

## Investigation on Post Treatment of Nano-size Silver Conductive Film

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**Abstract:** To achieve a satisfied conductivity of nano-size silver printed circuit, post deal with nano-size silver conductive film was investigated. Based on the preparation of nano-size conductive ink and conductive circuit, the coated conductive film was treated by series concentrations of hydrochloride solutions, and then scanned by laser beam. The influence of resolutions concentration and dipping time were investigated separately. Atomic force microscopy (AFM), fourier transform infrared (FTIR) and four-probe tester, were applied to characterize the different tested samples. It was found that when the coated silver conductive ink samples were dipped in 20% hydrochloride for 60min, 15°C before laser scanning, the conductivity reaches 0.3Ω/Υ. It is therefore considered that the “dip in” method provide an efficient alternative to improve the conductivity which from nano-size silver ink.

### Introduction

Generally, conductivity is one of the major metrics for conductive tracks in electrics. With the characteristic of direct-write approach of ink-jet printing [1], inks used as conductive tracks have been adopted for this technique. Nano-sized metallic particles, such as copper, gold and silver, have been used due to their excellent performance in conductivity. Silver based inks are most commonly used materials due to their low resistance and low prices [1].

There are several methods to improve the conductivity of nano-silver ink. Firstly, the coated silver nanoparticles were heated by an oven or laser scanning, as the nano-size effect, the sintering temperature has been decreased around 100°C as in the previous literature [2]. However, sintering treatment will limit the substrate (e.g. paper) as the temperature required for silver particles coalescing together, so as the energy [3, 4]. Secondly, the protect agents such as PVP can be removed by dipping method. Under this condition, the silver particles will be hand by hand without block.

In this paper, the method dipping in was used to study the post treatment of nano-silver coatings on conductivity.

### Experimental

The nano-silver colloids were synthesized by the well-known polyol method. The nitrate solution used as the precursor of silver particles was prepared by dissolving in distilled water, where polyvinylpyrrolidone (PVP) was added to protect the synthesized silver particles from agglomeration. This solution was stirred strongly in a beaker, meanwhile, the hydrazine hydrate was added to reduce the nitrate agent.

Photo paper has a special coated layer which can effectively absorb liquid in the ink, therefore it was used here to accelerate the drying of silver colloids. In the coating process, the nano-silver colloids were placed on photo papers, coating slowly by a lead screw. The coated samples were dried in the air at room temperature.

Samples coated with nano-sized silver colloids, were dipped in hydrochloride solution in room temperature. To study the influence of hydrochloride solution, the dipping time was varied from 10 to 120min and the concentrations of hydrochloride were 5%, 10% and 20%, respectively. After

dipping, the samples were washed by deionized water to remove the ions from dipping solution and then dried at 40°C. Laser scanner (RCTP-1S, Beijing print technology) is a laser apparatus commonly used in the laboratory; and the samples were exposed through the infrared laser treatment (100mW, 830nm). The sheet resistance was measured by a four-point probe (RTS-9, Guangzhou Four-probe Corporation). The samples' surface morphology and composition were observed by atomic force microscopy (AFM, SPM3000, Benyuan) and fourier transform infrared spectrometer (FTIR-8400, SHIMADZU). The as prepared samples were grinded with KBr particles together, and then pressed into a circle flake.

## Results and discussion

As shown in table 1, the samples' conductivity was improved rapidly with the concentration increased and dipping time expended, and then decreased slightly after 60min. The sheet resistance reaches the lowest value at  $0.3\Omega/\square$ , when samples are dipped in 20% hydrochloride for 60min. the sheet resistance of samples dip in 10% hydrochloride for 60min and 20% hydrochloride for 30min were below  $1\Omega/\square$ . The reason of conductivity decrease is partly attributed to the excess dipping time.

Table 1 The sheet resistance of samples dipping in three concentrations of hydrochloride solution [ $\Omega/\square$ ]

| Dipping Time [min] \ Concentration of hydrochloride Solution | 10               | 30               | 60   | 90    | 120    |
|--|------------------|------------------|------|-------|--------|
| 5%   | Non-conductivity | Non-conductivity | 12   | 35620 | 363626 |
| 10%  | Non-conductivity | Non-conductivity | 0.51 | 0.76  | 0.6    |
| 20%  | Non-conductivity | 0.59             | 0.3  | 0.35  | 0.40   |

After dipping in three concentrations of hydrochloride solution for 60min, the conductivity of samples after laser scanned were displayed as in Fig. 1. The sheet resistance of samples dipping in 5% hydrochloride solution drops apparently after laser scanning. However, the resistance is approximate, for samples before and after laser scan, when dipping in 10% and 20% hydrochloride solution.

