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Using nanoparticles as direct-injection printing ink to fabricate conductive silver features on a transparent flexible PET substrate at room temperature

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Abstract

Conductive metallic features that are flexible could have application in integrated circuits, ranging from large-area electronics to low-end applications. This paper shows the creation of conductive silver thin film and wire on the transparent flexible polyethylene terephthalate (PET) substrate by a room-temperature chemical reduction process. One-step synthesis and spectroscopic characterizations of size-controlled silver nanoparticles are also described. Transmission electron microscopy, Fourier transform infrared spectroscopy, thermal gravimetric-mass analysis, X-ray photoelectron spectroscopy and synchrotron radiation X-ray diffraction were used to characterize the dodecanoate-protected silver nanoparticles. Silver metal film and wire were produced by soaking the dodecanoate-protected silver nanoparticle film and wire, which were prepared, respectively, by spin-coating and by directly drawing with a commercial Epson T50 inkjet printer onto the flexible PET substrate using Ag nanoparticles suspended in cyclohexane (10 wt.%) as the ink, in an aqueous solution containing 80% N_2H_4. The resistivities of the Ag films are actually lower compared with the Ag thin films prepared by other conventional chemical routes, such as using silver salts as metallo-organic precursors. It is suggested that the use of nanoparticles as a precursor may be an explanation for the lower resistivity.

Keywords: Nanoparticles; Inkjet printing; Silver; Flexible electronics; Thin films

1. Introduction

Using low-cost liquid-based direct printing techniques for patterning and deposition is of great interest, because they have potential application in the fabrication of integrated circuits (IC), ranging from large-area electronics (LCD and light emitting diodes) to low-end applications (IC repair, smart labels and identification tags) [1–6]. Traditionally, the microfabrication of conductive patterns by electroplating and etching processes accompanied by lithography is time consuming and expensive, because the steps required in the construction of one layer of a circuit are complicated. Therefore, there is a need for direct printing to simplify the processes and to reduce manufacturing costs. The development of a convenient and fast processing technique to fabricate conductive lines by the direct printing of metallic nanoparticles that can be converted to a low resistance conductor after solvent removal and heat-treatment has attracted increased attention in recent years [7–9].

Gold nanoparticle dispersions have been used in printing highly conductive elements. Smooth gold films were produced by the thermal annealing of a film of alkanethiolate-protected gold clusters that were spin-coated on the Si

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wafer from a suspension of Au nanoparticles in toluene [10,11]. However, the high cost of gold has overshadowed its merits in electronic applications. Currently, there is interest in the application of metallic nanoparticles as printing inks to form conductor films [12–18]. Silver, rather than gold, is particularly interesting to study, because bulk silver has the highest electric conductivity among all metals. Recently, octanethiolate-protected Ag nanoparticles dispersed in toluene were used as precursors for metallic printing inks. A sulfide contaminant was observed in significant amounts upon the formation of a silver film by the thermal annealing of self-assembled alkanethiolate monolayers on a silicon wafer surface, which indicated that the deposited thin film was silver sulfide (Ag_2S) [19]. Therefore, the silver thin films were not conductive. In a previous report [18], a conductive silver metal film was produced by the thermal annealing of freshly prepared decanoate-protected Ag nanoparticles (Ag–$C_9H_{19}CO_2$) spin-coated on the Si wafer under an atmosphere of 90% N_2–10% H_2 at 300 °C. The resistivity, which was measured by a four-probe method, was $6.097 \times 10^{-6}\,\Omega$ cm (bulk silver, $1.587 \times 10^{-6}\,\Omega$ cm). However, it was found that the Ag–$C_9H_{19}CO_2$ nanoparticles were operationally stable only during 1 day at room temperature because of the desorption of CO_2 gas and other decomposition fragments. Another protecting agent is needed to stabilize the silver nanoparticles generated. Furthermore, the conversion temperature of Ag–$C_9H_{19}CO_2$ nanoparticles to silver film by thermal curing was 300 °C, which is too high for realistic use in industrial applications in flexible electronics.

