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Fabrication of conductive silver micropatterns on an organic–inorganic hybrid film by laser direct writing

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ABSTRACT

This paper describes fabrication of silver (Ag) micropatterns on a double-decker-shaped polysilsesquioxane (DDPSQ) hybrid film by laser-induced pyrolysis (LIP) of a film prepared from liquid-dispersed Ag nanoparticles. The line width of Ag micropatterns fabricated by LIP can be controlled flexibly by changing the numerical aperture (NA) value of an objective lens and the focusing point. By changing NA value of an objective lens, line widths of Ag micropatterns can be varied flexibly from 75 µm to 5 µm. The Ag micropatterns show an excellent adherence to DDPSQ surface as evaluated by adhesive tape test. The resistivity of the Ag micropattern is determined to be 4.3×10^{-6} Ω cm, which is comparable to that of bulk Ag (1.6×10^{-6} Ω cm).

1. Introduction

Recent years have witnessed an explosion of interest in the application of polymers as the substrates for various electronic and display devices. These applications include flexible organic light-emitting displays [1,2], thin film transistors [3,4], larger-area sensors [5], and polymer micro-electromechanical systems [6]. The advantages of polymers are their mechanical flexibility, lightweight, enhanced durability, roll-to-roll processing, and low cost compared with rigid materials (such as silicon and glass). In order to fabricate interconnect lines between device elements or layers in plastic electronic devices, metallization on the polymer substrates is essential. In this case, the width and conductivity of metallized line are extremely vital for minimizing the size of device. Therefore, the realization of metallization process with the scale of a few micrometers on the polymer substrate is required. Fabrication of conductive features such as electrodes, conductive lines, and interconnects on polymer substrates using conventional photolithography is not suitable because polymer substrates are chemically incompatible with resists, etchants, and developers used in the fabrication procedure. Moreover, this conventional process is subject to limitations in that it is multi-step, time consuming, expensive, and environmentally unfriendly as dischargement of many harmful chemical wastes during the development.

Therefore, there is a need for direct digital printing techniques that are simpler and less expensive. In this context, inkjet printing and laser direct writing are promising alternatives to traditional lithography. The inkjet printing technique has been applied to fabricate conductive patterns of Cu, Ag, and Au on plastic substrates using printable metal nanoparticle inks [7–9]. The inkjet printed metal nanoparticles, which are surrounded by organic surfactants and dispersed in a liquid, are dried on the substrate and then subjected to heat treatment. As a result organic components of the nanoparticle-dispersed film are decomposed and simultaneously converted to continuous metal conductor. The ink jet printing technique has several disadvantages such as high heating temperature of the substrate after printing, slow printing speed, and resolution of micropattern. Decreasing the size of nanoparticles can reduce the metallization temperature, however, the temperature is higher than 200 °C which causes thermal damage to conventional transparent polymer film substrate. The resolution of the inkjet printing technique is limited to the order of 50–100 µm due to the diffusion of the micro-droplet by air resistance [10–12]. Recently, laser direct writing of metal nanoparticles has emerged as an attractive technique for fabricating conductive patterns in microelectronics because of its fascinating features such as compatibility with a broad class of materials such as metals, glass, ceramics, polymers and polymer composites, high resolution, high degree of flexibility to control the resolution and size of the micropatterns, high printing speed, and a little environmental pollution. In addition, the shallow depth of the field of the objective lens reduces the thermal damage of the substrate during metallization.

Organic–inorganic hybrid polymers have drawn great attention because they offer the opportunity to prepare high-performance multifunctional advanced materials through the combination of properties of organic and inorganic segments. Recently, an approach to

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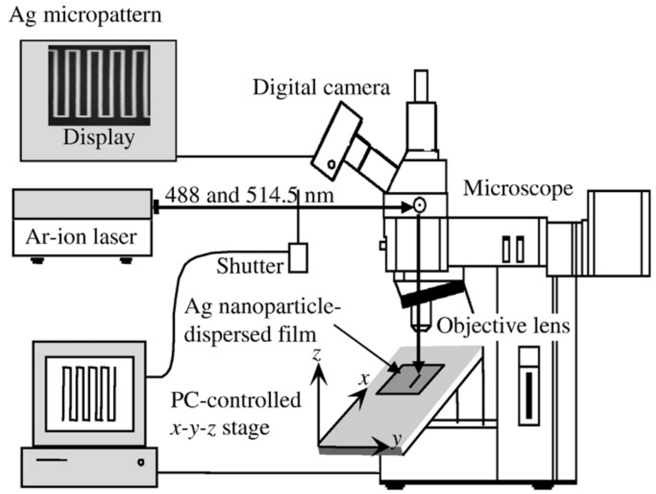

Fig. 1. Experimental setup for laser direct writing to fabricate Ag micropatterns on a DDPSQ film.

construction of nanohybrid materials based on polyhedral oligomeric silsesquioxne (POSS) as an inorganic moiety has attracted a lot of interest [13–15]. POSSs are ideal building blocks for the construction of organic–inorganic hybrid materials. Double-decker-shaped silsesquioxanes (DDSQs) are a family of silsesquioxanes consisting of nanometer-sized Si–O–Si cage structures functionalized with a wide variety of organic substituents [14], [16–19]. DDSQ-based hybrid polymers (double-decker-shaped polysilsesquioxane, DDPSQ) possess many exciting properties such as high thermal stability, good mechanical properties, low dielectric constant, excellent transparency, excellent flexibility, and so on [19]. Due to these exciting properties, DDPSQ can be used as a potential candidate substrate for various flexible electronic devices. For such applications drawing of conductive metal (Au, Cu, Ag) patterns on a DDPSQ substrate is required.

