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Magnetoresistance in Post-annealed Bi Thin Films on PbTe-buffered CdTe(111)B and on Mica Substrates

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We have observed a large increase in the magnetoresistance (MR) of Bi thin films, which were subjected to a post-annealing procedure at 268°C, 3°C below the Bi melting point. We have achieved an increase in the MR by 260-fold and 1200-fold at 5 K and 5 T after post-annealing, as compared with 190 and 620 for an as-deposited Bi film on PbTe/CdTe(111) and on mica, respectively. The large MR increase by post-annealing might be due to the improvement of crystallinity according to the x-ray analysis. However, post-annealing over a certain amount time showed the reduction in MR values.

Keywords : Bismuth film, Magneto-resistance, Post-annealing

I. Introduction

Recently, there have been several reports on Bi films with large magnetoresistance (MR) relative to those reported for GMR and CMR materials [1-3], which may have applications involving field and current sensing. A bulk Bi single crystal exhibits a huge MR of R(B)/R(0) $\approx 10^6$ at 4.2 K in a magnetic field of 5 T [4]. The large MR of Bi arises from its peculiar electronic structure. Bi is a group V semimetal with a rhombohedral A7 crystal structure. It has a small energy overlap (~38 meV) between the L conduction and T hole bands, small effective masses (at the band edge, $m_e = 0.002\ m_0$), and high carrier mobilities, good for electronic transport devices. Because of these properties, Bi has frequently been used for quantum confinement studies in quantum well and quantum wire geometries [5,6].

There have been several earlier efforts using conventional techniques to grow high-quality Bi thin films. However, the MR values obtained for Bi films, even those grown by molecular beam epitaxy (MBE), were limited [7]. Recently, a large magnetoresistance ratio, 1530 and 2560, at 5 T and 5 K was reported for 10 μm films prepared by electrodeposition and MBE, respectively [2,3]. This large magnetoresistance at low temperature is understood to be due to the curving of the carrier trajectories in a magnetic field by the Lorentz force. This so-called "ordinary" magnetoresistance is related to the quantity $\omega_c\tau$ ($= (eB/m^*c)\tau$), where ω_c is cyclotron frequency and τ is the relaxation time. In bismuth, ω_c is large because of the small effective masses of the electrons. For this reason, bismuth has a large magnetoresistance.

Annealing at a slightly lower temperature than the melting point may cause the inter-diffusion of the atomic species between the film and the substrate. Here we report influence of substrate and buffer layer as well

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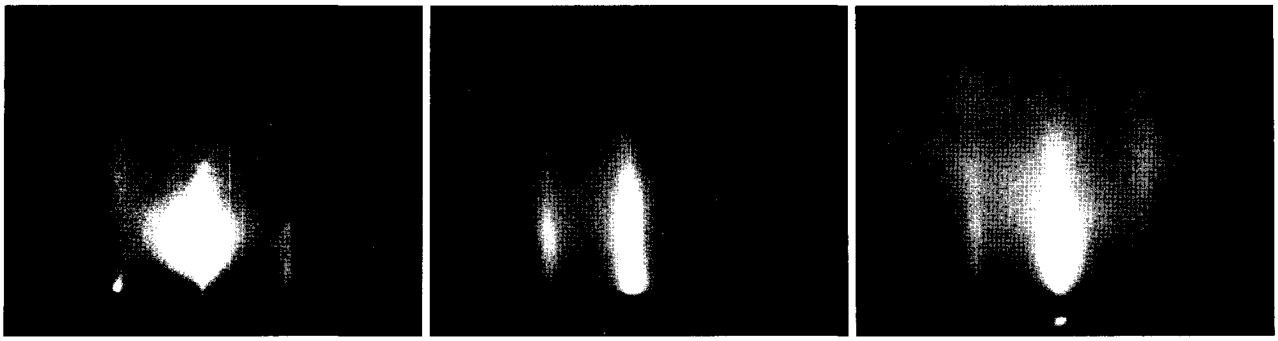

(a) (b) (c)

Fig. 1. RHEED pattern of (a) 200 Å PbTe buffer layer on CdTe(111)B, (b) 200 Å Bi layer on PbTe/CdTe(111)B, and (c) 2000 Å Bi layer on PbTe/CdTe(111)B along CdTe(1$\bar{1}$1) azimuth.

as the annealing time on the MR of MBE-grown Bi thin films on mica and CdTe with PbTe buffer later, which were subjected to a post-annealing procedure at 3° below the Bi melting point.

