Structural and thermal properties of a Bi nano-plane embedded in amorphous germanium.

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The synthesis and characterization by Raman spectroscopy of a bismuth nano-plane embedded in an amorphous germanium matrix is reported. The sample was prepared by alternate pulsed laser ablation. The structural properties were studied as a function of temperature. Upon heating the Bi nano-plane melts and as the sample is cooled down it re-crystallizes at a temperature well below the melting point. The melting-solidification hysteresis cycle was investigated and results compared with previous ones obtained on nanoparticles. Furthermore a metal induced crystallization effect was also observed in the germanium matrix.

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1. Introduction

In the last decade, a considerable amount of work on nanocomposite materials having novel magnetic, optical and electrical properties has been done. The main reasons for the reduced dimensions are the possible rise of quantum confinement effects [1] but thermodynamical aspects, while less explored, can also be of interest. The most interesting phenomenon which has been reported in this domain is a decrease of the melting point temperature of free standing nanocrystals (NC's) with respect to their bulk counterpart [2]. For NC's embedded in a solid matrix, the melting temperature can be below or above the melting temperature of the bulk. Furthermore a significant difference between the melting and re-solidification temperatures of the NC's typically referred as hysteresis can occur [3].

The Raman spectroscopy which is sensitive to size effects is a good characterization method to investigate these phenomena. It has been used earlier on Bi NC's with dimensions ranging from 2.3 to 23 nm [4]. For this study the Bi NC's have been embedded by pulsed laser deposition [5]. This nanocomposite system is particularly well suited to study thermal properties since the NC's are independent of each other and any contamination is prevented [6]. As a consequence, the successive cycles (fusion-solidification) do not exhibit in principle any drift with time. Moreover, Bi has a relatively low melting point (544 K) and Bi and Ge form an eutectic system with a low mutual solubility [5].

In a previous work, the kinetics of the solid-liquid phase transition of a Bi NC's was followed using Raman spectroscopy and X-ray diffraction [7]. In the present work, we have extended these studies from Bi NC's to a Bi nanoplane, both embedded in the same Ge matrix. Such a geometry allows to limit the confinement effects to one dimension only. Although this system behaves similarly to Bi NC's confined along the three dimensions, we have measured a much wider hysteresis effect: for the nano-plane, the temperature range at which Bi is in liquid state is of the order of 170 K compared to 70 K in the case of Bi NC's [7]. Furthermore, we have detected the crystallization of the amorphous Ge matrix above the Bi plane. This phenomenon is known as metal induced crystallization (MIC) and has been investigated in a variety of situations [9, 10, 11].

2. Experimental

2.1 Sample preparation

The sample is a thin nanocomposite film prepared by alternate pulsed laser deposition in vacuum, (ArF excimer laser at 193 nm, with a pulse duration of 12 ns and 5-Hz repetition rate), using a stainless steel mask with a square aperture of 5x5 mm to define the nano-plane. The samples were deposited on Si substrates at room temperature. The target to substrate distance was approximately 30 mm and the mask to substrate distance was about 5 mm. The growth sequence involved a number of pulses (7800) on the Ge target in order to deposit a continuous a-Ge layer of a few nm. Subsequently, the mask was placed in front of the substrate and after 3500 pulses on the Bi target the Bi nano-plane having a thickness close to 10 nm was deposited. Afterwards, a second deposit of a-Ge using 15600 laser pulses on the Ge target was deposited in order to ensure the complete encapsulation of the nano-plane. The density of amorphous Ge deposited by PLD is larger than when deposited by other techniques this in principle should result in a better confinement of the Bi nano-plane [12]. The resulting geometry is then a 10 nm thick square nano-plane of Bi, approximately 5x5 mm, embedded in two layers of amorphous Ge having a thickness of 3 nm underneath and 5 nm above the plane.

2.2 Raman scattering measurements

A Jobin-Yvon U1000 double monochromator was used for the Raman spectroscopy measurements. The 514.5-nm line of an Argon laser (Spectra Physics) was used as excitation source at a power level of 50 mW. For the macro-Raman measurements the diameter of the laser spot at the surface of the sample was of the order of 100 μm . The measurements were performed in vacuum. Due to the low Raman signal (the weaker signals correspond to scattering by a few atomic layers), each spectrum was the result of the addition of several scans. For the temperature measurements, a homemade oven reaching temperatures up to 750 K was used. The temperature was monitored by means of a thermocouple placed near the sample. The sample was heated step by step and once the desired temperature was reached, the system remained at that temperature at thermal equilibrium for several hours. Because of the low melting temperature of Bi, the black body emission in the visible range does not disturb the detection. The true temperature

of the sample was measured from the Raman frequency shift of the optical phonon of the silicon substrate [8]. For the micro-Raman measurements, a microscope coupled with the spectrometer was used; the diameter of the laser spot at the surface of the sample was of the order of $3\mu\text{m}$, in this case the measurements were performed in air at room temperature.

