This section is intended for the publication of (1) brief reports which do not require the formal structure of regular journal articles, and (2) comments on items previously published in the journal.

Large grain size CdTe films grown on glass substrates at low temperature

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Polycrystalline films of CdTe were prepared by the hot wall-close-spaced vapor transport technique on Corning glass substrates at substrate temperatures below 450 °C. The thickness of the films was constant at 25 μm for all samples grown at different substrate temperatures and different gas pressures. The film thickness was found to be a function of deposition time only (5 μm per min), and virtually independent of substrate temperature and control gas pressure. The grain size was a monotonic function of film thickness, reaching 40 μm for a film thickness of 50 μm. © *1995 American Vacuum Society.*

In recent years, films of II–VI compound semiconductors have been of interest due to their applications in optoelectronics, integrated optics, and thin film solar cells. Among these semiconductors, cadmium telluride (CdTe) is an attractive candidate because, among other characteristics, it has an optimum band gap (1.5 eV) for solar energy conversion.[1,2] Hot wall-close-spaced vapor transport (HW-CSVT) is a convenient method for growing semiconductor films because it is simple and allows large grains to be obtained.[3–7] This process is very efficient as more than 90% of the evaporated source material is transported to the substrate. It is also cost-effective as it can operate at atmospheric pressure under inert gas and uses moderate temperatures; its operation is simple, and films are compact with few voids and nearly theoretical density.

Fahrenbruch *et al.*[8] reported large grain size films (up to 70 μm) in CdTe films grown on glass substrates by the CSVT method in the substrate temperature range of 480–750 °C. Chu *et al.*[9] prepared CdTe samples with large grain size ($\sim$50 μm) by using the direct combination of the elements in a gas flow system; they utilized substrate temperatures in the 500–700 °C range. Zelaya *et al.*,[3] who used a modified CSVT technique, varied their substrate temperature from 450 to 650 °C. They obtained a grain size of about 70 μm at 650 °C. In all cases a high substrate temperature was required to obtain such grain size but the thickness used by Chu *et al.* and Zelaya *et al.* is not reported. Yet, to date, large grain size has not been reported at substrate temperatures below 450 °C and at low gas pressure. In this work we have grown CdTe polycrystalline films on glass substrates, using the HW-CSVT technique as described by Zelaya *et al.*[3] Our goal was to study the influence of the deposition time, the substrate temperature (for temperatures below 450 °C), and gas pressure on the stoichiometry, crystallinity, and grain size of CdTe polycrystallites.

The system utilized in the preparation of the films has been described in Ref. 3. We prepared three families of films, keeping the source temperature constant at 600 °C in all cases. The three families were: (a) series "TIM" in which the deposition time was varied from 1.5 to 10 min, keeping the substrate temperature constant at 400 °C, and the control gas pressure at 5×10^{-5} Torr; (b) series "TMP" in which the substrate temperature was varied from 300 to 450 °C, keeping the deposition time fixed at 5 min and the gas pressure at 5×10^{-5} Torr; and (c) series "PRS" in which the control gas pressure was varied from 5×10^{-5} to 5 Torr in steps of one order of magnitude, keeping the substrate temperature at 400 °C. For groups TMP and PRS, all the film thicknesses were about 25 μm.

The thickness of the films was measured with a Dektak 3030-ST stylus profilometer. Auger electron spectroscopy (AES) analyses were performed in a Perkin-Elmer PHI-560 ESCA-SAM system. Energy dispersive spectroscopy (EDS) measurements were performed in a scanning electron microscope (JEOL JSM-3500) with an EDS attachment from EDAX. A Siemens diffractometer type D5000 with a grazing incidence attachment was used to obtain x-ray diffraction (XRD) measurements. A scanning electron microscope (SEM) JEOL JSM-3500 was utilized to measure the average grain size of the films.

