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Abnormal resistance–temperature characteristic of the melting Bi nanowires

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ABSTRACT

There are no reports about the electronic transport behavior of the melting metal nanostructures because the morphology of nanostructures cannot be kept under the melting condition. Here, the electronic properties of the melting Bi nanowires are investigated using the pore confinement of anodic aluminum oxide template. The results indicate that with the increase of temperature the resistance of Bi nanowires has a transition from the positive temperature coefficient of resistance before fusion to the negative one after fusion. Moreover, as the temperature gradually increases, the resistance of the melting Bi nanowires rapidly decreases at first, and then tardily decreases. This research provides fundamental and valuable information for exploring and designing the new electronic devices under the high temperature.

1. Introduction

Recently, with the miniaturization of electronic and optoelectronic devices [1], metal nanowires have been considered to serve as nanoscale connecting elements and functional units [2–7]. In this way, the electronic properties of metal nanowires become the focus of attention [8–11]. In electronics with single molecules as active element, the resistance of metal nanowires will become bigger with the decrease of the diameter. In this case, the smaller current flowing through nanowires may make the metal nanowires melt. Compared with the solid metal nanowires, the melting metal nanowires have the more complex internal structure and may have the novel electronic properties. For the study of the electronic properties of the melting metal nanowires, on the one hand, it can provide insight into their physical behavior which is still incompletely understood under the melting state, such as the influence of the nanometer congeries produced during the fusion on the electronic properties. On the other hand, it can help designing nanoelectronic devices with an optimum performance under the extreme state. This indicates that it is necessary to know the electronic transport behavior of the melting metal nanowires. At present, the electrical performance research of liquid metal is mainly focused on the bulk material [12]. To the best of our knowledge, such electronic transport behavior of the melting metal nanowires has not been reported so far.

Because of the potential application of semimetal Bi nanowires as thermoelectric materials [13], the electronic transport behavior has attracted much attention in recent years [14–20]. To date, there are many reports about the relation between the electronic transport behavior of Bi nanowires and the diameter, temperature [21–25]. The measurement temperature is controlled in the range of lower temperature because the higher measurement temperature may result in the fusion of Bi nanowires, and the shape of nanowires can not be kept. Due to the chemically stable properties (up to 1100 K) and the pore confinement effects, the anodic aluminum oxide (AAO) template is propitious to study the properties of nanowires under the condition of higher temperature [26], and offers a unique opportunity to explore the electronic transport behavior of the melting metal nanowires. In this work, we take Bi nanowires as example to study the electronic transport behavior of the melting metal nanowires, and analyze the resistance–temperature characteristic of Bi nanowires before and after fusion. The correlative research will not only provide a basis for developing the electronic transport theory of the melting metal nanomaterials, but

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also afford the new notion and beneficial reference for the design of the liquid-state nanoelectronic devices.

2. Experimental details

The experiment mainly involved three aspects: fabricating AAO template with the uniform-diameter pores, depositing Bi nanowires in the pores of AAO template, and measuring their electronic transport behaviors. The AAO templates used in this work were prepared via a two-step oxidation method, and the detail process for preparing AAO template was as follows. Prior to anodizing, high-purity aluminum foils (99.999%) were annealed in a vacuum of 10^{-3} Pa at 500 °C for 5 h to remove the mechanical stress and obtain homogenous conditions for pore growth over a large area. Then, the aluminum foil was polished in the mixture of perchloric acid and absolute ethanol (the ratio is 1:9 in volume) for 3 min with the potential of 23 V. For the first anodization, the aluminum foils were anodized in the electrolyte of 0.3 M $C_2H_2O_4$ for 6 h at the potential of 40 V. After removing the alumina layer formed at the above step in a mixture of 6 wt% H_3PO_4 and 1.8 wt% H_2CrO_4 at 60 °C for 8 h, the Al sheet was anodized again in 0.3 M $C_2H_2O_4$ for 12 h at the potential of 40 V. After the second anodization, the AAO template was etched by saturated $CuCl_2$ solution to remove the remaining aluminum, and the alumina barrier layer was then dissolved in 5 wt% H_3PO_4 solution at 30 °C. Au layer was deposited by sputtering on the surface of AAO template. This Au layer served as a working electrode in the subsequent electrodeposition of Bi nanowires in a common two electrode plating cell, and a graphite plate was used as the counter electrode. The electrolyte for the deposition of Bi nanowires contained a mixture of $BiCl_3 \cdot 2H_2O$ (25 g/L), $C_4H_6O_6$ (70 g/L), $C_3H_8O_3$ (100 g/L), NaCl (100 g/L), and HCl (1 mol/L). The pH of the electrolyte was adjusted to about 1.0 by adding appropriate amounts of aqueous ammonia (5 mol/L). The electrodeposition was carried out under the current density of 2–2.5 mA/cm^2.

