APPLIED PHYSICS LETTERS **89**, 112112 (2006)

Monolayer protection for eletrochemical migration control in silver nanocomposite

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(Received 26 April 2006; accepted 20 July 2006; published online 12 September 2006)

The authors introduced an effective approach of using monolayer-protected silver nanoparticles to reduce silver migration for electronic device interconnect applications. Formation of surface complex between the carboxylate anion and surface silver ion reduces the solubility and diffusivity significantly of migration components and therefore contributes to effective migration control. A fundamental understanding of the mechanism of silver migration control was conducted by studying the current-voltage relationships of the nanocomposites with a migration model. The control of silver migration enables the application of the silver composites in fine pitch and high performance electronic device interconnects. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2353813]

Polymer-silver nanocomposites have seen dramatic applications in recent years due to the combined advantages of polymer matrices (i.e., low processing temperature and good physical and mechanical properties) and nano-Ag fillers (i.e., good electrical, thermal, and dielectric properties and high reactive surface area). Silver is also unique among all the cost-effective metals by nature of its conductive oxide (Ag_2O). In addition, silver nanoparticles are relatively easy to be formed into different sizes (a few nanometers to 100 nm) and shapes (such as spheres, rods, wires, disks, flakes, etc.)[1–4] and well dispersed in a variety of polymeric matrix materials. Therefore, silver nanocomposites are widely accepted as a promising material in electronic industry, such as lead-free conductive adhesives in electronic interconnects[5,6] and high dielectric constant composites in embedded passives.[7,8] However, a major problem that impedes the use of silver nanocomposite is the electrochemical migration of silver in the presence of moisture and applied bias.[9] In microelectronic devices, silver migration usually occurs between adjacent conductors/electrodes, which leads to the formation of dendrites, growing from the cathode to the anode, and finally results in an electrical short-circuit failure.[10,11] In particular, in polymer-Ag nanocomposite, polymers tend to absorb water and other ionic pollutants from the environment (i.e., H_2S, HNO_3, CO_2, and NO_2) which act as electrolytes and trigger silver to migrate fast between electrodes. DiGiacomo[12–14] proposed a semiempirical model of metal migration based on the electrochemistry of solutions, theory of adsorption and condensation, and transport through aqueous films and polymers characterized by Eq. (1),[12]

$$J = ZFDC_0\left(1-\exp\left(-\frac{ZFDE}{RT}t\right)\right)$$
$$= ZFC_0D_0\exp(-\Delta H_D/kT)$$
$$\times\left(1-\exp\left(-\frac{ZFD_0\exp(-\Delta H_D/kT)E}{RT}t\right)\right). \qquad (1)$$

In the equation, J is current density for the migration characterization, Z=valence, F=Faraday's electrochemical equivalent, D is the diffusivity of migration component, $D=D_0\exp(-\Delta H_D/kT)$, where ΔH_D is activation energy of diffusion component, C_0 is the ionic concentration of migration component, $E=V/d$ is the electric field, where V is the applied voltage, d is the distance between electrodes, t is time, and k and R are Boltzmann's constant and molar gas constant, respectively.

In this letter, carboxylic acid molecular monolayers are used in silver nanocomposites for migration control. Well-distributed silver nanoparticles of a diameter of 20 nm were purchased from nGimat Co. and dispersed in an epoxy matrix with a 60 wt % of nano-Ag filler. 2 wt % of dicarboxylic acid [glutaric acid, $HOOC-(CH_2)_3-COOH$] and monocarboxylic acid [heptanoic acid, $CH_3-(CH_2)_5-COOH$] were incorporated in the synthesized Ag-epoxy nanocomposite, respectively.

The formulated nanocomposites were stencil printed on the FR-4 boards with a spacing of 1.5 mm between electrodes (Fig. 1). The leakage current–voltage ($I-V$) relationship was measured by applying various voltages and testing

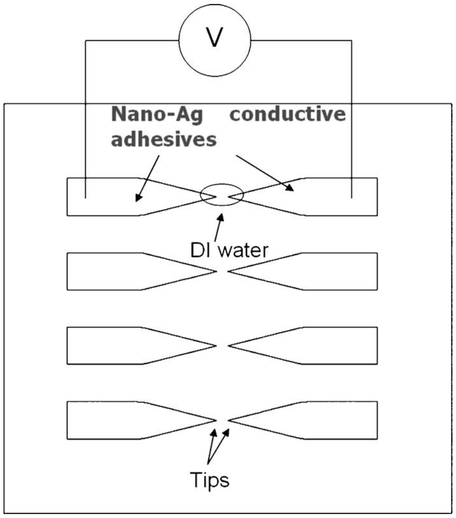

FIG. 1. Schematic illustration of migration test vehicle for nano-Ag composites.

