

The growth of CdTe thin film by close space sublimation system

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The effects of source and substrate temperature, ambient gas pressure and the separation between source and substrate on the growth rate of CdTe using the close space sublimation (CSS) system have been investigated. The growth rate increased as the source temperature increased with an activation energy of 1.9 eV and it was constant and independent of the substrate temperature, up to some breakpoint temperature, above which the rate decreased rapidly to zero. Free sublimation and transport is involved at low pressures such as 7.5×10^{-5} mbar, whereas diffusion-limited transport was involved at pressures of 2 and 6 mbar of N_2 . The growth rate increased as the separation between the source and the substrate decreased. The film's grain size increased from $<1 \mu\text{m}$ at 335 °C to more than $2.5 \mu\text{m}$ at above 445 °C. Analysis of the XRD traces indicated that the films grown at 335 °C were a highly preferred (111) orientation and the (111) texture coefficient reduced when the substrate temperature increased.

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1 Introduction

A common feature of all the most efficient laboratory scale CdS/CdTe cells has been the use of close space sublimation (CSS) [1, 2] to deposit the CdTe layer. The technique was first suggested by Nicoll in 1963 [3] for the heteroepitaxial growth of GaAs on Ge and is characterised by placing the source very close to the substrate. The growth rate depends on several interrelated parameters: the temperatures of the source T_{so} and the substrate T_{sub} , the separation between the source and the substrate, and the pressure, temperature and composition of gases in the deposition chamber.

Depending on the pressure, the deposition of CdTe by CSS may be described by either diffusion-limited transport or by Langmuir's expression for free sublimation. In the diffusion-limited transport model the Cd atoms and Te_2 molecules migrating to the substrate diffuse through the ambient gas, colliding several times with gas molecules before they condense on the substrate. According to this model, the deposition rate is an inverse function of gas pressure and is directly proportional to the exponential factor $\exp(-E_a/kT_{\text{so}})$, i.e. thermally activated with activation energy E_a , k is the Boltzmann constant. In the Langmuir theory, the Cd atoms and Te_2 molecules move directly to the substrate without any gas-phase collisions. The sublimation rate according to this theory is independent of the gas pressure, but is still proportional to $\exp(-E_a/kT_{\text{so}})$.

In this paper we shall investigate the effects of source and substrate temperature, ambient gas pressure and the separation between source and substrate on the growth rate of CdTe in a CSS system. The effects of substrate temperature on the orientation and grain size of CdTe films are investigated by X-ray diffraction and scanning electron microscopy.

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2 Experimental

The close space sublimation system used in the present study consisted of two heated graphite blocks, one containing the CdTe source material, the other the substrates. Initially the source and substrate blocks were heated by quartz-halogen lamps under the control of two Eurotherm programmable temperature controllers. Subsequently, the optical heating was replaced by Mo wire filament heaters embedded within the graphite. Temperatures were measured using type K thermocouples inserted into the graphite blocks. The entire assembly was housed in a turbo-pumped vacuum chamber capable of base pressures of $\sim 10^{-6}$ mbar.

The CdTe source was covered by a baffle to prevent the ejection of CdTe particles from the source onto the substrate. The baffle consisted of two stainless steel plates with non-overlapping arrays of holes drilled into them, such that there was no direct line-of-sight between the source material and the substrate. The separation between the source and the substrate could be varied up to 11 mm.

The substrates consisted of TCO-coated glass onto which ~ 100 – 150 nm of CdS had been previously deposited by vacuum evaporation. The substrates were loaded into the CSS evaporator immediately after deposition of the CdS and without any further processing.

