CONDUCTIVE SILVER FILMS ON PAPER PREPARED BY ATMOSPHERIC PRESSURE ARGON PLASMA CONVERSION OF SILVER NITRATE

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Abstract
We present a novel approach for deposition of metallic silver films from silver nitrate (AgNO₃) ink. The conversion of AgNO₃ is induced by argon plasma of the diffuse coplanar surface barrier discharge (DCSBD) generated at atmospheric pressure. The macroscopically homogeneous and diffuse plasma of high power density allows fast reduction of AgNO₃ into conductive metallic silver within two minutes. The process is carried out at temperatures below 70 °C and without the need for a complex vacuum chamber and is therefore highly suitable for deposition onto temperature-sensitive materials. In our study we used paper prepared from nanocellulose fibres, which offers mechanical flexibility, translucency and recyclability while having lower surface roughness and enhanced mechanical properties and thermal stability compared to regular paper. As a figure of merit, the resistivity of prepared films was measured. The X-ray photoelectron spectroscopy was used to study the conversion of AgNO₃ into metallic silver. Scanning electron microscopy revealed the morphology of the surface of the films giving insight on the nucleation and the growth process. The silver films prepared according to our methodology are an attractive possibility for applications in sensing devices or as conductive lines and other features in flexible electronics.

Keywords: Conductive films, silver nitrate, reduction, argon plasma, nanocellulose

1. INTRODUCTION
Printed electronics is an emerging technological field that focuses on utilizing deposition methods compatible with solution processing to prepare functional coatings for electronic devices. While conventional electronics are based on rigid substrates as silicon wafers; printed electronics aim towards flexible substrates such as polymer (PET, PEN) foils or (nano)paper, which can be designed for the highly desirable roll-to-roll processing with high throughput.

Printing of the metals is essential to create conductive features and paths in electronic circuits. There are several approaches for the formulation of metal inks for printing. Nanoparticle inks are the most studied in the metal ink technology [1]. Nanoparticles are dispersed within an organic solution together with some capping agents to control their shape and size. Another approach is formulation of particle-free inks, where metals exist in a form of ions from metal-metorganic complexes dissolved in volatile solvents. After printing the complexes can be transformed into pure metal patterns by decomposition at elevated temperature [2] or by chemical reduction [3].
Of particular interest are metal particle-free inks based on inorganic metal salts [4]. They have the same advantages against NP inks as the metal-organic complex inks, while the metal salts are readily available and do not require careful design and synthesis. Numerous metals have been printed by simple dissolving of the metal salt in water with addition of volatile organic solvents to adjust the fluid properties of the inks including gold, silver, copper, palladium, platinum, lead, bismuth and tin [5]. The drawback of metal salt inks is relatively high sintering temperature required for the decomposition.

Post-deposition sintering is typically required for removal of the organic parts of the inks that decrease the conductivity of the printed films. In case of particle-free inks the sintering is also needed for the conversion of the ionic metals to pure metal films. Sintering at elevated temperatures restricts the possible substrates used, as polymers or paper often cannot withstand temperatures exceeding 100 °C. Alternative sintering approaches have therefore been used such as photonic sintering [6], microwave sintering [7], chemical sintering [8] and plasma sintering [5,9–11].

In this contribution we present a method to prepare conductive silver films by reduction of silver nitrate AgNO₃ printed from a simple water-based ink by plasma treatment at low temperature (< 70 °C) at atmospheric pressure. The approach we present can completely convert silver nitrate film into pure metallic silver in just two minutes. It is highly suitable for printing on temperature-sensitive substrates and is capable of fast treatment of large areas and is compatible with roll-to-roll processing.

As a substrate we used nanocellulose paper. Compared to naturally-occurring cellulose, which consists of cellulose fibres 20–50 µm in diameter, the microfibrils that make up nanocellulose paper have diameters that lie in a measurement range of only tens of nanometres. This allows nanocellulose paper to match the desirable properties of plastic substrates, such as low surface roughness and thermal stability, while adding recyclability and enhanced flexibility [12,13].

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Silver nitrate was purchased from Merck KGaA (Germany). By dissolving 0.212 g of AgNO₃ in a mixture of 0.429 g water and 0.946 g ethylene glycol (Lach-ner s.r.o, Czech Republic) we obtained an ink with 15 wt.% of AgNO₃. The ink was very stable and retained its properties after up to a year of storage.

The nanocellulose paper was kindly provided by Dr. Juho Antti Sirviö of the Fibre and Particle Engineering Research Unit at the University of Oulu, Finland. The preparation process is thoroughly described in the works of Sethi et. al. and Li et. al. [14,15].

2.2. Deposition and plasma treatment

We deposited the silver nitrate ink using a spin-coater. A droplet with volume of 10 µl was placed in the middle of a 0.5 cm × 0.5 cm square nanocellulose substrate and spun for 45 s at 2000 RPM to distribute the ink.

Immediately after the deposition the coated samples were attached to the sample holder by a double-sided tape and inserted into the gas chamber, schematically visualized in Figure 1. The gas chamber had a volume of 50 cm³. An argon gas was continually flowing through the gas chamber at a rate of 1 l/min to achieve an argon atmosphere inside the chamber. The chamber was operated at atmospheric pressure. Plasma was generated by diffuse coplanar surface barrier discharge (DCSBD) – a dielectric barrier discharge withcoplanar arrangement of electrodes; commercialized by Roplass s.r.o. (Czech republic) [16].