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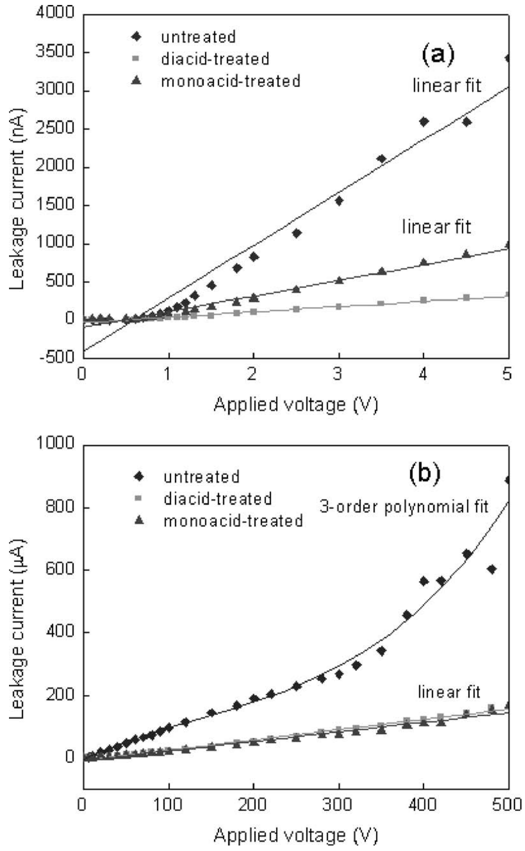

FIG. 2. *I-V* relationship of Ag nanocomposites at (a) low voltages and (b) high voltages.

the leakage current using a multimeter. The test was conducted under an accelerated condition of applying a drop of de-ionized water in between the electrodes, and thus, the time variation of the ion migration was very rapid and the characteristics shown were established within seconds of application of the field. Figure 2(a) (dots) shows the *I-V* relationship of different nanocomposites at low voltages (0–5 V). An obvious threshold voltage of migration was observed at 0.5 V for all the nanocomposites. Below the threshold voltage, the leakage currents were stabilized at a near-zero value; however, when the voltage increased over 0.5 V, the leakage current occurred. Although the untreated Ag nanocomposite showed a dramatic increase with increasing voltage, the nanocomposites incorporated with carboxylic acids showed much slower increase in leakage current. In comparison of two types of carboxylic acids, the dicarboxylic acid showed a more significant improvement than the monocarboxylic acid.

The obviously stabilized leakage current and subsequently the well-controlled electrochemical migration are due to the protection of silver ions with carboxylic acids by forming the chelating complexes. The adsorption of carboxylic acids on silver has been widely studied.[15–20] The reaction is considered as an acid-base reaction, and the driving force is the formation of chelating bond/complex between the carboxylate anion and the surface silver ion [Eq. (2)],

$$\mathrm{Ag} - e^- \rightarrow \mathrm{Ag}^+,$$

$$\mathrm{Ag}^+ + \mathrm{COO}^- \rightarrow \mathrm{Ag}^+ \cdots \mathrm{COO}^-. \qquad (2)$$

It was also reported that on Ag surfaces, the two oxygen atoms in carboxylate tend to delocalize and bind to the surface nearly symmetrically.[19,20] The bonding can change the surface properties of silver and control the properties of the metal-organic interfaces. Although the adsorption and alignment configurations of molecular monolayers on metal surfaces have been studied for over a decade, there were no reports on the applications of those organic monolayers until recently. Molecular monolayers such as thiolates were used to tune the chemistry as well as electrical and adhesion properties.[21–25] Studies have been conducted by surface analyses such as contact angle, x-ray photoelectron spectroscopy, infrared, and surface-enhanced Raman scattering for the understanding of bonding energy and alignment configurations between various carboxylic acids and silver. To reduce the energy, the molecules of monocarboxylic acids tend to have an all-*trans* conformation on bonding to silver surface. By adopting the all-*trans* forms, the molecule may lie close to the surface with a hydrophobic tail ($-\mathrm{CH}_3$), protecting the silver clusters. For dicarboxylic acid, it was found that both carboxylate groups were chelating to silver surface sites.[16,18] The molecule gains sufficient stability by bonding two carboxylate groups to the surface that it is able to adopt less favorable chain conformation. With the incorporation of carboxylic acid and the subsequent interaction between carboxylic acids and nanosilver fillers, the interface properties of the nanocomposites could be modified. Unlike typical nano-Ag composite in which Ag^+ is the major migration species, for carboxylic acid incorporated nano-Ag composite, the major migration component becomes the chelate $\mathrm{Ag}^+ \cdots \mathrm{COO}^-$. $\mathrm{Ag}^+ \cdots \mathrm{COO}^-$ has a lower solubility in water and higher activation energy (lower driving force) for migration towards cathode than that of free Ag^+, due to the neutral charge of the $\mathrm{Ag}^+ \cdots \mathrm{COO}^-$ complex. The lower solubility decreased the C_0 value, while the higher activation energy decreased the D value in Eq. (1). As such, migration became a kinetically unfavorable reaction and the leakage current of carboxylic acid incorporated nanocomposites was much lower than that of untreated composites. Comparing mono- and dicarboxylic acids, dicarboxylic acid performed better in terms of migration control, due to the more coverage on Ag surfaces; consequently, it provided a better protection of silver from migration.

