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https://doi.org/10.4224/23000709

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A Room-Temperature Process for Forming Highly Conductive Features

ABSTRACT

A process was developed to deposit highly conductive features on plastic films and papers. In this process, a reactive silver ink, which contains a weak reducing agent and is stable at room temperature, is directly cast or printed on a pre-coated substrate at room temperature. The strong reducing agent coated on the substrate instantly reacts with the ink on its surface and cause the rapid silver deposition locally. As the heat generated from the reaction is quickly transferred to the upper part of the ink, it initiates silver reduction reaction in the section, resulting in the continuous silver build up from the surface. Silver features with a conductivity almost the same as that of bulk silver and a thickness of up to 1 micrometer can be obtained from this bottom-up silver reduction and thus silver growth process. The whole reduction process happens at room temperature within minutes without any external energy applied.

INTRODUCTION

Conductive traces are the most basic elements in printed electronic devices. They are normally printed using silver conductive inks, either nano particles-based or micro particles-based. While the former one can be used to print conductive traces with a resistivity over 3 times of that of bulk silver, the later one is suitable for printing the races with a resistivity over 7 times of that of bulk silver. The nano particle-based silver inks are expensive to produce and are generally used in the area where high conductivity is essential and features are small. A post thermal annealing or solvent drying process at a typical temperature of 120°C or higher is required for treating the printed traces printed to get the optimum performance for all the inks.

Reactive inks have been considered as a potential replacement of nano particle-based ink due to its low cost[1]. We have developed a lower cost process that can be used to generate silver features, which have the same resistivity of bulk silver, at room temperature. The invention has been patented and is now disclosed in this conference.

EXPERIMENTS

Substrate preparation: The aqueous solution of hydroxylamine or its salt from reacting with formic acid was diluted using DI water by 20 to 50%. It was then coated onto a plastic film or photo paper with porous surface. For hydroxylamine, the substrate has to be used immediately before the chemical evaporates. For its salt, the coated film or paper was blown with compressed air to remove water to obtain dried films or papers for the use. The coated films or papers were used for accepting reactive silver inks.

Reactive silver inks: silver acetate was added into aqueous ammonium hydroxide and dissolved through a short mixing. Then, ammonium formic acid (as weak reducing agent) was added into the solution and dissolved. Afterwards, acetic acid was added into the solution to adjust its pH value. No precipitation was generated during the process, and the obtained solution would maintain the solution without precipitation at room temperature for over one week.

Silver deposition: The reactive silver ink was deposited on the coated substrate using casting and inkjet printing, and allowed the reaction at room temperature to complete.

RESULTS

All the reported silver reactive inks require a heating step to initiate and complete the reduction of silver ions to silver because the involved reaction is endothermic. Also, the reducing agent of the involved reactive ink has to be weak, otherwise the ink is not stable at room temperature for a sufficient long period. In order to develop a process that doesn't need the step, a supplementary exothermic reaction was introduced to the reported ink system to provide the heat required by the primary reduction. Figure 1 shows the concept of the design. On the substrate surface, the exothermic starts at room temperature when the ink is deposited on the substrate. The generated heat is quickly transferred to the upper ink layer and supports its energy need for reduction process.

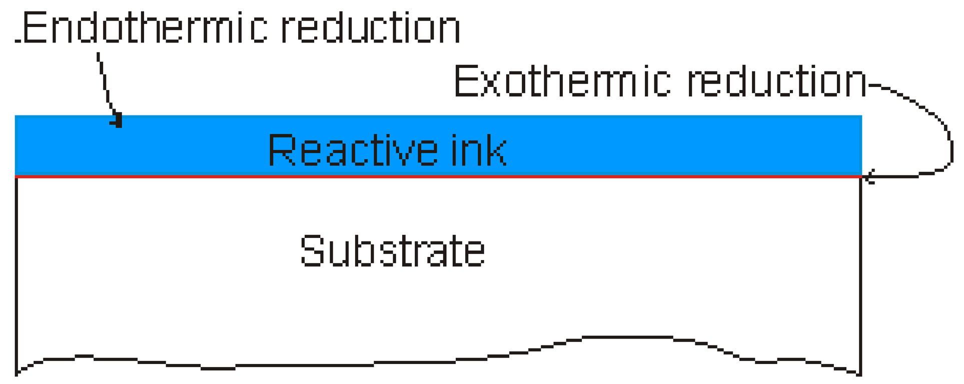

Figure 1. The design of a silver deposition process that doesn't need external heat

The selected exothermic reduction is based on the reaction of using hydroxylamine as a strong reducing agent. Figure 2 shows the room temperature DSC trace of a reactive silver ink when a tiny drop of hydroxylamine was added into the ink. Exothermic reaction instantly starts and quickly complete at room temperature. In comparison, the same silver ink undergoes an endothermic reaction when it is heated (Figure 3).

