# Large magnetoresistance of bismuth/gold films thermally deposited onto glass substrates

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Bismuth thin films deposited onto glass substrates by thermal sublimation are polycrystalline with short mean free paths, multiple grain orientations, and disappointingly small magnetoresistance when compared to single crystals. Direct deposition onto thin gold buffer layers followed by a post-deposition anneal leads to significantly improved properties, namely, large grains oriented in the trigonal direction and a 5-T magnetoresistance higher than 250% at room temperature. For a $Bi_{0.93}Au_{0.07}$ stoichiometry, we show that optimal results are obtained when the annealing temperature is above the BiAu eutectic point (241 °C) and below the melting temperature (271 °C) of bismuth, thus indicating a mechanism in which the presence of gold in the bismuth facilitates grain-boundary motion and grain growth. 
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Elemental bismuth is a semimetal with unusual properties, namely, a carrier density lower than that of normal metals by a factor of approximately $10^5$, small effective carrier masses, a long carrier mean free path, and an anisotropic Fermi surface. It is well known that bulk single crystals of bismuth exhibit a large magnetoresistance (MR) effect[1–3] and the recognition of this fact has stimulated a number of recent efforts[4–6] to grow thin films of bismuth having high magnetoresistance. Such films would be useful in magnetic sensing applications. Unfortunately, vapor deposition techniques, such as thermal sublimation and sputtering, are well-documented to give polycrystalline films having small grains and, accordingly, a significantly reduced MR.[7,8]

A judicious combination of lattice-matched substrates and carefully regulated post-deposition thermal annealing provides a strategy for growing Bi films with large grains. In early work on Bi films thermally deposited onto mica substrates,[7] it was found that post-deposition annealing close to the Bi melting temperature caused the helium temperature resistance to decrease by a factor of 15 when compared to unannealed films. In addition, the MR for fields perpendicular to the film surface (parallel to the trigonal axis) significantly improved with annealing, whereas very little improvement was noted when the field was oriented parallel to the film surface.[7] In the former case, the cyclotron orbits are in the plane of the film and are thus most sensitive to the size of the crystallites, which increases, as does the corresponding MR, with annealing. Epitaxial films of bismuth having a trigonal orientation have been grown on $BaF_2(111)$ (3.6% lattice mismatch)[9] and CdTe(111) (0.7% lattice mismatch).[6] In the latter case, post-deposition anneals at 3 °C below the melting temperature of Bi lead to significant increases in the MR, a result attributed to grain growth and associated enhancement of the carrier (electron and hole) mobilities.[6]

An alternative approach, which has been found to give large MR in Bi films 1–20-$\mu$m thick, is the technique of electrodeposition from aqueous solutions of $Bi(NO_3)_3 \cdot 5H_2O$.[4,5] An underlying Au layer, patterned onto a silicon substrate, serves as the working electrode for the electrodeposition. As is the case for vacuum-deposited Bi films,[6,7] post-deposition annealing of the electrodeposited films close to the melting temperature of Bi leads to a smaller resistivity $\rho$ and a large increase in the MR, equal to $[\rho(B)\text{-}\rho(0)]/\rho(0)$, with MR=2.5 at room temperature and MR=3800 at 5 K for the thickest 20-$\mu$m-thick film in a perpendicular magnetic field $B = 5$ T.[4] For technological applications, electrodeposition is economical and well suited for large-scale production. Similar advantages would likewise hold for thermal deposition, provided ultrahigh vacuums and specialized growth techniques, such as molecular-beam epitaxy, are not required.