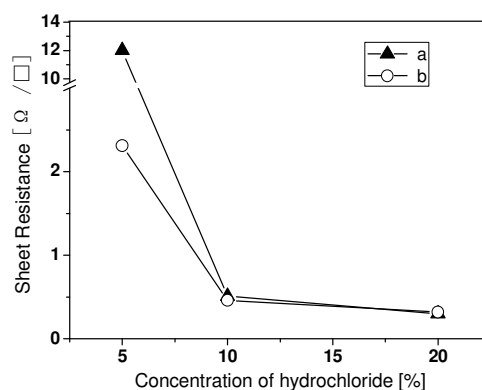


Fig. 1 The sheet resistance of samples after dipping in three concentrations of hydrochloride solution for 60min, (a) before laser scanning and (b) after laser scanning

To clarify the microstructure changes after dipping and laser scanning, AFM observations were carried out as shown in Fig. 2. In the initial stage, there is no treatment on the sample, the

particles can be seen clearly in Fig. 2a, and it can be supposed that the particles were separated by PVP. The resistance was so large and could not be detected by four-point probe. With the passage of dipping time, the Ag particles grew, as shows in Fig. 2b. Moreover, the coarsened particles become connected by forming metallic bonds [5]. And the resistance was  $0.3\Omega/\square$ . In the further stage, the dipped sample was sintering by laser scanner. After scanning, as shown in Fig. 2c, the Ag particles seems connected more closely, however, the resistance was slightly higher,  $0.32\Omega/\square$ . Above all, we may conclude that the dipping process plays an important role in removing the protect agent, PVP.

