

Effects of coating process on the characteristics of Ag–SnO₂ contact materials

X.M. Liu^{a,b}, S.L. Wu^{a,b}, Paul K. Chu^{b,*}, C.Y. Chung^b, J. Zheng^a, S.L. Li^a

^a School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

^b Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, PR China

Received 21 July 2005; accepted 29 September 2005

Abstract

Good wettability between the SnO₂ and silver matrix can improve the electrical contact performance of Ag–SnO₂ materials. In this work, Ag was deposited onto the surface of Ti-doped SnO₂ particles using chemical plating to enhance the wettability. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the Ag-coated SnO₂ particles. Scanning electron microscopy (SEM), conductivity tests, differential thermal analysis (DTA), and thermogravimetric analysis (TGA) were performed on the Ag–SnO₂ materials. Our results reveal that the chemical plating process can enhance the wettability between the Ti-doped SnO₂ particles and Ag matrix, and the Ag-coated SnO₂ particles are uniformly distributed in the Ag matrix. Both the thermal and electrical conductivity of the Ag–SnO₂ materials are significantly improved.

© 2005 Elsevier B.V. All rights reserved.

PACS: 81.40.Rs

Keywords: Chemical plating; SnO₂; Coating; Electrical conductivity

1. Introduction

As a pollution-free contact material, Ag–SnO₂ has been gradually replacing the toxic Ag–CdO materials in the last two decades. However, SnO₂ has higher thermal stability and is more difficult to be wetted by liquid silver than CdO [1]. Consequently, SnO₂ can easily aggregate to the interface between Ag and SnO₂. Furthermore, the mixture of Ag and SnO₂ can deposit from the silver melt onto the contact surface by the arc reaction. As a consequence, Ag–SnO₂ materials exhibit less favorable high temperature behavior than Ag–CdO materials. Generally, the high temperature properties of Ag–SnO₂ materials produced by powder metallurgical (PM) method can be improved by the addition of some metal oxides such as WO, MoO₃, Bi₂O₃, TeO₂, etc. [2–4], but this measure increases the brittleness of Ag–SnO₂ and makes it difficult to machine in practice. Therefore, it is necessary to develop new methods to enhance the wettability between Ag and SnO₂ while keeping the good properties of Ag–SnO₂.

The chemical plating method has been successfully used to improve the wettability between Ag and additives with high

melting point such as WC, TiC and graphite [5]. This is due to the higher adsorption affinity between newly precipitated Ag and additives during the plating process. Ti⁴⁺ has been successfully doped into the crystal lattice of SnO₂ by using the sol–gel method [6]. In the work reported here, we systematically investigated Ag cladding on the surface of Ti-doped SnO₂ powders using chemical plating and the characteristics of the Ag–SnO₂ contact materials.

2. Experimental details

The raw materials used in our experiments were nano Ti-doped SnO₂ powders with a purity of 99.5% prepared by the sol–gel method and sintered at 500 °C [6]. The nano Ti-doped SnO₂ powders were first added to deionized water with a weight ratio of 1:10 (SnO₂:H₂O), agitated by magnetic stirring, and then polyvinylpyrrolidone (PVP) containing of 1 wt.% of SnO₂ was dripped into the stirred solution as a stabilizing agent. Ammonia was then introduced into the silver nitride solution with continuous stirring to obtain a (Ag(NH₃)₂)NO₃ solution. Afterwards, the (Ag(NH₃)₂)NO₃ solution was poured into the SnO₂ suspended solution while keeping continuous agitation, and then a hydrazine hydrate (NH₄N₂·H₂O) solution was dripped into the stirred solution at a high rate to produce Ag-coated SnO₂ powders. Finally, the Ag-coated SnO₂ powders were dried at 100 °C for 48 h in the oven after rinsing with deionized water.

