deposition (MOCVD). A similar behavior was observed when thin-film CdTe was prepared on GaAs by metalorganic vapor-phase epitaxy, although the starting resistivity was substantially lower in this case.[11] Thus, our method seems more effective for this

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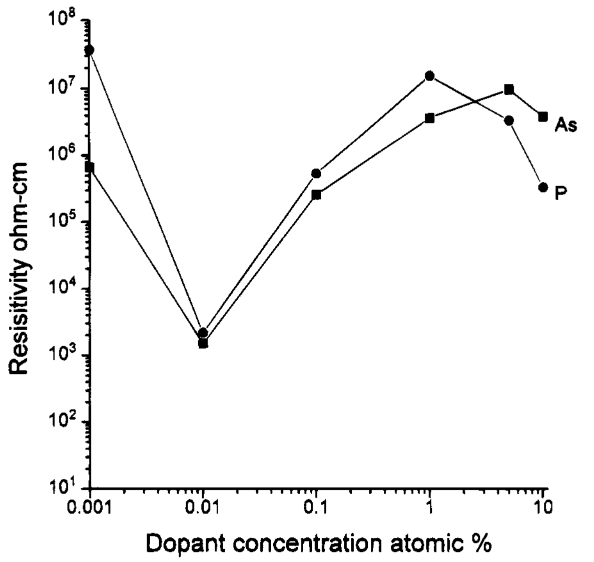

Figure 3. Resistivity of CdTe films as a function of the content of As and P in the spray solution. The atomic percent is relative to the amount of cadmium in the solution.

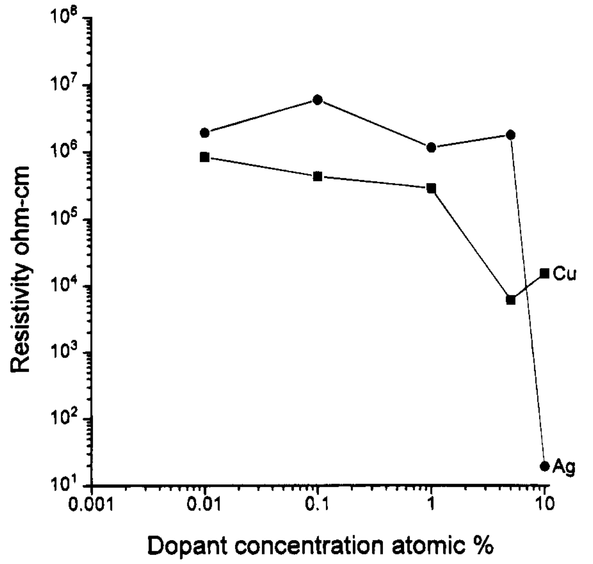

Figure 4. Resistivity of CdTe films as a function of the content of Ag and Cu in the spray solution. The atomic percent is relative to the amount of cadmium in the solution.

dopant. On the other hand, the MOCVD method[28] appeared to be effective for incorporation of Sb. Antimony reduced the resistivity to a minimum value of 200 Ω cm for a dopant concentration of 10^{19} cm^{-3}, and the dependence on dopant content followed a behavior similar to that in Figure 3 for As and P. In our experiments, antimony oxide had a solubility in water that was too low to affect the resistivity. Consequently, a comparison is not possible. At any rate, the minimum resistivity of our As and P doped films is within a factor of 7−10 of the lowest values obtained by others for As and Sb.

For Ag and Cu, the resistivity was not altered significantly at low additive content (Figure 4), but there was an abrupt decrease at high additive content. However, in this case, the film could no longer be considered to be predominantly CdTe. It is possible that these films consist of domains of Ag_2Te and Cu_2Te, which are very conductive small bandgap materials.[42] Chamonal et al. identified Cu and Ag as occupying Cd sites;[33] however, in their research, resistivities were not reported. Nishitami et al.[36] obtained a reduction of resistivity of CdTe from 10^6 Ω cm to 10^3−10^5 Ω cm after doping with Cu. One of the reasons for using our method was the expectation that the dopant would be uniformly dispersed through the film and a gradient would be avoided. However, as discussed above, it is possible that segregation occurs when large amounts of impurity are preferentially incorporated.

