A Novel Method for the Preparation of Ag/SnO$_2$ Electrical Contact Materials

Qiao Xiuqing$^1$, Shen Qianhong$^{1,3}$, Zhang Lingjie$^{1,3}$, Chen Lawson$^{2,3}$, Fan Xianping$^1$, Yang Hui$^{1,3}$

$^1$State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China; $^2$Wenzhou Hongfeng Electrical Alloy Co., Ltd., Wenzhou 325603, China; $^3$Zhejiang-California International NanoSystems Institute, Hangzhou 310029, China

Abstract: A novel method was presented to prepare Ag/SnO$_2$ (12 wt% SnO$_2$) electrical contact materials. First, Ag-SnO$_2$ nano composite powder with 42 wt% SnO$_2$ synthesized by a coprecipitation method was characterized. XRD results reveal that the synthesized composite powder is composed of cubic Ag and rutile type of SnO$_2$. SEM and TEM images show that nano-Ag and nano-SnO$_2$ particles are homogeneously dispersed in the composite powder. The preparation process of nano composite powder was analyzed with the help of the TG-DTA curves of the precipitation. Then, the obtained Ag-SnO$_2$ nano composite powder was mixed with Ag powder to prepare Ag/SnO$_2$ electrical contact materials (ECM) by powder metallurgy process and the prepared Ag/SnO$_2$ electrical contact materials was characterized. The results demonstrate that owing to the higher dispersion of nano SnO$_2$ particles in Ag matrix, the physical properties of ECM prepared by the new method, such as the density, hardness and conductivity are better than that by the traditional method.

Key words: Ag/SnO$_2$; nano composite powders; electrical contact materials; dispersive distribution

Ag/SnO$_2$ composite has attracted much attention in the field of electrical contact materials (ECM) due to its excellent properties such as long life time, better welding resistance and less arc erosion $^{[1-8]}$. There are mainly two approaches to prepare Ag/SnO$_2$ ECM: internal oxidation of Ag-Sn alloys$^{[9]}$ and powder metallurgy (P/M) technology$^{[10]}$. However, the internal oxidation of Ag-Sn alloys is complex due to the concurrence of external oxidation, leading to a passivation of the process due to the restriction of oxygen diffusion from the outside, particularly when their ratio of surface and volume is large. For the P/M process, the agglomerations of nano SnO$_2$ have been formed before the process, leading the difficulty to disperse them in Ag matrix, resulting in high contact resistance and temperature rise. Hence, great efforts have been made to improve the properties of the Ag/SnO$_2$ ECM and three major methods are developed, i.e. cladding Ag nanoparticles on the surface of SnO$_2$$^{[11]}$, adding other oxides$^{[12,13]}$ and utilizing nano SnO$_2$ particles$^{[14]}$. We have recently proposed a two-step process to overcome the aggregation and segregation of SnO$_2$ particles in Ag matrix$^{[15]}$. In a typical synthesis, Ag/SnO$_2$ composite powder with high weight percentage of SnO$_2$ (60wt% SnO$_2$) was prepared via mechanical alloying (M/A) process, and then the composite powder was mixed with Ag powder to prepare ECM with relatively low mass percentage of SnO$_2$ (12wt% SnO$_2$). By means of this process, the reinforcing phase of SnO$_2$ was uniformly dispersed in Ag matrix. However, it is more difficult to disperse nano SnO$_2$ by this M/A technique because the agglomeration have been formed during the synthesizing process of nano SnO$_2$. So the synthesis of monodispersed nano SnO$_2$ particles is of great importance for the preparation of Ag/SnO$_2$ ECM with
good properties. In the present work, we synthesized well dispersed Ag-SnO$_2$ nano composite powder with high mass percentage of nano SnO$_2$ particles (about 42wt%). Nano Ag particles in the composite powder serve as the space hindered additive and hinder the agglomeration of nano SnO$_2$. The nano composite powder synthesized via a coprecipitation method was then used as precursors to prepare Ag/SnO$_2$ ECM. The prepared ECM shows higher density, Vickers hardness and good electrical conductivity than that prepared by the traditional method.

1 Experiment

In a typical synthesis, 0.213 g of Na$_2$SnO$_3$ and 2.016 g of AgNO$_3$ were separately dissolved in deionized water to achieve their solutions with a concentration of 0.1 mol/L. Then AgNO$_3$ solution was added into the Na$_2$SnO$_3$ solution under vigorous stirring, and brown precipitate were immediately obtained. The resulting suspensions were further stirred at room temperature for 1 h. The products were collected by filtration, washed, dried and calcined at 900 °C for 3 h. Finally, nano composite powder with high mass percentage of SnO$_2$ was obtained. The mass percentage of SnO$_2$ in the nano composite powder was tested by the chemical titration method and used as precursor to prepare Ag/SnO$_2$ ECM by a powder metallurgy (P/M) technique.

