Microstructure and magnetoresistance of sputtered bismuth thin films upon annealing

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We investigated the microstructure and magnetotransport properties of sputtered Bi upon annealing. The grain size and the orientation of polycrystalline Bi thin films can be manipulated through a proper annealing treatment. Weak-oriented fine grains, of which size is about 0.1 μm, were found in as-sputtered Bi films. Careful annealing at 270 °C results not only in a grain growth of up to 1.1 μm but also in a [001]-preferred orientation structure. The grain size increases exponentially with annealing time in the temperature range of 266–270 °C. The grain-growth exponent (n) and the activation energy (Q) were evaluated to be 0.32±0.05 and 70.7 kJ/mol, respectively. The magnetoresistance (MR) of Bi films is strongly dependent on the microstructure and thickness of the film, and on the measured temperature. A very high MR of 30,000% can be observed in the annealed 7-μm-thick Bi films when measured at low temperature (4 K). The drastic increase in MR after annealing is largely attributed to the trigonal-axis-oriented texture diminishing anisotropy scattering as well as to the significant grain-growth decreasing grain-boundary scattering of carriers. The measured temperature and film thickness on which the phonon scattering relies are also important factors in determining the magnetoresistance of sputtered Bi films. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1989433]

I. INTRODUCTION

Semimetallic bismuth (Bi) is a fascinating material for spintronic devices because it intrinsically has a long mean free path and a small effective mass which are very advantageous in achieving a long spin-relaxation length in spin injection devices.[1,2] These unique properties leading to the high-magnetoresistance (MR) behavior are useful for realizing spin-based electronic devices.[3] Furthermore, as a semimetal, similar conductivity of Bi to the ferromagnetic materials can be a great advantage in reducing the effect of interfacial scattering of carriers, called conductivity mismatch.[4] Good observation of spin injection and detection is expected using ferromagnetic (FM)/Bi junction with peculiar characters of Bi.

The preparation of high-quality and uniform Bi thin films is essential in the fabrication of a spin device with such splendid physical properties of Bi. Comprehensive studies have focused on the high magnetotransport properties of Bi thin films grown by electroplating[2,5] and molecular-beam epitaxy (MBE).[6,7] MBE is estimated to be expensive and nominal with respect to the growth rate of thin film, even though it produces high-quality single-crystalline Bi films. There are some researches based on electrochemical methods for good Bi thin films: however, they are not suitable to microfabrication processes such as micropatterning and etching. Alternatively, the sputtering method was used to make Bi thin films which is known as an improper way to get a superior film in some previous studies,[8] in spite of its merits such as fast growing rate and easy control of thickness for microfabrication processes.

The sputtered Bi thin films show a quite low MR compared with those prepared by electroplating because they have very fine grains of 0.1 μm.[9] The MR of the electroplated films has greatly been increased by employing a suitable annealing treatment which finally produces single-crystal Bi films through active grain growth.[2,5,10] The grain growth is regarded as a promising way to increase the MR in polycrystalline Bi. However, there is rare work to be done on the grain growth of the sputtered Bi films with a very fine grain size.

In our work, we investigated the microstructural evolution of Bi upon annealing process which was carried out at 266–270 °C, a few degrees below the melting temperature of Bi (271.4 °C), for various holding times. The grain growth-exponent (n) and the activation energy (Q) were evaluated using the collected data in which the typical feature of grain growth was discussed. The texture evolution of Bi films upon annealing was also studied with electron backscattered diffraction (EBSD) method. We tried to clarify the relationship between the MR ratio and the microstructure of the film. The annealing effects on the large MR at 4 K and room temperature in the sputtered Bi thin films were discussed.

