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Silver metallization for microwave device using aerosol deposition

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Abstract

We examined the possibility of using aerosol deposition (AD) as a simple, environmentally friendly and dry metallization process capable of acting as an alternative to the electroless and electroplating methods. Silver thick films were fabricated, their characteristics evaluated, and the factors influencing their growth investigated. As a result, silver thick films were successfully fabricated by AD with high deposition rates ($10 \,\mu\text{m}/\text{min}$) at room temperature. The resistivity of the as-deposited silver thick films was 8–10 times larger than that of the bulk silver. Post-annealing increased the resistivity of the silver films by approximately 2–3 times compared to that of the bulk silver. Microstructural observations revealed an increase in the connectivity between the silver particles after the heat treatments, which reduced the resistivity of the as-deposited silver films. © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: C. Electrical conductivity; Silver thick films; Metallization process; Aerosol deposition (AD)

1. Introduction

With the ubiquitous and the rapid growth of wireless communication, the design and fabrication of miniaturized RF/ microwave devices are necessary [1]. Especially for the wireless and mobile communication, planar devices, such as patch antennas and planar bandpass filters, have attracted design attention for high frequency integrated circuits. Therefore, a metallization process is necessary according to the strong needs for planar device technology. Electroless and electroplating methods were usually used as conventional metallization processes. However, human health and the environment have been threatened by the wastewater generated from the plating manufacturing process and the rinse process. To remove heavy metals from effluent discharges, treatment processes, such as metal hydroxide precipitation, ion exchange and membrane separation, have been developed and used in advanced countries but not in developing countries due to their complexity and high cost [2,3]. Therefore, to solve these problems, this research proposes an environmentally friendly, simple, and dry metallization process with no chemical solutions.

Our research group has been studying an aerosol deposition (AD) process that has superior merits, such as a room-temperature process, a high deposition rate and a high density. Research on the AD process in other groups has primarily concentrated on the fabrication of ceramic thick films and the evaluation of their properties. In this study, we examine the potential of the AD process as an environmentally friendly, simple and dry metallization process that can be used as an alternative to the conventional plating method.

2. Experimental

The AD process is based on shock loading solidification due to the impact of ultra fine particles accelerated through a nozzle by carrier gases. The details of the AD process apparatus can be referred to elsewhere [4]. Silver powder with a purity of 99.99% (AGE09PB, Kojundo Chemical Laboratory Co., Ltd., Japan) and a primary particle size of approximately 1 μ m was selected as the starting power. The silver particles were aerosolized in the aerosol chamber and transported into a deposition chamber by He gas at a flow rate of 7 L/min. The orifice size of the nozzle was 10 mm \times 0.4 mm and the deposition area was 10 mm \times 5 mm. The distance between substrates and the nozzle was 0.5 mm, the working pressure was 36 torr, and the deposition time was 6 min 30 s. Under the above deposition conditions, silver thick films were fabricated on the glass

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(70010128H, LCI Co., Ltd., Korea) and Al₂O₃ substrates (ALO1005 (99.8%), JSLS Co., Ltd., Korea) at room temperature by AD. To confirm the effect of the conditions on the growth of the aerosol-deposited silver thick films, the microstructures of the AD-fabricated silver films were observed using a field-emission scanning electron microscopy (FE-SEM, S-4700, HITACHI Ltd., Japan) and X-ray diffractometer (XRD, X'Pert PRO, PANalytical). The resistivity of the aerosol-deposited silver films was measured using a 4-point probe (CMT-SR 1000N, Advanced Instruments Technology Co., Ltd., Korea) to evaluate the conductor loss. A post-annealing process was carried out at 300 °C for 2 h in a N₂ atmosphere to reduce the resistivity compared to that of the as-deposited silver films. To confirm the causes of the decreased resistivity, their microstructures were observed by SEM.