In this letter, we report on the large MR of Bi/Au films vacuum deposited onto glass substrates and then subjected to a thermal anneal close to the melting temperature of bismuth. We find that, upon annealing, the Au from the Au underlayer rapidly diffuses into the bismuth, giving rise to a film with large single-crystal grains oriented with trigonal axis perpendicular to the plane of the film (cf., Fig. 1) and having magnetotransport properties comparable to electrodeposited films.[4,5] We show that improvements of the MR are obtained only for annealing temperatures higher than the 241 °C eutectic temperature of the BiAu solid solution and below the 271 °C melting temperature of Bi. This 30 °C annealing window provides considerable latitude when compared to the narrow annealing window of a few °C confirmed here and reported previously for pure Bi films.[7]

All of our samples are grown by thermal evaporation of 99.999% pure Bi at $5\times10^{-7}$ Torr base pressure through shadow masks onto pre-cleaned glass substrates. Three categories of samples are prepared: (I) two pure bismuth films (1 $\mu$m thick) grown at 150 °C, followed by separate anneals at 265 and 270 °C for 6 h; (II) three different bismuth films (1 $\mu$m thick) grown simultaneously on pre-deposited 360-Å-thick gold films at 150 °C, followed by separate anneals at 238, 243, and 251 °C, respectively for 6 h, and (III) two

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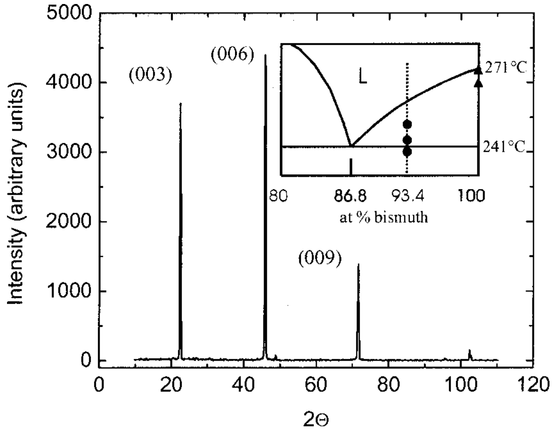


FIG. 1. X-ray diffraction pattern for a 4-$\mu$m-thick Bi/Au film grown at 150 °C and annealed at 251 °C, showing a pronounced single-crystal orientation with trigonal axis oriented perpendicular to the film plane. The inset shows the relevant portion of the Bi/Au phase diagram and the corresponding annealing temperatures for the Bi (solid triangles) and Bi/Au (solid circles) films discussed in this letter.

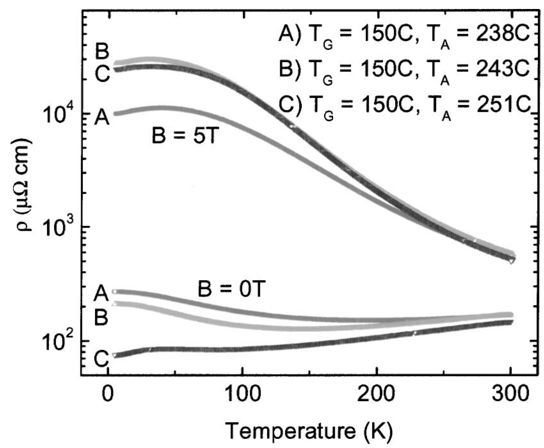


FIG. 3. Temperature dependence of the resistivity at 0 and 5 T for three category-II films grown simultaneously on a 150 °C substrate and then annealed separately at the respective temperatures of 238, 243, and 251 °C, indicated by the solid circles in the Fig. 1 inset.

bismuth films (1 $\mu$m thick) grown separately on 360-Å-thick pre-deposited gold films at room temperature and 150 °C, followed by a simultaneous anneal at 251 °C for 6 h. Annealing is performed in a quartz vacuum tube furnace with temperature calibrated with respect to the observed melting of a small bismuth crystal placed in close proximity to the samples. Magnetotransport measurements are carried out with the magnetic field applied perpendicular to the film.

The inset of Fig. 1 shows a schematic of the relevant portion of the Bi(Au) phase diagram.[10] A small amount of gold in bismuth reduces the melting point, and the lowest melting temperature, the eutectic temperature, occurs at 241 °C for the $Bi_{.868}Au_{.132}$ composition. In our experiment, the percentage of gold in the samples is controlled by the thickness of the gold and bismuth layers. Thus a pre-deposited 360-Å-thick layer of Au mixed by annealing into a 1-$\mu$m-thick overlayer of Bi represents a solid solution (vertical dashed line) with stoichiometry $Bi_{0.93}Au_{0.07}$. All of the Bi/Au films reported here are at this composition.