Two kinds of Ag/SnO$_2$ ECM were prepared in our work by the following process: (1) the precursor and nano SnO$_2$ particles were blended with 74 μm Ag powders in a plastic jug and milled for 4 h to get Ag/SnO$_2$(12) composite powder and the mass ratio of ball and powder (BPR) was 10:1. (2) the obtained Ag/SnO$_2$(12) composite powder was collected, sieved using an 12 μm screen and then pressed into wafers with Φ15 mm at 500 MPa for 2 min. (3) the wafers were sintered in a muffle furnace in air atmosphere at 850 °C for 6 h. (4) the wafers were repressed at 500 MPa for 2 min and resintered at 800 °C for 2 h and the Ag/SnO$_2$ ECM was got. The procedure for preparation of Ag/SnO$_2$ ECM is shown diagrammatically in Fig.1.

The structures of the as-synthesized and calcined composite powders were characterized by X-ray powder diffractometer (APEXII, Bruker Co., Germany) using Ni-filtered Cu Kα radiation (λ=0.1542 nm). Data were collected at 2θ angels from 20° to 90° with a step of 0.02°. Field emission scanning electron microscope (FE-SEM, SU-70, Hitachi Co., Japan) and transmission electron microscope (TEM, Tecnai G2 F20 S-TWIN, U. S.) were used to investigate the morphology. The elements mapping of the composite powders was determined using energy dispersive spectrometer (EDS) attached to FE-SEM. Thermo gravimetric analyzer and differential thermal analyzer (TG-DTA, WRT-3P and CRY-2P) were used to analyze the reaction process of the formation of the composite powder. The chemical composition ratio of the nano composite powder was determined according to the chemical titration described in national standard GB/T24268. The microstructures of Ag/SnO$_2$ ECM were observed using FE-SEM. The density of ECM was tested using the Archimedes method. Vickers hardness was determined by the HBRVU-187.5 hardness tester. The resistivity was characterized by the D60K digital metal conductivity measuring instrument.

2 Results and Discussion

XRD patterns of the as-synthesized and calcined composite powders are shown in Fig.2. The presences of broad peaks in the as-synthesized powders (Fig.2a) indicate the formation of amorphous tin compounds and pure cubic silver. For the calcined products, all of the sharp diffraction peaks in Fig. 2b are in good agreement with the tetragonal rutile SnO$_2$ (JCPDS Card No.41-1445, a$_0$=0.4738 nm, c$_0$=0.3187 nm, space group: P42/mmm) and face-centered cubic (fcc) Ag (JCPDS Card No.04-0783). No peaks are detected for other impurity phases, demonstrating the calcined powders are pure Ag and SnO$_2$ composite powders.

The TG-DTA profiles of the as-synthesized composite powder are shown in Fig. 3. The TG profile indicates about 12% mass loss from room temperature to 1000 °C. The mass loss observed at approximately 100 °C is associated with an endothermic peak can be assigned to the elimination of physically adsorbed water. The obvious exothermic peak near 213 °C is attributed to the decomposition of tin compounds and the mass loss continually. Thermal decomposition of AgO is formed by the poor thermal stability of Ag(OH), resulting in a slight mass loss between 250 and 500 °C. A heavy mass loss at 540 °C accompanied with an endothermic peak is ascribed to the decomposition of Ag$_2$O.

No obvious mass loss can be observed in the temperature range from 540 °C to 800 °C, indicating that no decomposition takes place in the temperature range. An obvious endothermic peak around 970 °C in the DTA profile,
accompanied with a small amount of mass loss can be assigned to the melt of Ag.

According to the TG-DTA and XRD results, we analyzed the possible chemical reactions involved in the formation of the uniformly dispersed Ag-SnO₂ nano composite powder:

\[
\text{SnO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \left[\text{Sn(OH)}_i\right]^{4-} + \text{OH}^- \quad (1)
\]

\[
\left[\text{Sn(OH)}_i\right]^{4-} + (4-i) \text{H}^+ \rightleftharpoons \text{Sn(OH)}_4 \downarrow + (4-i) \text{H}_2\text{O} \quad (2)
\]

\[
\text{Ag}^+ + \text{OH}^- \rightarrow \text{Ag(OH)} \downarrow \quad (3)
\]

\[
\text{Ag(OH)} \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O} \quad (4)
\]

\[
\text{Ag}_2\text{O} \rightarrow \text{Ag} + \text{O}_2 \uparrow \quad (5)
\]

\[
\text{Sn(OH)}_4 \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} \quad (6)
\]

In reaction (1), SnO₃²⁻ is hydrolyzed into [Sn(OH)]⁴⁻ and OH⁻. When AgNO₃ solution is added, the anions will react with H⁺ to form Sn(OH)₄ colloid, while Ag⁺ reacts with OH⁻ to produce Ag(OH), as shown in reaction (2) and (3). In reaction (4), AgOH decomposes quickly into Ag₂O due to its poor stability at room temperature. When calcined at 900 °C, Ag₂O and tin compounds further decompose into Ag and SnO₂ nanoparticles and the resulting Ag-SnO₂ nano composite powder is obtained. The chemical titration results show that the mass percentage of SnO₂ in the nano composite powders is 42%, while the remaining is Ag.

