Phase-change thin films
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CHAPTER 5

Effects of capping layers on the crystallization of Sb$_{3.3}$Te thin films

This chapter focuses on the influences of two different types of dielectric capping layers on the crystal nucleation and growth properties of Sb$_{3.3}$Te thin films. To reveal the effects, isothermal crystallization studies using TEM were performed. The following points should be noted: i) the electron beam influence on the crystallization process at elevated temperatures is explicitly excluded in this work, ii) the films analyzed in this work have a fixed Sb/Te ratio and were deposited using a single sputtering target, but the films discussed in the previous chapter were deposited using multiple targets, iii) carbon coated copper grids were used as substrates in this work, instead of silicon nitride membrane used in the previous work, to have an improved thermal conduction between the heating element and phase-change film, iv) in addition to the crystal growth parameters, the nucleation parameters were also quantitatively determined in this work and v) the effect of capping layer type on the crystallization was determined in this work by directly comparing the sandwiched phase-change films to the nonsandwiched films.

5.1. INTRODUCTION

Among the several types of materials for phase-change recording [1-4], doped alloys derived from eutectic Sb,Te, showing a growth-dominant crystallization behavior, appear to be the most obvious choice for both high data transfer rate and high density recording [5-10]. These materials are currently used in optical disc formats including rewritable digital versatile disc (DVD+RW and DVD-RW), Blu-ray disc [11] and high definition DVD [12], and also proposed for the line concept phase-change random access memory [14]. A good tradeoff between crystallization speed and data retention time is also expected in these materials, as they have a high activation energy for crystallization. In phase-change optical discs, the active layer is actually sandwiched between dielectric
layers, which are transparent to laser wavelength. Similar stacks are also relevant for PRAM, in particular for the recently proposed line concept [13]. Dielectric layer protection is necessary due to several reasons, particularly to control the fluidization and vaporization of the phase-change material during the recording process, and to protect the phase-change film from thermal stress cycle during repetitious overwriting [14]. Consequently, several properties of the phase-change film including crystallization are significantly altered by the capping layers [14-18]. Therefore, studies on the behaviour of the combination of the phase-change film and capping layers are crucial. Improving the understanding of the influence of capping layers on the crystallization kinetics of the phase-change film is important to optimize the disc characteristics.

Ohshima previously analyzed the influence of various dielectric capping layers on the crystallization of Ge$_{1}$Sb$_{2}$Te$_{4}$ thin films based on transmittance-change measurements [15]. However, transmittance measurements or other techniques [16-23] generally used, such as differential scanning calorimetry, X-ray diffraction, electrical (resistance) measurements and reflectance measurements, provide information only on the overall crystallization process, that is actually an interplay of both nucleation and growth processes. Transmission electron microscopy is capable of providing separate information on nucleation and growth parameters. Ruitenbergen et al. [24] have previously performed isothermal crystallization studies using in-situ TEM and determined the individual nucleation and growth parameters for the crystallization of nucleation-dominant type Ge$_{2}$Sb$_{2}$Te$_{5}$ thin films sandwiched between Si$_{3}$N$_{4}$ dielectric layers. However, there are some inconsistencies between the listed nucleation and growth parameters and the results predicted from the corresponding plots.

To the best of our knowledge, direct observations on nucleation and growth rates and the effects of the capping layers on these rates have not been reported yet for the so-called ‘fast-growth type’ phase-change materials. In this work, we have quantitatively determined both the nucleation and growth parameters of doped Sb$_{3.3}$Te amorphous films and study the influence of two types of dielectric capping layers, namely GeCrN and ZnS-SiO$_{2}$, using TEM with in-situ annealing experiments. During the experiments, we have explicitly excluded the effect the electron beam of the TEM has on the nucleation and growth rates we observed in our previous works [25-27]. This is a first major
difference of the present work with the results presented in Ref. 27. The other important differences are; i) in Ref. 27 nucleation rates were not obtained, but are reported here, ii) in Ref. 27 samples with various Sb/Te ratios were grown by sputtering from multiple targets on silicon nitride membranes. Here, a single fixed Sb/Te ratio is used for all samples, where the films were obtained by sputtering from a single target on carbon coated copper grids. These latter substrates exhibit a better heat conduction than the former, which is important for the new measurement strategy we adapted in the present work as will be explained in the following sections.

