Magnetotransport properties of bismuth films on p-GaAs

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Poly crystalline Bi films were deposited onto p-GaAs(100) by electrochemical deposition. Annealing resulted in the formation of large grains with a preferred [012] orientation. The p-GaAs/Bi junctions were rectifying and the barrier height and ideality factor decreased with increasing film thickness. For films greater than 0.5 μm in thickness, the barrier height was about 0.56 eV and the ideality factor was between 1.1–1.2 for both as-deposited and annealed films. The resistance of the as-deposited films exhibited a negative temperature coefficient whereas the annealed films exhibited a positive temperature coefficient due to the limiting carrier mean free path. The magnetoresistance (MR) exhibited a quasilinear field dependence with an MR effect as large as 560,000% at 5 K and 2.2 (220%) at room temperature. © 2000 American Institute of Physics. [S0021-8979(00)03824-X]

I. INTRODUCTION

Bismuth is a semimetal with unusual electronic properties related to its highly anisotropic Fermi surface, small carrier effective masses, and long carrier mean free path. As a result of these properties, finite size effects are easily observed in thin films, nanowires, and lithographically patterned crystals. The carrier mean free path may be as large as 1 mm at 4.2 K, many orders of magnitude larger than for most metals, giving rise to a very large magnetoresistance effect.1–10 The magnitude of the magnetoresistance (MR) in bismuth can be much larger than the giant magnetoresistance (GMR) obtained in multilayers and granular solids, although it is strongly dependent on the microstructure. Until recently, very large MR was only obtained in bulk single crystals or thin films grown by molecular beam epitaxy. Recently we have reported on large MR effects in bismuth nanowires and thin films fabricated by electrochemical deposition. In this article, we report on the electrical and magnetotransport properties of bismuth films electrochemically deposited on p-GaAs. Annealing of the electrodeposited films resulted in a large grained [012] texture with a MR effect as large as 5600 (560,000%) at 5 K and 2.2 (220%) at room temperature for 75 μm films.

II. EXPERIMENT

Bismuth thin films were electrochemically deposited from an aqueous 10 vol % glycerol solution with 0.15 M Bi(NO3)3 + 1 M KNO3 + 0.33 M 2R,3R–(CHOHCOOH)2 (L-tartaric acid) + 0.65 M HNO3 (pH 0.1–0.2). The solutions were prepared by adding the tartaric acid and potassium nitrate to water and then adding the glycerol and nitric acid. The solution is sufficiently acidic at this point that the bismuth nitrate readily dissolves; after adding the remaining water the pH increases to 0.1–0.2. Films were deposited onto Zn doped p-type GaAs (100) (Laser Diode Inc.) wafers with an acceptor density of about 1 × 1017 cm−3. Ohmic contacts were formed on the back side of the wafers by electrodeless deposition of gold from HAuCl4 solution. Prior to deposition the GaAs wafers were first rinsed in 6 M HCl, then chemically etched in a 3:1:1 (by volume) solution of H2SO4 (96 wt %), H2O2 (30 wt %), and H2O, rinsed in 6 M HCl solution to remove the native oxide, and finally rinsed in 1 M KNO3 + 0.33 M 2R,3R–(CHOHCOOH)2 (L-tartaric acid) + 0.65 M HNO3. The deposition was performed in a three electrode cell with a platinum current collector and a Ag/AgCl reference electrode [3 M NaCl, Ueq = 0.21 V (SHE)]. All potentials are given with respect to the Ag/AgCl reference. All experiments were performed at room temperature (297 K) and in the dark unless otherwise stated.

After deposition the films were rinsed in 1 M HCl and distilled water. Annealing was performed in an argon atmosphere by slowly heating up to 267 °C (at 1 °C/min from room temperature to 225 °C and at 0.2 °C/min from 225 to 267 °C). The temperature was held at 267 °C for 2–12 h, depending on the film thickness.