II. Bi Films on PbTe/CdTe

In order to investigate the influence of a buffer layer on the properties of Bi films which were subsequently annealed, 200 PbTe buffer layers were grown at a rate of 0.15 /s on CdTe(111)B using a custom built MBE similar in design to a Varian model 360 [8], followed by the growth of 10 µm of Bi at a rate of 0.95 /s, which was determined with a calibrated quartz thickness monitor. The in-plane lattice mismatch between PbTe (a = 4.58) and CdTe(111) (a = 4.58) is less than 0.1 %, and that between Bi (a = 4.546) and PbTe is ~ 0.7 %, respectively. The growth temperature for both the PbTe buffer layers and the Bi films was 170 °C. Bi and PbTe were evaporated from a high purity pyrolytic boron nitride crucible heated to 800 °C and 675 °C, respectively. After the deposition, we annealed the samples at 268 °C, 3 degrees below the Bi melting point of 271 °C, for 1, 4, and 12 hours under a 1 bar Ar atmosphere.

During the deposition of the PbTe buffer layer and the Bi film, reflection high-energy electron diffraction (RHEED) was used to examine the specific surface reconstruction of the deposited layers, growth mode, and the quality of the layers. PbTe layers on CdTe(111)B showed streaky RHEED patterns with Kikuchi lines and no surface reconstruction as shown in Fig. 1(a) The Bi films on the PbTe/CdTe(111) showed streaky RHEED patterns with Kikuchi lines and no reconstruction as shown in Fig. 1 (b) and (c), [8] attesting to high crystal quality with a layer-by-layer growth mode. This was confirmed by x-ray diffraction (XRD) patterns with an x-ray rocking curve (ω-scan) full width at half maximum (FWHM) at Bi(00.3) of 0.06°, near the resolution limit of our diffractometer.

Fig. 2 shows a θ-2θ XRD pattern of an as-deposited sample. In the θ-2θ scan, only $(00.l)$ peaks of Bi are seen, which implies that the 10 µm Bi films grow with the trigonal axis normal to the PbTe/CdTe(111). After the annealing, the XRD θ-2θ scan and rocking curves do not change significantly. For the 1 hour annealed sample, the measured rocking curve FWHM at Bi (00.3) was 0.07°, almost the same to that of the as-deposited sample, considering the resolution limit of the diffractometer. XRD measurement shows that the difference in the quality between as-deposited and annealed samples is very small in the average sense.

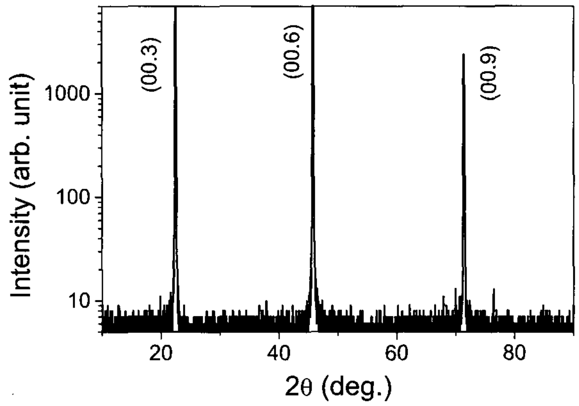

Fig. 2. XRD θ-2θ scan of a 10 μm as-deposited Bi film on PbTe/CdTe(111)B. The inset is a rocking curve (ω-scan) at the Bi(00.3) pole of the film.