It is noticed that the curves of leakage-current–voltage relationship can be well fitted into a linear relationship [Fig. 2(a), lines] by the polynomial fitting of the curves. The linear relationship can be explained by extracting Eq. (1). At low voltages, $ZFDE/(RT)t \ll 1$, then Eq. (1) can be rewritten as Eq. (3):

$$J = ZFDC_0\left(1 - \exp\left(-\frac{ZFDE}{RT}t\right)\right) \approx ZFDC_0\left(\frac{ZFDE}{RT}t\right)$$
$$= ZFDC_0\left(\frac{ZFDV}{RTd}t\right) \propto V. \qquad (3)$$

Therefore, the leakage current is almost proportional to the applied voltage.

When the nanocomposites were tested at higher voltages (5–500 V), the difference of leakage current of nanocomposites was more apparent [Fig. 2(b), dots]. The carboxylic acids incorporated nanocomposites showed a more stable leakage current value than the untreated nanocomposites, which had a dramatically increased leakage current, in par-

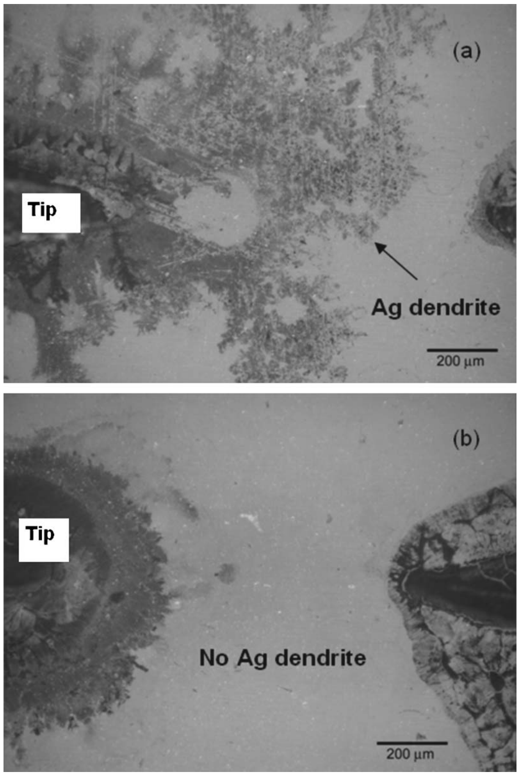

FIG. 3. Morphology of Ag dendrites after high voltage migration tests. (a) Untreated Ag nanocomposite showed obvious dendrite formation and (b) diacid incorporated Ag nanocomposite showed no dendrite formation.

ticular, at voltage higher than 200 V. By using the polynomial fitting of the curves of leakage-current–voltage relationship, it was found that under high voltage testing, the curve of untreated nanocomposite cannot be simply fitted linearly; instead, a three-order polynomial fits the curve very well. On the other hand, the carboxylic acid, both mono- and dicarboxylic acids, incorporated nanocomposites still follow a linear relationship [Fig. 2(b), lines]. The difference can also be explained by analyzing Eq. (1). For untreated nano-Ag composite at high voltage V, $ZFDE/(RT)t$ is not a near-zero value and Eq. (1) cannot be simplified as Eq. (3). According to the Taylor expansion, Eq. (1) can be expanded as Eq. (4):

$$J = ZFDC_0\left(1 - \exp\left(-\frac{ZFDE}{RT}t\right)\right) = ZFDC_0\left(\left(\frac{ZFDE}{RT}t\right) - \frac{1}{2}\left(\frac{ZFDE}{RT}t\right)^2 + \frac{1}{6}\left(\frac{ZFDE}{RT}t\right)^3 + \dots\right). \tag{4}$$

For the carboxylic acid incorporated nano-Ag composite, however, due to the much higher activation energy ΔH_D and subsequently the much lower D value, $ZFDE/(RT)t \ll 1$, and thus, Eq. (1) can also be simplified as a linear relationship as Eq. (3). Although diacid showed better protection of nanosilver fillers at low voltages than monoacid protection, the difference at high voltages was not obvious.

Figure 3 shows the photographs of test boards in the vicinity of nanocomposites after current-voltage tests. Obvious silver dendrites with several branches were observed for untreated composite, indicating the severe Ag migration upon high voltage. For the dicarboxylic acid incorporated nanocomposites, however, no obvious dendrites were detected which indicated effective silver migration control. The dark area around the edge of nanocomposite is considered from the typical interdiffusion between different materials rather than the ionic migration.

In summary, an effective method of using molecular monolayer of carboxylic acids is designed to protect nanosilver particles and control the silver migration in the silver nanocomposites. Formation of surface chelating complex between the carboxylate anion and a surface silver ion reduces the solubility and diffusivity of migration components and leads to effective migration control in silver nanocomposites. A better understanding of the mechanism of migration control is conducted by studying the current-voltage relationships of the nanocomposites. The control of migration of silver nanocomposite enables the application of the composite in fine pitch and high performance electronic devices.

The authors would like to thank the National Science Foundation and Environmental Protection Agency for the financial supports.

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