Two kinds of Ag–SnO₂ materials were prepared in our experiments. The coated Ag–SnO₂ materials were fabricated by mixing 99.99% Ag and the Ag-coated nano Ti-doped SnO₂ powders as follows. The Ag and Ag-coated SnO₂

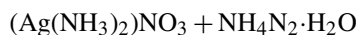
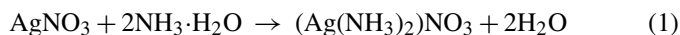
* Corresponding author. Tel.: +852 27887724; fax: +852 27889549.
E-mail address: paul.chu@cityu.edu.hk (P.K. Chu).

powders were fully mixed for 4 h and then sieved using an 800-mesh screen. The mixed powders were put into the die and pressed by a pressing machine at a pressure of 200 MPa for 1 min. Afterwards, the pressed samples were sintered as shown in Fig. 1 in a tube furnace under argon. Finally, the Ag–SnO₂ materials were stored in desiccators before use. The uncoated Ag–SnO₂ materials were fabricated as a control from the mixtures of Ag and the uncoated nano Ti-doped SnO₂ powders using similar procedures.

The density of the Ag–SnO₂ materials was measured by Archimedes method and their hardness was determined by using a Vickers hardness tester. The 7501 vortex conductivity apparatus was used to investigate the electrical conductivity of Ag–SnO₂ materials. The microstructure of the Ag–SnO₂ samples was examined by scanning electron microscopy (PHILIPS XL-20), transmission electron microscopy (TEM) (JEOL-100CXII) and XRD (Rigakudmax X-ray diffractometer with a 40 kV, 100 mA, Cu K α X-ray source) were employed to examine the chemical composition and the structure of the Ag-coated Ti-doped SnO₂ powders. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on the Ti-doped SnO₂ powders and the coated/uncoated Ag–SnO₂ contact materials.

3. Results and discussion

Chemical plating is one of the liquid coating techniques. It can significantly improve the bonding strength of the interface between the matrix and coated particles such as SiC, MgO, CaO and ZrO₂ as well as the mechanical properties [7–9]. In this work, the silver ions were deacidized by the reductant hydrazine hydrate and nucleated and grew preferentially around the surface of the suspended Ti-doped SnO₂ particles in a mixed solution because the Ti-doped SnO₂ particles in the solution acted as nucleation sites. The reactions in the chemical plating process are as follows:



As shown in Fig. 2, curve 1 shows an obvious peak corresponding to silver, implying that the Ti-doped SnO₂ powders are coated with Ag during chemical plating. The TEM image displayed in Fig. 3 reveals that the size of Ag-coated Ti-doped SnO₂ particles is in the range of 100–200 nm, whereas, the size

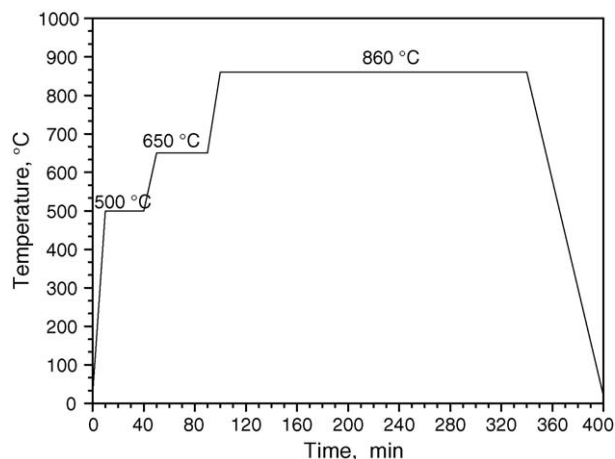


Fig. 1. Schematic diagram of the sintering process of Ag–SnO₂.