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II. EXPERIMENTAL PROCEDURES

Bi thin films were deposited on an oxidized Si (100) substrate in a dc magnetron sputtering system with a base pressure of 5×10^{-7} Torr. Prior to the Bi deposition, 0.2-μm-thick SiO_2 was formed on top of the Si substrate through thermal oxidation. The Bi films were deposited at 1 μm at a rate of 0.2 ± 0.01 μm/min at room temperature. The distance between the target and the substrate is kept at 10 cm in order to ensure high flatness and uniformity of thin films. Details on the deposition process were already reported in literature.[11]

Annealing is very important for the Bi thin films because it leads to the conspicuous improvement of magnetoresistance (MR) after a suitable thermal treatment. The conventional thermal annealing (CTA) was adopted in which the samples were loaded and vacuumed in the pressure of 10^{-6} Torr followed by Ar flowing by way of prevention of oxidation during annealing. Bi was heated to 240 °C with the rate of 4 °C/min after the vacuum state stabilized. For a 30-min preservation at 240 °C, the heating rate was reduced while the temperature reached the target temperature, so that the local melting of Bi thin films by overshooting was protected. Bi thin films were annealed at temperatures ranging from 266 to 270 °C for 5–25 h. The microstructures of as-sputtered and annealed Bi thin films were investigated by x-ray diffraction method (XRD, Philips) and by field-emmission scanning electron microscopy (FE-SEM, JEOL6500F) equipped with electron backscattered diffraction (EBSD) system. EBSD is a powerful analysis tool for notifying the general information about the crystallographic orientations of grains and the grain-boundary characteristics such as misorientation. By analyzing the Kikuchi lines generated from the area of concern in the specimen, the crystallographic orientations of each grain can be determined, which makes it possible to give valuable information on grain size with high-angle grain boundaries and to analyze the texture development. The grain size of Bi films was measured by linear counter method from five sets of SEM and corresponding EBSD grain maps covering different areas.

A conventional four-probe dc magnetotransport measurement was made on Bi films using physical property measurement system (PPMS, Quantum Design) in the temperature range of 4–300 K while an out-of-plane field was swept over ±9 T. The MR ratio defined by $((R_H-R_0)/R_0)\times100$ is evaluated at the magnetic field of 9 T for each Bi films.

III. RESULTS AND DISCUSSION

A. Grain growth

Figure 1 presents SEM images of Bi films: (a) as sputtered, (b) annealed at 268 °C and (c) at 270 °C for 10 h. Since annealing temperature of 270 °C is just 1.4° below the melting point of Bi (271.4 °C), a careful temperature control in a deviation of ±0.5 °C is needed during heat treatment. The as-grown film is polycrystalline and its grain size is evaluated to be about 0.1 μm, with large deviations. The films are always formed by columnar crystals with a grain size comparable to the film thickness which leads to surface roughness. Annealing yields a drastic change in the morphology of Bi films that individual fine grains grow into coarse grains. As coarse grains start to form, it becomes harder to define grain boundaries while fine grains can be easily counted in as-sputtered films. EBSD is expected to show clearly the grain size of annealed ones.

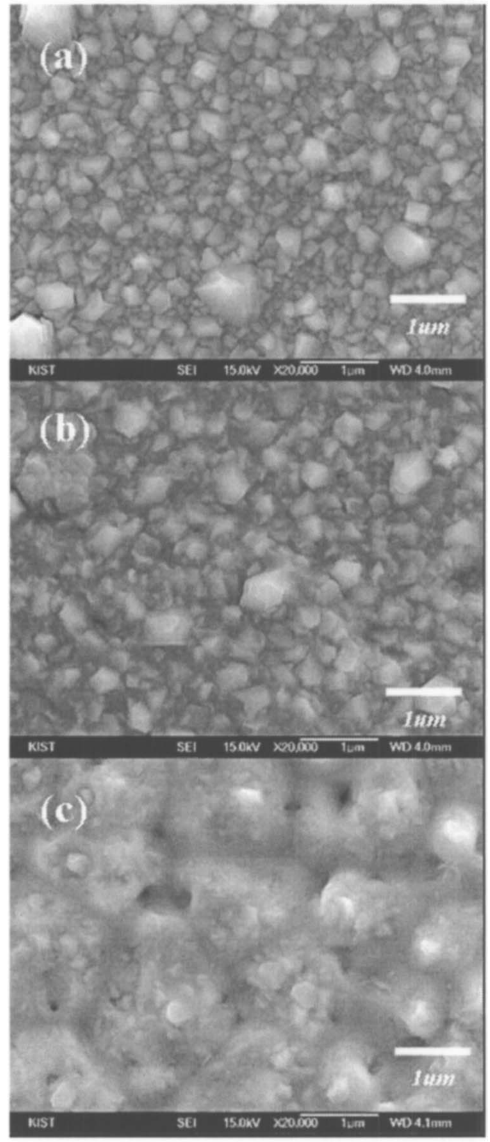

FIG. 1. SEM images of Bi thin films at different conditions: (a) as sputtered and (b) annealed at 270 °C for 5 h and (c) at 270 °C for 10 h.

