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Fabrication of single-crystal tin nanowires by hydraulic pressure injection

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Tin (Sn) nanowires, with 15 and 60 nm average diameter and up to 10 μm in length, were fabricated by an injection process using a hydraulic pressure method. The Sn melt was injected into an anodic aluminium oxide (AAO) template and solidified to form nanowires. By back etching the aluminium substrate and barrier layer, the nanowire array ends were partially exposed from the bottom face of the AAO template. The filling ratio of nanowires inside and through the thickness of the AAO template was found to be close to 100%. The nanowires were also found to be dense and continuous with uniform diameter throughout their length. Transmission electron microscope (TEM) and x-ray diffraction (XRD) studies on the 60 nm diameter nanowires revealed that the nanowires were single crystals with body-centred-tetragonal (bct) structure predominantly growing along the [100] direction. The current method of synthesizing nanowires is straightforward, low-cost and suitable for low-melting point ($<650\text{ }^{\circ}\text{C}$) metals including low-melting point alloys with stoichiometric composition.

1. Introduction

With the continued demand for miniaturization of electronic and optical devices, nanowires with enhanced mechanical and electrical properties are needed. To develop scaled-up functional devices highly ordered nanowire arrays are essential. Many candidate materials (metals, alloys, metal oxides and semiconductors) have been studied for various potential applications in nanotechnology and have shown some promising results [1–6]. In this work, tin (Sn) nanowires were fabricated using a pressure injection method, and their properties were characterized. The study of Sn nanowires has been motivated by the attractive properties of bulk Sn and the novel properties of nanostructures such as nanowires. Bulk Sn has excellent ductility, electrical conductivity, resistance to corrosion and has been extensively used in the electronics industry

[7–11].

Sn-based alloys are also among the most promising lead-free solders. On the other hand, recent experimental studies have shown some unique superconductivity and magnetization properties of Sn nanowires [5, 12, 13]. In addition, through oxidation of Sn nanowires, sensitive single SnO_2 nanowires can be synthesized for gas sensors [14]. Therefore, it is of interest to investigate whether cost-effective and efficient manufacturing methods for Sn nanowires maintain or even enhance the physical properties of bulk Sn at the nanoscale. Metallic nanowires, including Sn, have been widely produced by the electrodeposition process [2, 3, 5, 7, 13–27] using anodic aluminium oxide (AAO) templates. Relative to other deposition techniques such as chemical vapour deposition (CVD), the electrodeposition technique has been proven to be a

low-cost and a high-yield method for producing nanowires from different materials [17]. However, there are some drawbacks associated with most electrodeposition processes, including lack of nanowire length uniformity and length control. Another major challenge with electrodeposition is that the success of the process is highly dependent on finding the appropriate chemical precursor. A different approach that has been utilized for fabricating metallic nanowires and which overcomes most of the problems associated with deposition processes is based on an injection method. In this method, a molten metal is impregnated into the nanochannels of the AAO template. Various metallic nanowires (Sn, Bi, Al, In) with diameters larger than 200 nm have been fabricated by the injection method [18]. Recently, the use of a hightemperature gas pressure chamber has enabled the injection of bismuth (Bi) melt into AAO templates as small as 13 nm in diameter [19-20]. The smallest diameter nanochannel that can be filled is constrained by the maximum pressure the gas chamber can sustain and operate at safely. When a pressure higher than the chamber maximum is necessary, wetting agents with poor solubility in the molten metal are added to lower the surface tension of the molten metal and hence reduce the required injection pressure [20]. This article presents a hydraulic pressure injection method as an alternative to the aforementioned gas pressure injection, capable of achieving higher pressure ranges to inject molten Sn into nanochannels as small as 15 nm in diameter, without the aid of a wetting agent. The fabrication of Sn nanowires and their structural characterization are the focal points of this paper.

2. Experimental procedure

2.1. Fabrication of AAO template

Anodic aluminium oxide (AAO) templates with average channel diameter of 60 and 15 nm and thickness of 10 μm were fabricated by one-step anodization. The templates were generated by anodizing a commercial aluminium (Al, 99.7%) substrate. The 60 nm pore diameter

template (denoted as AAO60 hereafter) was then fabricated by anodizing the polished Al substrate at 40 V in 3 vol% oxalic acid. The anodization for the 15 nm pore diameter template (denoted as AAO15 hereafter) was performed at 18 V in 10 vol% sulfuric acid. More detailed description of the process can be found elsewhere [21]. It should be noted that the Al substrate was not removed after anodization; it was kept to serve as padding for the fragile porous AAO template during the injection process.

