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A Novel Growth Method of Single-Crystalline Bi Nanowires

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A novel growth method of single-crystalline bismuth (Bi) nanowires is presented. It is found that the growth of Bi nanowires on as-sputtered films occurs during heat treatment due to the relaxation of stress between the film and substrate, originating from thermal expansion mismatch. The diameter of Bi nanowires was found to decrease with the mean grain size of the film. The grains of Bi film grown at 100 W and annealed having preferred orientation, *i.e.*, (003) and (006), serve as Bi nanowire seeds. The largest MR values of 2246 % at T = 75 K and 286 % at T = 300 K in a 400-nm Bi nanowire were obtained, indicating that high-quality, single-crystalline Bi nanowires could be grown by the proposed stress-induced method. These results provide motivation for exploring the magneto-transport properties of single-crystalline Bi nanowires.

Keywords: Bi nanowires, stress-induced growth, ordinary magnetoresistance

Semimetallic bismuth (Bi) has been extensively investigated over the last decade. It exhibits very intriguing transport properties due to its highly anisotropic Fermi surface, low carrier concentrations, long carrier mean free path l, and small effective carrier mass m^*. The intense interest in Bi nanowires lies in the development of nanowire fabrication methods and the opportunity for exploring novel low-dimensional phenomena.

As the diameter of a Bi nanowire is much smaller than the mean free path of electrons, the electron will be confined by the boundary of the nanowire, giving rise to a reduction in the mean free path as the wire diameter decreases[1]. Very large magnetoresistance (MR) behavior associated with a long carrier mean free path l in Bi nanowires is of particular importance[1,2], since it can be exploited for spintronic device applications such as magnetic field sensors and spin-injection devices. With respect to "spintronics", it is expected that Bi can be used as a spin channel in a spin-injection device due to the very long spin diffusion length l_{sd} of a few ten μm, following the relation $l_{sd} = (l \upsilon_F \tau_{\uparrow\downarrow})^{1/2}$, where υ_F is the Fermi velocity and $\tau_{\uparrow\downarrow}$ is the spin relaxation time.

In spite of continued interest in exploring the unique properties of Bi, however, to date only a few methods have been reported for the preparation of Bi nanowires. Most of the existing high-temperature approaches to nanowire fabrication, such as laser ablation[3], plasma-arc[4], and chemical vapor-phase synthesis[5], are inappropriate for the growth of Bi nanowires, since Bi has a low melting point (271.3 °C). Furthermore, in most cases of Bi nanowire growth, additional processing steps are necessary to fabricate the nanowires. These include template-mediated methods such as pressure injection into the nanochannels of anodized aluminum oxide (AAO) templates[6,7,8] and electrochemical deposition using a template of nanometer-sized pores[1,2]. Other methods for growth of Bi nanowires require Bi-CrN composites[9] and aqueous bismuth nitrate[10] as a starting material.

In order to study the magneto-transport properties in a single-crystalline Bi nanowire, there are some difficulties and limits in the conventional methods with respect to device fabrication and high quality crystalline, including the proper removal of templates[1,2,6,7,8], The absence of straight nanowires in shape[9], small aspect ratio[10] and poor crystalline quality[1,2].

In the present work, we report a novel method to grow single-crystalline Bi nanowires. The proposed approach originates from the stress-relief phenomenon of Bi sputtered thin film based on thermodynamic and kinetic considerations during heat treatment. Our method provides high crystalline quality and straight nanowires with a high aspect ratio. It is neither template nor catalyst-assisted and is much simpler than the existing methods as well as cost-effective. We demonstrate the largest magnetoresistance (MR) reported in the literature for an individual 400-nm-diameter Bi nanowire, 2246 % at T = 75 K and 286 % at T = 300 K, reflecting high-quality, single-crystalline Bi nanowires.