The grain maps of Bi films annealed at 270 °C for (a) 150 min, (b) 300 min, and (c) 600 min were analyzed using EBSD, as shown in Fig. 2. The grain maps comprise a lot of mosaic pieces with different colors representing individual grains with a high-angle grain boundary of 15°. With EBSD grain maps, we can clearly see the grain growth of Bi films and measure the grain size at various annealing conditions. The grain size measured from SEM images agrees well with that from the EBSD grain maps.

Figure 3 shows the mean grain size of Bi films annealed for 150–600 min at temperatures as indicated. The error bar was determined by five sets of grain-size data measured from SEM images. An initial grain size of 0.1 μm in the as-sputtered samples increases drastically upon annealing. Annealing at 270 °C for 10 h causes an increase in the grain size up to 1.1 μm which is ten times larger than that of as-sputtered Bi films.

If the growth of the grain is caused by a decrease in its boundary area per unit volume,[12] then

$$\frac{d\bar{D}}{dt} = \frac{k}{\bar{D}}, \tag{1}$$

where $\bar{D}$ is the average grain size and k is a temperature-dependent constant. Integration of Eq. (1) yields

$$\bar{D}_t^2 - \bar{D}_0^2 = k' t, \tag{2}$$

where $\bar{D}_0$ and $\bar{D}_t$ are the initial grain size and the grain size at time t, respectively, and $k' = 2k$. Equation (2) is most commonly used in a simplified form:

$$\bar{D} = k' t^n, \tag{3}$$

which implies that $\bar{D}_0$ is negligible in comparison to $\bar{D}_t$. The grain-growth exponent n of Bi thin films was calculated from the data shown in Fig. 3 by plotting the average grain sizes and time in logarithmic scale which results in a straight line of the slope n.

The activation energy of grain growth may be obtained from the data at different temperatures.

$$k = k_0 \exp\left(\frac{-Q}{RT}\right), \tag{4}$$

where k_0 is a temperature-independent constant, Q is the activation energy for grain growth, R is the universal gas constant, and T is the absolute temperature.

The grain-growth exponents of 0.32±0.05, calculated from Fig. 3, are considered as one group because the temperature difference is quite small.

For a normal grain growth in a bulk sample, the grain-growth exponent $n = 0.5$ is usually expected. It turns out, however, that the magnitude of the grain-growth exponent is rarely equal to 0.5 and depends on the annealing temperature. In particular, in ceramics the grain-growth exponent is usually equal to 0.2–0.3.[13] For nanocrystalline materials, significant variations in n have been observed. The fact that the magnitude of n obtained from the experimental data is less than 0.5 may be explained on the assumption[12] that there is a drag force in the material investigated, which stops the grain-growth process when the mean grain size reaches a certain final value. During the early stages of the grain growth of thin films, the growth follows the patterns of a normal grain growth when grains grow in three dimensions. After the average grain size becomes comparable to the film thickness, a columnar grain structure develops and grain growth happens in two dimensions with free surfaces.[14] The thickness of sputtered Bi thin films is thin enough to confine grain growth in two dimensions when the grain grows to around 1 μm. Actually, grain size became stable after annealing at 270 °C for 10 h and no further increase was observed in spite of a longer duration of up to 15 h. The value of $n = 0.32$ obtained

