

SYNTHESIS OF SILVER NANOPARTICLES ON SILVER FLAKES TO ENHANCE ELECTRICAL PROPERTIES IN ISOTROPIC CONDUCTIVE ADHESIVES

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1 Introduction

For isotropic conductive adhesives (ICAs) have been used as an interconnection material for electronic applications for several decades owing mainly to their convenience related with processes, despite their relatively low conductivity and high contact resistance in comparison with those of solder. Numerous researches have recently been performed in order to enhance the electrical properties of ICAs. The main idea for improving the electrical properties involves adding silver nanoparticles as a conductive filler or a conductivity promoter in the fabrication of ICAs [1–6].

According to descriptions in literature, the electrical resistances of composites containing only nano-sized silver fillers are actually higher than those of conventional ICAs containing micro-sized silver flakes, and the resistances consistently increase with increasing particle content [1,2]. This can be attributed to the contact losses among fillers due to the relatively reduced filler content and the increased numbers of series contacts involving nano-sized particles. Using silver nanoparticles as a contact promoter in percolation linkages of micro-sized silver flakes is more favorable than using them as an entire structure material for percolation linkages [2,3]. As an example, the addition of only 1 wt% silver nanoparticles was effective in reducing electrical resistance in the content of micro-sized silver flakes comprising the percolation threshold [6]. On the other hand, in the case where percolation linkages are excessive, the addition of silver nanoparticles was negligible in or detrimental to reducing the resistance [3].

In the conventional adding step of nano-sized silver fillers during the formulation of isotropic conductive pastes (ICPs), only partial silver nanoparticles could perch on the contact sites

between micro-sized silver flakes. Most of the nanoparticles move freely in the binder and reside in the space among the flakes during ulterior high-rate shear mixing and curing steps. Moreover, the degree of dispersion of silver nanoparticles would be a very important factor for effectively enhancing the electrical properties of ICAs. To adopt the nanoparticles effectively as a contact promoter, nanoparticles should thus be anchored at the surfaces of micro-sized flakes before mixing.

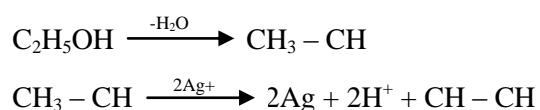
In this study, an anchoring technique of silver nanoparticles on micro-sized silver flake surfaces was attempted. The main purpose of the study was to broaden the contact area between micro-sized silver flakes in cured ICPs. After a synthesis of silver nanoparticles on flake surfaces, the treated flakes were mixed with a snap cure epoxy formation. Finally, electrical resistances of the ICP composites were measured with respect to filler content.

2 Experimental Procedures

2.1 Filler Materials

Micro-sized silver particles, consisting of flake shapes with a diameter of ~9.83 um (FAG-80A) and ~4.36 um (FAG-30A), were supplied by Chang Sung Corporation. The two powders were mechanically mixed at a large-to-small weight ratio of 5.08, which gives the maximum packing density in geometry.

Silver nitrate (AgNO_3) (Kojima Chemicals Co. Ltd, 99.9%) and ethanol (Duksan Pure Chemicals Co. Ltd, 99.9%) were purchased for the synthesis of silver nanoparticles. The reduction synthesis reaction can be expressed as follows:



2.2 Synthesis of Silver Nanoparticles on Micro-sized Silver Particles

A chemical reduction method using an ethanol vehicle has been reported in a previous article [6]. For the synthesis of silver nanoparticles on silver flake surfaces, 2 g bimodal silver flakes were placed into the 10 ml ethanol solution containing 0.085 g silver nitrate. The solution was heated to 60 °C indirectly using a water bath and maintained for 210 min. During the synthesis procedure, the solution was continuously stirred using a magnetic bar.

After the synthesis, the solution containing micro- and nano-sized particles was dried at room temperature using a vacuum chamber. The surfaces of the dried particles were then examined using a scanning electron microscope (SEM).

