Analysis of the crystallization kinetics of fast-growth doped Sb_xTe films

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ABSTRACT

Previous *in situ* TEM crystallization studies of phase-change films we have conducted suffered from the influence of the electron beam on the crystallization process. In our present work, we only performed TEM observations at room temperature, after crystallizing the samples at elevated temperatures for fixed time intervals without electron beam exposure. In this manner, the isothermal crystallization behavior of magnetron sputtered fast-growth doped Sb_xTe thin films with and without capping layers was investigated. As well as the crystal growth velocity, we have also been able to determine the nucleation rate as a function of time and temperature and the temperature dependent incubation time for nucleation. Further, the influence of the two types of capping layers (ZnS-SiO_2 and GeCrN) and the electron beam on crystallization properties were analyzed.

1. INTRODUCTION

Since the mechanisms underlying the reversible phase transition between crystalline and amorphous states control the erasing and writing processes, understanding the kinetics of crystallization is vital to optimize re-writable disc performance based on these materials. To the best of the authors knowledge, the isothermal crystallization behavior including separate information on nucleation and growth of Sb rich doped Sb-Te materials have not yet been investigated.

In this paper we present results on the isothermal crystallization behavior of doped Sb_xTe thin films, including the influence of capping layers and the electron beam on the crystallization process. The crystallization process is analyzed by Transmission Electron Microscopy (TEM) using *in situ* heating. Unlike most of the common techniques, such as differential scanning calorimetry (DSC), resistance and optical measurements, TEM with *in situ* heating provides a detailed information on nucleation and growth parameters separately in real time with a high spatial resolution. The main disadvantage of this technique is the possible influence of the electron beam on the crystallization process of the specimen at elevated temperatures. However, this can be avoided by doing the TEM imaging only at room temperature after crystallization occurs for fixed time intervals at elevated temperatures without electron beam exposure. This procedure is adopted in the present work.

2. EXPERIMENTS

Magnetron sputtering was used to prepare the samples for TEM analysis. 20 nm thick doped Sb_xTe amorphous films with and without capping layers were directly deposited on carbon coated copper TEM grids and on Si substrates containing silicon nitride (Si_3N_4) window. A constant dopant level of about 8 at. % of Ge + In was maintained with a well-defined Sb/Te ratio within the range 3.1 - 3.5. Henceforth, this ratio will be referred to as 'X'. Two types of dielectric materials namely ZnS-SiO_2 (ZSO) and GeCrN (GCN) were selected for the capping (protective) layer on both sides of the phase-change film, as they have been used in several phase-change optical discs. The capping layer thickness was 3 nm (see figure 1). The trilayer stack consisting of a Sb_xTe film sandwiched between the capping layers forms a quadrilayer structures with a 20 nm thick carbon layer on Cu grid (see figure 1a) and with a 25 nm thick Si_3N_4 membrane on Si substrate (see figure 1 b). The samples were stored in vacuum to prevent oxidation.

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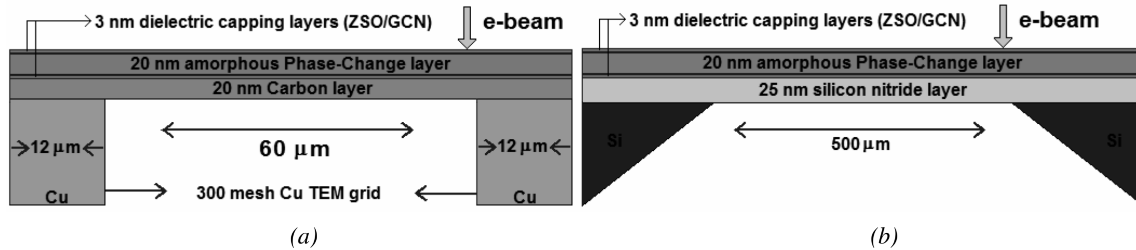
But, the uncapped samples might have oxidized to a very small extent while transporting them to the electron microscope.



