Nucleation of CdTe thin films deposited by close-space sublimation under a nitrogen ambient

J.D. Major [a], Y.Y. Proskuryakov [a], K. Durose [a],*, S. Green [b]

[a] *Department of Physics, Durham University, South Road, Durham, DH1 3LE, UK*
[b] *School of Engineering, Durham University, South Road, Durham, DH1 3LE, UK*

Abstract

The early stages of the close-space sublimation growth of CdTe/ITO (indium tin oxide) at 500°C under 26.7 kPa (200 Torr) of N_2 were investigated, the relatively high pressure being used to slow the growth. Film development was monitored over 60 mins by ex-situ AFM (atomic force microscopy), the growth being controlled by a shutter. The films formed by the 'island' or Volmer–Weber growth mechanism. Developments in the areal island growth rate, the island density and spatial distribution type were explained using growth mechanisms. Significant changes in these phenomena at $t \geq 10$ mins were attributed to a change in growth mechanism from surface migration limited, to a regime in which island coalescence and direct impingement of vapour species on the islands became important. Since the islands are characterised by distinct crystalline facets, this indicates the growth mechanism to be uninterrupted step-flow like addition of material to each island. Arguments are given to relate the final grain size in the films to the density of nuclei that are stable to re-evaporation after $t = 10$ mins.
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1. Introduction

Physical thin film crystal growth processes including nucleation and grain size development may be expected to have a profound effect on film continuity and microstructure. With reference to solar cell devices, both pinholes [1] and grain size/ grain boundary effects are known to have a direct effect on the conversion efficiency. For the case of CdTe growth by sublimation, it is known that the presence of low levels of O_2 in the processing ambient leads to more uniform coverage but smaller grain sizes [2,3]. Moreover the use of O_2 can influence other physical effects such as inter-diffusion at the CdTe/CdS interface [4]. In the wider literature, Barna has reported extensive studies of island growth phenomena. In particular he reports *in-situ* TEM (Transmission Electron Microscopy) observation of island growth by coalescence [5], and the influence of gas ambient on the formation of crystal habit planes that develop on islands during their formation. It was demonstrated that for the deposition of Al films, vacuum evaporation allowed the formation of distinct facets, while evaporation in the presence of oxygen yielded

islands with rounded morphologies [6]. It was inferred that step flow on crystal facets was interrupted by oxide formation.

In this work a study of the early stages of growth of CdTe on ITO/glass (indium tin oxide on glass) substrate was studied using *ex-situ* atomic force microscopy (AFM). The island morphologies, density and distributions were studied as a function of growth time under N_2. For the assessment of the spatial distribution of islands, a proximity method was used in which the nearest neighbour distribution parameter [7] is defined as: $R_n = 2\bar{d}\sqrt{(n/A)}$ where $\bar{d}$ is the average nearest neighbour distance, n is the sample size and A is the field area. A value of $R_n = 1$ indicates randomness, while $R_n < 1$ indicates clustering and $R_n > 1$ indicates 'well-spaced' or ordered points, as in a lattice for example.

2. Experimental

Samples were grown using a close-space sublimation (CSS) kit custom built by Electro-Gas Systems Ltd. Heating of the substrate and source was by independent temperature controlled electrical coil heaters with the operating temperatures being 500 °C and 600 °C respectively. Growth was controlled by a manually operated shutter. The growth ambient was chosen to be N_2 gas with pressures in the range 267 Pa to 26.7 kPa (2 to

200 Torr) being investigated. For the results presented here, the pressure was 26.7 kPa, this relatively high value being chosen to slow the growth down in order to resolve the initial nucleation phenomena. Growth times explored were in the range $1 \leq t \leq 60$ mins. The ITO/glass substrates were purchased from Merck and were cleaned by ultrasonic and reflux means in water, acetone and iso-propyl alcohol. Powdered CdTe of 99.999% purity was obtained from Alfa Aesar. AFM studies were performed in a Topometrix Explorer instrument. Image analysis made use of "UTHSCSA Image Tool" software, while spatial distribution analysis used "Spatial Analysis Utilities" software and spreadsheets. Morphology and crystallographic texture were further investigated by SEM (scanning electron microscopy)/EBSD (electron back scattered diffraction).