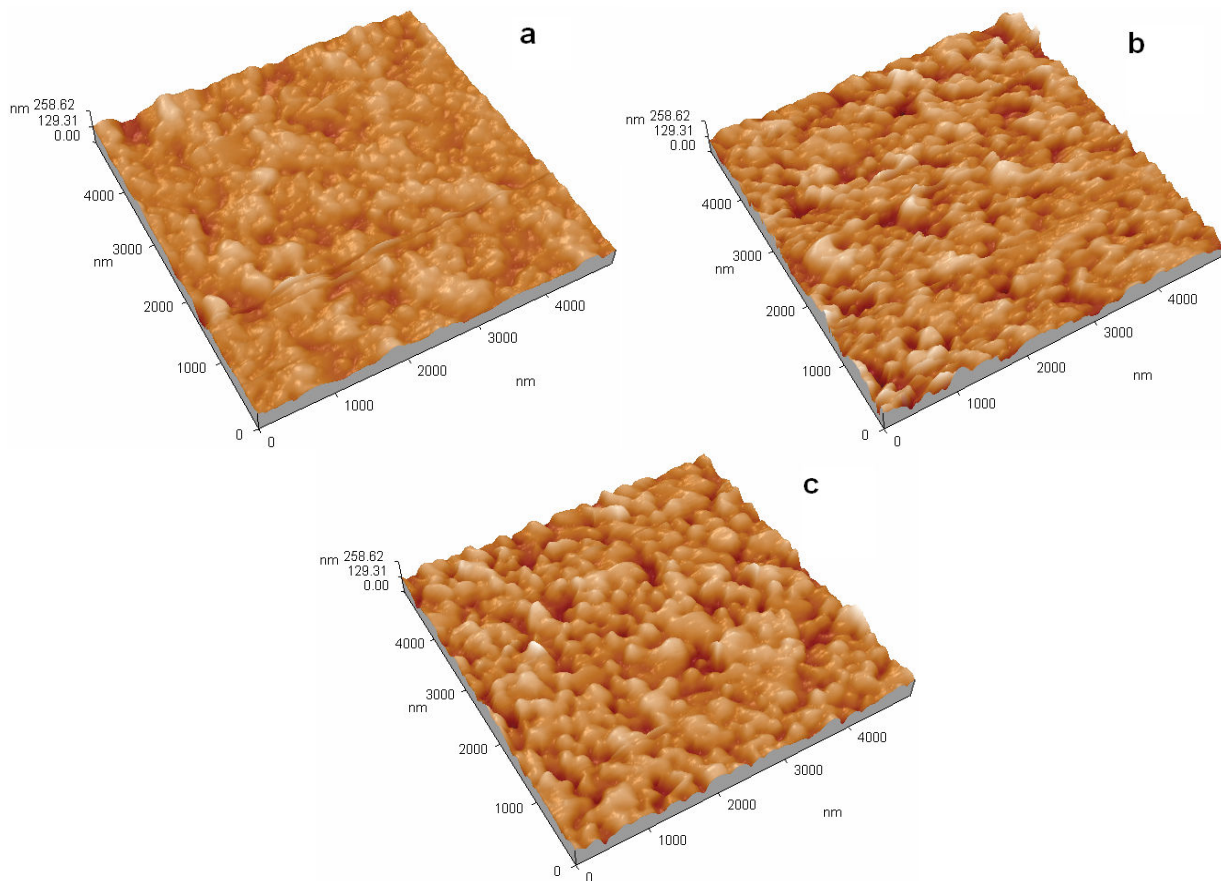


Fig. 2 AFM images of the microstructure of nano-silver coated samples: (a) no treatment; (b) only after “dip in” treatment; (c) after “dip in” and laser beam treatment

The results of Infrared (IR) spectrum are displayed in Fig. 3. The nano-silver ink IR spectra was shown in Fig. 3a, it is presumed that the C=O and C-N bond vibration absorption generated at the wavelength of about  $1654\text{cm}^{-1}$ , as well as  $1078$  and  $1020\text{cm}^{-1}$ , respectively, even though the latter is very slightly. The Fig. 3b is the IR spectra of nano-silver ink and hydrochloride, the wavenumbers of  $3128\text{cm}^{-1}$  is produced by positive ions. And compared with nano-silver ink, the peak of the C-N bond at  $1078$  and  $1020\text{cm}^{-1}$  are shifted to  $1080$  and  $1021\text{cm}^{-1}$ , even more apparently, which correspond to the changes of PVP and silver particles caused by hydrochloride. It is reported that there is a weak coordinative chemical bonding of C-N to Ag at the interface, and C=O absorption has bond weakening via partial donation of oxygen lone pair electrons of PVP to the vacant orbitals of the silver surface between PVP and the particles [6, 7]. Therefore, it is presumed that hydrochloride destroys the chemical bonding of C-N to Ag partly, and nano-silver particles are freed from the protect agent, the bare silver particles can connect because of their active surfaces. It is mainly  $\text{Cl}^-$  plays an essential role, as it has an effect on N of PVP. Finally, the samples after “dip in” method have improved the conductivity. The mechanism will be studied in the future work.

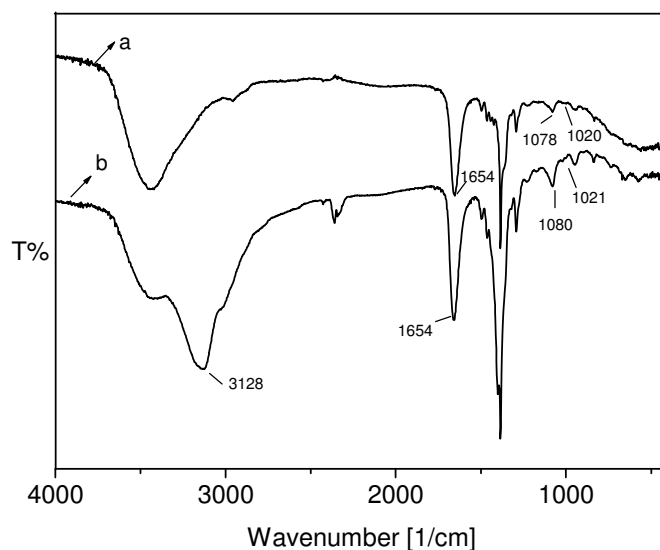


Fig. 3 IR spectra of nano-silver ink (a) and nano-silver ink and hydrochloride (b)

## Conclusion

We demonstrated a novel “dip in” method for post treatment of nano-Ag ink, which is carried out at ambient temperature in air atmosphere. The surface sheet resistance was  $0.3\Omega/\square$  when the sample was dipped in 20% hydrochloride solution for 60 min at  $15^{\circ}\text{C}$ . Thus, our “dip in” treatment effectively removes the dispersant and Cl<sup>-</sup> has played an important role on breaking the bonds between PVP and Ag particles. The mechanism of the effect will be studied in the next step. This method could become a standard procedure for the post treatment of nano-Ag ink coatings as it is both economic and rapid, while also being high conductivity.

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