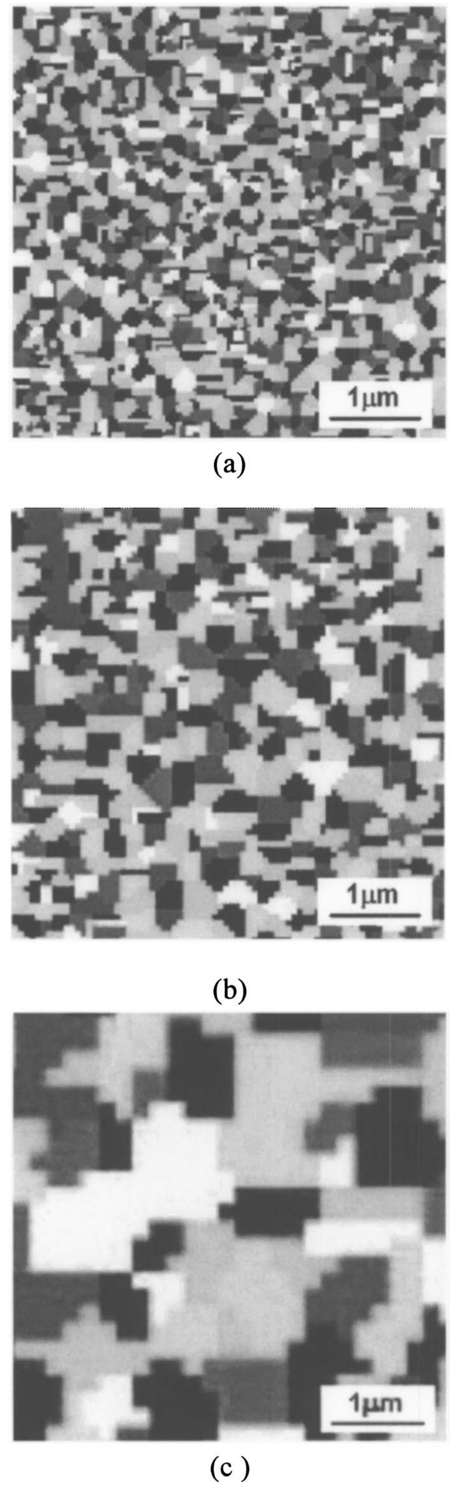

FIG. 2. Grain maps of Bi thin films (a) as sputtered and (b) annealed for 5 h, and (c) for 10 h at 270 °C. Each color represents the individual grains having misorientation angle larger than 15° from neighboring grains.

in the work which deviated from 0.5 seems to be reasonable considering the possible dragging effects in fine-grain-sized thin films as commented above.

We also calculated an activation energy of 70.7 kJ/mol by plotting $\ln k$ vs $1/T$. This value is much lower than the reported activation energy of self-diffusion in bulk Bi (580 kJ/mol).[15] Although such high activation energy of Bi is still controversial over the past decades, the low value of

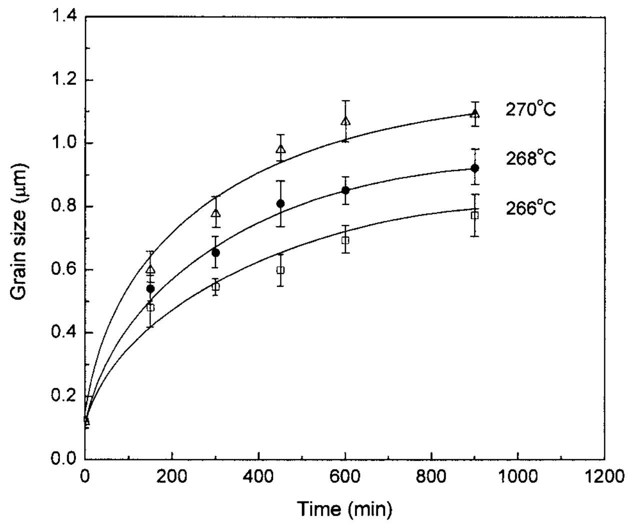

FIG. 3. The grain sizes of the samples annealed for 150–900 min at temperatures as indicated. Smoothed curves are fitted data based on the grain-growth equation.

obtained activation energy implies that the grain growth of the sputtered Bi films is dominated by grain-boundary diffusion and not by lattice diffusion. Ellis and Nachtrieb reported that the volume diffusion in Bi, even if close to its melting point, was an extremely slow process and the grain-boundary diffusion governed the self-diffusion of Bi.[16] Therefore, it is concluded that the grain-boundary diffusion is a major mechanism for the grain growth of Bi thin films.