3. Results and discussion

A series of AFM images, taken from samples with growth interrupt times of $t = 1, 5, 10, 30$ and 60 min and shown in Fig. 1 a–e are examples of the data sets from which quantitative data concerning the growth processes were extracted. Fig. 2a and b shows the time dependent development of island area and density respectively, while Fig. 3 shows the evolution of the nearest neighbour distribution parameter R_n. The images themselves also reveal qualitative information about the basic nucleation and growth processes.

The main features of the results that should be explicable by nucleation and growth mechanisms are as follows:

a) Growth proceeds by an island mechanism, in which discrete islands form (Fig. 1a), and these have distinct crystal habit planes (Figs. 1d−f and 4).
b) The rate of increase in island area is ~ 0.11 μm^2/min for the first 10 mins of growth, rising to ~ 0.44 μm^2/min thereafter.
c) There is a high initial density of islands ($\sim 2.3 \times 10^8$ cm^{-2} at $t = 1$ min) which falls very rapidly in the first 10 mins, but much more slowly thereafter.
d) During the first 5 mins of growth the islands are neither clustered nor random, but 'well spaced' with $R_n = 1.1–1.2$. At $t = 10$ mins, significant clustering has emerged ($R_n = 0.76$), but this reverts to the original 'well spaced' distribution type for $t \geq 20$ mins. A summary of the main findings and of the discussion which now follows is presented in Table 1. It is generally accepted that the first stages of vapour phase crystal growth on a substrate proceed by impingement, surface migration and then sticking. The latter is in competition with re-evaporation, with it being necessary for the sticking rate to be greater than the loss rate for film growth to occur. In the present case, growth proceeds not by monolayer formation, but by island growth i.e. the Volmer−Weber mechanism. This is direct evidence that the film–film bonds (Cd–Te) are stronger than the film-substrate
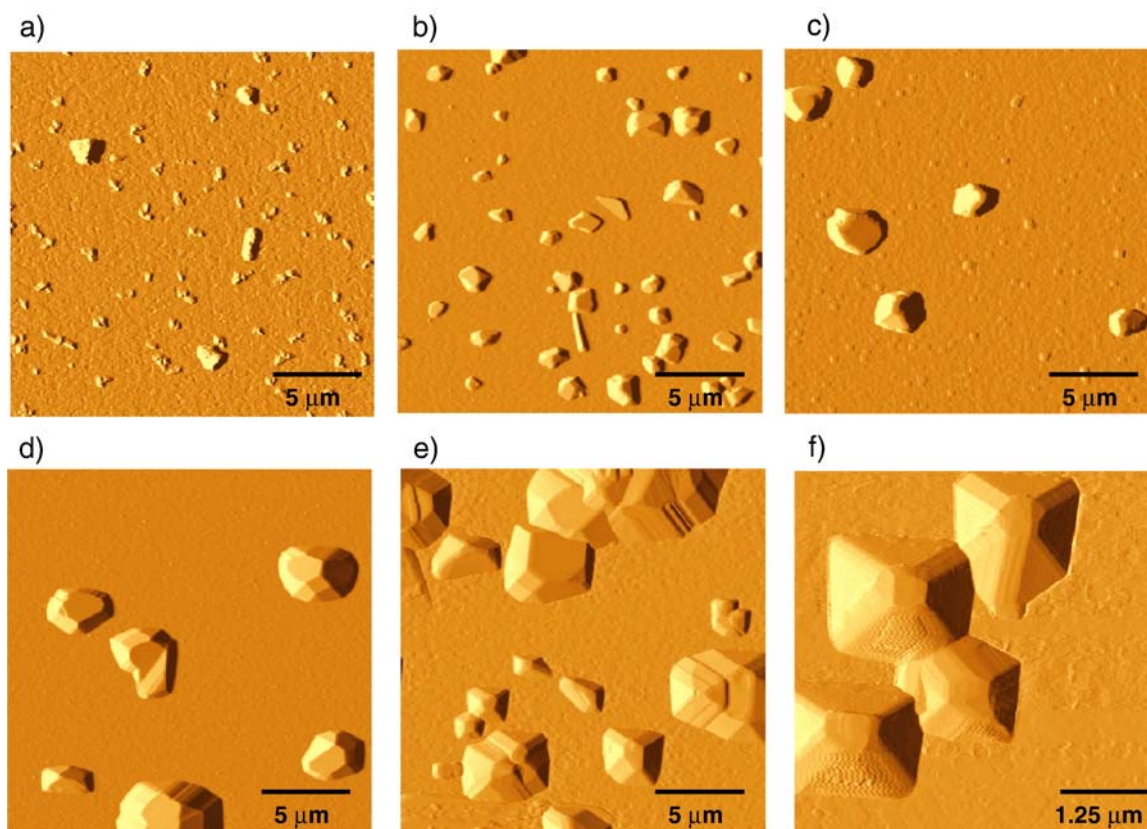