The composition of the bismuth films was examined using Auger electron spectroscopy (AES) (Perkin-Elmer, PHI 610 Scanning Auger Microprobe). Auger depth profiling was performed at an ion beam voltage of 4 kV and with the sputter raster set to 4 by 4 mm.

Transport measurements were performed in a conventional four point probe arrangement. Copper wires were attached to four indium dots at 1–2 mm spacings on samples with lateral dimensions of 6 mm by 1.5 mm with the current in the long direction. The resistivity ρ of the films was calculated from ρ = Rd(w/sC)1/8 where d is the film thickness, w is the width of the rectangular sample, s is the spacing of the probe tips, and C a geometric correction factor (~1 in our case). The MR was measured with the magnetic field perpen-

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dicular (P) and longitudinal (L) to the current flow and to the film plane.

III. RESULTS AND DISCUSSION

A. Microstructure and composition

Bismuth films were deposited at −0.5 V onto p-GaAs wafers using photoassisted nucleation. Samples were illuminated with a white light source to give a photodeposition current of 1–10 mA cm\(^{-2}\) for 5–10 s, corresponding to the deposition of about 100 equivalent monolayers of bismuth. Subsequent growth of the films was performed in the dark to a film thickness of 50 nm to 75 nm.

The as-deposited films were silver-white and had large equiaxed grains. In all cases, the grain size was of similar magnitude to the film thickness. Figure 1 shows an AFM image of an as-deposited 2 μm thick film illustrating that the grain size is close to the film thickness. After annealing the films were metallic gray and the grain size became much larger than the film thickness.

Figure 2(a) shows an Auger depth profile for a 2 μm thick film. For the as-deposited film, the oxygen concentration is high at the surface due to the air formed oxide, but is not present in the bismuth film or the GaAs/Bi interphase region. From the bismuth depth profile and the film thickness, an etch rate of 25 nm min\(^{-1}\) is obtained. Figure 2(b) shows a depth profile for the 2 μm film after annealing. In contrast to the as-deposited films, a small oxygen signal (<1 at. %) is observed in the bismuth layer for the annealed films suggesting diffusion of oxygen down the grain boundaries during annealing. The gallium and arsenic present at the bismuth surface is contamination from the GaAs wafer during the annealing process; the gallium and arsenic peaks are shifted about 5 eV lower in kinetic energy as compared to the respective peaks in the bulk, indicating that they are present as oxides. The etch rate for the annealed bismuth film is about 14 nm min\(^{-1}\), almost two times slower than for the as-deposited films due to the large increase in grain size.

Taking into account the different etch rates for the as-deposited and annealed films, the width of the GaAs/Bi interface region is the same in both cases showing that there is no interface broadening on annealing.

Figure 3 shows typical x-ray diffraction patterns for an as-deposited and an annealed 5 μm thick Bi film. The as-deposited films exhibit the characteristic diffraction peaks for polycrystalline rhombohedral bismuth.\(^{19}\) The diffraction patterns for the annealed bismuth films exhibited strong (012) peaks along with other small peaks that varied from sample to sample. These results indicate that the as-deposited films are polycrystalline with no preferred orientation, whereas the annealed films have very large grains with a preferential [012] orientation.

Bismuth has a rhombohedral crystal structure, however, a hexagonal primitive cell is usually used to describe the bismuth lattice. Figure 4(a) shows two rhombohedral unit cells (\(a=0.474\) nm, \(\alpha=57^\circ\) 14') on the hexagonal axes. The hexagonal primitive cell (\(a=b=0.455\) nm, \(c=1.186\) nm, \(\alpha = \beta = 90^\circ\), \(\gamma = 120^\circ\)) shown in Fig. 4(b) has atoms on the corners of the parallelepiped as well as atoms at the (2/3,1/3,1/3) and (1/3,2/3,2/3) positions. The (012) plane is also shown in Fig. 4(b). Figure 4(c) shows a normal view to the (012) plane, illustrating the twofold symmetry in this plane.