B. Texture development

Figure 4 displays XRD patterns of (a) as-sputtered Bi thin films and those annealed at 270 °C (b) for 5 h and (c) for 10 h. Bi has a rhombohedral structure, which is slightly distorted from a cubic structure. Its structure is often de-

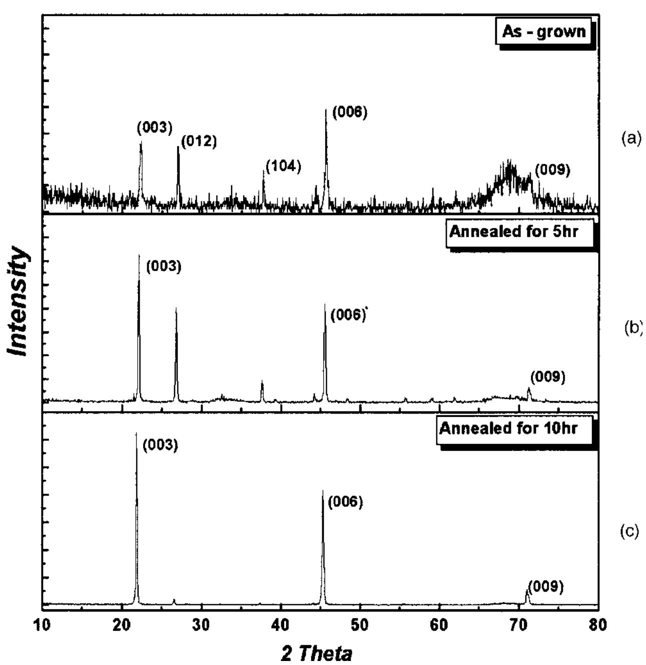

FIG. 4. X-ray diffraction patterns of (a) as-sputtered Bi films and those annealed at 270 °C (b) for 5 h and (c) for 10 h.

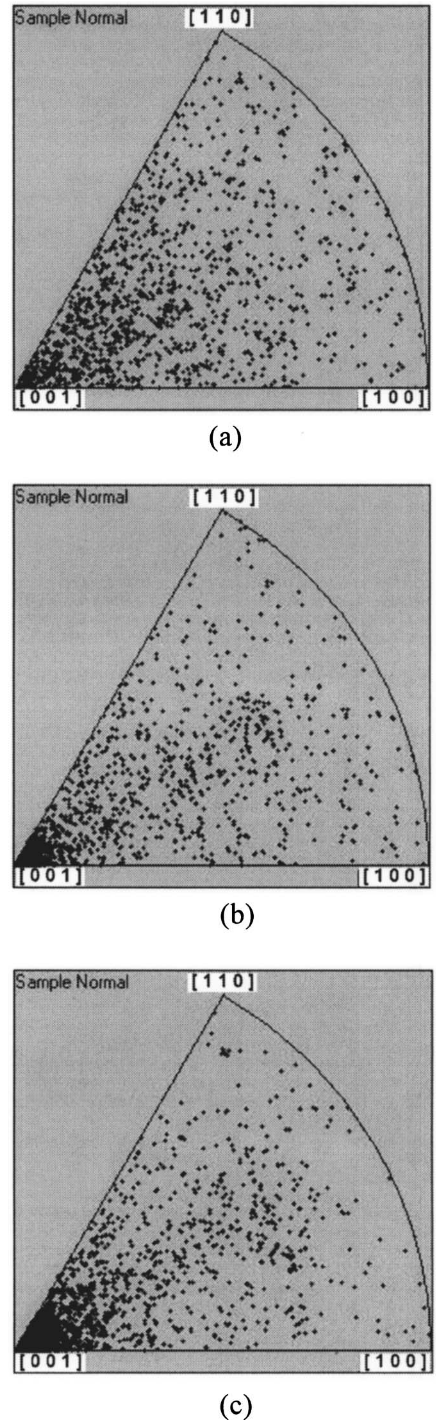

FIG. 5. Inverse pole figures showing the distribution of the plane-normal direction of Bi films upon annealing.

scribed as a hexagonal system. The XRD pattern of as-sputtered films exhibits major peaks of (003) and (006), with some minor peaks of (012) and (104). Upon annealing at 270 °C, the (003) peak remarkably increases while minor peaks get weaker. After 10 h annealing at the temperature, only major peaks of (003), (006), and (009) exist as minor peaks disappear, revealing that the sample becomes a trigonal-axis [001]-oriented film.

