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Philippe M. Vereecken, Kenneth Rodbell
IBM Research Division
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598

Chunxin Ji, Peter C. Searson
Johns Hopkins University
Department of Materials Science and Engineering
Baltimore, MD 21218

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Philippe M. Vereecken, Kenneth Rodbell

IBM, T.J. Watson Research Center

Yorktown Heights, NY 10591

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Abstract

Bismuth thin films are formed electrochemically on n-GaAs (110). Bismuth films up to a few hundred nanometers in thickness exhibit a strong (018) texture, while thicker films are polycrystalline. The barrier height of the n-GaAs/Bi Schottky contacts is 0.62eV, about 0.2eV lower than for electrodeposited bismuth films on GaAs (100).

Bismuth is a semimetal with unusual electronic properties related to its small carrier effective masses, low carrier concentration, and long carrier mean free path [1]. Bulk single crystals can be prepared by solidification from the melt [11-13], however, thin film deposition is complicated by its low melting point and low vapor pressure. Sputter deposition results in polycrystalline thin films with very small grain sizes, whereas large grained polycrystalline films can be obtained by electrodeposition. Epitaxial Bi thin films can be grown by evaporation [e.g. 5,6] and by molecular beam epitaxy (MBE) [e.g. 7-9].

In previous work we have shown that high quality, (012) textured bismuth films can be obtained on GaAs (100) by electrodeposition and subsequent thermal annealing [10]. In this paper, we report on the direct electrodeposition of highly oriented bismuth films on GaAs (110).

Bismuth films were electrodeposited from a solution containing 0.02 M BiO^+ in 2M $HClO_4$ on Te doped n-type GaAs (110) wafers (N_D of 1.2 x 10^{18} cm^{-3}, Wafer World, Inc.). Ohmic contacts were formed by thermal evaporation of In on the back side of the wafers followed by annealing at 400 ˚C in a N_2 atmosphere for 10 minutes. Solutions were prepared from 0.01M bismuth oxide (Bi_2O_3 Puratronic 99.9999%, Alfa Aesar) dissolved in 2M perchloric acid ($HClO_4$, 70% doubly distilled, Alfa Aesar). Deposition experiments were performed in a custom-built sealed Kel-F cell with inlets and outlets for gas purging and solutions. The cell included a platinum wire (Puratronic 99.9999%, Alfa Aesar) counter electrode and a Ag/AgCl (3M NaCl) reference electrode located in a separate compartment in contact with the solution in the cell through a Luggin capillary. All potentials are reported with respect to the Ag/AgCl reference (0.21 V vs. SHE). The GaAs wafers were assembled in the cell with an exposed surface area 1 cm^2.

Prior to each experiment, the wafer surfaces were pretreated by rinsing first in 1M NH_4OH for about 15 minutes and then in 6 M HCl for 10 to 15 minutes. The GaAs surface was then etched in a mixture of concentrated H_2SO_4, H_2O_2 (30 vol.%) and water (3:1:1 by volume) for 10 seconds with agitation, rinsed with distilled, deionized water, and finally rinsed in 6 M HCl solution to remove the formed oxide [11]. The cell was sealed with the HCl solution in the cell and Ar gas purged through the solution. After about 10 minutes the HCl solution was removed through the solution outlet and replaced with a de-aerated 2M $HClO_4$ solution (70% doubly distilled, Alfa Aesar). After about 15 minutes the supporting electrolyte solution was removed and the de-aerated 20 mM BiO^+ in 2M $HClO_4$ was introduced to the cell. Immediately before deposition, Ar flow through the solution was stopped while an Ar blanket was maintained above the solution. After deposition, the bismuth solution was replaced by 1.2 M HCl solution. Finally the films were rinsed with distilled, deionized water and dried in a nitrogen stream. All experiments were performed at room temperature (297 K). Rotating disk experiments were performed in a standard three-electrode cell (Radiometer RDE and controller) with a mountable wafer chip electrode holder.

Figure 1 shows typical current-voltage curves for n-GaAs (110) in 0.02M BiO^+ in 2M $HClO_4$. The onset potential for bismuth deposition is about -0.14 V. For the stationary electrode, a characteristic reduction peak is seen at -0.3 V due to the nucleation and diffusion-limited growth of bismuth. On the reverse scan, deposition continues to a potential of about 0 V. The total deposition charge during the scan (0.1 C cm^{-2}) corresponds to a Bi film of about 70 nm or 340 equivalent monolayers. The deposition of Bi results in the formation of a Schottky junction so that for $U > 0$ V the n-GaAs/Bi junction is under reverse bias and no anodic current is seen until 0.3 V when the band bending is sufficiently large that tunneling becomes possible and bismuth stripping is observed [12,13]. The stripping charge was 0.90 – 0.93 of the deposition charge indicating a small contribution of hydrogen evolution at the more negative deposition potentials.

