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Influence of dielectric capping layers on the crystallization kinetics of $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ films

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AgInSbTe alloys are attractive storage materials for phase change recording utilizing both optical and electronic contrast. The demand to decrease the thickness of such storage layers increases the significance of the surrounding dielectric layers, which can have a profound impact on the crystallization process. Hence we have investigated the influence of different capping layers on the crystallization kinetics of $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ films by measuring the electrical resistivity of the films as a function of temperature employing the van der Pauw method. While the phase transition temperature was found to only increase slightly for capped $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ films, a profound impact on the activation barrier for crystallization was observed. Activation energies of 2.39 ± 0.10 eV and 3.24 ± 0.12 eV were determined for films capped with 5 nm of ZnS-SiO_2 and Si_3N_4 , respectively, in comparison with a value of 3.03 ± 0.17 eV for an uncapped film. Additional stress measurements reveal that this change in activation barrier is not caused by stresses induced by the dielectric films but must rather be due to the different activation barriers for heterogeneous nucleation at the different interfaces. In the amorphous state the temperature dependence of the sheet resistance follows an activation-type relation, where the activation energy is not affected by the capping layer. © 2004 American Institute of Physics. [DOI: 10.1063/1.1774265]

I. INTRODUCTION

Phase change materials are based upon the reversible switching between an amorphous and a crystalline state. Since they offer a pronounced contrast for both optical and electronic properties they can be used for rewritable optical data storage as well as nonvolatile electronic data storage.^{1,2} In both types of storage devices the active layer is sandwiched between surrounding layers. The active layer is usually a Ge-Sb-Te- or a Ag-In-Sb-Te alloy. The surrounding layer which is typically a dielectric prevents vaporization during the heating process and protects the recording film from fatigue encountered upon the cyclical volume change during overwriting.³ It has been found that the choice of the dielectric layer is of tremendous importance, since it influences the rate of crystallization.⁴ The effect of several transparent dielectric films, employed as capping layers (protective layers) on the crystallization kinetics of Ge-Sb-Te recording film, has been studied.⁵⁻⁷ The Ge-Sb-Te alloys employed in those studies belong to the class of fast nucleation materials. It has been reported that not only do the protective films influence the crystallization mechanism but they also affect the number of achievable overwrite cycles. Results from previous work have shown that a combination of the recording film and the protective film is one of the dominant factors determining the characteristics of the optical disk.^{3,8} In this work, we investigate the influence of different dielectric layers on the crystallization and electrical properties of $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ thin films. This material belongs to the second class of phase change materials, the so-called growth

dominated materials where the nucleation rate frequently is lower than in nucleation dominated materials. Hence it is not clear *a priori* if for this class of materials also a strong influence of capping layers has to be expected.

II. EXPERIMENTAL PROCEDURES

dc magnetron sputtering was used to deposit $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ films while rf sputtering was used to deposit the dielectric layers of ZnS-SiO_2 , SiO_2 , and Si_3N_4 from targets with the corresponding nominal chemical compositions. The composition of the ZnS-SiO_2 target was 60% ZnS and 40% SiO_2 . The purity of $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ and SiO_2 targets was 99.99% while those of ZnS-SiO_2 and Si_3N_4 had a purity of 99.9%. Ordinary glass slides and silicon wafers were used as substrates. Preliminary deposition experiments were performed to investigate the rate of deposition at different sputtering conditions. The sputtering rate was determined by x-ray reflectometry measurements. An Ar pressure of 7.3×10^{-3} mbar and a power of 100 W were used to deposit all films except for ZnS-SiO_2 and SiO_2 films where a power of 60 W was employed. The resulting growth rates were determined to be 0.5 nm/s for $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$, 0.018 nm/s, 0.010 nm/s, and 0.013 nm/s for ZnS-SiO_2 , SiO_2 , and Si_3N_4 , respectively. Samples of 100 nm $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ coated with 5 nm of the different dielectric layers were prepared. Subsequently the sheet resistance was measured with a four-point probe setup following the procedure proposed by van der Pauw.⁹ The setup allows us to monitor the sheet resistance upon annealing in argon ambient. The sample temperature was measured by a NiCr/Ni thermocouple. Wafer curvature