2.2. Fabrication of nanowires by hydraulic pressure injection

The nanowires were fabricated by vacuum melting and pressure injection of the Sn melt into the nanochannels of the AAO template. The vacuum hydraulic pressure injection set-up has been described previously [22]. The external pressure for the AAO60 and AAO15 templates was estimated to be ~ 350 and ~ 1400 bar, respectively. For the fabrication of Sn nanowires, a disc-shaped Sn foil was placed on the top side of the AAO template and both were put inside a mould. The mould, containing the AAO/Sn foil, was then placed inside a vacuum chamber and heated up to the melting temperature of Sn (230°C) using a hot plate. The hot chamber was removed from the hot plate and pressure was applied on the melt, through the sliding column of the chamber, using a hydraulic jack to impregnate the molten Sn into the nanochannels of the AAO template. The chamber was immediately placed in cold water to cool down for a period of 10–15 min to solidify the impregnant inside the nanochannels.

The filling ratio of the hydraulic injection method was investigated by examining the top and bottom surfaces of the Sn-filled AAO template. The top face of the AAO template was studied after mechanically removing (peeling by hand) the excess surrounding bulk Sn from the top surface of the Sn-filled AAO template. To examine the bottom surface of the AAO template, the Al substrate was first removed with a CuCl_2 -based solution [23] which revealed the barrier layer that capped the nanochannels. The barrier layer and a few nanometres of AAO template were etched away using NaOH solution which exposed the

ends of the nanowires. Free-standing Sn nanowires were collected after the AAO template was dissolved thoroughly in 0.4 M H_3PO_4 + 0.2 M CrO_3 mixture solution at $\sim 60^\circ\text{C}$ for 1 h [23]. The released nanowires were suspended in isopropanol and dispersed by sonication. The morphology of the top and bottom surfaces of Sn-filled AAO template, after the injection process and various etching procedures, were studied using an SEM (FE-SEM, Zeiss 1530). The crystal structure of the Sn nanowire arrays was determined by using an advanced powder diffractometer (XRD, Bruker D8). Differential scanning calorimetry (DSC, PerkinElmer Pyris 1) was used to determine the melting point of both the precursor bulk Sn and Sn nanowire arrays. A TEM (JEOL 2010) was employed to characterize the crystallinity and growth orientation of free-standing Sn nanowires.

3. Results and discussion

3.1. Sn nanowires

Figure 1 shows SEM micrographs of the top surface of an AAO60 template after the injection of molten Sn. When the applied pressure was equal to the estimated value (350 bar), the filling ratio was found to be only about 60% (figure 1(a)). The filling ratio improved to almost 100% (figure 1(b)) by increasing the applied pressure to about 700 bar. Even though other pressure values between 350 and 700 bar might have equally improved the filling ratio, because 700 bar was within the capability of the apparatus, a decision was made to double the applied pressure in order to ensure the maximum filling ratio. One plausible explanation why a higher pressure value than the value estimated from the analytical expression (Washburn equation) was needed for complete filling is the possibility of not having complete molten state of the Sn metal just before injection. Although the nominal reading of the thermocouple in the apparatus was the expected melting temperature of Sn, the position of the thermocouple inside the chamber and possible thermal gradients in the chamber may have led to a thermocouple reading overestimating the actual temperature of the Sn metal.

Figure 2 shows a range of etching times and their corresponding morphologies for AAO60 that was etched by 0.2 wt% NaOH at 23°C . When the barrier layer was etched for 120 min, nanochannels were opened exposing the tips of the nanowires, as shown in figure 2(a). Increasing the etching period to 150 min dissolved the barrier layer completely and the tips of the nanowires stuck out a few nanometres (figure 2(b)). As the etching time was further increased to 180 min, the pore walls started to break down, leading to Sn nanowires adhering to each other (figure 2(c)). The AAO template was completely dissolved after 210 min of etching and the nanowires collapsed on the Al substrate as shown in figure 2(d). Similarly, the morphologies of the etchings of Sn-filled AAO15 template are illustrated in figure 3. Since the barrier layer of the AAO15 template was thinner than that of the AAO60 template, the etching time required to expose the nanowire tips after completely removing the barrier layer of the AAO15 sample was 30 min (figure 3(a)), in contrast to the 150 min needed for the AAO60 sample (figure 2(b)). The thickness of a barrier layer is determined mainly by the anodizing voltage although there is a slight deviation depending on the anodization electrolyte and temperature. Early experimental studies on the morphology and mechanism of pore formation on aluminium films showed that the barrier layer thickness is proportional to the anodization voltage [24]. According to the correlation between the barrier layer thickness and anodizing voltage given in the literature [24], the thickness of the barrier layer of the templates used in this study are estimated to be 18 nm and 40 nm for AAO15 and AAO60 templates respectively, and hence the significant difference in etching time.

