Alkoxysilane Adhesion Promoter for Ag Nano-Ink

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The low-cost printing techniques have facilitated the development of affordable electronics for a variety of applications, including solar cells, memory devices and other flexible electronics.[1-9] In contrast to the complex and time-consuming photolithography method, printed electronic devices are produced by directly printing electrical elements with any solution-based materials, including metal nanoparticles, polymers, and carbon nanotubes. Noble metal nanoparticles, especially silver nanoparticles (AgNPs) possess high electrical conductivity on the order of 10^5 S cm^{-1} and high operational stability.[1,5] These nanoparticles were used for the direct printing of conductive elements on substrates with common printing techniques, such as screen printing, flexography, gravure offset lithography, and ink-jet printing.

Although printed electronics provide a promising potential pathway toward the realization of low-cost electronic devices, some technical problems must be resolved before widespread application. One of the major issues is the poor adhesion of the conducting lines to substrates. The patterned conductive lines tend to crack after sintering, both for glass or flexible polymer substrates. Therefore, the selection of an appropriate adhesion promoter (A.P) for Ag nano-ink is crucial for fabricating conducting thin films.

In early studies, glass frit A.Ps were developed for inorganic substrates.[1,10-13] However, glass frits are not suitable for organic polymer substrates due to a lack of flexibility and the high annealing temperatures required (above 500 °C). Some organic adhesive primers have been considered as A.Ps for flexible polymer substrates, like PET. However, polymer primers suffer from yellowing at high temperature, and the adhesion strength deteriorates during sintering.

Alkoxysilanes such as tetramethoxysilane, tetraethoxysilane (TEOS), and 3-glycidoxypropyltrimethoxysilane (GPTMS) are the most commonly used protective coating materials for various substrates. They polymerize *via* the well-known sol-gel reaction, and create organic-inorganic hybrid coating films. The methoxy or ethoxy groups of the alkoxysilanes can also react with various forms of hydroxyl groups, and provide a linkage with inorganic substrates, pigment or filler to improve coating integrity and adhesion. In addition, alkoxysilane with a functional organic group,

such as GPTMS with an epoxy group, can be used as a coating material for organic substrate. The epoxy rings can polymerize to form an organic network and increase the adhesion strength to an organic substrate. Additionally, the flexible organic segments reduce the formation of cracks during the reaction. Unlike organic polymers, inorganic polymers from alkoxysilanes are stable at elevated temperatures of up to 400 ºC, due to the stable Si-O bond at the backbones. Furthermore, alkoxysilanes have been customized to enhance the adhesion of AgNPs to substrates. According to Tee *et al.*, a strong interface can form *via* the formation of Si-O-Ag covalent bonding, and silane groups act as binding bridges for AgNPs. These bonds cause better binding of AgNPs to the substrate.[14] Based on such characteristics, alkoxysilanes are expected to be a promising A.P for Ag nano-ink for both inorganic and organic substrates (Scheme 1(a)).

In this manuscript, we presented alkoxysilane-based A.P for Ag nano-ink for both glass and PET substrate.

TEOS and GPTMS were selected as A.P candidates for
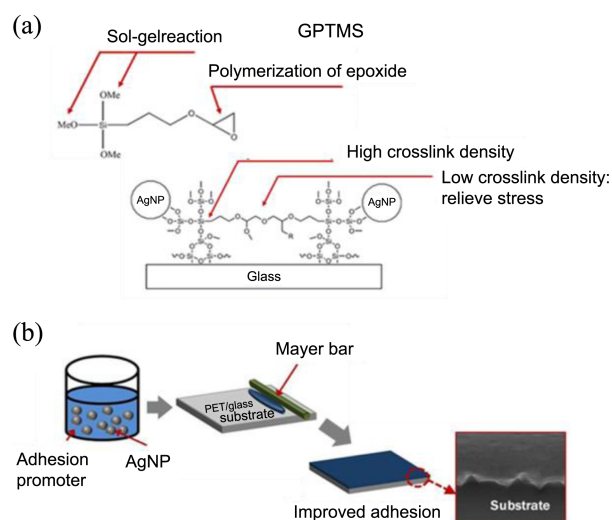
Scheme 1. (a) Adhesion mechanism of Ag NPs on substrate with GPTMS at the interface of the film. (b) Schematic representation of conducting film preparation of glass/PET substrate.

