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Preparation of Highly Textured Bi and MnBi Films by the Pulsed Laser Deposition Method [*]

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Textured Bi and MnBi/Bi thin films are prepared by the pulsed laser deposition method. The highly c-axis textured MnBi films are obtained by annealing the bilayer consisting of textured Bi and Mn films. The coercivities of the MnBi/Bi film are 1.5 T and 2.35 T at room temperature and at 373 K, respectively, showing a positive temperature coefficient. Microstructural investigations show that the textured MnBi film results from the orientated growth induced by the textured Bi under-layer.

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MnBi is a magnetic material with many favorable properties such as high uniaxial magnetocrystalline anisotropy and a positive temperature coefficient of the coercivity, which is unique for magnetic materials.[1,2] It was found that different preparation processes can obtain MnBi with different phases,[3] while in these phases, only the low-temperature phase (LTP) and quenched high-temperature phase (QHTP) can exhibit ferromagnetism at room temperature. It is remarkable that the LTP has strong uniaxial magnetocrystalline anisotropy ($H_{\rm A}$) of 9.0 T[1] and a coercivity (${}_iH_{\rm C}$) of 2.5 T has been achieved for MnBi powders at 540 K.[4] Therefore, LTP MnBi has considerable potential as a permanent magnet at high temperature.[5–12] In view of a large magnetic anisotropy constant (K) of the order of 10^7 erg/cc, LTP MnBi thin films show an extraordinarily large Kerr rotation,[13] a high value of spin polarization,[14] and an unusual Kondo effect with doping.[15,16] LTP MnBi films have been prepared using magnetron sputtering, e-beam evaporations, and molecular beam epitaxy (MBE).[17–20] PLD has become an extensive technique for fabricating high quality thin films which can be prepared at a lower-growth temperature or even at room temperature.[21,22] In previous studies, hard magnetic films such as NdFeB and FePt have been prepared by the PLD method.[23–26] In this Letter, a MnBi/Bi thin film is successfully obtained using the PLD method. Highly textured MnBi films can be achieved by annealing the bilayer consisting of textured Bi and Mn films. The coercivities of the MnBi/Bi film are 1.5 T and 2.35 T at room temperature and at 100℃, respectively, showing a positive temperature coefficient.

The Bi/Mn films were deposited at room temperature on glass substrates by using a KrF excimer laser source ($\lambda = 248$ nm) with a base pressure lower than 5×10^{-8} Torr. The depositing argon gas was kept at 5 mTorr. The distance between the target and the substrate was 5 cm. Before deposition, the substrates were placed in acetone solution, subjected to ultrasonic cleaning for 20 min, then were rinsed with deionized water and finally dried using nitrogen. The Bi and Mn films were deposited on the glass substrates with the pulse deposition frequency 0–5 Hz and laser energy 200–700 mJ. The thickness of the films was controlled by changing the number of pulses. At the same time, to ensure the uniformity of the film, the target and substrate were rotated simultaneously at a certain speed during the deposition process. After the Bi/Mn film was prepared, the sample was annealed in situ in the temperature range 300–600℃ for 0.5–2 h, then a Au layer with a proper thickness was deposited on the surface as a protective layer.

The structures were investigated using x-ray diffraction (XRD) with Cu-Kα radiation, The microstructure and morphology of the films were observed using a scanning electron microscope (SEM), a transmission electron microscope (TEM) and an atomic force microscope (AFM), respectively. The magnetic properties were measured by an alternating gradient magnetometer (AGM) and a physical property measurement system (PPMS). The content of the phases in the samples is refined with the Rietveld method by using the Fullprof program.

Both Bi and Mn films are prepared on the glass substrates by the pulsed laser deposition method. Figure 1 shows the x-ray diffraction patterns of the Bi films prepared with different thicknesses. As can be seen from Fig. 1, when the Bi film is thin, there is still

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a (012) peak in addition to (003) and (006) diffraction peaks, which indicates that the crystalline texture along (001) is not very good. With the increase of the Bi film thickness, the diffraction peak intensities of (003) and (006) peaks increase, while the intensity of the (012) peak decreases, and that of the (009) diffraction peak starts to appear. This indicates that the thicker Bi film is helpful in promoting the crystalline texture along the *c*-axis.

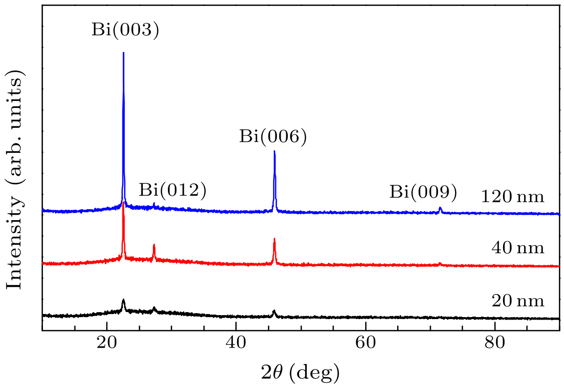

Fig. 1. X-ray diffraction patterns of Bi films with different thicknesses.