Bi thin films were grown on a thermally oxidized Si substrate in a radio frequency (rf) sputtering system with a Bi

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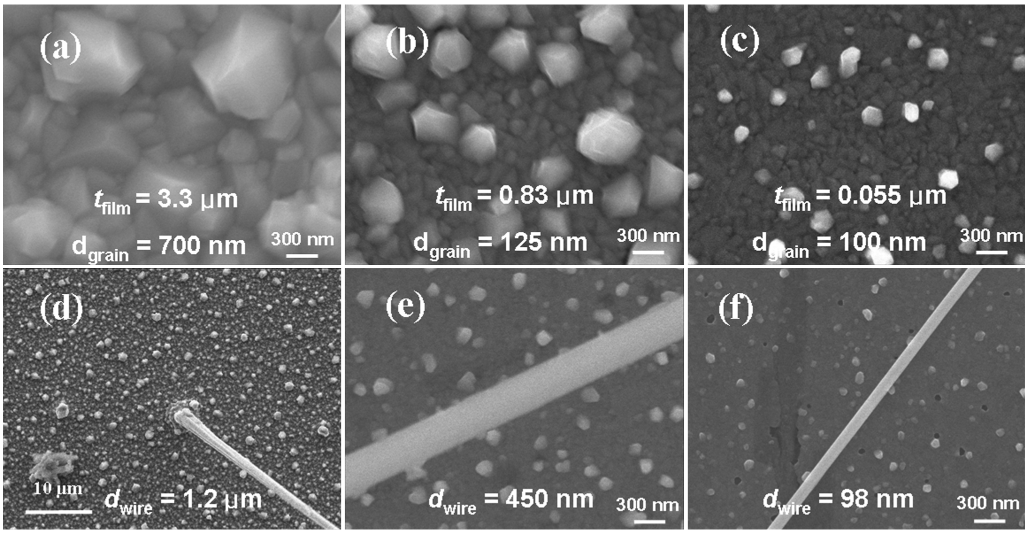

Fig. 1. Scanning electron microscopy (SEM) images of surface morphology of as-grown Bi films deposited at 100 W in rf power [(a), (b), (c)] and the same films annealed at 270 °C for 10 hours [(d), (e), (f)]. The thickness of 3.3 µm (a), 0.83 µm (b), and 0.055 µm (c) in the as-grown films correspond to average grain sizes of 700 nm (a), 125 nm (b), and 90 nm (c). The average grain sizes of 700 nm (a), 125 nm (b), and 100 nm (c) in the as-grown films yield Bi wire diameters of 1.2 µm (d), 450 nm (e), and 98 nm (f).

target of 99.9 %. The deposition of Bi was carried out in a vacuum chamber with a base pressure of 5.0 × 10^{-7} Torr. Rf power of 100 W and Ar working pressure were utilized, yielding a growth rate of 27.5 Å/sec. The film thickness (0.04~3.3 µm) depended on the deposition time. For growth of the Bi nanowires, the sputtered Bi thin films were transferred to a furnace for heat treatment at 270 °C for 10 hours. During heat treatment, a vacuum level of 5.0 × 10^{-7} Torr was kept in order to prevent additional oxide layers on the surface of the Bi nanowires. A combination of photo-lithography, electron-beam lithography, plasma etching, and lift-off process was used to fabricate an individual Bi nanowire device. The microstructure of the Bi thin films was investigated by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The magnetoresistance (MR) measurement was performed by applying a magnetic field up to 9 T in a temperature range of 2 – 300 K in order to investigate the electrical and magneto-transport properties in individual Bi nanowires.

Figure 1 presents SEM images showing the surface morphology of as-grown Bi thin films [(a), (b), (c)] and films annealed at 270 °C for 10 hours [(d), (e), (f)]. As-grown Bi thin films with a thickness of 3.3 µm (a), 0.83 µm (b), and 0.055 µm (c) were obtained by controlling the deposition time. It was found that as the thickness of the as-grown film decreases, the size of the grains of the films also decreases. The thickness of 3.3 µm (a), 0.83 µm (b), and 0.055 µm (c) in the as-grown films correspond to average grain sizes of 700 nm (a), 125 nm (b), and 90 nm (c). Surprisingly, after heat treatment, uniform and straight Bi nanowires with a high aspect ratio were found to be extruded from the surface of the as-grown films. These nanowires continued to grow to as long as hundreds of micrometers, as seen in Figs. 1(d), (e) and (f). This is believed to be due to induced stress between the film and substrate, which acts as a thermodynamic driving force during heat treatment. In other words, the growth of Bi nanowires on the films is attributed to the relaxation of stress originating from a thermal expansion mismatch between the film and the substrate. This mismatch arises from the large difference in the coefficient of thermal expansion of Bi and SiO_2, i.e., 13.4 × 10^{-6}/°C and 3.0 × 10^{-6}/°C, respectively. It was also found that as the mean grain size of the as-grown film decreases, the diameter of the nanowires grown on the films after heat treatment decreases. The average grain sizes of 700 nm (a), 125 nm (b), and 100 nm (c) in the as-grown