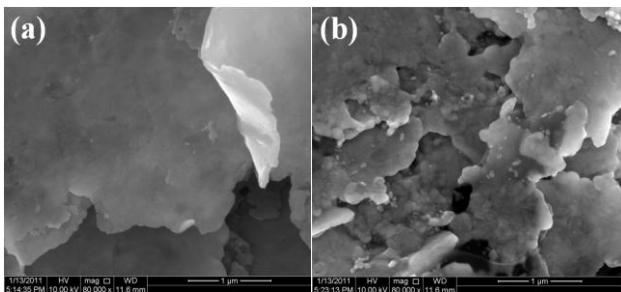


Fig. 1. SEM morphologies of silver flakes (a) in raw state and (b) after the synthesis of silver nanoparticles.

2.3 Preparation of Composites

The bimodal silver flakes were mixed with in-house epoxy formulation having snap cure properties using a homogenizer as a function of filler content. Prior to this, the formulation was first prepared by mixing epoxy resin (Hexion Specialty Chemicals, Inc., EPON 862) with other ingredients such as a hardener (Sigma-Aldrich Co., hexahydro-4-methylphthalic anhydride). The fabrication procedure of epoxy formulation was similar to that shown in another article [7]. The paste was plastered on a slide glass and cured at 140 °C for 60 s. The cured composite was ground to ~150 µm thick before an electrical resistance was measured.

2.4 Measurement of Electrical Resistance

The resistance of a composite was measured using a multimeter (Keithley Instrument, Inc., Keithley

2400) with a four-point probe. At least five samples were prepared, and five points were measured for each specimen.

3 Results and Discussion

3.1 Synthesis of Silver Nanoparticles without PVP

Chen et al. used poly(N-vinylpyrrolidone) (PVP) as a capping agent in the ethanol-based chemical reduction synthesis [6]. In this case, a complex compound containing silver ions and PVP is easily reduced at the early stage because of the presence of PVP. Thus, the nucleation rate increases and results in a higher number of nuclei formed. Moreover, the presence of PVP decreases the mean size of collected final particles. PVP also plays a role in preventing silver nanoparticles from agglomeration by covering the nanoparticle surfaces. However, the method has a big drawback in considering the next usage of nanoparticles. The silver nanoparticles synthesized in this case should be washed again by acetone because the PVP covering layer is an electrically insulated material. To conclude, the PVP agent should not be used during the synthesis to prepare conducting fillers easily. In this study, a prolonged reaction time of 210 min was tried to complete the synthesis without PVP. As a result, the synthesis was successive as observed in Figs. 1–3.

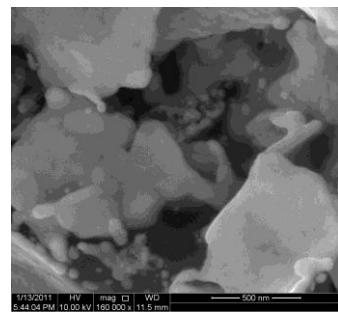


Fig. 2. SEM image indicating homogeneous nucleation and aggregation of silver nanoparticles during the synthesis without PVP.

3.2 Morphologies of Synthesized Silver Nanoparticles

Fig. 1(b) shows the morphologies of silver nanoparticles synthesized without PVP in the condition of being silver mediums containing micro-

sized silver flakes. The amount of reduced silver was 4% of the initial silver flake weight. As shown in Fig. 1, most of the silver nanoparticles were formed on the surfaces of the silver flakes. More specifically, the silver nanoparticles were formed preferentially on the edge surfaces of the flakes, not on smooth surfaces. The activation energy barrier of heterogeneous nucleation is well known to be smaller than that of homogeneous nucleation [8]. Therefore, heterogeneous nucleation may become more feasible. Edge surfaces can also be considered as a preferential site for atom attachment. In Fig. 1(b), the uniformly sized, extremely small protuberant morphologies observed in the flat surfaces of flakes properly indicated the synthesis behavior in the atomic level because silver is not corroded in ethanol. However, the rough-shaped structures observed on the edges of the flakes implied that the structures are aggregates of nanoparticles. Considering the absence of capping on nanoparticle surfaces from the synthesis without PVP, the aggregation behavior is not astonishing.

