Reduction in crystallization time of Sb:Te films through addition of Bi

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ABSTRACT

The electrical, optical and phase change properties of bismuth doped Sb_8Te_2 as-deposited and re-amorphised films have been characterised. Thin films of the material, with up to 15 atomic percent bismuth, have been synthesised by sputter deposition. As deposited amorphous films were stable at room temperature with a bismuth concentration upto 13 atomic percent. We show that effect of bismuth on the phase change properties of the films is to reduce the crystallization time by an order of magnitude. Both static and dynamic measurements of the as-deposited and re-amorphised films have showed similar decreases of crystallisation time with bismuth increases. The crystallisation activation energy reduction appears unaffected by the bismuth atoms up to a concentration of 13 atomic percent. The structure of the films after annealing at 180°C has been measured by X-ray diffraction; the material shows the same A7-type structure as that previously reported for the well known phase change film $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$. A reduction in the material viscosity with increasing bismuth is suggested as a means by which the reduction in crystallisation time is achieved while a negligible change in activation energy and structure is possible. The effect of bismuth dopants on the Sb_8Te_2 material's physical properties and the consequent performance of optical media and electrical devices will be discussed.

Key words: phase change, antimony telluride, bismuth doping, crystallisation

1. INTRODUCTION

Over the past 30 years[1] phase change materials have been investigated extensively for optical data storage applications. Phase change recording is based on the reversible switching between the crystalline and amorphous states. The rate that data can be erased and directly overwritten is reliant on the crystallization time of the material; thus understanding the effect of compositional variations on the crystallization times of these materials is of key importance. The effect of Bi doping, in the well researched $Ge_2Sb_2Te_5$ (GST) phase change alloy, has been reported by a number of groups[2-4]. Experimental results demonstrate that the use of Bi as a dopant could play an important role in the demonstration of improved data storage materials. When doped in GST, Bi is known to reduce the transition temperatures without affecting the crystal structure or its lattice parameters[2]. In addition to the well known GST composition, the Sb:Te binary compositions are also known phase change materials[5].

The appreciation of bismuth's mechanism in Sb:Te compounds could aid the understanding in the somewhat more complex Bi doped ternary systems. The Sb-Te system is characterised by two congruent melting points, the first at Sb_2Te_3 and the second with a wide composition range centred at 29 at.% Te. In the Te rich zone there is a eutectic at 89 at.% Te. The Sb_2Te phase shows a wide compositional tolerance with Sb content ranging from 63 to 81 at.%[6] . In this work, samples containing 80% Sb have been doped with Bi; close to the maximum Sb concentration at which the Sb_2Te phase is formed. Since this crystal can form over a wide Sb compositional range it is anticipated that it will show some acceptance of the Bi atom. The structural, electrical and optical properties of the film have been characterised and particular emphasis is given to the crystallisation speed. Insight into the influence of Bi on these aformentioned properties has been gained through simulating the structural relaxation of Bi doped Sb_8Te_2.

2. EXPERIMENTS

The Bi content was varied between 0 and 15 atomic percent by attaching pure Bi pieces to a Sb_8Te_2 sputtering target. Sputtering was performed in an argon atmosphere, controlled at 0.5Pa, with a RF power of 100W. Films, of thickness 100nm, were deposited onto Si and SiO_2 substrates. The film composition was measured by X-ray fluorescence spectroscopy using a Rigaku RIX 2100 system. The crystallization temperature and its activation energy were measured by monitoring the reflection as a function of temperature, using a Linkam microscope furnace in conjunction with a broad visible source and a monochromator-detector setup. Measurements of the crystallization temperature were made at heating rates of 5, 10, 15, 20 and 25°Cmin^{-1} in an Ar atmosphere. These heating rates are many orders of magnitude lower than that of laser or Joule heating. However for the purpose of comparing samples

measured in the same fashion, these heating rates were deemed sufficient. A non-isothermal Kissinger analysis[7] of crystallization was used to determine the activation energy of each composition; the results are given in figure 1 and table 1. The mean measurement error in activation energy was found to be 0.2eV.