Table 1. Summary of the adhesion strengths and the sheet resistances of the conducting Ag films

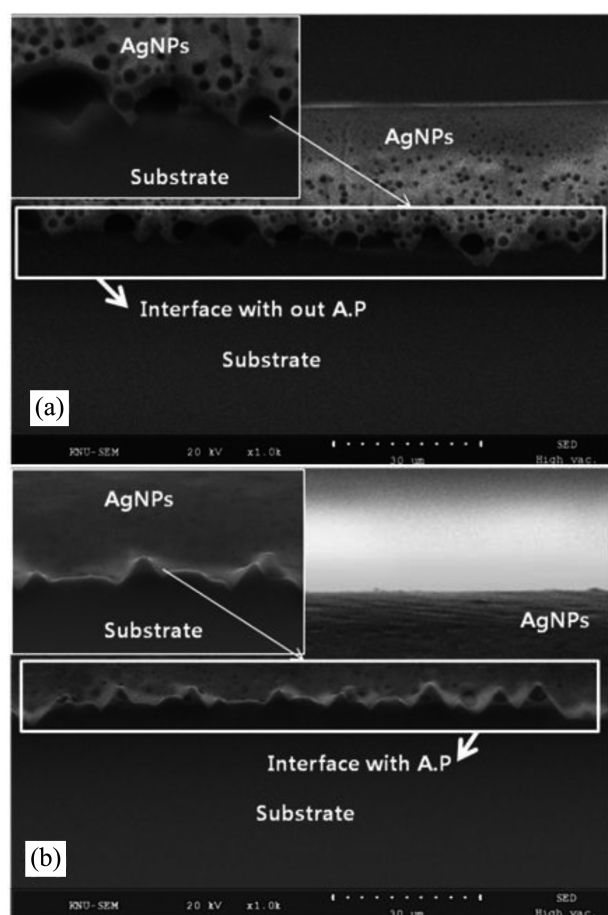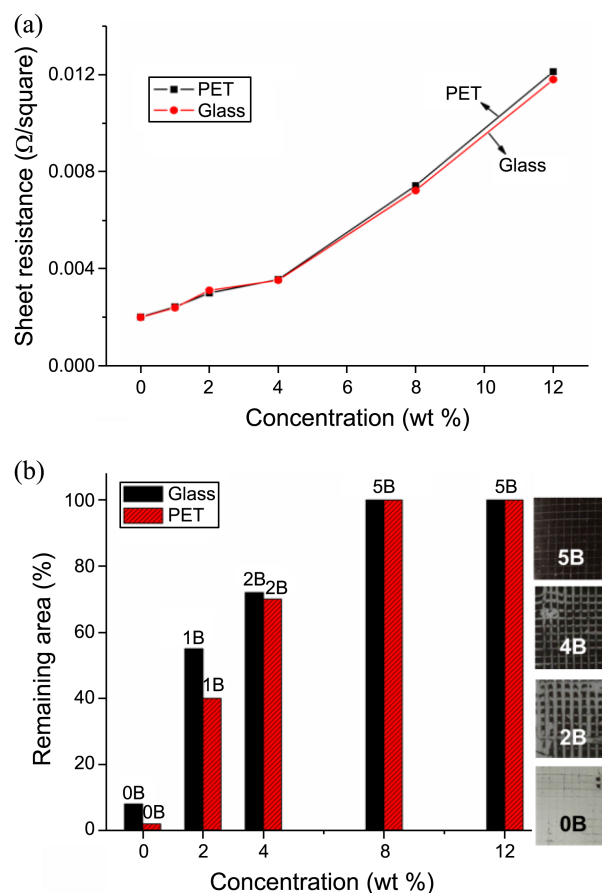| A.P	ASTM D3359		Sheet resistance (mΩ/)	
	glass	PET	glass	PET
0 w t% A.P	0B	0B	2.01	2.10
8 wt % TEOS	3B	0B	4.40	4.44
8 wt % GPTMS	5B	5B	7.31	7.29

