

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

R. E. Simpson,<sup>1,a)</sup> D. W. Hewak,<sup>1</sup> P. Fons,<sup>2</sup> J. Tominaga,<sup>2</sup> S. Guerin,<sup>3</sup> and B. E. Hayden<sup>3</sup>

<sup>1</sup>*Optoelectronics Research Centre, University of Southampton, Southampton SO17 1BJ, United Kingdom*

<sup>2</sup>*Center for Applied Near-Field Optics Research (CAN-FOR), AIST, Tsukuba, Japan*

<sup>3</sup>*School of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom*

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The electrical, optical, and phase change properties of bismuth doped  $\text{Sb}_8\text{Te}_2$  films have been characterized. Thin films of the material, with up to 15 at. % percent Bi, have been synthesized; amorphous films were stable at room temperature with a Bi concentration of up to 13 at. %. The effect of Bi on the phase change properties of the film is shown to reduce the crystallization time by an order of magnitude while the crystallization activation energy reduction is minimal; 0.2 eV. Bismuth doped  $\text{Sb}_8\text{Te}_2$  materials show potential as the active material in phase change data storage media. © 2008 American Institute of Physics. [DOI: 10.1063/1.2901161]

Over the last 30 years,<sup>1</sup> phase change materials have been extensively investigated 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  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (GST) phase change alloy, has been reported by a number of groups.<sup>2–4</sup> 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.<sup>2</sup>

In addition to the well known GST composition, the Sb:Te binary compositions are also known phase change materials.<sup>5</sup>

The appreciation of bismuth's mechanism in Sb:Te compounds could aid the understanding in the somewhat more complex Bi doped ternary systems. The  $\text{Sb}_2\text{Te}$  phase shows a wide compositional tolerance with Sb content ranging from 63 to 81 at. %.<sup>6</sup> In this work, samples containing 80% Sb have been doped with Bi; close to the maximum Sb concentration at which the  $\text{Sb}_2\text{Te}$  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 crystallization, optical, and electrical properties have been investigated.

The Bi content was varied between 0 and 15 at. % by attaching pure Bi pieces to a  $\text{Sb}_8\text{Te}_2$  sputtering target. Sputtering was performed in an argon atmosphere, controlled at 0.5 Pa, with a rf power of 100 W. Films, with thickness of 100 nm, were deposited onto Si and  $\text{SiO}_2$  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 °C min<sup>-1</sup> 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 nonisothermal Kissinger analysis<sup>7</sup> of crystallization was used to determine the activation energy of each composition; this is given in Table I. The mean measurement error in activation energy was found to be 0.2 eV.

A NFT I-Elli2000 imaging ellipsometer has been used to measure the films' ellipsometric parameters at 532 nm as a function of Bi content. The real  $n$  and imaginary  $k$  components of the refractive index dependence on Bi are also presented in Table I.

The crystallization time for each composition was measured using a static tester pump probe system.<sup>8,9</sup> A 658 nm diode laser was focused to a diffraction limited spot, through a 0.65 NA objective, and used to locally heat the sample. The incident power was incremented from 5 to 58 mW, and for each power setting, the pulse duration was varied from 10 to 500 ns in steps of 10 ns. The reflectivity of a second, 635 nm diode laser, with an optical power of 100  $\mu\text{W}$  coincident 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  $\text{SiO}_2$  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 Fig. 1.

The electrical sheet resistance was measured with a four point probe, before and after annealing at 180 °C in a nitrogen atmosphere. A curve showing the effect of Bi on the resistivity is given in Fig. 2.

Room temperature, x-ray diffraction (XRD) was performed before and after annealing at 180 °C. Figures 3(a) and 3(b) show the respective diffractograms. One can see that there is a clear dopant threshold between 13 and 15 at. % Bi, the point at which the material is crystalline at room temperature.

The effect of Bi on the optical, electrical, and crystallization properties of  $\text{Sb}_8\text{Te}_2$  films is summarized in Table I. It should be noted that the  $(\text{Sb}_8\text{Te}_2)_{85}\text{Bi}_{15}$  sample was con-

<sup>a)</sup>Electronic mail: robert.simpson@asit.go.jp.

TABLE I. Summary of measurements on  $(\text{Sb}_8\text{Te}_2)_{100-x}:\text{Bi}_x$  where  $T_x$ =crystallization temperature,  $E_a$ =crystallization activation energy ( $\pm 0.2$  eV),  $n$ =refractive index,  $k$ =extinction coefficient,  $\rho$ =electrical resistivity, and  $R_{\text{inc}}$ =increase in reflectivity.