Printed IC or systems on flexible polymer substrate, such as polyethylene terephthalate (PET) and polyimide (PI), have been of great interest in recent years. One reason for the growing interest in using polymer-based flexible substrates is low-cost and large-area manufacturing. PET films [20], which have the advantages of transparency, light weight, low cost, mechanical flexibility, good chemical resistance and low coefficients of thermal expansion have been used as substrates in the fabrication of plasma display panels [21], organic LED [22] and Ge–Al micro-sensors [23] by various evaporation techniques. The transparent PET film can withstand temperatures only up to 120 °C. As the temperature increases beyond 120 °C, the transparent surface starts to turn translucent. It was reported [24] that the resistance of printed patterns on a PET film using conductive silver paste is as high as 50 Ω after curing the printed film at 120 °C for 30 min. Silver nanowire direct road-coating onto PET substrates was also reported previouly [25–27]. Using non-transparent PI as substrate instead of PET is another alternative. The PI film can withstand temperatures up to 250 °C. Aqueous silver nitrate or acetate solution was used as an ink to fabricate conductive patterns on PI by a direct-printing process [28]. When the curing condition was 200 °C for 60 min, the resistivity could fall to $6.6 \times 10^{-6}\,\Omega$ cm.

Until now, the fabrication of conductive silver features using silver nanoparticle suspensions as inks by direct-printing on PET and PI substrates has not been reported. Previously, polyvinylpyrrolidone–silver nanoparticle suspension was used as an ink to fabricate conductive patterns on PI by a complicated laser patterning technique [29]. A UV laser was used to trigger silver nanoparticles to convert light into heat. After UV laser beam irradiation on the silver nanoparticle thin film and washing away the unirradiated nanoparticles, a silver conductive line with resistivity $2.01 \times 10^{-5}\,\Omega$ cm was obtained after 120 °C and 1 h thermal annealing. The present study creates conductive silver film and wire using a direct printing process and a room-temperature chemical deprotection method for the saturated alkylcarboxylate-protected silver nanoparticles deposited onto plastic substrates from a suspension consisting of 10 wt.% silver nanoparticles in cyclohexane. As illustrated in Fig. 1, the conductive films and wires can be printed onto the substrate in one step, and room-temperature processing makes it potentially suitable for use in printed flexible electronics.

2. Experimental methods

2.1. Materials

All chemicals were of analytical grade and were used as received without further purification. All manipulations involving air-sensitive materials were carried out using standard Schlenk techniques under an atmosphere of nitrogen. Human occupational data and studies on laboratory animals suggest that people exposed to hydrazine may develop adverse systemic health effects or cancer.

2.2. Silver nanoparticles of Ag–$C_{11}H_{23}CO_2$ and Ag–$C_{17}H_{35}CO_2$

A toluene solution (31.69 nl) containing either dodecanoic acid or octadecanoic acid (16.67 mmol) was added to 1.4156 g (8.33 mmol) $AgNO_3$, resulting in a concentration [Ag^+] of 0.25 M, and then the mixture was stirred vigorously. Then 1.65 nl (16.67 mmol) of *n*-butylamine was added dropwise to the solution over a period of 2.5 min. After the mixture was stirred for a further 3.5 min, the solution became milk white. A 25 nl aqueous hydrazine solution prepared from 80 wt.% $N_2H_4{\cdot}H_2O$ (0.2607 g, 4.17 mmol) as reducing reagent was added dropwise over 15 min with vigorous stirring. After the addition of reductant, the solution was stirred for 3 h. Products were precipitated by addition of 200 nl acetone. Following the steps of centrifuging, resuspending with methanol, precipitating and washing with acetone gave the desired dark-brown silver nanoparticles.

2.3. Deprotection by chemical reduction to form silver features at room temperature

A suspension of silver Ag–$C_{11}H_{23}CO_2$ nanoparticles (10 wt.%) in cyclohexane was spin-coated by Swienco PM490