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Microstructural Analysis of Sintered Ag Interconnections through Different Reduction Methods

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Abstract

Taking the advantage of low sintering temperature and high processing flexibility, Ag nanoparticles have been widely used to fabricate interconnections and joints. This report studies the preferred orientation of the sintered nanoparticles and electrical resistivity subjected to thermal or/and chemical reductions using grazing incidence XRD and EBSD. Compared to chemical reduction which develops (111) out-of-plane texture, thermal sintering of nanoparticles tends to form (100)-oriented grains and more twin boundaries. A decrease in sintered film thickness further intensifies (111) texture in the case of chemical sintering. A proportional relationship between electrical conductance and twin boundary ratio was also proposed.

1. Introduction

Taking the advantage of low sintering temperature and high processing flexibility, metallic nanoparticles (NPs) have been widely used to fabricate interconnections [1-5]. For the preparation of silver NPs, a variety of stabilizers for silver nanoparticles, such as a thin layer of poly(vinyl pyrrolidone) [6], polyacrylate [7], oleylamine [8], and alkylthiol [9] coated on the surfaces, have been proposed for NP preservation. Besides, our previous report suggested carboxylate can protect Ag NPs up to months without changing the properties [10].

To obtain excellent electrical conductivity, capping molecules protecting the nanoparticles have to be removed by thermal or chemical ways to form conductive sintered films. The reduction mechanism of carboxylate on Ag NPs has been proposed [11], but there are very few reports investigating the growth texture of sintered structure, and the contribution to electrical performance. The literatures indicate that the microstructure of metal films is closely related to their physical properties, e.g. electrical resistivity [12-17]. It has been suggested that heat treatment and film thickness both strongly affect the preferred orientation of metal films. In this study, we investigated the relationship between growth texture, grain boundary characteristics and electrical conductance of NP-sintered films prepared by different reduction methods.

2. Results and Discussion

In this study, chemically synthesized nano silver particles (NP) (Fig. 1) were prepared using silver nitrate as the precursor. Carboxylic acid (lauric acid) was used to form a self-assembled protective monolayer. Ag NPs were mixed with α-terpineol and a small amount of ethyl cellulose to form pastes, which was named Ag-NPs-EC. The weight ratio of the particles to the solvents was 7:3. The nanoparticles were also suspended in toluene at the ratio of 1:6.

As for thermal sintering, the paste was applied to 1x1 cm^2 silicon wafer using blade casting and was heated at 275°C for 30 minutes in two different kinds of atmospheres N_2-H_2 (namely NH) and FA/N_2 (namely FAV), respectively. Chemical sintering was performed by means of soaking the sample into a chemical reduction agent including liquid formic acid liquid (designated as FAD) at room temperature and 1M ascorbic acid solution at 75°C (designated as AAD) respectively. NP suspensions were deposited on a PET substrate by spin coating, named FADS and AADS. Table 1 tabulates the conditions and corresponding designations of the samples

Table 1. Sample designations

NH	N_2-H_2 atmosphere
FAV	Formic acid vapor
FAD	Dipping in liquid formic acid (paste)
AAD	Dipping in liquid formic acid (paste)
FADS	Dipping in liquid formic acid (suspension)
AADS	Dipping in liquid formic acid (suspension)

Difference in sintering processes resulted in texture difference. XRD patterns of the sintered structures of different samples are illustrated in Fig. 2. The calculated relative texture coefficients are given in Fig. 3. Those data indicate that chemical sintering generally forms a (111) oriented structure (yellow triangle). Compared with those with pastes (AAD and FAD), sintered structures prepared using suspensions using spin-coating (AADS and FADS) show a reduced film thickness, and an enhanced (111) texture. With respect to thermal sintering (NH and FAV), a weak (100) preferred orientation (blue circle) can be detected.

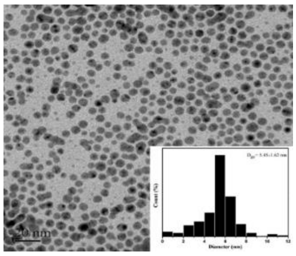

Fig. 1 (a) TEM image of Ag NPs, and (b) SEM image of Ag SMPs.

