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Epitaxial Bi/GaAs(111) diodes via electrodeposition

Zhi Liang Bao and Karen L. Kavanagh
Department of Physics, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia V5A 1S6, Canada

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Bismuth films formed by electrodeposition on *n*-GaAs (111) at 70 °C are found to be single crystalline, (0001) oriented, with trigonal surface morphologies typical of high quality single crystals. Diode current-voltage characteristics display low reverse-bias leakage currents and average barrier heights of 0.77 ± 0.02 eV ($n = 1.07$). A necessary requirement for single crystalline growth is the presence of ammonium sulfate in the electrolyte.
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Bismuth is a semimetal that has many extraordinary transport properties due to its highly anisotropic Fermi surface and small effective carrier mass.[1] It is the most diamagnetic of metals, has the largest magnetoresistence,[2–4] and quantum size effects were also first reported in Bi.[4,5] Using vacuum deposition techniques, epitaxial Bi has been obtained on cleaved mica,[5] BaF_2,[6] GaSb,[7] GaAs(110),[8] and CdTe[9] using molecular-beam-epitaxy (MBE) techniques, or on Au/Si(100) obtained by annealing electrodeposited polycrystalline Bi films.[4] Highly textured films have also been reported for (001) and (011) GaAs orientations using electrochemistry.[10] However, the direct epitaxial growth of single crystalline Bi films using electrochemistry has not been reported.

Recently, we have shown that the addition of ammonium sulfate, $(NH_4)_2SO_4$, into iron sulfate ($FeSO_4$) aqueous solutions can lead to the electrodeposition of high quality epitaxial Fe films on GaAs (111), (110), and (001) substrates.[11] In this paper, we report on a similar effect of $(NH_4)_2SO_4$ on the electrodeposition of single crystalline Bi films epitaxially on GaAs (111) substrates.

The substrates were oriented (±0.5°), *n*-type (Si-doped, $1-2 \times 10^{18}$ or $2-3 \times 10^{17}$) GaAs (111)-B (As-terminated) epiready wafers cleaved into 5×6 mm^2 pieces. The electrolyte was composed of a saturated solution of reagent-grade, bismuth (III) nitrate pentahydrate, $Bi(NO_3)_3 \cdot 5\,H_2O$, $(NH_4)_2SO_4$, and deionized water. Photoresist was used to mask the substrate backside and to define the deposition windows exposed to the electrolyte. Prior to the electrodeposition, the substrates were dipped into an aqueous ammonium hydroxide solution (10%) (10 s) to remove the native oxide, rinsed in distilled water (10 s), and then immediately transferred into the electrolyte. An InGa ohmic contact was used to connect the GaAs substrate to the constant current power supply. Galvanostatic electrodeposition (10 mA/cm^2) was carried out at 70 °C without electrolyte agitation. Growth rates were approximately 70 nm/min based on cross-sectional transmission electron microscopy (TEM).

Low-resolution x-ray diffraction θ-2θ scans for 70 ± 5 nm thick Bi/GaAs films are shown in Fig. 1(a). Bismuth (003), (006), and (009) diffraction peaks and the GaAs (111) and (333) substrate peaks are detected, indicating a rhombohedral Bi structure with its trigonal axis normal to the substrate surface. The peak positions indicate that the Bi film is relaxed in the out-of-plane direction.

High-resolution x-ray measurements (monochromated beam, width 12 arcsec) comparing θ-2θ scans to tilt scans showed that the Bi (006) peak width was 0.14° comparable to the theoretical width expected for a perfect 70 nm thick Bi film (0.12°).[12] Thus, a very small broadening occurred due to defects. X-ray pole figures using the Bi $\{02\bar{2}4\}$ reflections showed the expected threefold symmetry [Fig. 1(b)] of a single Bi crystal. The spots at higher tilt angles are due to the GaAs {311} planar reflections which are tilted 3° away from the Bi $\{02\bar{2}4\}$ reflections. They confirm the epitaxial in-plane arrangement between the two materials. The weak extra spots visible in between at the hexagonal symmetry positions (circled) are likely due to twinning defects.[13] We see further evidence of these from secondary electron images of the surface obtained by field emission, scanning electron microscopy (SEM). Figure 2 is a typical example showing triangle-shaped surface facets visible, consistent with the trigonal Bi crystal symmetry. The dark lines are likely surface steps at twinning boundaries inferred from the rotation in surface facet direction inside these regions.

