Fabrication of bismuth nanowires with a silver nanocrystal shadowmask

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We fabricated bismuth (Bi) nanowires with low energy electron beam lithography using silver (Ag) nanocrystal shadowmasks and a subsequent chlorine reactive ion etching. Submicron-size metal contacts on the single Bi nanowire were successfully prepared by *in situ* focused ion beam metal deposition for transport measurements. The temperature dependent resistance measurements on the 50 nm wide Bi nanowires showed that the resistance increased with decreasing temperature, which is characteristic of semiconductors and insulators. © *2000 American Vacuum Society.* [S0734-2101(00)03704-0]

I. INTRODUCTION

Nanometer-size structures such as wires and dots have aroused considerable interests as ideal systems for testing predictions about quantum confinement and reduced dimensionality, and as building blocks for nanostructured materials. A more practical reason for the study of nanostructures is the ever present drive towards smaller sizes in the electronics industry.[1] In particular, semimetallic bismuth (Bi) with very small effective mass and high carrier mobilities is reported to be a good candidate to study quantum-confinement effects in one-dimensional systems and a very promising material for thermoelectric applications.[2]

Recently, a number of fabrication techniques have been utilized to produce Bi nanowires. For example, filling porous anodic alumina with Bi from the liquid phase resulting in single-crystal nanowire arrays having the same crystal structure and lattice parameters as bulk.[3] However, it would be difficult to make contacts to a single Bi wire to study its one-dimensional properties.

We previously demonstrated a new fabrication technique for the fabrication of nanometer-size polymethyl methacrylate (PMMA) patterns using Ag nanocrystal shadowmasks.[4] In this work, we used same technique and a subsequent reactive ion etching to fabricate Bi nanowires. 100 nm wide platinum (Pt) lines were written to contact a Bi single nanowire by the FIB to permit transport measurement.

II. EXPERIMENTAL RESULTS

First, we prepared 40 nm thick Bi single-crystal films by molecular beam epitaxy (MBE) system. The substrates for the MBE growth were indium doped semi-insulating CdTe(111)B pieces, 1 cm^2 in size. X-ray diffraction showed only sharp (000*l*) peaks, which implied *c*-axis growth of Bi perpendicular to the substrates as shown in Fig. 1. Self-assembled high-aspect ratio Ag wire structures were transferred as a Langmuir–Schaeffer film to 40 nm thick 1% PMMA coated MBE-grown Bi/CdTe substrates. Substrates with the transferred Ag wires were exposed by a JEOL 6401F field emission scanning electron microscope (FESEM) at 700 V to provide samples with an electron dose of 50 $\mu C/cm^2$. At 700 V, 40 nm thick PMMA was thought to be exposed all the way to surface of Bi film. The penetration depth of electron in silver was found to be 4 nm at 700 V by a previous Monte Carlo simulation.[4] That penetration depth is smaller than the thickness of Ag nanocrystal shadowmask. Following the electron beam exposure, a sample was developed for 1 min in a mixture of methyl isobutyl ketone and isopropanol in the ratio 1:3. A subsequent anisotropic reactive ion etching (RIE) process was carried out by a PlasmaMaster Model PME 1200 chlorine etcher. With a BCl_3 to Ar_2 mixture at 20 mTorr, and a plasma sustaining power of 200 W, RIE process transferred Ag nanowire patterns to Bi/CdTe substrates. The mask material is believed to consist of 30 nm thick Ag and 40 nm thick PMMA layers.

Its electronic orbital configuration of Bi implies that Bi prefers to have two ionization states. The following simple model of the Bi etching mechanism for the case of Bi^{+3} ionization state is proposed:

$$\mathrm{Bi} \rightarrow \mathrm{Bi}^{+3} + 3e^-$$

$$\frac{3}{2}\mathrm{Cl}_2 + 3e^- \rightarrow 3\mathrm{Cl}^-$$

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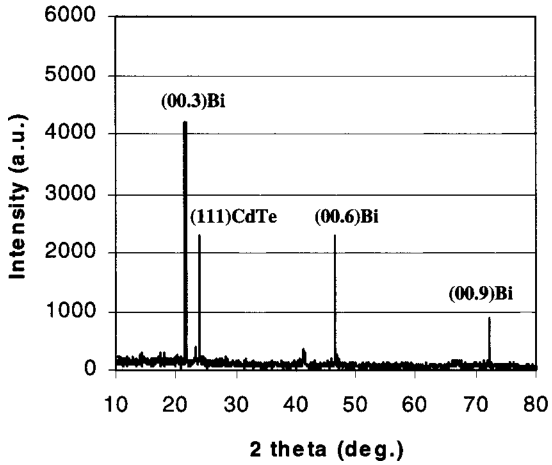