3. Results and discussion

3.1. Growth of silver thick films fabricated by AD process

In order to research the AD-induced growth of the silver thick films, they were fabricated on the glass and Al_2O_3 substrates by AD. As a result, the silver thick films were successfully fabricated by AD with high deposition rates (10 μ m/min) at room temperature.

Fig. 1 shows the XRD patterns of the silver powders, and the aerosol-deposited silver films on the Al_2O_3 substrates. The XRD patterns of the aerosol-deposited silver films exhibited

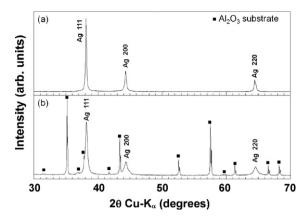
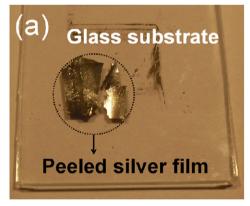


Fig. 1. XRD peak patterns of the films deposited by AD: (a) silver powder and (b) fabricated silver films on Al_2O_3 substrates.

peak broadening in comparison with that of the as-received silver powders. A literature survey revealed that the peak width is increased during the deformation of metals [5]. In this article, greater peak broadening of the silver peaks in Fig. 1(b) was observed in comparison with that in Fig. 1(a), implying that plastic deformation of the silver powders occurred during the AD process. However, the appearance of the silver thick films formed on the glass and Al₂O₃ substrates differed, as shown in Fig. 2. The former peeled off easily from the substrate in comparison with the latter. In general, the fabrication process of a metal film for planar circuits should provide strong adhesion strength between the metal films and the substrates. Therefore,



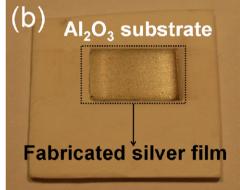
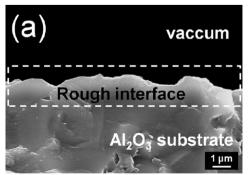


Fig. 2. Appearance of aerosol-deposited silver films on the (a) glass and (b) Al₂O₃ substrates.



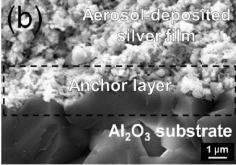


Fig. 3. Cross-sectional SEM images (a) before and (b) after deposition of silver films on the Al₂O₃ substrates by AD.

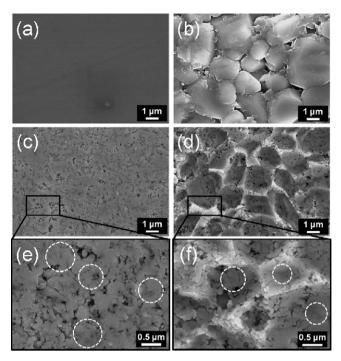


Fig. 4. SEM micrograph of surface of (a) glass and (b) Al_2O_3 substrates and backside of silver films (c) on the glass and (d) Al_2O_3 substrates and (e), (f) their enlarged images.

we investigated the factors influencing the adhesion strength were. We hypothesized that the adhesion strength between the aerosol-deposited silver films and the substrates was related to the interface between them. Therefore, the glass and Al₂O₃ substrates, which has flat and rough surface, respectively, were used to support the hypothesis. In addition, the use of a surface profiler revealed that the surface roughness ($R_a = 4.6 \text{ nm}$) of the glass substrates was much lower than that $(R_a = 270 \text{ nm})$ of the Al₂O₃ substrates. Firstly, the SEM cross-sectional images of the aerosol-deposited silver films on the Al₂O₃ substrates, which had good adhesion strength, were observed in Fig. 3. Fig. 3(a) shows the rough surface of the as-received Al₂O₃ substrates. After the deposition of the silver films on the Al₂O₃ substrates, inspection of Fig. 3(b) revealed that the silver particles filled the rough surface of the Al₂O₃ substrates. As for the films on the glass substrates, the cross-sectional SEM image was very difficult to observe due to the ease with which the aerosoldeposited silver films peeled off. However, observation of the backside of the peeled silver films enabled the growth of the aerosol-deposited silver films to be inspected. After initially peeling off the aerosol-deposited silver films on the two substrates, the backsides of the peeled silver films were observed by SEM, as shown in Fig. 4(c)-(f). The backside of the silver films on the glass substrates was flat, while that on the Al₂O₃ substrates was rough, in line with the morphology of each substrate surface shown in Fig. 4(a) and (b).