(a) *(b)*

***Figure 1:** Quadrilayer sample structures; (a) on Cu grid and (b) on Si substrate used for TEM measurements (The electron beam is always focused near the edge of the electron transparent window)*

The amorphous samples were annealed between 160 and 185°C within the column of a TEM (JEOL 2010F) operating at 200 kV. A Gatan double tilt heating holder with a PID controller was used to control the furnace temperature within ± 0.5°C accuracy and for a fast ramp rate to attain the final temperature without any overshoot. The point to be noted here is that the temperature of the phase-change layer that is imaged by TEM might be generally a bit lower than the measured (furnace) temperature. However, the temperature gradient between the heating element and the phase-change layer can be significantly minimized by using substrates with high thermal conductivity (e.g. Cu). Also, the gradient is expected to increase from the edges of the electron transparent window towards the centre, with a maximum at the centre. This can also be minimized by reducing the window size to a minimum possible dimension and/or by choosing an area very close to the edges for TEM observations. All precautions to minimize the temperature difference with the PID controller were employed in the present study.

It should also be noted that in our previous *in situ* measurements with TEM, the crystallization was shown to be influenced by the electron beam at elevated temperatures[1]. In our present investigation, this effect is avoided by crystallizing the samples for fixed time intervals (hold-on time) in the absence of an electron beam and subsequently cooling down to room temperature for recording the TEM images. The hold-on times were made longer at lower annealing temperatures, where the crystal growth velocity is relatively slow (e.g. 45 minutes at 160°C and 3 minutes at 185°C).

Nucleation and growth of crystal nuclei were clearly observed by TEM in bright field imaging mode and the images were digitally recorded using a CCD camera. In order to measure both the nucleation and growth rates accurately, optimum magnification of 40 kx (corresponds to the field of view of 3.6 by 2.9 μm^2) within the microscope was selected. This field of view was sufficient to follow the growth of individual crystallites clearly and also low enough to survey a substantial number of nuclei. Here, it is assumed that the nucleation and growth viewed on the screen is representative for the crystallization process across the sample. The average crystal radius and number of nuclei were precisely measured as a function of time by monitoring at least 6 areas (as defined above) at each annealing temperature.

3. RESULTS AND DISCUSSIONS

3.1 Influence of the capping layers on growth

A typical example for the formation and growth of Sb_xTe crystallites in an amorphous matrix during an isothermal anneal is illustrated in figure 2. This example shows the crystallization process at 180°C, within the Sb_xTe film sandwiched between ZSO capping layers. From a sequence of images like those shown in figure 2, the number of crystal nuclei formed and the crystal radius are measured in real time. Isotropic crystal nuclei start to appear after a certain incubation time. The incubation time can be defined as the time taken by the material to produce a visible crystal nucleus after reaching the annealing temperature. However, a different (more accurate) definition is provided below.

The measured average crystal radius was found to increase more or less linearly with time (see figure 3). The example shown in figure 3 holds for the Sb_xTe film without any capping layers for annealing at 160, 165, 170, 175, 180 and 185°C. The slope of the straight line fits in figure 3 gives the growth velocity of the crystallite, which is more or less constant for a particular annealing temperature. The effective incubation time was determined by extrapolating the linear regression in the crystal radius versus time plot to the radius of zero (see figure 3 and figure 10).

