Magnetism and Magneto-Optics of MnBi Nano-Particles

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Abstract- Thin MnBi films have been grown by molecular beam-epitaxy technique in combination with an alloying process. The formation of MnBi is driven by an enhanced intermixing due to diffusion close to the eutectic temperature where Bi becomes liquid. The growth process of MnBi was investigated in detail by preparing a wedge-shaped thin film. Highly c-axis oriented nano-particles of MnBi are formed in a Bi matrix. The particles show two magnetic phases with magnetic moments of 744 kA/m and 113 kA/m and coercivities of 20 kOe and 7 kOe, respectively. They have a large magnetic energy product of 171 kJ/m³. The magneto-optical Kerr rotation in the visible spectral range is determined.

Key words: molecular beam epitaxy, manganese bismuth, magnetic properties, magneto-optical medium, nano-particles

1. Introduction

For more than 4 decades it is known that the binary compound MnBi has a large potential to store information magnetically which can be read out optically¹⁾. As the material has a large Kerr rotation peak in the blue spectral range²⁾, storage media with high recording densities can be developed.

MnBi is a hard magnetic material. At room temperature the coercivity is 20 kOe and increases at higher temperatures³⁾. Thus, the stability of the information stored is guaranteed even when the particle size is reduced in order to increase the data density. However, MnBi exhibits some important drawbacks regarding magneto-optical recording. The material undergoes an irreversible crystalline first-order ferromagnetic-to-paramagnetic phase transition at 628 K upon heating^{4,5)}. This instability implies severe difficulties in the Curie point writing process and the possibility of information loss.

We have prepared thin MnBi films by molecular beam-epitaxy (MBE) technique followed by an alloying process. To study the properties of the films as function of the layer thickness we have grown a wedge-shaped sample. In this way, we obtained 9 MnBi layers which have been grown under the same conditions and differ only in their thickness. We were able to clarify the connection between the structural quality of the MnBi layers and their magnetic and magneto-optical properties.

2. Sample Preparation

Thin MnBi films were prepared by the MBE technique. *In situ*-RHEED analysis was used to investigate the surface morphology during the growth process. Generally, our films can be grown on several substrates, e.g. glass, GaAs, BaF₂, CaF₂, Si. The first step is the preparation of a textured Bi layer which is grown directly onto the substrate. Initially, the Bi forms islands which begin to coalesce at a thickness of about 20 nm. This leads to a smooth Bi film for a thickness larger than 60 nm. Subsequently, a Mn layer is deposited at room temperature onto the Bi buffer. Afterwards, the Mn/Bi bilayer is heated to 500 K, which makes the Mn layer alloy into the Bi film to form MnBi.

The alloying process has been investigated by tempering a Mn (100 nm)/Bi (100 nm) bilayer on a BaF₂ substrate in a SQUID magnetometer (*Quantum Design* MPMS-5S) and measuring the remanent magnetization M_r while annealing the sample (Fig. 1). Before tempering the bilayer already shows a small magnetic coupling. This indicates the occurrence of MnBi directly at the interface between the Bi and the Mn layer. Below 490 K the remanence increases slowly with increasing temperature. At 490 K the magnetization starts to rise rapidly and reaches its maximum value at 520 K. The fact that ferromagnetic MnBi occurs directly after growth at room temperature shows that the enhanced formation of MnBi at 490 K is not due to a chemical activation process. The mechanism is rather diffusion. The Bi becomes liquid at the eutectic point of 535 K⁶⁾. Thus, the

Fig. 1 Remanent magnetization M_r of a Mn (100 nm)/Bi (100 nm) bilayer during the alloying process.

increase of the mobility causes a better mixing of Mn and Bi close to the eutectic temperature. When all Mn atoms have reacted with the Bi, the remanence remains constant.

In order to obtain samples which differ only in the thickness, a wedge-shaped MnBi film on Si substrate has been prepared. During the evaporation of Mn the main shutter of the MBE system is pushed slowly across the substrate. In this way, the same growing conditions for all thicknesses are obtained. The wedge has been cut into 9 single pieces which can be investigated separately. The maximum thickness of the samples is 140 nm, which was determined during growth by a quartz oscillator with an uncertainty of less than 10 %.