3.2 DSC, TEM and XRD studies of nanowires

Differential scanning calorimetry (DSC) studies were carried out to examine the size-dependent and dimension-dependent melting behaviour of Sn nanowires embedded in the AAO template. Figure 4 compares results of the Sn nanowires embedded in the AAO matrix with that of bulk Sn. The melting point shows a slight reduction as the

nanowire diameter decreases from 60 to 15 nm. Various researchers [23–26] have shown that low-dimensional crystals, including metallic nanocrystals, embedded in a matrix can melt below or above the melting point of their corresponding bulk crystal. The embedded nanocrystals could be spherical particles, thin films, disc-like particles or nanowires. The enhancement or reduction of the melting temperature was found to depend on the nature of the interface structure between the embedded nanocrystals and the matrix. For an incoherent interface, where there is no lattice matching between the two interfacing phases, the melting point was found to decrease as a function of the size of nanocrystals. Both theoretical predictions and experimental results for Sn nanocrystals indicate that the reduction in the melting point was especially significant for nanocrystals whose radius was less than 15 nm [25]. In the current study, the interface between the AAO template and the Sn nanowires is incoherent because there is no interaction between the two phases since the AAO template is essentially stable at temperatures lower than 800 °C [26].

X-ray diffraction (XRD) was used to study the phase and crystal structure of the Sn nanowire arrays. The XRD experiment was performed on the bottom face of the AAO/nanowire composite after removing the Al and barrier layer. The XRD patterns, as shown in figure 5, were indexed to the body-centred-tetragonal (bct) β -Sn structure. All the observed peaks, both for the AAO60 and AAO15 samples, were found to match very closely to the standard polycrystalline β -Sn (JCPDF, 4-673). For the AAO60 sample, the intensity for (200) was almost 4.0 times higher than that of the secondary peak (101). This is higher than expected as the ratio of the intensities of (200) and (101) for polycrystalline β -Sn is 1.1. On the other hand, for the AAO15 sample, the relative intensities of the peaks were very similar to that from the standard polycrystalline β -Sn with no preferred orientation. The reason for this is not clear yet, but further investigation is underway. A transmission electron microscope (TEM) was employed to further study the morphology, crystallinity and growth orientation of

individual nanowires. TEM micrographs taken from various randomly selected 60 nm diameter Sn nanowires revealed that the nanowires were dense, continuous, and uniform in diameter along the length of the nanowire. A typical TEM micrograph of a randomly selected individual nanowire is shown in figure 6. Selected-area electron diffraction (SAED) patterns taken along the length of a 60 nm diameter nanowire showed the same single set of ED patterns along the length of the wire, verifying single crystallinity of the nanowires. After analysing several SAED patterns from randomly selected nanowires, it was concluded that although other directions were observed, the growth direction for the majority of the wires was along [100]. This is basically in good agreement with results reported previously where it was found that the majority of the Sn nanowires synthesized by electrochemical deposition also had preferred [100] growth direction. From the XRD and TEM observations, it can be deduced that the nanowires in the AAO60 sample are predominantly oriented along the [100] direction. In addition, from the current results and earlier reported results it appears that regardless of the fabrication process [100] may be the preferred growth direction for Sn nanowires in the 40–160 nm diameter range.

4. Summary

Sn nanowires with 15 and 60 nm diameter were successfully fabricated by injecting molten Sn into the nanochannels of an AAO template by applying hydraulic pressure. SEM and TEM examination of the Sn nanowires showed that the nanowires were dense and continuous, with uniform wire diameter along their entire length. Structural characterization on the 60 nm diameter Sn nanowire arrays and freestanding nanowires through XRD and using a TEM revealed that the nanowires are highly oriented along the [100] direction. DSC results showed that the melting point decreased with the decrease of the nanowire diameter.