5.2. EXPERIMENTAL PROCEDURE

Two types of Sb$_{3.3}$Te films, named as single-layer film and sandwiched film, were prepared for the TEM experiments and the structures of the films are shown in Fig. 5.1. In the single-layer film structure (see Fig. 5.1a), an amorphous phase-change film is deposited on a carbon coated copper grid (300 mesh). In the sandwiched film structure (see Fig. 5.1b), the phase-change film is sandwiched between two amorphous dielectric layers and this trilayer stack is deposited on the carbon coated Cu grid.

![Fig. 5.1. Structure of the Sb$_{3.3}$Te specimens used in the TEM experiments.](image)

A constant dopant level of about 8 at.% of Ge + In was maintained with a fixed value for the Sb/Te ratio of 3.3 in the phase-change film. This dopant is of crucial importance for the performance of the phase change material in particular providing a high activation energy for growth that enables the combination of a good archive stability (low growth rates at low temperature) and high speed direct overwriting (high growth rates at high...
temperature). The dielectric capping layers were composed of either ZnS-SiO$_2$ (80 at.% of ZnS + 20 at.% of SiO$_2$) or GeCrN. DC and RF magnetron sputtering techniques were used to deposit the phase-change and dielectric layers, respectively. The samples were stored in vacuum to prevent possible oxidation. However, the uncapped samples can become oxidized to a small extent when they are transferred through air to the vacuum system of the TEM.

The samples were isothermally annealed at various temperatures between 160 and 185$^\circ$C inside a JEOL 2010F TEM operating at an accelerating voltage of 200 kV. A Gatan 652 double tilt heating holder with a 901 SmartSet Hot Stage Controller is used for the temperature control. A proportional integral derivative (PID) controller equipped with the furnace controls the temperature within ±0.5$^\circ$C accuracy and provides a fast ramp rate to attain the set point temperature without any overshoot. However, the measured temperature is the furnace temperature, but not the actual film temperature, which is expected to be slightly lower than the measured value and will show a time lag. To minimize this temperature difference and time lag, substrates with relatively good thermal conductance are desirable. Therefore, carbon coated copper grids were used in these experiments, instead of silicon substrates containing silicon nitride membranes used in the work of chapter 4 and our earlier works [25-27]. Moreover, to maximally reduce the temperature gradient, we chose areas as close as possible to the grid edges where a physical contact with the furnace is made and close to the grid bars as well.

Our previous works [25-27] showed that the crystallization of the phase-change film is sensitive to irradiation by the electron beam of the TEM; i.e. nucleation and growth rates increased. A detailed investigation of the influence of electron beam on the growth properties of SbTe films is given in chapter 6 and also in Ref. 28. In order to entirely avoid such an influence in the present experiments, crystallization was carried out without electron beam exposure for fixed time intervals at elevated temperature. After each interval, the sample is cooled to nearly room temperature (below 30$^\circ$C) for TEM measurements, i.e. the measurement of nucleation and growth were made in discrete heating and cooling steps unlike our previous studies [25,26], where it was done in a more or less continuous manner. Using this procedure, it was important to switch from the silicon nitride membranes to the carbon coated copper grids with their better thermal
conduction. Nucleation and growth of crystals were monitored in bright-field mode of the TEM on a fluorescent screen and the images were digitally recorded using a CCD camera. A magnification of 40 kX, corresponding to 10.4 μm² field of view on the camera, was found to be most suitable to get a good statistics on the nucleation and growth parameters. It means that this magnification is high enough to follow the growth of individual crystal nuclei and at the same time it is low enough to count a substantial number of nuclei. However, to perform a more accurate and representative measurement on nucleation and growth for the entire sample, we monitored the crystallization at (6 to 10) different areas on the sample. Sufficient statistics on nucleation is obtained by considering a combination of the individually monitored areas. The crystal radius is precisely measured by averaging the radii of more than 6 crystals monitored in the different sample areas. During each isothermal annealing, the number of crystal nuclei, the crystal radii and the crystallized area fraction were measured as a function of time.

5.3. RESULTS

5.3.1. Growth properties

An example for the formation and growth of Sb₃.₃Te crystals in an amorphous surrounding during crystallization is shown in Fig. 5.2. These TEM images hold for a
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ZnS-SiO₂ capped Sb₃.₃Te film annealed at 180°C. The crystals nucleate after a certain incubation time and grow more or less isotropically by maintaining their circular shape. Radius of the crystal increases more or less linearly with time i.e. the crystal growth rate is (almost) constant during isothermal annealing, implying an interface controlled growth mechanism.