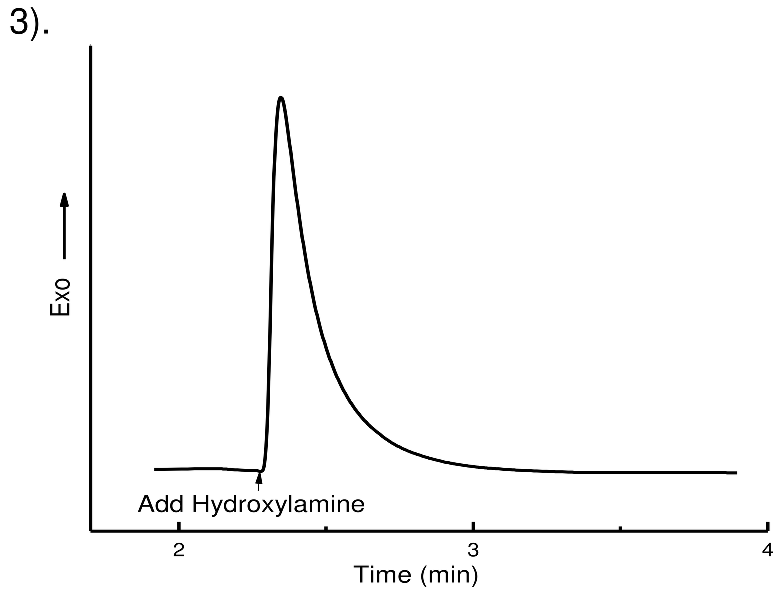

Figure 2. DSC trace of the reactive silver ink at room temperature when hydroxylamine was added.

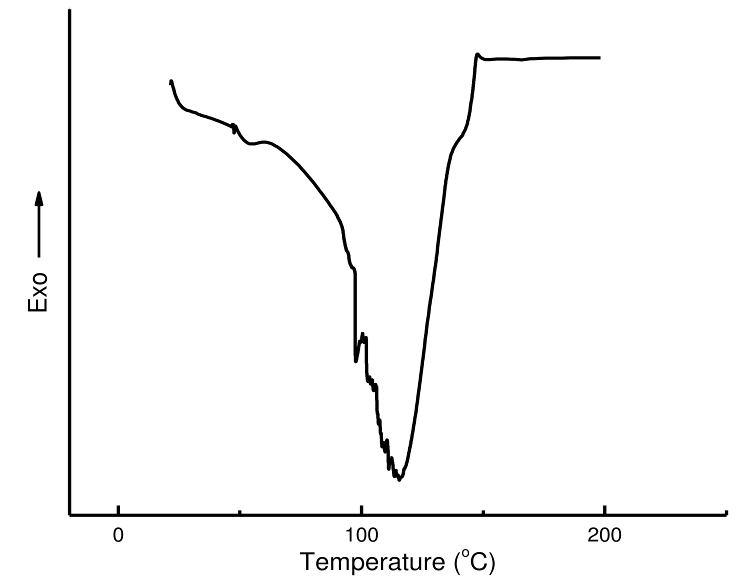

Figure 3. DSC trace of the reactive silver ink during its heating process.

The hydroxylamine-caused reduction and silver deposition was implemented by doping hydroxylamine into the surface pours of a substrate. For this, a solution was prepared by diluting commercial hydroxylamine aqueous solution with water and coated on the substrate. When the silver reactive ink which carries its weak reducing agent was deposited on the surface of the coated substrate, the exothermic reaction quickly starts at the surface and leads to the deposition of very small amount of silver into the pours and onto the substrate surface. Subsequently, its released heat initiates and supports the reduction of the majority ink and major silver deposition in upper layer. Many substrates with a porous surface layers, such as some PET films and photo printing paper for inkjet printing, are suitable for the application. For better handling, hydroxylamine can be reacted with formic acid to generate a salt which can stay on the substrate for a long period.

For the same amount of ink, the heat released by the first reaction is much more than the one absorbed by the second reaction, making it possible to use the released heat to support the whole second reaction when the targeted silver film is thin. In fact, the heat release is so intensive that it may deform the substrate if the weak reducing agent of the reactive silver ink was removed and the ink doesn't absorb heat. When the targeted silver is thick, the released heat is not enough for completing the reaction on the top layer. In this case, a further diluted solution of hydroxylamine or its reacted product with formic acid, can be applied on the surface to complete the reaction, and their residual can be wash with water.

