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Preparation of Au-paste by liquid-phase reaction

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Preparation of Au-paste by sol–gel-like reactions from the liquid phase was investigated. The Au-paste thus obtained was a well dispersed colloidal gold. The films sintered from the paste were good metallic conductors. These films showed good resistivity despite the presence of included metal oxides such as titania or zirconia in the matrix. The resistivity of the films thus obtained is about $3.0 \times 10^{-7}\Omega$ m, which is not so different from that of pure gold ($2.35 \times 10^{-8}\Omega$ m).

1. Introduction

In recent years, the improvement of electronic devices has been a remarkable ramification of fine-ceramics research. Hybrid integrated chips and sensors are indispensable for the fabrication of functional electrical appliances; and finding a suitable electrical conductor is one of the most important problems in the development of these devices.

Metalic materials, particularly noble metals, have been used as conductors for electrical circuits because of their low resistivity and high stability. Normally, noble-metal pastes are used as precursors of the metal conductors used for electroceramic devices. High-quality pastes need very fine and homogeneous metal powders which are very difficult to prepare. The form of metal particle is influenced by their own sinterbility, which governs the resistivity; however, the extra-high malleability and ductility of metal make it difficult to prepare the fine-powder state. Consequently, these metal fine powders are normally prepared by tiresome methods such as vapour-phase reactions or chemical reduction from their solution.

Sakka *et al.* [1–3] have reported that the sol–gel method is just appropriate for preparing fine-ceramics powders; this method is a liquid-phase reaction using metal alkoxides or related metal organic compounds as starting chemicals. The most striking characteristic of this method is the hydrolysis of an organic substrate in a solvent which enables well-dispersed fine particles to be obtained by controlling reaction conditions such as pH, temperature, humidity, etc. Those reactions can be applicable to the fabrication of fine metal powders.

The goal of this study is to find an easy preparation method for gold conductive paste on a laboratory scale. Finely dispersed colloidal gold was obtainable by photodecomposition of gold chloride in an alcohol solution containing titanium or zirconium alkoxide; a process which includes a sort of sol–gel-like liquid-phase reaction. In this paper, the properties of the paste obtained were also investigated.

2. Experimental procedure

2.1. Preparation of Au paste

Diethanolamine (DEA) was diluted with half of a prescribed amount of ethylalcohol, to which a metal alkoxide, $Ti(O\text{-}iC_3H_7)_4$ or $Zr(OC_3H_7)_4$, was added. After half an hour, a mixture of 99% hydrogen tetrachloroaurate ($HAuCl_4$ from the Nacali teque Company) and the remaining solvent (ethylalcohol) was dropped into the solution and stirred. The solution obtained, whose container was sealed by parafilm, was aged about for 2 days. The solvent was then removed by decantation and a viscous precipitate (Au paste) was recovered.

2.2. Characterization of the products obtained

The precipitate obtained was painted on a silica-glass plate and then sintered at 800 °C. The structure of the film thus obtained was examined by X-ray diffraction (XRD), electron spectroscopy for chemical analysis (ESCA) and electron probe microanalysis (EPMA). The resistivity of the sintered sample was measured by a four-terminal method in the temperature region 17–300K.

3. Results and discussion

3.1. Effect of the synthesizing composition on the products obtained

The compositions of the starting materials are shown in Fig. 1. The dropping of the $HAuCl_4$ (HAC) solution in the mixture of DEA and alkoxide solution makes a yellow precipitate, which dissolves in the mixture when it is stirred. After dropping, an orange clear solution or a yellow suspension is obtained. The high concentration of DEA tends to form the orange clear solution [4–6].

Each solution was kept in a covered beaker in the laboratory. A large amount of gold was gilded on the

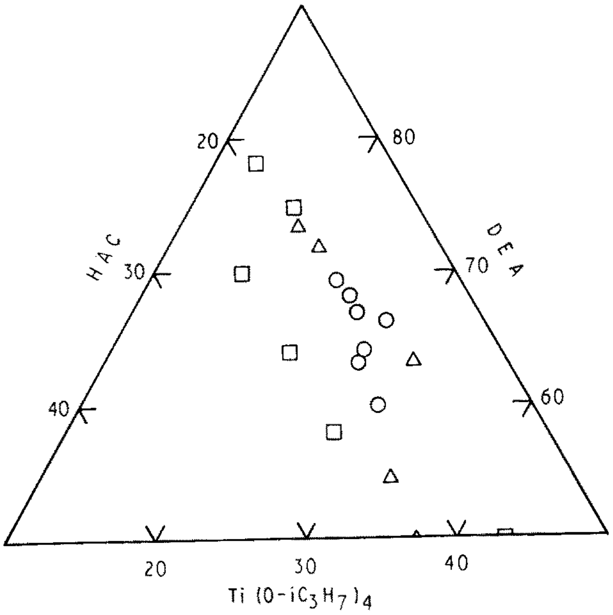

Figure 1 Composition diagram for the starting materials in molar ratio: (○) A, (△) B, (□) C (see text).

