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Enhanced resistance to metal induced crystallization of amorphous Ge in contact with Bi

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The metal-induced crystallization (MIC) of amorphous Ge (α -Ge) has been studied in two different Bi/ α -Ge bilayer film systems prepared by dc sputtering: films with nm-size columnar Bi grains and films with micron-size laminar Bi grains produced by pulsed laser irradiation. Both systems were annealed *in situ* in a transmission electron microscope in order to determine the temperature at which the semiconductor crystallizes as a function of the metal grain size and the mechanism by which crystallization occurs. The results show that increasing the grain size by two orders of magnitude leads to an increase in the Ge crystallization temperature above the eutectic temperature of the Ge–Bi system and, thus, to a system with an enhanced resistance to MIC. © 1996 American Institute of Physics. [S0003-6951(96)00440-8]

Amorphous semiconductors are known to crystallize at temperatures well below their normal crystallization temperature when in contact with metals, with crystallization temperatures of the order of 0.7–0.8 of the eutectic temperature of the metal/semiconductor system usually reported.^{1,2} The determination of the parameters that can improve the stability of metal/ α -semiconductor interfaces is an important technological contribution to the development of devices in which metal and α -semiconductor are in contact, since the crystallization of the semiconductor usually destroys the device characteristics.

The causes of metal-induced crystallization (MIC) are not yet fully understood, but interdiffusion at the interface between the metal and semiconductor seems to play an important role in the activation of the process.^{2–4} The degree of interdiffusion achievable in polycrystalline materials depends strongly on their microstructural features and is enhanced by the presence of a high density of grain boundaries and/or defects. Furthermore, the grain boundaries are known to act as centers of thermal instability at which the nucleation of crystallization is promoted.⁵ Although an increase in grain size of one or two orders of magnitude will notably reduce the grain boundary density, to our knowledge no systematic studies of the role of metal grain size on MIC of amorphous semiconductors have been reported. The aim of this work is to show that an increase in the grain size of the metal (Bi) improves the resistance of the amorphous semiconductor (Ge) to MIC.

Pulsed-laser irradiation has often been found to induce grain growth in polycrystalline metallic^{6,7} and semiconductor thin films.^{8,9} A recent work¹⁰ has shown that pulsed laser melting changes the microstructure of sputtered Bi thin films, by significantly reducing their surface roughness and increasing the grain size of the Bi crystals by two orders of magnitude. In this work, Bi/Ge bilayer films with a 20 nm thick Bi layer on top of a 40 nm Ge layer were grown onto carbon-coated mica substrates by alternate sputtering from Ge and Bi targets (99.999% purity). The background pressure was 3×10^{-4} Pa and the argon operating pressure was 5×10^{-1}

Pa. Pulsed-laser irradiation has been used to change the structure of the Bi layer as reported elsewhere¹⁰ by means of single pulses from an ArF excimer laser ($\lambda = 193$ nm, $\tau = 12$ ns).

Plan-view transmission electron microscope (TEM) specimens were prepared by floating the films off the mica substrates in distilled water. The microstructure of the irradiated samples was analyzed using a Philips EM-420 TEM. The study of the kinetics of MIC in the as-grown and laser irradiated films was performed by controlled heating of the films *in situ* in a JEOL 4000 EX TEM (0.25 nm point-to-point resolution). The annealing temperatures were measured by a thermocouple mounted in the heater body and the microstructural changes were recorded onto video tape for subsequent analysis using a Gatan television/image pickup system. Further details of the *in situ* annealing experiments can be found elsewhere.¹¹

Figure 1 shows TEM images of the as-grown film and the film after laser irradiation with two different energy densities. Figure 1(a) shows a TEM image of the as-grown film, and the inset selected area diffraction pattern (SADP) shows that the film is composed of a polycrystalline Bi layer and an amorphous Ge layer, with the contrast in the image, therefore, only arising from the Bi layer. The Bi grains are columnar and their diameters range from 40 to 80 nm. A TEM image and SADP of the film irradiated with a low laser energy density (20 mJ/cm^2) can be seen in Fig. 1(b) and, although the Ge remains amorphous, important changes are observed in the Bi layer. The Bi is now composed of laminar crystals with a grain size approximately two orders of magnitude higher than those in the as-grown film ($1\text{--}2 \mu\text{m}$ as opposed to 40 nm). The high magnification image (inset) shows a large number of voids within the grains. SADPs taken from single Bi grains across the film all show the same Bragg reflections indicating that a high degree of preferential orientation is promoted after irradiation, the fiber axis being along the $[2, -2, -1]$ direction. These features are very similar to those reported earlier for Bi films following laser melting and rapid solidification.¹⁰

FIG. 1. TEM images and SAD patterns from Bi/Ge bilayer films: (a) as-grown, and laser irradiated with (b) 20 and (c) 50 mJ/cm². The image inset in (b) is magnified 18 times.

Figure 1(c) shows a TEM image and SADP of the film after irradiation with a high laser energy density (50 mJ/cm²). The Ge layer has now clearly crystallized, since diffraction rings corresponding to crystalline Ge (c-Ge) have appeared in the SADP. The Bi layer again shows an increase in grain size and a preferred orientation. The grains look different to those observed upon lower energy irradiation, since they appear to contain a larger number of small features whose contrast is typical of voids, in addition to some evidence for Ge crystals that have precipitated during the solidification process, due to the low mutual solubility of Bi and Ge.¹²

In an earlier work,¹³ it has been reported that laser irradiation of Bi–Ge bilayers, over a wide range of energy densities, did not induce significant intermixing between the layers, thus, maintaining a “sharp” interface between the layers. The diffusion lengths estimated for a configuration similar to that studied in this work (Bi at the surface) were below the experimental resolution (<approx. 2.5 nm) for energy densities lower than 25 mJ/cm², and were approximately 5 nm for energy densities around 50 mJ/cm².

