



ELSEVIER

Contents lists available at SciVerse ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

In situ preparation and sintering of silver nanoparticles for low-cost and highly reliable conductive adhesive

Shilong Chen^a, Konghua Liu^a, Yuanfang Luo^a, Demin Jia^a, Hong Gao^b,
Guojun Hu^b, Lan Liu^{a,*}

^a College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, PR China

^b No.38 Research Institute of China Electronics Technology Group Corporation, Hefei 230088, PR China

ARTICLE INFO

Article history:

Accepted 8 April 2013

Available online 2 May 2013

Keywords:

Epoxy
Adhesive
Silver
Sinter

ABSTRACT

A facile method to prepare low-cost, highly conductive and reliable silver-coated copper (Ag-coated Cu) flakes filled isotropic conductive adhesive (ICAs) by in situ generation and sintering of silver nanoparticles (AgNPs) during the curing process is presented. The silver–triethanolamine complex is derived from the complexing reaction between AgNO₃ and triethanolamine in the epoxy matrix. At the curing temperature, AgNPs are in situ generated by the thermal decomposition of silver–triethanolamine complex. The sintering of AgNPs anchored on the surface of Ag-coated Cu flakes could effectively prevent the exposed Cu from oxidizing. Compared with the ICAs without AgNPs which has a resistivity of $9.6 \times 10^{-4} \Omega \text{ cm}$, the ICAs filled with AgNPs shows a much lower volume resistivity of $6.62 \times 10^{-4} \Omega \text{ cm}$. Furthermore, the contact resistance of the ICAs is only 6.7% increase after aging at 85 °C and 85% RH for 500 h, while the increase in contact resistance of the controlled ICAs reaches to 23%. The facile approach will pave the way towards high performance and low cost ICAs for electronic packaging applications.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Isotropically conductive adhesives (ICAs) have been considered as a major alternative to Sn/Pb solders for electronics packaging applications due to many advantages over metallic solders, such as environmental friendliness, mild processing conditions, fewer processing steps, and fine-pitch interconnect capability [1–5]. ICAs are composed of polymeric resin (epoxy, silicone, polyurethane, polyimide, etc.) that provide physical and mechanical properties, and metallic fillers (such as silver, gold, nickel or copper) that provide electrical conductivity. Among various conductive fillers, silver is commonly used due to its excellent electrical conductivity and oxidative stability, but the high cost hinders its wide applications in the preparation of low-cost ICAs. Copper can be promising conductive filler owing to its similar electrical conductivity, lower cost and less migration tendency compared to silver. However, it readily reacts with oxygen in the air to form oxide and the oxidized layer will dramatically degrade the electrical property of ICAs. In recent years, some researchers have turned their attentions to the preparation of ICAs filled with Ag-coated Cu flakes [6–8]. Ag-coated Cu flake retains the electrical conductivity of Ag, and effectively protects Cu from the oxidation. Furthermore, it

significantly decreases the cost of ICAs. It has been utilized commercially in conductive inks [9,10] and also be promising filler in adhesives [11,12].

Due to partial plating of Cu flakes with Ag, the oxidation of the exposed Cu still occurs. Lin [8] discovered that the Ag-coated Cu filled ICAs have excellent oxidation resistance at the moderate temperature, but the resistivity of ICAs increased from $1.6 \times 10^{-3} \Omega \text{ cm}$ to $2.5 \times 10^{-3} \Omega \text{ cm}$ after heat at the curing temperature. This result indicates the presence of oxidation of the Ag-coated Cu powders at high temperature that deteriorates the electrical conductivity of ICAs. Organic compounds are usually used to prevent Cu from oxidizing, such as triazoles [13], thiol [14,15]. Zhang et al. [16] has prepared ICAs filled with Ag-coated Cu flakes which were modified by the amine-based silane coupling agent. Both the conductivity and reliability of the ICAs have remarkable improvement. They contributed the improvement to the coordination of nitrogen on the silane coupling agent to the exposed Cu, thus protecting Cu from oxidation. Instead of using the amine-based silane coupling agent, they directly used an amine curing agent for in situ protection of the exposed Cu of Ag-coated Cu flakes. The amine-cured ICAs also have low electrical resistivity [17]. Nevertheless, the non-conductive organic layer absorbed on the surface of Cu could form a barrier film between the fillers, which may produce negative impact on the electrical property of ICAs. Many research efforts [18–20] have been focused on the preparation of Ag filled ICAs by in situ generation of silver

* Corresponding author. Tel.: +86 2087114857.
E-mail address: psliulan@scut.edu.cn (L. Liu).