The surface morphology with respect to the annealing time was examined using an atomic force microscope (AFM) manufactured by Nanosurf (Easyscan 2). Fig. 3 (a), (b) and (c) are the surface images of an as-deposited, a 4 hour annealed and a 12 hour annealed Bi films, respectively. The image sizes of the samples are 46.4 × 46.4 μm^2 for the as-deposited film, 43.2 × 43.2 μm^2 for the 4 hour annealed film, and 59.8 × 59.8 μm^2 for the 12 hour annealed film, respectively. As seen in the fig., as the annealing time increases, the Bi grains become more and more to look like an equilateral triangle. During the annealing process, Bi atoms look to diffuse across the surface and re-align with higher nucleation rate to make triangular shape Bi crystallites whose planes are normal to the trigonal axis of the rhombohedral Bi, which is reported by earlier researchers [7,9,10]. The root mean square average roughnesses for the three samples are 10 nm, 9.7 nm, and 15 nm, respectively.

The magnetoresistance (MR) of the samples were measured at both 5 K and 300 K using a Quantum Design magnetometer (MPMS). The conventional four-probe method was used to measure the perpendicular MR (with a magnetic field along the film normal direction) of as-deposited and annealed 10 μm Bi films in magnetic fields up to 5 T. As shown in Fig. 4 (a), the MR ratio $(R_B/R_0(=R(B)-R(B=0)))$ measured at 5 K showed a quadratic behavior at very low field, changing to a quasi-linear behavior which holds up to 5 T. The MR ratio for the as-deposited sample was 190. For the 1 hour annealed sample, the ratio increased to 260 at 5 K and 5 T, which is small increase compared with the 6 hour annealed Bi on CdTe case of 2560 [3]. After that point, as the annealing time increased, the MR ratio decreased. The MR ratios at 5 K for a 4 hour annealed and a 12 hour annealed samples were 105 and 55, respectively. The decrease in MR ratio when

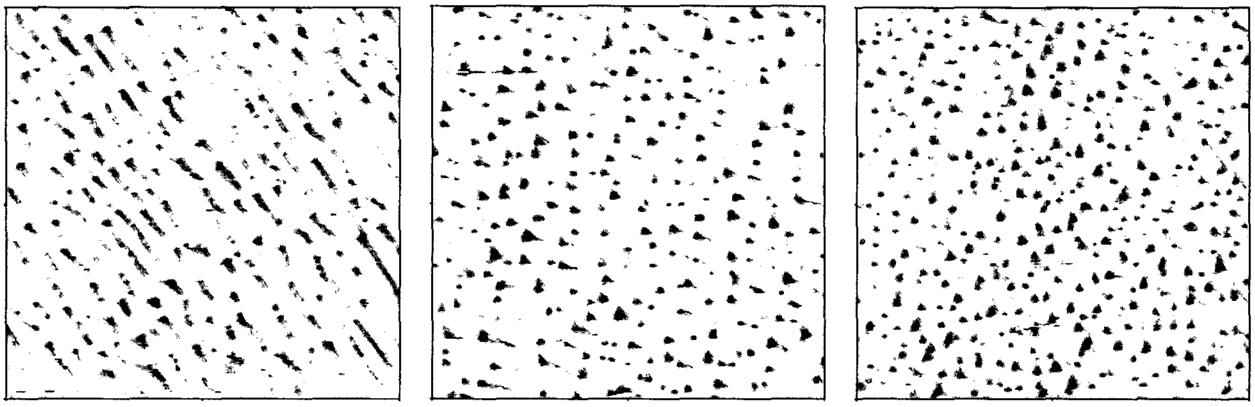
(a) (b) (c)

Fig. 3. AFM images of (a) an as-deposited Bi film, (b) a 268 ℃ 4 hour annealed Bi film, and (c) a 12 hour annealed Bi film. The image sizes are 46.4 × 46.4 μm^2 for (a), 43.2 × 43.2 μm^2 for (b), and 59.8 × 59.8 μm^2 for (c). respectively.