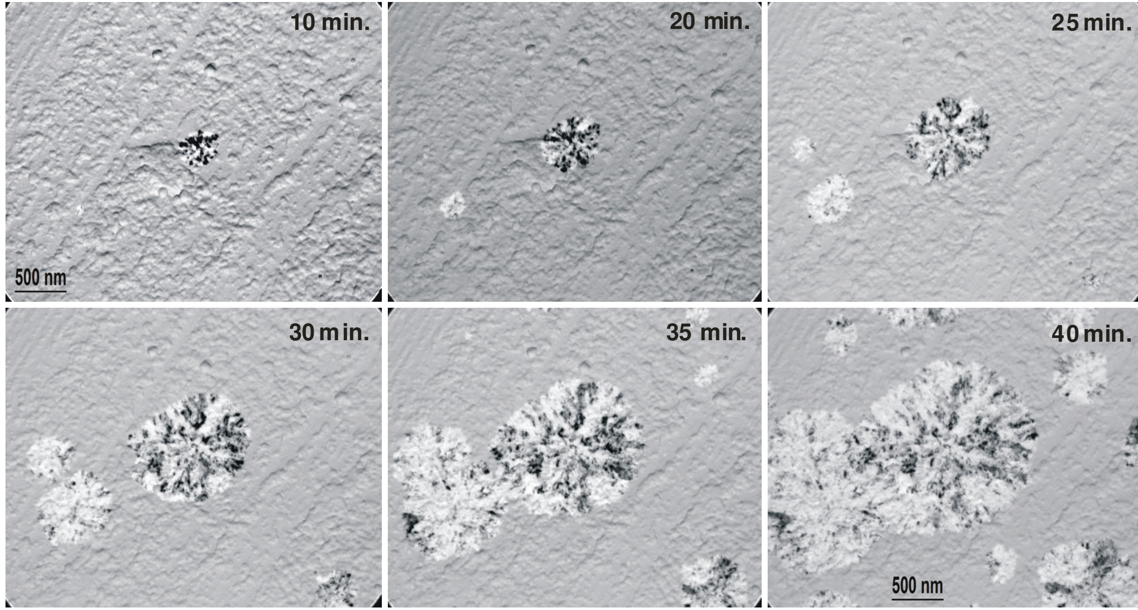


Figure 2: *TEM images of the Sb_xTe crystallites in an amorphous surrounding during annealing at 180°C after various times indicated. (Sample: Sb_xTe film with $ZnS\text{-}SiO_2$ capping layers on carbon film)*

The growth velocity was measured for all the samples (with and without capping layers) at various temperatures between 160 and 185°C. The measured growth velocity was found to increase with the annealing temperature and its temperature dependence is adequately described by the following Arrhenian type equation 1.

$$G(T) = G_0 \exp\left(\frac{-E_g}{k_B T}\right) \tag{1}$$

Where, G is the crystal growth velocity, E_g is the activation energy for crystal growth, G_o is the pre-exponential constant for growth and k_B is the Boltzmann constant and T is the annealing temperature.

In order to determine the activation energy for growth, the growth velocities were plotted as a function of reciprocal temperatures. The slope of the Arrhenius plot yields E_g and the intercept corresponds to $ln(G_o)$. The growth activation energies for the Sb_xTe films with and without capping layers were determined and compared as shown in figure 4.

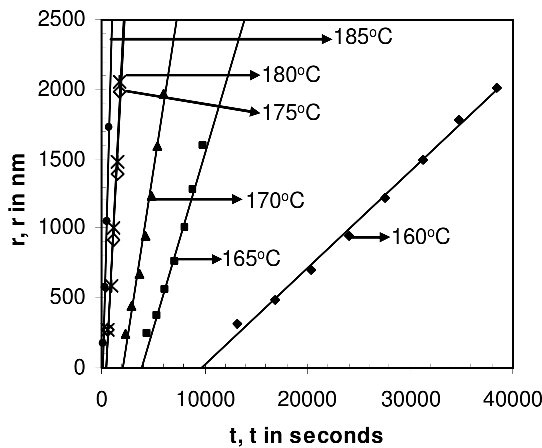


Figure 3: *The average crystal radius (r) as a function of time (t) at various annealing temperatures (Sample: Sb_xTe films without capping layers)*

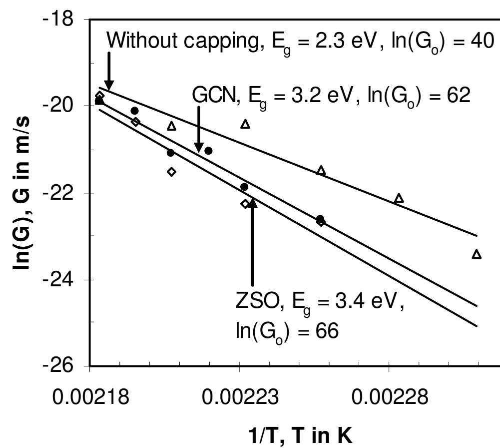


Figure 4: *Arrhenius plot of growth velocity (G) as a function of annealing temperature (T) (Sample: Sb_xTe films with and without capping layers)*

The calculated activation energy for growth is 2.3 eV for the Sb_xTe film without capping layers. This value is in good agreement with E_g of 2.37 ± 0.15 eV reported for 5 at. % Ge-doped $Sb_{3.6}Te$ thin film in one of our previous works[2], where the films were deposited by electron beam evaporation. Figure 4 shows that E_g of the Sb_xTe film is significantly increased by both the capping layers (ZSO and GCN) and the increment of 40 - 50 % is about the same for both ZSO and GCN. At lower temperatures around 160°C, the growth velocity of the Sb_xTe film is reduced about 7 times by the ZSO capping layers and about 5 times by the GCN capping layers. At higher annealing temperatures around 185°C, this discrepancy becomes less and the growth velocity is just reduced about 2 times by both the ZSO and GCN capping layers.