Fig. 1. AFM images of islands after various growth times: a) $t = 1$ min, b) $t = 5$ mins. c) $t = 10$ mins d) $t = 30$ mins, e) $t = 60$ mins. f) shows coalescence of growth islands ($t = 30$ mins).
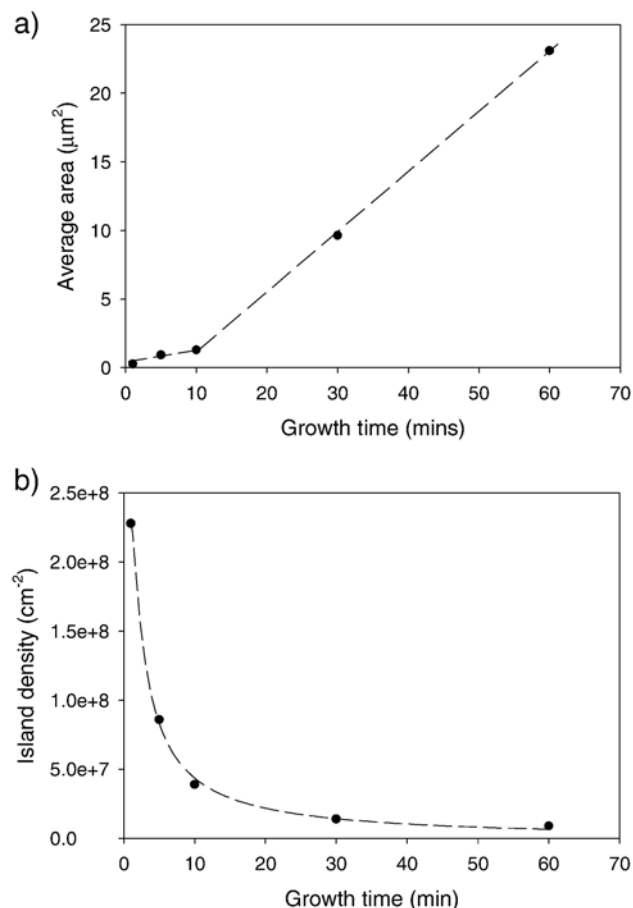
a)

b)

Fig. 2. Variation of a) island area, and b) island density with growth time.

Fig. 3. Variation of the nearest neighbour distribution parameter, R_n, with growth time.

