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ORIGINAL ARTICLE

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A novel method of centrifugal processing for the synthesis of lead–bismuth eutectic alloy nanospheres and nanowires

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Abstract In the present study, lead–bismuth (Pb–Bi) eutectic alloy nanospheres and nanowires were fabricated using a process based on centrifugal force. When various centrifugal forces were applied, nanospheres and nanowires were formed on/inside the highly ordered anodic aluminum oxide (AAO) templates. The X-ray diffraction spectrum showed that nanoscale wires were composed of Pb_7Bi_3 and Bi phases. The scanning electron microscopy (SEM) images proved the formation of nanospheres and nanowires on/inside the alumna channel templates. During centrifugation, the repulsive force between the nanochannel and the alloy melt was calculated from the surface tension on the ultra-fine tube. The force applied to the melt of Pb–Bi inside the AAO was controlled by the centrifugal force.

Keywords Lead–bismuth eutectic · Nanosphere · Nanowire · Centrifugal force · Anodic aluminum oxide template · Ultra-fine tube

Nomenclature

AAO	Anodic aluminum oxide
l	Liquid length of injection
γ	Surface tension of liquid
θ	Contact angle between liquid and substrate
ΔP	External pressure forcing the liquid into the channel
r	Radius of channel
η	Viscosity of liquid
ε	Coefficient of slip
F	Centrifugal force
ω	Angular speed of the centrifuge
m	Sample weight
R	Rotation radius of the centrifuge

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1 Introduction

In recent years, nanostructure materials have inspired great interest in fundamental study and in high-tech industry, as they are expected to exhibit very different properties from their bulk forms. Low-dimensional systems represent one of the most important fields in advanced materials research. The quantum confinement effect in low-dimensional systems not only provides a forceful tool for managing their optical, electrical, and thermoelectric properties [1–3], but it also creates possibilities for nanotechnological applications [4].

Applications of nanowires in the future include integrated circuits, nanosensors, nanodevices, nano-thermocouples, and so on. Nanospheres are a kind of useful solder for joining nanowires together; additionally, nanoscale spheres have potential applications to serve as devices such as single-electron transistors, memory units, sensors, optical detectors, thermoelectric chips, and catalyzers. Metal and semiconductor nanomaterials can be synthesized by several methods, such as electrodeposition [5, 6], the sol gel method [7], chemical vapor deposition [8, 9], physical vapor deposition [10, 11], the vapor–liquid–solid method [12], thermal evaporation [13–15], and the rapid solidification process [16], etc. The procedure studied in this paper, namely, the centrifugal process, is considerably different from electrochemical and vapor methods. Its advantages are as follows: (1) the composition of alloys can be maintained correctly; (2) the operating conditions are easy

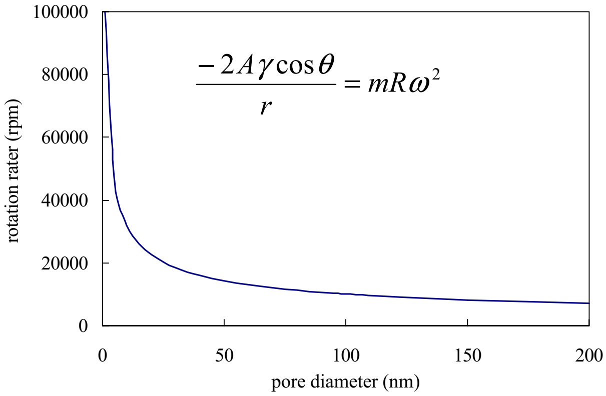

Fig. 1 Curve of rotation rate with pore size when melted lead–bismuth (Pb–Bi) eutectic alloy is injected to the nanochannel

to use and maintain; and (3) the process is efficient. Moreover, applying a force is much more antipolluting than using an electrolyte, and this process is more suitable for fabricating nanostructures within a large area.

Current literature is not available on the use of a centrifugal force to fabricate nanospheres and nanowires. In this study, the lead–bismuth (Pb–Bi) nanoscalar spheres and wires were fabricated using the novel technique of vacuum melting and centrifugation, which could generate isolated, uniform nanospheres or continuous, straight, and dense nanowire arrays. Washburn [17] declared relationships between the surface tension and the contact angle. The length of the injection with time is given by:

$$l^2 = \frac{\left(\Delta P + \frac{2\gamma}{r}\cos\theta\right)\left(r^2 + 4\varepsilon r\right)t}{4\eta}$$

where ΔP is the external pressure, γ is the surface tension of the liquid, θ is the contact angle, r is the radius of the channel, η is the viscosity of the liquid, and ε is the coefficient of slip. At the critical condition, $l \approx 0$, $\Delta P + \frac{2\gamma}{r}\cos\theta = 0$. The required pressure ΔP to overcome the surface tension for the liquid material to fill the pores with a radius of r can be determined as $\Delta P = -\frac{2\gamma}{r}\cos\theta$.

