

***In situ* TEM study of the crystallization of fast-growth doped Sb_xTe alloy films**

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ABSTRACT

Crystallization of amorphous thin films composed of doped Sb_xTe with x=3.0, 3.6 and 4.2 and constant dopant level was studied by *in situ* heating in a TEM. Magnetron sputtering was used to deposit 20 nm thick films sandwiched between two types of 3 nm thick dielectric layers on 25 nm thick silicon-nitride membranes. One type of dielectric layer consists of ZnS-SiO₂ (ZSO), the other of GeCrN (GCN).

Crystallization was studied at temperatures ranging between 150 and 190 °C. The type of dielectric layer turned out to strongly influence the crystallization process. Not only the nucleation rate appeared to depend sensitively on the dielectric layer type, but also the growth rate. The velocity of the crystalline/amorphous interface is about 5 times higher for the x=4.2 film than for the x=3.0 film if ZSO is used. In case of GCN the interface velocity is about 2 times higher for the x=4.2 film than for the x=3.0 film. The activation energy for crystal growth is not strongly dependent on the Sb/Te ratio, but clearly different in case of ZSO and GCN at 2.9 eV and 1.9 eV, respectively. The incubation time for the crystal nuclei formation is longer for ZSO than for GCN. Although the effects of the Sb/Te ratio and of the dielectric layer type on the growth rates is strong, their effects on the nucleation rate are even more pronounced; a higher Sb/Te ratio results in a lower nucleation rate and the use of GCN instead of ZSO leads to much higher nucleation rates.

1. INTRODUCTION

The crystallization rate in phase change optical recording, known from the rewritable CD and DVD formats, is becoming increasingly important because of the increasing demands on the data-transfer rates. Crystallization is the rate-limiting process, because amorphization is inherently a much faster process that in principle can be performed within femto-seconds¹. Ge₂Sb₂Te₅ shows nucleation-dominated crystallization, i.e. it nucleates easily and fast, but it shows only limited growth, with final sizes of the crystallites within a disc of 10-30 nm^{2,3}. With the ongoing decrease of the amorphous-mark sizes due to a decrease in laser wavelength and an increase in numerical aperture of the focusing lens, phase-change materials showing very fast growth (i.e. growth-dominated crystallization) tend to become more preferable than Ge₂Sb₂Te₅, that is to say at least with respect to attainable data-transfer rates^{3,4}. If the bit size decreases, the distance a fast growing crystal has to proceed from the edge of the amorphous mark to its center decreases and consequently the rewriting speed increases. For decreasing mark sizes, nucleation becomes less an issue since 'nuclei' are always available near the edge of the mark. Therefore, phase-change materials showing very low nucleation rates, but fast growth rates become increasingly important. Apart from application to optical recording, phase change materials are also of considerable interest for electrically-based memory devices due to the large difference in resistivity (up to three to four orders in magnitude) for the amorphous and crystalline phase.

The fast-growth type of phase-change materials is investigated in the present work. These materials are based on a Sb-rich Sb-Te eutectic composition (Sb_xTe with x=3.0, 3.6 and 4.2), since it is known that these Sb-rich alloys show highest crystallization rates^{3,4}. A systematic study is made of the influence of these three different Sb/Te ratios on the crystallization kinetics, in particular the crystal growth rate. The 'dopant' level (about 8 at.%) is kept constant for these three ratios. In previous work the strong effect of varying the Ge dopant level in Sb_{3,6}Te was studied⁵. In addition the present work addresses the influence of two types of thin dielectric layers, between which the phase-change layer is sandwiched, on the crystallization kinetics.

The crystallization process is studied by Transmission Electron Microscopy (TEM) using *in situ* heating. Advantage of this technique is that it provides detailed information with a high spatial resolution (nuclei with a size of 5 nm are easily detected), allowing nucleation (rates) and growth (rates) to be monitored separately. Most

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techniques for the determination of crystallization kinetics measure the overall crystallization rate, which is an interplay of nucleation and growth, but are unable to unravel these separate contributions. Crystal structure(s), crystal size distributions, crystal shapes, crystal orientations and defects within the crystals grown can be assessed using TEM. A disadvantage of TEM could be that the electron beam of the TEM affects the crystallization process. In a previous study on $\text{Ge}_2\text{Sb}_2\text{Te}_5$ the electron beam turned out to strongly enhance the nucleation rate, obscuring a normal (isothermal or isochronal) analysis of the transformation kinetics⁶.

