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Influence of dielectric capping layers on the crystallization kinetics of Ag$_5$In$_6$Sb$_{59}$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 Ag$_5$In$_6$Sb$_{59}$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 Ag$_5$In$_6$Sb$_{59}$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$_3$N$_4$, 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. In both types of storage devices the active layer is sandwiched between surrounding layers. The active layer is usually a Ge-Sb-Te- or an 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. It has been found that the choice of the dielectric layer is of tremendous importance, since it influences the rate of crystallization. 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. 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. In this work, we investigate the influence of different dielectric layers on the crystallization and electrical properties of Ag$_5$In$_6$Sb$_{59}$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 Ag$_5$In$_6$Sb$_{59}$Te$_{30}$ films while rf sputtering was used to deposit the dielectric layers of ZnS-SiO$_2$, SiO$_2$, and Si$_3$N$_4$ 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 Ag$_5$In$_6$Sb$_{59}$Te$_{30}$ and SiO$_2$ targets was 99.99% while those of ZnS-SiO$_2$ and Si$_3$N$_4$ 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 Ag$_5$In$_6$Sb$_{59}$Te$_{30}$, 0.018 nm/s, 0.010 nm/s, and 0.013 nm/s for ZnS-SiO$_2$, SiO$_2$, and Si$_3$N$_4$, respectively. Samples of 100 nm Ag$_5$In$_6$Sb$_{59}$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. 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...
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.\(^\text{10}\)

### III. RESULTS AND DISCUSSION

Figure 1 compares the temperature dependence of the sheet resistance of Ag\(_5\)In\(_6\)Sb\(_{59}\)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.\(^\text{11}\) 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.\(^\text{12}\) 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 single layer of 100 nm Ag\(_5\)In\(_6\)Sb\(_{59}\)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.

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

**FIG. 2.** Temperature dependence of sheet resistance upon annealing single layer of 100 nm Ag\(_5\)In\(_6\)Sb\(_{59}\)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.

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 thick films of Ag\(_5\)In\(_6\)Sb\(_{59}\)Te\(_{30}\) capped with 5 nm of ZnS-SiO\(_2\) and Si\(_3\)N\(_4\), 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\(_3\)N\(_4\) 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\(_3\)N\(_4\) occurs in a relatively larger temperature range. These results prove unequivocally that the crystallization process of Ag\(_5\)In\(_6\)Sb\(_{59}\)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,\(^\text{13}\)

\[
\sigma = \sigma_0 \exp\left(-\frac{E_{\text{a,trans}}}{kT}\right).
\]

Here \(\sigma\) is the conductivity, \(\sigma_0\) is a preexponential factor and \(E_{\text{a,trans}}\) 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.
They attributed the crystallization at the top interface and the higher transition temperatures. They suggested that the crystallization of amorphous Ag5In6Sb59Te30 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 Ge2Sb2Te5 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 capping layers reduce and increase the activation energy, respectively. Hence the value of the activation energy for crystallization of amorphous Ag5In6Sb59Te30 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 Ge2Sb2Te5 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 double transition to different stresses at the two interfaces. By employing an argument put forward by Situ et al. 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 SiO2 (200 MPa) and compressive stress for ZnS-SiO2 (−250 MPa) and Si3N4 (−400 MPa) films. These values of stress were determined from the substrate curvature measured before and after film deposition applying Stoney’s equation. This implies that employing SiO2 as a capping layer induces compressive stress to the Ag5In6Sb59Te30 layer, which should lead to a lower crystallization temperature while capping layers of ZnS-SiO2 and Si3N4 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 Ag5In6Sb59Te30 films is reduced and increased when ZnS-SiO2 and Si3N4 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 Ag5In6Sb59Te30 films has recently been shown unequivocally by atomic force microscopy measurements of the crystallization process. Different dielectric materials will lead to bonds of different strengths to the phase change films offering a plausible explanation for these effects.

Ohshima et al. 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-SiO2 and Si3N4 on the crystallization of...
Ag$_5$In$_6$Sb$_{59}$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. 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 Ag$_5$In$_6$Sb$_{59}$Te$_{30}$ films. The capping layers introduced either a compressive or tensile stress on the Ag$_5$In$_6$Sb$_{59}$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$_3$N$_4$, 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; $E_{a,\text{trans}}$ was around 0.28±0.01 eV in all experiments.

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