Figure 5.3 shows the increase of the average crystal radius ($r$) as a function of time ($t$) at various annealing temperatures in uncapped Sb₃.₃Te films as an example. The slope of the ($r$ versus $t$) straight line fit corresponds to the crystal growth rate that strongly increases with the annealing temperature (see Fig. 5.3). Careful analysis shows that the growth velocity is actually not a constant at each temperature, but is slightly increasing with time. This effect of an increasing growth velocity with time was also observed in our previous work mentioned in chapter 4 and attributed it to the so-called relaxation process [27]. Hereafter, in the following results and discussions sections, this effect is disregarded, but it is addressed in chapter 6 (and in Ref. 28) where also the influence of electron beam of the TEM (that is now absent for the present measurements) on the growth velocity is analyzed in detail.

The temperature, $T$, dependence of the crystal growth rate, $V_g$, is adequately represented by the following Arrhenian-type equation:

$$V_g = A e^{-E_a / kT}$$
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\[ V_g(T) = C_g \exp\left(\frac{-E_g}{k_BT}\right) \]  

(5.1)

where, $E_g$ is the activation energy for crystal growth, $C_g$ is the preexponential constant and $k_B$ is the Boltzmann constant. According to equation (5.1), plotting $\ln(V_g)$ against $1/T$ should provide a straight-line. The slope of the line yields $E_g$, whereas the intercept represents $\ln(C_g)$. Arrhenius-type plots based on the measured crystal growth rates at various annealing temperatures for the capped & uncapped samples are shown in Fig. 5.4.

![Fig. 5.4. Arrhenius plots of the growth rate, $V_g$, as a function of the annealing temperature, $T$, for the three types of capped Sb$_{3.3}$Te films.](image)

- Single-layer, ■: GeCrN sandwiched, ▲: ZnS-SiO$_2$ sandwiched

This figure clearly shows that sandwiching the phase-change film between ZnS-SiO$_2$ or GeCrN layers leads to a reduction in growth rate. Variation in growth rate between the capped and uncapped film is larger at lower temperatures (~ 160°C) compared to that at higher temperatures (~ 185°C). Quantitative measurements reveal that the growth rate is reduced by ~ 7 and 5 times due to ZnS-SiO$_2$ and GeCrN layers, respectively, at ~ 160°C. The magnitude of this effect becomes smaller at ~ 185°C, where the growth rate is lowered only ~ 2 and 1.5 times by ZnS-SiO$_2$ and GeCrN layers, respectively. Hence, the influence of capping layers on growth rate reduces with increasing temperature and expected to be insignificant at higher temperatures (~ 200°C).

Growth parameters, $E_g$ and $\ln(C_g)$, determined from the $\ln(V_g)$ versus $1/T$ linear fit (see Fig. 5.4) are listed in table 5.1 for uncapped and capped samples. The activation energy for crystal growth of an uncapped Sb$_{3.3}$Te film is 2.4 ± 0.3 eV and increases to
3.3 ± 0.3 eV and 3.4 ± 0.6 eV when the film is capped with GeCrN and ZnS-SiO₂ layers, respectively. These results show that the activation energy for crystal growth of Sb₃.₃Te films is strongly influenced by the capping layers and the variation in activation energy (~ 40%) is not significantly dependent on the type of the capping material. The activation energy for crystal growth of the uncapped Sb₃.₃Te film is in good agreement with that of 2.37 ± 0.15 eV reported in Ref. 26 for electron beam evaporated (5 at.%) Ge doped Sb₃.₆Te films, and is also very close to the activation energies found for the (uncapped) nucleation-dominant GeSbTe films ($E_g = 2.35 \pm 0.05$ eV for Ge₂Sb₂Te₅ on Si [29] and 2.4 ± 0.3 for Ge₂Sb₂Te₅ on SiO₂ [30]). Ruitenberg et al. [24] reported $E_g$ of 1.6 ± 0.6 eV for a Ge₂Sb₂Te₅ film sandwiched between Si₃N₄ layers. This value is rather low compared to the activation energies of the sandwiched Sb₃.₃Te films ($E_g > 3$ eV) listed in table 5.1.