Resulting films were dark gray in color, uniform in thickness, and fairly adherent to the substrate surface. The relative atomic concentration values for all the series were determined by AES and we found that the concentrations were nearly stoichiometric. The TMP series was measured by EDS in order to compare them with the Auger results. All concentrations were close to the stoichiometric expected values, in

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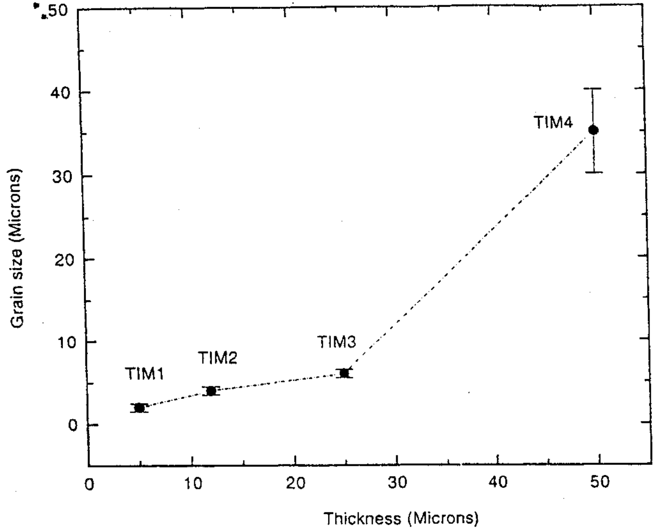


FIG. 1. Average grain size of CdTe films as a function of thickness.

good agreement with the AES results. The XRD patterns measured on the films have peaks corresponding to planes of CdTe in the cubic phase, whereas peak heights show a markedly preferential growth of film crystallites toward the (111) plane parallel to the substrate. For series TIM we obtained a different thickness for each film. In Fig. 1 we show the variation of the average grain size with the thickness of these films. It shows that the grain size increases from about 2 to 35 μm when the thickness increases from 5 to 50 μm. A very steep increase in the average grain size is noted from 25 to 50 μm thickness. Figure 2 shows average grain size as a function of substrate temperature for the series TMP. The error bar in each point represents one standard deviation of all the measured grain diameters for that sample. Typically, the central area of the films presented larger grains, by a factor of about 2, than the edges. For the series PRS, the average grain size remains constant at about 6 μm. The Dektak profile of all films was fairly uniform, having an average thickness of about 25 μm and variations between 23 and 27 μm. Typical SEM photographs of samples TIM2 and TIM4 are shown in Fig. 3. It is possible to observe that the grains of the films grown with a thickness of 50 μm (sample TIM4) appear in a large variety of orientations.

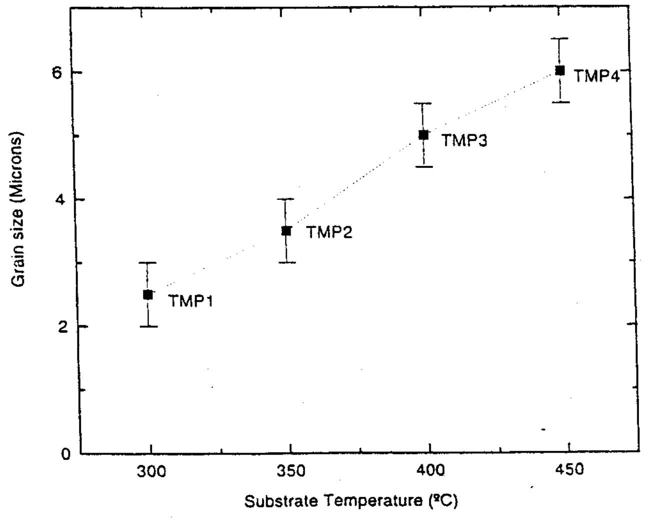
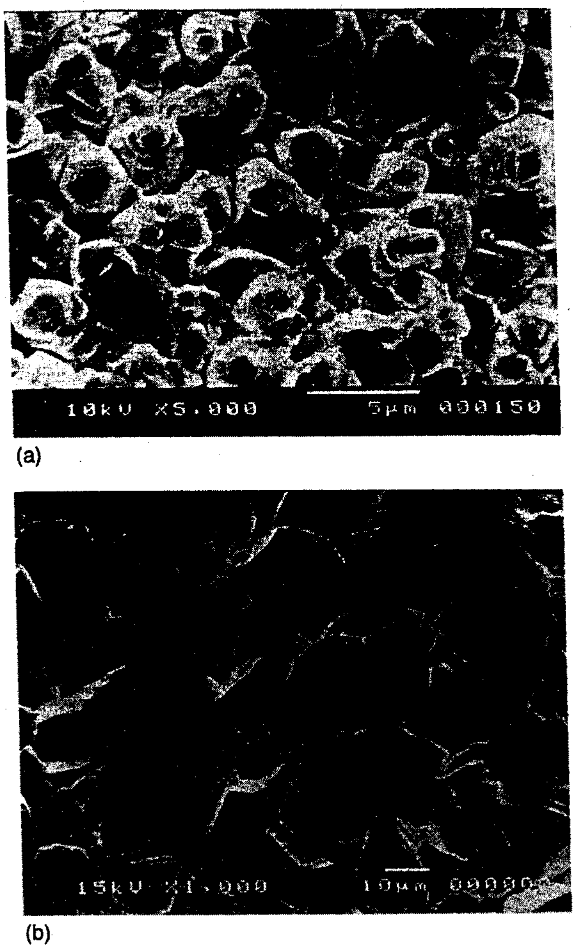