Figures 5 and 6 exhibit the inverse pole figures showing the orientation distributions of Bi films upon annealing, measured with EBSD. Figures 5 and 6 were achieved from the

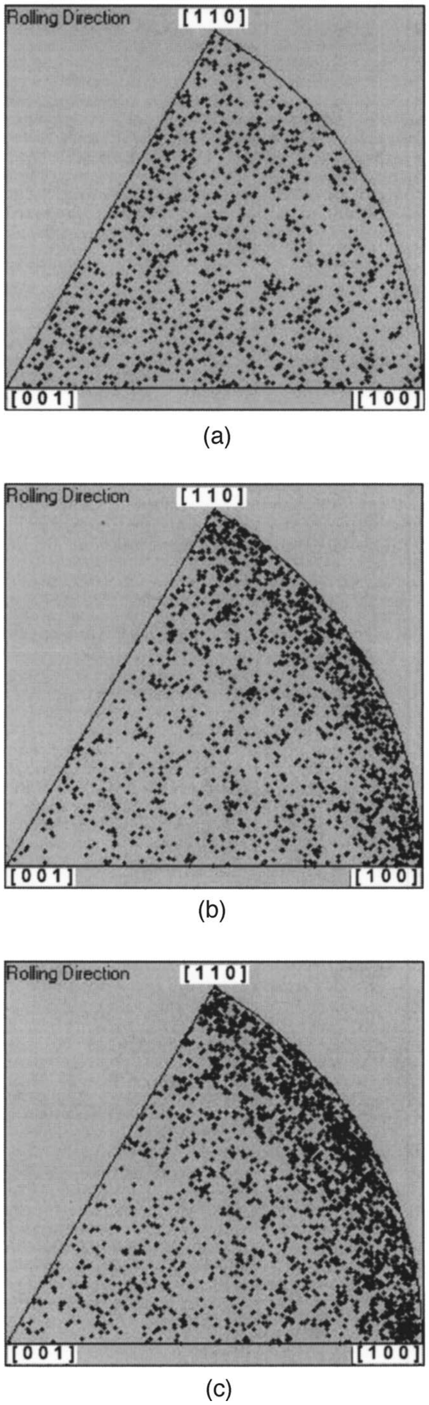

FIG. 6. Inverse pole figures showing the distribution of the in-plane direction of Bi films upon annealing.

perpendicular and parallel directions to the film surface, respectively. Since individual spots in the inverse pole figures correspond to the orientation of each pixel within the microstructural area scanned by EBSD, the specific orientation with high population of spots indicates the preferred orientation of the film that is texture. For the as-deposited samples [Fig. 5(a)], the spots indicating the plane-normal direction of the film are dispersed over the inverse pole figure, but majority of the spots are found around the [001] direction. The as-prepared samples have a weak preferred orientation of (001). Upon annealing, the more spots gather around [001], the less spots gather around the periphery between [110] and [100] directions. This agrees well with the XRD patterns already shown in Fig. 4(c) where only major (003) peaks still exist after annealing at 270 °C for 10 h. On the other hand, viewing the distribution of the in-plane direction of the films (Fig. 6), the spots from the as-grown samples [Fig. 6(a)] are uniformly distributed in the inverse pole figure, meaning the random distribution of in-plane directions of Bi films. More spots move to the periphery of the triangle between [110] and [100] upon annealing, and finally most of the spots exist around the periphery. From the observation, it is believed that the fine grains tend to align to the preferred orientation of (001) in a perpendicular direction and to randomly distribute in a parallel direction to the film surface. In combination with the active grain growth, very fine grains of 0.1 μm in the as-sputtered samples grow to form coarse grains as well as change their orientations to the preferred orientation during annealing.

By the way, we failed to obtain single crystalline Bi, which is in contrast to the result that single crystalline Bi can be achieved from electroplated polycrystalline Bi through annealing at 270 °C for 10 h.[2,5] The failure to obtain single-crystal films in the work is mainly attributed to the fact that the film thickness we prepared is quite thin compared to that of Chien *et al.*[5] The grain size remarkably increases during the early stage of growth and it gradually stabilizes to 1 μm at 270 °C for 10 h. Further annealing for 15 h does not increase the grain size anymore. The grain growth is largely confined in two dimensions (2D) in the thin film when the grain size is comparable to the film thickness.[17,18] Since the 1-μm grain size is almost equivalent to the film thickness, the grain shapes round after substantial annealing. By the time the grain size reaches 1 μm, no driving force acts on the grain growth because the major driving force for grain growth decreases in boundary area per unit volume.

