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Electrical and stoichiometric characteristics of CdTe films deposited by the hot-wall flash-evaporation technique

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The electrical and stoichiometric characteristics of polycrystalline CdTe films deposited by the hot-wall flash-evaporation technique are reported for different deposition parameters. The crystallites in these films grow in a columnar type of grain. The stoichiometry of the films is largely dependent on substrate (T_s) and wall temperatures (T_w) during deposition. At low values of T_s and T_w ($\sim$92 and 425 °C, respectively) a large excess of Te is present ($\sim$30 at. %). At $T_s \simeq 192$ °C and $T_w \simeq 560$ °C, nearly stoichiometric films were obtained. The electrical characteristics were strongly dependent on the amount of excess Te present in the samples. A change in the resistivity of up to seven orders of magnitude was measured between the samples with $\sim$30 at. % of excess Te and those with a stoichiometry close to 1:1. Also a large difference in the resistivity measurements was observed on the surface and across the samples for the different deposition conditions studied. The behavior of the resistivity with temperature in the 100–500 K range is also discussed.

INTRODUCTION

Cadmium telluride is a II-VI compound widely investigated because of its possible use in a large variety of applications. Among the most common of these are photovoltaic devices such as solar cells and infrared detectors.[1] The preparation of good quality CdTe thin films is of great importance for many of these applications. Several techniques have been used to fabricate CdTe films. The most common are, molecular-beam epitaxy (MBE),[2,3] close-spaced vapor transport (CSVT),[4,5] and thermal evaporation.[6] In the present work, we have used the hot-wall flash-evaporation (HWFE) technique[7] to prepare our samples. This technique is a low-cost process used to obtain good quality polycrystalline films. The CdTe films deposited by HWFE are p type. In this work, it was found that these films have an excess amount of Te which is strongly dependent on the deposition parameters such as substrate (T_s) and hot-wall temperatures (T_w). The electrical conductivity of these films changes up to seven orders of magnitude with the excess of Te present in the film. The dependence of the electrical and stoichiometric characteristics on deposition parameters as well as the behavior of the resistivity measured on the surface and across the film with temperature are also reported in this work.

EXPERIMENTAL DETAILS AND RESULTS

The CdTe films were deposited on a Pyrex glass slide with or without a conductive oxide layer. The hot-wall flash-evaporation apparatus is described in detail in previous work.[7] The technique consists of a flash evaporation of the material achieved by feeding CdTe powder to a previously heated molybdenum boat ($\sim$950 °C). The CdTe vapors reach the substrate through a cylindrical quartz wall. The substrate and wall temperatures are continuously monitored and kept at a constant value throughout the deposition process. The samples deposited on glass slides without conductive oxide coating were used for electrical measurements along the surface of the film. For this purpose, two parallel gold contacts were vacuum evaporated on the sample. The separation between these contacts was 0.3 cm and the width of each contact was 0.4 cm. In the case of electrical measurements across the film, circular gold contacts of 0.1 cm in diam were evaporated on films deposited on conductive oxide covered slides. Some samples were deposited on a glass slide coated with evaporated gold to check the effect of the contacts on the electrical characteristics of the sample. The current versus voltage characteristics of the sample were measured with a regulated power supply and a logarithmic picoammeter. The samples were placed in a commercial cryostat with a temperature controller to obtain the electrical characteristics of the films at temperatures up to room temperature. At higher temperatures, a resistance-heated

TABLE I. The substrate (T_s) and hot-wall (T_w) temperatures during deposition as well as the final film thickness are tabulated for the types of samples used in this work.

Sample	T_s (°C)	T_w (°C)	Thickness (μm)
M1	92 ± 5	425 ± 5	3.33
M2	100 ± 10	560 ± 5	1.33
M3	192 ± 5	560 ± 5	1.13