The influence of the capping layers on the crystallization properties of phase-change films has already been analyzed by a few authors[3,4]. The structure of the interface between the phase-change and capping layer is one of the important factors determining the crystallization properties of the phase-change film. Ohshima et al.[3] showed that the growth mechanism of the phase-change film can be varied by the interfacial atomic arrangement, which depends on the chemical affinity between the phase-change and capping layers at the interface. It is also pointed out by Martens et al.[4] that the crystal-growth velocity of the intermediate phase-change layer can be directly affected by the adjacent capping layers as the phase-change-capping layer interface energy determines the maximally achievable crystallization speed in thin phase-change films. The increase in activation energy for crystallization by sandwiching the phase-change film between the capping layers is also previously observed by Ohshima et al.[5] in Ge-Sb-Te films. The activation energy was 2.2 eV for the single layer and increased to 3.0 and 2.9 eV with SiO_2 and ZnS protective layers respectively in a very similar manner what we observe here.

The phase-change films with high activation energies (might be induced by the capping layers) are attractive for data storage applications as they can show a good trade-off between the programming speed and data retention[6].

3.2 Influence of the electron beam on growth

The crystallization process of the phase-change materials can be affected by electron beam irradiation during *in situ* heating measurements within the TEM[1]. In the present investigation, we analyzed the influence of the electron beam on growth properties as well. For this analysis, Sb_xTe films deposited on silicon substrates containing silicon nitride window (similar to the sample structure used in our previous studies and also shown in figure 1b) were examined. The measured growth parameters of these films were compared with the results of our previous investigation[1], where the films were continuously exposed to the electron beam throughout the crystallization process. Since the composition of the present samples, x = X (precise value in-between 3.1 - 3.5) fits in-between the formerly analyzed compositions (x = 3.0 – 3.6), it is possible to compare with the previous ones.

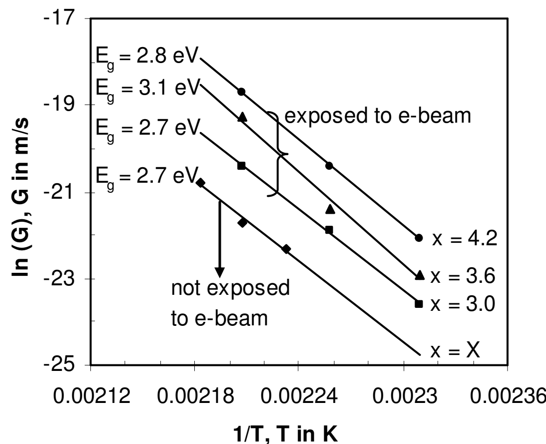


Figure 5: *Arrhenius plot of growth velocity as a function of annealing temperature (Sample: Sb_xTe thin films with ZSO capping layers)*

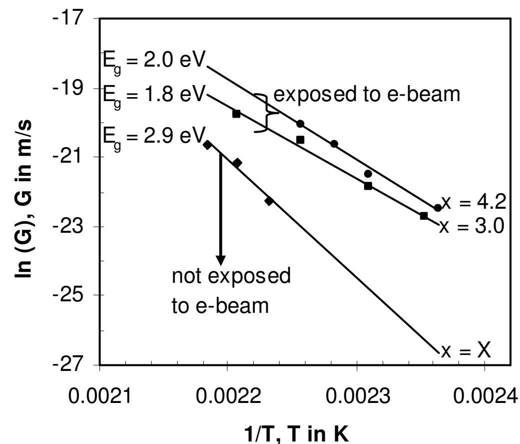


Figure 6: *Arrhenius plot of growth velocity as a function of annealing temperature (Sample: Sb_xTe thin films with GCN capping layers)*

Figure 5 shows how the growth parameters of an Sb_xTe film are influenced by the electron beam exposure during crystallization at elevated temperatures if sandwiched between ZSO capping layers.

The conclusions drawn from figure 5 are: 1) the crystal growth velocity of the electron beam exposed sample is about 4 times higher than that of the unexposed sample and 2) the activation energy for growth of the sample is not significantly affected by the electron beam exposure, i.e. about 2.7 eV.

Generally, if the beam energy is sufficiently high, then the electron beam exposure on soft materials like phase-change materials can cause one or more of the following effects; raise of the sample temperature, bond breaking (radiolysis), atom movement (knock-on or collision), relaxation processes, electron-hole pair formation etc. The effect(s) can be more pronounced when the material is at higher temperatures, particularly above the glass-transition temperature. So the electron beam exposure is expected to influence the crystallization process significantly during annealing at elevated temperature.