3. Results

3.1 Structural Characterization

The samples are characterized by X-ray diffraction (XRD) measurements. The choice of the substrate has considerable influence on the structural quality of the Bi buffer. Measurements of films which are grown on BaF₂ (111) show only the Bi (001)-orientation as indicated by the appearance of the Bi (003) reflex only (Fig. 2 a). Films on a quartz substrate reveal (101)-oriented Bi perpendicular to the (001) direction (Fig. 2 b). Regarding the peaks related to MnBi only the (002) reflex is ob-

Fig. 2 X-ray diffraction measurements of a MnBi layer on a) BaF₂ and b) quartz substrate. On BaF₂ the Bi buffer is (001)-oriented, whereas on quartz substrate (001)- and (101)-oriented crystallites are observed. In spite of that, on either substrate the MnBi shows only (001)-orientation.

served on both BaF₂ and quartz substrate. Despite the different quality of the Bi buffer, this synthesis technique yields only c-axis oriented MnBi thin films.

3.2 The Role of Surface Morphology on Magnetism

The surface morphology has an important influence on the formation of MnBi. In order to grow MnBi nanoparticles it is necessary to produce a smooth Bi buffer layer. Then, MnBi clusters can be formed on the surface (Fig. 3a) with an average size of 200 nm × 500 nm. The magnetization of these particles is shown in Fig. 4a to be ferromagnetic as already published⁷⁾. If the Bi buffer shows too large facets, the segregation of Mn is enhanced and, unregularly distributed Mn islands on the Bi surface are observed (Fig. 3b). The facetting behaviour

Fig. 3 Micrographs of the surface of MnBi films on a smooth (a) and a rough (b) Bi buffer (size: 172 μm × 142 μm).

Fig. 4 Hysteresis loops of a) MnBi particles on a smooth Bi layer and b) Mn clusters on a highly faceted Bi layer normalized to the maximum magnetization M_s of curve a).

could be proved by "V"-shaped reflexes in the RHEED analysis. In this case, only a small amount of MnBi is formed. This is clearly supported by the magnetic properties of these samples which are dominated by an antiferromagnetic coupling of the Mn islands (Fig. 4b).

To obtain a closer insight into the growth process of MnBi on a smooth Bi buffer the surface of the wedge-shaped sample (Fig. 5) is investigated by optical microscopy. In the lower part of Fig. 5 the surfaces of all samples are shown as observed with an optical microscope. MnBi clusters can be seen in a Bi matrix. After an initial state, in which these clusters are still small and MnBi begins to form, one observes that the size reaches a constant value, and the clusters become more dense with increasing thickness.

3.3 Magnetic Properties

Magnetic measurements performed perpendicular to the surface at room temperature (Fig. 6) reflect the morphology observed in the optical micrographs of Fig. 5. The initial state (sample 1) exhibits only a narrow magnetization curve with a coercivity of about 7 kOe. With increasing island size, a second component to the magnetization curve occurs with a coercivity approx. 20 kOe (Nos. 2-3). This contribution is known to belong to the high coercivity phase of MnBi and is related to a small particle size⁸⁾.

Fig. 5 Wedge-shaped MnBi layer on Si substrate (top). The layer was cut into 9 single samples which were investigated separately. Below, optical micrographs show the surface of these samples (size of each picture: 172 μm x 142 μm).

As shown in Fig. 5 the size and the shape of the MnBi islands do not change with increasing thickness. Therefore, the shape of the magnetization curves of the samples 4-6 is not changing, either, and it is dominated by the high coercivity loops. With increasing thickness, the contribution of the 7 kOe becomes a little more pronounced (Nos. 7-9). The absolute magnetization increases and reaches values of 744 kA/m and 113 kA/m for the 20 kOe and the 7 kOe phase, respectively, which results in a total magnetization of 857 kA/m.

Fig. 6 Magnetization curves of the 9 pieces of the wedge-shaped MnBi sample (see Fig. 1). The hysteresis loops consist of two different contributions (see text).