C. Magnetoresistance

Figure 7 shows the MR of the 7-μm-thick Bi thin films measured at (a) 4 K and (b) 300 K, before and after annealing at 270 °C for 10 h. For low-temperature measurement, no MR change can be found in the unannealed Bi films in spite of applying a high external magnetic field of 9 T. On the contrary, a very high MR ratio of 30,000% was recorded for the annealed ones. The low-temperature measurement yields an obvious difference in the MR ratio between as-sputtered and annealed samples. By contrast, the room-temperature measurement does not yield such a big difference in MR for both samples. The as-grown samples still have a very low MR ratio of 1–2% and the annealed ones shows just 600% MR which is 1/60 as low as that of the low-temperature measurement. The MR of the as-sputtered samples has nothing to do with the measurement temperature, while that of the annealed ones largely depends on the temperature. The large dependence of MR on measured temperature (600% at room temperature and 30,000% at low temperature) found in the annealed samples is probably due to the phonon scattering of carriers.[5,10] The phonon scatter-

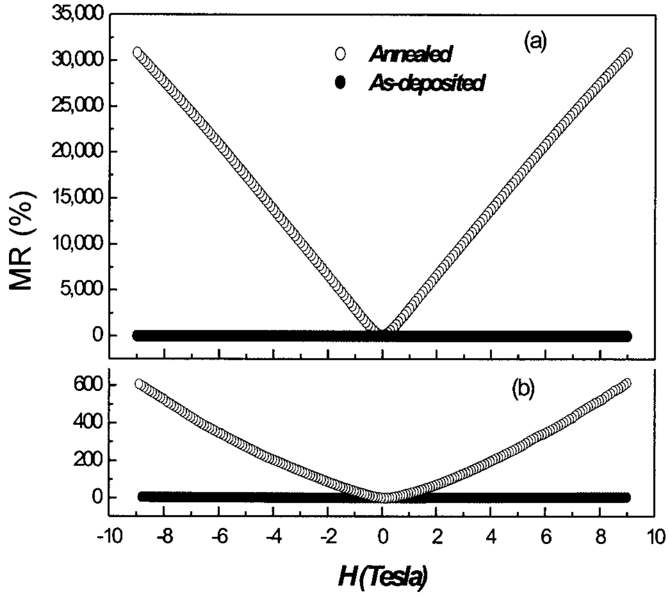

FIG. 7. Variation of magnetoresistance ($\Delta R/R$) against magnetic fields for 7-μm-thick Bi films measured at (a) 4 K and (b) 300 K.

ing should be dominated at room temperature by which relatively low MR was observed in both samples.

Although high MR of 30,000% was observed in the 7-μm-thick Bi films measured at low temperatures, such thickness is not allowed for the fabrication of a microscale device. Considering photolithography followed by lift-off or dry etching process for device fabrication, it would be better to make Bi film as thin as 1 μm as possible. The MR measurement was also carried out on the 1-μm-thick Bi films.

Figure 8 shows the MR of 1-μm-thick-Bi thin films after annealing at 270 °C for 10 h. Both MR values measured at 5 and 300 K from thin Bi films appear noticeably low compared with those from 7-μm-thick films. Only the MR effect of 920% was found at low temperature and that of 330% was found at room temperature. The maximum MR of 920% was achieved even after annealing at 270 °C for 10 h which is the same annealing condition producing 30,000% MR for 7-μm-thick Bi films. The low-temperature MR of 1-μm-thick films is much smaller ($\sim 1/32$) than that of the