2. EXPERIMENTAL

Magnetron sputtering was used to deposit 20 nm thick doped Sb_xTe films sandwiched between 3 nm thick dielectric layers. Three different values for the Sb/Te ratio were used, $x=3.0, 3.6$ and 4.2 , and sandwiching occurred between two types of dielectric layers. One layer type is based on ZnS-SiO_2 (ZSO), the other on GeCrN (GCN). A constant dopant level of Ge+In below 12 at.% was used. As substrates for deposition 25 nm thick silicon-nitride membranes were used. These transparent substrates were obtained by etching $1 \times 1 \text{ mm}^2$ windows in a Si wafer containing the thin Si-nitride film on one side. Specimens were stored in vacuum to prevent oxidation of the films.

For TEM a JEOL 2010F operating at 200 kV was used. A Gatan double tilt heating holder (model 652 with a model 901 SmartSet Hot Stage Controller) was used that employs a PID controller for accurately control of the temperature (within ± 0.5 °C) and for a fast ramp rate to attain the desired final temperature without overshoot. Note that the temperature of the thin area that is imaged using TEM is generally lower than the nominal temperature indicated by the heating element within the specimen holder, i.e. the higher the temperature, the larger the discrepancy. In order to allow a correct comparison of the various samples, it turned out important to always measure a not too large area (with identical dimensions) directly at the edge of the Si-nitride window. A clear gradient in number of crystal nuclei that develop and in their size due to subsequent growth was observed as a function as distance from the edge to the center of the window. Within the relative small analysis area this gradient is irrelevant.

In order to measure the crystal growth rates accurately, crystallization is monitored at relative high magnifications (100 kx) within the TEM. This has two main disadvantages. First, the number of nuclei that develop in the observed area is very low (say 4 to even below 1), preventing a statistical accurate analysis of the nucleation rate. However, this is not a serious disadvantage, since previous work^{5,6} showed that the electron beam of the TEM clearly increased the nucleation rate, which therefore should not be analyzed by continuous monitoring at the transformation temperature, but after cooling down to room temperature. Second, the higher the magnification, the higher the current density of the electron beam of the TEM that is transmitted through the sample. This increases the possible influence of the electron beam on nucleation and growth. Previous work showed that the influence on nucleation was large, but negligible on growth⁵. In the present work, however, the electron beam turned out to also clearly increase the crystal-growth rate. This difference between the present and the previous work is likely to be the result of using sputtered films at present and electron-beam evaporated films previously. More details on this difference are presented within the results below. In order to analyze the effect of the activation by temperature care was taken to always use an identical current density of the electron beam through the sample. Nucleation and growth can of course also be measured by intermittent heating within the TEM (without observation) and cooling to room temperature where the observations takes place.

3. RESULTS AND DISCUSSION

Reasonable incubation times for crystallization (within one hour) and absence of crystallization before the desired isothermal transformation temperatures is reached put clear bounds on the temperature interval which is suitable for the (*in situ* TEM) study of crystallization. For the alloy films in this study the temperature interval turned out to be in-between 150 and 190 °C. The incubation time for crystallization appeared to be clearly shorter when the dielectric layers GCN were used instead of ZSO. Therefore crystallization of the phase-change films sandwiched between GCN was possible starting at about 150 °C, whereas for sandwiching between ZSO was possible starting at about 160 °C. An example of the results of *in situ* TEM monitoring of the crystallization is shown in Fig.1; this specific example is for an Sb/Te ratio of 3.0, ZSO dielectric layers and an isothermal transformation temperature of 170 °C. The incubation time in this case was about 4.5 minutes (starting when the temperature reached 169 °C). The images show that the growing crystals are more or less circular, so that growth is more or less isotropic.