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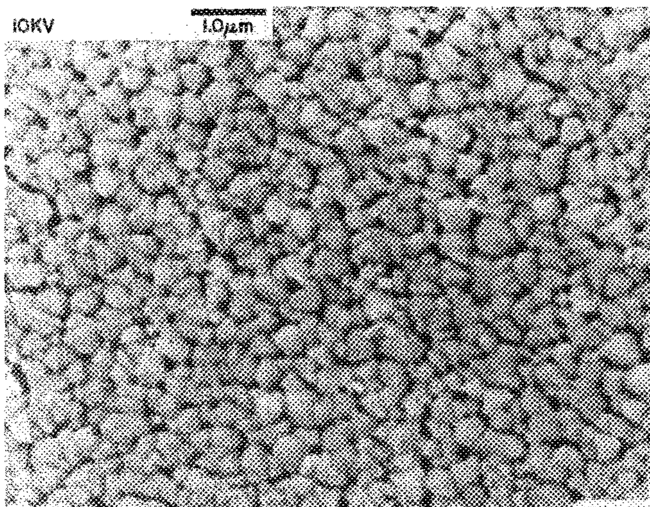

FIG. 1. Scanning-electron-microscope picture of the surface of a CdTe polycrystalline film (sample M3).

hot plate was used instead of the cryostat. The chemical composition of the films was determined with an x-ray fluorescence system adapted to a Jeol electron microscope. The measurements were calibrated with pure Cd and Te samples. The electron beam diameter was $\sim 0.1\ \mu m$. This measurement was corrected for x-ray absorption in the film.

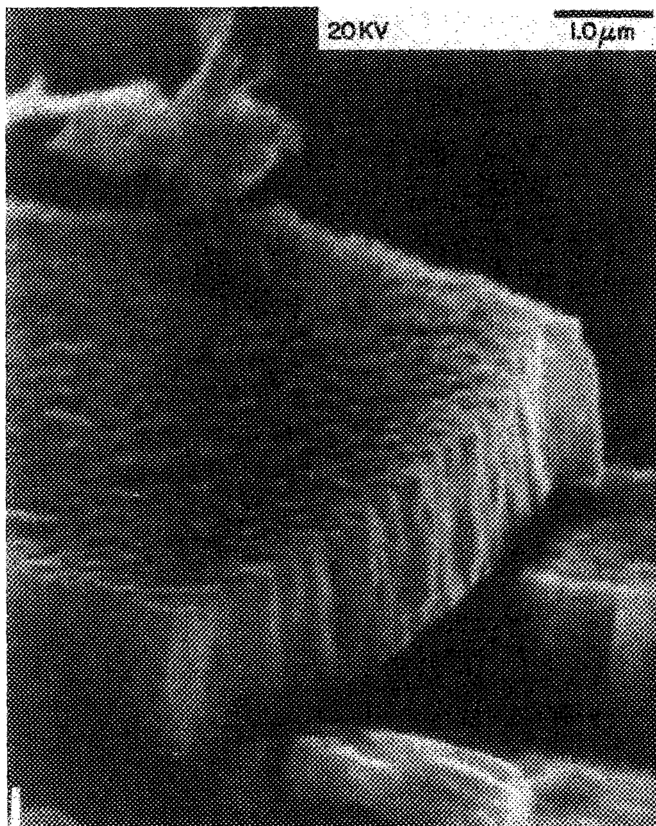

FIG. 2. Cross-section scanning-electron-microscope picture of the CdTe film shown in Fig. 1. The columnar growth of the CdTe crystallites is clearly observed in this picture.

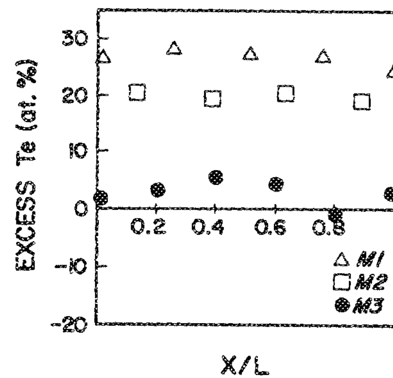

FIG. 3. Excess Te vs normalized film thickness for samples M1 (△), M2 (□) and M3 (●).

Table I summarizes the deposition conditions for the three types of samples used as well as the thickness of the films. The polycrystalline nature of the films was determined by x-ray diffraction measurements. The CdTe crystallites have a cubic structure highly oriented with the (111) direction perpendicular to the substrate surface. Figures 1 and 2 show scanning-electron-microscope pictures of the surface and cross section of sample M3. From these pictures the columnar growth of the grains is clearly observed. At lower values of T_w and T_s, the size of the grains was smaller but the columnar growth of the grains still remained. The chemical composition across the samples was performed on the cross-section geometry of the films. The profile of the excess Te versus the distance measured from the substrate and normalized to the total thickness of the film is plotted in Fig. 3 for the three types of samples studied. The excess of Te was calculated by subtracting the at. % of Cd detected from the total amount of at. % Te. The excess of Te present in the film was almost 30 at. % at low values of T_s and T_w (sample M1). As T_w was increased, the excess of Te in the film decreased (sample M2). However, when both T_s and T_w were increased a nearly stoichiometric CdTe film was obtained (sample M3).

