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## DEPOSITION OF CdTe BY SPRAY PYROLYSIS

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We report the spray pyrolysis of thin films of CdTe which show promise as a base material for solar cell applications. The films predominately show a zinc blende structure and appear to be intrinsic. Microprobe analysis indicates an excess of cadmium but this is not detectable by X-ray diffraction or from electrical conduction measurements. Measurements indicate a nominal direct bandgap of 1.47 eV and an absorption coefficient of the order of  $10^4 \text{ cm}^{-1}$ . The room temperature electrical resistivity is of the order of  $10^7 \Omega \text{ cm}$ .

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### 1. INTRODUCTION

There is a need for the development of low cost solar cells which would permit large-scale utilization of solar energy. In order to reduce solar cell cost, it is necessary to reduce the material and device fabrication cost while maintaining a relatively high conversion efficiency. One approach is to synthesize the material in the form of thin polycrystalline films such that the device geometry is established during the growth process.

Chemical spray deposition (spray pyrolysis) is a low cost process which has recently been utilized to prepare thin polycrystalline films of a wide variety of compound semiconductors by a number of investigators<sup>1–5</sup>. Most of this pyrolysis work has been an outgrowth of initial efforts by Hill and Chamberlin<sup>6</sup> and subsequent work as reported by Chamberlin and Skarman<sup>7</sup> on II–VI compounds, principally CdS. The spray pyrolysis of these binary semiconductors involves the spraying of an aqueous solution containing soluble salts of the constituent atoms onto a heated substrate. The preparation of CdS from a solution containing CdCl<sub>2</sub> and NH<sub>2</sub>CSNH<sub>2</sub> (thiourea) has been achieved by several investigators, and various studies relative to the effects of synthesis parameters on the properties of the films have been conducted. The preparation of CdSe from a solution containing CdCl<sub>2</sub> and NH<sub>2</sub>CSeNH<sub>2</sub> (selenourea) has been accomplished, but has not received as much attention probably because of a lesser interest in CdSe as a photosensitive material.

To achieve the ultimate goal of a low cost solar cell, the low cost synthesis must be accompanied by a relatively high conversion efficiency. Based on the energy gap, CdTe is an optimal absorber material and both the CdS/CdTe heterojunction and

the CdTe p-n junction look promising in terms of their high theoretical efficiencies as solar cells<sup>8</sup>. Logically, devices utilizing polycrystalline CdTe as a base material should display relatively high conversion efficiencies, provided that grain sizes of at least 1  $\mu\text{m}$  can be achieved. As a solid state device material, there are many unanswered questions concerning doping, contacts, junction formation etc. However, the same situation existed for silicon 20 years ago.

The successful synthesis of CdTe thin films through spray pyrolysis represents a first and important step towards an ultimate goal of low cost solar cells.

## 2. DEPOSITION METHOD

A reducing solution was prepared from a mixture of water, ammonium hydroxide, hydrazine and hydrochloric acid; to this, near-stoichiometric amounts of tellurium and cadmium were added in the form of  $\text{TeO}_2$  and  $\text{CdCl}_2$ . This solution was sprayed onto a heated substrate using nitrogen as the carrier gas. The substrate rested on a stainless steel surface which was heated indirectly by an electrical resistance heater. The entire apparatus was located inside a glove box which was purged with nitrogen prior to each deposition operation. The stainless steel surface temperature was monitored with thermocouples to provide a reference. The exact temperature of the substrate surface was unknown and varied as a function of the heater temperature, the spray rate and the surface coverage.

The substrates were Corning glass (7059) with dimensions of 1.9 cm  $\times$  1.9 cm  $\times$  0.16 cm or 1.27 cm  $\times$  1.9 cm  $\times$  0.16 cm. The heater temperature during deposition ranged from 425 to 500  $^\circ\text{C}$ , depending on the spray rate. Spray rates were usually of the order of 3–5 ml  $\text{min}^{-1}$ . Deposition times of 15–60 min resulted in films of thickness 2–4  $\mu\text{m}$ . Complete details of the spray apparatus as well as preliminary results have previously been reported<sup>9</sup>.