In the present case, the increased crystal growth velocity observed in the e-beam exposed sample might be due to a raise in sample temperature of about 10 K by electron beam heating. Since the growth velocity is governed by the annealing temperature above the transition point T_c (see equation 1), a raise in sample temperature consequently raises the growth velocity.

The influence of the electron beam on growth properties of the Sb_xTe film with GCN capping layers is illustrated in figure 6. If the film is exposed to the electron beam, then its Arrhenius plot is expected to lay in-between the plots for the previous film compositions x = 3.0 and 4.2, with E_g between 1.8 and 2 eV. So, the important conclusions to be drawn are: 1) The electron beam increases the growth velocity of the sample. The increment is different at different annealing temperatures in contrast with the previous sample (Sb_xTe with ZSO). The growth velocity is increased about 26 times at the temperature around 160°C and about 5 times at the temperature around 185°C. 2) The activation energy for growth of the sample is reduced by about 1 eV by the electron beam and such a reduction in E_g is also not observed in the sample with ZSO capping layers.

The reduction of the activation energy by electron beam exposure in case of GCN capping layers is not yet fully understood, though can be explained by the concept of relaxation. Then, the electron beam exposure is able to relax the amorphous phase/material, and the relaxed material can have a reduced activation energy for growth and an increased crystal-growth velocity compared to the unexposed one. A similar type of relaxation process, induced by pulsed laser irradiation was observed by Morilla et al.[7] in the $Sb_{0.87}Ge_{0.13}$ phase-change thin films. It was shown that the relaxed amorphous material had a lower activation energy for crystal growth and a higher growth velocity than the un-relaxed sample. E_g of 4.2 eV for the unexposed material and 0.5 eV for the relaxed material were reported, i.e. an even much stronger effect than what we find in the present investigation.

3.3 Influence of the capping layers on nucleation

The number of nuclei per unit area of the untransformed material, N can be determined by counting the total number of visible crystalline nuclei on the screen and then dividing the number with the observed area, A. As an example, figure 7 shows how the average number of nuclei within the observed area (A = 10.44 μm^2) varies with time in the Sb_xTe film with GCN capping layers at various annealing temperatures.

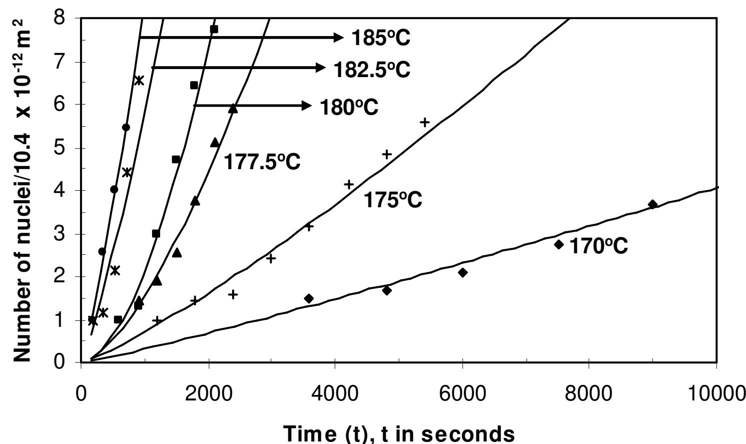


Figure 7: *The number of nuclei per 10.44 μm^2 of the untransformed material as a function of time at various annealing temperatures (Samples: Sb_xTe films with GCN capping layers)*

The time dependence of the number of nuclei per unit area, N, is given by the following phenomenological relation[8]

$$N \propto t^{a} \tag{2}$$

Where, a is the nucleation index, which can be approximated from equation 2 by first calculating a_i from two successive frames,

$$a_i \approx \frac{\ln N_{i+1} - \ln N_i}{\ln t_{i+1} - \ln t_i} \tag{3a}$$

and then averaging,

$$a = \frac{\sum_i a_i (1 - x_i)}{\sum_i (1 - x_i)} \tag{3b}$$

Where, x_i is the area fraction of the transformed material. At each annealing temperature, x_i is directly determined by measuring the fraction of the screen-area covered by the crystalline phase, for a number of frames throughout the crystallization process as a function of time. The weighing term (1- x_i) is used in equation 3b, since the contribution of nucleation to the growth process becomes less when the crystallization proceeds.