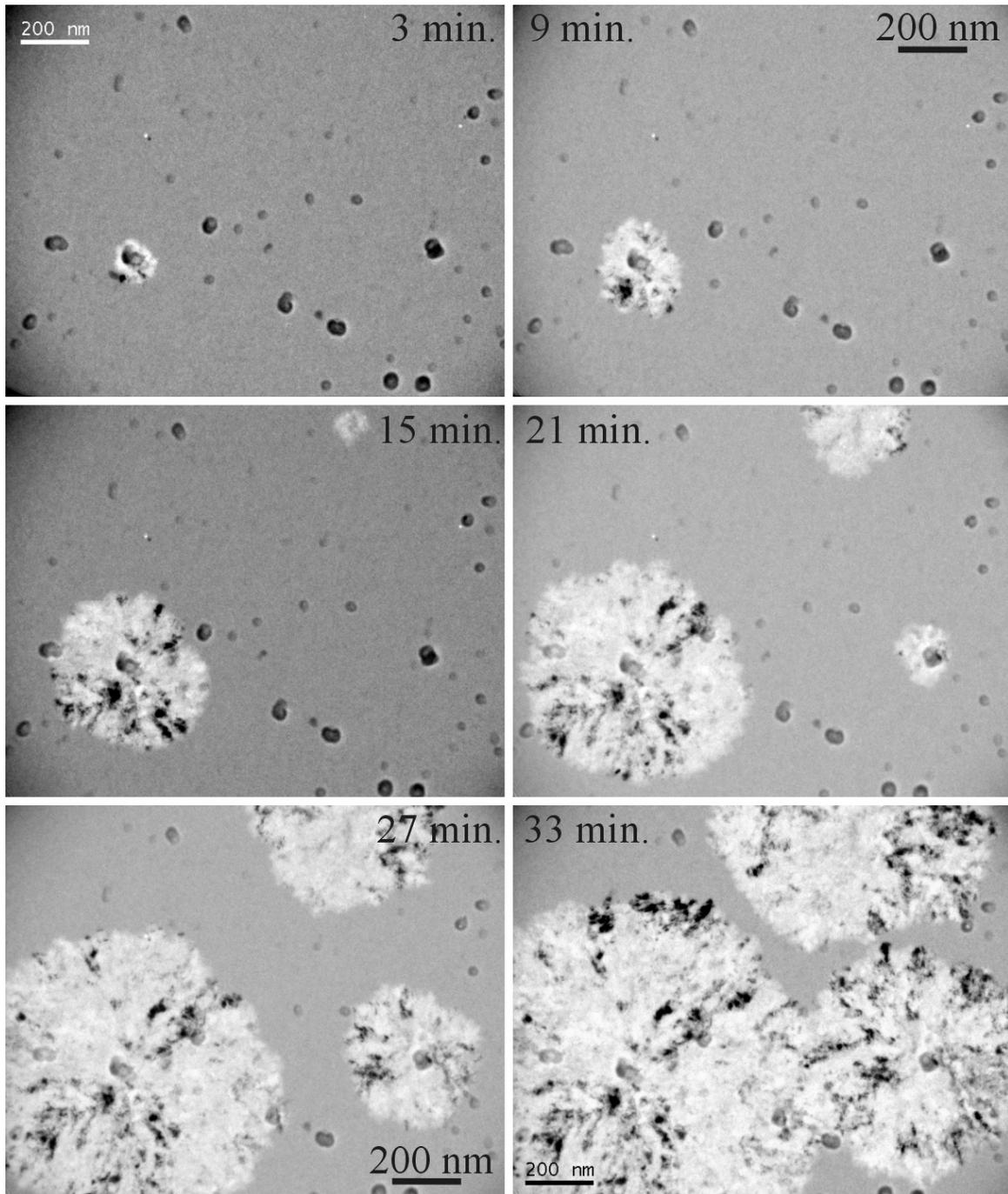


Fig.1 Bright-field TEM images of crystal growth during heating at 170 °C of a phase-change film with an Sb/Te ratio of 3.0 that is sandwiched between ZnS-SiO₂. The time indicated in the images is the time used for growth after the incubation time, that for this example was 4.5 min.

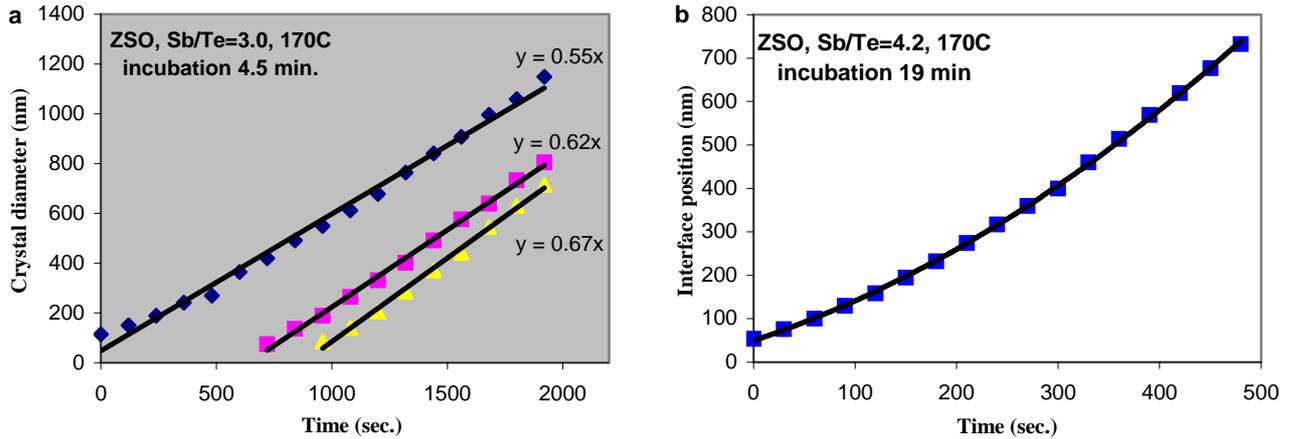


Fig.2 From the change of the crystal diameter or the interface position (corrected for drift) as a function of time the crystal growth rate can be obtained. The growth rate is not constant, but appears to increase proportional with time. The crystal growth shown in Fig.1 is the basis for the results shown in Fig.2a.