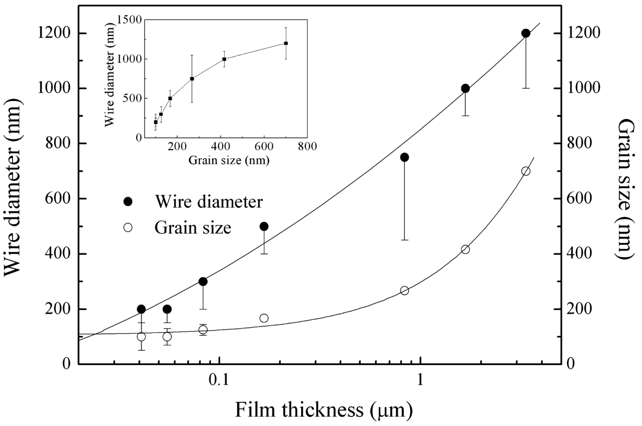

Fig. 2. Correlations between the thickness and mean grain size of the Bi films deposited at 100 W rf power. The diameters of the Bi wires are shown in log scale. The inset shows that the diameter of the Bi wires decreases in proportion to the grain size of the films.

films correspond to Bi wire diameters of 1.2 μm (d), 450 nm (e), and 98 nm (f).

Figure 2 shows correlations between the thickness and mean grain size of the Bi films and the diameter of the Bi nanowires. The diameter of the Bi wires was found to decrease in proportion to the thickness and the grain size of the films. Therefore, it is concluded that the diameter of Bi nanowires is dependent upon the mean grain size in as-grown films, which in turn is determined by the thickness of the films. This indicates that the diameter of Bi nanowires can be controlled in the proposed method. With this regard, the present method is much more effective than a previously reported stress-induced growth method of Bi nanowires[9]. In the present work, nanowire with a diameter as small as 59 nm was obtained.

In order to clarify the mechanism of Bi nanowire growth, the microstructures of Bi thin films have been investigated. Figure 3 exhibits x-ray diffraction (XRD) patterns of Bi thin film after heat treatment at 270 °C for 10 hours grown at a deposition rate of (a) 3.4 Å/sec (rf power : 10 W) and (b) 27.5 Å/sec (100 W). Regardless of the deposition rate, 50-nm-thick Bi films were obtained by controlling the deposition time, corresponding to films with 95 nm mean grain size. Interestingly, whereas no nanowires were observed in the film grown at 10 W and annealed, numerous nanowires were observed in the film grown at 100 W and annealed. From Fig. 3, while the grains of the Bi film grown at 10 W and annealed were observed to be randomly oriented, the grains of the Bi film grown at 100 W and annealed were found to have preferred orientations, (003) and (006). This implies that the grains having preferred orientation of (003) and (006) play a role as seeds for the Bi nanowires.

Figure 4 shows the variation of ordinary magnetoresistance (MR) for a representative 400-nm-diameter single nanowire (see the inset of Fig. 4), fabricated by a combination of photo-lithography, electron-beam lithography, plasma etching, and a lift-off process. The ordinary MR measured with a magnetic field perpendicular to the Bi nanowire is defined as

$$\Delta R\,(B)\,/\,R\,(0) = [\,R\,(B) - R\,(0)\,]\,/\,R\,(0)$$

where R (0) is the zero-field resistance and R (B) is the resistance at a given magnetic field B. For the 400-nm Bi nanowire, the largest MR (2246 %) was found at 75 K, which is nearly 2-times larger than the largest MR (35 K) of electodeposited 400-nm-diameter Bi nanowire arrays.[1,2] MR values of 1577 % and 286 % were observed at 2 K and 300 K, respectively.