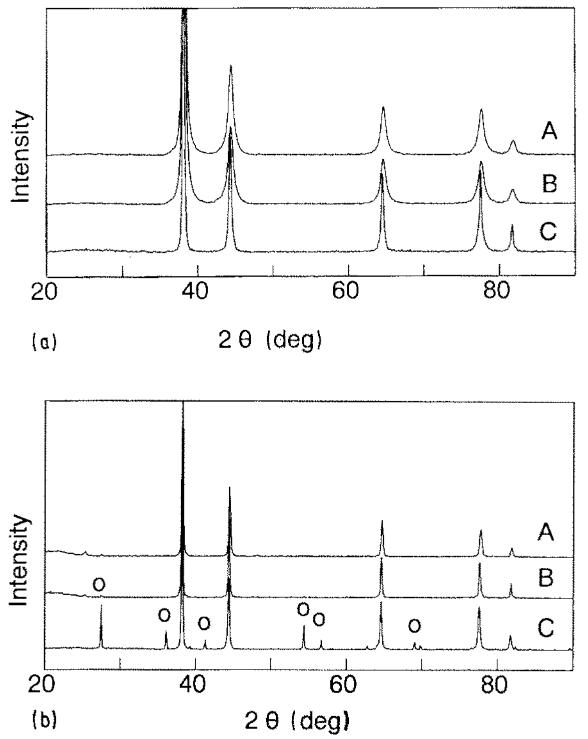

Figure 2 XRD of the three types of precipitates : (a) heated at 100 °C, and (b) reheated at 800 °C: (○) rutile.

surface of the beaker containing the clear orange solution, which was a non-viscous and non-dispersive precipitate; while a viscous brown or navy-blue paste was precipitated from the yellow suspension. No colour change was observed even for long aging in a dark place. This shows that the formation of a colloidal-gold precipitation is accomplished by the decomposition of HAC by visible light [7]. In Fig. 1, the formation map of gold paste is shown in the HAC–DEA–Alkoxide (Ti) system. The gold precipitate obtained was divided into three categories depending on the starting composition: (A) a viscous dark-brown precipitate, which showed metallic lustre when painted on a substrate and dried at 100 °C; (B) a navy-blue viscous precipitate which showed no metallic lustre when treated in the same way as (A); (C) a violet powder which showed no viscosity. As shown in Fig. 1, the gold paste of type A is obtained over a relatively wide region. In the case of preparation without a metal (Ti or Zr) alkoxide, only an aggregation of Au particles were observed and no viscous precipitate was prepared. The metal alkoxide acts as a regulating agent for the agglutination of Au particles. It is considered that the presence of excess DEA hinders good dispersion of the gold colloidal precipitate and enhances the stability of the metal alkoxide against hydrolysis; while too low a content of DEA tends to form a powder product (type C), as a result of the formation of an oxide and/or a hydroxide by losing the stability of metal alkoxide against hydrolysis [4–6].

3.2. Composition and resistivity of synthesizing paste

Fig. 2a shows XRD patterns of the three types A–C of precipitates heated at 100 °C. The peaks of the samples were attributed to the presence of Au alone. The XRD patterns of the same samples reheated at 800 °C are shown in Fig. 2b. The diffraction pattern of the powder for precipitate C is considerably different from the patterns of the other two. Strong peaks of rutile-type TiO_2 are realized in the case of precipitate C, while the other two samples showed only weak peaks. The Au colloid from types A and B is fundamentally the same; the difference between the viscosity of pastes A and B being due only to the concentration of residual organic compound. The metal lustre of the film surface appeared after heat treatment (600–800 °C) for the navy-blue precipitate, type B. The small quantity of titanium alkoxide is considered to be resisted in a precipitate. It dissolves in the supernatant liquid when the precipitate forms. In the case of the HAC–$Zr(OC_3H_7)_4$ system, exactly the same phenomena were observed.

Fig. 3 shows the surfaces of the paste printed on silica glass and heated at 800 °C for 1 h. The film is made from a fine matrix and small particles (1–8 μm).