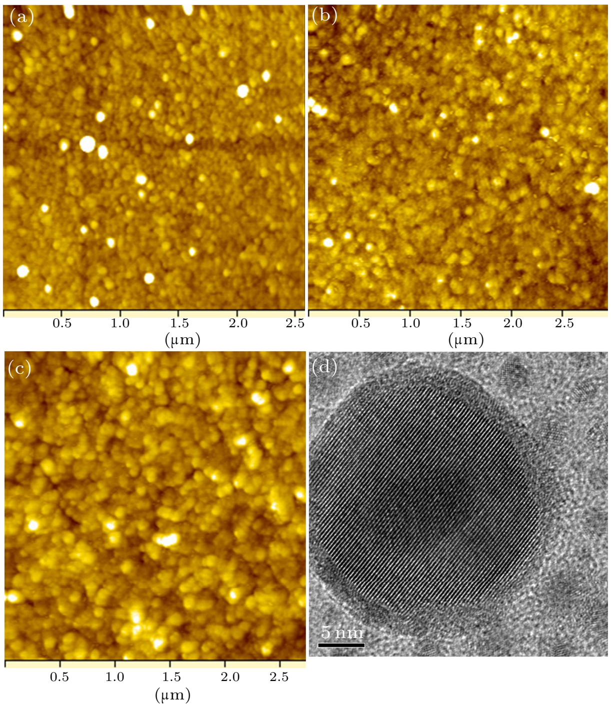

Fig. 2. AFM and TEM images of Bi films with different thicknesses (a) 20 nm, (b) 40 nm and (c) 120 nm, and (d) TEM image of grains in (b).

To understand the relationship between the thickness of the Bi film and its crystal structure, the microstructure of the Bi films is observed by AFM and TEM. As can be seen from Fig. 2, the average grain sizes of the Bi films increase from 10 nm to 40 nm when the film thicknesses increase from 20 nm to 120 nm. Figure 2(d) is the TEM image of the Bi film with the thickness of 40 nm. It is found that there are grains with different sizes. The size of the large grains is about 25 nm, while the small grains show sizes of about 4–5 nm. This indicates that the small grains should gradually grow into the large grains during the PLD process, which suggests that during the deposited process, an obvious preferential nucleation appears in the beginning stage of the nucleation. The anisotropic nuclear aggregation and gradual growth leads to the formation of the Bi film with a crystal texture. This shows that the continuous Bi film with a crystal texture can be prepared on a glass substrate via the optimizing process, which is very important for the preparation of anisotropic MnBi films with good crystal textures.

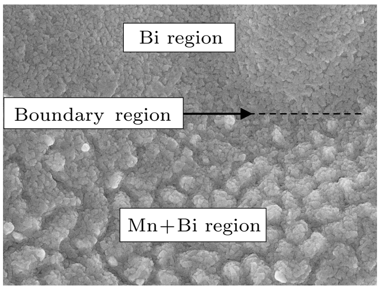

Fig. 3. The SEM image of the Bi film with and without the Mn toplayer annealed at 350℃ for 20 min.

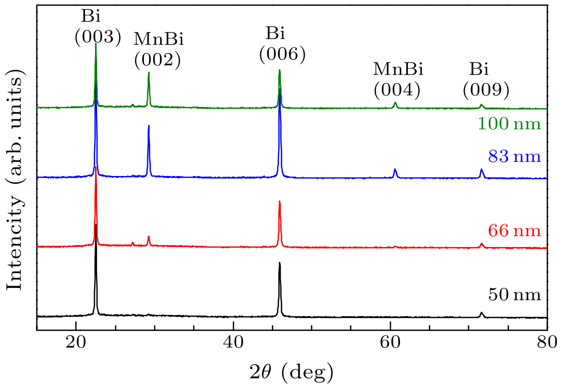

Fig. 4. X-ray diffraction patterns of Mn/Bi bilayer films with different Mn film thicknesses annealed at 345℃ for 20 min.

We have tried to prepare the Mn films on the glass substrate. Compared with the process conditions for preparing the Bi film, a much higher laser energy is required for the preparation of the Mn film since the melting point of Mn is much higher than that of Bi (Mn 1244℃, Bi 271.3℃). The preferential growth phenomenon was not observed in the Mn film. Therefore, to prepare the anisotropic MnBi film, the textured anisotropic Bi film was used as a template to deposit the Mn film, and then the composite films were annealed at an appropriate temperature.

