Rapid Two-Step Metallization for Highly Conductive Black Electrodes

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Abstract

A novel two-step metallization scheme for the formation of highly conductive "black" metal electrodes is presented and its underlying physics is investigated with electrical, morphological and optical characterization techniques. It is found that silver oxide microparticles converted to silver nanoparticles at a temperature as low as 150 ℃ just for 10 min in the course of the first metallization step. Although this first metallization step has a much shortened sintering time, it does not produce silver electrodes with high enough electrical conductivity. By performing the second metallization step with an aqueous ionic solution, however, the electrical conductivity of silver electrodes is found to be enhanced by six to seven orders of magnitude, approximately 1.0×10^{7} *S/m, only in 10 sec. Moreover, the color of silver electrodes is blackened by a factor of 1.7. This rapid two-step metallization scheme is found more amenable to an open continuous roll-to-roll printing process and the resulting sheet resistance of a "black" transparent conductive film exhibits 0.9 Ω/□ with an optical transparency of 81%.*

Introduction

Low cost transparent conductive films (TCFs) have been demanded by industries as touch based smart devices become the mainstay of daily electronic appliances. Though Indium-Tin-Oxide (ITO) based TCFs have been the mainstream in TCF industries, their cost and electrical performance cannot fulfil the requirements for large area touch screen panels (TSPs) due to the high cost required for patterned ITO electrodes rather than the cost of ITO itself [1]. As a result, solution based techniques to construct highly conductive TCFs using various coating and printing processes have been devised.

Among many possible routes to construct highly conductive printed TCFs, those with silver nanowires or metal meshes using silver paste have become the most promising ones [2,3]. For example, silver nanowire based TCFs have a strong advantage in terms of manufacturing simplicity because they can be manufactured with two coating steps, one for the underlying silver nanowire layer and the other for the overcoat layer. On the other hand, metallic mesh based TCFs using silver paste have an advantage over silver nanowires with respect to material cost.

Whatever approaches are taken, either silver nanowires or metallic meshes using silver paste, silver based TCFs have the major drawback, i.e. metallic reflectivity. As can be seen in Fig. 1(a), conventional silver electrodes have high metallic reflectivity so that they look hazy when viewed at a glancing angle.

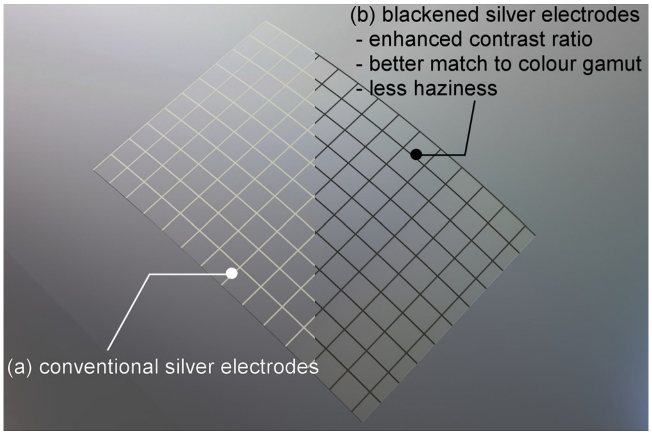

Figure 1*. Illustration of the visual impact of silver electrodes, (a) without blackening and (b) with blackening.*

If this metallic reflectivity is not suppressed, the value of lightness increases and hence the color coordinates are deviated from the target specifications. Therefore, the achievement of black silver electrodes, as shown in Fig. 1(b), is essential for printed TCFs in touch screen panels because black silver electrodes contribute to (1) the enhancement of contrast ratio, (2) better color matching, and (3) less haze. In this sense, the use of silver nanowires has a disadvantage because silver nanowires are too small in diameter to be electrochemically blackened. To now, the most effective means to reduce the haze of silver nanowire based TCFs is the use of silver nanowires with a smaller diameter [4] but it eventually increases the material cost of silver nanowire based TCFs.

Another vital requirement is the rapid metallization of highly conductive silver electrodes at a low sintering temperature. When flexible touch screen panels are manufactured using a roll-to-roll printing process, the sintering time required to achieve the targeted conductivity, 10^{4} S cm^{-1}, must be as short as possible. Even with silver nanoparticulate ink, however, the required sintering time is likely to be more than 30 min at 150 °C [5]. Since this sintering time requires unacceptably long footprint of an IR dryer, it must be substantially shortened.

Therefore, this study investigated a novel two-step metallization to fulfill both rapid metallization and blackening of silver electrodes through the physicochemical conversion of the used silver oxide paste.