Bi (%)	$T_x$ ( $^{\circ}\text{C}$ )	$E_a$ (eV)	As-deposited			Annealed			$R_{\text{inc}}$ (%)
			$n$	$k$	$\rho$ (k $\Omega$ m)	$n$	$k$	(k $\Omega$ m)	
0	165	3.2	3.37	3.66	794	1.59	4.61	0.88	16
3	168	2.9	3.28	3.62	591	1.42	4.63	1.07	17
8	115	3.0	3.05	3.82	92.1	1.78	4.53	1.22	11
13	103	2.47	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

firmed crystalline at room temperature by XRD.

Doping with just 3 at. % Bi decreases the crystallization time by a factor of 2. An order of magnitude reduction was achieved for concentrations of 8 at. % Bi, the point at which 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 reamorphized material. It is anticipated that the crystallization time of the reamorphized state will be shorter than that of the as-deposited state due to the existence of “frozen-in” crystalline nuclei from which crystal growth can occur.<sup>10</sup> Further measurements will be undertaken on the reamorphized material to understand these effects and the results will be duly published. 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  $^{\circ}\text{C}$  shows consistency with that previously reported for  $\text{Ag}_{3.4}\text{In}_{3.7}\text{Sb}_{76.4}\text{Te}_{16.5}$ ,<sup>11</sup> an A7-type structure with Sb and Te randomly occurring on all sites. Assuming an  $R\bar{3}m$  space group, the lattice parameters are found to be  $a=4.29$   $\text{\AA}$  and  $c \approx 11.22$   $\text{\AA}$ . The 15 at. % Bi sample, which was crystalline at room temperature also seems to hold this A7-type structure with lattice parameters,  $a=4.45$   $\text{\AA}$  and  $c \approx 11.36$   $\text{\AA}$  for the  $R\bar{3}m$  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 while its impact on the absorption coefficient is minimal. By consideration of the refractive index and Fresnel reflectivity for 532 nm light at normal incidence, the resultant increase in reflectivity has also been included in Table I. It can be seen that Bi reduces the optical contrast

between phases, however, at 8 at. % Bi, the increase in reflectivity is still 11%.  $\text{Sb}_8\text{Te}_2$  materials have been identified as having growth dominated crystallization.<sup>12</sup> Figure 1 shows 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,<sup>13</sup> 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  $\text{Sb}_8\text{Te}_2$  materials to Bi is contrary to that reported in the nucleation dominated GST material, where doping with Bi reduces the activation energy for crystallization allowing a correlated reduction in the crystallization time.<sup>2</sup>

From a thermodynamic perspective, heteronuclear bonding is favorable 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.<sup>14</sup> 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 favor 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  $^{\circ}\text{C}$  for an undoped film

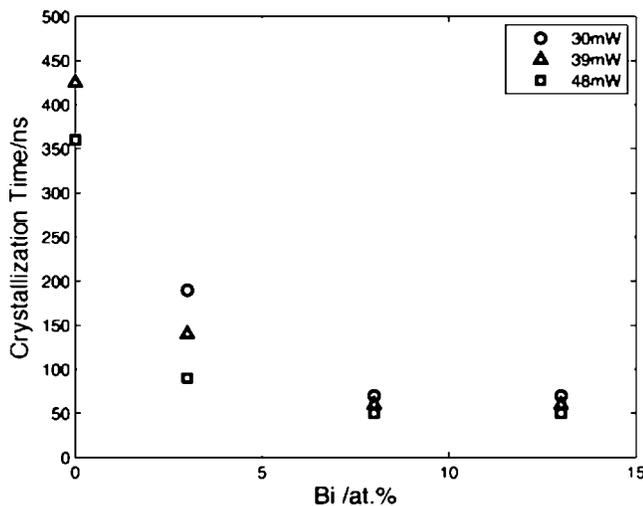


FIG. 1.  $(\text{Sb}_8\text{Te}_2)_{100-x}:\text{Bi}_x$  crystallization time as a function of Bi content.