2 Experimental details

To investigate the properties of a zero-dimensional (0D) quantum dot system and a one-dimensional (1D) quantum wire system, a template was used to fabricate a variety of material nanospheres and nanowires. The template, generated by anodizing a purity Al substrate (99.7%) in 0.3 M oxalic acid electrolyte, was porous anodic aluminum oxide (AAO).

Our method was based on the vacuum melting and centrifugal processing of melted metal. It was applied with a large force to push the melt into the AAO template. The investigated Pb–Bi eutectic alloy was prepared by a weighing method under an ultra-vacuum. The purity of the initial lead and bismuth was 99.99 mass%, while the content of impurities did not exceed 10^{-3} mass% in each of them. Then, a piece of Pb–Bi eutectic alloy and AAO template were put in a titanium tube, within which the vacuum pressure was maintained at 10^{-6} Torr, using the molecular turbo pump to prevent the active metal oxidation. The titanium tube was heated up to the melting point of alloy before it was put on the centrifuge. The melt of Pb–Bi eutectic alloy was dispersed on the AAO template and the centrifugal force determined whether nanospheres or nanowires were formed on/inside the AAO template.

In this experiment, the centrifugal radius was 2 cm and the total mass of the titanium tube, AAO, and metal were fixed at 10 g. The centrifugal force was calculated from the centrifugal formula. The diameter of the nanochannel at particular rates of rotation was decided from the Washburn equation and the centrifugal formula.

The morphology and crystal structure of the isolated Pb–Bi eutectic nanospheres and nanowires were characterized by scanning electron microscopy (SEM, JSM-6500F) and X-ray diffraction (XRD, D/max 25.50 V, Cu kα radiation). The diameter distribution of nanospheres on the template was assessed using Matlab, a tool for performing numerical computations.

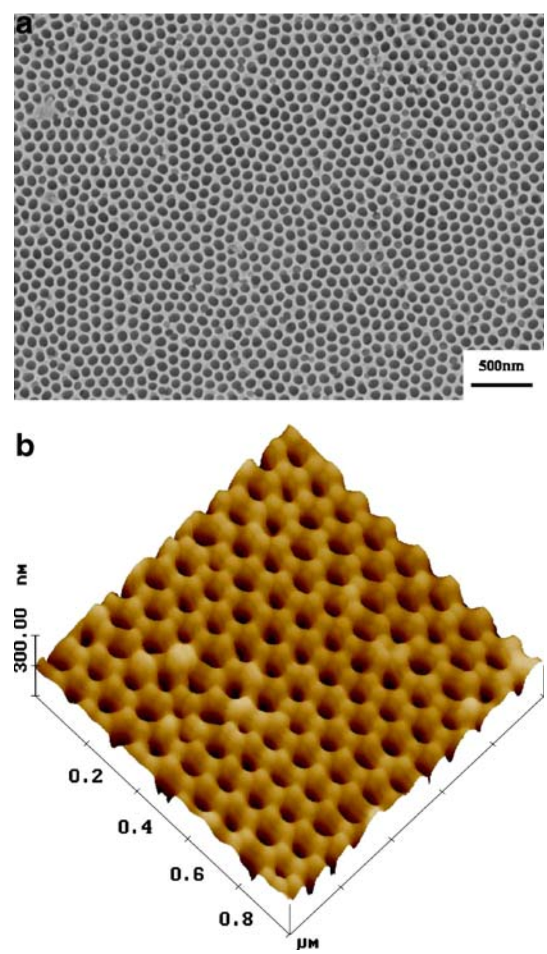

Fig. 2 **a** Scanning electron microscopy (SEM) image of the AAO template with ordering pore diameter of 80 nm. **b** Three-dimensional atomic force microscopy (AFM) tapping mode image of the patterned surface after anodization

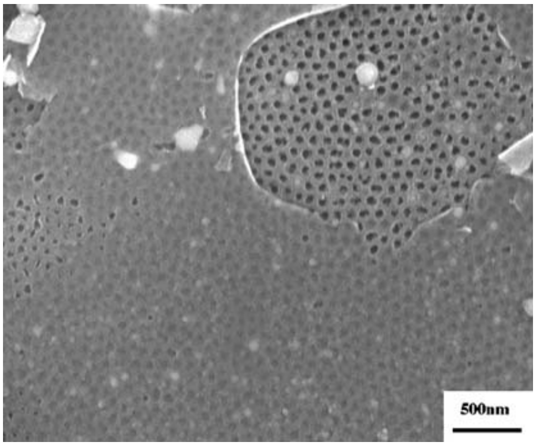

Fig. 3 Thin film spread out on the AAO template when the applied centrifugal force was 19.7 N (3,000 rpm)