B. Electrical properties of p-GaAs/Bi junctions

Typical current–voltage curves for as-deposited p-GaAs/Bi junctions with 150 nm and 10 μm thick bismuth...
films are shown in Fig. 5. All contacts showed rectifying properties characteristic for \( p \)-type semiconductor-metal Schottky junctions.\(^{20}\) In the inset of Fig. 5 the current–voltage curves (corrected for the iR drop) are replotted according to thermionic emission theory:

\[
i = i_0 \exp \left( \frac{eU}{nkT} \right) \left[ 1 - \exp \left( -\frac{eU}{nkT} \right) \right],
\]

where \( i_0 \) is the saturation current density and \( n \) is the ideality factor. For films thicker than 2 \( \mu \)m, Eq. (1) was followed over the whole potential region, whereas for films less than 2 \( \mu \)m the saturation current was significantly larger and the linear region did not extend into the reverse bias region (see inset).

The barrier heights and the ideality factors determined from the forward bias region in the current–voltage curves are shown in Fig. 6. For film thicknesses greater than 0.5 \( \mu \)m the barrier heights were about 0.56 eV and the ideality factors were between 1.0 and 1.2. For the 50 and 150 nm films, the ideality factors were considerably larger but decreased on annealing. These values are in good agreement with a barrier height of 0.58 eV and an ideality factor of 1.08 reported for evaporated \( p \)-GaAs/Bi junctions.\(^{21}\)

C. Resistivity of bismuth films

Figure 7 shows the temperature dependence of the resistance for 0.5, 1, and 7.5 \( \mu \)m thick as-deposited and annealed bismuth films. Due to the variation in spacing of the indium contacts, the resistance is plotted relative to the resistance at room temperature. The resistance of the as-deposited films
increases with decreasing temperature (negative temperature coefficient) although the magnitude of the change is dependent on the film thickness. For the 0.5 \( \mu m \) film the resistance at 5 K is almost three times larger than at room temperature whereas for the 7.5 \( \mu m \) film the resistance is almost independent of temperature. In contrast, the resistance of the annealed films decreases with decreasing temperature (positive temperature coefficient). For the 7.5 \( \mu m \) film, the resistance is about three times lower than at room temperature whereas the resistance of the 0.5 \( \mu m \) film is almost independent of temperature. Similar features have been reported for bismuth nanowires\(^4\) and bismuth films deposited on gold.\(^1\)

In general, the resistance of an ideal crystal lattice is determined by the carrier concentration and the carrier mobility. The carrier concentration increases with increasing temperature, whereas the carrier mobility decreases with increasing temperature. Hence the carrier concentration will contribute to a negative temperature coefficient, whereas the carrier mobility, or carrier mean free path, will contribute to a positive temperature coefficient.

For the as-deposited films the grain size is small in comparison with the carrier mean free path so that grain boundary scattering will suppress the influence of the carrier mobility. In this case, the resistance will be determined by the temperature dependence of the carrier concentration resulting in a predominantly negative temperature coefficient. Since the grain size is comparable to the film thickness, the effect is the largest for the thinnest films. After annealing, the mean free path is no longer limited by the grain size and the resistance is determined by the carrier mobility resulting in a positive temperature coefficient. In this case finite size effects are important since the mean free path is larger than the film thickness and hence surface scattering significantly influences the resistance.

The average room temperature resistivity is plotted versus film thickness in the inset of Fig. 7. The resistivity for the as-deposited films decreases from about 1000 \( \mu \Omega \) cm for 0.15 \( \mu m \) thick films to 120 \( \mu \Omega \) cm for thicker films, corresponding to the value for bulk bismuth. The resistivity for the annealed films exhibits more scatter but in general fluctuations around the bulk value.