Clearly anisotropic growth was observed in previous work on undoped $Sb_{3.6}Te$, where intermediate dopant level (5 at.% Ge) clearly increased the isotropy⁵. When the dielectric layers were GCN, growth appeared to be slightly less isotropic compared to ZSO. A larger number of images than shown in Fig.1 allow the measurement of the average crystal diameter as function time. The result is shown in Fig.2a. The slopes of the linear regressions in Fig.2a allow the determination of the crystal growth velocities (i.e half the slope, because the diameter corresponds to the advancement of two interfaces). Two systematic effects are observable in Fig.2a. First, the crystal size is generally not a linear function of time, but the growth rate increases with time. In order to observe this, the number of data points has to be sufficiently large and the time interval sufficiently long. Therefore this effect was up to now not detected in previous growth studies on sputtered phase-change films^{7,8,9}. Fig.2b shows another example of the deviation from linear growth. It turns out that the positive curvature can be accurately

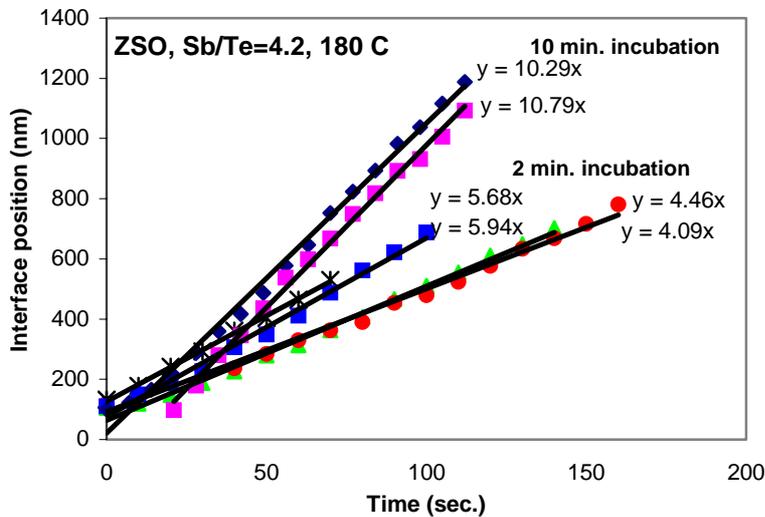


Fig.3 Interface positions (corrected for drift) as a function of time during crystallization of a film with an Sb/Te ratio of 4.2 at 180 °C after two different incubation times. The growth velocities in-between 4 and 6 nm hold for after incubation time of 2 min. and in-between 10 and 11 nm after an incubation time of 10 min.

described by a parabolic fit. This shows that the increase of the growth velocity is approximately a linear function of time. The second connected effect is that crystals that nucleate later show on average a higher growth velocity. This is observable in Fig.2a and another example is shown in Fig.3. For the case shown in Fig.3 crystallization of the observed area occurs within the order of a few minutes and therefore an incubation time clearly longer than this crystallization time results in a difference in growth velocity. The growth velocities in-between 4-6 nm/s hold for a short incubation time of 2 min., whereas the growth rates in-between 10-11 nm/s hold for an incubation time of 10 min. These results clearly show that during heating (and simultaneous electron beam exposure) relaxations with the sputtered amorphous matrix take place,

that enable a subsequent faster growth. These relaxations are pronounced for the presently studied sputtered films and therefore easy to detect, but were not detected in our similar previous study on electron-beam evaporated phase-change films⁵. Apparently the amorphous phase after sputtering is in a much less stable condition than after (e-beam) evaporation. A likely origin of the difference in stability is the presence of clearly larger residual stresses within the sputtered film. These stresses were easily observable at low magnifications under a light microscope, due to fringe fields showing buckling of the membrane. In this context it has to be mentioned that also the dielectric layers can have some additional influence on the residual stresses. In the previous study the phase change layer was directly evaporated on the Si-nitride membrane, whereas in the

present work they are also sandwiched between thin dielectric layers. Therefore relaxations within the present phase-change films are more constrained, can maybe not occur very fast and are therefore more apparent. A future study of films which are directly sputtered on the membranes, should show how important is the influence of the dielectric layers on the relaxations within the amorphous matrix. As a last example, Fig. 4 shows that relaxation occurs as a function of annealing at temperature, and is not a dominant effect of electron beam exposure. Fig. 4a shows crystallization at 170 °C, for a sample that was not previously heated and Fig. 4b another area of the same sample after it had subsequently been heated for 2 hours at 160 °C and 9 minutes at 180 °C. The second time heating at 170 °C shows a shorter incubation time. According to the results shown in Fig.3 this would mean a lower growth velocity. However, in Fig.3 the difference in incubation time is just a difference in statistical probability that crystallization starts in a certain area. In Fig.4 it will be clearly, on average, shorter the second time at 170 °C than the first time due to the annealing that has taken place in the mean time. Moreover, due to this annealing the amorphous matrix is more relaxed allowing a higher growth velocity. This increase in growth velocity apparently outweighs the decrease in incubation time.