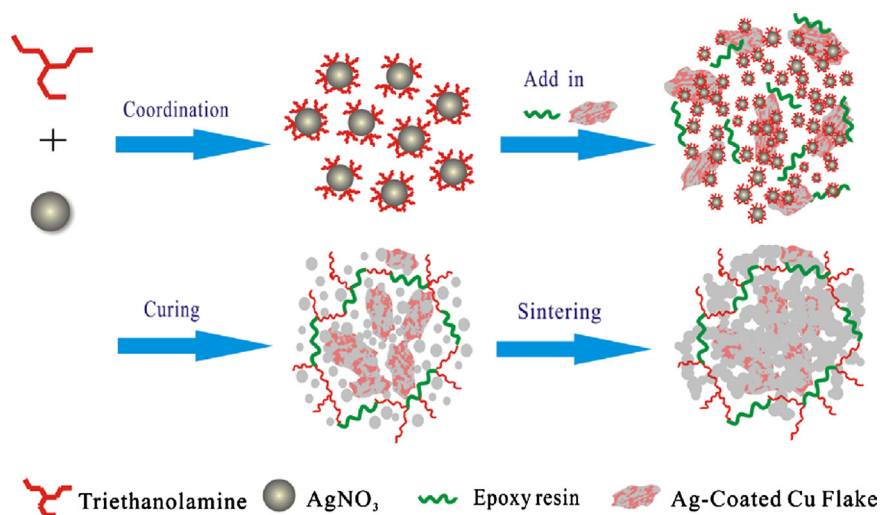


Fig. 1. Schematic illustration of preparation of Ag-coated Cu filled ICAs by in situ preparing and sintering AgNPs on the surface of Ag-coated Cu flakes.

nanoparticles (AgNPs). The sintering of AgNPs enables the formation of metallurgical bonds between the conductive fillers and effectively reduces the contact resistance, leading to highly conductive ICAs. Therefore, we consider that the AgNPs sinter on the surface of Ag-coated Cu flakes to prevent Cu from oxidizing is feasible.

In this paper, we describe the preparation of high performance, low-cost ICAs filled with Ag-coated Cu flakes by in situ generation and sintering of AgNPs during the curing process. AgNPs are in situ generated by the thermal decomposition of silver–triethanolamine complex in the epoxy matrix. Triethanolamine is simultaneously released to participate the curing of epoxy resin. The increased viscosity of the cured epoxy network prevents the AgNPs from agglomerating. The subsequent sintering of AgNPs on the surface of Ag-coated Cu flakes effectively prevents the exposed Cu from oxidizing. Moreover, the sintered AgNPs also increase the contact areas among the Ag-coated Cu flakes, which lead to the improvement of the electrical conductivity of ICAs. The overall process is shown in Fig. 1.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol F (DGEBF 862) is supplied by Shell Chemical Company. Boron–amine complex (594#) and triethanolamine are selected as curing agent and curing accelerator, respectively. The two compounds are provided by Shanghai JuXing chemical Co., Ltd. Silver nitrate and Ag-coated Cu flakes are donated by Guangzhou yinfeng Co., Ltd. The diluting agents used are acetic ether and ethanol. They are used as received.

2.2. Preparation of ICAs filled with Ag-coated Cu flakes

Silver nitrate (AgNO_3) was first dispersed in ethanol by magnetic stirring. Then triethanolamine was slowly injected into the AgNO_3 solution, the molar ratio of AgNO_3 to triethanolamine was kept at 1:3. The dispersion was sonicated for 30 min until the AgNO_3 powder completely dissolved and the mixture became uniform black. After the removal of solvent by vacuum distillation under reduced pressure, the silver–triethanolamine complex was obtained. Then the complex and curing agent were added to the epoxy resin, respectively. Finally micron-sized Ag-coated Cu flakes

were added to the mixture and the mixture was stirred uniformly, the content of the filler was kept at 70 wt% in the total amount of the adhesive. The adhesive was spread onto a glass slide and cured at 150°C for 1 h. The cured samples were conducted to the electrical conductive measurement. For comparison, the controlled sample was prepared through the following steps: epoxy resin, curing agent and curing accelerator were uniformly mixed. Then Ag-coated Cu flakes were added in the pre-mixture. After adequate mixing, the mixture was spread onto a glass slide and cured at 150°C for 1 h.

2.3. Measurements

Oxidation of Ag-Coated Cu Flakes: Ag-coated Cu flakes were dispersed in appropriate amount of silver triethanolamine complexes in ethanol and stirred at 40°C for 12 h. The mixture was centrifuged at a speed of 4800 r/min for 20 min and washed with ethanol repeatedly. Then the powders were dried in a vacuum oven at 400°C in order to decompose the silver triethanolamine complexes to Ag NPs and remove the organic compounds on the surface of Ag-coated Cu flakes. Thermogravimetric analysis (TGA), which conducted on a TA Instruments Q5000 thermogravimetric analyzer, was used to investigate the oxidation of Ag-coated Cu flakes in air. Temperature was raised from 30°C to 300°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Characterization of AgNPs: AgNPs were obtained by heating the ethanol solution of silver triethanolamine complex at 150°C for suitable times. X-ray diffraction (XRD) of Ag NPs prepared in different condition was performed on a Bruker D8 ADVANCE diffractometer with a $\text{Cu-K}\alpha$ source. The samples were measured at 2θ from 10° to 90° at a scanning rate of $0.01^\circ/\text{s}$. The UV–visible extinction spectra were taken on a HP 8453E spectrometer. All the solutions were diluted with ethanol before taking spectra. TEM images were taken using a Hitachi H-7650 instrument.

Surface morphology: The morphological characteristics of Ag-coated Cu flakes and ICAs were investigated by scanning electron microscope (SEM, Nano 430).

Electrical measurements: The electrical resistances (R) of ICAs were measured by Keithley 2182A (Nanovoltmeter) and Keithley 6220 (DC Current Source) with the four-point probe method.

Reliability tests: The samples were aged under 85°C and 85% RH conditions for 500 h in a temperature/humidity chamber (Guangzhou Gongwen Tryout Equipment Co., model GDS-100).

Download English Version:

<https://daneshyari.com/en/article/776109>

Download Persian Version:

<https://daneshyari.com/article/776109>

[Daneshyari.com](https://daneshyari.com)