3 Results

3.1 Effect of source temperature on growth rate

Several layers of CdTe were deposited by CSS at different source temperatures between 873 K and 958 K. The substrate temperature was maintained at 773 K and the chamber vacuum was maintained at around 7.5×10^{-5} mbar during the deposition. Layer thickness was measured by a Tencor α -step 200 surface profiler at the centre of the film. The growth rate increased from 1.1 $\mu\text{m}/\text{min}$ at 915 K to 3.3 $\mu\text{m}/\text{min}$ at 958 K indicating that the growth rate (R) depends strongly on source temperature. Plotting the data as $\log(R)$ versus $1/T$, as shown in Fig. 1, gives a straight line and suggests that the deposition rate may be expressed in terms of an Arrhenius equation: [4]

$$R = R_0 \exp(-\Delta E_a/kT_{so}), \quad (1)$$

where R_0 is a constant. The slope of the line in Fig. 1 gives a value for the activation energy of 1.9 eV, comparable with values reported Sosa et al. [5] of (1.9 ± 0.1) at 4×10^{-4} Torr, Fahrenbruch et al. [6] and Saraie et al. [7] of (1.8 eV) and Mitchell et al. [8] of 1.83 eV at 1 atm of H_2 .

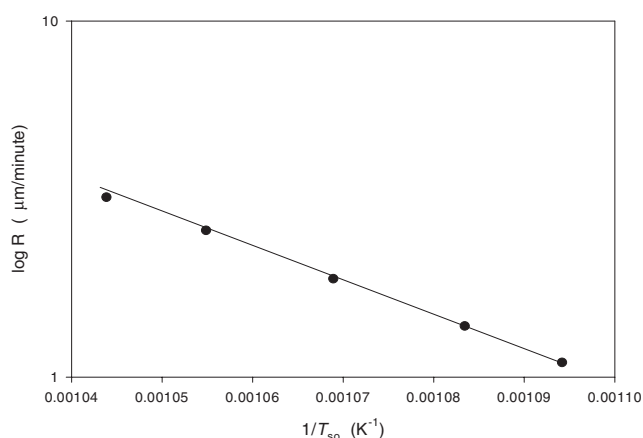


Fig. 1 $\log R$ versus $1/\text{source temperature}$ at 500°C substrate temperature.

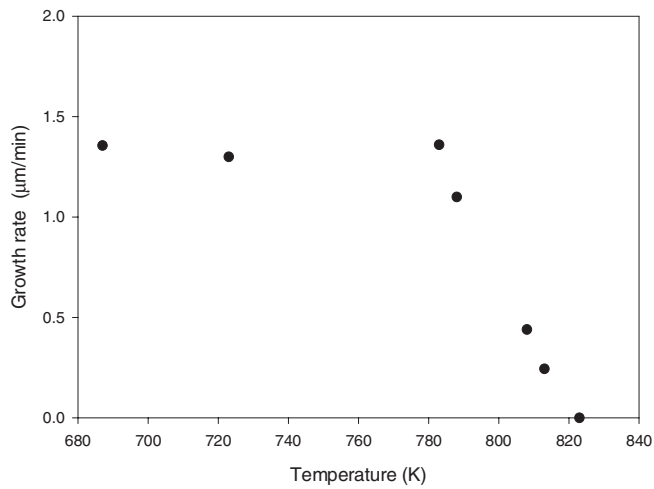


Fig. 2 Growth rate versus substrate temperature at 650 °C source temperature and 7.5×10^{-5} mbar.

3.2 Effect of substrate temperature on growth rate

Layers of CdTe were also deposited at different substrate temperatures between 687 K and 823 K. The source temperature was maintained at 923 K and the chamber was maintained at a pressure of 7.5×10^{-5} mbar during growth. Figure 2 shows the dependence of the growth rate on the substrate tem-