FIG. 1. X-ray diffraction pattern of MBE-grown Bi film on CdTe (111)B substrate.

$$Bi+\frac{3}{2}Cl_2\rightarrow Bi^{+3}+3Cl^-\rightarrow 3BiCl_3(\text{volatile}).$$

Following formation of Bi^{+3} and Cl^{-3} ions by plasma, volatile products of BCl_3 were formed and washed away. Ar in the etch gas mixture might contribute to the reduction of the undercut profile. We have found a mixture of BCl_3 and Ar_2 to be an excellent choice of gases to be used in RIE of Bi, producing vertical profiles and etching rates at about 100 nm/min. The RIE chemical mechanism for Bi is found to be similar to that of GaAs etching by chlorine gases. Through the RIE process, 50 nm wide and 40 nm high Bi nanowires were fabricated on CdTe substrates.

Submicron-size platinum (Pt) contacts on a Bi single nanowire were prepared by *in situ* FIB metal deposition at 25 kV, 6 pA to allow temperature dependent resistance measurements. Figure 2 shows the FESEM micrograph of a 50 nm wide, 40 nm high Bi nanowire to which Pt contacts were made by the FIB. The electrical resistance of the wire measured was typically on the order of 1–20 Ω. The temperature dependence of the resistance of 50 nm wide Bi nanowire is shown in Fig. 3. The data show that resistance increases with decreasing temperature, which is characteristic of semiconductors and insulators. As quantum confinement is introduced into the Bi nanowire system, the external conduction subband and valence subband edges move in opposite directions to eventually form a positive energy band gap (E_g) between the lowest L-point conduction subband edge and the highest T-point valence band edge, thereby leading to a semimetal-semiconductor transition ($E_g=0$) as the wire size is decreased below the critical wire width of Bi. Dresselhaus *et al.* found that Bi makes a transition at critical wire radius of 52 nm.[5] In the Bi nanowires, the carrier mobility is suppressed by carrier confinement along the direction of wire and by surface imperfection.

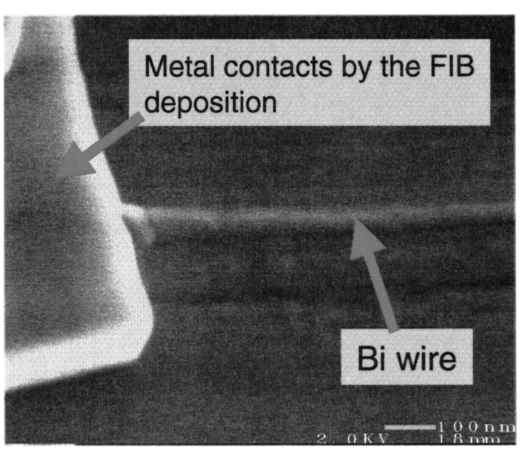

FIG. 2. FESEM micrograph of a 50 nm wide Bi nanowire with metal contacts. Pt contacts to the wire were prepared by *in situ* FIB metal deposition.

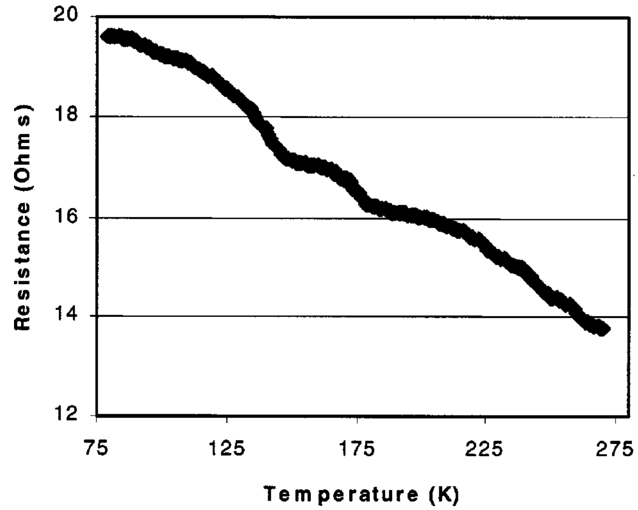

FIG. 3. Temperature dependence of the resistance of the 50 nm wide Bi nanowire.

III. CONCLUSIONS

In conclusion, 50 nm wide Bi nanowires were fabricated by low energy electron beam lithography using Ag nanocrystals as a shadowmask and a subsequent chlorine reactive ion etching process. Temperature dependent resistance measurements show that the Bi nanowire fabricated has semiconductor properties rather than metallic properties. Our method may be a good candidate of fabrication technique for studying Bi nanowires.

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