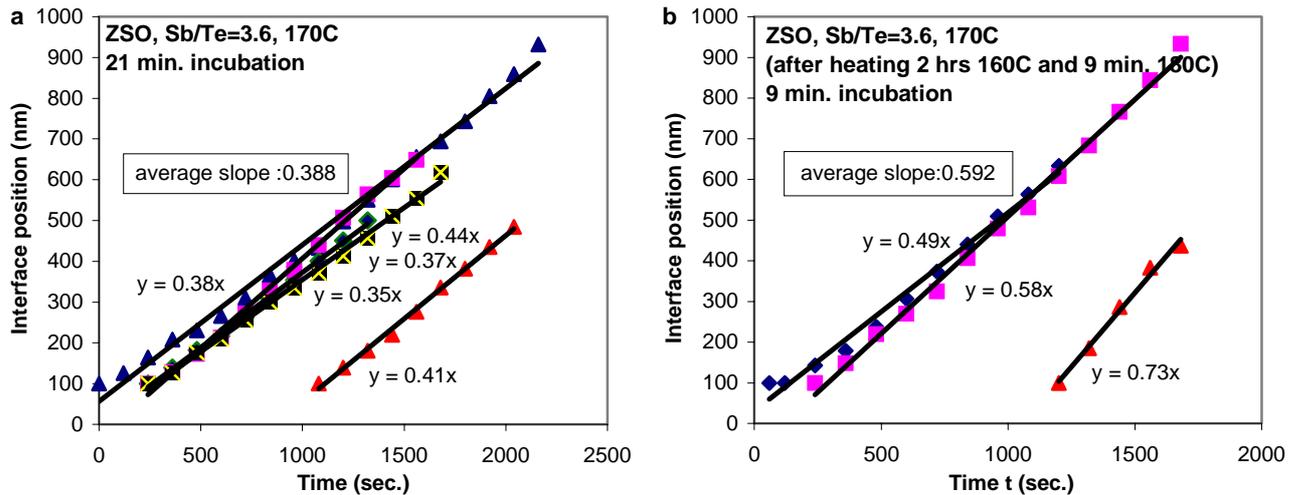


Fig.4 Interface positions (corrected for drift) as a function of time during crystallization of a film with an Sb/Te ratio of 3.6 at 170 °C after two different annealing conditions. In **a** the film is not annealed previously, whereas in **b** the film is annealed 2 hours at 160 °C and 9 min. at 180 °C before the crystal growth is measured.

The main results of the present work are shown in Fig.5. It shows the measured crystal growth velocities for the various Sb/Te ratios and the two types of dielectric layers as a function of transformation temperature. The plot is of Arrhenius type, i.e. showing the logarithm of the crystal growth velocity as a function of reciprocal temperature. The slopes of the linear regressions in Fig.5 allow the assessment of the activation energy for growth. Most data points shown in Fig.5 are an average of about 5 separately measured interface velocities. Despite the large influence of the relaxations, which make an accurate determination (without systematic errors) of the crystal growth rate difficult, it turns out that the differences between the various Sb/Te ratio and the two dielectric layers are so pronounced that important conclusions can still be drawn:

1. When the dielectric layers are ZSO, the crystal-growth velocity within the Sb/Te=4.2 films is about 5 times higher than within the Sb/Te=3.0 films. For Sb/Te=3.6 the growth velocity is intermediate.
2. When the dielectric layers are GCN, the crystal-growth velocity within the Sb/Te=4.2 films is about 2 times higher than within the Sb/Te=3.0 films.
3. The activation energy for growth is not strongly dependent on the Sb/Te ratio, but is clearly different for growth between the two types of dielectric layers. The activation energy for growth is on average about 2.9 eV in case of ZSO and about 1.9 eV in case of GCN. So a difference of about 50% exists.
4. For the temperature interval considered the growth rate within phase-change films with the same composition is generally higher if the dielectric layers are of type GCN. However, since the activation energy for growth is clearly higher in case of ZSO, this distinction will reverse at higher temperatures. The transition for this reversal for Sb/Te=4.2 already occurs around 175 °C and for Sb/Te=3.0 around 190 °C.
5. The incubation time for crystallization is longer in case of ZSO than GCN.
6. More tentative conclusions are that a larger Sb/Te ratio leads to a slightly longer incubation time and higher activation energy.