Ag nano-ink. These two alkoxysilanes are extremely low in viscosity, which significantly affects the rheological behavior of the Ag nano-inks. Furthermore, the monomers undergo polymerization *via* polycondensation reaction, and cause severe volume shrinkage. Prepolymerization was conducted in order to increase the viscosity and avoid such shrinkage. Prepolymers of TEOS and GPTMS were synthesized according to the experimental section, and mixed with Ag nano-ink. The solutions were coated onto glass/PET substrates and annealed at 150 ºC for 20 min. The adhesion strengths and resistances of the coating films are listed in Table 1.

Table 1 shows that the adhesion strength of the film for glass substrate increased from 0B to 3B after the addition of TEOS prepolymer, while there was no change for PET substrate. However, the GPTMS prepolymer, which possesses epoxy groups, dramatically increased the binding strengths for both glass and PET substrate, from 0B to 5B.

In order to investigate the role of the GPTMS A.P, we examined the interfaces of the films from cross-sectional scanning electron microscopy (SEM) images (Figure 1). These images are potential evidence of the binding properties of GPTMS. Figure 1(a) shows very poor adhesion of the AgNPs to the substrate and holes can also be observed at the interface of the two layers without any A.P. These holes indicate the weak binding of AgNPs to the substrate. This weak binding property is caused by the non-uniform dispersion of AgNPs on the substrate. However, in Figure 1(b), with the GPTMS prepolymer, highly uniform and dense layers could be observed without any holes. This confirmed that the GPTMS causes potential adhesion of the Ag layer on the substrate.

According to Table 1, it is clear that the electrically inherent alkoxysilane A.P not only influences the adhesion properties, but also the electrical properties of the conducting film. In order to optimize the adhesion and electrical properties, we studied the relationship between the adhesion strength and the sheet resistance upon changing GPTMS prepolymer concentration. (Figure 2) The sheet resistances of the Ag thin films increased from 2.0 to 12.1 mΩ/ for the glass substrate, and to 11.8 mΩ/ for the PET substrate,

Figure 1. (a) The cross-sectional image of film without GPTMS and (b) film with 8 wt % GPTMS.

Figure 2. (a) A relation between GPTMS concentration and sheet resistance (b) the ASTM-D3359 test results and optical microscope images.

when increasing the concentration of GPTMS from 0 wt % to 12 wt %. The adhesion strength also increased with increasing the concentration of the GPTMS A.P. Optical microscope images of the test panels after the cross cut test are shown in Figure 2. Without GPTMS prepolymer, almost all of the films were detached by the tape test, and categorized as class 0B. 56 and 72% of the Ag thin films with 2 wt % and 4 wt % GPTMS prepolymer remained after the tape test, and were categorized as 1B and 2B, respectively. When the concentration of the A.P reached 8 wt %, almost 100% of the film remained, indicating excellent adhesion strength with 5B binding strength. The film with 8 wt % GPTMS prepolymer showed a sheet resistance of 7.31 mΩ/ , and a tape test binding strength of 5B on glass, and a 7.29 mΩ/ sheet resistance with a 5B binding strength on PET substrate. The Further addition of the GPTMS prepolymer would not provide more film adhesion strength, but would lower the film conductivity. Based on these results, the optimum concentration of the GPTMS prepolymer for glass or PET was determined to be 8 wt %.

In order to evaluate the applicability of the prepared Ag nano-ink with GPTMS prepolymer for printed electronics, conducting films were constructed on glass and PET substrates by Mayer rod coating and ink-jet printing respectively. Figure 3(a) and (b) show the shiny Mayer-road-coated Ag film on PET and glass substrates, and Figure 3(c) and d show the ink-jet printed Ag lines, respectively. The formation of a shiny Ag mirrored surface indicates that the AgNPs are closely packed in the film. The developed Ag nano-ink with GPTMS exhibited good dispersion on both glass and PET substrates with good adhesion.