Finally, single crystalline structure was also confirmed from TEM. A plan-view electron diffraction pattern is shown in Fig. 1(c). The corresponding images reflect single crystalline material, consistent with the diffraction pattern, which clearly shows the expected hexagonal symmetry. The extra spots around each hexagonal spot are due to double diffraction[14] in the Bi and GaAs. Indexing of this pattern confirms that the Bi out-of-plane trigonal axis (0001) is parallel to the GaAs (111), and that the Bi in-plane hexagonal $\{10\bar{1}0\}$ directions are parallel to the GaAs in-plane hexagonal $\langle 110 \rangle$ directions, consistent with the x-ray diffraction results.

Film crystalline quality declined for growths at room temperature, as indicated by broader x-ray peak widths and lower peak intensities, however, a preferred (0001) texture remained. The $Bi(NO_3)_3 \cdot 5\,H_2O$ electrolyte by itself is strongly acidic and the addition of ammonium sulfate inhibits the formation of metal oxide ions in the electrolyte and at the film surface. Electrodeposition without the addition of $(NH_4)_2SO_4$, resulted in textured or polycrystalline films at all growth temperatures, typical of Bi deposited in acidic electrolytes.[9,10,12] No evidence of oxygen in the films or an interfacial oxide layer was detected in our films using cross-sectional TEM investigations.

A typical current-voltage characteristic for a Bi/GaAs (111) diode grown on a lower doped substrate at 70 °C is shown in Fig. 3. All diodes displayed close to ideal thermi-

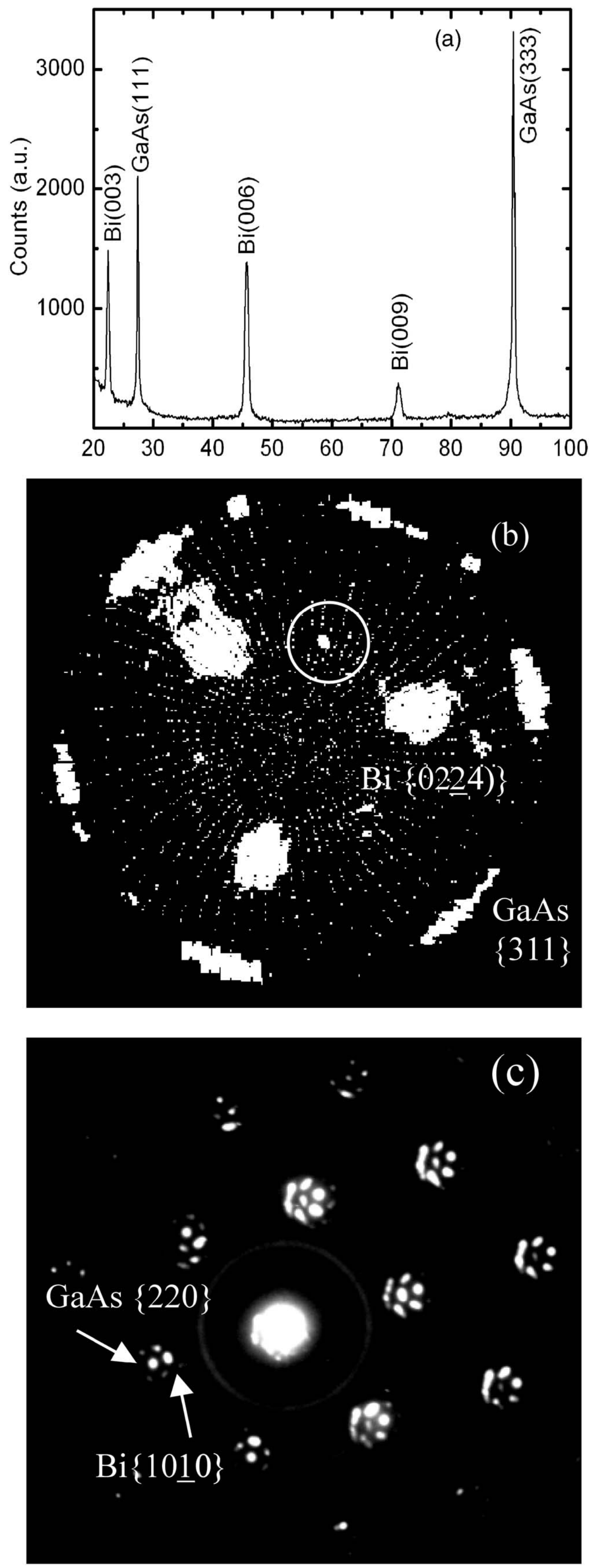

FIG. 1. (a) X-ray diffraction spectra (θ-2θ) of Bi films electrodeposited from saturated $Bi(NO_3)_3$ and $(NH_4)_2SO_4$ (0.3 M) solutions at 70 °C on GaAs (111); (b) Bi {02̲24} x-ray pole figure; (c) A plan-view TEM diffraction pattern with the beam normal to the film and substrate surfaces. The extra spots around each of the Bi {101̲0} and GaAs {220} primary spots are due to double diffraction.