Table 5.1. Growth parameters, $E_g$ and ln($C_g$), for the single-layer and sandwiched Sb₃.₃Te films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ (eV)</th>
<th>ln($C_g$); $C_g$ in m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-layer</td>
<td>2.4 ± 0.3</td>
<td>42 ± 8</td>
</tr>
<tr>
<td>GeCrN sandwiched</td>
<td>3.3 ± 0.3</td>
<td>63 ± 8</td>
</tr>
<tr>
<td>ZnS-SiO₂ sandwiched</td>
<td>3.4 ± 0.6</td>
<td>67 ± 16</td>
</tr>
</tbody>
</table>

From the application point of view, high $E_g$ as exhibited in our sandwiched samples would be beneficial to improve the data retention (i.e. low growth rates at low temperatures) with still holding high crystallization rates (i.e. fast data transfer) at high temperatures. The preexponential constants listed in table 5.1 for the sandwiched samples are larger than those reported in Ref. 24 for Si₃N₄ capped Ge₂Sb₂Te₅ film. However, it should be noted that there is a large data scatter in Ref. 24, where also the reported preexponential constant 43 ± 25 is definitely inconsistent with the corresponding fit. Moreover, using the relevant growth parameters given in table 1 of Ref. 24, a growth rate of about 5.8 m/s is predicted at 450 K, but this is incorrect and the correct value would be 6 nm/s.

5.3.2. Nucleation properties

A nonlinear time dependence of the number of nuclei per unit area of untransformed material, $N$, is described by the following phenomenological relation [24]
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\[ N \propto t^\alpha \]  

(5.2)

for \( t > t_0 \) with \( t_0 \) the incubation time and \( \alpha \) denoting the ‘nucleation index’.

It should be mentioned that \( N \) can be related to \( (t-t_0)^\alpha \) in order to show that \( N = 0 \) for \( t < t_0 \). However, in our case, although there exists an incubation time, including \( t_0 \) in equation (5.2) i.e. having \( N \propto (t-t_0)^\alpha \) led to clearly less consistent analysis, because:

(i) The fitting in \( N \) versus \( t \) plots (see e.g. Fig. 5.5) could be performed very well on the basis of \( t^\alpha \) and deteriorated if we performed them on the basis of \( (t-t_0)^\alpha \), where \( t_0 \) was obtained from (linearly) extrapolating the average crystal radius versus time back to a radius of zero;

(ii) So-called Avrami plots of \( \ln(\ln(1-x)) \) versus \( \ln(t) \) (where \( x \) is the area fraction of the transformed material) showed data exhibiting a good linear dependence whereas \( \ln(\ln(1-x)) \) versus \( \ln(t-t_0) \) resulted in data showing a clearly curved dependence;

(iii) The Avrami exponent \( n \) (as obtained from the Avrami plot) should be equal to \( \alpha + D\beta \) with \( D \) the dimensionality of growth (which is 2 for the present thin film case) and \( \beta \) is the growth index (\( \beta = 1 \) for interface-controlled growth and 0.5 for the diffusion-controlled growth). In the analysis excluding \( t_0 \) the equality is obeyed (within the error limits with \( n \) is about 3 to 4, depending on the capping layer type), whereas in the analysis including \( t_0 \), \( n \) has a value of about 2 clearly inconsistent with the value of \( \alpha + D\beta \).

The nucleation index \( \alpha \) can be approximated from equation (5.2) by first calculating \( \alpha_i \) from two consecutive images,

\[
\alpha_i = \frac{\partial \ln N_i}{\partial \ln t_i} \approx \frac{\ln N_{i+1} - \ln N_i}{\ln t_{i+1} - \ln t_i}
\]  

(5.3a)

and then averaging \( \alpha_i \) as given below.

\[
\alpha = \frac{\sum_i \alpha_i (1-x_i)}{\sum_i (1-x_i)}
\]  

(5.3b)

where \( x_i \) is the area fraction of the transformed material, and it can be measured directly from the TEM images. Note that in equation (5.3b) not just a simple arithmetic average is taken, but also a weighing term \((1-x_i)\) is used, since the accuracy of determine \( \alpha_i \) is
strongly decreasing when the untransformed area becomes smaller and approaches zero during the course of transformation.

![Graph showing the number of nuclei per unit area as a function of time during isothermal annealing.](image)

**Fig. 5.5.** Number of nuclei per unit untransformed area, \( N \), as a function of time, \( t \), during isothermal annealing of ZnS-SiO\(_2\) capped Sb\(_{3.3}\)Te films at various temperatures.