Figure 2 shows the resistivity versus temperature at 0 and 5 T for two category-I pure Bi films (no Au underlayer)

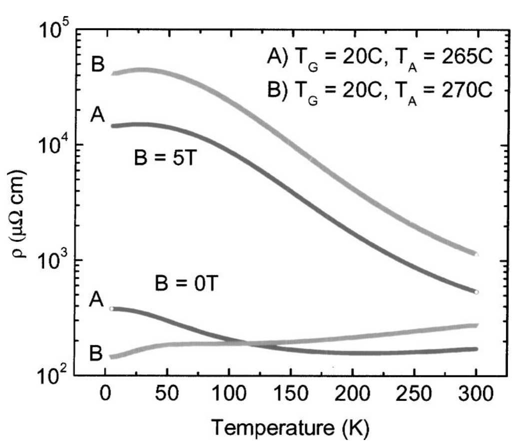


FIG. 2. Temperature dependence of the resistivity at 0 and 5 T for two category-I pure Bi films (no Au underlayer) annealed for 6 h at 265 and 270 °C, indicated by the solid triangles in the Fig. 1 inset. The magnetic field is oriented perpendicular to the film surface.

annealed at 265 and 270 °C, respectively. We note that a small difference of annealing temperature at close to the 271 °C melting point of bismuth produces a drastic change of the properties of the films. The film annealed at 270 °C just starts to melt and is recrystallized during the slow cooldown. As observed through the quartz tube, the film develops a shiny surface just below the melting temperature, but at higher temperatures begins to fully melt and ball up. The positive slope in the resistance–temperature curve in zero magnetic field indicates that the film is metallic. Also, at 5 T, the MR=286 at 5 K indicates the good quality of this film. In contrast, the film annealed at 265 °C does not change its appearance during the annealing process. The unannealed film also shows a characteristic minimum[7] near 200 K and then an increase in resistance as the temperature is further lowered. In addition, the MR of this film is much smaller than the one annealed at 270 °C throughout the whole temperature range. These results are in accord with previous studies,[6,7] which have shown that post-annealing near the melting point followed by recrystallization is an effective way to get high-quality metallic bismuth films. However, the temperature control must be accurate to a few °C and must not be allowed to go above the melting point where there will be a loss of film adhesion leading to agglomeration and discontinuity between grains.

As shown in Fig. 3 for the temperature dependent resistivity of the category-II films, the presence of a gold underlayer leads to completely different behavior. The three films are grown simultaneously on a 150 °C substrate and then annealed separately at the respective temperatures of 238, 243, and 251 °C, indicated by the solid circles in the Fig. 1 inset. Prior to each post-deposition anneal, a gold color can be observed from the backside of each glass substrate. After anneal, the gold color is gone and the underside of each Bi/Au film is silver colored and indistinguishable from the underside of a pure Bi film. These color changes indicate that during annealing, the gold atoms no longer remain segregated beneath the bismuth film but diffuse into the bismuth. For an annealing temperature of 238 °C, which is below the eutectic temperature of 241 °C, all of the film remains in the solid form, and the surface texture of the film does not

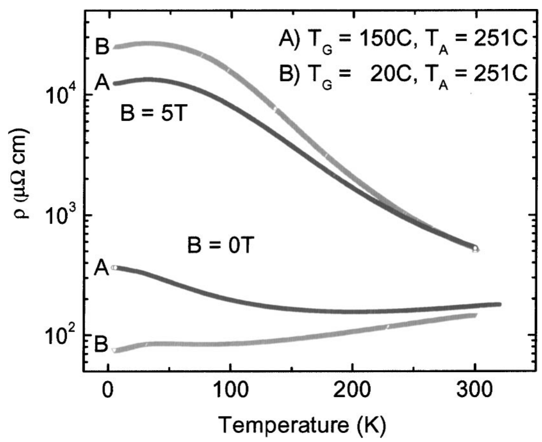


FIG. 4. Temperature dependence of the resistivity at 0 and 5 T for two category-III films showing the beneficial effect of growth temperature (150 °C) on transport properties for the same anneal (251 °C) conditions.