more annealing time is applied may be caused by atomic diffusion from the buffer or the substrate to the Bi film which mainly contributes the carrier conduction. As the annealing proceeds, the crystallinity of the sample may be improved, but after it reaches a certain point, the diffusion from the buffer or the substrate overcomes any further improvement from annealing and eventually degrades the electrical properties of the sample. Though PbTe has a perfect lattice match with CdTe and Bi, it looks not good enough as a buffer layer between CdTe and Bi because it may react with Bi or it cannot prevent the atomic diffusion from CdTe to Bi. The increase in MR ratio at 300 K was small compared to the 5 K case. Field dependent MR ratio curves at 300 K with respect to the annealing time were relatively similar regardless of the annealing time as shown in Fig. 4 (b) Zero field resistance ratios at 5 K normalized with the values at 300 K for the four samples were also very similar with one another, with the values 0.44, 0.45, 0.42, and 0.46, respectively.

III. Bi on Mica Substrate

Mica has been used to grow Bi films for a long time [11]. It is well known that Bi films grow epitaxially on mica with the film normal to the trigonal axis [9,11]. In this experiment, commercially cleaved mica substrates were used. MBE was used to grow 10 μm thick Bi films. The growth temperature was 130-200 °C, and the growth rate was 0.95 Å. After the deposition, we annealed the sample at 268 °C for 1, 4, 8, 16 hours in Ar.

XRD studies were performed on an as-deposited and a 1 hour annealed film samples. In a θ-2θ scan of a film deposited at 170 °C, the (01.2) peak and its harmonics as well as the (00.l) peaks are seen, as shown in Fig. 5 (a), implying that both (00.1) oriented and (01.2) oriented Bi grains have grown on the mica substrate. After one hour of annealing at 268 °C, the XRD pattern changes significantly as shown in Fig. 5 (b) The intensity of the (00.l) peaks increased and that of the (01.2) peaks decreased. The rocking curve for the (01.2) peak became broader for the annealed sample (FWHM: from 0.15° for the as-deposited to 0.20° for the annealed sample), while the curve for the (00.3) peak changed from broad to sharp (FWHM: from 0.38° to 0.18°). Note that the edge of mica substrate is not clean and the substrate is easy to be bent, so that