FIG. 2. Average grain size of CdTe films as a function of substrate temperature.



(a)

(b)

FIG. 3. SEM micrographs of (a) sample TIM2 and (b) sample TIM4.

For our samples prepared by varying the gas pressures from 5×10^{-5} to 5 Torr, the average grain sizes were constant; this result is different from that reported by Zelaya *et al.*[3] who obtained a variation of grain size as a function of gas pressure. This difference could be due to the fact that we obtained the same thickness in the films and Zelaya *et al.* did not report the thickness and, as we can see in Fig. 1, this is an important parameter of the grain size. In Ref. 7 Zelaya and co-workers reported nearly stoichiometric CdTe films for high pressure and $T_{su}>500$ °C; we found that the films are still nearly stoichiometric for low pressure and low substrate temperature between 300 and 450 °C. Cárdenas *et al.*[6] reported poor crystalline quality for films grown with a temperature gradient $\Delta T=T_{so}-T_{su}=300$ °C using the same technique. In our work, we find that the films grown with ΔT have good crystalline quality. For the series TIM, we maintained the deposition rate at 5 μm per min and, to obtain different grain sizes, we employed deposition times of 1.5–10 min. At 1.5 min we obtained a grain size of about 5 μm and for 10 min we obtained a grain size of about 40 μm, as shown in Fig. 1. The increase of grain size with the thickness may be explained using the Langmuir's model for free evaporation. The sublimation rate of the CdTe in this model[10] is very rapid ($\sim 2.5\times10^{-3}$ g cm^{-2} min^{-1}). This high sublimation rate causes a high number of vapor atoms of Cd and Te and consequently a lower number of collisions of the vapor Cd and Te atoms with the control gas, which permits them to arrive at the substrate with higher kinetic energy. This mean that the mobility of the adsorbed molecules at the substrate is high enough to favor growth in a reduced number of centers and, with this, large grain size—nearly 40 μm.

From the measurements obtained on three sets of CdTe films deposited using HW-CSVT onto glass substrates, series TIM, TMP, and PRS, we can conclude the following. All films present a polycrystalline structure, zinc-blende type, with a preferential orientation toward the (111) plane parallel to the surface. All films grow with the stochiometry of CdTe as measured by AES, EDS, and XRD. The average grain size of the films increases as a function of deposition time from 2 μm at 1.5 min up to 40 μm at 10 min, and as a function of substrate temperature from 2 μm at 300 °C up to 6 μm at 450 °C, showing a linear increase. For the series TMP and PRS all films were uniform in thickness with average values of 25 μm. The control gas pressure in the chamber apparently did not influence the stoichiometry, structure, or grain size of the films.

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