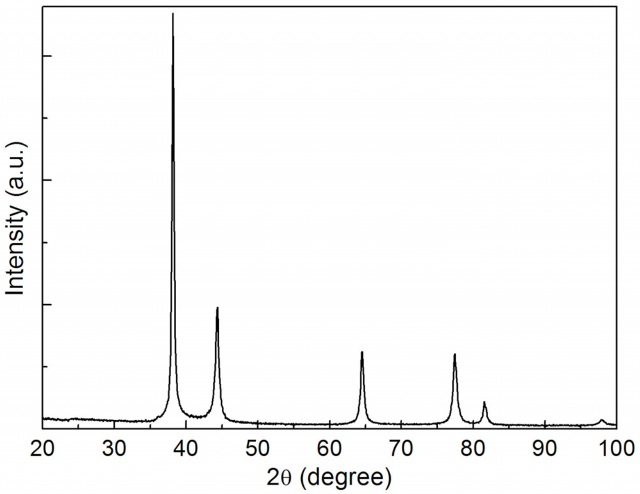

Figure 2*. XRD spectra of the silver oxide paste after thermal treatment at 150 ℃ for 10 min.*

Experimental Details

The used silver oxide paste was prepared with silver oxide microparticles (D50≈1.89 μm, Kojundo Chemical Laboratory, Co. Ltd, Japan) and silver neodecanoate ($C_{10}H_{19}AgO_2$, LG Chem Research Park, Republic of Korea) in α-terpineol (Kano Chemical Co. Inc., Japan) at a weight ratio of 2:2:1. The used specimens were prepared using a four-sided applicator (PA-2020, BYK-Gardner GmbH, Germany) on a PET film and thermally sintered on a hot plate at 150 °C for 10 min for the first metallization step. For the second metallization step, the prepared specimens were dipped in 6 wt.% of $FeCl_3$ (Kanto Chemical Co. Inc., Japan) in DI water at room temperature for 10 sec. For the visual demonstration of black silver electrodes, the developed silver oxide paste was screen-printed.

Results and Discussion

The initial particle size of the silver oxide paste was 1.80 μm on average. However, when the silver oxide paste was thermally treated at 150 °C for 10 min, silver oxide microparticles turned into silver nanoparticles and its crystalline size became 35 nm, , as shown in Fig. 2. This physicochemical conversion is known to be contributed by the used organic silver compound, silver neodecanoate in this case [6]. Due to this physicochemical conversion at the first metallization step, the electrical conductivity of the thermally sintered parts could be comparable to that with conventional conductive ink based on silver nanoparticles. However, the lack of thermal sintering time caused relatively poor electrical conductivity, approximately 1.33 S/m. Moreover, the measured blackness was approximately 36.29 B, which implies that the metallic reflectivity of the sintered parts was not suppressed at this stage.

At the second metallization step, the specimens were dipped in 6 wt.% of $FeCl_3$ in DI water for 10 sec and its electrical conductivity and blackness were re-measured. It is noteworthy that the electrical conductivity of the specimens was greatly enhanced by approximately six to seven orders of magnitude from 1.33 S/m to 1.0×10^7 S/m. This great enhancement of electrical conductivity is caused by self-catalytic addition [7]. In the presence of chloride anion (Cl^-) and oxygen (O_2), silver nanoparticles are slowly dissolved into silver cation (Ag^+) and re-deposited onto the silver surface. Due to this self-catalytic addition, the crystalline size of silver nanoparticles grew up around 50 nm, as shown in Fig. 3.

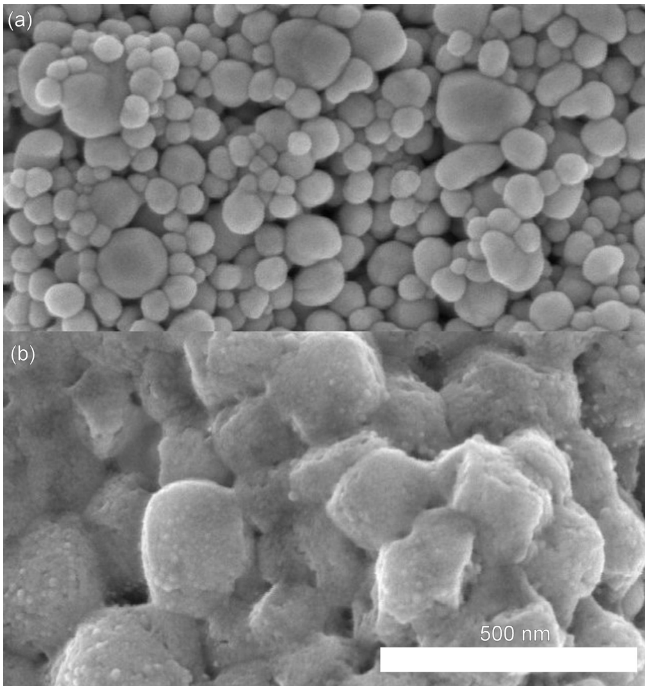

Figure 3*.SEM images of silver nanoparticles, (a) before and (b) after the second metallization step.*