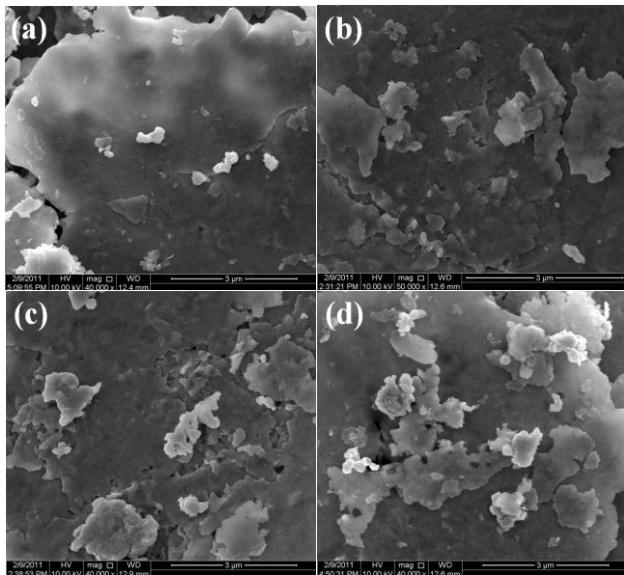


Fig. 3. Surface morphology changes of silver flakes with respect to the amount of synthesized silver: (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, and (d) 4 wt% of initial silver flake weight.

In another observation in Fig. 2, many individual elongated spheres or irregular shapes were also observed to be about to be synthesized. The shapes of the perfectly disjoined particles, thought to be

synthesized just through homogeneous nucleation, were observed to be very similar to the rough-shaped nodule structures in flake edges. Hence, microstructural features by homogeneous nucleation and aggregation of silver nanoparticles during the reduction synthesis are simultaneously shown in Fig. 2. Moreover, aggregation behavior among small disjoined particles was evidently observed in other regions of Fig. 2, resulting in the formation of larger disjoined particles that were irregular in shape and size. The result also strongly confirmed that the particles several hundred nanometers in size were formed from the coarsening and aggregation of primary nanoparticles, and could attach to flake surfaces.

In brief, heterogeneously nucleated nanoparticles could be anchored directly on micro-sized silver flakes through the chemical reduction of silver. Some homogeneously nucleated particles could not settle down on the flakes initially, but they were ready to aggregate with the flakes.

Fig. 3 presents the SEM images revealing surface morphology change of silver flakes with respect to the amount of synthesized silver nanoparticles. The figure shows that the protuberant morphologies in silver flake surfaces continued increasing along with the increasing percentage of synthesized silver. Furthermore, the sizes of the protuberant morphologies suddenly grew to micro scale with an increase in the amount of synthesized silver. As shown in Fig. 3(a), initial nano-sized nodules have a large surface area and many edge surfaces. Thus, the initial nodules would be preferential sites for heterogeneous nucleation. Nevertheless, it is still difficult to explain how the nano-sized nodules were transferred to micro-sized irregular skins in an instant. Analysis showed that the irregular skins were formed by the attachment or aggregation of particles synthesized from homogeneous nucleation. The irregular distribution of the skins may also be evidence of the attachment or aggregation behavior of particles. Consequently, the number of particles anchored on flake surfaces would increase abruptly with the increasing percentage of synthesized silver.

3.3 Electrical Properties of Cured ICAs

The electrical resistances of composites cured with only micro-sized or mixed-sized silver pastes are plotted simultaneously in Fig. 4 as a function of silver flake volume fraction. In the composite

containing only micro-sized silver flakes, the percolation threshold range was measured to be around 11–14.3 vol%. The resistance decreased continuously with the increase in silver flakes to $\sim 1.77 \times 10^{-2} \Omega$ at 20.6 vol%.

