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Electroless silver coating of rod-like glass particles

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ABSTRACT

An electroless silver coating of rod-like glass particles was performed and silver glass composite powders were prepared to impart electrical conductivity to these non-conducting glass particles. The low density Ag-coated glass particles may be utilized for manufacturing conducting inorganic materials for electromagnetic interference (EMI) shielding applications and the techniques for controlling the uniform thickness of silver coating can be employed in preparation of biosensor materials. For the surface pretreatment, Sn sensitization was performed and the coating powders were characterized by scanning electron microscopy (SEM), focused ion beam microscopy (FIB), and atomic force microscopy (AFM) along with the surface resistant measurements. In particular, the use of FIB technique for determining directly the Ag-coating thickness was very effective on obtaining the optimum conditions for coating. The surface sensitization and initial silver loading for electroless silver coating could be found and the uniform and smooth silver-coated layer with thickness of 46 nm was prepared at 2 mol/l of Sn and 20% silver loading.

1. Introduction

Recently, as the use of electronic products and communication instruments increases, electromagnetic interference (EMI) has been a problem for the lifetime and efficiency of the instruments. Although EMI-transmitted electromagnetic waves can easily damage electronic components, good conductive materials can act as a shield against electromagnetic penetration [1–3], and metals such as gold, silver, copper, nickel, and aluminum are the best material for shielding. In addition, gold and silver provide excellent conductivity properties but they are expensive [4]. Nickel and copper also display good electrical conductivities but are susceptible to oxidation, resulting in the concomitant diminution of desirable properties such as quality and stability. In order to overcome the problems associated with the oxidation and the high cost simultaneously, the substitution by silver-coated copper particles for solid silver particles have been proposed [5,6]. However, copper is still heavy and expensive as a core material. Accordingly, silver-coated glass powders can be a desirable option in electronic industry to solve those problems since glass has the favorable properties such as design capabilities, lightweight, and anti-corrosion. Besides, silver-coated inorganic particles or polymer microspheres can be used as the filler for conductive adhesives since the electrical conductivity of silver is much higher than that of inorganic particles [7]. In addition, the silver-plated particles can be used as biosensor materials. The potential use of surface plasmon resonance (SPR) for gas detection and biosensing was first demonstrated by Nylander et al. [8]. Since then, SPR biosensing has received growing attention from the scientific community. The advantage of employing SPR in biosensing lies in its capability of monitoring binding interactions without the need for labeling and fluorescence of the biomolecules. In addition, this technique has shown great promise in the real-time determination of the concentration, kinetic constant and binding specificity of individual biomolecular interactions. Antibody–antigen interactions, peptide–protein interactions and DNA hybridization conditions can all be analyzed [9].

In general, in order to prepare metal-coated ceramics, a wet chemistry method is usually used, such as precipitation, ball milling, electroless deposition, and reduction. Among these methods, electroless deposition has a greater advantage in obtaining an evenly dispersed metal coating [10]. Electroless plating is a process in which a metal salt is reduced to metal onto a surface from a solution without the use of an electrical potential [11]. Thus, the surface does not have to be electronically conducting, while the kinetics of electron transfer should be slow enough to avoid the reduction of the metal ions and nucleation in solution. This process has been widely utilized in coating many materials with metal films for numerous applications [12] due to its ease of use, its relatively quick results (usually <20 min), and uniform coatings.

In the present work, an electroless silver-coating process was employed on rod-like fine glass particle and silver glass composite powders were prepared. Rod-like glass particle was utilized since

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the glass is light and the high aspect ratio can provide the good conductivity at relatively low loading when used as shielding fillers. For the surface pretreatment, Sn sensitization was performed and the optimum conditions were found for the preparation of the thin uniform silver-coating layers. The coating powders are characterized by scanning electron microscopy (SEM), focused ion beam microscopy (FIB), and atomic force microscope (AFM). The purpose of the present work was mainly focused on controlling the uniform thickness of silver coating by characterization with various microscopic techniques since the thickness control is very important in preparation of biosensing materials for SPR and other materials for microelectro-mechanical systems (MEMS).

2. Experiments

2.1. Materials

Glass fiber (mean diameter of 5 μm and length of 50 μm) was obtained from Fluoro Chemical. $SnCl_2$ (anhydrous, 98%), $AgNO_3$ (99%), L-ascorbic acid, NH_4OH, and hydrofluoric acid were supplied by Aldrich and used as received. In all preparations, absolute methanol and distilled water were used.