\( N \) is determined by a similar procedure as proposed and used in Ref. 24. First it is started by counting the number of crystal nuclei, \( n \), in a sample area, \( A \). Note that here \( A \) is not the area of a single field of view, but the sum of number of fields of view (6 to 10) taken into account for counting \( n \). To convert \( n \) to \( N \) (i.e. to make it the number per unit of untransformed area) the following recursive procedure is used:

\[
N_i = N_{i-1} + \frac{(n_i - n_{i-1})}{1 - x_{i-1}}
\]

(5.4)

This procedure is exact for infinitesimally small steps in \((1-x_i)\) and \( n_i \). During the crystallization process, \( N \) and to a lesser extent \( n \) (particularly less at the later stage of the transformation) increase with time. Figure 5.5 shows an example for the profound nonlinear variation of \( N \) with time during crystallization of ZnS-SiO\(_2\) capped Sb\(_{3.3}\)Te films at various annealing temperatures.

At each annealing temperature, by having \( N_i \) and \( x_i \) for each time step \( t_i \), first \( \alpha_i \) and then \( \alpha \) are calculated using equations (5.3a) and (5.3b), respectively. The nucleation index derived using the procedure outlined is shown as a function of the inverse temperature for the single-layer and sandwiched Sb\(_{3.3}\)Te films in Fig. 5.6. In the figure, the nucleation index does not show any detectable temperature or capping layer
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dependence. The average nucleation index is 1.8 ± 0.4, where the error is the standard deviation of the nucleation indices of single-layer and sandwiched Sb$_{3.3}$Te films. This value is significantly lower compared to that of 2.8 ± 0.6 reported for Ge$_2$Sb$_2$Te$_5$ films by Ruitenberg et al. [24]. For a nucleation-dominant material it is probably not surprising that a higher nucleation index holds than for a fast growth type material, although the essential point is the trade-off between the nucleation and the growth rates.

Fig. 5.6. Arrhenius plots of the temperature dependence of the nucleation index ($\alpha$) for the three types of capped Sb$_{3.3}$Te films.

The nucleation rate per unit area of the untransformed material, $V_n$, can be expressed as [24]

$$V_n(T) = C_n T^\alpha e^{-\frac{E_n}{k_BT}}$$  \hspace{1cm} (5.5)

where, $E_n$ is the activation energy for nucleation and $C_n$ is a preexponential constant with respect to temperature and time. By counting the number of nuclei, $n$, on a screen area, $A$, as a function of time, the nucleation rate per unit area is determined for each isothermal annealing process using the following equation:

$$V_n = \frac{dN}{dt} = \frac{dn}{dt} \frac{1}{A(1-x)}$$  \hspace{1cm} (5.6)

Referring to equation (5.5), plotting ln($V_n^{1-\alpha}$) against the reciprocal temperature, $1/T$, yields a straight line. The slope and intercept of the line correspond to the activation energy for nucleation and preexponential constant, respectively.
Figure 5.7 shows the $\ln(V_{n/1-\alpha})$ versus $1/T$ plots for the single-layer and sandwiched Sb$_{3.3}$Te films. The comparison made in Fig. 5.7 indicates that the nucleation rate is accelerated ~ 1.7 times and decelerated ~ 5 times when the film is sandwiched between GeCrN and ZnS-SiO$_2$ layers, respectively. Thus, the nucleation rate of the Sb$_{3.3}$Te film is significantly dependent on the capping layer type. From an application point of view, the influence of the capping layer effect on the nucleation rate can be useful, because the nucleation rate of the recording layer can be controlled by using proper capping layers. Such a control on nucleation is important for fast-growth materials to show a nucleation free characteristic with advantages of low jitter and high amorphous phase stability.

Table 5.2. Nucleation parameters, $E_n$ and $\ln(C_n)$, for the single-layer and sandwiched Sb$_{3.3}$Te films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_n$ (eV)</th>
<th>$\ln(C_n)$; $C_n$ in s$^{-\alpha}$m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-layer</td>
<td>6.1 ± 0.4</td>
<td>171 ± 10</td>
</tr>
<tr>
<td>GeCrN sandwiched</td>
<td>6.2 ± 0.2</td>
<td>174 ± 5</td>
</tr>
<tr>
<td>ZnS-SiO$_2$ sandwiched</td>
<td>6.4 ± 0.2</td>
<td>178 ± 4</td>
</tr>
</tbody>
</table>