The electrical current (I) versus voltage (V) characteristic curves of these films showed an ohmic behavior over three orders of magnitude variation in current regardless of the electrical contact geometry. The conduction type of these films was determined to be p type.[7] The maximum applied voltage was 70 V when the measurements were performed on the surface of the film and up to 2 V across the film. The resistivity (ρ) of the films was calculated from the slope of the I vs V curves using the relation: $\rho = (A/D)(V/I)$ where A was given by the thickness of the film times the width of the electrical contact and D was the separation between contacts for measurements on the surface of the film (surface ρ). In the case of measurements across the film (transversal ρ), A was determined by the area of the electrical contacts and D was given by the thickness of the film. The behavior of the resistivity with temperature (T) of all the samples studied is illustrated in Figs. 4–6 where $\ln \rho$ is plotted as a function of $1/KT$ for both geometries (K is the Boltzmann constant). No difference in the electrical characteristics measured across the film was observed between samples deposited on conductive oxide and those deposited on an evaporated gold film. Sample M1 showed no change in the resistivity with temperature. How-

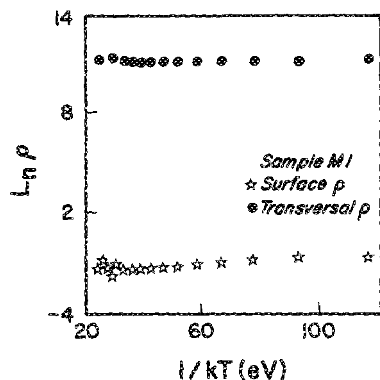

FIG. 4. The logarithm of the resistivity vs inverse of KT for sample M1. There is almost no variation of ρ with temperature and a large magnitude difference between surface and transversal ρ.

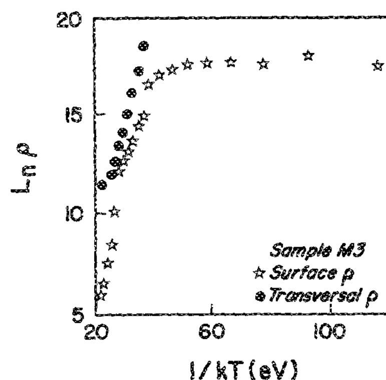

FIG. 6. The logarithm of resistivity vs inverse KT for sample M3. In this sample, surface and transversal ρ show similar behavior with temperature but a difference in magnitude exists between them.

ever, there was a large magnitude difference between the resistivity values measured across and on the film (Fig. 4). In the case of sample M2, the surface resistivity showed some dependence on the temperature, although the variation of the transversal resistivity remained small in the range of temperatures studied. Also there was an overall difference in the magnitude of both resistivities. Sample M3 (Fig. 6) showed a similar behavior with temperature for either electrical contact geometry. At large temperatures (small values of $1/KT$) ρ showed an exponential behavior with $1/KT$. However, at low temperatures a deviation towards saturation was observed.

DISCUSSION AND CONCLUSIONS

The lateral resolution of the chemical analysis technique used in this work was not good enough to determine to what extent the excess Te was segregated in the grain boundaries of the polycrystallites. However, it is very likely that at low substrate and wall temperatures (samples M1 and M2) a large amount of the excess Te is located at the grain boundaries. The excess Te present in the CdTe films grown by the HWFE technique is strongly dependent on both substrate and hot-wall temperatures as shown in Fig. 3. It was possible to change the amount of excess Te present in the films from 30 to $\lesssim 5$ at. % by increasing T_s and T_w from 365 and 698 K to 465 and 833 K, respectively. The profile of excess Te has some fluctuation across the CdTe film for the samples considered in this work (Fig. 3). Although, in some cases, at intermediate temperatures of T_s and T_w a large variation of the excess Te distribution across the films was found.