2.2. Coatings preparation

Electroless plating was carried out by multistep processes which included: scouring, rinsing, etching, rinsing, sensitization, rinsing, electroless silver plating, rinsing, and drying. Ten grams of glass fiber was scoured in 0.1 mol/l HF solution at room temperature prior to use. The samples were rinsed in distilled water and etched in a mixture of ethylene glycol solution. Then, surface sensitization was conducted by immersion of the samples into an aqueous solution containing 1–3 mol/l of acid $SnCl_2$ solution (with 38% HCl at 30 °C). The specimens were rinsed in distilled water and completely dried off about 80 °C, then immersed in the electroless silver-plating bath for 10 min. The electroless silver-plating bath contained silver nitrate: 5–40% (the weight percentage of total silver to glass fiber). Finally, L-ascorbic acid was added and the samples were rinsed with distilled water, methyl alcohol and dried in an oven at 80 °C.

2.3. Characterization

The surface resistivity of the conductive coatings was measured in a plastic cylinder (1 cm in diameter and 4 cm in length) by Agilent 34401A Multimeter after pressing the composite particles at 4 atm. The microstructure of glass fiber coatings were observed by SEM (Hitachi S-4700). The thickness of the silver coating was measured by utilizing FIB (FEI Nova 200 STEM) micrographs and the surface image was scanning by AFM. The AFM images were acquired in non-contact mode using a PSIA Xe-150 (Korea). Silicon cantilevers were used and the AFM scanner and position sensors were calibrated using standard samples from Mikromash.

3. Results and discussion

3.1. Effect of $SnCl_2$ concentration and silver loading

In Fig. 1, surface resistance of silver-coated glass particles as a function of $SnCl_2$ concentration at 20% of initial silver concentration is given. The figure shows the optimum $SnCl_2$ concentration exists for the minimum surface resistance at 1 mol/l probably due to the saturation of glass surface with tin atoms in sensitizing process. The technique for electroless metal plating is based on the use of a chemical agent that permits the reduction of the metal from solution on the surface of the substrate. For this process, the surface does not have to be electronically conducting, while the kinetics of electron transfer should be slow enough to avoid the reduction of the metal ions and nucleation in solution [13]. In sensitizing process for the present systems, Sn^{2+} ions adsorb on the surface of the glass. Then, ammonical $AgNO_3$ is added to the solution and a redox reaction occurs involving the oxidation of surface Sn^{2+} to Sn^{4+} and reduction of Ag^+ to Ag^0 [13]. Accordingly, one atom of Sn molecule on the surface can attach two Ag atoms. As the tin concentration increases, the more deposition of silver can be expected as shown in Fig. 1. However, after the glass surface is saturated with tin atoms (probably at 1 mol/l), the excess tin atoms may provide some bigger Ag clusters on silver monolayer on glass particle surfaces. Therefore, it appears that the resulting silver multilayer and bigger silver clusters can form irregular and thick Ag coatings on glass, which allow slight increase in resistivity of the composite. In Fig. 2, the similar results were observed for the effect of initial silver

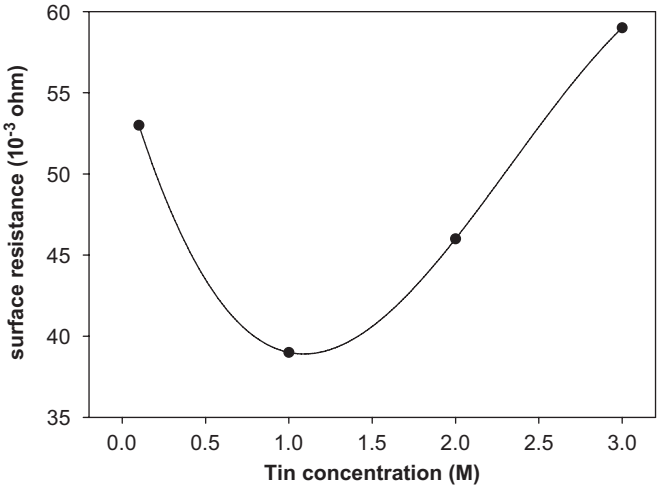

Fig. 1. Surface resistance of silver-coated glass powder as a function of $SnCl_2$ concentration at initial silver concentration of 20%.

