Characteristics of nano Ti-doped SnO$_2$ powders prepared by sol–gel method

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Abstract

Ti$^{4+}$-doped SnO$_2$ nano-powders were prepared by the sol–gel process using tin tetrachloride and titanium tetrachloride as the starting materials. The crystallinity and purity of the powders were analyzed by X-ray diffraction (XRD) and the size and distribution of Ti$^{4+}$-doped SnO$_2$ grains were studied using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The results show that Ti$^{4+}$ has been successfully incorporated into the SnO$_2$ crystal lattice and the electrical conductivity of the doped materials improves significantly.

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1. Introduction

AgSnO$_2$ contact materials are gradually replacing toxic AgCdO materials in switching devices such as contactors and circuit breakers [1,2] partly due to the more favorable properties of AgSnO$_2$ such as long lifetime, better welding resistance and less arc erosion [3]. Furthermore, growing environmental concerns have spurred the replacement of AgCdO by nontoxic AgSnO$_2$ [4]. However, Ag$_x$Sn$_{1-x}$O$_2$ suffers from inadequate welding behavior compared to AgCdO [5]. Generally, Ag$_x$Sn$_{1-x}$O$_2$ made by traditional metallurgical processes at high temperature exhibits high contact resistance caused by surface layers of accumulated SnO$_2$. This also leads to poor wettability of SnO$_2$ grains in the silver melt [6–9]. The large size and high hardness of SnO$_2$ particles prepared by traditional processes degrade the properties of Ag$_x$Sn$_{1-x}$O$_2$ contact materials [10].

The welding and thermal behavior of Ag$_x$Sn$_{1-x}$O$_2$ can be improved by incorporating oxides such as TeO$_2$, Cu$_2$O, Bi$_2$O$_3$ and W$_2$O$_5$ [5,11,12]. However, few studies have reported on the preparation and performance of tin oxide doped with ions such as Ti$^{4+}$. In this work, we prepared Ti$^{4+}$-doped SnO$_2$ using the sol–gel technique and investigated the microstructure, size, distribution and crystallization of Ti$^{4+}$-doped tin oxide grains as well as the effects of doped Ti$^{4+}$ on the electrical conductivity of Ag$_x$Sn$_{1-x}$O$_2$.

2. Experimental details

The SnO$_2$ gel was prepared by the sol–gel technique [13,14]. Tin tetrachloride (SnCl$_4$·5H$_2$O) was first dissolved in a solution composed of ethanol and de-ionized water (volume ratio is 1:1) to a concentration of 2 mol/l with vigorous stirring for 20 min. Titanium tetrachloride (TiCl$_4$) was then added to the solution with the dispersant of polyethylene glycol (PEG 400) and stirred for 30 min at 80°C. The atomic ratio of Ti to Sn was 5.95. Ammonia was then added to the metal chloride solution until the pH of the mixture reached 7. After 48 h of aging in the air, the SnO$_2$ gel was centrifuged (Centrifugal machine, LD4-2, Beijing, China) at 3000 rpm for 5 min and only the solid gel was collected. In order to remove both the ammonia and chloride components, centrifugation in de-ionized water and ethanol was repeated until all chloride ions had been removed (by examining the centrifuged solution using 3 mol AgNO$_3$). The macrostructure of the SnO$_2$ gels with and without the dispersant were evaluated using transmission electron microscopy (TEM, JEOL 100CXII).

The gel was then dried in an oven at 60°C for 4 h to remove moisture. In order to investigate the effect of the treatment tem-
perature on the particle size of Ti$^{4+}$-doped SnO$_2$ powders, the dried gel was sintered for 2 h at 350, 500 and 700 °C in a furnace. To find the suitable particle size and crystallization, the morphologies of the Ti$^{4+}$-doped SnO$_2$ powders were studied by scanning electron microscopy (SEM; PHILIPS XL-30 TMP ESEM) and X-ray diffraction (XRD) patterns were obtained using a Rigaku X-ray diffractometer with a Cu Kα X-ray source operated at 40 kV and 100 mA.