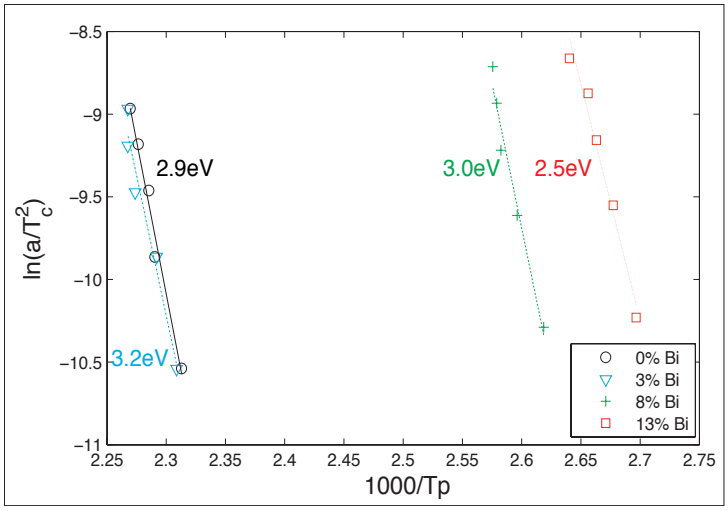

Figure 1: Arrhenius plots used to calculate the activation energy for Bi doped Sb_8Te_2

A NFT I-Elli2000 imaging ellipsometer has been used to measure the films' elipsometric parameters at 532 nm as a function of Bi content. A Simplex fitting routine was then used to determine the real, n, and imaginary, k, components of the refractive index dependence on Bi; the results are also presented in table 1.

The crystallization time for each composition was measured using a static tester pump probe system[8-9]. A 658nm diode laser was focussed to a diffraction limited spot, through a 0.65NA objective, and used to locally heat the sample. The incident power was incremented from 5mW to 58mW and, for each power setting, the pulse duration was varied from 10ns to 500ns, in steps of 10ns. The reflectivity of a second, 635nm diode laser, with an optical power of ~0.1mW co-incident on the sample, was used to monitor the change in reflectivity of the film surface. Measurements were conducted on uncapped films prepared on top of the SiO_2 substrates. For each composition, a matrix of optical power, pulse duration and change in reflectivity was generated and plotted. The pulse time necessary to invoke the highest crystallization rate was found for three different incident optical powers. These times were then plotted as a function of Bi content and the results are given in figure 2.

In practicle data storage media, it is not the as-deposited state which is crystallised but the melt-quenched or laser amorphised state. Differences in the crystallisation time are apparent and dependant on the way in which the amporphous film is prepared[10]. For this reason the crystallisation time for amorphous marks of lengths ranging from 500nm to 11um have been investigated. Films were prepared on a DVD, polycarbonate, substrate. The disc structure consisted of Substrate/$(ZnS)_{85}(SiO_2)_{15}$/$Bi(Sb_8Te_2)$/ZnS-SiO_2/AlCr with layer depths described by: Substrate/140nm/ 20nm/20nm/50nm. All films were RF-sputter deposited at 0.5 Pa. A Dynamic Disk Unit (DDU) was employed to prime the discs with a focussed 650nm set at 4mW on the film and a disc tangential rotation velocity of $2ms^{-1}$. The same setup was then used to write marks at a linear velocity of 4ms-1 whilst alttering the lasers modulation frequency to control the amorphous mark length. The laser write power was controlled between 6mW and 8mW in order to achieve a Carrier to Noise Ratio (CNR) greater than 33dB. The decrease in signal was then measured after applying CW laser light to erase the written marks. The maximum difference in CNR before and after the erasing laser pulse is termed: erasability. The erasability has been plotted against the amorphous mark length in figure 3 for Sb_8Te_2 samples doped with 0, 3 and 8% Bismuth. Clearly, at a fixed disc linear velocity, the longer the amorphous mark length which can be erased, the greater the rate of crystallisation.