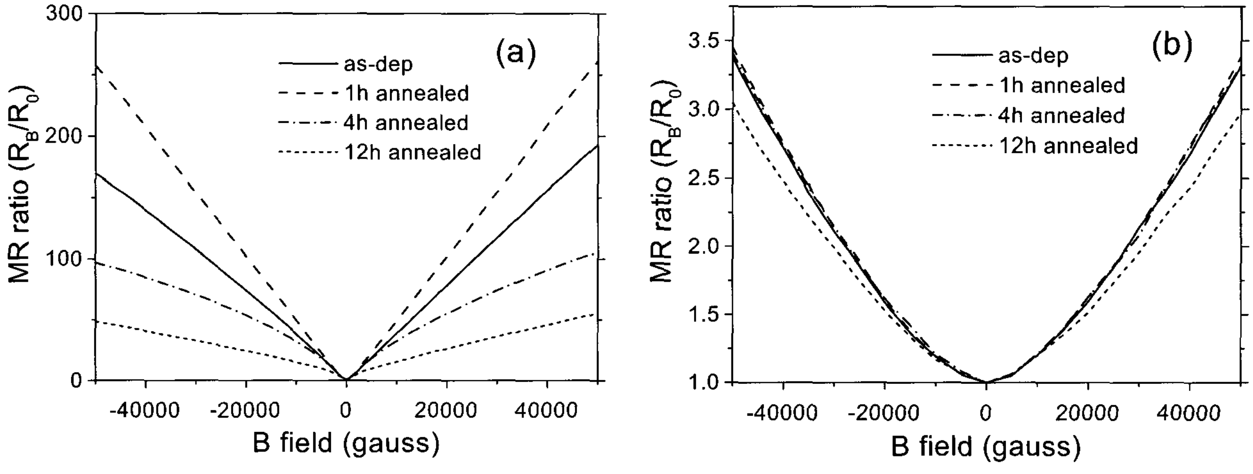

Fig. 4. (a) Perpendicular MR (with a magnetic field along the film normal direction) at 5 K of an as-deposited (solid line), a 1 hour annealed (dash line), a 4 hour annealed (dash-dot line), and a 12 hour annealed (dot line) Bi film. (b) Perpendicular MR at 300 K.

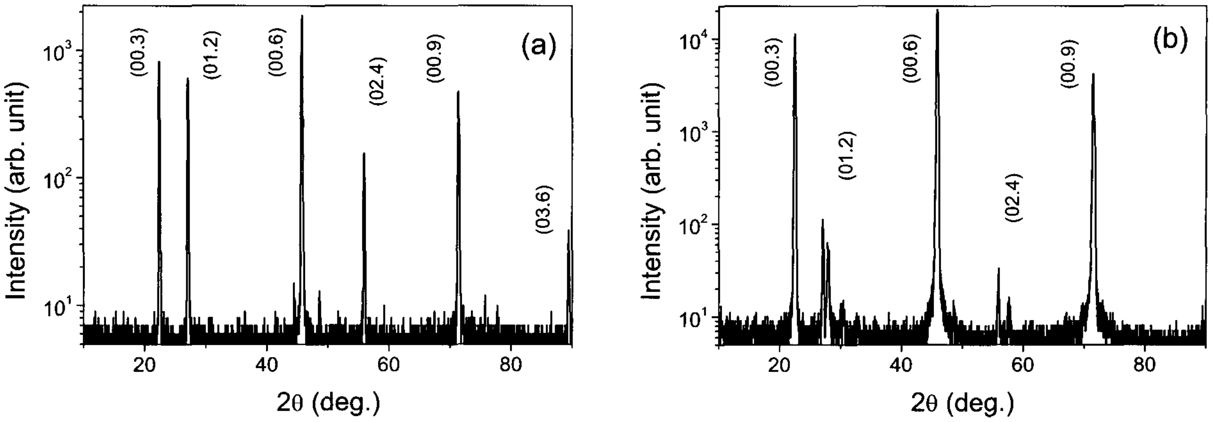

Fig. 5. XRD θ-2θ scans of a 10 μm Bi film on mica (a) as-deposited and (b) after 268℃ 1 hour annealing, in the logarithmic scale.