Afterwards, the selected powders were passed through an 800 mesh sieve. In order to measure the electrical conductivity and density, 2.5 g of the Ti$^{4+}$-doped SnO$_2$ powders were compacted by hydraulic pressing at 100 MPa to make plates with a diameter of 9.3 mm. Because the solution temperature of SnO$_2$ was about 800 °C [15] the plates were calcined at 600, 800, 1000 and 1200 °C, respectively, about 2 h [16] to measure the change of electrical conductivity and density. The resistance of the plates was determined employing a bridge resistance instrument (LCR Databridge, KTI-401D). The instrument was set in the resistance mode ($R$) and both probes were put on the two sides of the plate coated with some silver conductive paint. The resistance value of the plates in air and water was determined respectively using an FR-300 MKI electronic balance with a precision of 0.1 mg. The density of the plates was then obtained according to ASTM B 328 [17] and ISO 2738 [18].

### 3. Results and discussion

The microstructure and distribution of the Ti$^{4+}$-doped SnO$_2$ gel grains are shown in Fig. 1. For the gel with polyethylene glycol (PEG) as the dispersant (Fig. 1a), it can be observed that the size of the grains varies from 10 to 100 nm and the grains are quite evenly distributed during gel formation. This indicates that PEG can effectively prevent the SnO$_2$ gel grains from agglomeration. Yang et al. [19] ascribed this phenomenon to the steric hindrance mechanism. With PEG as the dispersant, the gel particles can absorb long chain molecules of PEG on the surface, and it can inhibit the aggregation of the gel particles. Besides, the surface tension can be reduced due to the gel particles being surrounded by the PEG [20]. With regard to the gel formation without PEG, the gel particles in the solution are unstable because of their high surface tension. Moreover, the gel particles tend to agglomerate together without the interaction of steric hindrance. As shown in Fig. 1b, the Ti$^{4+}$-doped SnO$_2$ gel is poorly dispersed.

Fig. 2 displays the XRD spectra of the Ti$^{4+}$-doped SnO$_2$ powders sintered for 2 h at 350, 500 and 700 °C, respectively. The spectra indicate the presence of SnO$_2$ only and the peaks associated with Ti$^{4+}$ cannot be observed. It reveals that Ti$^{4+}$ has been successfully incorporated into the crystal lattice of SnO$_2$ by the sol-gel technique. As shown in Fig. 2, the intensity of the SnO$_2$ peaks increases with increasing treating temperature and the full-width half-maximum (FWHM) widths of the peaks decrease with increasing temperature as well. It indicates that crystallization of the SnO$_2$ powders progresses gradually as the
Table 1
Grain size of Ti⁴⁺-doped SnO₂ powders sintered at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>10–20</td>
</tr>
<tr>
<td>500</td>
<td>30–50</td>
</tr>
<tr>
<td>700</td>
<td>70–90</td>
</tr>
</tbody>
</table>

treating temperature increases. Our experimental data show that crystallization of the SnO₂ gel is not complete at a temperature of 350 °C, but perfect crystals can be obtained at higher treating temperatures at 500 and 700 °C. The grain size of the Ti⁴⁺-doped SnO₂ powders treated at different temperatures can be obtained from the FWHM of the diffraction peaks. The FWHM’s can be expressed as a linear combination of the contributions from the strain and particle size by the following equation [21]:

\[
\beta \cos \theta \frac{1}{\lambda} = \frac{1}{D} + \varepsilon \sin \theta \frac{1}{\lambda},
\]