Considering the surface roughness of the substrates and the observed morphology of the aerosol-deposited silver films, the growth of the silver films on the two substrates was depicted in Fig. 5. Because of the flat surface of the glass substrates, no anchoring layer was formed, as shown in Fig. 5(a). However,

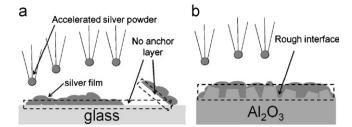


Fig. 5. Schematic of appearance of aerosol-deposited silver films on the (a) glass and (b) Al₂O₃ substrates.

the rough surface of the Al₂O₃ substrates can give strong adhesion strength, by acting as the anchoring layer, as shown in Fig. 5(b). During the AD process, the anchoring layer acts to increase the adhesion strength between the aerosol-deposited films and the substrates [4]. Using ceramic particles as the starting powders allows the accelerated ceramic particles to form the anchoring layer on the glass substrate because of high hardness of ceramic particles [4]. However, the anchoring layer is formed via a different mechanism in the fabrication of the silver films compared to that of the ceramic films. The enlarged images of the backsides of the aerosol-deposited silver films on the glass and Al₂O₃ substrates shown in Fig. 4(e) and (f) revealed the plastic deformation and bonding between the silver particles, as marked with dashed circles. Moreover, no anchoring layer was formed by the silver particles. In the case of the Al₂O₃ substrates, the anchoring layer was formed by the rough surface of the Al₂O₃ substrate itself, rather than by the accelerated silver particles.

These results were attributed to the Vickers hardness variation between the silver (about 51 Hv) [6], glass (about 635 Hv) [7], and Al_2O_3 (about 2040 Hv) [8] materials. As the silver material was by far the softest, the silver particles were easily deformed during the impact on the substrates for AD deposition with high deposition rates. On the other hand, the silver particles were too soft to form anchor points on the flat and hard surface of the glass substrates. Therefore, metal particles with high hardness are required to increase the adhesion strength.

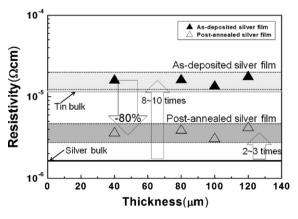
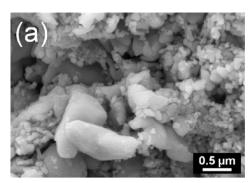


Fig. 6. Comparison of the resistivity of the as-deposited and post-annealed silver films.



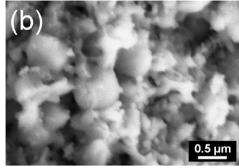


Fig. 7. Cross-sectional SEM images of the (a) as-deposited and (b) post-annealed silver films.

3.2. Resistivity of silver thick films grown by AD process

The resistivity of the aerosol-deposited silver thick films on the Al_2O_3 substrates at room temperature was measured by using 4-point probe measurements. The resistivity of the asdeposited silver films ranged from 13.4 to 17.5 $\mu\Omega$ cm, as shown in Fig. 6, which was approximately 8–10 times larger than that of the bulk silver (1.6 $\mu\Omega$ cm) [9]. Post-annealing was used to decrease the resistivity of the as-deposited silver films. The resistivity of the post-annealed silver films at 3.1–4.2 $\mu\Omega$ cm was approximately 2–3 times larger than that of the bulk silver. The resistivity of the post-annealed silver films was decreased to approximately 20–30% of that of the as-deposited silver films.