D. Magnetoresistance

The MR was measured for the as-deposited and annealed films in a magnetic field \( (H) \) up to 50 kOe. Figure 8 shows typical curves for the MR effect potted as \( \frac{R(H) - R(0)}{R(0)} \) versus the applied magnetic field for a 75 \( \mu m \) Bi film at 5 and 298 K before and after annealing. In all cases, the MR shows a quasilinear field dependence. In the perpendicular
FIG. 9. Magnetoresistance at 50 kOe in longitudinal (L) and perpendicular (P) geometry, and at room temperature (298 K) and at 5 K as a function of film thickness for (a) as-deposited and (b) annealed bismuth films: (C) P, 298 K; (□) L, 298 K, and (△) P, 5 K; (◆) L, 5 K.

measuring geometry and with an applied magnetic field of 50 kOe, the MR of the as-deposited film increases from 2.1 at room temperature to 78.0 at 5 K. After annealing, the room temperature MR increases slightly to 2.2 whereas the MR at room temperature to 78.0 at 5 K. After annealing, the room temperature MR increases to 5600, significantly larger than the value of 3800 reported for bismuth films electrochemically deposited on gold.\(^1\)

Figure 9 shows the dependence of the MR at 50 kOe on film thickness. The MR for the as-deposited films increases with film thickness and reaches a saturation value of 2.1(P) and 0.9(L) for film thicknesses greater than 5 \(\mu\)m at room temperature and of 100(P) and 6(L) for film thicknesses greater than 25 \(\mu\)m at 5 K. Annealing resulted in a slight increase of the room temperature MR [2.2(P) and 1.0(L)] and in a very large increase in the MR at 5 K. In the latter case the MR had not reached saturation for a film thickness up to 75 \(\mu\)m (5600(P) and 460(L)) so that a magnitude in excess of 10 000 (1 000 000\%) may be anticipated for thicker films.

The MR effect in bismuth is related to the bending of the electron trajectory in the presence of a magnetic field that leads to a reduction in the effective mean free path and hence an increase in the resistance. The magnitude of the MR effect is related to the average angle of the helical path swept out by the charge carriers between two consecutive collisions. The angle is given by \(\omega \tau\), where \(\omega\) is the cyclotron frequency and \(\tau\) is the relaxation time, i.e., the average time between consecutive scattering events. The cyclotron frequency is proportional to the magnetic field (\(\omega_m = eH/m^*\)) and the relaxation time \(\tau\) is related to the mean free path \(l\) of the charge carriers (\(l = v_F\tau\)) and the conductivity (\(\sigma = ne^2/\tau m^*\)) where \(v_F\) is the Fermi velocity and \(n\) is the carrier concentration. From their respective dependencies it can be seen that \(\omega_m \tau = eH/\pi ne\). In general, significant MR can be achieved if \(\omega_m \tau \gg 1\), i.e., for materials with large carrier concentration and mean free path, and small effective mass. For bismuth, the carrier concentration is relatively low, on the order of \(3 \times 10^{17} \text{ cm}^{-3}\), and the effective mass is small \((m^* = 0.02m_0)\) so that a large MR can be obtained for high-quality films where the mean free path is large and not limited by structural defects.

The largest MR values were obtained for the perpendicular measuring geometry. Under a magnetic field, charge carriers will move in a cyclotron orbit of radius \(r_c = m^*v_F/eH\) perpendicular to the magnetic field with a cyclotron frequency \(\omega_c\). Thus the orbit of the charge carriers is in the plane of the film for the perpendicular geometry and perpendicular to the film plane for the longitudinal geometry. Since the current is also in the film plane, all carrier motion will contribute to the MR in the perpendicular geometry whereas only a small fraction of the carrier motion will contribute to the MR in the longitudinal case.

Finite-size effects can be observed when \(l\) is comparable to, or larger than the film thickness. For very thick films \((d \gg l)\) with comparable quality \((\tau \approx \pi)\) the MR will be comparable and independent of the thickness. However, for thin films \((d \approx l)\) surface scattering of the charge carriers will decrease the relaxation time and hence the MR will be the lowest for the thinnest films. Figure 9 shows that for the as-deposited films the perpendicular MR at 5 K becomes constant at a film thickness of about 25 \(\mu\)m suggesting that the mean free path is about 25 \(\mu\)m. For the annealed films, the perpendicular MR has not reached a constant value for 75 \(\mu\)m films suggesting that the mean free path is greater than 75 \(\mu\)m. A mean free path of 60 \(\mu\m) at 5 K was estimated for annealed bismuth films deposited on gold.\(^2\)