The major limitation of this method arises mainly due to the Al substrate, whose melting temperature is 660 °C. Although the AAO template is stable up to 800 °C, the Al

substrate that should remain attached to the AAO template during the injection process would not stand temperatures higher than its melting temperature. However, this fabrication process can be readily extended to low-melting point ($<650\text{ }^{\circ}\text{C}$) metals as well as alloys with stoichiometric composition.

Acknowledgments

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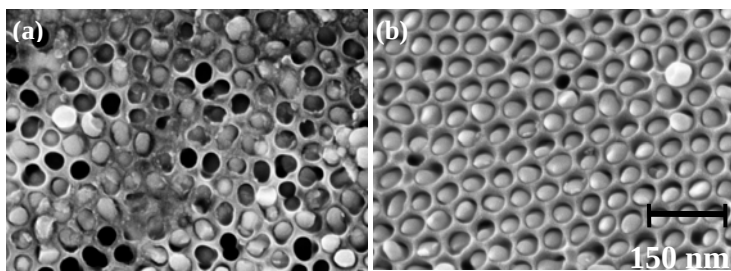


Figure 1. SEM micrograph taken from the top surface of AAO60 samples injected pressure of (a) 350 bar and (b) 700 bar.

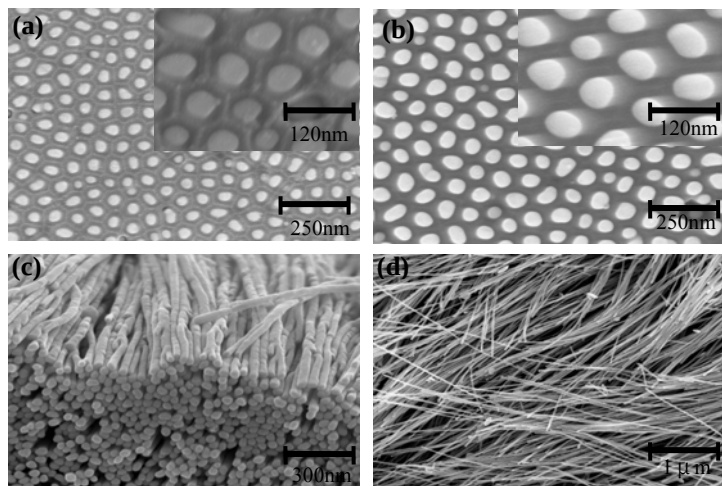


Figure 2. SEM images of the bottom surface of an AAO60 sample after the barrier layer was removed by 0.2 wt% NaOH at 23°C for (a) 120 min, (b) 150 min, (c) 180 min, (d) 210 min.

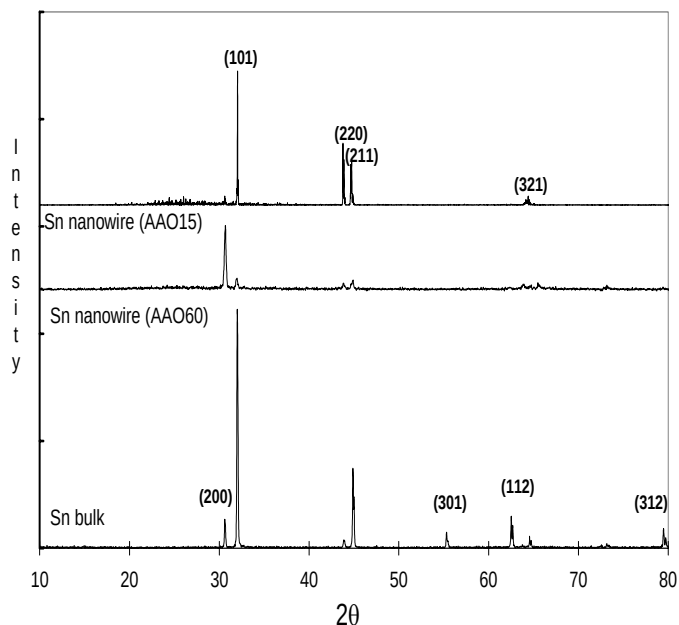


Figure 5. XRD patterns of large scale AAO/Sn nanowire composite.