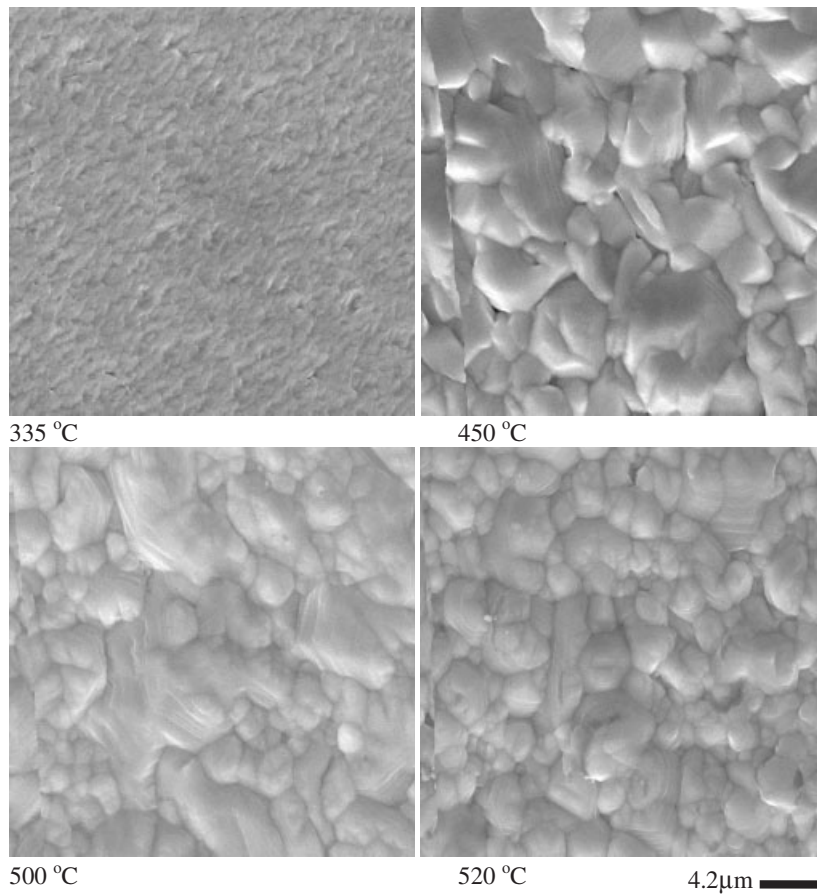


Fig. 3 Scanning electron microscopy images of CdTe films deposited at different substrate temperatures and 7.5×10^{-5} mbar of air.

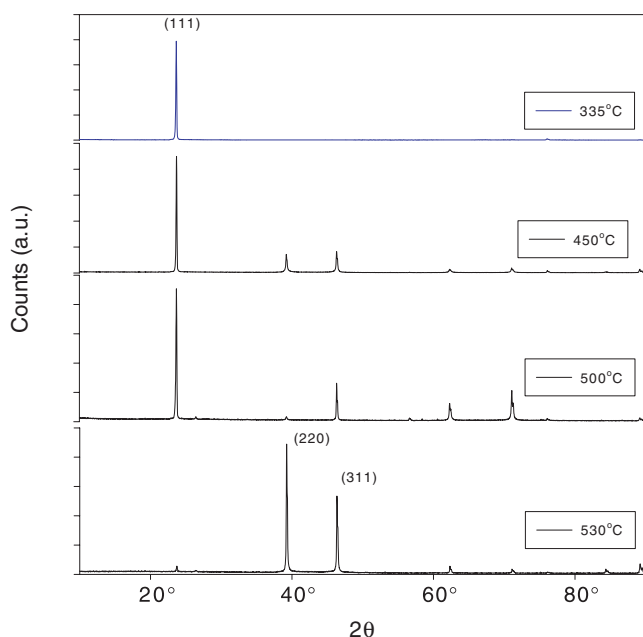


Fig. 4 (online colour at: www.interscience.wiley.com) XRD trace of CdTe films deposited at different substrate temperatures in 7.5×10^{-5} mbar of air.

perature. The results show that the growth rate was constant (i.e. independent of temperature) up to some characteristic breakpoint temperature, above which the rate decreased rapidly to zero. Below this breakpoint temperature, where the growth rate was temperature independent, growth was limited by the supply of Cd and Te₂ vapours. Above the breakpoint temperature the growth was limited by surface-kinetic processes of adsorption, compound formation and evaporation. As the temperature was increased beyond this point, the evaporation losses become increasingly dominant, until virtually no growth occurred at all.