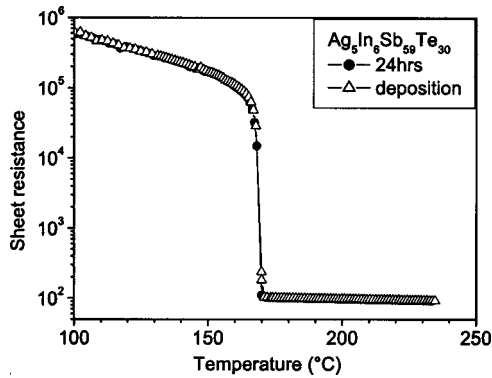


FIG. 1. Temperature dependence of the sheet resistance of 100 nm $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ films for samples measured immediately after deposition (open symbols) and one day after deposition (solid symbols).

measurements are employed to determine the stress induced by crystallization in thin films of phase change material sputter deposited onto thin glass or Si substrates. The wafer curvature is measured by a laser scanning technique using a rotating mirror and a position sensitive detector. The stress is determined from Stoney's equation.¹⁰

III. RESULTS AND DISCUSSION

Figure 1 compares the temperature dependence of the sheet resistance of $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ films measured immediately after deposition and one day after deposition. The two measurements exhibit an abrupt change around 168°C which is attributed to a phase change from amorphous to crystalline. This has been confirmed by our earlier structural studies.¹¹ Upon crystallization the sheet resistance changes by three orders of magnitude. Thus, this material can also be used for electronic solid-state memories. Another notable feature in Fig. 1 is the close agreement of the two measurements. One measurement was performed immediately after deposition while the other one was measured one day after deposition. The close agreement of both data sets is a clear evidence for the absence of a pronounced aging effect. Such an aging effect has been reported for a Ge-Sb-Te alloy.¹² The aging effect has been attributed to oxide formation on the film surface. These oxides on the film surface act as nucleation sites, which increase the nucleation rate hence lowering the transition temperature.

Figure 2 compares the temperature dependence of the sheet resistance upon annealing a single layer of 100 nm $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ and when the film is covered with a 5 nm thick protective layer. Figures 2(a) and 2(b) were obtained using heating rates of 0.5 and 3.0 K/min, respectively. The capping layers are indicated inside the individual graphs. It is observed that the heating rate only influences the phase transition temperature. The heating rate of 3.0 K/min leads to higher transition temperatures than that of 0.5 K/min. The transition temperatures for the samples with the protective layers are only slightly higher than those of the uncapped, single layer. The single layer curve and the curve of the film coated with Si_3N_4 exhibit an abrupt sheet resistance change in a very narrow temperature range. On the contrary the resistance change observed for films covered with ZnS-SiO_2

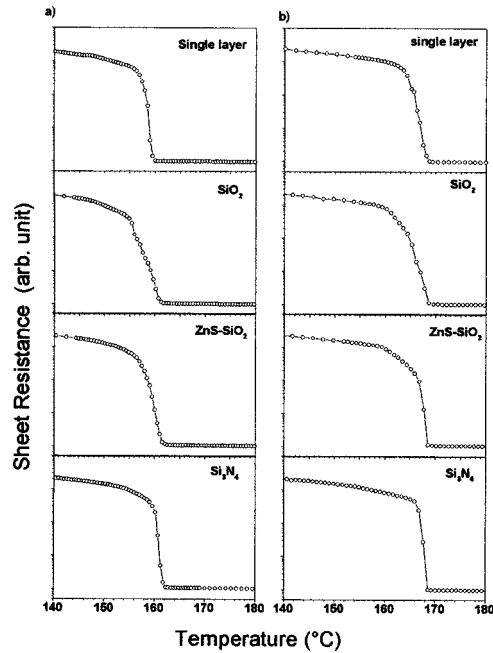


FIG. 2. Temperature dependence of sheet resistance upon annealing single layer of 100 nm $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ film and films covered with different protective layers having a thickness of 5 nm. The different protective layers are indicated inside the individual graphs. Curves of (a) and (b) were obtained using a heating rate of 0.5 K/min and 3.0 K/min, respectively.

and SiO_2 occurs in a relatively larger temperature range. These results prove unequivocally that the crystallization process of $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ films is influenced not only by the mere existence of a capping layer but also by the material of the capping layer used. In the amorphous phase the temperature dependence of the sheet resistance follows an activation-type relation,¹³

$$\sigma = \sigma_0 \exp\left(\frac{-E_{a_trans}}{kT}\right). \tag{1}$$

Here σ is the conductivity, σ_0 is a preexponential factor and E_{a_trans} is the activation energy for electronic transport. It is observed from Fig. 3 that the slope of the sheet resistance in the amorphous state does not depend neither on heating rate nor on the capping layer. Using Eq. (1) to fit the sheet resistance in the amorphous state leads to an activation energy for carrier transport of 0.28 eV, which is independent of both the capping layer and heating rate, as shown in Table I.