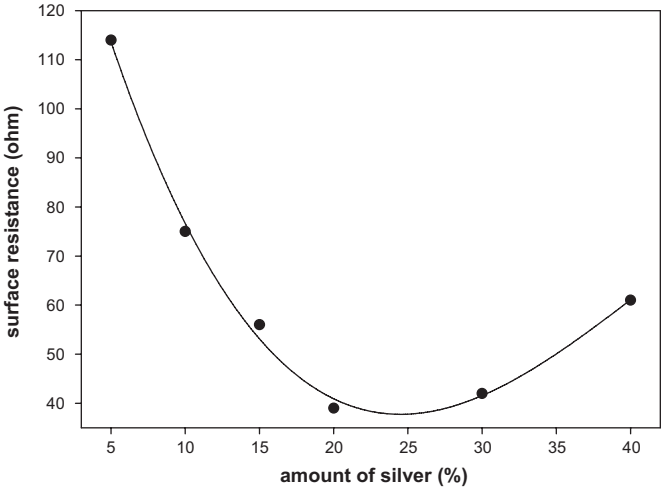

Fig. 2. Surface resistance of silver-coated glass powder as a function of initial silver concentration at $SnCl_2$ concentration of 1 mol/l.

concentration on the surface resistance. When the silver content increases, the more compact and smoother deposits of silver can be attained. However, silver loading (total silver weight to total glass fiber weight) reaches to the minimum resistance at 20%, and the additional increase in initial silver concentration provides even higher surface resistance of silver glass composite.

3.2. Coatings characterization

The morphology of the silver-coated surface was studied by scanning electron microscope (SEM). For direct measurements of the Ag-coating thickness under various processing conditions, we employed FIB since the SEM and AFM measurements could were provide enough information on the thickness. The steps involved in the thickness measurement via FIB was described in the previous work [14].

SEM photographs of the silver-coated powder surface obtained at different plating conditions are shown in Fig. 3 and the cross-sections of the silver glass composite created by FIB sputtering are shown in Fig. 4. Without Sn sensitizing, no silver deposition was observed (Figs. 3(a), 4(a), and 5(a)). As Sn concentration was increased at a fixed silver content (20%) in the order of (b), (e), and (c) in Figs. 3 and 4, SEM photographs revealed that compact deposition could be obtained on glass fiber and the images showed the grain size was almost kept constant with increasing Sn concentration. On the other hand, FIB and AFM images clearly revealed that the optimum deposition was attained at 1 mol/l of Sn. As shown in Figs. 4(b) and 5(b), the thickness of silver coating was 22 nm at 0.1 M of Sn but the glass surface was not completely