bonds. While the islands are small, and the surface coverage fraction is low, then island formation and growth may only occur by the surface migration mechanism. At $t = 1$ min, (the first point of growth monitoring), the islands have an average area of 0.26 μm^2 and their distribution is of a 'well-spaced' or 'ordered' type, that is the islands are generally surrounded by an area within which there is a reduced possibility of finding another island. This is consistent with the surface migration model in which growth nutrients for a certain area are all gathered by a central sink site. Moreover no new nuclei form according to this model, and experimentally a very strong decrease in the island density is observed for $t \leq 10$ mins (Fig. 2b). Of the two possible mechanisms that could be responsible for this, island coalescence was not observed by AFM at this stage (although it becomes very significant later). The dominant mechanism active in the first 5 min is most likely to be re-evaporation. Further to this it may be inferred that it is the smaller islands that are reduced in numbers most strongly, since thermodynamically they are known to have a higher vapour pressure than the larger ones. An additional factor making evaporation more likely is that while growth is instigated after the substrate and source temperatures are stabilised, opening the shutter between the two exposes the substrate to thermal radiation that induces a thermal transient lasting several minutes. This additional substrate heating will act to encourage evaporation of the
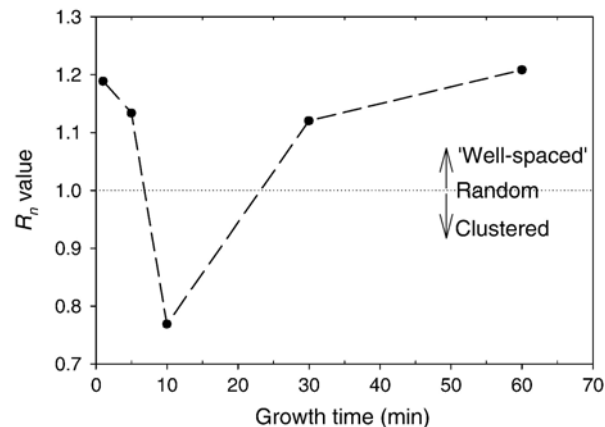
less stable islands. This decrease in island density is accompanied by a change in distribution type from 'well-spaced' to clustered. As the rate of island density decrease is high in this phase of growth, it is reasonable to suppose that no new islands form. The change in distribution must therefore result from the distribution of those islands that is most stable to re-evaporation i.e. the largest ones remain in their original positions, and the clustered distribution is therefore drawn from the 'well-spaced' distribution that preceded it. The fact that at $t = 10$ mins the islands are present in clusters may be interpreted as indicating that there are patches of the substrate that initially favoured sticking, or else there are regions of the source that contributed in the same way.

For growth times exceeding 10 mins there is a profound change of behaviour: the rate of island growth increases by a factor of 4, the island density decreases much more slowly, and the distribution reverts to a 'well-spaced' one. These changes may be explained by invoking two additional growth mechanisms. Firstly, as the surface coverage and island size increase, the possibility of vapour species impinging directly on the islands and contributing to growth is increasingly probable (In
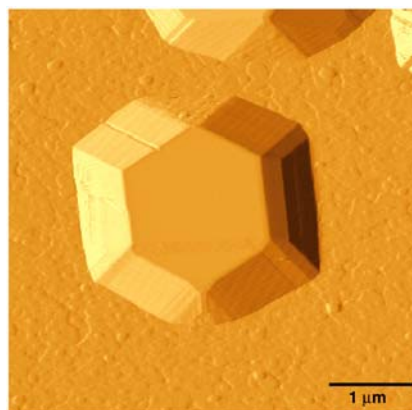

Fig. 4. Example of a hexagonal/octagonal growth island exhibiting smooth crystallographic facets.

Table 1
Summary of main observations and their interpretation using growth mechanisms

Time	Observation	Mechanism
$t=0$	Shutter opened. nucleation is initiated.	Islands begin to form by surface migration of absorbed species.
$t=1$ min	$\sim 2.3 \times 10^8$ cm^{-2} islands have formed, but this number decreases very rapidly until $t=10$ mins. Island growth rate is 0.1 µm/min. There is a 'well-spaced' distribution. Clear facets are established on each island.	Re-evaporation of smaller islands presumed to be responsible for island density reduction. Each stable island has a region free of other islands surrounding it, supporting the surface migration mechanism of growth.
$t=10$ mins	There is now a clustered distribution. Island density becomes more stable, but continues to fall slowly. Island growth rate increases by a factor of ×4. Coalescence of islands is observed by AFM from here on.	The clustered distribution is presumed to reflect the distribution of islands that is stable to re-evaporation. Re-evaporation slows markedly for $t \geq 10$ mins and the mechanism for island density reduction becomes dominated by coalescence. This new mechanism also accounts for the dramatic increase in island growth rate.
$t \geq 30$ mins+	The 'well-spaced' distribution is re-established. The fast island growth rate, and slowed island loss rate, are maintained.	Clusters have been eliminated by island coalescence and hence the distribution reverts to its earlier form. Secondary nucleation is not observed, and hence each island is presumed to develop into a single grain in the film under these growth conditions.

the limit of a continuous film the impingement fraction trivially becomes 100%). Secondly, island coalescence begins to occur, as may be seen for the AFM images for $t \geq 10$ mins (Figs. 1c–e and 4). We postulate that from hereon island coalescence replaces re-evaporation as the dominant mechanism of reducing island density for the following reasons: Firstly, the temperature transient passed after 3–5 min and the steady state has been regained at the 10 min point. Secondly, coalescence arising from the expansion of separate islands at this stage is necessarily a slower phenomenon than is re-evaporation — which for small islands could be almost instantaneous. This is consistent with the observation that the island density reduction rate is slowed very greatly at this point. Thirdly, since coalescence is intrinsically possible only for closely spaced islands, the tendency to annihilate clusters is to be expected. The fact that by $t=30$ mins, a well-spaced distribution prevails is itself evidence for the coalescence model.