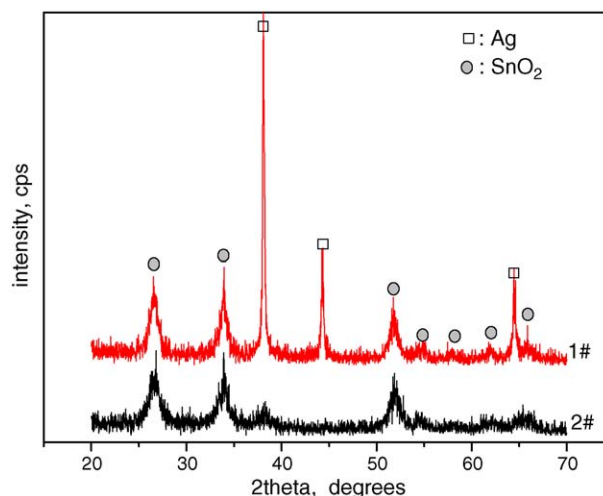


Fig. 2. XRD spectra of Ti-doped SnO₂ powders: (1) coated with Ag and (2) uncoated (as a control).

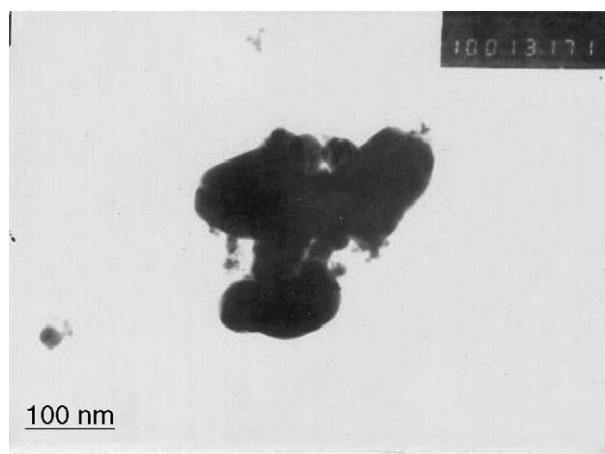


Fig. 3. TEM image of nano Ti–SnO₂ particles coated with silver.

of the uncoated Ti-doped SnO₂ particles before coating varies from 8 to 10 nm [6]. It indicates that Ag deacidized by the reductant hydrazine hydrate successfully nucleates and grows on the surface of the Ti-doped SnO₂ particles suspended in the mixed solution.

The SEM image of the coated Ag–SnO₂ materials is depicted in Fig. 4. The Ag-coated Ti-doped SnO₂ particles (white color) are uniformly distributed in the Ag matrix. It arises from the improvement of wettability between the Ag-coated SnO₂ particles and Ag matrix.

Table 1
Physical and electrical properties of Ag–SnO₂ contact materials

Samples	Hardness (Hv-MN/m ²)	Density (g/cm ³)	Electric conductivity (% IACS)
Coated	98.4	9.74	68.3
Uncoated	95	9.71	58.1

Note: The value in the form is the average of three samples. IACS: International Annealed Copper Standard.

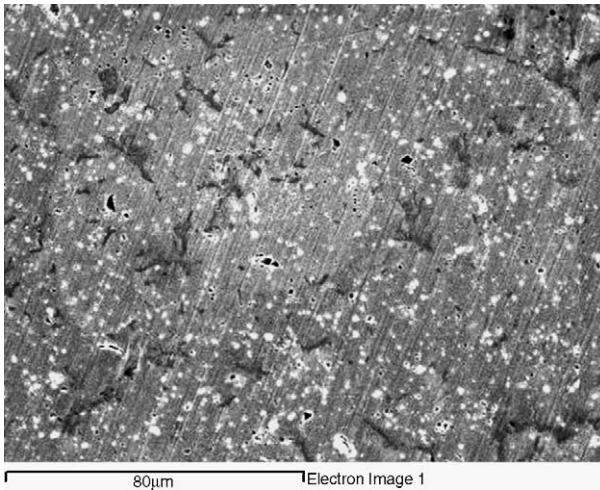


Fig. 4. SEM image of coated Ag–SnO₂ contact materials.