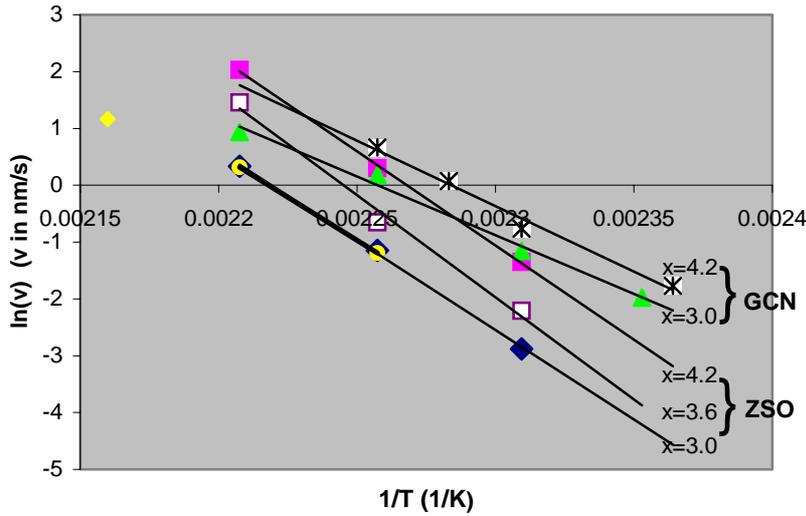


Fig.5 Logarithm of the crystal growth velocity versus the reciprocal temperature for the various Sb/Te ratios x and the two types of dielectric layers (ZnS-SiO₂ or GeCrN).

lot of scatter)⁷ and 2.4 eV (on SiO₂)⁸ for Ge₂Sb₂Te₅, 2.35 eV for Ge₂Sb₂Te₅ (on Si(100))⁹, 2.74 eV for Ge₄SbTe₅ (on Si(100))⁹ and 2.90 eV for Ag_{5.5}In_{6.5}Sb₅₉Te₂₉ (on Si(100))⁹. The composition of the films used to obtain this last result is most comparable to the present ones (i.e has a Sb/Te ratio near to 3.0 and a similar dopant level) and the result is also the same as obtained in case of dielectric layer type ZSO. The crystal shapes and sizes observed for Ag_{5.5}In_{6.5}Sb₅₉Te₂₉ with AFM⁹ are also comparable with the results obtained here. However, an important difference is that in Ref.9 only growth of pre-existing nuclei was observed (so all crystals have always a similar size), whereas in the present work, although nucleation is also dominant at the beginning of crystallization, nuclei still develop during later stages of the transformation (cf. Figs.6, 7 below). This results here in a broader crystal-size distribution. In both cases nucleation is (expected to be) heterogeneous; at the film surface (influence of native oxide?) in Ref.9 and at the interface between the phase-change and the dielectric layers in the present work.

Images of the as-deposited amorphous films show the presence of distinct particles with a size up to 40 nm. These nano-clusters were clearly detected by TEM (cf. Figs.1, 6 and 7), but also by tapping mode AFM. These clusters were observed for the three types of Sb/Te ratios and the two types of dielectric layers. Energy-Dispersive X-ray Spectro-metry connected to the TEM indicated that these particles appear to be slightly enriched in GeTe (and depleted in Sb). They probably develop because several targets instead of one compound target were used for sputtering in order to arrive at the films with the large variation in Sb/Te ratio. During the sputter process in the gas/plasma phase atoms from the different targets may aggregate and form clusters that are subsequently deposited. Chemical bonding preferences (e.g. between Ge and Te) during this aggregation possibly explains the composition of the clusters that deviates from the average one of the phase change layer. These clusters had clear influence on nucleation; they appeared preferential sites for nucleation. Nevertheless, significant differences in nucleation rate were still observed for the various Sb/Te ratios and the two dielectric layer types. Moreover, the overall growth rates within the films measured were not affected by the presence of these particles. Since the thickness of the phase change layer is controlled by the mass change, the presence of the clusters reduces the thickness of the phase change film. From the particle density and their size it can be estimated accurately that the film thickness will not be smaller than 18 nm instead of the nominal 20 nm.