Figure 3 shows the scanning electron microscope images for some CdTe films deposited at a variety of substrate temperatures from the lowest attainable substrate temperature of 335 °C, to 520 °C, close to the upper limited of deposition (Fig. 2). The colour of the film deposited at 335 °C appeared to be blacker than the other films that had a blue tint. From Fig. 3 it is clear that the grain sizes of the layer deposited at 335 °C were very much smaller (<1 μm) than for the other layers (>2.5 μm). The SEM images indicate a progressive reduction in grain size in the temperature-dependent part of the growth-rate characteristic (i.e. $T_{\text{sub}} \geq 780$ K). In particular there were fewer very large grains and the grain size distribution was narrower. Terracancy is also more evident on the layers grown at higher substrate temperature. These results suggest that above the breakpoint temperature (~780 K) growth was more self-limiting.

X-ray diffraction traces for CdTe films deposited at 7.5×10^{-5} mbar are illustrated in Fig. 4. At 335 °C substrate temperature only a single sharp (111) peak was found, indicating that all the grains were oriented along the (111). Preferred ordering in a thin film may be identified using Harris analysis. This compares the observed relative peak intensities in the X-ray trace with those expected from a powder (assumed to be fully random) to give the texture coefficient, i.e. the probability that a given plane is parallel to the substrate. The texture coefficient is given by [9]:

$$\text{TC}(hkl) = \frac{I/I_0(hkl)}{(1/N) \sum_N I/I_0(hkl)} \quad (2)$$

where N is the number of diffraction peaks (reflections) expected in the XRD diffraction pattern from a random powder sample, $I_0(hkl)$ is the intensity of the hkl peak from a random powder, $I(hkl)$ is the measured intensity of the same peak from the layer. If the $\text{TC}(hkl)$ is equal to the number of peaks expected

Table 1 The texture coefficient of CdTe layers deposited in 7.5×10^{-5} mbar of air.

substrate temperature	111	220	311	331	400	422	440	511	531	σ
335 °C	9	—	—	—	—	—	—	—	—	2.8
450 °C	4.8	1.3	2.9	—	—	—	—	—	—	1.64
500 °C	1.6	—	1.5	2.2	—	3.7	—	—	—	1.3
530 °C	—	2.6	3.17	—	—	—	—	—	3.17	1.3

(N) all the grains of the films are oriented in the (hkl) direction. A $TC(hkl)$ value of unity indicates a random grain orientation, whereas $TC(hkl)$ larger than unity implies that the (hkl) planes are preferentially oriented parallel to the substrate plane.

Unification may be obtained by calculating the standard deviation [10]:

$$\sigma = \left[\frac{\sum_N \{TC(hkl) - TC_R(hkl)\}^2}{N} \right]^{1/2}, \quad (3)$$

where the $TC_R(hkl)$ is the value for a randomly oriented sample, i.e. unity. Values of standard deviation, σ , close to zero indicate the absence of order.

The (111) texture coefficient reduced to zero as the substrate temperature was increased as recorded in Table 1. Values of σ confirm the loss of ordering with increasing substrate temperature. A reduction in the (111) peak intensity and increased intensities of the (220), (311) and (440) peaks after annealing of electrodeposited CdTe films has also been reported by Morris and Das [11, 12] and by Bin Qi et al. [13].