Accordingly, the MnBi film was prepared by firstly depositing a Bi layer, and then a Mn layer was deposited to cover one part of the Bi layer. Figure 3 is the SEM image of the annealed film with and without Mn layers. As compared with the relatively flat pure Bi region, one can see that the column-like structures are formed for the Mn covered region due to the diffusion between Mn and Bi layers. This column-like structure consists of many nanosized MnBi grains (confirmed by x-ray data). This may be the key to form the anisotropic (textured) MnBi films. The effect of the Mn/Bi atomic ratio on the texture of the MnBi phase is subsequently investigated. Figure 4 shows the x-ray diffraction patterns of Mn/Bi bilayer films with different atomic ratios annealed at 350℃ for 30 min. The different Mn/Bi atomic ratios are achieved by fixing the Bi film thickness and varying the Mn film thickness. The Bi film thickness is fixed at about 200 nm, and Mn films with different thicknesses of about 50 nm, 66 nm, 83 nm and 100 nm are deposited. As can be seen from Fig. 4, the peak intensity of the MnBi (002) increases gradually with the Mn film thickness, and it reaches a maximum when the Mn film is about 83 nm. When the thickness of the Mn film further increases to 200 nm, the peak intensity of the MnBi (002) starts to decrease. This is related to diffusion ability within Mn and Bi layers. The increase of the Mn layer thickness leads to the deterioration of the c-axis texture of the Bi films and the appearance of the Bi (012) peaks.

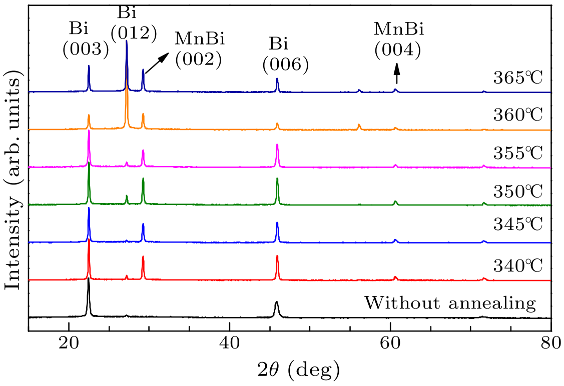

Fig. 5. The effect of annealing temperature on the MnBi phase.

The effect of annealing temperature on the MnBi phase purity was investigated. Figure 5 shows the x-ray diffraction patterns of the Mn (200 nm)/Bi (100 nm) bilayer annealed with different temperatures for 20 min. As can be seen from Fig. 5, when the annealing temperature is between 340℃ and 355℃, there is slight difference in the relative intensity of the (002) peaks for MnBi films. However, with the increase of the annealing temperature, except the (003), (006) and (009) diffraction peaks, the (012) diffraction peak of the Bi appears. When the annealing temperature is higher than 360℃, the peak intensities of (003), (006) and (009) of the Bi phase decrease and that of the (012) peak increases abruptly. This leads to a decrease of the content of the MnBi phase and a deterioration of the texture. These results indicate that the annealing temperature has a great influence on the formation of the MnBi phase and its crystal texture. Annealing the sample at a lower temperature may be helpful for the formation of the MnBi phase with a good crystalline texture.

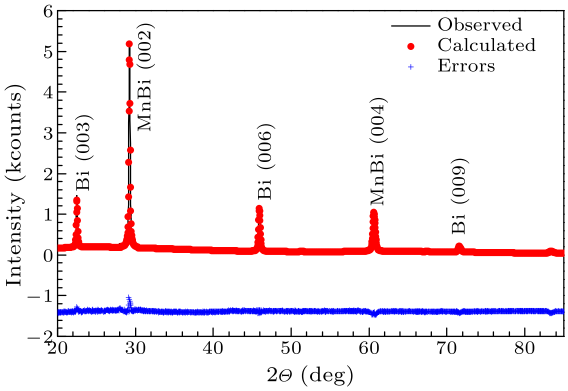

Fig. 6. X-ray diffraction pattern of the MnBi film.

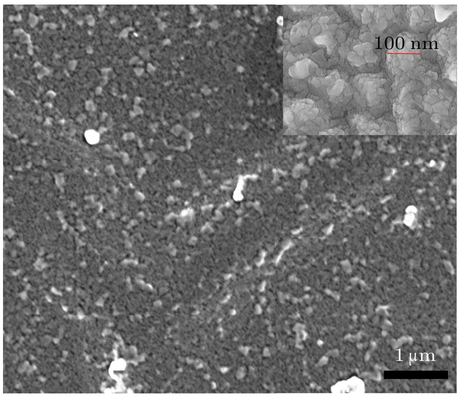

Fig. 7. SEM images of the MnBi film.