As shown in Table 1, both the Vickers hardness and density of the coated Ag–SnO₂ contact materials are higher than those of the uncoated ones because the Ag coat on the surface of SnO₂ can increase the wettability between the SnO₂ and Ag matrix. It can avoid aggregation of SnO₂ particles and make them uniformly disperse in the Ag matrix. The SnO₂ dispersed in the Ag matrix can strengthen the matrix. Furthermore, the bonding strength of the interface between the matrix and the second phase particles can be strengthened after the second phase particles are coated with the matrix metal by chemical plating [7]. Here, the Ag deposited on the surface of SnO₂ can eliminate the gap between the SnO₂ and Ag matrix. Therefore, the hardness and density of the coated Ag–SnO₂ are enhanced slightly. The electrical conductivity of two kinds of Ag–SnO₂ contact materials listed in Table 1 shows significant improvement of up to 68.3% that is higher than that of uncoated Ag–SnO₂ materials. Based on the International Annealed Copper Standard (% IACS), it is 58.1% IACS. In general, the uncoated Ag–SnO₂ materials consist of a mixture of two phases, i.e. Ag and SnO₂ powders. Consequently, the contact resistance between the uncoated SnO₂ particles and Ag matrix is higher due to direct contact between the SnO₂ particles and Ag matrix [10]. However, Ag deposited on the surface of SnO₂ particles converts the two phase mixture into a homogeneous single phase substance, i.e. Ag(SnO₂), thereby significantly reducing the contact resistance between the SnO₂ particles and Ag matrix.

Figs. 5–7 display the thermal and thermogravimetric properties of the Ti-doped SnO₂ powders produced by the sol–gel methods as well as uncoated and coated Ag–SnO₂ contact materials. All three DTA curves show one exothermic peak at about 300 °C corresponding to dehydration reaction of Ti-doped SnO₂. Both of the DTA curves acquired from the coated and uncoated Ag–SnO₂ contact materials show another endothermic peak at about 960 °C corresponding to the melting point of Ag. There are two weight loss steps in the TG curves of the Ag–SnO₂ contact materials (Figs. 6 and 7). Both the coated and uncoated Ag–SnO₂ contact materials show weight losses at lower temperature similar to the Ti-doped SnO₂ powders produced by

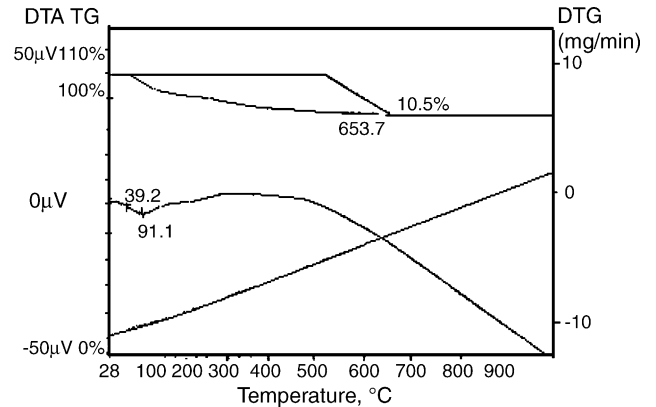


Fig. 5. DTA–TG curve of nano Ti-doped SnO₂ powders.

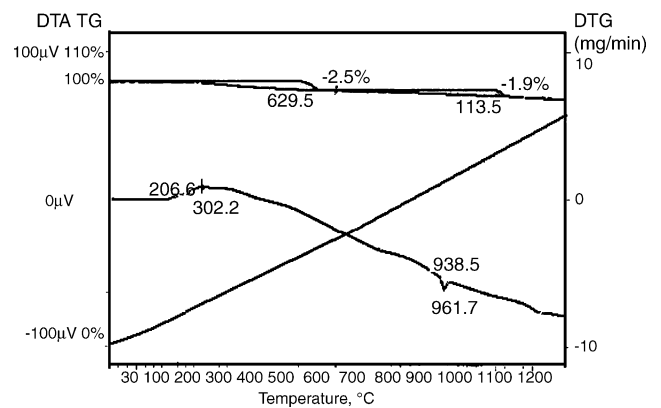


Fig. 6. DTA–TG curve of uncoated Ag–SnO₂ contact materials.

the sol–gel method. It reveals that the weight loss is mainly caused by dehydration of the Ti-doped SnO₂ at a low temperature. Another weight loss of the Ag–SnO₂ contact materials occurs at a higher temperature. This is induced by evaporation of Ag. The weight losses from the coated Ag–SnO₂ contact materials are 0.5% at the low temperature and 0.3% at the high temperature. They are much less than those of the uncoated ones due to Ag deposition. Furthermore, the higher bonding strength between the Ag matrix and Ag-coated SnO₂ particles helps to reduce evaporation of Ag at higher temperature.