3.3 Effect of the pressure on growth rate

To investigate the effects of pressure on growth rate, CdTe thin films were deposited at different pressures of ambient gas. These latter depositions were carried out using the embedded filament heating. In particular, films were grown in 6 mbar and 2 mbar of N_2 at a source temperature of 700 °C. The growth rate data is shown in Fig. 5. In all cases the growth followed the same general behaviour observed for high vacuum grown layers i.e. temperature-independent growth at temperatures below some threshold, and a rapid decrease in growth rate at higher temperatures. However, the growth rate values and threshold temperatures differ quite substantially. The growth rate at 7.5×10^{-5} mbar was $\sim 1.35 \mu\text{m}/\text{min}$ up to

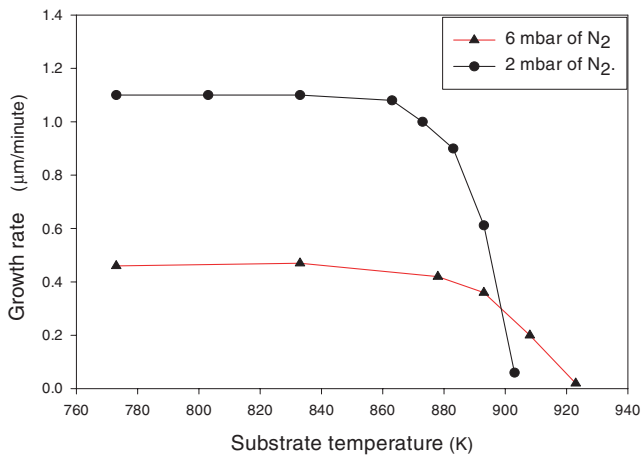


Fig. 5 (online colour at: www.interscience.wiley.com) Growth rate versus substrate temperature at 2 mbar and 6 mbar of N_2 .

783 K, above which it reduced rapidly to zero at 822 K. Figure 5 shows that the introduction of 2 mbar N_2 suppressed the growth rate to $\sim 1.1 \mu\text{m}/\text{min}$, increasing the ambient pressure further to 6 mbar reduced the growth rate even further to $0.47 \mu\text{m}/\text{min}$. However, the threshold temperature was only slightly increased from $\sim 863 \text{ K}$ to 877 K .

3.4 Effect of source–substrate separation on growth rate

The effects of too small a separation between the substrate and the source was apparent when the pattern of baffle holes was reproduced on the CdTe film. Parts of the film, located directly above a baffle hole were darker in colour, indicating that this area was thicker than other parts of layer (i.e. not located above holes in the baffle). Figure 6a shows the thickness of the peak is around $72.7 \mu\text{m}$ at when the substrate was placed directly on the baffle. The reduction in layers thickness is shown in Figs. 6b, c, d, and f at separation distances of 1, 2, 3, 8 and 11 mm, respectively, and summarised in Fig. 7. The peak growth rate (i.e. above the hole) also reduces as the separation between the substrate and the baffle (source) increases [14] as shown in Fig. 7. Interestingly there is an abrupt change in the slope at a separation of $\sim 3 \text{ mm}$, suggesting a change in the deposition mechanism.