## 3. FILM CHARACTERIZATION TECHNIQUES

The primary objective of our work has been to produce polycrystalline films of intrinsic CdTe with optical and electrical properties comparable with those of the bulk material. Crystallinity, orientation and, to some extent, purity are evaluated through X-ray diffraction. Optical absorption data have been used to evaluate the energy gap, to ascertain direct transitions and to detect the presence of undesired energy states and band tailing. Photoluminescence studies on some earlier samples<sup>10</sup> have shown a spectrum similar to that for the bulk material except that the intensity was much greater. It was concluded that most of the luminescence was associated with the intergranular regions and consequently is of little value in evaluating the quality of our material. Microprobe analysis has been used to provide an indication of stoichiometry although the accuracy of these measurements is questionable.

Electrical conductivity *versus* temperature measurements have been made to provide some information on the energy gap, impurity levels and carrier transport. This report is concerned with material which has not been intentionally doped such that the samples have a small electrical conductivity. No Hall measurements have been made on these low conductance samples.

## 4. RESULTS

The X-ray diffraction results for a typical sample are shown in Fig. 1. In all cases, the material deposits in the zinc blende (cubic) structure, and there is no indication of any other crystalline material. In some samples, we have observed a tendency for the [111] direction to orient perpendicular to the substrate. This situation seems to occur when the spray rate is less than  $1 \text{ ml min}^{-1}$  and the cadmium and tellurium concentrations are 0.05 M. As with sprayed CdS<sup>11</sup>, the possibility exists for phase mixing. However, we have never observed the  $3.98 \text{ \AA}$   $d$  spacing which would be indicative of the wurtzite (hexagonal) structure.

Optical absorption measurements on four samples are shown in Fig. 2. The absorption edges are abrupt and show an absorption coefficient of the order of  $10^4 \text{ cm}^{-1}$ . Figure 3 shows plots of  $(\alpha h\nu)^2$  versus  $h\nu$ ; these indicate a direct gap of 1.44–1.46 eV. In some of the initial films, there was a tendency to get h.c.p. tellurium mixed with the CdTe when the deposition temperature was low. We have never detected elemental cadmium in any of our films.

Electrical conduction measurements versus temperature in the range 20–150 °C indicate intrinsic material with a resistivity in excess of  $10^7 \text{ \Omega cm}$ . Plots of  $\ln G$  versus