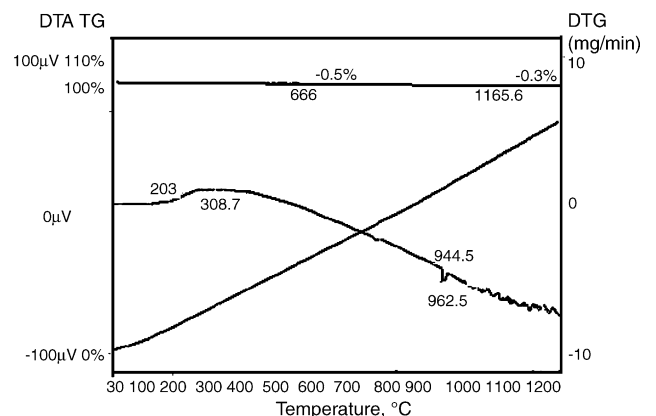


Fig. 7. DTA–TG curve of coated Ag–SnO₂ contact materials.

4. Conclusion

Nano Ti-doped powders have been successfully coated with Ag by using the chemical plating process. Our results indicate that the Ag-coated particles are uniformly distributed in the Ag matrix and the coating process can improve the wettability between the Ti-doped SnO₂ particles and Ag matrix. The coating process can enhance the physical properties such as the density and hardness as well as the electrical conductivity of the AgSnO₂ contact materials. The DTA–TG analysis shows that the weight loss of AgSnO₂ at higher temperature decreases significantly after the nano Ti-doped SnO₂ particles are coated with Ag. It suggests that the coating process can improve the thermal stability at higher temperature.

Acknowledgements

The work was financially supported by City University of Hong Kong Direct Allocation Research Grant 9360110.

References

- [1] R. Michal, K.E. Saeger, *IEEE Trans. Comp. Hybrids Manuf. Technol.* 12 (1989) 71–81.
- [2] B. Gengenbach, U. Mayer, R. Michal, K.E. Saeger, *IEEE Trans. Comp. Hybrids Manuf. Technol.* 8 (1985) 58–63.
- [3] D. Jeannot, J. Pinard, P. Ramoni, E.M. Jost, *IEEE Trans. Comp. Hybrids Manuf. Technol.* 17 (1994) 17–23.
- [4] M.Z. Rong, Q.P. Wang, Effects of additives on the AgSnO₂ contacts erosion behavior, in: *Proc. 39th IEEE Holm Conf. Electr., Contacts*, 1993, p. 33.
- [5] X.Y. Zhang, J.D. Zhang, Z.C. Wu, R.S. Song, X.J. Cheng, Z.C. Cao, *J. Shanghai Univ. (Nat. Sci. Edn.)* 6 (2000) 91–94 (in Chinese).
- [6] X.M. Liu, J. Zheng, S.L. Li, Q.Y. Li, Y.T. Li, *Electr. Eng. Mater.* 1 (2003) 12–15 (in Chinese).
- [7] A.M. Davidson, D. Regener, *Compos. Sci. Technol.* 60 (2000) 865–869.
- [8] A.P. Fang, H. Gu, J. Vleugels, B.O. Van der, *J. Inorg. Mater.* 19 (2004) 1003–1010.
- [9] H.Z. Gu, H.Z. Wang, Y.R. Hong, W.J. Zhang, Y.T. Li, *J. Wuhan Univ. Sci. Technol. (Nat. Sci. Edn.)* 26 (2003) 229–233 (in Chinese).
- [10] S.S. Yuan, L. Gould, S. Swann, *IEEE Trans. Comp. Hybrids Manuf. Technol.* 8 (1985) 352–358.