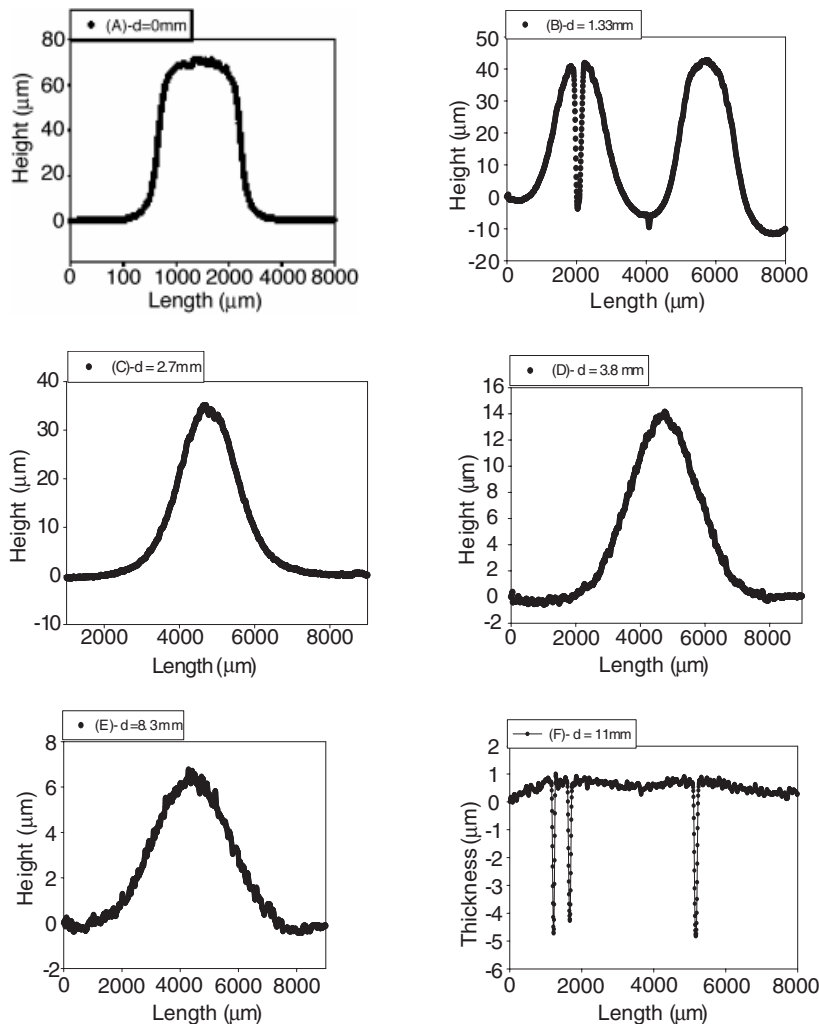


Fig. 6 Film thickness as function of separation between the baffle and substrate.

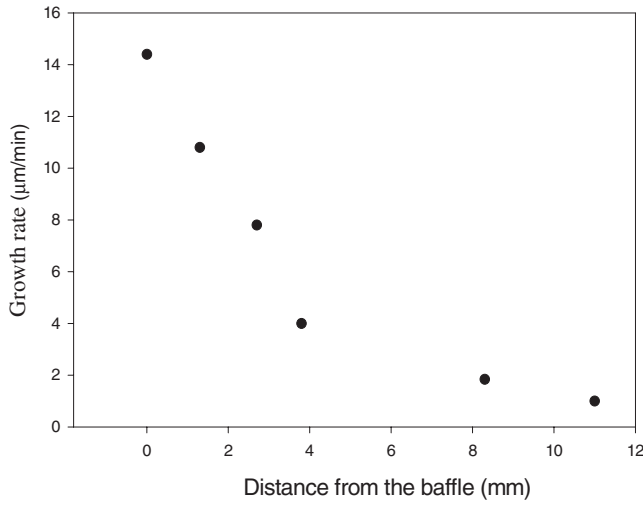


Fig. 7 Peak height versus the separation between the substrate and baffle.

4 Discussion

The vapour pressures of Cd and Te₂ may be calculated from the mass action law [15]:

$$K_{\text{CdTe}}(T) = P_{\text{Cd}} P_{\text{Te}_2}^{1/2}, \quad (4)$$

where the P_{Cd} and P_{Te_2} are the vapour pressures of Cd and Te₂, respectively, and $K_{\text{CdTe}}(T)$ is the equilibrium constant. For a stoichiometric source Eq. (1) gives:

$$P_{\text{Cd}} = 2 P_{\text{Te}_2}, \quad (5)$$

and therefore:

$$P_{\text{Cd}} = 2^{1/3} K_{\text{CdTe}}^{2/3}(T). \quad (6)$$

The equilibrium constant may be calculated from the expression given by deLargy et al. [16] for 912 K < T < 1324 K:

$$\ln K(T) = -(69446 \pm 786)/RT + (45.842 \pm 1.532)/R, \quad (7)$$

where R is the universal gas constant. Substituting in Eq. (6) gives

$$P_{\text{Cd}} = 2^{1/3} (\exp((-69446 + 45.842T)/RT))^{2/3}. \quad (8)$$

The vapour pressures of Cd at 923 and 973 K (source temperatures) are 0.067 and 0.243 mbar, respectively, and the corresponding vapour pressures of Te₂ are 0.033 and 0.12 mbar respectively. Similar values have been reported by Chu and Chu [17] at 973 K. The mean free paths in the vapour would be 6.5 and 1.8 mm, respectively. The value of mean free path at 6.5 mm is comparable to the distance between the baffle and the substrate, suggesting that at a vacuum pressure of 7.5×10^{-5} mbar, deposition at 923 K was by free sublimation and transport of CdTe.