In summary, the use of GPTMS prepolymer as an A.P results in excellent adhesion to glass and PET substrates. GPTMS prepolymer can provide crucial molecular interactions between the AgNPs and the substrate to improve the adhesion. Furthermore, sintering was conducted at lower temperatures (< 200 °C) suitable for polymer substrates like PET films. All of these characteristics succeeded not only in solving the problem of the adhesion, but also in facilitating the fabrication of an Ag layer with a lower resistance (0.01 Ω/). The results of this work can be applied directly to industries for manufacturing conductive films either on glass/PET films.

Experimental

Materials and Methods. Silver nitrate, ethylene glycol, ethanol, tetrahydrofuran (THF), and polyvinylpyrrolidone (PVP, Mw = 360,000) were purchased from Sigma-Aldrich and used as received. The interface of the film was investigated by a Hitachi (Japan) S-4800 field-emission SEM. The sheet resistances of the films were measured using 4-terminal measurement on a probe station. The adhesion strength of the film was qualitatively evaluated according to an American Standard Test Method (ASTM D3359). The adhesion strength is rated according to a scale ranging from 0B (weakest) to 5B (strongest). AgNPs were prepared by the polyol process.

Synthesis of Ag NPs. AgNPs were prepared by reducing $AgNO_3$ with ethylene glycol in the presence of PVP as a stabilizer. In a typical polyol synthesis of AgNPs, PVP dissolved in ethylene glycol (0.711 M) under stirring. The prepared solution of $AgNO_3$ dissolved in ethylene glycol (1.766 M) was added to the PVP reaction solution at 165 °C, resulting in an immediate solution color change from colorless to dark yellow. The resultant solution was centrifuged with acetone and THF to remove the excess PVP. The precipitate was collected and dispersed in ethanol. The SEM images and particle size distribution graph are presented in Figure S1 and S2.

Preparation of the Adhesion promoter. TEOS (20.8 g, 0.1 mol) and distilled water (7.2 g, 0.4 mol) were dissolved in THF (200 mL). In the case of the GPTMS A.P, GPTMS (24.8 g, 0.1 mol) and distilled water (5.4 g, 0.3 mol) were used in place of TEOS and distilled water. 0.1 N HCl (5 mL) was added as a catalyst. The mixture was refluxed for 8 h and diluted with ethyl acetate (300 mL), and finally washed 3 times with distilled water. The prepolymer was dried over anhydrous $MgSO_4$, and the solvents were removed under vacuum to produce a light-yellow viscous liquid.

Fabrication of AgNPs Conducting Film. AgNPs and A.P solution in ethanol (50 wt %) were bar-coated on glass/PET substrate (Scheme 1(b)). They were then dried using an IR heater, and annealed at 150 °C for 20 min.

Ink-jet Printing. An Epson T50 home printer with a resolution of 5,260 dpi was used in this experiment. This printer has a piezoelectric head with 90 openings, and the volume of each droplet is approximately 1.5 pL. 30 wt % Ag ink was poured into the black container and used to print a line pattern on glass/PET substrates.
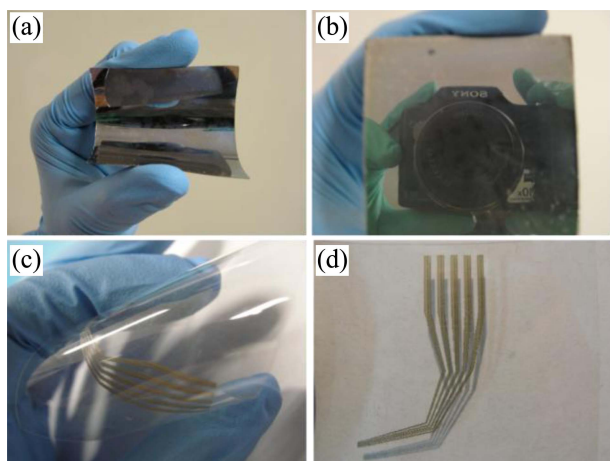
Figure 3. Rod-coated films (a) on a PET substrate, (b) on a glass substrate. Ink-jet printed films (c) on a PET substrate (d) on a glass substrate.

Supporting Information. The SEM images and particle size distribution of AgNPs.

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