The nucleation parameters, $E_n$ and $\ln(C_n)$, determined for the single-layer and sandwiched Sb$_{3.3}$Te films are listed in table 5.2. $E_n = 6.1 \pm 0.4$ eV and $\ln(C_n) = 171 \pm 10$ for the single-layer film and these values are not strongly altered by sandwiching the film between GeCrN or ZnS-SiO$_2$ layers. Comparing these nucleation parameters with those
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reported for the nucleation-dominant Ge2Sb2Te5 films in Ref. 24 is not appropriate. The reason is that the reported activation energy for nucleation (4.7 ± 1.1 eV) and the natural logarithm of the preexponential constant (166 ± 43) in Ref. 24 are too high compared to those estimated from the fit shown in Fig. 5 of Ref. 24. Another in-situ TEM study [30] reports an activation energy for nucleation of 2.8 ± 0.3 eV for a 50 nm thick Ge2Sb2Te5 film on a SiO2 layer. On the basis of ex-situ AFM measurements an activation energy for the steady state nucleation rate of 3.50 ± 0.17 eV and 4.09 ± 0.20 eV were obtained for 30 nm thick uncapped Ge2Sb2Te5 and Ge4Sb1Te5 films, respectively [31]. All these results show that the activation energy for nucleation is clearly smaller for the nucleation-dominant material than for the fast-growth material we studied.

5.4. DISCUSSION

5.4.1. Why do the capping layers affect the growth rate?

In chapter 4 (and in Ref. 27), we explained the influence of the adjacent dielectric layers on the crystal growth rate in the phase-change film on the basis of the following equation:

\[
V_g = C_g \exp\left(-\frac{E_g}{kT}\right) \left[1 - \exp\left(-\frac{\Delta G}{kT}\right)\right]
\]

(5.7)
equation (5.7) can be derived at the atomic scale where two atomic positions on both sides of an interface are considered with a Gibbs free energy difference \(\Delta G\) \((\Delta G < 0)\). \(E_g\) is activation energy required for an atom to jump across the interface and \(C_g\) is equivalent to an attempt frequency, \(v\), times the jump distance, \(d\). It makes a substantial difference if these atomic positions are considered at the amorphous-crystalline \((a-c)\) interface near the middle of the phase change film or at the \(a-c\) interface in contact with the dielectric layers. The thinner the phase-change film the larger the fraction of atomic positions influenced by the dielectric layers and the stronger the influence of the dielectric layers on the crystal growth rate. The presently investigated 20 nm phase-change films are expected to be about 60 to 70 atoms thick.

Figure 5.8 shows various interfaces associated with the crystallite growing in a sandwiched amorphous phase-change film. In general, the interfacial energy of an amorphous-amorphous interface is lower than that of amorphous-crystalline one \(\gamma_{a-c}\). Therefore it is possible that the amorphous dielectric layers are not favorable for the
crystal growth, if the amorphous-dielectric interface energy ($\gamma_{a-D}$) is less than the crystalline-dielectric interface energy ($\gamma_{c-D}$). This consideration is consistent with our observation that both ZSO and GCN capping reduces the growth rate. Also, it does not have to imply that the nucleation rate is reduced by the capping layers, because if $\gamma_{c-D} < \gamma_{a-c}$ nucleation can still be accelerated by the capping layer as is maybe the case with GCN, whereas for ZSO then $\gamma_{c-D} > \gamma_{a-c}$ and the nucleation rate is reduced. Unfortunately, these interfacial energies are not known. However, Kalb et al. [32] recently measured (a lower limit for) the crystal-melt interfacial energy for various phase-change materials including a Sb-rich alloy via DTA based under cooling experiments.

Our results show that the reduction in growth velocity (by the dielectric capping layers) is dramatic only at relatively low temperatures, it would hence improve the data retention. But this effect is insignificant at high temperatures, which can be advantageous for high data transfer rate. In our analysis (shown in section 5.3.1) we can incorporate this reduction in a phenomenological way in the activation energy for growth $E_g$. However, it is not obvious by what physical mechanism the type of dielectric layer affects the activation energy for growth that is in principle an intrinsic property of the $a-c$ interface within the phase change film. On the other hand, the effect on $\Delta G$ is obvious, because, when considering $\Delta G$ on a continuum scale, it is the sum of the bulk, interface and strain

![Diagram of amorphous-crystalline interface](image)