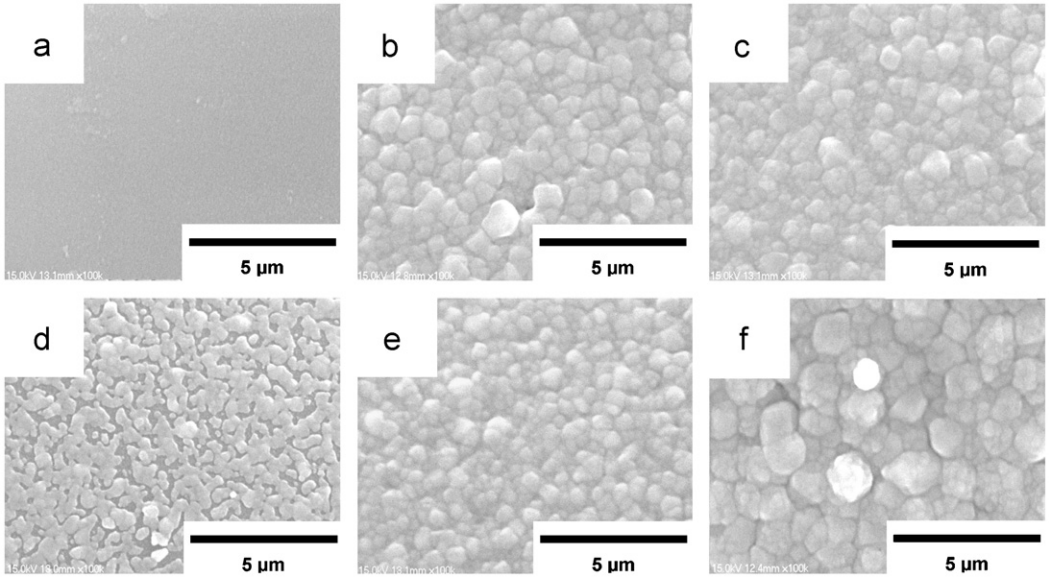

Fig. 3. SEM images of the silver-coated powder surface obtained at different initial silver and $SnCl_2$ concentrations in the bath: (a) $SnCl_2$ 0 mol/l, silver 20%; (b) $SnCl_2$ 0.1 mol/l, silver 20%; (c) $SnCl_2$ 2 mol/l, silver 20%; (d) $SnCl_2$ 1 mol/l, silver 5%; (e) $SnCl_2$ 1 mol/l, silver 20%; and (f) $SnCl_2$ 1 mol/l, silver 40%.

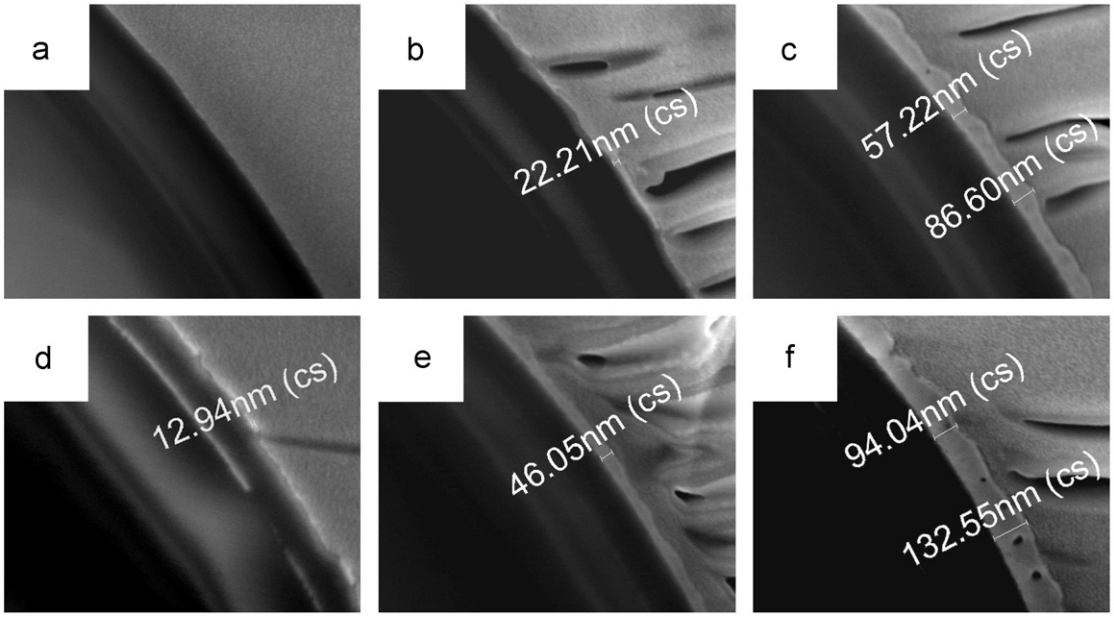

Fig. 4. FIB photographs of the silver-coated powder surface obtained at different initial silver and $SnCl_2$ concentrations in the bath: (a) $SnCl_2$ 0 mol/l, silver 20%; (b) $SnCl_2$ 0.1 mol/l, silver 20%; (c) $SnCl_2$ 2 mol/l, silver 20%; (d) $SnCl_2$ 1 mol/l, silver 5%; (e) $SnCl_2$ 1 mol/l, silver 20%; and (f) $SnCl_2$ 1 mol/l, silver 40%.