Next, evidence is considered to indicate the growth processes involved in the formation of continuous films from a distribution of islands. Importantly, there is no evidence from either the AFM images or from the island density time graph (Fig. 2b), that there is any secondary nucleation i.e. new, smaller nuclei forming between the original ones. Hence it may be inferred that the island growth/coalescence mechanism is ultimately responsible for the formation of a continuous film (It is assumed here that the film growth mechanism operating is the same as that during low pressure higher speed CSS growth used in practice). Furthermore, where islands are seen to coalesce (Fig. 1e and f for example) there is no evidence that the orientation of one island is assumed by another. It follows logically therefore that each island becomes a single grain in the film. Further to this, the average grain area should be given by the reciprocal of the areal density of islands in the film, taken at the point when island reduction by evaporation has ceased to dominate. This model gives insight into the temperature dependence of grain size for vapour growth: for higher growth temperatures, the extent of re-evaporation of the smaller islands will be greater i.e. evaporation will persist as the dominant island density reduction mechanism for longer — and hence a smaller fraction of islands will remain than at low temperature. Since it is the remaining islands that will form grains in the film, higher temperatures may therefore be

expected to yield larger grain sizes. In practice larger grains are indeed found for higher substrate temperatures [8]. However, any attempt to confirm the proposed mechanism by experiment should also take into account both i) the grain coarsening phenomena that may accompany growth, and ii) the grain size development with increasing thickness that is common for polycrystalline films [9].

Finally, the morphology of the islands and facets are considered. The fact that all of the islands seen develop smooth flat facets is itself evidence that they are crystalline and grow by uninterrupted addition of condensed species to steps on flat growth surfaces [5]. The presence of impurities in either the source (99.999%) or process gas (purified dry N_2) has therefore not impeded significantly the growth processes. Whilst various habits are displayed by the islands, square based pyramids (Fig. 1f) and hexagon/octagons (Fig. 4) are frequently seen. However, attempts to identify their orientations by electron backscattered diffraction (EBSD) were frustrated by problems with identifying specific features at the 70° tilt angle required, and by shadowing effects.

4. Summary and conclusions

Initial phases of the close-space sublimation vapour growth of CdTe/ITO under 26.7 kPa (200 Torr) of nitrogen were investigated by ex-situ AFM in order to explore the growth mechanisms. Growth proceeds by the Volmer–Weber island growth mechanism, this being evidence that the bonds between atoms within the film are stronger than the film–substrate bonds. Since the islands have distinct crystallographic facets it is inferred that the addition of material to each island proceeds by a step flow process that is uninterrupted by impurities in either the source material or the processing ambient.

After 10 min the island growth mechanism changes from surface migration to being island-coalescence dominated. (A contribution from direct impingement of vapour species on the islands themselves also becomes increasingly likely as the substrate coverage increases). At the same point in time, the dramatic reduction in island density, presumed due to the rapid re-evaporation of small islands – is arrested – this corresponding with the onset of island coalescence as the dominant

mechanism for the reduction in the density of islands. A similar mechanistic argument may be used to account for the changes in the spatial distribution type observed experimentally as the 10 min growth time is passed – a transition from a clustered to a 'well-spaced' distribution is consistent with island coalescence within the clusters – as is described in detail in the previous section. Since no secondary nuclei were seen to form, it is assumed that under these conditions of film growth, a complete film forms by expansion and coalescence of the islands. Hence the grain size (area) at the substrate in a completed film may be expected to be the inverse of the island density present when island re-evaporation declines and island coalescence takes over. (This assumes that the as-grown grain structure is stable to coarsening effects in the grown film).

We expect that this study shall form the starting point for growth methodologies that will influence the grain size and surface coverage of films for use in improved solar cell devices.

Acknowledgements

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