*Fig. 5.8. Representation of the amorphous-crystalline interface during a steady state growth, its wetting angle, $\theta$, with the adjacent dielectric layer and the three interfacial energies $\gamma_{a-c}$, $\gamma_{a-D}$ and $\gamma_{c-D}$.\*
energy terms. Neglecting the strain energy term (more on this in section 5.4.2), $\Delta G$ can be expressed as:

$$\Delta G = (G_c - G_a)\pi r^2 d + \gamma_{c,a} 2\pi r d + (\gamma_{c,c} - \gamma_{a,c}) \pi r^2$$

where, $G_c$ and $G_a$ are the bulk energies of the crystalline and amorphous phases, respectively. $r$ is the crystal radius and $d$ is the phase-change film thickness (i.e. 20 nm). The last term involving the film-dielectric interfacial energy becomes more important the thinner the phase-change film. At the melting temperature ($T_m$), $G_c - G_a$ is zero and the value becomes increasingly more negative at lower temperatures. Our measurements are performed at relatively low temperatures just above the glass transition temperature, $T_g$, and well below $T_m$. Therefore, it is expected that $\Delta G$ is not small and does not strongly change within the temperature interval of our measurements. Hence, the last term in equation (5.7) can account for about 10% constant reduction in growth rate, but cannot explain the strong (up to a factor of 7) reduction, that is also strongly varying with temperature, as we observe.

A more plausible physical origin for the large variations in $C_g \exp(-E_g/kT)$ we observe can be the viscosity of the phase-change material, which is often taken according to the Stokes-Einstein relation directly proportional with the reciprocal of the jump attempt frequency $1/\nu$ [33-35]. In some cases the viscosity is described by an Arrhenian temperature dependence [35-38]. However, in most cases the (strongly temperature dependent) Vogel-Fulcher-Tammann (VFT) relation (that holds particularly in the temperature range $T_g < T < T_g + 100$ K) is used to describe the viscosity $\eta$ [32,39-42].

$$\eta(T) = \eta_0 \exp\left(\frac{A}{T - T_0}\right)$$

where $\eta_0$ and $A$ are constants. $T_0$ is the ideal glass transition temperature that is generally about $T_g - 50$ K. Again, the viscosity is in principle an intrinsic property of the phase-change material. Nevertheless, it is likely that the viscosity within a certain phase is largely influenced if this phase is strongly confined at the nanometer scale by more or less rigid walls. Such a confinement should in general result in an increase in viscosity (i.e. atomic rearrangements are limited), leading to a reduction in growth rate. This is in accordance with our observations that adding capping layers to the phase-change film
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reduces the growth rate. If the capping layers cause for instance a small variation in $A$ or $T_0$ in the VFT relation, its effect will be most pronounced near $T_g$ and will decrease at higher temperatures and can thus explain our observation that the reduction in growth rate by the capping layers is most pronounced at the lowest temperatures.

5.4.2. How do the capping layers affect the overall crystallization rate?

Crystallization is a two step process involving nucleation and subsequent growth of critical nuclei. In actual applications of fast-growth type phase-change materials nucleation is in principle not required at all, since crystallization (i.e. erasing) of an amorphous written mark proceeds by growth from the crystalline rim to the centre of the mark without requiring any crystal nucleation. Moreover, very low nucleation rates are beneficial for having a good archival stability and a low jitter level. When the phase-change film is sandwiched, both the nucleation and growth processes are dominated by: (i) the interfaces between the phase-change film and capping layers when the phase-change film is very thin and (ii) the bulk when the phase-change film is thick. The interfacial effect of the capping layers can be attributed to factors such as interface morphology, stress at the interface and the so-called \textit{interfacial confinement}.

Since the crystals nucleate at the interface [17,24,43], the interface morphology is expected to have some influence on nucleation. However, it has been shown that the morphology does not play a vital role in the crystallization [15] although it can differ due to different types of capping layers and/or different deposition procedures. Considering the second factor, capping layers can induce either tensile or compressive stress within the phase-change film at the interface depending on their material type. These induced stresses should then affect the crystallization temperatures, i.e. tensile and compressive stresses should correspond to higher and lower crystallization temperatures, respectively [17,18]. However, it is reported [15] that the magnitudes of these stresses are low (~80 MPa) and do not differ significantly with capping layer type. In another work [18] both tensile (200 MPa) and compressive (250 to 400 MPa) stresses were measured for different types of capping layers, but in all cases the crystallization temperature went up, indicating that the stresses (of these magnitudes) do not play an important role in crystallization. Thus, in principle only the third and fourth factor, i.e. a kind of ‘pure’ interfacial energy that is only based on (chemical/physical) bonding states at the interface
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or the interfacial confinement, remain as origin for the difference in the crystallization, where the role of the interfacial energy has already been emphasized by a few authors [15,18,43].