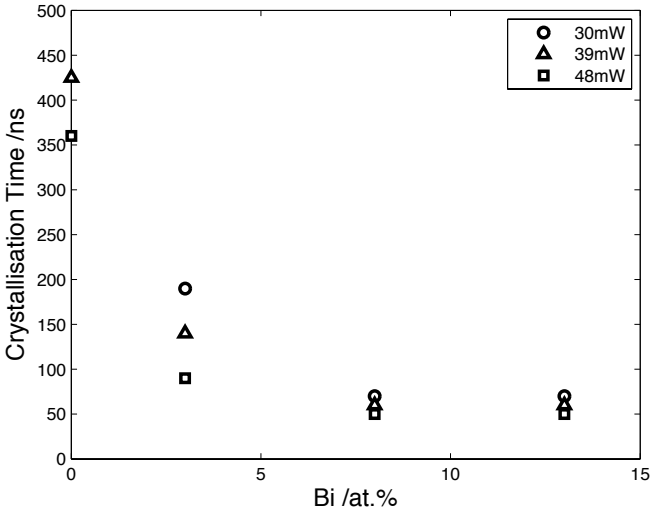

Figure 2: Crystallisation time of Sb8Te2 as a function of Bi content

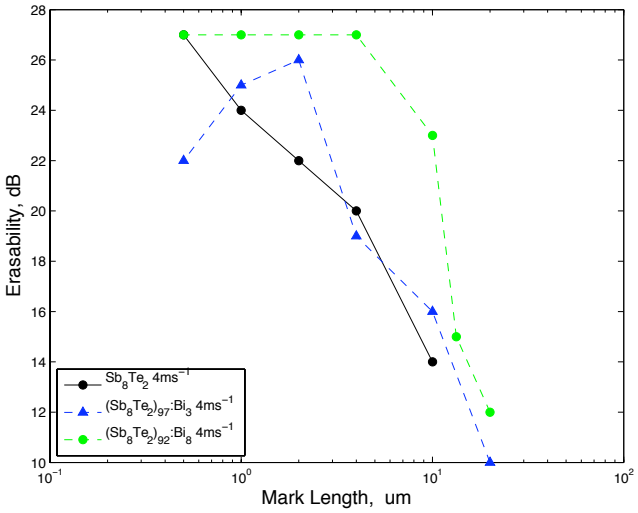

Figure 3: Erasability of laser amorphised marks as a function of mark length at a linear velocity of 4ms^{-1}

The electrical sheet resistance was measured with a four point probe, before and after annealing at 180ºC in a nitrogen atmosphere. A curve showing the effect of Bi on the resistivity is given in figure 4.

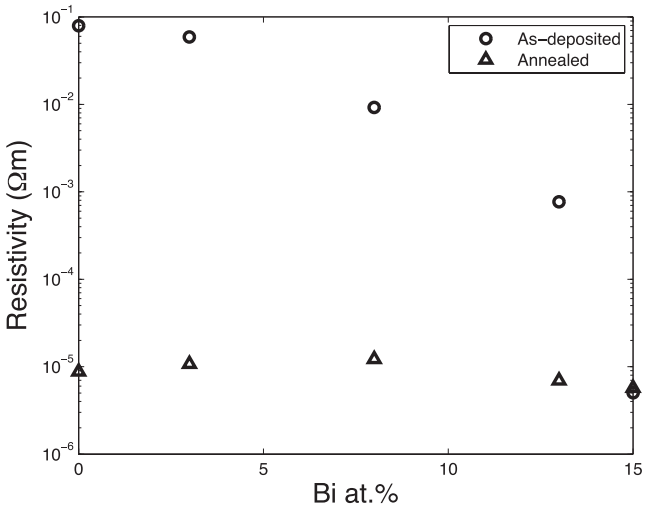

Figure 4: Electrical resistivity before and after anealing at 180 ºC

Room temperature, X-Ray Diffraction (XRD) was performed on the as-deposited samples before and after annealing at 180ºC. Figure 5(a) shows the diffractograms for the as-deposited samples, whilst figure 5(b) shows the same films after annealing at 180ºC. One can see that there is a clear dopant threshold between 13 and 15 atomic percent Bi at which point the material is crystalline at room temperature. The effect of Bi on the optical, electrical and crystallization properties of Sb_8Te_2 films is summarized in table 1. It should be noted that no change in optical reflectivity of the $(Sb_8Te_2)_{85}Bi_{15}$ sample was observed below 180ºC; hence no crystallization temperature was measured. The XRD spectra of the sample has shown it to be in a crystalline state at room temperature.