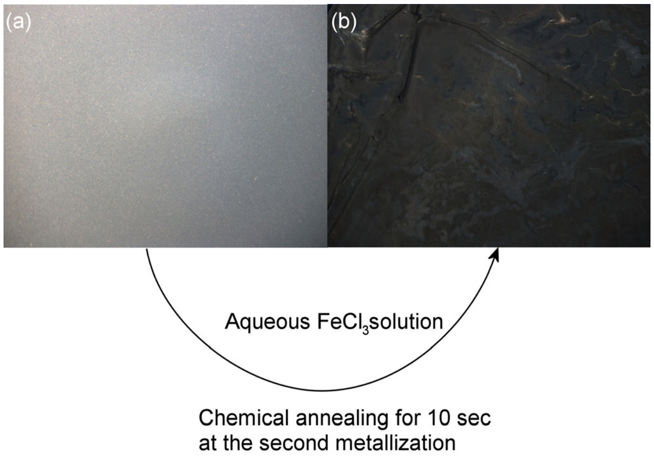

Figure 4*. Visual impact of blackness, (a) before and (b) after the second metallization step.*

In addition, the blackness of the specimens after the second metallization step increased from 36.29 B to 61.51 B, as shown in Fig. 4. This color change was found to be attributed by the formation of AgCl on the top surface of the silver layer.

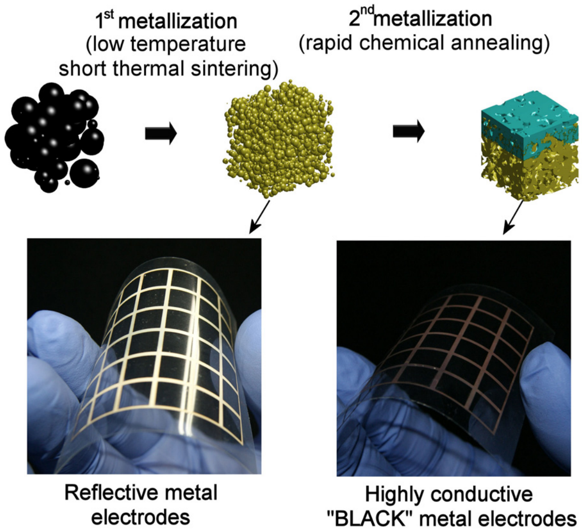

***Figure 5**. Illustration of rapid two-step metallization scheme for highly conductive “Black” metal electrodes.*

This bilayer structure of Ag/AgCl enhances the surface plasmon resonance and hence makes the specimens visually dark [8]. The formation of the topmost AgCl layer also serves as a protective layer from subsequent processes. As an example, O2 plasma treatment is likely to be used in the fabrication of most types of displays and the AgCl layer prevents the underlying silver layer from unwanted oxidation.

The visual impact of black silver electrodes are shown in Fig. 5 with the overall two-step metallization scheme. Contrary to conventional silver electrodes, those after the second metallization step became much darker.

Conclusions

In this study, a rapid two-step metallization for black silver electrodes are investigated. At the first metallization step, silver oxide microparticles physicochemically converted to silver nanoparticles in the presence of silver neodecanoate when thermally treated at 150 °C for 10 min. This physicochemical conversion of silver oxide microparticles to silver nanoparticles contributes to the reduction of sintering temperature even without the use of metallic nanoparticles. However, the lack of sintering time results in relatively low electrical conductivity, around 1.33 S/m. For the electrical conductivity enhancement and blackness of thermally sintered metallic parts, chemical annealing with an aqueous $FeCl_3$ solution was employed at the second metallization step, which resulted in the enhancement of electrical conductivity up to 1.0×10^7 S/m. Moreover, the blackness of silver electrodes increased from 36.29 B to 61.51 B. Therefore, the proposed two-step metallization scheme makes the rapid metallization of silver electrodes more amenable to a continuous roll-to-roll printing process.

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Author Biography

Dong-Youn Shin received his BS in mechanical engineering from Seoul National University (1997) and his MS and PhD in mechanical engineering (1999) and materials science (2003) from UMIST, UK. After a postdoctoral period at UMIST, he served at LG Chem Research Park to develop ink-jet printed color filters for TFT LCD and at Korea Institute of Machinery and Materials to develop ink-jet related equipments and applications. He is currently an assistant professor at Pukyong National University. His research has focused on the theoretical and experimental analysis of the microfluidic behaviors in a piezo DOD ink-jet print head and fine pattern generation for displays, electronics and photovoltaic applications.

Sangki Chun received his BS and MS in Agricultural Chemistry (1991) and in Chemistry (1993) from Seoul National University and his PhD (2001) in Chemistry from Texas Tech University, USA. He is currently general manager at LG Chem. His work has focused on the printed electronics such as printed mesh films for PDP EMI filters and touch screen panels.