Ohshima [15] studied the influence of various dielectric protective layers (including ZnS + 20 mol% SiO$_2$) on crystallization process of Ge$_1$Sb$_2$Te$_4$ film. It was reported that the activation energy for total (or overall) crystallization of the single-layer film is 2.2 eV and it increases up to 3 eV (for SiO$_2$) when the capping layers are included. Since the activation energy as used by Ohshima is the activation energy for total crystallization, which includes both the nucleation and growth processes, a direct comparison between our $E_g$ (or $E_n$) and the abovementioned activation energy cannot be made. However, the total activation energy ($Q$) can be calculated for our samples as

$$Q = \frac{E_n + D\beta E_g}{\alpha + D\beta}$$

(5.10)

where, $D$ is the dimensionality of growth ($D = 1, 2$ and $3$ for one dimensional, two dimensional and three dimensional growth, respectively) and $\beta$ is the growth index ($\beta = 1$ for interface-controlled growth and $0.5$ for the diffusion-controlled growth). For our case $D = 2$ and $\beta = 1$. The calculated $Q$ values are $2.9 \pm 0.3$, $3.4 \pm 0.2$ and $3.5 \pm 0.4$ for the single-layer, GeCrN and ZnS-SiO$_2$ sandwiched Sb$_{3.3}$Te films, respectively. Note that in fact $Q$ is (generally) close to the corresponding $E_g$.

It has been shown earlier that sandwiching the nucleation-dominant films such as Ge$_1$Sb$_2$Te$_4$ and Ge$_2$Sb$_2$Te$_5$ with ZnS-SiO$_2$ layers leads to an increase of 0.4 to 0.5 eV in $Q$ [15,22]. An almost similar increase of 0.5 to 0.6 eV in $Q$ is found in our case for Sb$_{3.3}$Te films. However, from the present measurements it is clear that this increase is caused by the increase in the activation energy for crystal growth and not by the one for nucleation. Njoroge et al. [18] determined $Q$ to be $3.03 \pm 0.17$ eV for an uncapped Ag$_5$In$_6$Sb$_{59}$Te$_{30}$ film and they found that this value increases to $3.24 \pm 0.12$ eV and decreases to $2.39 \pm 0.10$ eV when the film is sandwiched between Si$_3$N$_4$ and ZnS-SiO$_2$ layers, respectively. The reduction in $Q$ they found for ZnS-SiO$_2$ sandwiching contrasts with our results and also the results of both Refs. 15 and 22, where ZnS-SiO$_2$ sandwiching leads to an increase in $Q$. The capping layer influence on the nucleation rate observed in the present investigation has also another interesting similarity with Ohshima’s work [25],
where it is reported (for Ge$_1$Sb$_2$Te$_4$ films) that the nucleation is accelerated and retarded by Si$_3$N$_4$ and SiO$_2$ capping layers, respectively. In our case (for Sb$_{3.3}$Te films), the nucleation is accelerated by GeCrN and decelerated by ZnS-SiO$_2$.

5.5. CONCLUSIONS

The influence of amorphous GeCrN and ZnS-SiO$_2$ capping layers on the crystallization of doped Sb$_{3.3}$Te thin films was analyzed using a TEM. Direct and quantitative information on crystal nucleation and growth was obtained. The temperature dependent crystal growth rate reduces if Sb$_{3.3}$Te film is sandwiched between the capping layers and turns out to be dependent on the capping layer type. The effect of capping layers on the growth rate is pronounced at lower temperatures (about 160°C) and it tends to disappear at higher temperatures (about 200°C). The activation energy for crystal growth is 2.4 ± 0.3 eV for Sb$_{3.3}$Te single-layer and it increases about 40% when the capping layers, GeCrN or ZnS-SiO$_2$, are added. The nucleation rate shows temperature and time dependence. The ‘nucleation index’ is found to be independent of temperature and the capping layer type. It is determined as 1.8 ± 0.4. GeCrN layers accelerate the nucleation by a factor of about 1.7 whereas ZnS-SiO$_2$ layers decelerate it about 5 times. The activation energy for crystal nucleation is almost unaffected by the capping layers and is about 6.2 eV for all the samples. The variations observed in both the growth and nucleation parameters are attributed to the interfacial energy (chemical bonding) between the phase-change and capping layer material and to the confinement of the phase-change material by the capping layer where we expect that it increases the viscosity within the phase-change film.
REFERENCES