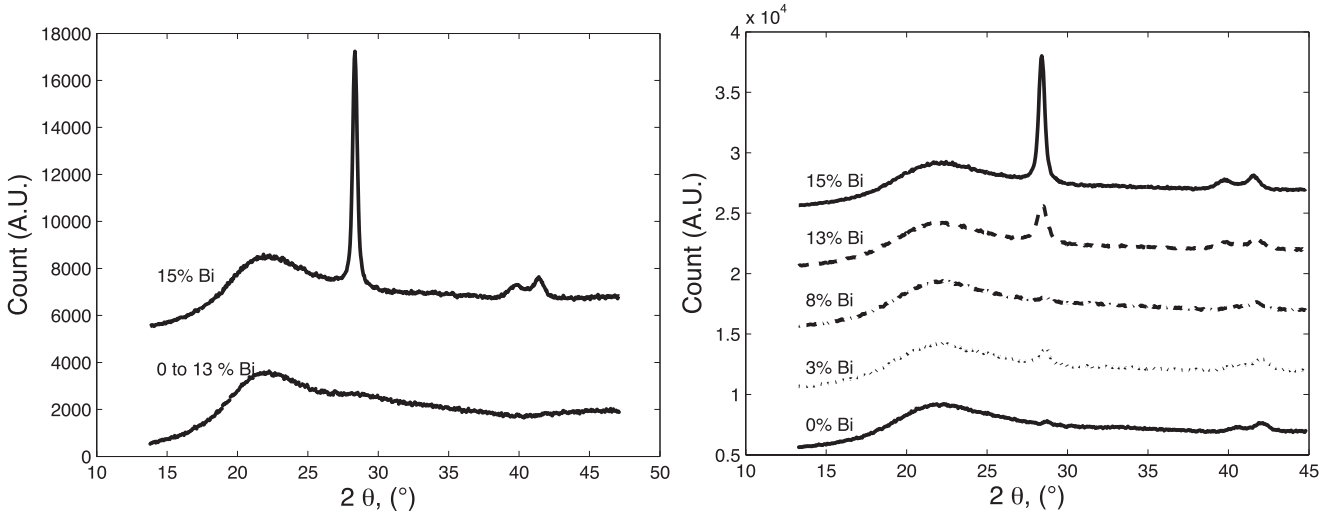

Figure 5: X-ray diffraction spectra for bismuth doped Sb_8Te_2 before (a) and after (b) annealing at 180°C

Bi / at.%	Crystallization			As-Deposited			Annealed			R_{inc} / %
	T_x / °C	E_a/eV	Time/ns	n	k	R/kΩ.m	n	k	R/kΩ.m	
0	165	3.2	430	3.37	3.66	794	1.59	4.61	0.88	16
3	168	2.9	150	3.28	3.62	591	1.42	4.63	1.07	17
8	115	3	60	3.05	3.82	92.1	1.78	4.53	1.22	11
13	103	2.5	60	2.98	3.53	7.71	1.76	4.38	0.69	10
15	--	--	--	1.21	4.57	0.51	1.46	4.38	0.57	-2

Table 1: Summary of crystallisation, optical and electrical values

3. DISCUSSION

Doping with just 3 at.% Bi decreases the crystallization time by a factor of two. An order of magnitude reduction was achieved for concentrations of 8 at.% Bi, at which point the effect saturates. Although the crystallization time has been measured from the as-deposited state, it is important to know the crystallization rate of the re-amorphised material. The crystallisation time of the laser quenched amorphous marks showed consistency with the as-deposited film. Figure 3 shows that maximum re-amorphised mark length which could be erased at 4ms-1 was 0.5um for the undoped film and 8um for the film doped with 8 at.% Bi. Doping the films with concentrations of bismuth greater than 13 at.% resulted in the deposition of a crystalline film at room temperature; this was confirmed by XRD. The structure of this film and those annealed at 180^{o}C shows consistency with that previously reported for $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$[11]; an A7-type structure with Sb and Te randomly occurring on all sites. Assuming an R-3m space group, the lattice parameters are found to be a=4.29Å and c~11.22Å. The 15 at.% Bi sample, which was crystalline at room temperature also seems to hold this A7-type structure with lattice parameters, a=4.45Å and c=11.36Å for the R-3m space group.

The effect of Bi on the film's optical properties has been measured by ellipsometry; 13 at.% Bi reduces the refractive index by 0.4 whilst its impact on the absorption coefficient is minimal. By consideration of the refractive index and Fresnel reflectivity for 532nm light at normal incidence, the resultant increase in reflectivity of the material has also been included in table 1. It can be seen that Bi reduces the optical contrast between phases, however, at 8 at.% Bi the increase in reflectivity is still 11%. Sb_8Te_2 materials have been identified as having growth dominated crystallization[12]. Figures 2 and 3 show that the crystallization time for this material is reduced by an order of magnitude through the addition of Bi. The rate of crystal growth is dependent on activation energy for crystallization[13]; however from the measurements reported here, the activation energy is only marginally reduced by addition of Bi. Thus the effect of Bi atoms on the crystal growth for this composition can be neglected. The values of crystallization activation energy for as-deposited films are susceptible to some change for melt quenched or annealed films. The activation energy insensitivity of Sb_8Te_2 materials to Bi is contrary to that reported in the nucleation dominated $Ge_2Sb_2Te_5$ material, where doping with Bi reduces the activation energy for crystallization allowing a correlated reduction in the crystallization time[2].