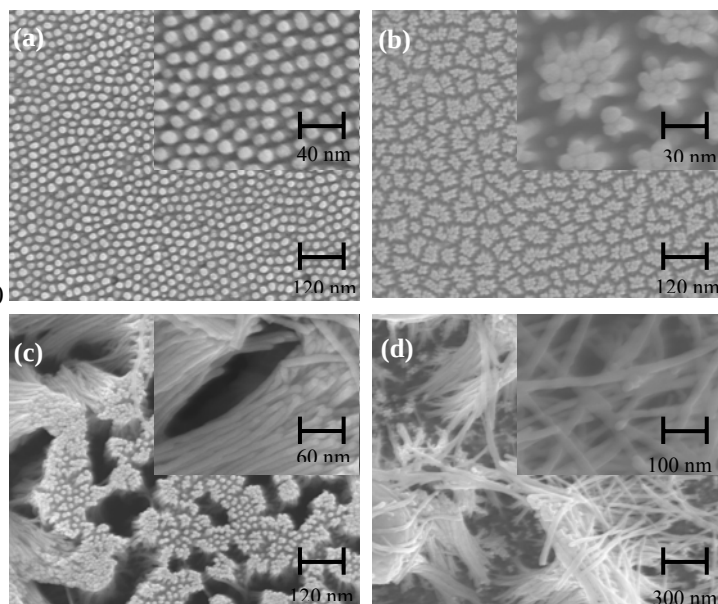


Figure 3. SEM images of the bottom surface of an AAO15 sample after the barrier layer was removed by 0.2 wt% NaOH at 23°C for (a) 30 min, (b) 40 min, (c) 50 min, (d) 60 min.

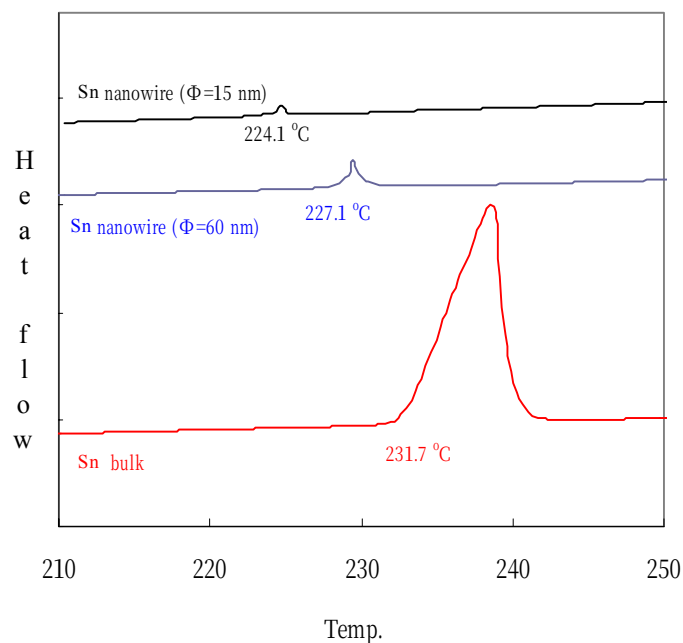


Figure 4. DSC curves of the melting point on bulk Sn is 231.7 °C, 60 nm diameter and 15 nm diameter Sn nanowires decrease to 227.1 °C and 224.1 °C.

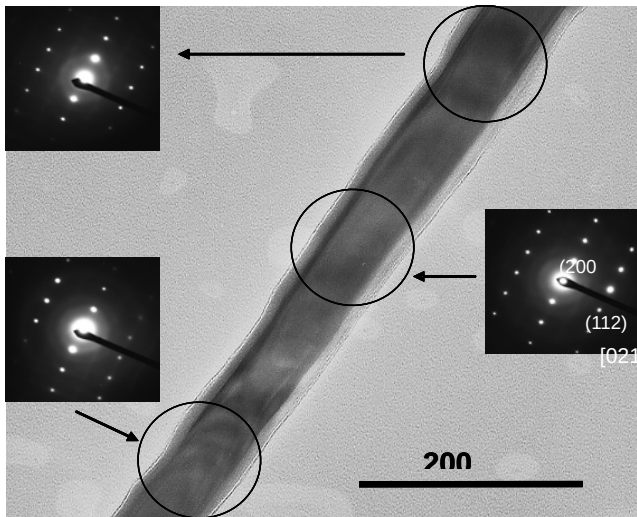


Figure 6. TEM micrograph of a randomly selected single nanowire (60 nm). The black circles indicate the areas from which the electron diffraction pattern (ED) was taken. Note that the ED patterns remain the wire length. The zone axis in this case was [021] and the growth direction is [100].