3 Results and discussion

Since liquid Pb–Bi eutectic alloy has a high surface tension (410.5 dyne/cm) at 300°C [18], a high rotation rate was needed to force liquid Pb–Bi eutectic alloy to enter the nanochannels of the AAO template. The simplified equation, $\Delta P = -\frac{2\gamma}{r}\cos\theta$, could be used to estimate the extra pressure required to form Pb–Bi eutectic nanowires 80 nm in diameter, where γ is the surface tension of liquid Pb–Bi eutectic alloy and θ is the contact angle between the liquid Pb–Bi eutectic alloy and the AAO template. In this research, γ is 410.5 dyne/cm and θ is 105.8°.

The centrifugal force is a physical force that increases with the rate of rotation, centrifugal radius, and the sample mass on the centrifuge. The centrifugal force [19–23] is given by:

$$F = mR\omega^2 \tag{1}$$

where F is the centrifugal force (N), m is the sample weight (kg), R is the radius of the centrifuge (m), and ω is the angular speed (rad/s). In the experiment herein, the mass of the sample was 10 g, the radius of centrifugation was 2 cm, and the sample area (A) in this experiment was 1 cm^2. Therefore, the centrifugal force can be expressed as:

$$\frac{-2A\gamma\cos\theta}{r} = mR\omega^2 \tag{2}$$

In the foregoing equation, the relationship between the rate of rotation and the diameter of the pores can be calculated, as indicated in Fig. 1. The critical rate of rotation for the

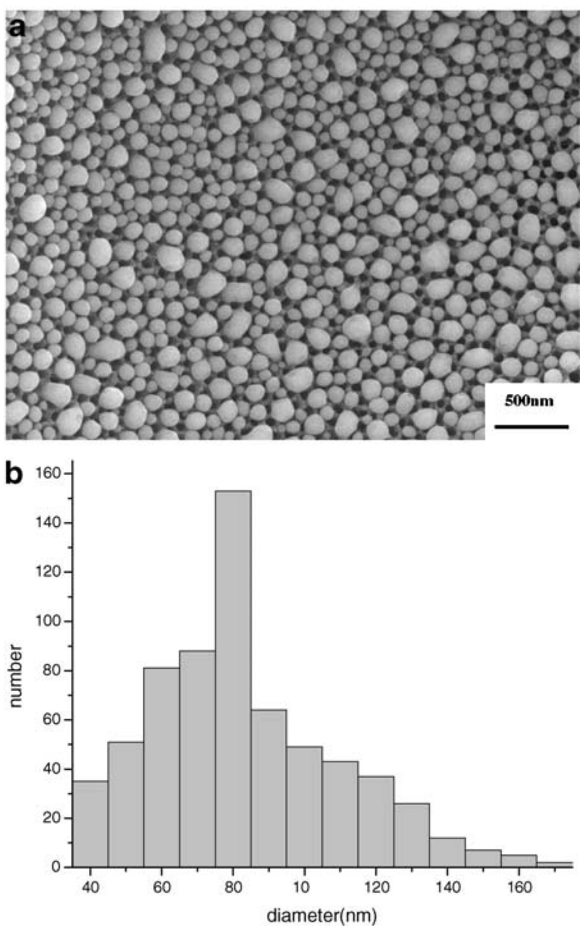

Fig. 4 **a** Isolated nanospheres on the AAO template when the applied centrifugal force was 140.3 N (8,000 rpm). **b** Diameter distribution of the nanospheres

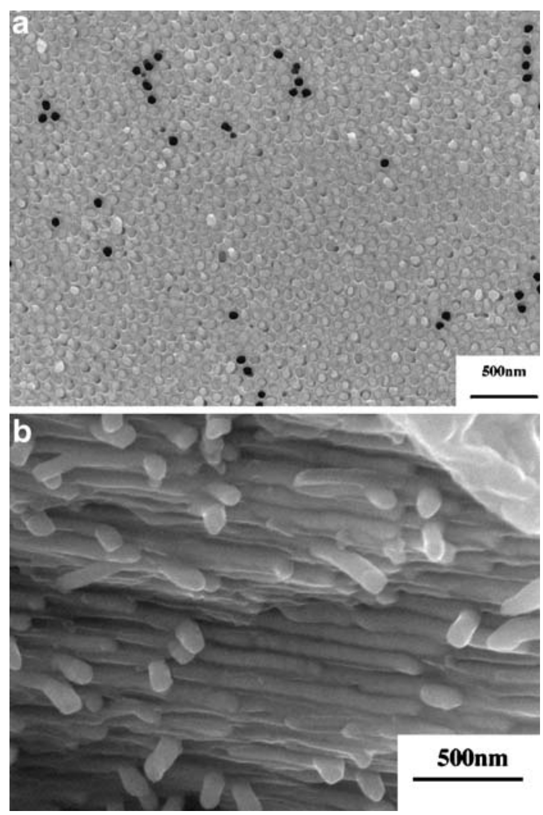

Fig. 5a, b The nanowires were formed inside the AAO template when the applied centrifugal force was 633.9 N (17,000 rpm). The SEM images of the Pb–Bi eutectic nanowires: **a** plane view; **b** cross-section view