where \( \beta \) is the measured FWHM in radians, \( \theta \) the Bragg angle of the diffraction peak, \( \lambda \) the X-ray wavelength, \( D \) the effective particle size and \( \varepsilon \) is the effective strain. The results are shown in Table 1. It can be concluded that the Ti⁴⁺-doped SnO₂ powders sintered at 500 °C are more suitable because the grains aggregate easily at 700 °C, and it is supported by the SEM images shown in Fig. 3, which depicts the microstructure of the Ti⁴⁺-doped SnO₂ powders sintered for 2 h at 500 and 700 °C. The grain size of the SnO₂ powders sintered at 700 °C is much larger than that of the powders sintered at a lower temperature. Furthermore, the grains in the sample sintered 500 °C are distributed evenly whereas those in the sample sintered at 700 °C exhibit agglomeration, which is very similar to ripening process [22,23]. At the expense of the small grains, some larger grains emerge. Hence, based on the above result, we chose the powders treated at 500 °C to conduct secondary calcination. Fig. 4(a) and (b) show the graphs of the density and electrical conductivity of the Ti⁴⁺-doped SnO₂: (a) density; (b) electrical conductivity.

![SEM micrographs of Ti⁴⁺-doped SnO₂ powders sintered at different temperatures for 2 h. (a) 500 °C and (b) 700 °C.](image)

![Temperature dependence on density and electrical conductivity of Ti⁴⁺-doped SnO₂: (a) density; (b) electrical conductivity.](image)
Prepared by the same method, the density and electrical conductivity of the pure SnO$_2$ are 6.053 g/cm$^3$ and 1.84 × 10$^{-10}$ Ω$^{-1}$ cm$^{-1}$, respectively. The introduced Ti$^{4+}$ can make the SnO$_2$ lattice more compact decreasing the lattice parameters [24], possibly due to the shorter Ti-O bond [25]. Hence, the doped SnO$_2$ has a higher density than the undoped SnO$_2$. In addition to the higher density, the Ti$^{4+}$-doped SnO$_2$ powders possess electrical conductivity that is 10$^4$ times higher than that of pure SnO$_2$. After Ti$^{4+}$ incorporation into the SnO$_2$ lattice, the electric resistance decreases [26–28]. In fact, SnO$_2$ is an n-type semiconductor in which the intrinsic oxygen vacancies (V$_{O}$) are compensated by electrons. The equilibrium between oxygen vacancies and electrons is responsible for the semi-conducting characteristics of SnO$_2$. The mechanism of can be expressed by the following equation [29]:

\[
\text{SnO}_2 \rightarrow \text{SnO}_{2-} + \text{V}_O^- + \text{O}_2^+.
\]

As the ionic radius of Ti$^{4+}$ (0.68 nm) is close to that of Sn$^{4+}$ (0.71 nm), it is easy for Ti$^{4+}$ to be doped into the crystal lattice of SnO$_2$ and occupy the substitutional positions [30]. This can create a large number of oxygen vacancies and increase the electrical conductivity of SnO$_2$. The process is shown in the equation:

\[
\text{Ti}^{4+} + \text{SnO}_2 \rightarrow \text{TiO}^2- + \text{V}_O^- + \text{O}_2^+.
\]

In general, the electrical conductivity of the materials is determined by the following equation:

\[
\sigma = \frac{c \cdot \mu \cdot \rho}{\Omega},
\]

where $c$ is the electrical conductivity, $\rho$ the concentration of charge carriers, $\mu$ the chemical valence of charge carriers, $\epsilon$ the charge of electron and $b$ is the drift velocity of charge carriers. It is obvious that $\epsilon$ increases significantly with Ti$^{4+}$ doping according to Eq. (3). Therefore, the electrical conductivity ($\sigma$) of Ti$^{4+}$ doped SnO$_2$ is improved significantly, which is in good agreement with our results.

4. Conclusion

We have demonstrated the fabrication of nano-sized Ti$^{4+}$ doped SnO$_2$ powders using the sol–gel technique. Polyethylene glycol (PEG) can effectively prevent the SnO$_2$ grains from agglomerating during the formation of the gel. We have obtained high quality Ti$^{4+}$-doped SnO$_2$ crystals and fine grains after Ti$^{4+}$-doped SnO$_2$ gel is sintered at 500°C. After secondary calcination at 1000°C, the Ti$^{4+}$-doped SnO$_2$ samples exhibit higher density and electrical conductivity. Our test results reveal that the doped materials possess significantly enhanced electrical conductivity and density compared to the undoped SnO$_2$ materials made by conventional methods.

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