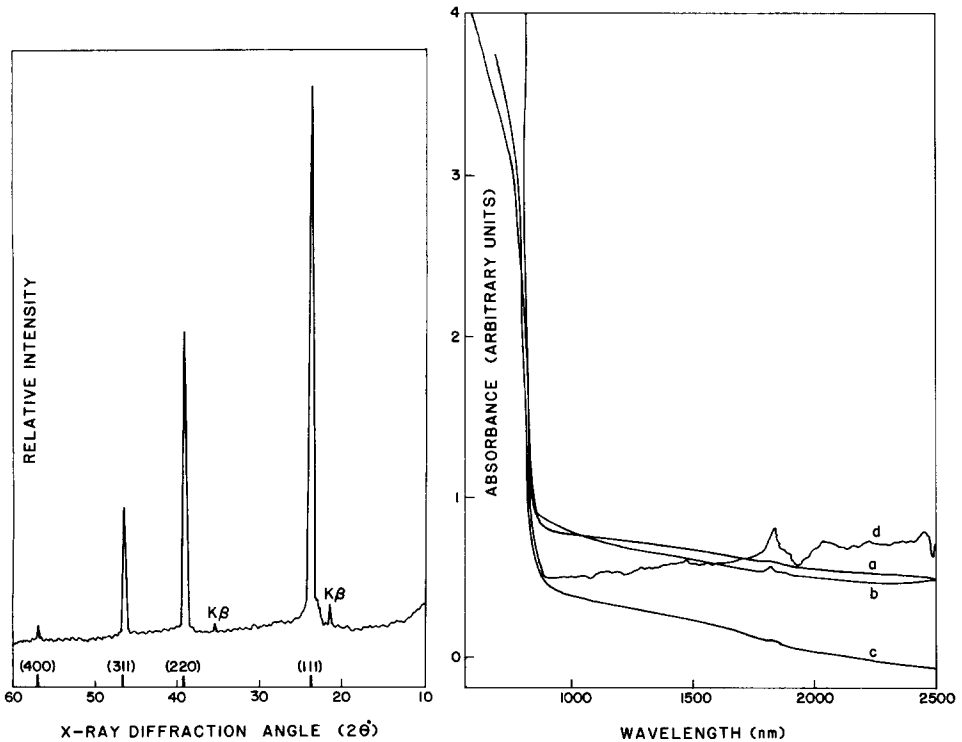


Fig. 1. Cu  $K\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) X-ray spectra of CdTe sprayed films. The peaks are at the correct location and have the proper relative magnitudes for the zinc blende structure.

Fig. 2. Absorbance vs. wavelength for four CdTe sprayed samples. The location of the absorption edge is correct for cubic CdTe and is repeatable from sample to sample.

$1000/T$  are shown in Fig. 4. The slopes of these curves indicate a band gap of 1.45–1.5 eV with an apparent absence of any intermediate states. These conductivity measurements were made using a Hewlett–Packard model 4140B picoammeter. Low temperature data were not obtainable because of the extremely large resistance of the samples.

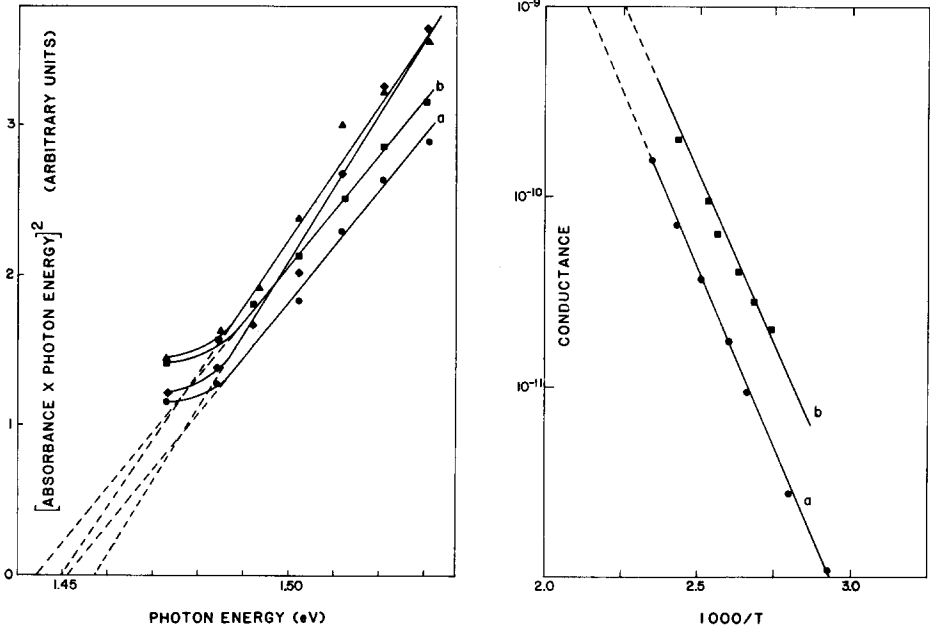


Fig. 3. A plot of  $(ah\nu)^2$  vs.  $h\nu$  for four CdTe sprayed samples. These data indicate a direct gap in the range 1.44–1.46 eV.

Fig. 4. A plot of  $\ln G (\Omega^{-1})$  vs.  $1000/T (K^{-1})$  for samples a and b. The slope indicates a thermal band gap in the range 1.45–1.5 eV. No active states within the band gap are indicated over the temperature range shown.