The morphologies of Bi nanowires were observed with field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F), and transmission electron microscope (TEM, JEOL JEM-2100). The crystal structures of Bi nanowire arrays were characterized by X-ray diffractometer (Rigaku D/MAX2500) with Cu Kα_1 radiation ($\lambda = 0.154056$ nm). For FE-SEM observation, the AAO was partly dissolved with 0.5 M NaOH solution, and then the obtained Bi nanowires were carefully rinsed with deionized water for several times. For TEM observations, the AAO was completely dissolved with 1 M NaOH solution and then rinsed with absolute ethanol. For X-ray diffraction (XRD) measurements, the overfilled nanowires on the surface of the AAM template were mechanically polished away. The electronic transport behaviors were automatically recorded using a digital source-meter (Keithley 2400) and controlled using a laptop PC via KUSB-488A interface using a Labview program. During the electronic measurement under high temperature, the pores of AAO template with Bi nanowires are placed by the level, and two sides of pores are obturated.

3. Results and discussion

Fig. 1a shows the typical FE-SEM image of Bi nanowires embedded in the pores of AAO template. It can be seen from Fig. 1a that high filling, ordered and uniform Bi nanowires are obtained. The nanowires have filled the pores of the AAO, implying that the diameter of Bi nanowires is the same as the diameter of pores. The corresponding TEM image is shown in Fig. 1b, indicating that Bi nanowires have the uniform-diameter. The XRD pattern of the as-prepared Bi nanowires is shown in Fig. 2. One can see that the positions of the peaks for Bi nanowires are all in good agreement with those of the standard diffraction peaks of Bi (JCPDS, 44-1246), which indicates that Bi nanowires are rhombohedral lattice structure. The intensity of these peaks has no obvious difference, which indicates that Bi nanowires have no preferred orientation and are polycrystalline structure.

In our experimental, the characteristic of the sample geometry do not allow four-point measurements of the resistance and only two-probe measurement is feasible by bringing two silver wires with silver paste to a small area on both sides of the AAO template. In order to understand the contact mode between Bi nanowires and the measurement electrode, we measure the I–V curve of Bi nanowires filled in the pores of AAO before the fusion, which is shown in Fig. 3. From their I–V curves, the electronic transport of the Bi nanowires presents symmetric and linear behaviors, which indicates that Bi nanowires and the measurement electrode forms ohmic contact before the fusion. Using the same method, we also analyze the contact mode between the melting Bi nanowires and the measurement electrode. The correlative results are shown in Fig. 4. From their I–V curves, the melting Bi nanowires and the measurement electrode also forms ohmic contact. The change trend of I–V curves shows that with the increase of the temperature the curve slope increases for the melting Bi nanowires. That is to say, the resistance of the melting Bi nanowires decreases with the increase of the temperature.

In order to know the change trend of Bi nanowires during the increase of the temperature, we use Keithley-2400 to measure the current under the invariable voltage of 4.0 V with the increase of the temperature. Here, the holistic resistance of Bi nanowire array is calculated. According to the measurement results, the resistance $R(T)$ of Bi nanowires can be obtained under the different temperatures. Fig. 5 shows the temperature dependence of the resistance

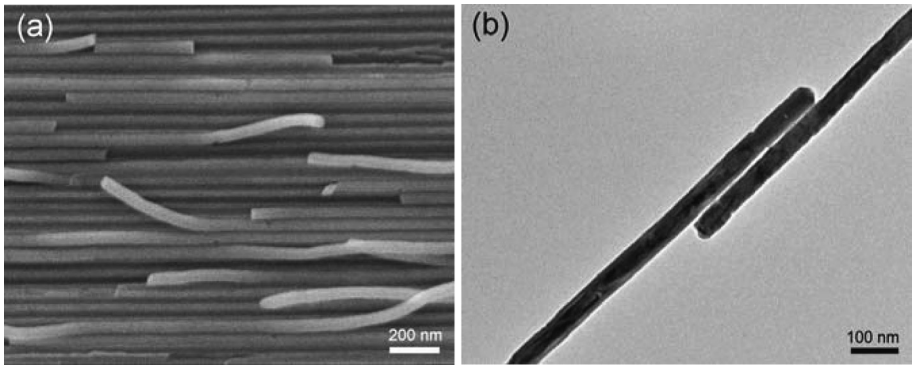

Fig. 1. FE-SEM and TEM images of Bi nanowires: (a) FE-SEM image for the side of the sample after breaking AAO; (b) the corresponding TEM image shown in (a).