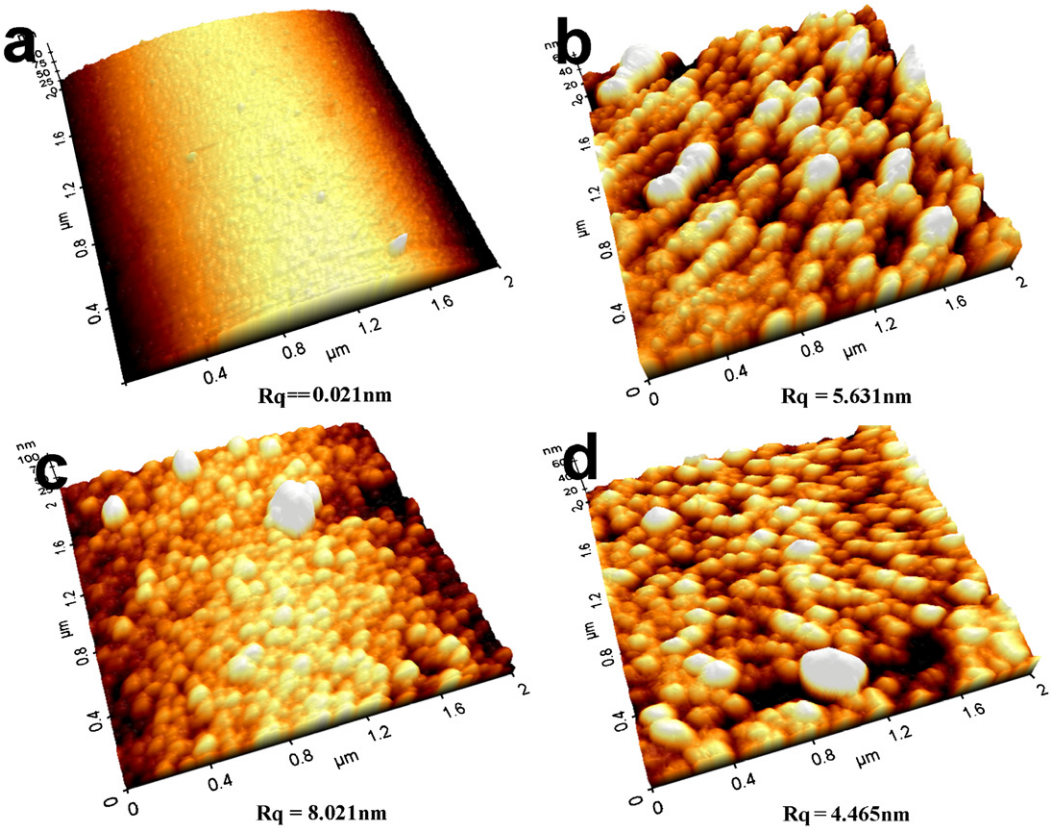

Fig. 5. AFM images of the silver-coated powder surface obtained at different initial silver and $SnCl_2$ concentrations in the bath: (a) $SnCl_2$ 0 mol/l, silver 20%; (b) $SnCl_2$ 0.1 mol/l, silver 20%; (c) $SnCl_2$ 1 mol/l, silver 5%; and (d) $SnCl_2$ 1 mol/l, silver 20%.

covered by silver, while Figs. 4(e) and 5(d) showed that the uniform and smooth silver layer was formed and thickness of silver was 46 nm at 1 mol/l of Sn. In addition, the root mean square roughness (Rq) for Fig. 5(d) is 4.46 nm and slightly smaller than that for Fig. 5(b), i.e., 5.63 nm. Besides, Fig. 4(c) shows that the thickness was increased at 2 mol/l of Sn, but the silver layer was not smooth and relatively non-uniform deposition was formed.

When the initial silver concentration was increased under constant sensitizing conditions, SEM photographs showed that deposition became more compact but bigger grains were obtained as given in Fig. 4(d) and (e). The similar results were observed in FIB photographs and AFM images. The silver-coating thickness was increased with increasing total silver loading. However, Fig. 4 shows the optimum silver-coated deposition was obtained when 20% silver was loaded compared to the sample Fig. 4(d) and (f) since 5% silver loading for sample (d) did not provide full coverage on the glass surface and sample (f) showed much thicker and irregular silver deposition was obtained with 40% silver loading. From the AFM measurements, it was found that 20% silver loading (Rq; 4.46 nm) allowed more compact deposition than 5% loading (Rq; 8.02 nm). Accordingly, it is to be noted that the variation in the coating thickness as a function of coating variables can be studied precisely by the use of FIB, which appears to be the most convenient technique to measure the Ag-coating thickness directly.

4. Conclusion

The electroless Ag coating of rod-like glass particles has been performed and characterized by SEM, AFM, and FIB along with surface resistivity measurements. It was found that silver coating over the glass by electroless technique is feasible and efficient. In particular, the use of FIB technique for determining directly the Ag-coating thickness was very effective on obtaining the optimum conditions for coating. The optimum conditions of surface sensitization and initial silver loading for electroless silver coating were 2 mol/l of Sn and 20% silver loading. Under these conditions, the uniform and smooth silver-coated layer could be attained with thickness of 46 nm.

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