At a rotating disk electrode the deposition current becomes diffusion controlled at about -0.3 V depending on the rotation rate. The inset of Figure 1 shows that the diffusion limited deposition current is proportional with the square root of the rotation rate in accordance with convective-diffusion mass transport. The diffusion coefficient for BiO^+, determined from the slope, is 0.6×10^{-5} cm^2 s^{-1}.

Bismuth thin films up to 1 μm in thickness were deposited at constant potential using a two step process, without agitation. A short (0.1 to 0.25 s) nucleation pulse at -0.275 V was followed by growth at -0.02 or -0.025 V to the final film thickness. During the nucleation pulse the current density was between 5 and 40 mA cm^{-2}, corresponding to 1 - 5 nm of bismuth. The as-deposited films were bright and silver colored although they became gold colored after rinsing and drying.

Figure 2 shows images of bismuth films for deposition charges of 5, 22, and 135 mC cm^{-2}. For a deposition charge of 5 mC cm^{-2} (17 ML), the surface is covered by isolated 20 – 50 nm diameter bismuth islands up to 10 nm in height. The relatively flat islands are in contrast to the hemispherical islands typically associated with diffusion-limited growth. For a deposition charge of 22 mC cm^{-2} (74 ML) the islands have coalesced resulting in a relatively smooth 16 nm thick film. For a deposition charge of 135 mC cm^{-2} (454 ML), the films are polycrystalline with grain sizes of 50 - 100 nm and an average thickness of 100 nm.

Figure 3 shows 2D plane ($2\theta - \chi$) x-ray diffraction pattern for 100 nm and 1 μm bismuth films [14]. The spots in the diffraction pattern for the 100 nm films, characteristic of films up to several hundred nanometers in thickness, indicate that the films have very strong in-plane texture. Perpendicular to the film plane ($\chi = 0$), only the spots for GaAs (220) and Bi (018) are seen. The unit cell for the GaAs (110) plane is 4.0 Å x 5.65 Å with four atoms in the corners. The Bi (018) plane has two layers, one slightly above the other, with a rectangular unit cell. The unit cells, with four atoms in the corners, are 4.546 Å x 5.486 Å and 4.546 Å x 5.755 Å, corresponding to misfits of 13% in the short direction and -2.9% or 1.8% in the long direction. These results suggest that the Bi (018) plane can form an epitaxial 1x1 overlayer on GaAs (110). Formation of epitaxial (1x1) bismuth overlayers up to a few monolayers thick on GaAs (110) have been reported using MBE [15,16] and PVD at low substrate temperatures [17].

For the 1 μm thick film, the appearance of rings shows the gradual loss of texture and the emergence of a polycrystalline film. Perpendicular to the surface, streaks corresponding to Bi (006), (024), (205), and (207) are evident. We note that strong (012) texture has been previously reported for electrodeposited Bi films on GaAs (100) [10].

Figure 4 shows a typical semi-logarithmic current-voltage curve for a n-GaAs(110)/Bi junction with a 200 nm bismuth film. The n-GaAs/Bi junctions showed rectifying behavior with an exponential forward current at negative potentials and a reverse current of about 10^{-4} A cm^{-2} at positive potentials. The barrier height Φ_B, determined from the forward bias current region according to the thermionic emission theory [18] was about 0.62 eV with an ideality factor, n = 1.19. Previously, we have measured barrier heights of about 0.80 eV for bismuth films electrodeposited on n-GaAs(100) ($N_D = 3 \times 10^{16}$ cm^{-3}) solution [12]. Hence, the measured barrier height for n-type GaAs/Bi Schottky junctions is about 0.2eV lower for (110) than for (100) single crystal GaAs. The relatively high value for the ideality factor n is due to the high donor density ($N_D = 1.2 \times 10^{18}$ cm^{-3}).

The time dependence of the barrier height of a n-GaAs(110)/Bi contact is shown in the inset of Figure 4. The small 10 meV increase from an initial value of 0.616 eV to 0.626 eV after one month suggests that the bismuth film is dense and continuous completely covering the GaAs surface. The 10 meV change is probably due to slow oxidation at the edges of the sample [12].