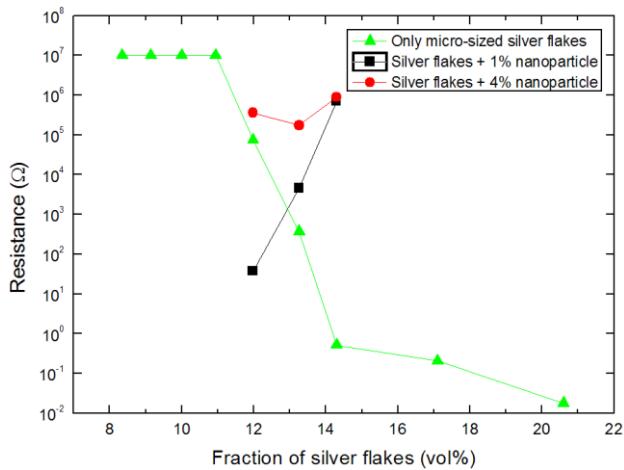


Fig. 4. Average electrical resistance of epoxy composites measured as a function of silver flakes volume fraction and addition of silver nanoparticles.

In the case where 1 wt% nanoparticles were synthesized on ~ 12 vol% silver flakes, the resistance was observed to decrease outstandingly. Analysis showed that the enhancement was mainly attributed to the supply of nanoparticles for deficient contact points between flakes. The contact resistance between nanoparticle and flake would be lower than that of the binder. However, this improved result is only obtained by anchoring silver nanoparticles in our study. In the presence of 1 wt% nanoparticles, the resistance tended to increase rapidly with increasing volume fraction of silver flakes to $\sim 14.3\%$. Hence, although the anchored nanoparticles are very effective in making contact points at the beginning region of percolation threshold, the anchored nanoparticles demonstrate a detrimental effect in electrical conduction because the contacts between the flakes increased with increasing flake content. Considering that a representative electrical conduction path in the only flakes added composite, there would be just one contact resistance between the flakes per unit linkage. However, the number of contact resistance per unit linkage in some linkage structures that consist of flakes and nanoparticles can increase to at least two. Even though contact

resistance in the interface between anchored nanoparticle and flake may be lower than that in the interface formed while making the composite, the additional contact resistance should be considered because the interface is not a perfect integration. Considering that the percolation linkage is a series connection, the increased number of contact resistance may present an influence directly detrimental to electrical resistance. Relatively big nanoparticles formed near the flake surface in Fig. 3(a) can also hinder the enhancement of contact area by multi-contacts between flakes. Consequently, the positive effect of anchored nanoparticles is not observed except at the beginning region of the percolation threshold mainly because the increase of contact resistance is more dominant than the enhancement of contact area from the middle range of the percolation threshold.

In the case with 4 wt% nanoparticles, all composites containing flakes of around 12–14.3 vol% showed higher resistance compared with the only flakes added composite. This is clearly revealed from the result of Fig. 3(b). Immoderately protuberant thick silver skins on flakes would lower the possibility for multi-contact between flakes, therefore increasing contact resistance between flakes. Moreover, the skins characterized as a multilayer structure would multiply total resistance owing to the increasing number of series contact.

To reduce the resistance of resin-based composites more effectively, fundamental methods lowering interfacial resistance among filler particles are necessary. For example, a surface functionalization technique of filler particles can be considered by using surfactants [5]. This can expedite sintering behavior among the nanoparticles, resulting in low interfacial resistance among nanoparticles. The technique is judged to be still valid for the silver fillers containing nano-sized nodules considered in this study if the nodules can participate in the sintering reaction with another particle during cure.

4 Conclusions

For the purpose of decreasing the electrical resistance of ICPs, reduction synthesis of silver in an ethanol solution containing micro-sized silver flakes was conducted to anchor the synthesized nanoparticles on the flake surfaces. Although some

nanoparticles in separated shape were formed due to homogeneous nucleation, the amount of particles anchored on flake surfaces increased suddenly as the amount of reduced silver increased. This was probably due to the attaching or aggregation behavior of the individual nanoparticles under stirring condition, indicating successive synthesis without PVP. The cured epoxy composites containing 1 wt% nanoparticles anchored silver flakes indicated enhanced electrical conductivity by reinforcing for deficient contact points between flakes in the beginning region of percolation threshold. In the case that the amount of anchored nanoparticles or flakes is higher, the anchored nanoparticles presented a detrimental effect to the conductance.

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