The crystallization process can be analyzed quantitatively based on the change of sheet resistance upon annealing at different rates employing Kissinger's analysis. Figures 3(a) and 3(b) illustrate the temperature dependence of the sheet resistance measured at different heating rates upon annealing 100 nm thin films of $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ capped with 5 nm of ZnS-SiO_2 and Si_3N_4 , respectively. Figure 4 displays the corresponding Kissinger's plots including the plot for a single layer. A good linear relationship is obtained between $\ln\{(dT/dt)/T_c^2\}$ and $1000/T_c$. The activation energies deduced for the samples capped with ZnS-SiO_2 and Si_3N_4 are 2.39 ± 0.10 eV and 3.24 ± 0.12 eV, respectively. Comparing these values to the value obtained for a single layer which is 3.03 ± 0.17 eV, it can be concluded that ZnS-SiO_2 and Si_3N_4

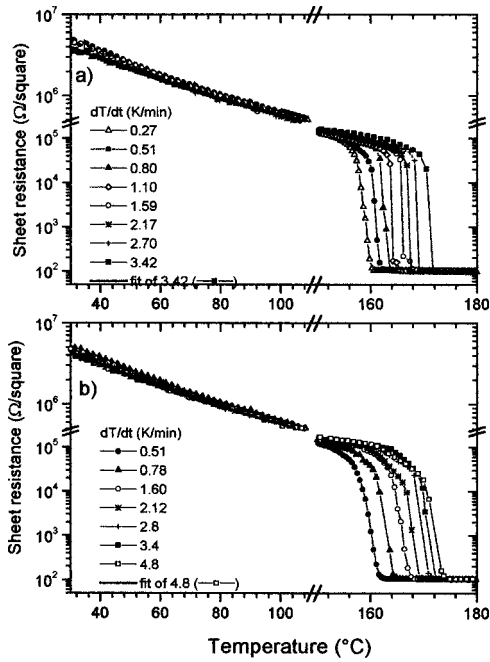


FIG. 3. Temperature dependence of sheet resistance for 100 nm of $Ag_5In_6Sb_{59}Te_{30}$ films covered with 5 nm $ZnS-SiO_2$ (a) and Si_3N_4 (b) measured at different heating rates. The heating rates are shown in the inset. The solid line represents the fit for electronic transport with an energy barrier E_{a_trans} .

capping layers reduce and increase the activation energy, respectively. Hence the value of the activation energy for crystallization of amorphous $Ag_5In_6Sb_{59}Te_{30}$ films depends on the protective layer used. Two explanations have been proposed to describe the influence of protective layers on crystallization.

The first explanation is based on the stresses induced in the phase change layer by the capping layer while the other explanation is based on a modification of chemical bonds at the interface. Tominaga *et al.* used an optical method to investigate the crystallization mechanism of $Ge_2Sb_2Te_5$ thin films sandwiched between SiN layers and observed two transition temperatures. They suggested that the crystallization occurred at the interfaces and related the lower transition to crystallization at the top interface and the higher transition to crystallization at the bottom interface. They attributed the

TABLE I. Activation energy for electronic transport for different capping layers and heating rates.