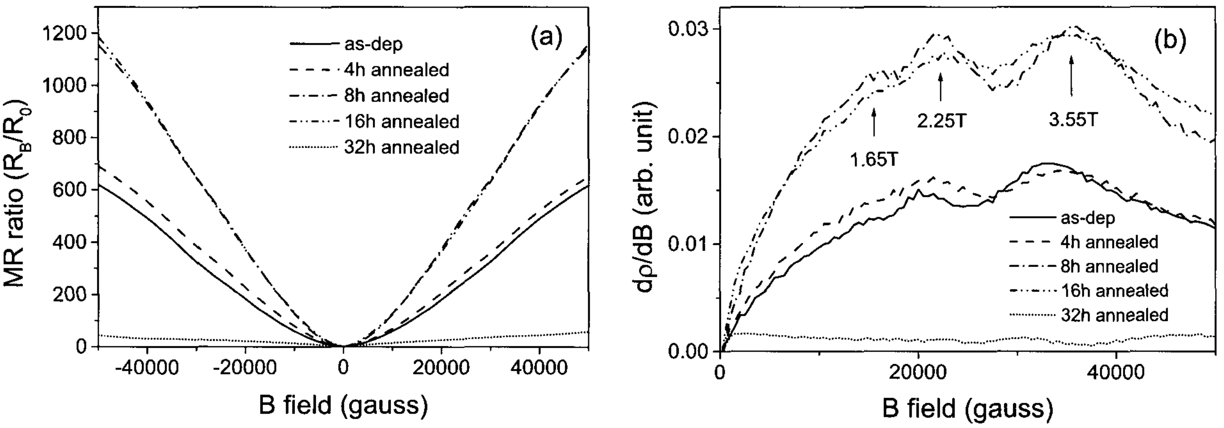

Fig. 6. (a) Perpendicular MR at 5 K of an as-deposited (solid line), a 4 hour annealed (dash line), a 8 hour annealed (dash-dot line), 16 hour annealed (dash-dot-dot line), and a 32 hour annealed (dot line) Bi film. (b) SdH oscillation for a magnetic field applied perpendicular to the film plane at 5 K. The arrows indicate the peak positions of the oscillations.

the FWHMs were not accurately determined. However, the trend that the intensity of the (00.*l*) peaks gets larger with the annealing time is clear.

The magnetoresistance of 10 μm thick Bi films on mica measured at 5 K is shown in Fig. 6 (a) MR increase with magnetic field at 300 K was small and similar for all the measured samples with the values at 5 T of 3.2-3.6. An as-deposited film showed an increase in MR ratio, 619 at 5 K and 5 T. 1, 4, 8, 16, 32 hour annealed films showed an increase, 622, 650, 1150, 1200, and 60, respectively. The MR ratio increases with annealing time upto 16 hours, then decreases, which probably is explained same as in the Bi on PbTe/CdTe case. Some atomic diffusion from mica degraded the Bi film even though the annealing process improved the crystallinity of the sample. Considering that the intensity of the XRD (01.2) peak decreases and the (00.3) peak increases with the annealing time as shown in fig. 5 (a) and (b), the increase in MR may also be contributed in part by the increase of the portion of the Bi grains with their trigonal axes normal to the substrate surface with the annealing time. For the 8 or the 16 hour annealed Bi film, even for the as-deposited or the 1 hour annealed sample, as shown in Fig. 6 (b), Shubnikov-de Hass (SdH) oscillations were apparent, indicating that the film is of high quality. The oscillation positions are determined to be at 1.65, 2.25 and 3.55 T, with the period of $\Delta(H^{-1})\sim0.16\ T^{-1}$, which are in agreement with the previous reports [1,3,12]. Zero field resistances at 5 K normalized with the values at 300 K for the as-deposited, 1, 4, 8, 16, and 32 hour annealed samples were 0.56, 0.52, 0.62, 0.44, 0.42 and 1.13, respectively. Note that, in metal sample, the decrease in resistance with temperature is expected. However, in the 32 hour annealed sample, the resistance increased probably due to the diffusion from the substrate.

In summary, post-annealing of 10 μm thick Bi films on mica makes a large increase in magnetoresistance ratio to 1200 at 5 K and 5 T for a 16 hour annealed sample. The larger MR values for the Bi film on mica than those on PbTe/CdTe might be caused by the difference between mica and PbTe/CdTe in the reactiveness with Bi, which leaves mica as a better substrate candidate than PbTe or CdTe.

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PbTe / CdTe(111)B와 마이카 기판 위에 성장된 Bi 박막의 후열처리 전후의 자기저항

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비스무스의 녹는점보다 3도 낮은 온도인 268℃ 에서 후열처리를 하여 비스무스 박막에서 자기저항의 큰 증가를 관측하였다. 레드텔러라이드/케드뮴텔러라이드 기판 위에서는 온도 5 K, 자기장 5 T 하에서 190에서 260으로, 마이카 기판 위에서는 620에서 120으로 자기저항의 큰 증가를 나타내었다. 이러한 자기저항의 큰 증가는, 열처리에 따른 결정도의 향상에 기인한 것으로 보인다. 하지만 일정 시간 이상의 오랜 시간의 열처리는 자기저항을 감소시키는 것으로 관측되었다.

주제어 : 비스무스 박막, 자기저항, 후열처리

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