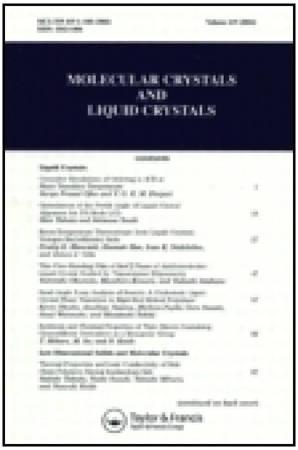

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Direct Drawing of Submicrom Wiring By Laser-Induced Pyrolysis of Film Prepared from Liquid-Dispersed Metal Nanoparticles

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The direct-drawing of submicron Ag wiring was achieved by laser-induced pyrolysis (LIP) of a precursor film prepared from liquid-dispersed Ag nanoparticles. This new method provided the micro-wiring by wet and maskless process toward printed electronics. The linewith of the Ag wiring was easily controlled by changing the objective lens magnifications and the focusing point. The resistivity of the Ag wiring fabricated by this technique ($1.9 \times 10^{-6}\,\Omega$ cm) is comparable with that of bulk Ag ($1.6 \times 10^{-6}\,\Omega$ cm).

Keywords: laser-direct drawing; laser-induced pyrolysis; liquid-dispersed metal nanoparticle, micro-wiring; nanometalink

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INTRODUCTION

Printed electronics toward flexible devices have recently attracted much interest. To realize the devices, a new production process without high vacuum system, that is, a wet process using soluble materials is desired. Micro-wiring by a wet process is one of the key technologies in the printed electronics. In a conventional process, a micro-wiring substrate was prepared as illustrated in Figure 1 (a). A metal thin film is deposited on a substrate by sputtering in vacuum, and then, photoresist is spin-coated and patterned by UV-irradiation through photomask. After the development of the photoresist, the micro-wiring patterns are fabricated by etching and stripping using plasma processing.

Such multistage processes can be simplified in the inkjet printing [1–4] as shown in Figure 1(b). A precursor solution is printed on a substrate directly without photomask, and then, the precursor micro-patterns are converted to metal micropatterns by heat treatment. In the case of a micro-wiring by conventional inkjet printing, a micro-droplet with the diameter of about 16 μm is sprayed onto a substrate. In general, the resolution of the inkjet printing is larger than 20 μm due to the diffusion of the micro-droplet by air resistance. The limitation of the printing speed and the necessity of the heat treatment process are also additional problems.

In this paper we report a new micro-wiring method by laser-direct drawing as illustrated in Figure 1(c) [5]. A precursor solution is spin-coated on a substrate, and then, laser beam is scanned on the

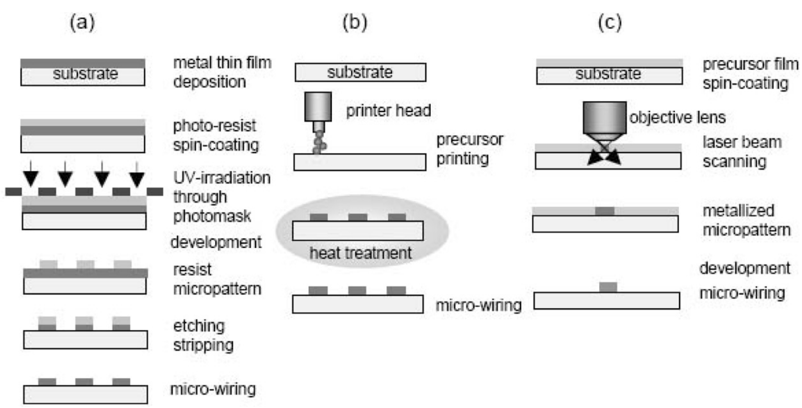

FIGURE 1 Comparison of micro-wiring processes. (a) conventional method, (b) inkjet printing method, (c) laser-direct drawing method.

film. The laser-irradiated area is converted to metal and the unirradiated area is removed by solution development process. This is also wet and maskless process. The characteristic feature of the laser-direct-drawing is the high resolution. Using an objective lens, the spot size of the laser beam can be reduced to smaller than 1 μm. Flexibility to control the resolution and the size of the micorpatterns by changing the focusing spot size is also advantageous. This feature enables to enhance the efficiency of the microwiring with various line widths. In addition, the shallow depth of field of the objective lens reduces the heat damage of a substrate during metallization. These features supply the weak points of the inkjet printing, especially, the resolution of the micro-wiring. We call this process LIP method because the formation of the micropattern is caused by the laser-induced pyrolysis of the precursor. We have reported the application of the LIP method to micropatterning of Si, Ge and Si/Ge semiconducting films [6,7] and PZT and BT dielectric films [8,9].

EXPERIMENTALS

A nano-Ag-dispersed film was prepared by the spin-coating of a diluted toluene solution (5 wt%) of Ag nanoparticle ink (Ag Nanometalink, ULVAC) on a glass substrate. Figure 2 shows the experimental setup for laser-direct drawing. An Ar-ion laser beam (488 nm) was introduced into a microscope and focused onto the precursor film. The focused laser beam was scanned by PC-controlled x-y-z stage. During drawing of micropattern, the shape was observed by CCD camera. The change of the chemical structure can be measured by micro-Raman spectroscopy [8].

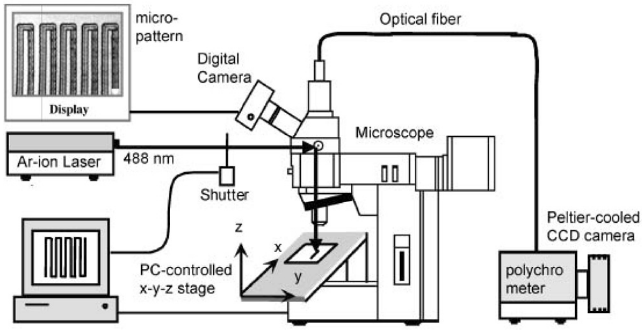

FIGURE 2 Experimental setup of laser-direct drawing.