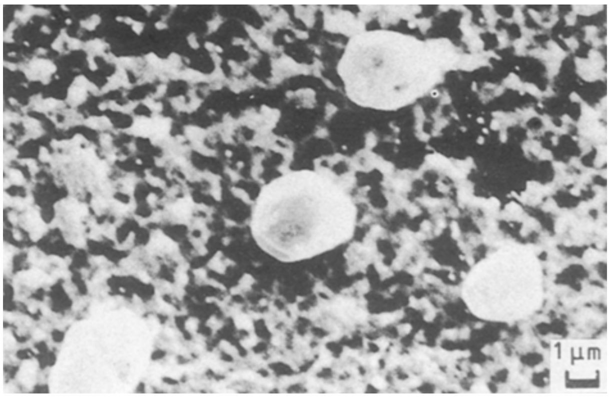

Figure 3 Surface morphology of a heated paste (type A).

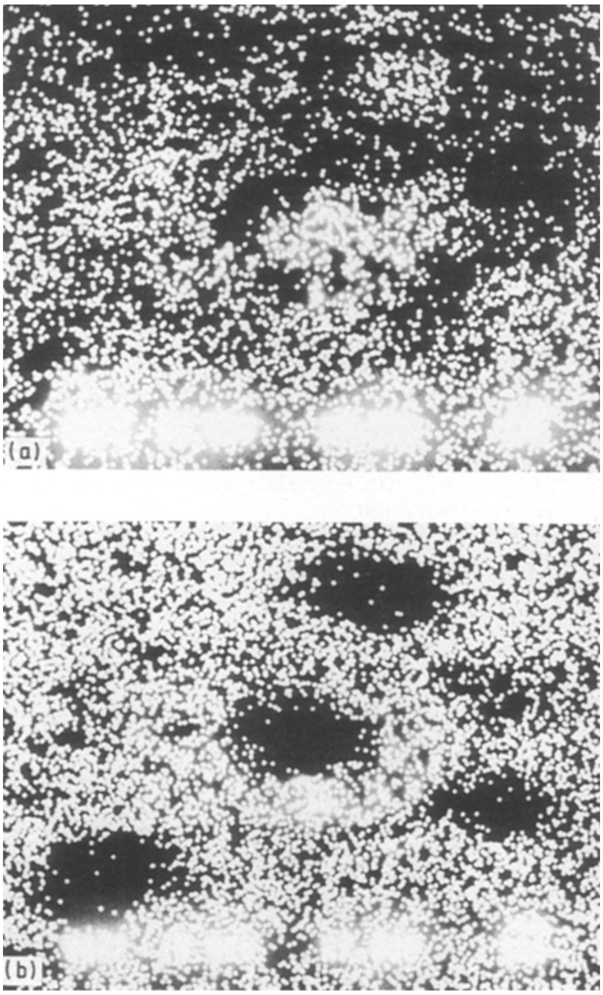

Figure 4a EPMA analysis of Fig. 3 (Au), and (b) EPMA analysis of Fig. 3 (Ti).

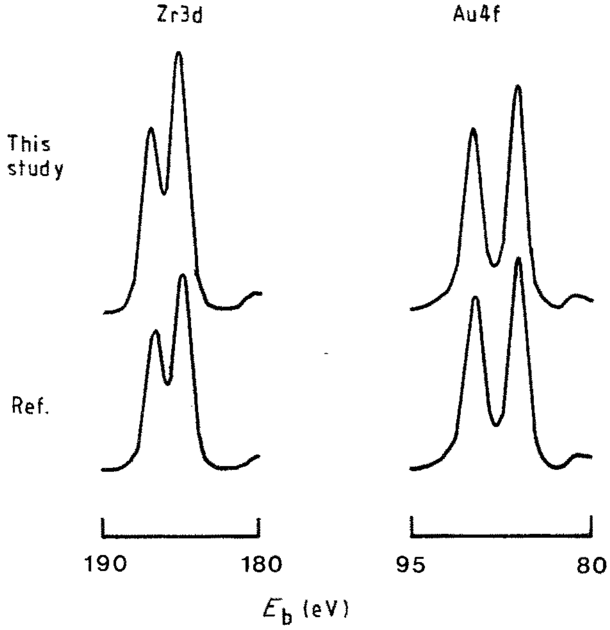

Figure 5 Electron spectra of Au–Zr paste.

Fig. 4a, b shows composition analysis by EPMA of the same samples. The bright points in these photographs show the presence of each element. The X-ray images of Au and Ti show that both elements are mixed homogeneously in the matrix, while small particles (1–8 μm) form from Au only.