Microprobe analysis of our films indicates that the material is nearly stoichiometric, and the results always indicate a slight cadmium excess; however, the samples are p type which could be explained as a result of cadmium vacancies. Further analysis will be required to resolve this apparent inconsistency. Figure 5 shows the element peaks for one such microprobe test. In some thin samples, silicon and barium peaks from the substrate have been observed. No additional impurities have been detected. Figure 6 shows scanning electron micrographs of the films. These reveal an irregular surface with larger structures of the order of 10–20  $\mu\text{m}$  and smaller features which are typically 0.25–0.5  $\mu\text{m}$  in size. The larger structures are attributed to variations in the nucleation and growth rates that result from irregularities in the substrate surface. The smaller features are indicative of grain size. It does not appear likely that control of the grain size through variations in the substrate temperature is practical since the range of useful deposition temperatures is quite narrow. The spray rate does have an effect, lower spray rates resulting in smaller grains, but there is a tendency to cool the substrate as spray rates are

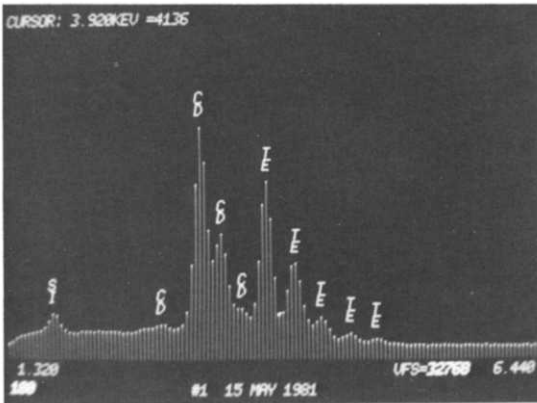


Fig. 5. A microprobe spectrum for one of the sprayed CdTe films indicating near-stoichiometric amounts of cadmium and tellurium. The silicon peak comes from the substrate.

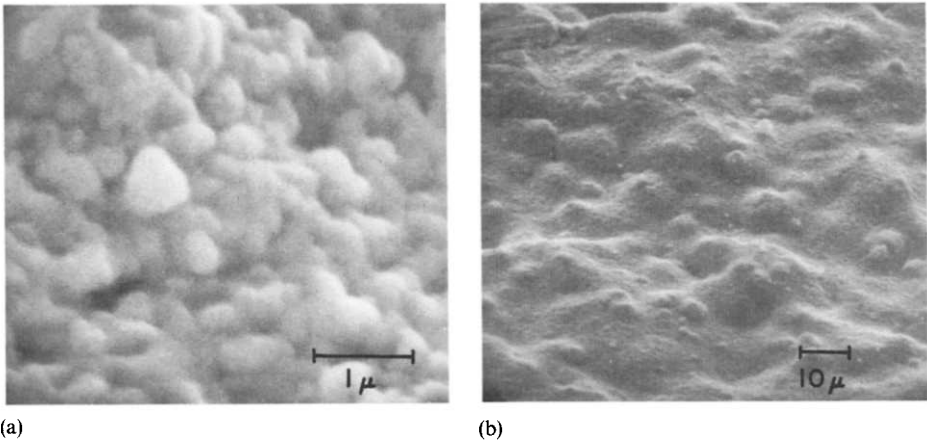


Fig. 6. Scanning electron micrographs of the sprayed CdTe film showing (a) the apparent grain size for the CdTe crystallites and (b) larger surface irregularities which reflect the substrate influence on nucleation and growth.

increased so that the films shown in Fig. 6 represent the largest grain size achieved with the present apparatus.

## 5. DISCUSSION

Spray pyrolysis of CdTe appears to be a promising approach for forming the base material for photovoltaic devices. The material produced in our laboratory is apparently near-intrinsic CdTe and can be grown rapidly without the need for special or costly equipment. The material is very photoconductive but we have no quantitative results to report. Given the proper set of parameters, films with similar properties are readily produced. Pursuant to fabricating p-n junctions or CdS/CdTe heterojunctions, it will be necessary to dope the material, preferably from solution, and to achieve film growth on a conducting substrate. Indium and phosphorus

appear to be viable candidates for n- and p-type doping<sup>12</sup>. Preliminary studies with these two elements in solution have produced an increase of about three orders of magnitude in the conductivity but these studies are incomplete. Attempts have been made to spray onto metallic substrates with little success. Copper substrates resulted in the continued formation of Cu<sub>2</sub>Te with no subsequent formation of CdTe. Marginal success has been achieved with brass substrates.

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