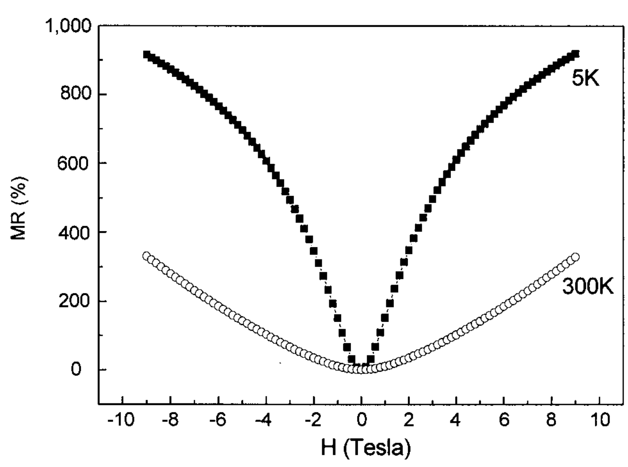

FIG. 8. Variation of magnetoresistance ($\Delta R/R$) against magnetic fields for 1-μm-thick annealed Bi films measured at (a) 4 K and (b) 300 K.

7 μm, but the high-temperature MR of the thin one is only half of the thick one. Compared with MR in Figs. 7 and 8, we believe that the MR of Bi films strongly depends on the film thickness, called thickness effect.[6]

The MR effect is the so-called ordinary MR caused by the curving of the carrier trajectories in a magnetic field. Since the MR is directly proportional to the carrier mean free path and inversely proportional to the effective mass, both unique properties of Bi (small effective mass m^* and long carrier mean free path l) are expected to lead comparable high MR in Bi. Bi is also characterized by highly anisotropic Fermi surface which exhibits different MR behaviors depending on the relative direction of the applied magnetic field with respect to the crystal orientations.[19] The magnetic field applied along the trigonal axis [001] (perpendicular) causes the largest MR over transverse and longitudinal MR, indicating that the texture developed during annealing also affects MR.

In this work, we should consider the grain size effect on MR because the sputtered Bi films show an extremely small grain size of 0.1 μm. Such small grains are common for polycrystalline metal films prepared by conventional deposition techniques but are unacceptable for achieving a large MR in Bi because the small grains result in a small mean free path.

In the case of polycrystalline Bi thin films, conductivity depends sensitively on the grain size and the crystal structure. The smaller the grain size is, the lower the conductivity is, owing to the electron scattering in the grain boundary. A lot of grain-boundary scattering that resulted from fine grain size obviously decreases MR as well as increases the resistivity. As already shown in Figs. 1–3, annealing produces coarse grains that are ten times larger than that of as-sputtered films and accommodates a preferred orientation of trigonal axis. Large grains eventually suppress the possibility of boundary scattering, and a strong texture structure along the [001] axis increases the trigonal-axis carrier mobility (decreases anisotropy scattering). This is one of the reasons that annealed samples display relatively large MR. It is well supported by the fact that a very low MR is found in as-sputtered samples with very fine grains less texture structure.

Another interesting thing is the thickness effect of the films on MR which is clearly demonstrated by comparing both MR values of 1- and 7-μm-thick films. The effective carrier mean free path of the single-crystal films determined for Bi thin films with 1–20-μm thickness was comparable to, and usually slightly less than, the film thickness.[8] This indicates that the intrinsic carrier mean free path in the Bi films is longer than the thickness of the film and is limited by the film thickness. It is actually expected that Bi has an enormous carrier mean free path of tens of microns which is most favorable in utilizing Bi as a transport medium for spin injection devices.

IV. SUMMARY

In conclusion, we have successfully fabricated polycrystalline Bi films using the sputter and demonstrated that the grain size and orientation of polycrystalline Bi thin films can be manipulated through postannealing. Careful annealing at 270 °C results not only in a grain growth up to 1.1 μm but also in the [001] preferred orientation structure of Bi. The grain size increases exponentially with annealing time at a temperature range of 266–270 °C. The grain-growth exponent (n) and the activation energy (Q) were evaluated to be 0.32 ± 0.05 and 70.7 kJ/mol, respectively. The magnetoresistance of Bi films is strongly dependent on the microstructure and thickness of the film, and on the measured temperature. A very high MR of 30,000% can be achieved in 7-μm-thick Bi films annealed at 270 °C for 10 h when measured at low temperature (4 K). The drastic increase in MR after annealing is largely caused by the trigonal-axis-oriented texture diminishing anisotropy scattering as well as by the significant grain-growth decreasing and grain-boundary scattering of carriers. The measured temperature and film thickness on which the phonon scattering relies are also important factors in determining the magnetoresistance of sputtered Bi films.

ACKNOWLEDGMENT

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