From a thermodynamic perspective heteronuclear bonding is favourable for increasing the entropy of mixing, leading to a more homogeneous mixture of atoms. Whereas homonuclear bonds lead to a reduction in the glass transition temperature and an increase in the Gibbs free energy, resulting in a less stable amorphous film[14]. This may explain the effect of Bi introduction on the crystallization temperature. The Bi atoms may strongly compete with Sb and tend to inhibit Sb-Te bonding in favour of Bi-Te bonds. This could, in turn, increase the proportion of Sb-Sb bonds and reduce the stability of the structure. The combination of a lower mean dissociation energy and the instability in the amorphous structure incurred due to an increased proportion of Sb-Sb, homonuclear bonds, allows a significant reduction in the crystallization temperature from 165^{o}C for an undoped film to 115^{o}C for a film doped with 8 atomic percent Bi. This compositional range also corresponds to an order of magnitude reduction in crystallization time. Since the material crystallises at lower temperatures, for increasing amounts of bismuth, the viscosity is expected to show a corresponding reduction. It is therefore deduced that the Bi dopant decreases the viscosity and thus, by the Becker and Doring equation[13], provides an increase in the crystal growth rate.

The electrical resistivity in the amorphous state is, reduced by two orders of magnitude. The heating efficiency of electrical phase change memory is linearly dependant on electrical resistivity. Doping with Bi would therefore reduce this efficien of the cell.

In comparison to $Ge_2Sb_2Te_5$ has a much lower tellurium concentration. A reduction in the concentration of tellurium has the effect of reducing the proportion of dangling bonds, point defects and, in turn, the concentration of charge carrier traps. Adding Bi, which prefers to form metallic bonds and enters the amorphous networks with 6-fold coordination[14], to Sb_8Te_2 may further reduce these charge traps permitting a strong, correlated, reduction in the amorphous electrical resistivity, this is seen in figure 4.

Electrical phase change RAM (PCRAM) is reliant on the ability to amorphise materials at low electrical currents. Low Bi concentrations, <8 at.%, increase the electrical resistivity of the crystallised state of Sb_8Te_2. This would allow a reduction in the writing current for a potential electrical PCRAM device. The difference in electrical resistivity between phases decreases with increasing proportions of Bi. At the 8 at.% Bi level, the amorphous phase is three orders of magnitude greater in electrical resistivity than that of the crystalline. Such a large difference is encouraging for electrical phase change applications whereby scaling to small dimension cells will result in a need for materials with a large, intrinsic, difference in electrical resistivity. Since the crystallization of Sb_8Te_2 is growth dominated, the

crystallization time would scale with the PCRAM cell area. For a practical electronic device, there is a need for the material to retain data at elevated temperatures. Clearly these Bi doped Sb_8Te_2 materials are limited by their low crystallization temperatures. However the fact that Bi can reduced the crystallization time of growth dominated materials without resulting in any significant changes to the crystallization activation energy could mean that the crystallization time of other, stable, growth dominated materials will benefit from Bi inclusion.

4. CONCLUSION

We have shown, experimentally, that the optical crystallization of Sb_8Te_2:Bi can occur in just 50ns. This material shows growth dominated crystallization and therefore it has potential for shorter crystallization times in a PCRAM device where the cell dimensions can be just tens of nanometers[15]. The material demonstrated two orders of magnitude reduction in electrical resistivity and this has been attributed to saturation of trapping states, thus allowing metallic conduction.

Previous work has shown that a $Sb_{45}Te_{65}$ alloy will crystallise in the shortest time in relation to other compositional proportions of the alloy. In this manuscript we have demonstrated that the addition of Bi to much larger concentrations of Sb has far superior properties and decreases the crystallization time by an order of magnitude. The general trend of Bi doping in Sb_8Te_2 seems to be consistent with Bi inclusion in GST; that is, for low concentrations of Bi, the crystal structure is not affected and that the introduction of Bi reduces the crystallization time and temperature. However, in this case, the reduced crystallization time is suspected to be due to a reduction in viscosity with increasing bismuth rather than a reduction in activation energy which has been described for GST [2].

Acknowledgement

R Simpson is grateful to the Japanese Society for promotion of Science (JSPS) for his summer studentship which helped support this work and Ilika Technologies for funding the static tester which was employed to measure the crystallisation time.

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