In our previous study on Sb_xTe films we found an activation energy of 1.6 eV for the undoped film and about 2.4 eV in case of 5 at.% Ge addition⁵. The present films contain about 8 at.% dopants and are thus expected to be similar to the second type of film in the previous study. However, these previous films were not sandwiched between dielectric layers. Therefore it is intriguing that for ZSO the activation energy for growth is about 0.5 eV higher and for GCN about 0.5 eV lower than the previous result of 2.4 eV. Other growth studies show activation energies of 1.6 eV (Si₃N₄ sandwich, but data show a

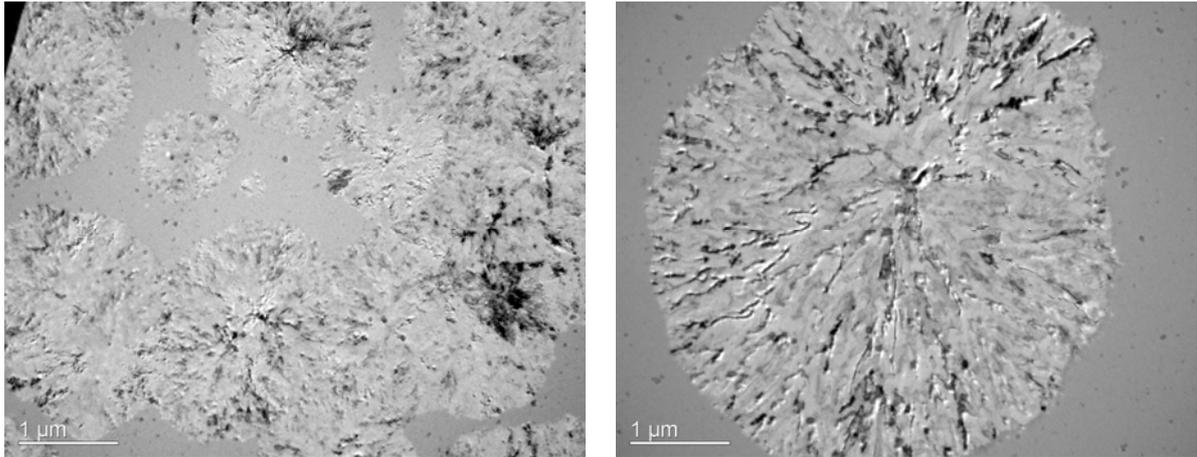


Fig.6 After crystallization at 170 °C a grain size of 1,5-2 μm develops within the films with an Sb/Te ratio 3.0 as shown left and a grain size of about 6 μm within the films with an Sb/Te ratio 4.2 as shown right. In both cases ZnS-SiO₂ was used as sandwich.

Although direct measurements of the nucleation rate were not performed in the present work, an analysis of the grain-size and its distribution still enable useful information on the nucleation rate to be obtained. Fig.6 shows images with identical scales of crystals formed at 170 °C in the films with $x=3.0$ and $x=4.2$ sandwiched between ZSO. It is clear that the grain size is several times larger in case of the faster growing $x=4.2$ film. Now the question is, can this faster growth, together with a constant nucleation rate explain the difference in average grain size? Based on the theoretical analysis described in Ref.7, it can be derived relatively easily that the average crystal diameter or radius (during later stages of the transformation, i.e. fraction transformed larger than 0.5) scales with $(G^2/I_0)^{1/(a+d)}$, where G is the constant growth rate with growth occurring in d dimensions and where the nucleation rate per unit of untransformed area obeys $I=I_0t^{a-1}$, with t the time and a thus an exponent for the time dependence of the nucleation rate. Assuming for the present work that $d=2$ and a is between 1 (i.e. continuous nucleation rate) and 0 (i.e. nucleation rate clearly decreases as a function of time, is similar to pre-existing nuclei), shows that the average grain size scales with factors in-between $(G/I_0)^{1/3}$ and $(1/I_0)^{1/2}$, where the latter I_0 can also be regarded as the number of pre-existing nuclei per unit of area. The difference in growth rate between the $x=3.0$ and $x=4.2$ films is about 5 times and the difference in crystal diameter is 3 to 4 times (see Table 1). This indicates with the above information that I_0 is between 5.4 to 16 times larger for the $x=3.0$ than the $x=4.2$ film. To explain the difference in grain size an even larger difference in nucleation rate than growth-rate is needed. An example of the influence of the sandwich layer on the nucleation rate is depicted in Fig.7; Fig7a holds for ZSO and Fig7b for GCN. Despite a growth rate that is 3.5 to 4 times faster at 170 °C in case of GCN than ZSO, the grain size is a factor 2 smaller. This means that the nucleation rate in case of GCN is in-between 4 to 32 times faster than in case of ZSO. So, also here the difference in nucleation rate is more pronounced than the difference in growth rate. A strong influence of the type of dielectric layers on the heterogeneous nucleation could of course be anticipated *a-priori* (see also earlier results and discussions on this matter^{7,10}). However, the direct measurement of the strong influence of the dielectric layers on the growth rate is a new, less expected and exciting result. An indirect indication that the dielectric layers directly affect the growth velocity is recently presented in Ref.11 and is based on finding a maximum in the crystallization velocity for a certain phase change film thickness (9 nm in their case). Both thinner and thicker films lead to a clear decrease of the crystallization velocity. Although the theoretical analysis to explain this observation as performed in Ref.11 is not fully correct (with flaws in the interpretation of the activation energy and the Gibbs-free energy change upon crystallization as used in the equation to describe the temperature dependence of the growth velocity), their conclusion that the dielectric layers adjacent to the phase-change layer directly affect the crystal-growth rate remains valid and is consistent with the present results.