Previously, we have reported the fabrication of metal (Ag, Cu) micropatterns with submicron resolution on a glass substrate by laser direct writing technique using the metal nanoparticle-dispersed film as a precursor [20–22]. This technique is based on the efficient and fast conversion of photon energy to thermal energy by direct excitation of the plasmon absorption of a metal nanoparticle. In this paper, we describe fabrication of Ag micropatterns on a DDPSQ film by laser direct writing. In this fabrication process, the laser-irradiated area is quite narrow which reduces the thermal damage of the polymer film due to the thermal diffusion and the strain. Moreover, Ag micropatterns are characterized by optical microscopy, atomic force microscopy (AFM), surface profilometry, and resistivity measurements.

2. Experimental details

DDPSQ (Sila-DEC, $M_w = 6.63 \times 10^3$, $M_w / M_n = 2.29$) was obtained from Chisso Petrochemical Co., Japan. A thin film of DDPSQ on a glass substrate was prepared using a spin-coater (Mikasa Spin Coater, 1H-D7, Mikasa Co. Ltd., Japan) from a solution (10 wt.%) of DDPSQ in toluene at 2000 rpm for 30 s and the obtained film was baked at 110 °C for 1 min in order to evaporate the solvent. The thickness of the DDPSQ film was estimated to be 412 nm as measured by a surface profiler (Dektak^{3}ST, ULVAC). Ag nanometal ink (Ag1TeH) was purchased from ULVAC Technologies Inc. and used as received. The nanometal ink contained 50–60 wt.% Ag nanoparticles with an average particle size of 4.5 nm. Ag nanoparticles are individually dispersed in tetradecane solvent. The viscosity and density of the ink were 10.5 mPa s and 1.6 g/mL, respectively. Nanometal ink prepared by the gas evaporation method has several advantages compared with liquid-dispersed metal nanoparticles produced by chemical reaction in the liquid phase such as high quality and purity due to gas phase reaction in an inert gas, high-quality crystalline structure due to particle formation in a quasi-thermal equilibrium state, and uniform particle distribution etc [20–22]. Nanoparticle surfaces were modified with organic surfactants to prevent agglomeration during preparation [23]. Prior to preparation of Ag nanoparticle-dispersed film on a DDSPQ thin film, DDPSQ film was subjected to deep ultraviolet (UV) irradiation (wavelength: 185 and 254 nm, intensity: 16 mW/cm^2, Photo Surface Processor, SEN Lights Co.) in the presence of atmospheric oxygen for 5 min. The thickness of the deep UV modified DDPSQ film was 380 nm. An Ag nanoparticle-dispersed film was prepared on the deep UV modified DDPSQ film by spin coating of an Ag nanometal ink (50–60 wt.%) at 2000 rpm for 30 s and the obtained film was dried by heating at 110 °C for 30 s. Before laser irradiation, the thickness of nanoparticle film was 730 nm, which was also determined by a surface profiler. Absorption spectra of an Ag nanoparticle-dispersed film on a deep UV modified DDPSQ film were measured by a JascoV-670 spectrophotometer.

Fig. 1 shows the experimental setup for laser direct writing to fabricate Ag micropatterns on a DDPSQ film. A continuous wave Ar ion laser (wavelength: 488 nm and 514.5 nm, MELLES GRIOT 543-300A) was introduced into an optical microscope (Olympus, BX51 M, Japan)

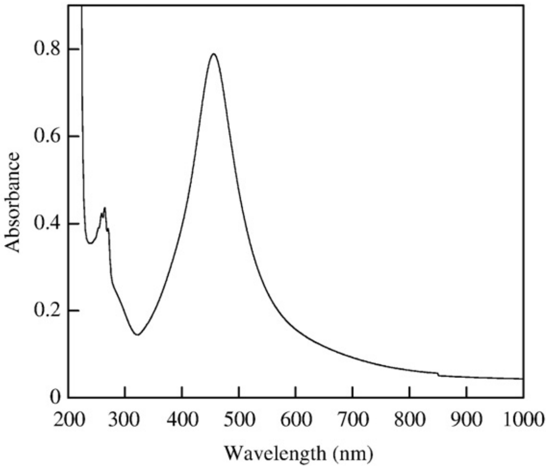

Fig. 2. Absorption spectra of an Ag nanoparticle-dispersed film on a deep UV modified DDPSQ film.

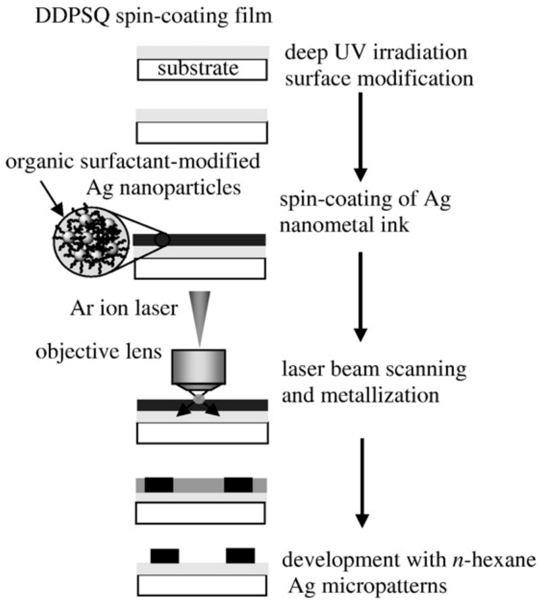

Fig. 3. Schematic illustration of Ag micropatterns fabrication process on a DDPSQ film by laser directs writing.