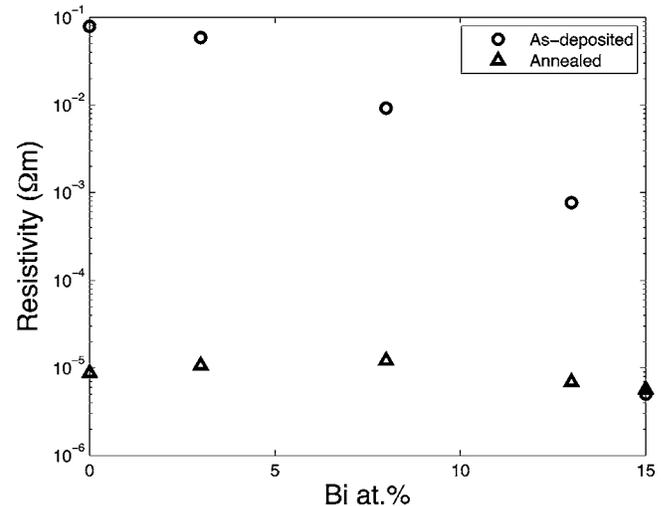


FIG. 2.  $(\text{Sb}_8\text{Te}_2)_{100-x}:\text{Bi}_x$  electrical sheet resistance as a function of Bi content.

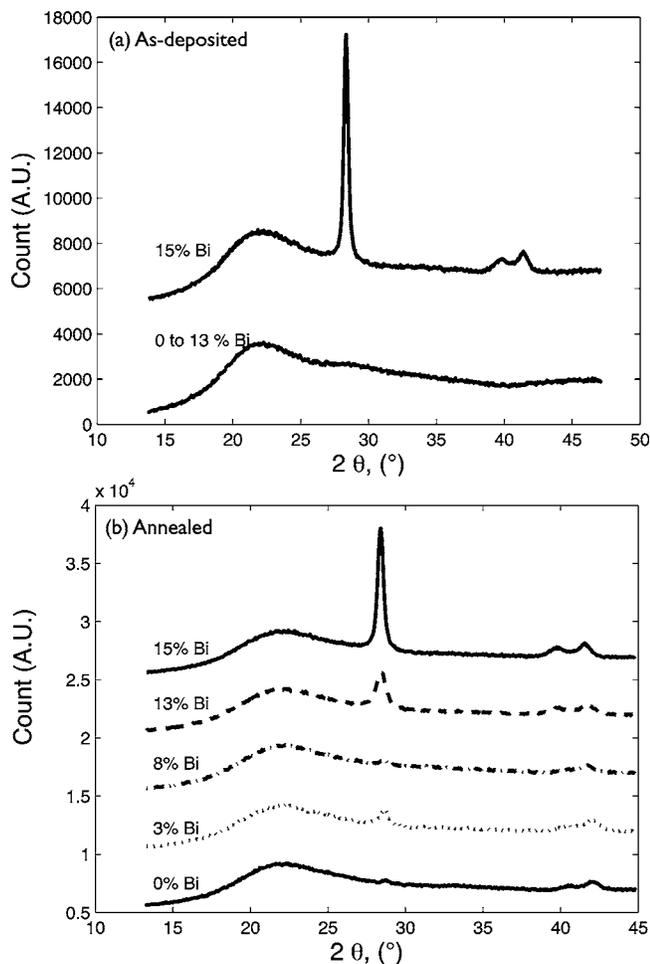


FIG. 3. X-ray diffraction spectra as a function of Bi content for (a) as-deposited and (b) annealed samples.

to 115 °C for a film doped with 8 at. % Bi. This compositional range also corresponds to an order of magnitude reduction in crystallization time. Since the material crystallizes 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 Döring equation,<sup>13</sup> provides an increase in the crystal growth rate.

In comparison to GST,  $\text{Sb}_8\text{Te}_2$  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 sixfold coordination,<sup>14</sup> to  $\text{Sb}_8\text{Te}_2$  may further reduce these charge traps permitting a strong, correlated, reduction in the amorphous electrical resistivity; this is seen in Fig. 2.

Electrical phase change random access memory (PCRAM) is reliant on the ability to amorphise materials at low electrical currents. Low Bi concentrations (<8 at. %) increase the electrical resistivity of the crystallized state of  $\text{Sb}_8\text{Te}_2$ . 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  $\text{Sb}_8\text{Te}_2$  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  $\text{Sb}_8\text{Te}_2$  materials are limited by their low crystallization temperatures. However, the fact that Bi can reduce 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.

We have experimentally shown that the optical crystallization of  $\text{Sb}_8\text{Te}_2:\text{Bi}$  can occur in just 50 ns. This material shows growth dominated crystallization and, therefore, it has a potential for shorter crystallization times in a PCRAM device where the cell dimensions can be just tens of nanometers.<sup>15</sup> 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  $\text{Sb}_{45}\text{Te}_{65}$  alloy will crystallize in the shortest time in relation to other compositional proportions of the alloy. 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  $\text{Sb}_8\text{Te}_2$  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.<sup>2</sup>

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