3. Results and discussion

The Stokes Raman spectra as a function of temperature in a heating and cooling cycle: 297 K , 498 K, 563 K, 570 K, and finally a 389 K is presented in Fig. 1. At low temperatures one observes the well-known modes E_g (70 cm^{-1}) and A_{1g} (97 cm^{-1}) of the Bi. However in the parallel polarization configuration (H-V) used in this case, the A_{1g} mode is much less intense [4] and is at the limit of our detection. Due to anharmonic effects , the peaks shift towards lower wave numbers when the temperature increases. When the melting point is reached, the nano-plane becomes liquid and as expected the peaks disappear completely. As the temperature decreases, the liquid Bi nano-plane re-solidifies and the crystalline peaks appear again. However, this occurs at a significantly lower temperature than the melting temperature (almost 170 K below). In this temperature range, the liquid bismuth is then in a supercooled state which disappears when the first crystal seed appears in the liquid Bi, this seed can often be a soluble or insoluble impurity [13]. The most important feature that can be inferred from Fig. 1 is this hysteresis behaviour of the melting-solidification cycle [3, 14]. In Fig. 2 the hysteresis behaviour of the heating-cooling cycle is presented by plotting the intensity of the E_g (70 cm^{-1}) of Bi as a function of temperature. One observes that the intensity of the peak vanishes abruptly at 570 K and the peak re-appears, although less intense, at 389 K. In the case of Bi NC's [7], we have yet reported an hysteresis effect in the heating cooling cycle of only 50 K as compared to the 170 K observed here.

At 570 K, apart from the disappearance of the Bi peaks due to its liquefaction, one can see, as an inset in Fig. 1, a Raman peak near 300 cm^{-1} characteristic of crystalline germanium. This effect of recrystallization of Ge at low temperature has been widely studied and is known as metal induced crystallization [9-11]. On the last spectrum taken after decreasing the temperature to 389 K, the peak characterizing the crystalline bismuth reappears indicating the solidification of the material. The intensity of this peak is lower than that observed at similar temperature when increasing the temperature. This

is probably due to a loss of Bi material by thermal diffusion in the re-crystallized germanium [9]. Further experiments are needed in order to observe the possible presence of Bi in the germanium matrix.

In figure 3, the spatial distribution of the metal induced crystallized germanium is analyzed with a micro-Raman setup, after the heating-cooling cycle, when the sample has thermalized at room temperature. The position of the laser beam probe with respect to the nano-plane is shown in the first column of the figure and the corresponding Raman spectra are shown for Bi, Ge and Si in each row. On the top row (laser spot near the center of the Bi plane), the Bi spectrum can be clearly observed as well as the one of re-crystallized Germanium. On the middle row, the laser spot is situated at a few tens of micrometers away from the edge of the Bi plan. Bi Raman signal has disappeared, however, crystalline Germanium is still detected. This result is due to metal induced crystallization of Ge induced by small clusters of Bismuth probably scattered by the edge of the mask during the deposit (remember that the distance mask-sample is 0.5 cm). The silicon signal intensity is higher since it is only absorbed by small Bi clusters and a mixed of crystalline and amorphous germanium. Finally, in the lower row (laser spot far from the Bi plan), the Raman signals of both Bismuth and crystalline germanium have disappeared as expected (no Bi deposited and the Germanium is still amorphous here) and the Si signal is larger since it corresponds to the signal of the Si wafer only slightly absorbed by a 8 nm layer of amorphous Germanium.

4. Conclusions

The solid $\leftrightarrow$ liquid $\leftrightarrow$ solid transitions of a bismuth nanoplane, embedded in amorphous germanium, have been investigated by Raman spectroscopy.

At room temperature the system is composed of a Bi nanoplane embedded in an amorphous germanium matrix. At 570 K and above, the system is composed of a liquid bismuth plane embedded in an amorphous Ge matrix. The Raman spectroscopy results allow to confirm the phase transition from crystalline to liquid bismuth since, as expected, the phonon peaks disappear. A melting-solidification temperature hysteresis of the order of 170 K is observed as compared to 50 K measured previously on NC's. Further investigations need to be performed in order to understand the origin of this difference (one dimension vs. three dimensions, size of the smaller or larger

dimension...). Finally MIC is detected by micro-Raman spectroscopy indicating that the whole nano-plane is surrounded by crystallized germanium.

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Figure Captions

Fig. 1. Raman spectra of Bi nano-plane embedded in a-Ge as a function of temperature. In the inset the Raman spectrum of crystalline germanium is shown.

Fig. 2. Raman intensity of the E_g (70 cm^{-1}) peak of Bi as a function of temperature.

Fig. 3. Micro-Raman spectra at three different positions of the probe beam with respect to the nano-plane.