The mechanism of electrical conduction in polycrystalline semiconductor films has been addressed theoretically by several authors.[8–10] The models developed by them assume a thermionic emission of carriers through energy barriers formed at the grain boundaries.[8] If a voltage drop across the barriers is small compared with $1/KTq$; $q =$ electron charge (i.e., small grain sizes), then an ohmic behavior is predicted for the electrical current as a function of voltage.[8,9] The resistivity on the other hand, is expected to have an exponential dependence with $1/KT$ with an activation energy E_0. In these models,[8] the height of the energy barriers is assumed to be uniform throughout the entire film. The electrical characteristics of the films studied in this work present an ohmic behavior, as predicted theoretically. However, the resistivity dependence of $1/KT$ is not exponential. Samples with large amounts of excess Te have a resistivity almost independent of temperature for both geometries (sample M1). On the other hand, the resistivity of samples with small amounts of excess Te (sample M3) have an exponential behavior for low values of $1/KT$ ($\lesssim 40\ \mathrm{eV}^{-1}$), but at higher values of $1/KT$ ρ becomes almost constant (Fig. 6). In the case of sample M2 with an intermediate content of excess Te, ρ is approximately constant with $1/KT$ if measured across the film. However, for the resistivity measured on the surface of the film, the behavior was also exponential at low values of $1/KT$, and nearly independent of temperature at larger values of $1/KT$. If a linear fitting is performed to $\ln \rho$ vs $1/KT$ data at low values of $1/KT$, an activation energy of 0.73 and 0.51 eV is obtained on the surface and across the film measurements of ρ, respectively, in the case of sample M3. For sample M2, an activation energy of 0.75 eV is obtained for the surface ρ. The activation energies are close to the midgap of CdTe in all cases. The behavior of ρ in the case of sample M3 is similar to that reported for neutron transmutation-doped polycrystalline Si[9] with a doping concentration of P above $2\times 10^{15}\ \mathrm{cm}^3$. In that case, the deviation from the exponential behavior of ρ with $1/KT$ was associated with a large variety of grain-boundary barrier heights. It is possible that a similar situation is present in this case. The resistivity for sample M1 on the other hand has no dependence on the temperature. Since this sample contains a large amount of excess Te, it is possible that a considerable quantity of Te is segregated to the boundary of the grains. This phenomena could lead to a percolation type conduction mechanism through the excess Te

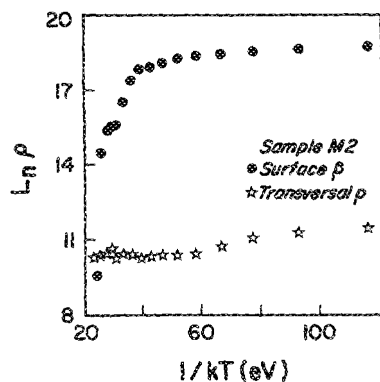

FIG. 5. The logarithm of the resistivity vs inverse KT for sample M2. In this case there is a difference in magnitude and also in the behavior with temperature between surface and transversal ρ.

at grain boundaries. In this case, low dependence on temperature of ρ would be expected. The asymmetry of the temperature dependence of ρ measured across and on the surface of sample M2 could be related to the fact that it contains less excess Te than sample M1. Then the Te at the grain boundaries might not be enough to create continuous percolation paths on the surface due to the large number of grains involved. However, across the film the probability of finding such paths is very large. The magnitude differences observed between ρ measured across and on the film for all samples might be due to the columnar growth of the CdTe crystallites.

In summary, a large dependence of the excess Te present in polycrystalline CdTe films on substrate and wall temperatures has been observed when these films are deposited by the hot-wall flash-evaporation technique. A variation of 30 to $\lesssim 5$ at. % of excess Te in the films resulted in up to seven orders of magnitude change in their resistivity. The CdTe crystallites grow in a columnar fashion giving rise to asymmetries in the electrical characteristics of the films measured across and on the surface of the samples. The current versus voltage characteristics were ohmic as predicted theoretically for the general case of conduction in semiconducting polycrystalline films. However, the behavior of ρ vs $1/KT$ is not exponential over the temperature range studied. Only for small values of $1/KT$ and low concentrations of excess Te was it possible to fit an exponential behavior with an activation energy close to that of midgap. At high concentrations of excess Te in the film, a low dependence of ρ with temperature was observed. This behavior might be associated with segregation of the excess Te to the grain boundary.

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