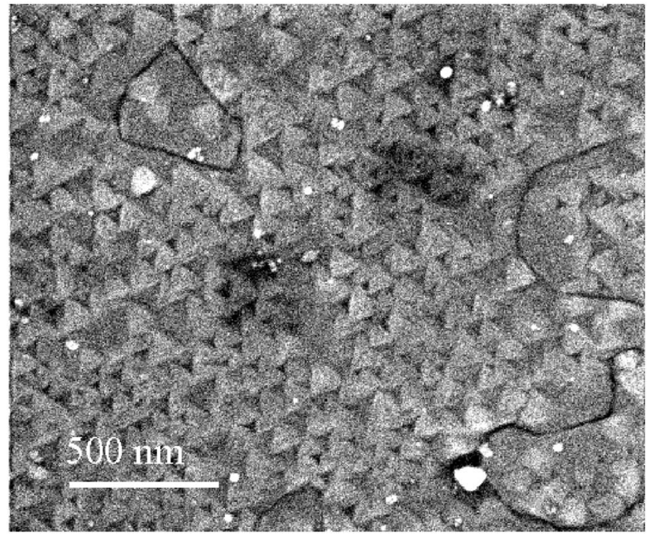

FIG. 2. A secondary electron image from scanning electron microscopy of the surface of a Bi/GaAs (111) film. The triangle shapes indicate the development of a threefold symmetric surface facet consistent with single crystalline Bi. Also visible are rotation boundaries due to twinning.

onic emission behavior with an average barrier height Φ_B^{IV} and ideality factor n of 0.77 ± 0.02 eV and 1.04 ± 0.03, respectively. These characteristics were compared to our own (001) diodes (textured) prepared under identical electrochemical conditions which displayed an average Φ_B^{IV} of 0.73 ± 0.02 eV ($n=1.07$). Other reports of barriers for Bi/GaAs (001) diodes include, 0.83 or 0.80 eV, for polycrystalline or textured electrodeposited diodes[15] and values of 0.72 and 0.85 eV for a UHV vacuum-prepared diode (image force correction not applied).[8,16]

In summary, we have electrodeposited single crystalline Bi films on GaAs (111) substrates from bismuth nitrate, ammonia sulfate solutions. Bi (0001) films are obtained at 70 °C while at room temperature, crystal growth is poorer but strong (0001) texture remains. Diode current-voltage

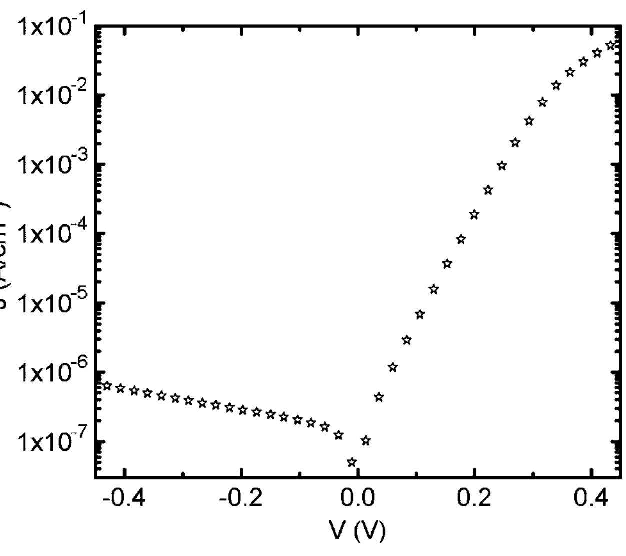

FIG. 3. Current-voltage characteristics from a typical Bi(0001)/GaAs(111) diode grown at 70 °C. The extracted barrier height from the intercept of the I-V curve was $\Phi_B^{IV}=0.77$ eV, with an ideality factor $n=1.05$.

characteristics give a barrier height 0.77 ± 0.02 eV ($n=1.07\pm0.03$) slightly higher than those formed on (001) substrates electrochemically (0.73 eV), or by vacuum techniques (0.72 eV).

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