Research Article

Nanowires of Lead-Free Solder Alloy SnCuAg

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1. Introduction

Recently, a number of methods have been developed to fabricate one-dimensional or linear nanostructures, namely, nanotubes and nanowires [1–5]. In the electronic sector, nanowires and nanotubes are attractive nanostructured materials for electronic, optoelectronic, and sensor applications because of their unique properties [1–9]. However, one of the main problems is the nanoscale contact in these nanowires.

As an essential part of electronic circuits, soldering has been made with materials containing Pb until the beginning of 2000. Pb-based materials show good mechanical properties and low melting temperature. Since Pb-based materials have toxic properties and may be harmful for health and the environment, interest in and production of lead-free solder materials have increased enormously. More recently studied lead-free solder materials include Sn96Ag3.5 [10, 11], Sn99.5Cu0.7 [12], Sn42Bi58 [13], Sn48In52 [14], SnSb [15], Sn91Zn9 [16, 17], Sn95.5Ag3.8Cu0.7 [18], and Sn63Cu37Ni [19]; the melting temperatures of these materials are 221°C, 217°C, 138°C, 118°C, 235°C, 199°C, 217°C, and 227°C, respectively. Among these solder material alternatives, SnAgCu has begun to be used for making microscale contacts due to its better creep-fatigue resistance and microstructural stability [20].

Technology is developing as a result of the miniaturization of devices as well as the production of nano-sized circuits. Lead-free solder materials have been extensively produced in bulk, powder and thin film forms by different methods over the past decade. Different kind of solder nanowires such as Sn, In, Sn-Ag, Au-Sn, Cu-Sn, Sn-Au-Ni-Au-Sn have been synthesized directly using an electrodeposition method in nanoporous templates [21–23]. However, for nanoscale soldering, SnAgCu material in the form of nanowires is required for production, but until now no studies have been performed on this material. In this work, SnCuAg nanowires have been fabricated by electrodeposition in structured nanoporous Al2O3 using various values of the deposition potential.

2. Experimental

A three-electrode cell was used for the electrochemical experiments. The volume of the electrochemical bath was approximately 85 mL. An Ag/AgCl electrode (BAS, 3 M NaCl, and −35 mV versus SCE at 25°C) was used as the reference electrode. Anopore Aluminum Oxide (AAO) membranes, with specified pore diameters of approximately 200 nm and pore length 60 μm, were used as a cathode, with an exposed area of approximately 1 cm² for the nanowire synthesis. These membranes were supplied by the Whatman Company. Before the electrodeposition, one side of the AAO templates was coated with Au to a thickness of 5–10 nm and stuck on...
was performed over the potential range −0.75 V to −2 V, versus Ag/AgCl. The bath pH was adjusted to 4 by adding 0.1 mM HCl or 0.1 mM NaOH while reagent-grade chemicals in distilled water. The bath pH was given in Table 1. All solutions were prepared by dissolving carbon disc on copper plate for electrical contact. A platinum electrode approximately 5 times larger than the cathode was used as an auxiliary electrode. The bath contents are listed in Table 1 (colour online).

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration</th>
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<tbody>
<tr>
<td>SnCl₂ · 2H₂O</td>
<td>40 mM</td>
</tr>
<tr>
<td>CuCl₂ · 2H₂O</td>
<td>1 mM</td>
</tr>
<tr>
<td>Ag(NO₃)₂</td>
<td>5 mM</td>
</tr>
<tr>
<td>C₆H₁₇N₃O₇ 95 mM</td>
<td></td>
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</tbody>
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<table>
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<tr>
<th>Operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bath pH 4</td>
</tr>
<tr>
<td>Bath temperature = room temperature</td>
</tr>
<tr>
<td>Deposition duration = 180 min</td>
</tr>
<tr>
<td>Deposition potential = −0.75 V to −2 V, versus Ag/AgCl</td>
</tr>
<tr>
<td>Agitation paddle (5 cycles/s)</td>
</tr>
</tbody>
</table>

Figure 1: Cyclic voltammograms of Sn-Ag-Cu at 25 mV/s from the bath solution in Table 1 (colour online).

Differential scanning calorimetry (DSC) was performed in a nitrogen atmosphere with a heating rate of 10°C min⁻¹, using a Shimadzu DSC-60 thermal analyzer.

3. Results and Discussion

A typical cyclic voltammogram for the CV plating of SnAgCu deposition is shown in Figure 1. The CV curve generally shows three reaction regions corresponding to cathodic deposition, no reaction, and anodic oxidation processes, as previously described [24]. In Figure 1, at potentials negative to −0.8 V, on both the positive and negative sweeps, a cathodic current is clearly found, indicating that tin, silver, and copper ions can be deposited into the AAO template. It was observed that neither cathodic deposition nor anodic oxidation occurs when electrode potentials are larger than −0.75 V. The growth rate increases suddenly at potential exceeding −1.25 V.

