Laser Direct Writing of Conductive Silver Film on Polyimide Surface from Decomposition of Organometallic Ink

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Laser direct writing of organometallic ink to manufacture silver films was investigated by using a continuous-wave, Yb-doped fiber laser beam at a wavelength of 1071 nm. The organometallic ink consisted of an organometallic silver complex and a carrier vehicle, which was prepared by reaction of silver oxide with ammonium carbamates in methanol. The organometallic silver decomposed at a laser power of 0.1 W. The electrical resistivity values of silver conductors that were fabricated at a laser power of 0.5 W were about four times that of bulk silver. The morphology and electrical properties of the silver film were observed to be controllable as a function of laser processing parameters. The fabricated silver film exhibited excellent adherence to the polyimide substrate surface according to evaluation using the peel-off testing method.

Key words: Laser direct writing, organometallic ink, silver film, polyimide, electrical resistivity

INTRODUCTION

Laser direct writing of noble-metal-based inks has emerged as an attractive technique for fabrication of conductive patterns in microelectronics because of its fascinating features, such as its compatibility with a broad class of substrates (e.g., polymer, silicon, alumina), high control tunability in terms of micropattern resolution and size, ability to form patterns without a mask, and potential to reduce waste of noble metals.1–3

Noble-metal-based inks can be divided into two major types: micro or nanoparticle based4,5 and organometallic based6,7. Laser direct writing of conductive patterns using organometallic inks has many benefits in comparison with writing with ink made with metal micro- or nanoparticles. For example, organometallic inks do not contain any solids and do not clog the nozzle during inkjet, mesoscale material depositon (M3D),8 or micropen9 direct-write processing. The conversion of organometallic inks to metal can be achieved at relatively low temperatures, such as 180°C, which is lower than that reported as required for sintering silver nanoparticles in organic solvents.10 Organometallic inks that contain platinum,11 gold,12 and copper13 have been printed and subsequently processed to obtain conductive tracks of the desired metal on a range of substrates. Silver conductive lines have the lowest resistivities of all of the elements that are used to fabricate conductive lines and play an important role in high-density packaging and ultra-large-scale integrated devices; however, few studies14 that investigate laser direct writing of organometallic silver inks have been published in the open literature.

Therefore, we report herein a chemical reaction method for formation of organometallic silver ink and studied the formation of silver conductive film on polyimide surface through localized decomposition of organometallic ink by laser irradiation. The influence of laser power on the bulk resistivities and microstructures of the conductive lines was investigated.

EXPERIMENTAL PROCEDURES

Preparation of the Organometallic Silver Ink

The general synthesis strategy that was used to synthesize the organometallic silver ink proceeded as follows. First, ammonium carbamates were...
prepared by reacting dry carbon dioxide with primary or secondary aliphatic amines in absolute methanol solvent at a temperature below 0°C to 5°C. Next, the ammonium carbamates were reacted with silver oxide in methanol to produce the target, which could be purified by crystallization from a solution of 1:1 (volume to volume) methanol and ether. The synthetic reactions are presented in Eqs. 1 and 2. The probable structure of the organometallic silver complex is displayed in Fig. 1.

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\begin{align*}
2C_6H_5CH_2NH_2 + CO_2 & \rightarrow C_6H_5CH_2NHCOO^- \\
& + NH_3CH_2C_6H_5 \\
+ 4C_6H_5CH_2NHCOO^-NH_3^+C_6H_2CH_3 & \rightarrow 2C_6H_5CH_2NHCOOAg(C_6H_2CH_3C_6H_5)_2 \\
& + 2C_6H_5CH_2NH_2 + 2CO_2 \uparrow + H_2O 
\end{align*}
\]

**Laser Direct Writing of the Organometallic Silver Ink**

In the experiments, polyimide (120 μm thickness, Kapton) was used as the substrate, and it was cleaned with ethanol and attached to a rigid support (such as glass) by double-sided adhesive tape. The ink was deposited via micropen printing using a pen head (such as glass) by double-sided adhesive tape. The ink was studied with DTA/TGA. The corresponding DTA/TGA response curves are depicted in Fig. 2. Two endothermic processes were observed to occur during the heating process of the ink: one at approximately 112°C (peak A) and another at approximately 153°C (peak B). Peak A occurred due to volatilization of the solvent, which absorbs heat from the ink, and the TGA curve confirms this result. The mass began to decrease rapidly at 112°C. The endothermic peak, peak B, indicates decomposition of the organometallic silver complex. The decomposition concluded at 170°C, which is close to the value reported by Kaydanova (180°C). Corroboratively, the sample weight remained nearly constant when the ink was heated to a temperature beyond 170°C. The final weight ratio was 22.70 wt.%, which was assigned to the content of elemental silver in the compound.

**RESULTS AND DISCUSSION**

**Thermal Behavior of the Organometallic Silver Ink**

The thermal behavior of the organometallic silver ink was studied with DTA/TGA. An ESEM Quanta 200 scanning electron microscope (SEM) equipped with an energy-dispersive x-ray analyzer (EDS) was used to observe the microstructures of the silver lines. The cross-sectional profile was measured using a profilometer (KLA TENCOR P16+). Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using a simultaneous thermal analyzer (Diamond TG/DTA 6300; PerkinElmer Instruments) at a scanning rate of 10°C/min in ambient nitrogen environment. A four-point probe ohmmeter was used to measure resistance. Electrical resistivity was calculated from the resistance R, the length l, and the cross-sectional area A of the line, using \( \rho = RA/l \), and the results were compared with the resistivity of bulk silver (1.6 × 10⁻⁶ Ω cm). The adhesion strength of the silver film was assessed by peel-off testing using 3M Scotch tape in accordance with ASTM D3359 (standard test methods for measuring adhesion by the tape test method).

**Microstructure of the Silver Films**

When the continuous-wave laser beam scans the surface of the organometallic silver thick film, the organometallic film begins to generate heat due to the photothermal effect. Increasing the laser power induces a local temperature increase within the laser spot area. As soon as the temperature in the film exceeds the decomposition point of the organometallic silver complex, it will decompose and form silver particles. Furthermore, the decomposition threshold laser power depends on the concentration and composition of the organometallic compound. In this experiment, decomposition occurred at a laser power greater than a threshold of 0.1 W on the