Based on the above results, by optimizing the process, we successfully prepared MnBi thin films with a high crystallographic texture. The deposited thicknesses of Bi and Mn films are about 200 nm and 80 nm, respectively. After the Bi/Mn films were prepared, the sample was annealed in situ at 350℃ for 20 min. The main problem with MnBi is difficulty in obtaining single phase material, and only a few reports show almost phase pure MnBi films.[27] Figure 6 shows the x-ray diffraction pattern of the MnBi film, from which we can find that the main phase of the thin film is the MnBi low temperature phase. Certainly, there is still a small amount of Bi. The actual content of the MnBi LTP phase is about 84 wt% calculated from the Rietveld refinement by using the Fullprof program. The calculated average grain size from XRD by using Scherrer's equation is about 44 nm, which was confirmed by the TEM observation (data not shown here).

Figure 7 shows the morphology of anisotropic MnBi/Bi film prepared by the optimized process, from which we can find that the MnBi/Bi film is compact. The MnBi granular can be observed from the enlarged image (see the inset of Fig. 7), which is composed of a plurality of MnBi grains with an average size of about 40–50 nm.

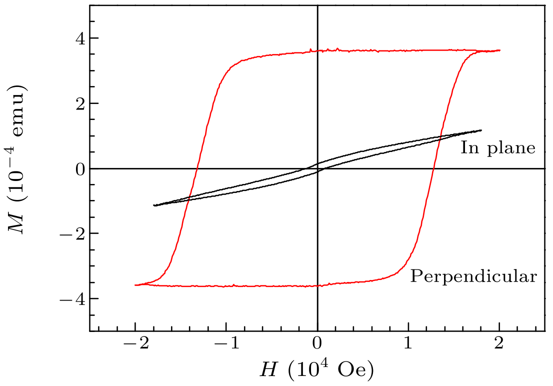

Fig. 8. Room-temperature hysteresis loops for MnBi films.

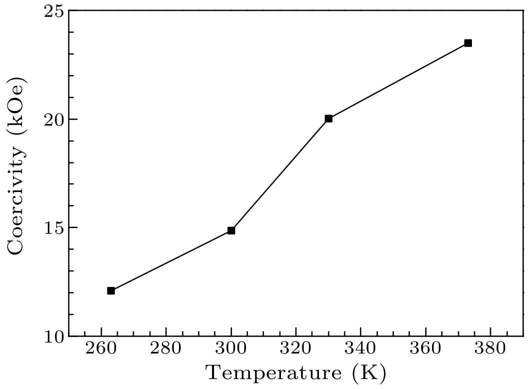

Fig. 9. The coercivities of the MnBi film at different temperatures.

Both the perpendicular and in-plane hysteresis loops of the prepared MnBi/Bi film were measured at room temperature as shown in Fig. 8. The nearly square loop is observed from the perpendicular curve, while the in-plane curve exhibits an almost overlapped curve with nearly zero remnant magnetization. The estimated full saturation anisotropic field is approaching 7 T, which is approximate to the magnetocrystalline anisotropic field of bulk MnBi.[1] The squareness ratio (M_r/M_s) is about 0.98, indicating a high degree of crystalline texture in the MnBi films. This observation offers a direct evidence for the giant perpendicular anisotropy, which is consistent with the XRD data. The room-temperature coercivities of the MnBi/Bi film are about 1.5 and 0.0 T along perpendicular and in-plane directions, respectively. This suggests that the magnetic reverse process of the MnBi/Bi film is mainly controlled by coherent rotation of single domain grains (the single domain size of MnBi is 250 nm) according to the Stoner–Wohlfarth model.[28]

The temperature dependence of coercivity for the MnBi film is shown in Fig. 9. With the increase of temperature, the coercive force increases and reaches 2.35 T at 373 K. This indicates that the MnBi film shows a positive coercivity temperature coefficient. This positive temperature coefficient is related to the anisotropy field of the MnBi.[1] From 100 to 550 K, the anisotropy field increases with temperature, which is related to the change of lattice constant when temperature changes.[4] This shows a benefit over the rare-earth permanent magnetic materials such as $Nd_2Fe_{14}B$ materials, thus it could be used as high-temperature magnetic recording media.

In summary, the anisotropic MnBi/Bi film has been obtained using the pulsed laser deposition method. The coercivities of the MnBi film are 1.5 T and 2.35 T at room temperature and 373 K, respectively. A positive temperature coefficient is obtained for the synthesized MnBi film, which can be a potential permanent magnetic material due to its excellent high temperature magnetic properties.

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