Figure 2 shows the current behavior as a function of deposition potential during the electrodeposition of nanowires. Electrodeposition curves were obtained in a stirred electrolyte at pH 4. The current versus time plot shows that growth of the nanowires was often not a steady-state process, and it appears that there was significant current oscillation as the voltage was applied to the cathode. At the first stage of the current–time transient curve, the increase in the current when the pores are empty is strongly dependent on the deposition potential. Then the current falls gradually with filling of the pores although there were broad peaks overlapping the decaying current with decreasing deposition potentials. The growth rate increases suddenly at potential exceeding −1.25 V (Figure 2).

It is well known that bath contents and electrochemical deposition parameters have great effects on characteristics of nanowires such as length, appearance. The higher growth
rate corresponds to faster metal ions on the tip of the nanowire surface to higher charge density there. Some bubbles are trapped in the nanowire because of higher deposition potentials of $-1.5$, $-1.75$, and $-2$ V. These bubbles electrolyze the water and make the surface rough. The morphology of the SnAgCu nanowires for various values of deposition potential are shown in Figure 3, after complete dissolution of the membrane in 1 M NaOH for 7 minutes. The diameter and length of regular nanowires electrodeposited at $-1$ V were determined to be approximately 200–250 nm and 8 μm by scanning electron microscopy (SEM) (Figure 3(b)). The nanowires produced at higher potentials of $-1.25$ V are not uniform along the entire nanowire length.

The average composition of nanowires on the AAO template was evaluated by EDX microanalysis. The unsigned peak rises from the AAO template (Figure 4). It is clearly seen that apparent decrease in intensity of Sn and Ag peaks, if the deposition potential is changed from $-1$ to $-1.25$ V. The results indicate that the electrodeposition potential had a marked effect on the Sn, Ag, and Cu content of the SnAgCu deposits (Figure 5). Under the same bath conditions, SnAgCu deposits at $-1$ V contain more Sn content than those deposited at 0.75 V, $-1.25$ V, $-1.5$ V, $-1.75$ V, $-2$ V. As can be observed from Figure 5, the compositions of the deposited nanowires were Sn$_{58}$Ag$_{18}$Cu$_{24}$, Sn$_{78}$Ag$_{16}$Cu$_{6}$, Sn$_{90}$Ag$_{4}$Cu$_{6}$, Sn$_{87}$Ag$_{4}$Cu$_{9}$ for potentials $-0.75$ V, $-1$ V, $-1.25$ V, $-1.5$ V, $-1.75$ V, $-2$ V, respectively. Significant differences in the morphology of the electrodeposits were observed for different Sn content. When the Sn content is below 93%, SnAgCu nanowires appear in a tree-like pattern, which resembles the branches of the nodes as shown in Figures 3(a) and 3(c).

XRD presented data in Figure 6, mostly in agreement with the recent XRD results for SnAgCu alloy nanoparticles by Jiang et al. [25]. As shown in Figure 6, diffraction pattern of SnAgCu nanowire arrays within AAO demonstrates strong Sn reflections and minor Ag$_3$Sn and Cu$_{10}$Sn$_3$ reflections, indicating the successful alloying of Sn–Ag and Cu–Sn during electrodeposition process. No prominent oxide peak was observed from XRD.

Gao et al. [26, 27] reported the size-dependent melting temperature effect of SnAgCu nanoparticles by differential scanning calorimetry (DSC). They observed from the DSC curves of SnAgCu nanostructures that the instability becomes obvious and usually the nanostructures lose stability at lower temperature than their bulk precursors. They have also reported that the depression in melting temperature of SnAgCu nanoparticles can be attributed to the large particle free energy caused by the size effect. Our results agree well with Gao et al. [26, 27]. The melting temperature of
Figure 4: EDX spectrum of SnAgCu nanowire arrays at (a) −1 V and (b) −1.25 V.

the embedded nanowires was determined using a DSC heating rate of 10°C/min (Figure 7). The measured melting temperature was 221.77°C for sample produced at −1 V. The melting onset temperature of Sn93Ag4Cu3 nanowires is about 204°C. The corresponding latent heat of melting of Sn93Ag4Cu3 nanowires is about 59.43 J/g.

Figure 8 shows the full XPS spectra of SnAgCu nanowires embedded in AAO template on the surface. The XPS spectrum indicates that surface mainly contains O, C, Sn, Ag, Al, and Cu. XPS is presented in Figure 8, mostly in agreement with the recent XPS results for SnAgCu lead-free solder alloys by Zhang et al. [28]. Existence of C is due to the accumulation of contaminants during exposure to air. Al and most especially O peak is due to from the AAO template.

4. Conclusions

In conclusion, we have successfully, for the first time, fabricated SnAgCu nanowires using template-based electrodeposition. It was shown from SEM micrographs that the nanowires are around 200 nm in diameter and 8 μm in length...
for a deposition potential of \(-1\) V. SEM and EDX results show that the morphological and composition changes of the nanowires are highly dependent on the deposition potential. It was also observed that the DSC measurement of SnAgCu alloy nanowires shows broad endothermic peak. The melting onset temperature for the nanowires with \(-1\) V deposition potential was about 204°C, which is lower than that of SnAgCu bulk alloy (217–219°C) [29].

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**References**


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