Capping layer	Heating rate (K/min)	E_{a_trans} (eV)
None	0.5	0.268
None	3	0.297
SiO ₂	0.5	0.288
SiO ₂	3	0.280
ZnS-SiO ₂	0.5	0.275
ZnS-SiO ₂	3	0.260
SiN	0.5	0.296
SiN	3	0.292
ZnS-SiO ₂	3.4	0.270
SiN	4.8	0.284
Average		2.28±0.01

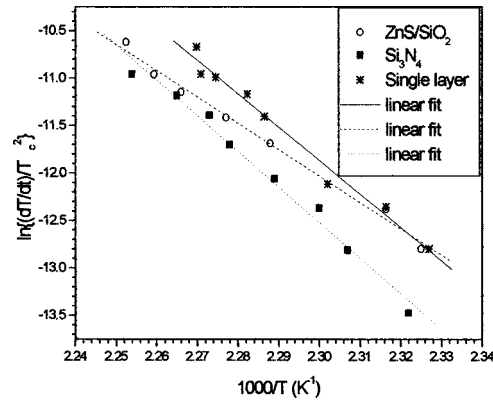


FIG. 4. Kissinger plots from which the activation energy E_a of the amorphous to crystalline transition at T_c is determined. Plots of a single layer of 100 nm $Ag_5In_6Sb_{59}Te_{30}$ film (star) and film covered with 5 nm thick protective layers of $ZnS-SiO_2$ (open circles) and Si_3N_4 (solid squares) are presented. The lines show the linear fit.

double transition to different stresses at the two interfaces. By employing an argument put forward by Situ *et al.*¹⁴ that tensile stress prevents or delays the crystallization, leading to higher transition temperatures, they concluded that the top interface possesses a lower tensile stress while the bottom has a higher tensile stress. Our stress measurements revealed tensile stress for SiO_2 (200 MPa) and compressive stress for $ZnS-SiO_2$ (-250 MPa) and Si_3N_4 (-400 MPa) films. These values of stress were determined from the substrate curvature measured before and after film deposition applying Stoney's equation.¹⁰ This implies that employing SiO_2 as a capping layer induces compressive stress to the $Ag_5In_6Sb_{59}Te_{30}$ layer, which should lead to a lower crystallization temperature while capping layers of $ZnS-SiO_2$ and Si_3N_4 induce tensile stress that should lead to higher crystallization temperatures. However our results show that all the three capping layers increased the crystallization temperature. In addition, the activation energy of amorphous $Ag_5In_6Sb_{59}Te_{30}$ films is reduced and increased when $ZnS-SiO_2$ and Si_3N_4 films are applied as protective layers, respectively. Considering that these two types of protective layers possess the same type of stress, it can be concluded that the activation energy is not linked to stress. Therefore, stress of this magnitude may not play an important role in crystallization. This leaves the second explanation which is based on heterogeneous nucleation at the interface. The relevance of heterogeneous nucleation for the crystallization of $Ag_5In_6Sb_{59}Te_{30}$ films has recently been shown unequivocally by atomic force microscopy measurements of the crystallization process.¹⁵ Different dielectric materials will lead to bonds of different strengths to the phase change films offering a plausible explanation for these effects.

Ohshima⁴ used transmittance measurements to investigate the crystallization of $Ge-Sb-Te$ films sandwiched between various dielectric layers. They reported higher activation energies (2.6 eV) for films with the protective layers compared to 2.2 eV for films without the protective layer. They attributed this to the surface reactivity and chemical affinity of the film materials. This could also possibly explain the influence of $ZnS-SiO_2$ and Si_3N_4 on the crystallization of

$\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$. However, to justify this reason more investigations using different types of dielectric materials are necessary. Such studies should include taking cross section TEM images of the interfaces possibly also helping to determine how the phase change alloy wets the dielectric material.⁸ From such an experiment one might determine or at least estimate the interface energy between the dielectric and the phase change film.

IV. CONCLUSION

We have investigated the influence of different capping layers on the crystallization kinetics and the electrical resistivity of thin $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ films. The capping layers introduced either a compressive or tensile stress on the $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$ film. The magnitude of the stresses introduced ranged between 200 and 400 MPa. It was established that stresses of this magnitude played no important role in crystallization. An analysis of the crystallization kinetics showed that the crystallization process depends on the type of the capping layer. Activation energies of 2.39 ± 0.10 eV and 3.24 ± 0.12 eV were determined for films capped with 5 nm of ZnS-SiO_2 and Si_3N_4 , respectively, as compared to

3.03 ± 0.17 eV for unprotected film. The different activation energies may be attributed to different interface energies. The influence of the capping layer on the electrical resistivity and on the activation barrier for electronic transport in the amorphous state was found to be minimal; E_{a_trans} was around 0.28 ± 0.01 eV in all experiments.

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