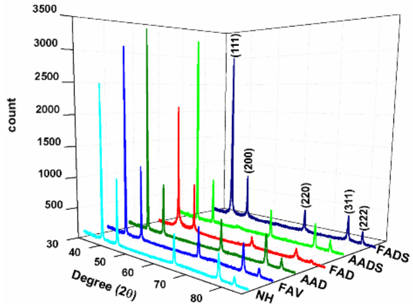

Fig. 2 X-ray diffraction patterns of sintered Ag-NPs-EC pastes and Ag-NPs suspensions

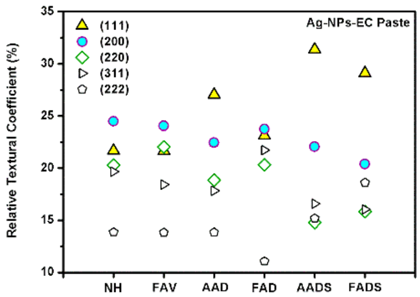

Fig. 3 Relative texture coefficient of sintered silver NPs

Based on EBSD mesh texture results, Fig. 4 show the ratio of each special grain boundary (coincidence site boundary) for selected samples, i.e. NH, FAV and AAD. The relationship between the electrical properties and Σ3 grain boundary as well as twin boundary is shown in Fig. 5. The electrical resistivity shows an inversely proportional relationship with the twin boundary fraction. As for FAV with the lowest resistivity of 11.21 μΩ-cm, the twin fraction reached 22.3%. Compared with general high-angle grain boundaries, twin boundaries usually possess smaller lattice mismatch, and much lower boundary energy, thereby cause less electron scattering [18].

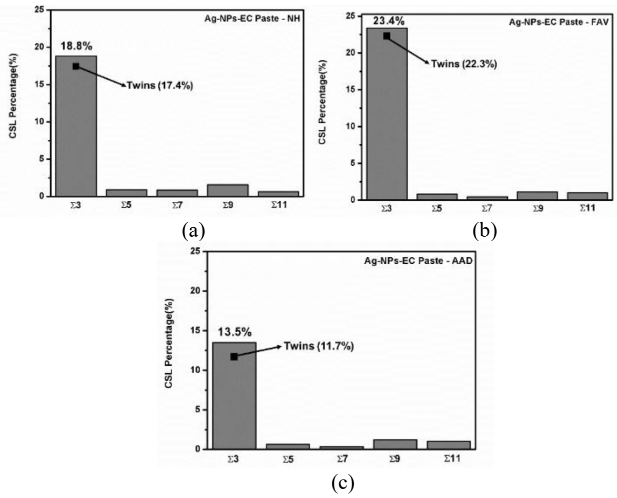

Fig. 4 Grain boundary distribution and low angle grain boundary percentage after sintering (a)NH(b)FAV(c)AAD.

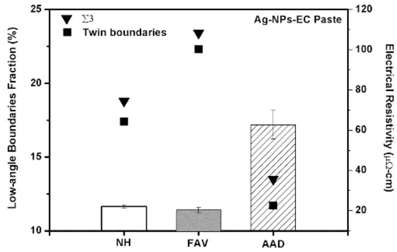

Fig. 5 Relationship between electrical resistivity and low-angle grain boundary ratios for sintering of NH, FAV, and AAD.

3. Conclusions

An investigation of Ag particle sintering behavior with respect to particle sizes and reduction methods was carried out. With the studied particle sizes, thermal reduction gave rise to a (100) texture for sintered structure. Dissimilar behavior can be observed in chemical sintering. NP-films show (111) texture especially when the film thickness was reduced. On the other hand, SMP films show a random texture with a very weak (311) preferred orientation. A close relationship was found between electrical resistance and grain boundary feature. A higher percentage of ∑3/twins brings about a lower electrical resistivity.

Acknowledgements

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