MnBi undergoes a phase transition at 628 K from the ferromagnetic low temperature phase (LTP) into a paramagnetic high temperature phase (HTP)^{4,5)}. Upon quenching back to room temperature the HTP can be stabilized forming a quenched high temperature phase (QHTP) which orders ferromagnetically below 440 K. The magnetization of the QHTP is reduced to 50 % of the LTP at room temperature⁹⁾. The HTP can already be formed in part at a temperature of 500 K at which the sample has been annealed¹⁰⁾. The 20 kOe phase in our samples has a magnetization of 744 kA/m, which is close to the value of 760 kA/m found in literature⁶⁾ for the LTP. Thus, this 20 kOe phase should be attributed to the LTP.

One might speculate that the 7 kOe phase is related to the QHTP of MnBi. In this case, however, a magnetization of 113 kA/m would imply that about 1/3 of the material is in the QHTP phase and 2/3 is in the LTP of MnBi. As a consequence, the measured magnetization of 744 kA/m for only 2/3 of the material in the film indicates for our LTP a magnetization of about 1116 kA/m which is much higher than the literature value⁶⁾ and which appears unlikely. In addition, the coercivity of the QHTP is reported to range between 0.45 kOe and 4 kOe^{9,11)}. The larger value of 7 kOe measured in our samples does not support the identification of the 7 kOe phase as the QHTP. The fact that the contributions of the

two phases to the magnetization curves change with thickness also speaks for a pinning effect rather than for a chemical phase transition.

Despite the fact that a structural magnetic phase transition occurs below the ferromagnetic Curie temperature, MnBi remains a potential candidate for an application in the magneto-optical storage field. In addition, the large magnetic energy of approx. 200 kJ/m^3 makes this material interesting for other magnetic devices where permanent magnets are used in the nanotechnology.

3.4 Magneto-Optical Properties

The determination of the intrinsic magneto-optical properties of MnBi as a thin films is limited by the circumstance that the film consists of small particles. Thus, when the Kerr rotation is measured experimentally not only the MnBi but also the visible Bi surface is illuminated. As a consequence, the observed spectrum is a superposition of the MnBi and the Bi contribution to the Kerr signal. The Kerr rotation of Bi is small and of opposite sign to the rotation of the ferromagnetic MnBi¹²⁾. In addition the reflectivity of the rough surface is poor and, thus, the signal-to-noise ratio is low.

Fig. 7 Kerr spectra of selected layers of the wedge-shaped MnBi sample (see Fig. 5). The measured data are compared to theoretical calculations by Koehler and Kuebler¹³⁾.

In Fig. 7 the Kerr rotation of the samples Nos. 5-8 of the wedge-shaped MnBi film are shown in comparison to a theoretical MnBi spectrum¹³⁾. For the samples Nos. 1-4 a Kerr rotation has not been observed. The measured spectra are qualitatively similar but smaller than the theory because of the Bi contribution to the Kerr rotation. In addition, the optical constants of small particles are different from those of bulk material and they influence directly the magneto-optics. Going from No. 5 to No. 8,

the coverage of MnBi at the surface increases. Therefore, the effective Kerr rotation becomes larger. The maximum effective rotation obtained from the nano-particle samples is -0.83 deg at 1.97 eV . A second broad maximum occurs in the UV spectral range between 3.5 and 4.0 eV . In this region, the Kerr rotation is around 0.2 deg .

4. Conclusion

Using MBE technique in combination with an alloying process, MnBi nano-particles have been grown onto several substrates. The formation of MnBi, which is driven by enhanced diffusion at 500°C , depends on the surface morphology of a pre-grown Bi layer.

XRD measurements have confirmed a c-axis orientation of the MnBi. Further investigations by optical microscopy yield an initial growing state with small MnBi clusters on the Bi surface. With increasing thickness the islands grow up to a maximum size of $200 \text{ nm} \times 500 \text{ nm}$ and begin to coalesce. The morphology of the islands can be related to the magnetism of the nano-particles showing wide hysteresis loops. The shape of the loops indicates the occurrence of two MnBi phases. The magneto-optical investigation results in a maximum Kerr rotation of -0.83 deg at 1.97 eV and also a considerable rotation in the UV spectral range.

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