Having obtained N_i and x_i as functions of time, the nucleation index, a is calculated via equations 3a and 3b for each sample at various annealing temperatures. Figure 8 shows the nucleation indices as a function of inverse temperature for the Sb_xTe film with and without capping layers. The nucleation indices do not show any clear temperature dependence. Moreover, the nucleation index is not significantly influenced by the capping layers. The average nucleation index is estimated as 1.5 ± 0.3 for the Sb_xTe films, where the error is determined from the standard deviations of all the values of a. This value is significantly lower compared to 2.8 ± 0.6, which is the nucleation index reported by Ruitenberg et al.[8] for the $Ge_2Sb_2Te_5$ film sandwiched between Si_3N_4 capping layers.

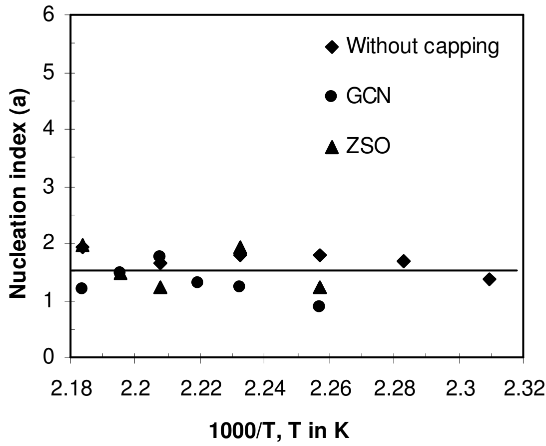


Figure 8: *Arrhenius plot of temperature dependence of the nucleation index (a)*

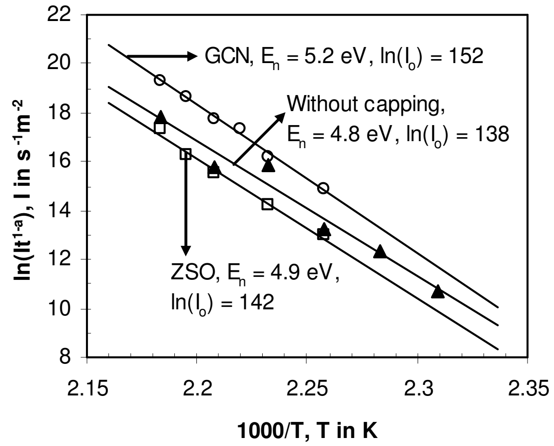


Figure 9: *Arrhenius plot of temperature dependence of the nucleation rate (I)*

If the time dependence of N is governed by the nucleation index (see expression 2), then the time dependent nucleation rate per unit area of the untransformed material, I can be written as

$$I = aN_0 t^{a-1} \tag{4}$$

Where, N_0 is a constant for a constant temperature.

When I varies with the annealing temperature, its Arrhenian temperature dependence is given by[8,9]

$$I(T) = I_0 t^{a-1} \exp\left(\frac{-E_n}{k_B T}\right) \tag{5a}$$

Where,

$$I_0 = aN_0 \exp\left(\frac{E_n}{k_B T}\right) \tag{5b}$$

E_n is the activation energy for nucleation and I_0 is a pre-exponential constant with respect to temperature and time.

By having the total number of nuclei per unit area, N and the area fraction of the transformed material, x as a function of time, the nucleation rate per unit area, I is determined for each isothermal anneal using

$$I = \frac{dN}{dt}\frac{1}{A(1-x)} \tag{6}$$

The term $(1-x)$ is due to the fact that nucleation only occurs in the untransformed area.

According to equation 5a, plotting $ln(It^{1-a})$ as a function of reciprocal temperature, gives a straight line with slope E_n and intercept $ln(I_0)$. Figure 9 shows such Arrhenius plots for the Sb_xTe film with and without capping layers. The activation energy for nucleation, E_n is not significantly affected by the capping layers and it is 5 ± 0.2 eV for all samples. But, the time dependent nucleation rate, I is strongly influenced by the capping layers. I is accelerated about 3 times by the GCN capping layers, whereas it is decelerated about 3 times by the ZSO layers.