In order to research the distribution of nano SnO₂ in the composite powder, we made an element mapping analysis of the powder using EDS, as shown in Fig.4a–4c, which represent the samples, Ag element and Sn element, respectively. As shown in SEM image of the composite powder, individual nanoparticles with mean diameter of about 0.50 nm are distributed homogeneously. The map of Ag, Sn and O element (not listed) are fitted into the sample morphology, which indicates that Ag and SnO₂ nano particles are uniformly dispersed in the composite powder. The corresponding TEM image in Fig.4d corroborates the uniformity and dispersity observed in the FE-SEM image. The high
resolution transmission electron microscopy (HRTEM) images of the area marked with A and B are shown in Fig. 4d and 4f. The spacing between two lattice planes shown in Fig. 4e is 0.236 nm, corresponding to the (111) planes of fcc silver \[^{[17]}\]. The distance between fringes in Fig. 4f are 0.335 and 0.264 nm, respectively, and they are found to correspond to the (110) and (101) planes of the rutile SnO\(_2\). The clear lattice fringes confirm the high crystallinity of the nano SnO\(_2\). The results are in good agreement with the XRD results.

A homogeneously distributed composite powder is basic condition for high quality contact materials with stable mechanical switching characteristics. The synthesized highly dispersed nano composite powder is used as precursor to prepare Ag/SnO\(_2\) (12) composite powder. SEM images of the Ag/SnO\(_2\) (12) composite powders from the precursor and pure SnO\(_2\) are shown in Fig. 5. It can be seen that the composite powder has irregular micro particles with nano nanoparticles coated. For the Ag/SnO\(_2\) (12) composite powder forms the precursor, nano Ag particles dispersed in the composite powder may serve as the space hindered additive and hinder the agglomeration of nano SnO\(_2\) and this is a contribution to the dispersed distribution of nano particles. However, for the Ag/SnO\(_2\) (12) composite powder forms pure SnO\(_2\), the very fine SnO\(_2\) particles adhered to the Ag powders are packed with each other. The packed nano particles are hard to be dispersed and may block the interconnection of Ag particles after consolidation and deteriorate the performance of the ECM.

The microstructures of the two different ECM fabricated in our work are given in Fig. 6. As is evident to see the microstructures, ECM made form the precursor gives the more uniform microstructure and without any pore. An enlarged view of the ECM shows that the SnO\(_2\) nano particles are uniformly distributed in the Ag matrix and better connectivity of individual Ag grains. For the ECM made form the pure SnO\(_2\) nano particles, it may be noticed that many pores are observed (black color) and the aggregation of nano SnO\(_2\) in Ag matrix is severe, which is in accordance with the analysis of SEM image in Fig. 5. As is known, pores are potential scattering centers for the electrons and consequently reduce the conductivity \[^{[17]}\] of ECM. The very uniform distribution of nano SnO\(_2\) in Ag matrix and dense structure of the ECM fabricated from the precursor can help to improve the density, conductivity and hardness.

The physical properties of the Ag/SnO\(_2\) ECM prepared from Ag-SnO\(_2\)(42) precursor and pure nano SnO\(_2\) particles are compared in Table 1.

As shown in Table 1, ECM prepared form the precursor gives higher density, Vickers hardness and conductivity than those fabricated from the pure nano SnO\(_2\) particles, illustrating the nano composite powder synthesized in our work is a good choice for the fabrication of high performance ECM. However, the hardness and conductivity of the ECM fabricated in our work are still lower and this may be caused by the simple preparation technique. The properties of the ECM are expected to be significantly improved after hot-extrusion or other special working techniques.
Table 1  Physical properties of Ag/SnO$_2$ ECM prepared by the two different methods

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Density/ g·cm$^{-3}$</th>
<th>Hardness, HV/MPa</th>
<th>Resistance/ $\mu\Omega$·cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgSnO$_2$(42)</td>
<td>9.81</td>
<td>848.4</td>
<td>3.37</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>9.79</td>
<td>814.1</td>
<td>3.44</td>
</tr>
</tbody>
</table>

3  Conclusions

1) The novel method can be used to prepare Ag/SnO$_2$ ECM with highly dispersed SnO$_2$ nano particles in Ag matrix.

2) The good dispersion of nano SnO$_2$ particles improves the density, hardness and conductivity of ECM.

3) The coprecipitation method used for the synthesis of the precursor is facile, efficient and controllable and can be applied in industrial production.

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