The effect of additive on hole density mirrored the effect on the resistivity. When the resistivity decreased, the hole density increased by a somewhat larger factor because the mobiltiy decreased. The carrier concentration varied from 10^9 to 10^{14} cm^{-3}, while the mobilities varied from 20 to about 0.5 cm^2 V^{-1} s^{-1}. The decrease in mobility with increased carrier density is due to increased scattering by the higher density of impurities. It is interesting to compare the carrier densities obtained by other methods. Incorporation of antimony by the MOCVD method[28] resulted in a carrier density of 10^{19} cm^{-3} when the resistivity reached a minimum of 200 Ω cm, indicating a mobility of 3×10^{-3} cm^2 V^{-1} s^{-1}. The incorporation of P into single-crystal CdTe resulted in hole densities around 10^{16} cm^{-3} with mobilities of 7 cm^2 V^{-1} s^{-1}. Apparently, impurity scattering in the P doped single crystal is comparable to our films, whereas it is much higher in the films that were doped with As by MOCVD.

Heat treatment of undoped CdTe films coated with a very thin layer of $CdCl_2$ had a moderate but real effect on the resistivity. The four films treated in this manner were more conductive than the untreated, undoped film. In each case, the resistivity decreased by at least a factor of 10. This change was due to an increase in hole density by more than this factor because the Hall mobility decreased. Although the crystallite size appeared to increase as a result of this treatment, this increase cannot account completely for the observed behavior. The increase in hole density is consistent with a decrease in grain boundary state density; however, it should be accompanied by an increase in hole mobility not a decrease.[24] Although Cl often acts as a donor, it can also form acceptor-like complexes, which could account for the increase in hole density. Oxygen is known to act as an acceptor; however, the amount of oxygen in the nitrogen annealing ambient would be quite low.

Conclusions

The efficiency of the spray deposition depends critically on a number of parameters associated with the spray system. For 0.1 M $Cd(NO_3)_2$, a spray duration of 15 min over a substrate surface of 2.5 × 5.0 cm resulted in a deposition efficiency of 25%, which compares favorably with other spray methods. The films were of uniform thickness within these limits. However, to obtain films of desired thickness reproducibly, periodic recalibration of the system is necessary.

The reaction period required for complete conversion of CdS to CdTe increases as the film thickness increases. It is possible that no sulfur remained because the sulfur content is very close to the limit of detection of 0.1%.

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When the conversion was incomplete, almost complete removal of sulfur from the partially converted films was achieved by annealing. The thickness increased by about a factor of 2 upon conversion from CdO to CdTe.

Any impurity added to the spray solution was incorporated into the CdO film and, subsequently, into the final CdTe film. Impurities such as Ga, Cu, Ag, and As could be incorporated into CdO in appreciable quantities. The presence of P was inferred from alteration of the carrier transport properties. The extent to which the impurities were incorporated into the film depended on their nature. The behavior ranged from a very low degree of incorporation for As, Ga, and P to preferential incorporation of Ag and Cu.

One interesting consequence of introducing additives in the spray solution was that the thickness of the resultant CdO film increased as a function of additive concentration. The extent of the increase depended on the nature of the additive. It would appear that the presence of small amounts of these additives are effective in increasing the efficiency of the spray process.

Undoped CdTe prepared by this method had resistivity values that were typically 10^7-10^8 Ω cm. The resistivity of As and P doped CdTe were both lowered to a minimum resistivity value of 10^3 Ω cm. For Ag and Cu, the resistivity was not altered significantly at low additive content, but there was an abrupt decrease at high additive content. However, in this case, the film could no longer be considered to be predominantly CdTe. The effect of additive on hole density mirrored the effect on the resistivity. When the resistivity decreased, the hole density increased by a somewhat larger factor because the mobility decreased.

Acknowledgment. This work was supported in part by a grant to M.C. from the Natural Sciences and Engineering Research Council of Canada. It is a pleasure to acknowledge contributions of Bill Teesdale of the Physics Department for the data obtained by PIXE, Graeme Spiers and Glen Wilson from Land Resource Science for ICP and XRD data, respectively, and Sandi Smith of Food Science for SEM and EDS data. We thank the reviewer for pointing out the possibility of Cl acceptor complexes.

CM9405279