Figure 4 shows the silver deposited on PET film. Except the nano porous on the very top surface, the obtained silver film is solid dense. For performance evaluation, silver films, 5x5 (cm^2) large and 1 mm thick, on PET films were prepared and measured using 4 point probing method. The films were measured to have a resistivity of 1.89 x10^{-8} (Ω·m), which is almost identical to the resistivity of bulk silver at 1.59 x10^{-8} (Ω·m).
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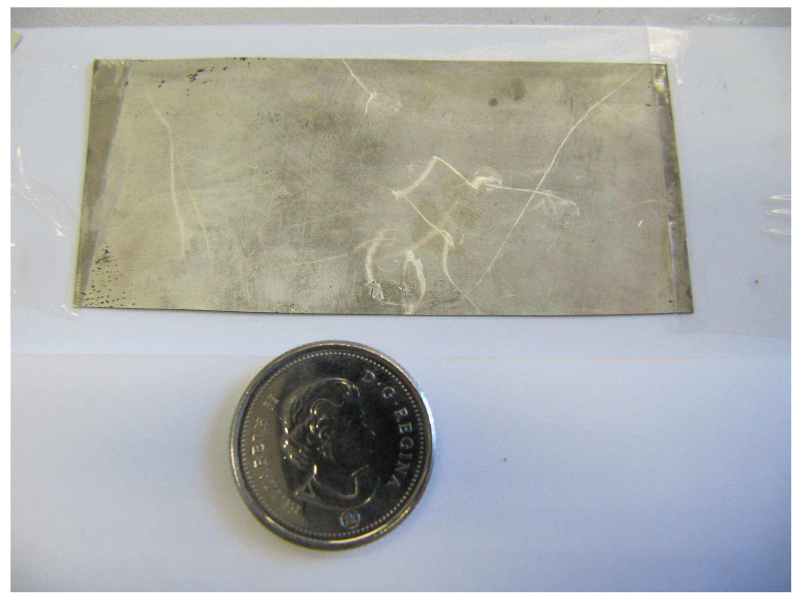

Figure 4. Silver film deposited on PET film using the reported process. PET films from Novacentrix were used.

The reactive silver inks could be directly printed on the coated substrates using an inkjet printer. Figure 5 shows some lines printed with a commercial inkjet printer (Dimitix). The lines were tested highly conductive without any post treatment after the printing.

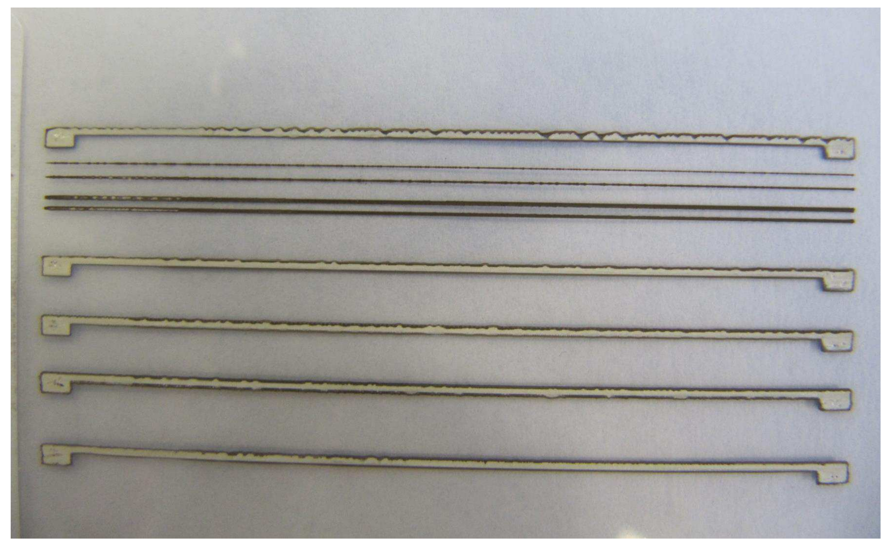

Figure 5. Silver lines printed using inkjet printer on PET film. Printed at room temperature and without any post treatment

As the described silver deposition happens at room temperature, it is possible to print silver patterns on papers. Commercial photo printing papers with smooth surface and nano pores were tested suitable for the application. Figure 6 shows the silver lines printed on Canon photo paper. With the addition of a suitable surfactant, the line quality could be substantially improved.

Figure 6. Silver lines printed using inkjet printer on Canon photo paper. Printed at room temperature and without any post treatment.

CONCLUSION

By combining a strong reducing agent--based exothermic reduction reaction and a weak reducing agent-based endothermic one, it was proved to be possible to deposit silver and print highly conductive silver patterns at room temperature using reactive silver inks. The associated process can be applied on PET and even papers.

Reference

1. S. Brett and J. A. Lewis, J. Am. Chem. Soc. 2012, 134 1419