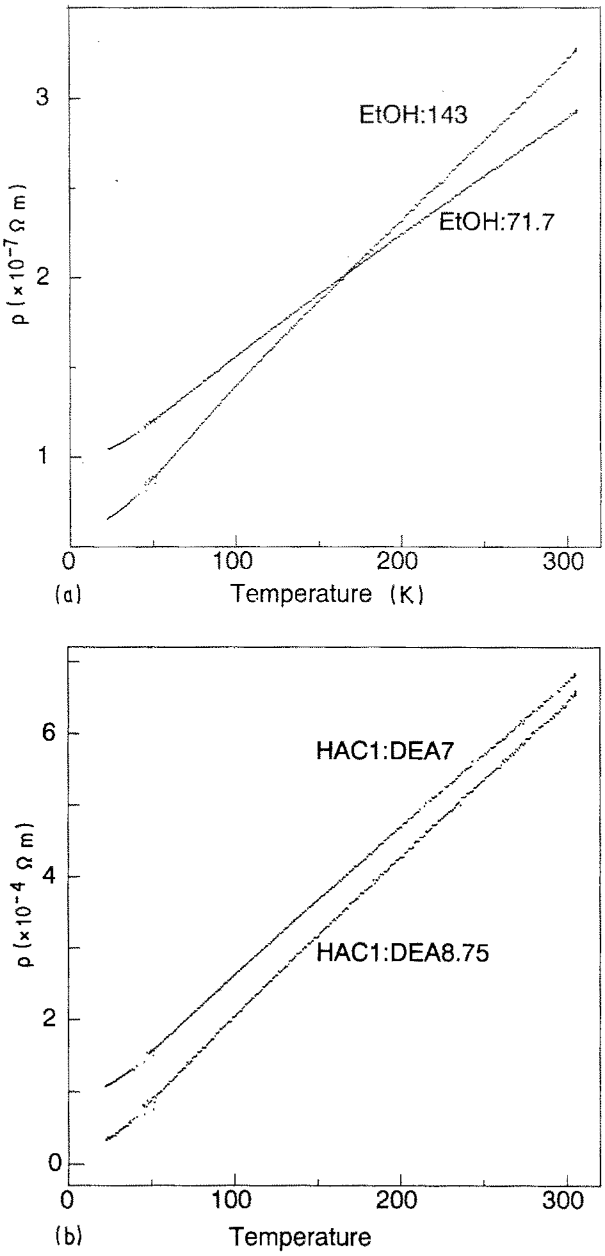

Figure 6 Temperature dependence of the resistivity of: (a) Au–Ti paste, and (b) Au–Zr paste.

This phenomena could be explained by two hypotheses. The grains were precipitated from a composite matrix (Au and Ti) and/or small gold particles existed in the paste obtained and they act as seed crystals and grow. However, neither conclusion could be established in this study. The same results could be obtained for the HAC–Zr(OC_3H_7)$_4$ system.

To confirm the electrical state of each element, ESCA measurement was carried out. Fig. 5 shows the results of an ESCA study for an Au–Zr heated film. ZrO_2 (TOSOH Company) was used as a reference. Zirconium exists as an oxide in the film. The formation of Au alloy is excluded because the ESCA measurement data shows good agreement with pure Au.

The temperature dependence of the resistivity for the film painted on an α-Al_2O_3 plate and heated is shown in Fig. 6a, b. These films exhibit good resistivity which is about 3.0×10^{-7} Ω m at room temperature. The resistivity of those films decreased with decreasing temperature. This result suggests that the film thus obtained is a good metallic conductor, despite the titanium (or zirconium) compound included in the matrix. The titanium (or zirconium) oxide has no effect on the conductivity of this film.

4. Conclusion

The liquid-phase preparation of Au-paste and its properties were investigated. A good conductive paste was obtained from a sol–gel-like liquid-phase reaction. This method is not only simple, but also easy to do in a laboratory. The sintered film showed good resistivity, $3.5 \times 10^{-7} \Omega\,\mathrm{m}$, despite included titania or zirconia. This value is not so different from that of pure gold which is $2.35 \times 10^{-8} \Omega\,\mathrm{m}$. Generally, Au–$TiO_2$-composite films show lower resistivity than Au–ZrO_2-composite films except in a few cases.

5. Acknowledgement

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References

1. S. SAKKA, "Treatise on materials science and technology", Vol. 22, Glass III (Academic Press, New York 1982) p. 129.
2. E. BARRINGER, N. JUBB, B. FEGLEY, R. L. POBOR and H. K. BOWEN, "Ultrastructure processing of glasses, ceramics and composites", edited by L. L. Hench, D. R. Ulrich, (John Wiley, New York 1984) p. 315.
3. B. E. YOLDAS, *J. Mater. Sci.* **21** (1986) p. 1080.
4. Y. TAKAHASHI and Y. MATSUOKA, *J. Mater. Sci.* **23** (1988) p. 2259.
5. K. KAMIYA, T. NISHIJIMA and K. TANAKA, *J. Am. Ceram. Soc.* **73** (9) (1990) 2750.
6. K. KOHNO, *J. Mater. Sci.*, **27** (1992) 658.
7. "Merck Index", 10th Edn, edited by M. Windholz (Merck, Rathway, 1983) p. 650.

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