The mean free path of Cd atoms and Te₂ molecules evaporated from a CdTe source, depends on the source temperature and the pressure according to the following equation [18]:

$$h = \frac{kT}{2^{1/2} \pi d^2 P}, \quad (9)$$

Table 2 Mean free paths of Cd and Te₂ at different pressures and source temperatures.

pressure (mbar)	7.5×10^{-5}	2	6
source temp. (K)	923	973	973
h of Cd (cm)	563	0.022	7.42×10^{-3}
h of Te ₂ (cm)	343	9.61×10^{-3}	3.2×10^{-3}

where k is Boltzmann's constant, P is the pressure (Pa), T is the source temperature (K) and d is the molecular diameter. The molecular diameters of Cd and Te₂ are 2.606 and 3.966 Å [19], respectively. Table 2 shows values of the mean free paths of Cd and Te₂ at different pressures and source temperatures.

These results suggest that the deposition at 7.5×10^{-5} mbar is by free molecular transport because the mean free path is longer than the space between the baffle and the substrate so the Cd and Te₂ molecules move directly to the substrate and the growth rate is independent of pressure. The deposition at 6 and 2 mbar is probably diffusion limited because the mean free path is short compared to the space between substrate and baffle and the Cd and Te₂ vapour molecules will collide several times with nitrogen molecules before they condense on the substrate. In the diffusion-limited transport model, the deposition rate is an inverse function of pressure, consistent with Fig. 5.

5 Conclusion

The growth rate increased as the source temperature increased with an activation energy 1.9 eV. For a given source temperature the growth rate was constant and independent of the substrate temperature, up to some breakpoint temperature, above which the rate decreased rapidly to zero. A reduction in growth rate as the substrate temperature is increased beyond some threshold has also been reported by Sosa et al. [5]. Their system was similar to that used here, although the separation between the source and substrate was around 6 mm, approximately half that in the present study. Uda et al. [20] also have reported that the growth rate decreased as both the substrate temperature and the separation between the source and the substrate were increased.

The pressure of ambient gas defines the mechanism for the deposition involved in the CSS system. Free sublimation and transport is involved at low pressures such as 7.5×10^{-5} mbar because the mean free path is longer than or equal to the space between the source and substrate. There were no pinholes in the films deposited at this pressure. Diffusion limited transport was involved at pressures of 2 and 6 mbar of N₂, because the mean free path is short compared to the space between the substrate and the source. There were pinholes in these films, possibly as a result of collisions between the Cd, Te₂ and N₂ molecules during the deposition.

The growth rate increased as the separation between the source and the substrate decreased. This is as expected, due to vapour beam divergence.

The use of the baffle between the source and the substrate had a significant effect on the uniformity of the film. When the substrate was too close to the baffle (less than 11 mm) at high vacuum (7.5×10^{-5} mbar), then those parts of the film that were directly above the holes, were considerably thicker than the rest of the layer. The baffle was necessary to prevent spitting of CdTe particles onto the layer. Fortunately, the increased separation did not restrict growth rate too severely.

The grain size increased from <1 µm at 335 °C to more than 2.5 µm at above 445 °C. The CdTe films grown at 335 °C showed a highly preferred (111) orientation. The intensity and the (111) texture coefficient reduced when the substrate temperature increased. Analysis of the XRD traces indicated that there was a general reduction in the degree of ordering as the substrate temperature was increased.

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