Such an influence of capping layers on nucleation properties, especially on nucleation rate was observed by Ohshima et al.[5] as well. The nucleation of the Ge-Sb-Te film is accelerated by the Si_3N_4 and Ta_2O_5 capping layers, whereas it is retarded by the SiO_2 layers. Their results show that the chemical factors such as the surface reactivity and chemical affinity are predominant for the difference in crystallization. According to them, these differences might have originated from chemical bonding states at the interface between the phase-change film and capping layers.

It is confirmed by Ruitenberg et al.[8] that the nucleation occurs predominantly at the interfaces between the phase-change film and capping layers. Therefore the capping layers are sometimes called as 'seeding layers' and the nucleation parameters are expected to be influenced by the structure of the interface. As the interface structure varies with capping layer material, the nucleation parameters will be different for different capping layers as we observe here.

3.4 Influence of the capping layers on incubation time

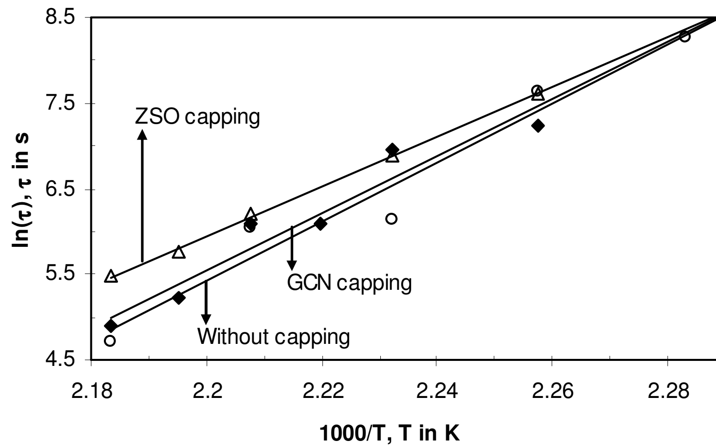


Figure 10: *Arrhenius plot of the temperature dependence of the incubation time (τ)*

The effective incubation time, τ was determined for each isothermal anneal and it was found to increase with decrease in annealing temperature. The incubation time for the Sb_xTe films, as a function of reciprocal temperature is shown figure 10. In all the films, the incubation time shows a strong temperature dependence and is not much affected by the capping layers at lower temperatures around 165°C.

But, at higher annealing temperatures around 185°C, τ is lengthened about 2 times by ZSO, while not drastically affected by the GCN capping layers.

4. CONCLUSIONS

Isothermal crystallization properties of doped Sb_xTe thin films, and the effects caused by the capping layers and electron beam on crystallization, were investigated using TEM with *in situ* heating, in the temperature range 160 – 185°C. With this technique, the formation and growth of crystal nuclei were observed in real time and the growth and nucleation parameters were determined separately. Two types of capping layers composed of dielectric materials were tested; one was GeCrN (GCN) and the other was ZnS-SiO_2 (ZSO).

At lower annealing temperatures around 160°C, the growth velocity of the Sb_xTe film is reduced about 7 times by the ZSO capping layers, whereas it is reduced about 5 times by the GCN capping layers. But, the growth velocity is not considerably controlled by both the capping layers at higher annealing temperatures around 185°C. The activation energy for growth of the Sb_xTe film is raised from 2.3 to about 3.3 eV by both the capping layers.

The influence of the electron beam on the growth properties of the samples, during in situ TEM measurements at elevated temperatures, was confirmed. In Sb_xTe film with ZSO capping layers, the growth velocity is increased about 4 times and the activation energy for growth is left unaffected by the electron beam exposure. When the sample is sandwiched between GCN layers, the electron beam alters both the growth velocity and the activation energy for growth. The growth velocity is accelerated about 26 times at lower annealing temperatures around 160°C and about 5 times at higher annealing temperatures around 185°C. The activation energy for growth is reduced about 1 eV.

The nucleation index is not strongly affected by sandwiching the Sb_xTe film between the GCN or ZSO capping layers. It is estimated as 1.5 ± 0.3 for all the Sb_xTe films with and without capping layers. The time dependent nucleation rate of the Sb_xTe film is accelerated about 3 times by the GCN capping layers, whereas it is retarded about 3 times by the ZSO capping layers. The activation energy for nucleation is almost unaffected by both the capping layers and it is 5 ± 0.2 eV for all the samples.

The temperature dependent incubation time is determined for Sb_xTe films and it is also influenced by the capping layers. The incubation time is increased about 2 times using ZSO capping layers, but not appreciably modified with GCN capping layers.

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