Acknowledgements

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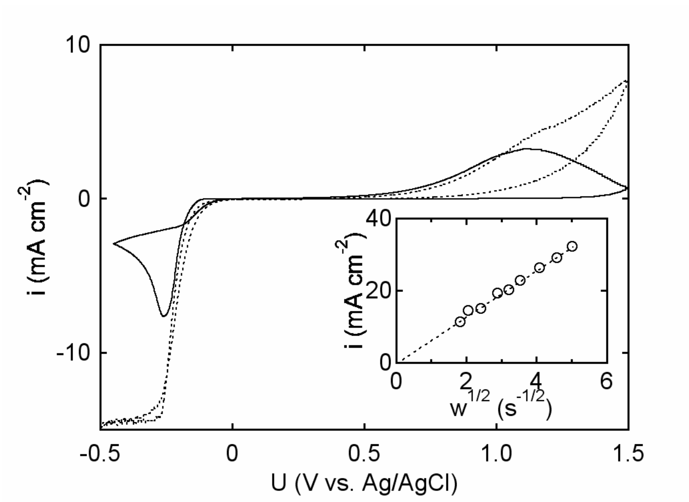

Figure 1. Current – voltage curves for n-GaAs (110) in solution containing 20 mM BiO^+ and 2M $HClO_4$ at a scan rate of 20 mV s^{-1} : (a) stationary conditions and (b) rotating disk electrode at a rotation rate of 5 s^{-1}. The inset shows the diffusion limited deposition current at -0.5 V versus the square root of the rotation rate.

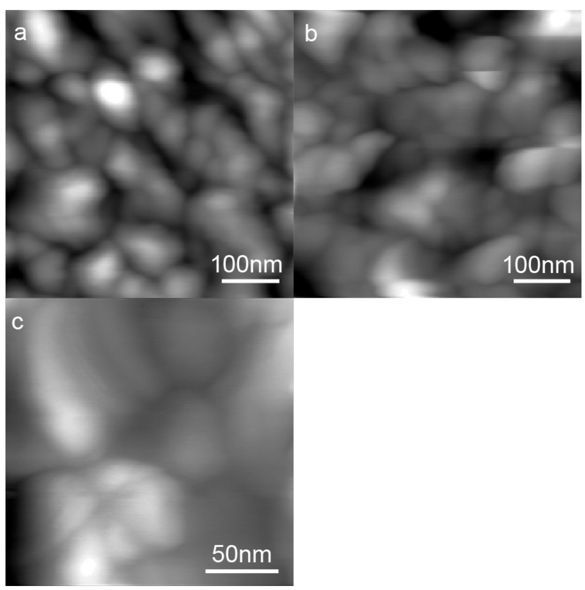

Figure 2. Atomic force microscope images of (a) 3.5nm, (b), 16 nm, and (c) 100 nm electrodeposited bismuth films on n-GaAs (110).

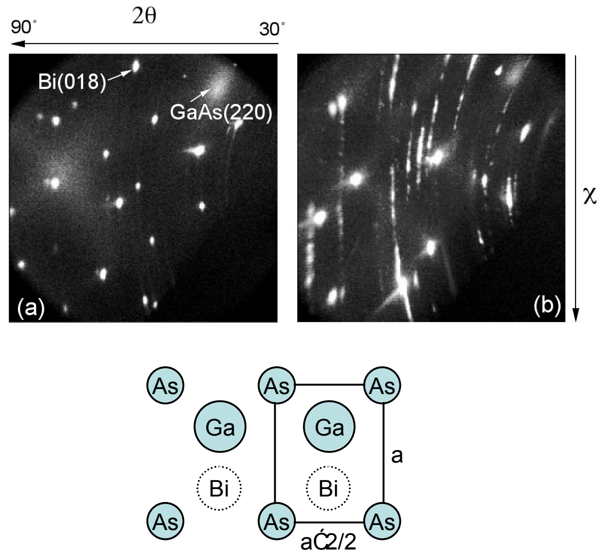

Figure 3. 2θ vs. χ x-ray diffraction patterns for (a) 100 nm and (b) 1 μm thick bismuth films deposited on GaAs (110).

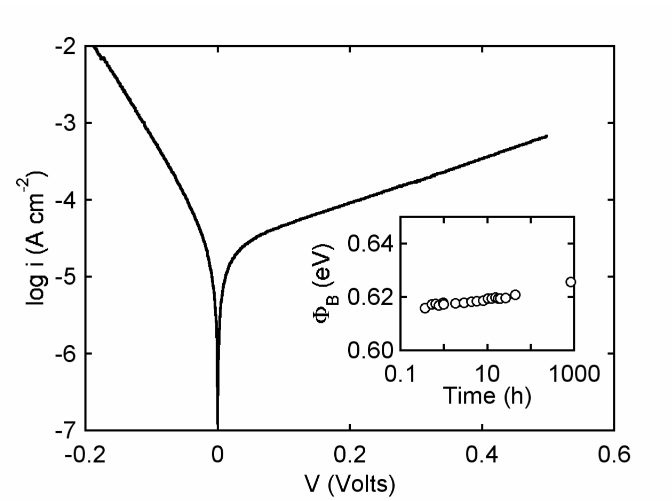

Figure 4. Current-voltage curves for a n-GaAs(110)/Bi junction with a 200 nm bismuth film. The series resistance was about 3 Ω cm^2. The inset shows the time dependence of the barrier height after deposition.