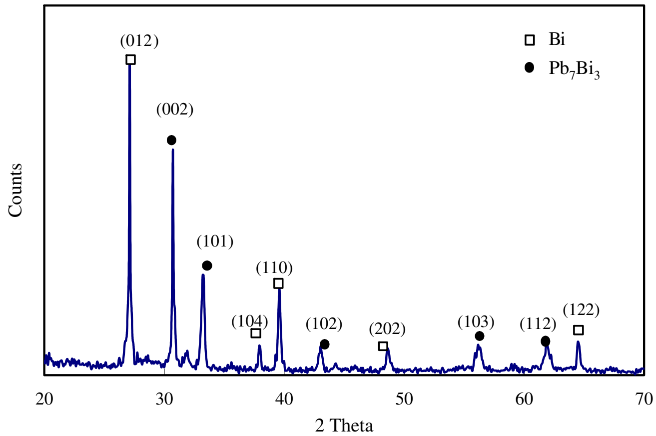

Fig. 6 The X-ray diffraction (XRD) spectrum of Pb–Bi eutectic nanowires consisted of Pb_7Bi_3 and Bi phases

formation of nanowire inside the AAO template with an 80-nm pore size is 15,963 rpm, and the centrifugal force is 558.9 N.

Due to the heating and high-pressure process, the substrate must be chemically stable and able to maintain its porous structure. Therefore, AAO film is a typical material used as a template. Figure 2a, a typical plan view of an SEM micrograph of the AAO template, shows that the pores were regularly arranged and their size was 80 nm. A topographical image of the surface of the AAO template taken with atomic force microscopy (AFM) also indicates the six cusps which formed at the hexagonal corners of each pore, as shown in Fig. 2b.

In addition, the centrifugal process is a rapid solidification process, and it is possible to fabricate nanomaterials with various features. When the rate of rotation reached 3,000 rpm, the thin film of the Pb–Bi eutectic alloy was spread out on the AAO template, as shown in Fig. 3. When the rate of rotation was increased to 8,000 rpm, nanospheres formed, as shown in Fig. 4a. The AAO template provided positions for the nucleation of the formation of nanospheres when the centrifugal force was sufficiently high to disperse melted Pb–Bi eutectic alloy throughout the pores of the AAO template. Figure 4b reveals that nanospheres have a narrow distribution in diameter by numerical computation. The mean diameter of nanospheres is 82.7 nm, and this value also corresponds with the pore size of the AAO template. Moreover, the critical rate of rotation for the formation of nanowire into AAO is 15,963 rpm. In order to produce a dense Pb–Bi nanowire and improve the filling ratio, a higher rotation rate (17,000 rpm) is needed. The Pb–Bi eutectic nanowires were formed and the filling ratio was almost 100%, as shown in Fig. 5a,b. In the binary phase diagram, the eutectic phase of Pb–Bi alloy is consisted of the Pb_7Bi_3 and Bi phases. In Fig. 6, the diffraction pattern proves that the crystal phase structure of the nanowires and the XRD spectrum identified the composition of nanowires in agreement with the theoretical values.

4 Conclusions

Lead–bismuth (Pb–Bi) eutectic alloy nanospheres and nanowires were successfully fabricated on/inside the anodic aluminum oxide (AAO) template by the convenient process of centrifugation. The critical pressure and the rate of rotation to form nanowires inside the AAO template with diameter 80 nm were 55.89 bar and 15,963 rpm, respectively. The experimental results demonstrate that, when the centrifugal force was 19.7 N (3,000 rpm), the thin film of Pb–Bi was spread out on the AAO template. When the force was 140.3 N (8,000 rpm), nanospheres were formed. When the force was increased to 633.9 N (17,000 rpm), the melted Pb–Bi inside the AAO template formed nanowires. Additionally, the composition of Pb–Bi eutectic alloy nanowires was Bi and Pb_7Bi_3 detected by X-ray diffraction (XRD). Furthermore, the nanospheres and nanowires were fabricated using a method that was cost-effective, simple, and efficient.

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