### E. Shubnikov–de Haas oscillations

The MR results for the annealed sample at 5 K shown in Fig. 8(d) exhibit Shubnikov–de Haas (SdH) oscillations superimposed on the quasilinear field dependence. These oscillations are due to the Landau quantization of the cyclotron orbits of the charge carriers.\(^2\) At low field the oscillations are periodic in \(H^{-1}\) with a period:

\[
\Delta(H^{-1}) = 2\pi e/\hbar A,\]

where \(A\) is the extremal cross-sectional area of the Fermi surface in the plane normal to the applied magnetic field. Figure 10(a) shows the anisotropic Fermi surface of Bi with a single hole pocket (symmetrical ellipsoid) along the trigonal axis and three electron pockets (asymmetrical ellipsoids).
planes for the perpendicular and transverse measuring geometries in determined from the angle between the sectional area of the hole pocket in the pockets in the \( D \) out of the \( x-y \) \( z \) perpendicular to the \( \) magnetic field \( H \) determined to be 25 \( \) reciprocal space correspond to the threefold \( c \).

The projections of the hole and electron pockets in the \( (012) \) plane are shown in Fig. 10(b). Three different cross sectional areas exist, one originating from the hole pocket \( (h) \) and two from the electron pockets \( (e_1 \) and \( e_2) \). The cross-sectional area of the hole pocket in the \( (012) \) plane can be determined from the angle between the \( (001) \) and \( (012) \) planes \( (56.42^\circ) \), and the periods of the hole ellipsoids found for the perpendicular and transverse measuring geometries in \( (001) \) single crystal bismuth \( \Delta(H^{-1})_{p,h} = 0.20 \ \text{T}^{-1} \) and \( \Delta(H^{-1})_{T,h} = 0.08 \ \text{T}^{-1} \) (Ref. 23). From this we determine a period \( \Delta(H^{-1})_{p,h} = 0.14 \ \text{T}^{-1} \) for the hole pocket with the magnetic field \( H \) perpendicular to the \( (012) \) plane. This value is in good agreement with the positions of the peak minima of the SdH oscillations for bulk single crystal Bi tilted \( 56^\circ \) \( 25' \) with respect to the \( z \) axis.

The periods for the electron pockets \( (e_1 \) and \( e_2) \) are determined to be \( \Delta(H^{-1})_{e_1} = 0.30 \ \text{T}^{-1} \) and \( \Delta(H^{-1})_{e_2} = 0.74 \ \text{T}^{-1} \) for \( H \) perpendicular to the \( (012) \) plane. The calculated value for \( \Delta(H^{-1})_{e_1} \) agrees with experimental SdH data for bulk bismuth for this orientations (no data at \( H^{-1} > 0.5 \) were available).

Figure 11 shows the resistance at 4 and 0.3 K referenced to the resistance at 11 K for magnetic fields up to 8 T perpendicular to the film showing two distinct minima at 0.29 and 0.57 \( \text{T}^{-1} \). Since the mobility of the electrons is about ten times larger than that of the holes, the large peaks around 0.3 and 0.6 can be, at least partially, attributed to electrons. From the difference in the resistance at 4 and 0.3 K, shown in Fig. 11(b), smaller perturbations are seen at 0.45 and 0.67 \( \text{T}^{-1} \).

Since the electron period \( \Delta(H^{-1})_{e_1} \) is very close to being a multiple of the hole period \( (0.14 \ \text{T}^{-1}) \), the peaks at 0.3 and 0.6 \( \text{T}^{-1} \) correspond to the second and fourth hole oscillations. The small perturbations at 0.45 \( \text{T}^{-1} \) can hence be attributed to the third hole oscillation. At lower fields the oscillations die out very quickly due to grain boundary scattering. Finally, the perturbation at 0.67 \( \text{T}^{-1} \) is close to the expected value for the fifth hole oscillation.

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