Since the aim of this work is to study the role of metal grain size on the MIC of α -Ge in contact with Bi, we intend to compare results from a small grain-size (SGS) system

FIG. 2. TEM images and SAD patterns taken during *in situ* annealing of sample containing both LGS and SGS regions. In each case, the SADP is shown below the corresponding image. (a) SGS and LGS film before annealing; (b) and (c) SGS film at 250 °C, just before and after crystallization of Ge respectively; and (d) and (e) LGS film at 250 °C [this image was taken only a few minutes after (b) and (c)] and at 295 °C after crystallization of Ge, respectively.

with those from a large grain-size (LGS) system. We have, therefore, chosen for comparison the as-grown film with a Bi grain size of tens of nm (SGS system) and the film after laser irradiation with 20 mJ/cm² pulses (LGS system). The latter has micronsized Bi grains, no crystallization of the Ge and negligible interdiffusion at the interface.

A TEM specimen containing both SGS and LGS areas was prepared, so that the *in situ* TEM heating experiment could be carried out with exactly the same experimental condition for both systems. Figure 2(a) shows images and SADPs (showing polycrystalline Bi and α -Ge) of the SGS and LGS regions at room temperature prior to heating, respectively. The temperature was increased at a rate of approximately 10 K/min up to 250 °C, since it has been reported that the MIC in the SGS region could be triggered for

temperatures above 200 °C.¹⁴ The first changes are observed in the SGS areas as shown in Fig. 2(b), which was recorded at a temperature of 250 °C after 20 min of heating. The grain size has slightly increased, large voids have appeared, preferentially located at the grain boundaries, and the boundaries have broadened. No changes are observed in SADP at this state of the transformation. The image in Fig. 2(b) was taken just before a crystallization front, moving parallel to the interface with a constant velocity (approx. 10^{-8} m/s), appeared in this region. The boundary between the crystallized and noncrystallized regions can be seen in the low magnification image shown in Fig. 2(c). The SADP included in the Fig. 2(c) shows that Ge has now crystallized.

Figure 2(d) shows the LGS region at the same temperature as the image of the SGS region seen in Fig. 2(c). [Figures 2(c) and 2(d) were taken only a short time apart.] No significant changes are observed in the LGS film, even at regions such as grain boundaries or points where three or more grains meet, at which crystallization might be expected to nucleate at a lower temperature. Even after 40 min heating at 250 °C the LGS region remained perfectly stable, so the temperature was increased to 295 °C, at which temperature crystallization front was then observed to appear in the LGS film. The velocity of the crystallization front in the LGS film is of the same order of magnitude as that for the SGS film. An image and a SADP of the laser-irradiated LGS film after crystallization of the Ge is shown in Fig. 2(e). Analysis of the sample after cooling to room temperature showed that the Ge layer had crystallized over most of the SGS region, while over large areas of the LGS region the Ge was still amorphous.

The results presented here clearly show that the changes induced by heating appear at lower temperature in the SGS film than in the LGS film. The MIC temperature of Ge in contact with Bi has been observed to occur at temperatures between 170 and 250 °C, depending on the layer configuration, in the SGS system.¹⁴ These temperatures correspond to approximately 81%–95% of the eutectic temperature ($T_e = 544$ K) of the Bi–Ge system expressed in K. This result is in agreement with results reported earlier for the Bi–Ge system¹ and other metal/semiconductor systems.^{1,2}

In the LGS system, however, the MIC temperature is not only higher than that observed in the SGS system but also higher than the eutectic temperature of the Bi/Ge system, and this occurs even when laser irradiation has produced defects (such as voids) that in principle are expected to favor interdiffusion and, consequently, the nucleation of c-Ge. The MIC temperature *increase* cannot be related to any structural relaxation within the α -Ge layer that might occur upon laser irradiation, because previous work has shown that in fact the relaxed material has a *lower* crystallization temperature.¹⁵

The properties of the interface are known to depend on the microstructure since a reduction in the total grain boundary area^{16,17} or crystallization in a preferred orientation^{17,18} can lead to a decrease of the free energy of a polycrystalline

system. Laser irradiation of the bilayer films has induced an increase of the metal grain size and a crystallographic texture, both of which will reduce the interface free energy with respect to the as-grown material and, therefore, enhance the interface stability to thermal annealing, as observed experimentally. Despite the large difference in the crystallization temperature observed for the SGS and LGS films, most likely as a result of a difference in interface energy, crystallization occurs via a fundamentally similar mechanism. The crystallization fronts of α -Ge are observed in both systems moving parallel to the interface with an approximately constant velocity, which is similar in SGS and LGS films. The crystallization process cannot, therefore, be related to grain boundary interdiffusion. Furthermore, the nucleation sites are not obviously related to the Bi grain structure. These results, thus, suggest that the mechanism of Ge crystallization in both SGS and LGS systems is “interface controlled.”

In conclusion, it has been demonstrated that an increase in the metal (Bi) grain size leads to a system that is more thermally stable to MIC of the semiconductor (Ge), the crystallization temperature being higher than the eutectic temperature of the metal–semiconductor system. Laser irradiation of eutectic systems in which the elements have low mutual solubility, such as Bi–Ge, is demonstrated to be a suitable means to modify the properties of the interface by reducing its energy through microstructural changes in the metal layer with no significant intermixing.

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