The plasma region of the DCSBD unit was around 0.3 mm thick. To ensure a good contact of the sample surface with the plasma region the sample holder was distanced from the ceramics of the DCSBD unit by 0.3 mm of Kapton tape. The exposure time of the treated sample surface was varied from 0 s to 128 s.
2.3. Film analysis

Mira3 scanning electron microscope (SEM) from Tescan (Czech Republic) was employed for the analysis of the morphology of the reduced silver film and the evaluation silver nanoparticles dimension. The images were captured at with 20x up to 100x magnification, 5 kV accelerating voltage and at a working distance of 5 mm.

The surface chemistry of the reduced silver films was determined from X-ray photoelectron spectra (XPS) obtained by AXIS Supra spectrometer from Kratos Analytical Ltd. (United Kingdom). The instrument uses Al Kα spectral line (1486.6 eV photon energy) and an electron flood gun was utilized for charge compensation. The acquisition of narrow regions of the spectrum was performed with the pass energy 20 eV. For analysis of the spectra CasaXPS software was used. The spectra were calibrated to C—C/C—H peak of C 1s at 284.8 eV binding energy.

The sheet resistance of the reduced silver films was determined by the four-point probe measurement using the Four-Point Probe System from Ossila Ltd (United Kingdom).

3. RESULTS AND DISCUSSION

The sheet resistance of the as-deposited AgNO₃ film and the converted silver films after treatment for 16 s, 64 s and 128 s are shown in Table 1. Because of the insulating nature of the AgNO₃ caused the sheet resistance of the reference sample was too high to be measured. With increasing exposure to the reduction atmosphere of the argon plasma the sheet resistance of the film decreased down to 0.6 ± 0.1 Ω/□ for the film treated for 128 s. The energetic species in the plasma, specifically the argon ions and electrons are thought to be responsible for the conversion of the AgNO₃ into metallic silver. The plasma has a limited penetration depth into the treated film given by the porosity of the substrate and the film. There is a possibility that the converted metallic silver film forms a crust around non-converted AgNO₃ below, that has not been exposed to the plasma species.

The XPS spectra of the film treated for 128 s were analysed for the atomic concentrations and displayed 48% of silver, 35% of carbon, 14% of oxygen and 3% of fluorine. The carbon and oxygen that were detected can be attributed to surface contamination as well as the signal from the underlying nanocellulose substrate, which can be significant due to its porosity. The fluorine signal was also detected in the XPS spectra of the nanocellulose without the coating, therefore it can be attributed to the substrate as well. Interestingly, no nitrogen was detected in the coating. This suggests complete removal of the AgNO₃ during the conversion process.
Table 1 Sheet resistance of as-deposited AgNO₃ reference film and plasma reduced silver films

<table>
<thead>
<tr>
<th>Treatment time</th>
<th>Sheet resistance [Ω/□]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>n/a (&gt; 10 MΩ/□)</td>
</tr>
<tr>
<td>16 s</td>
<td>160 ± 30</td>
</tr>
<tr>
<td>64 s</td>
<td>50 ± 20</td>
</tr>
<tr>
<td>128 s</td>
<td>0.6 ± 0.1</td>
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</table>

The narrow XPS region of the Ag 3d 5/2 of the 128 s treated sample is shown in Figure 2a. A metallic Ag displays a single peak at around 368.4 eV and the signal from AgNO₃ is typically shifted by 0.4 eV towards higher binding energies. This small difference in the binding energies makes it difficult to assess the chemical form of the film. If we look at the Ag MNN auger peak in Figure 2b we can better see the pronounced features typical for the metallic silver rather than those in the position for the AgNO₃ [17].

Figure 2 Narrow XPS regions of the film treated for 128 s a) Ag 3d 5/2 peak b) Ag MNN auger peak

The SEM images of the film treated for 128 s are shown in Figure 3. The image with lower magnification in Figure 3a shows the homogeneity of the converted film. The reduced silver film copies the fibres of the underlying nanocellulose substrate. The image with higher magnification in Figure 3b shows details of the nanoparticles of silver which formed by agglomeration of silver atoms during the conversion from AgNO₃ by plasma. The average diameter of nanoparticles was 36 ± 1 nm. The tight packing of the nanoparticles that can be seen in Figure 3b and the necks that formed between them explain the excellent sheet resistance of the film.

Figure 3 SEM images of the reduced silver film after 128 s treatment with a) 20 kx magnification and b) 100 kx magnification
4. CONCLUSION

Silver nitrate dissolved in a mixture of water and ethylene glycol was printed using spin-coating on the nanocellulose substrate. Exposure of the printed film to the argon plasma generated by the diffuse coplanar surface barrier discharge led to the conversion of the silver salt to metallic silver as a result of reduction by energetic species from the plasma, specifically electrons and argon ions. The sheet resistance of 0.6 Ω/□, which is about 10x the resistance of bulk silver, was achieved after treatment for just 128 s. X-ray photoelectron spectroscopy suggested a complete conversion of the AgNO₃, as there was no nitrogen detected on the surface and the auger peak of silver displayed a shape typical for metallic silver, not a mixture of silver and silver nitrate. The nanocellulose paper substrate was used because of its compatibility with the ink, good mechanical and thermal properties and it’s flexibility and recyclability. Scanning electron microscopy images showed homogeneous coating copying the rough surface of the nanocellulose. The agglomerated nanoparticles were densely packed and formed connections during conversion. The high conductivity of the prepared films and the compatibility with the roll-to-roll processing makes this method very attractive for applications in flexible and printed electronics.

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