change during the anneal. In addition, the temperature dependent resistance is nonmetallic and the 5 K MR is low (MR=37). In contrast, for the two anneals above the eutectic temperature, the films undergo a definite change in appearance in which they become shiny and remain metallic after cooldown, the temperature-dependent resistance becomes progressively more metallic, and both films exhibit significantly larger MR. MR(5 K)=130 for the 243 °C anneal and MR(5 K)=327 for the 251 °C anneal. We note that the MR of our 251 °C annealed Bi/Au film is higher than the MR(5 K)=250 of a comparable 1-$\mu$m-thick "single-crystal" film grown by electrodeposition.[4,5] Further increase of the annealing temperature to slightly above 260 °C but well below the 271 °C Bi melting temperature leads to severe melting and loss of electrical connectivity, as would be expected from the intersection of the vertical dashed line with the solid/liquid phase boundary shown in the Fig. 1. inset.

The plots in Fig. 4 for the category-III films show the effect of growth temperature on transport properties for the same anneal conditions. The film grown at 150 °C shows metallic behavior at zero field and has MR(5 K)=327. The film grown at room temperature, however, shows nonmetallic temperature dependence similar to that of the unannealed Bi film (see Fig. 2) along with a significantly lower MR(5 K)=34. For pure Bi films grown on CdTe substrates, growth temperatures in the range of 80 to 220 °C are required to obtain epitaxial behavior.[6] For our Bi/Au films, the higher growth temperature promotes the growth of larger grains, thus facilitating the effectiveness of the annealing procedure by starting with larger grains. We also note, as shown by the x-ray diffraction pattern in Fig. 1 for a 4-$\mu$m-thick Bi/Au film grown at 150 °C and annealed at 251 °C, that the annealed films exhibit a pronounced single-crystal orientation with trigonal axis oriented perpendicular to the film plane. Similar behavior has been noted for annealed electrodeposited films.[4,5]

Optical microscopy verifies a smoother topography and larger grain size (1–10 $\mu$m) for the films annealed at high temperature and exhibiting a large MR. This result is consistent with the aforementioned conclusions that large grain size achieved either by epitaxy and/or annealing is a prerequisite for large MR. The primary factors that affect the quality of Bi/Au films are the growth temperature and the annealing temperature. A moderate growth temperature (~150 °C) encourages the formation of large grains, but should not be so high as to cause the film to agglomerate and to become discontinuous.

The effect of the diffusion of the Au into the Bi during the post-deposition annealing process can be qualitatively understood by referring to the phase diagram depicted in the Fig. 1 inset. If equilibrium is assumed, then, for the isotherm (tie line) drawn at a given annealing temperature, application of the "lever rule" for binary phase diagrams will determine a gold-rich melted phase and a bismuth-rich solid (unmelted) phase. It is the presence of this melted phase that facilitates grain boundary migration and grain growth resulting in the high MR that we have observed. We suspect that this melted phase is most likely associated with the grain boundaries although detailed microcompositional analysis would be necessary to verify such a scenario.

In oversimplified terms, the Au can be thought of as a lubricant that facilitates the growth of large grains during the post-deposition anneal. However, one should not forget that Au is an impurity that gives rise to increased carrier scattering and an associated lower MR, thereby preventing the MR from approaching the high values reported for single crystals.[2,3] Accordingly, the use of annealed Bi/Au bilayers to obtain large MR requires a judicious balance between using enough gold to assure large grain growth, but not using so much gold that the additional scattering compromises the MR. We believe that these considerations also apply to the Bi/Au films deposited by the electrodeposition technique reported previously by Yang *et al.*[4,5]

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