We considered that the resistivity of the post-annealed silver films is capable of satisfying the required resistivity for the metal trace in microwave devices. To explain the decrease in the resistivity after the heat treatments, cross-sectional SEM images of the as-deposited and post-annealed silver films were observed, as shown in Fig. 7(a) and (b), respectively. The connectivity between the silver particles was increased in the post-annealed silver films, which reduced the resistivity of the as-deposited silver films. In addition, we considered that the nozzle-ejected metal particles need to be more accelerated in the AD process in order to fabricate the dense silver films, and that this greater acceleration decreased the resistivity of the as-deposited silver films without heat treatment.

This research confirmed the superior merits of the AD process such as its high deposition rates ($10 \,\mu\text{m/min}$), capability for room-temperature processing, and low resistivity. Moreover, the densification of the silver films and the increased adhesion strength between the deposited films and the substrates both helped to improve the characteristics of the metal films fabricated by AD. Consequently, the capability of the AD-metallization process to be used in the fabrication of microwave devices was confirmed.

4. Conclusions

The AD process was proposed as a simple, environmentally friendly and dry metallization process. The silver thick films

were fabricated on the glass and Al_2O_3 substrates, which has flat and rough surface, respectively, by AD with high deposition rates (10 μ m/min) at room temperature. The hardness and surface roughness of the substrates affected the growth of the aerosol-deposited silver thick films. The resistivity of the asdeposited silver films was approximately 8–10 times larger than that of the bulk silver. Post-annealing increased the resistivity of the silver films approximately 2–3 times compared to that of the bulk silver. The connectivity between the silver particles was increased after the heat treatments, which reduced the resistivity of the as-deposited silver films.

Acknowledgements

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References

- [1] G.M. Yang, A. Shrabstein, X. Xing, O. Obi, S. Stoute, M. Liu, J. Lou, N.X. Sun, Miniaturized antennas and planar bandpass filters with self-biased NiCo-ferrite films, IEEE Transactions on Magnetics 45 (2009) 4191–4194.
- [2] A. Khelifa, S. Moulay, A.W. Naceur, Treatment of metal finishing effluents by the electron flotation technique, Desalination 181 (2005) 27–33.
- [3] H. Katsumata, S. Kaneco, K. Inomata, K. Itoh, K. Funasaka, K. Masuyama, T. Suzuki, K. Ohta, Removal of heavy metals in rinsing wastewater from plating factory by adsorption with economical viable materials, Journal of Environmental Management 69 (2003) 187–191.
- [4] J. Akedo, Room temperature impact consolidation (RTIC) of fine ceramic powder by aerosol deposition method and applications to microdevices, Journal of Thermal Spray Technology 17 (2008) 181–198.
- [5] A.R. Kilmametov, G. Vaughan, A.R. Yavari, A. LeMoulec, W.J. Botta, R.Z. Valiev, Microstructure evolution in copper in copper under severe plastic deformation detected by in situ X-ray diffraction using monochromatic synchrotron light, Materials Science and Engineering A 503 (2009) 10–13.
- [6] T. Kizuka, H. Ichinose, Y. Ishida, Structure and hardness of nanocrystalline silver, Journal of Materials Science 32 (1997) 1501–1507.
- [7] M. Yamane, J.D. Mackenzie, Vicker's hardness of glass, Journal of Non-Crystalline Solids 15 (1974) 153–164.
- [8] T. Tani, Y. Miyamoto, M. Koizumi, Grain size dependence of Vickers microhardness and fracture toughness in Al₂O₃ and Y₂O₃ ceramics, Ceramics International 12 (1986) 33–37.
- [9] J.R. Greer, R.A. Street, Thermal cure effects on electrical performance of nanoparticle silver inks, Acta Materialia 55 (2007) 6345–6349.