Table 1 Average crystal diameter obtained after crystallization at 170 °C

Sb/Te=3.0 GCN	Sb/Te=3.0ZS O	Sb/Te=3.0 ZSO	Sb/Te=4.0 ZSO
~0.8 μm	1.5-2 μm	~4 μm	~6 μm

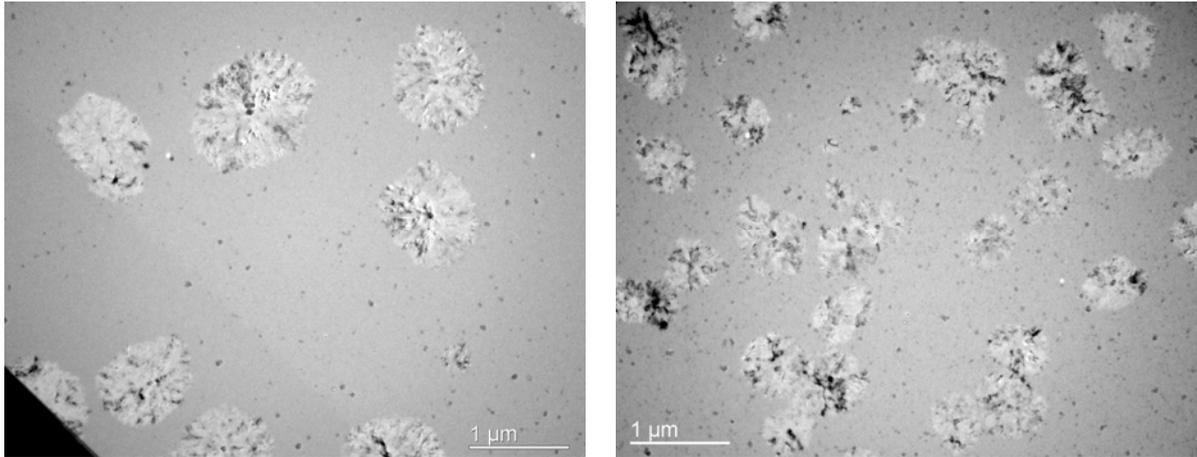


Fig.7 Despite a growth rate that is a factor 3.5 to 4 higher at 170 °C when GeCrN is used instead of ZnS-SiO₂, the grain size after crystallization attains a value that is a factor 2 smaller, pointing at a clearly higher nucleation rate for in case of GeCrN. In both cases the Sb/Te ratio of the films was 3.0.

4. CONCLUSIONS

In situ heating in a TEM in the temperature range 150-190 °C allowed the measurement of the crystal-growth velocity in sputtered phase change films based on three different Sb/Te ratios (3.0, 3.6 and 4.2) and as sandwiched between two types of dielectric layers: ZnS-SiO₂ (ZSO) or GeCrN (GCN). During annealing and electron beam exposure relaxations within the sputtered amorphous phase lead to a growth rate that slowly but continuously increases with time. The growth rate within the Sb/Te=4.2 films is about 5 times higher than within the Sb/Te=3.0 ones when ZSO is used. With GCN, the crystal-growth velocity within the Sb/Te=4.2 films is about 2 times higher than within the Sb/Te=3.0 ones. The activation energy for growth is not strongly dependent on the Sb/Te ratio, but is clearly different for growth between the two types of dielectric layers. The activation energy for growth is on average about 2.9 eV in case of ZSO and about 1.9 eV for GCN. For the temperature interval considered the growth rate within phase-change films with the same composition is generally higher if the dielectric layers are of type GCN, but this reverses after a relative small temperature increase due to the higher activation energy for growth in case of ZSO. The incubation time for crystallization is longer if ZSO is used instead of GCN. The average grain size after crystallization indicates that the nucleation rate *decreases* more strongly than the growth rate *increases* when changing the Sb/Te ratio from 3.0 to 4.2 (in case of ZSO) and that the nucleation rate *increases* more strongly than the growth rate *increases* when changing from ZSO to GCN (for an Sb/Te ratio of 3.0).

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