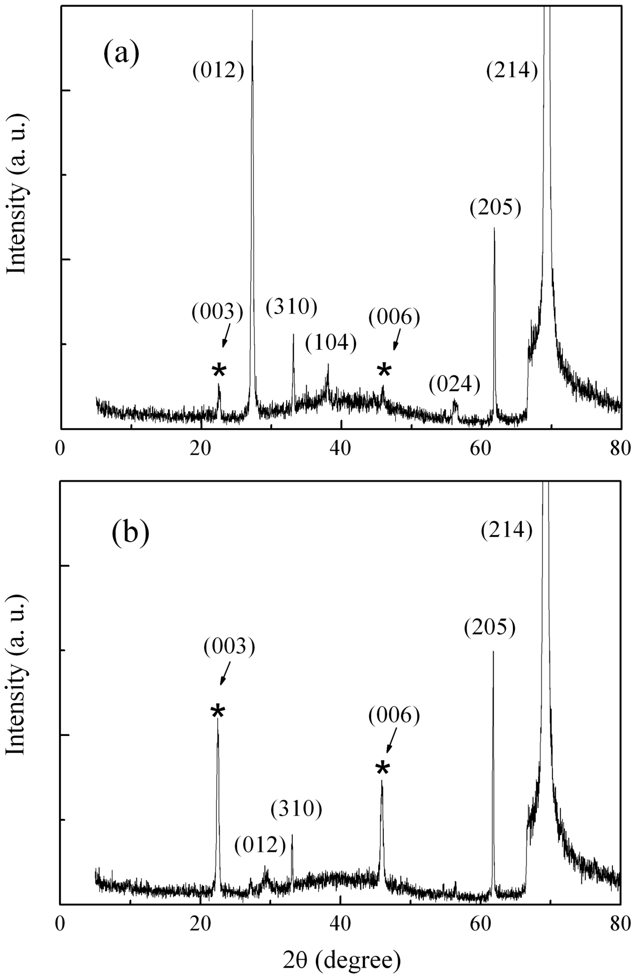

Fig. 3. X-ray diffraction pattern of Bi sputtered films (50 nm) after heat treatment at 270 °C for 10 hours; with a deposition rate of (a) 3.5 Å/sec (rf power : 10 W), (b) 27.5 Å/sec (100 W).

The ordinary MR effect in Bi is caused by curving of the carrier trajection in a magnetic field. The magnitude of the MR effect is determined by $w_c\tau$, where $w_c = eH/m^*c$, the cyclotron frequency, τ is the relaxation time, e the electron charge, m^* the effective carrier mass, and c the speed of light. At a given value of H, the value of w_c is an intrinsic property of a given material. Since m^* is much smaller in Bi than in common metals, w_c is about two orders of magnitude larger[11]. Longer relaxation time (τ), which reflects the crystal quality of a sample, is associated with higher MR. In this work, the very large MR observed in the 400-nm Bi nanowire reflects the high quality of the nanowire, i.e., single-crystalline.

In summary, we have investigated a growth method and magneto-transport of Bi nanowires. The growth of Bi nanowires on as-sputtered films was found to occur during heat treatment due to the relaxation of stress between the film and substrate, originating from thermal expansion mismatch. The diameter of Bi nanowires was found to decrease with the mean grain size of the films, indicating that the diameter of the Bi nanowires can be controlled in our method. The grains of a Bi film grown at 100 W and annealed was found to have preferred orientation, *i.e.*, (003)

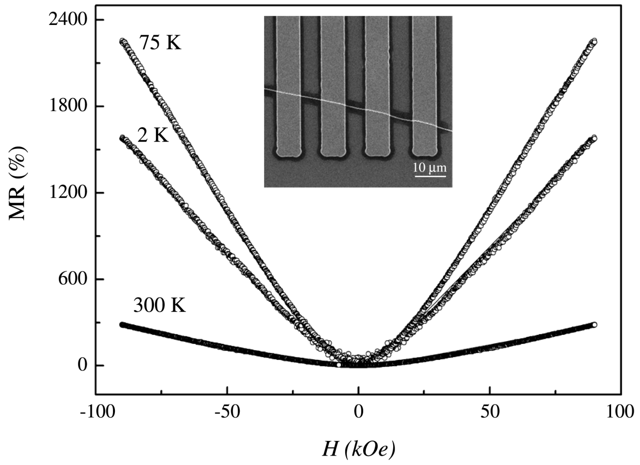

Fig. 4. Ordinary magnetoresistance (MR) of 400-nm Bi nanowire at 2 K (2246 %), 75 K (1577 %), and 300 K (286 %). The inset shows a SEM image of a 400-nm Bi nanowire with Au contacts fabricated by a combination of photo-lithography, electron-beam lithography, plasma etching, and a lift-off process.

and (006), while the grains of a Bi film grown at 10 W and annealed were observed to be randomly oriented. The grains having the preferred orientation play a role as seeds for the Bi nanowires. MR values of 2246 % at T = 75 K and 286 % at T = 300 K in a 400-nm Bi nanowire were obtained. Thus, high-quality, single-crystalline Bi nanowires could be grown by the proposed stress-induced method.

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