RESULTS AND DISCUSSION

The Nanometalink is produced by the gas evaporation method, where Ag nanoparticles (average particle size 4.5 nm) are individually dispersed in an organic solvent by covering the surfaces with a surfactant [10]. Nanometalink prepared by the gas evaporation method has some advantages compared with liquid-dispersed metal nanoparticles produced by chemical reaction in the liquid phase, that is, high quality and purity due to the gas phase reaction in an inert gas, high-quality crystalline structure due to the particle formation in a quasi-thermal equilibrium state, and uniform particle distribution. The relationship between diameter of the nanoparticle and the melting point has been reported by Buffer and Boel [11]. With decreasing in the size, the melting point drops remarkably. The metallization temperature of the Ag Nanometalinks is 220°C in air, where organic moieties covering the Ag nanoparticles are thermally decomposed and the metallic Ag phase is formed by fusion of the Ag nanoparticles.

The resolution of the Ag micropattern was investigated by changing laser intensity under the following conditions: the objective lens; 100 magnifications, scanning speed; 10 μm/s. Ag Nanometalink was spin-coated on a quartz substrate and then preheated at 120°C.

Figure 3 shows the optical micrographs of the Ag micropatterns before development process, where the repetition length of the Ag line was 5 μm. The laser intensities at the focal point through the 100x objective lens were estimated assuming a beam waist diameter of 0.74 μm for the 488 nm line of the Ar-ion laser. The linewidth of the Ag wiring depended markedly on the laser intensity. The micropatterns obtained at lower laser intensities showed submicron resolution: the linewidths drawn with the laser intensities of 0.0395, 0.198, and 0.395 MW/cm^2 were 0.48, 0.69, and 0.89 μm, respectively. With increasing the laser intensity, the linewidth was increased due to the thermal diffusion: the linewidths drawn with the laser intensities of 1.58b and 2.77 MW/cm^2 were 1.63 and 3.60 μm, respectively. After the development process using n-hexane for 10 sec, unirradiated area was removed easily as shown in Figures 3(f)–(j). When the laser intensity is lower than 1 MW/cm^2, micro-wiring with submicron resolution can be achieved as shown in Figure 3(h). However, Ag patterns drawn with lower laser intensities were peeled off from the substrate during the development process using n-hexane and the scrap was observed as shown in Figure 3(f) and (g). When the laser intensity is not sufficient to reach the bottom of the spin-coated film, the elution of the unirradiated layer at the interface of the substrate caused the peeling.

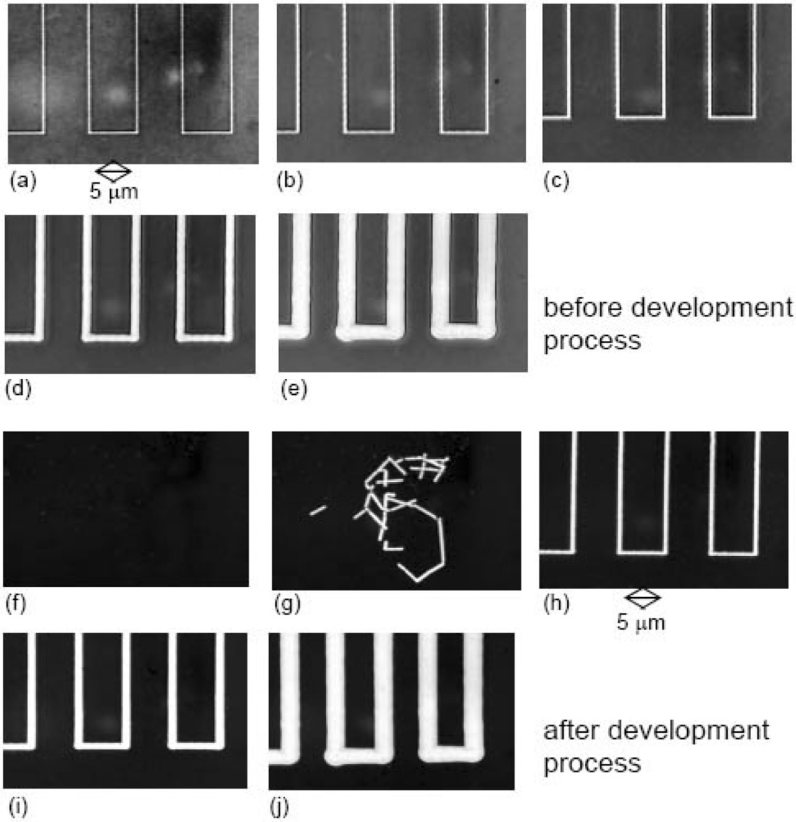

FIGURE 3 Optical micrographs of the Ag micropatterns. The Ar-ion laser beam (488 nm) was scanned under the following conditions: objective lens magnification = 100x, scanning length = 50 μm, interval between scanning lines = 5 μm and scanning speed = 10 μm/s. Laser intensities: (a) 0.0395, (b) 0.198, (c) 0.395, (d) 1.58, (e) 2.77, (f) 0.0395, (g) 0.198, (h) 0.395, (i) 1.58, and (j) 2.77 MW/cm^2.

Micro-wiring with higher resolutions may be obtained by using a thinner nano-Ag-dispersed film.

The line width of the Ag pattern also depends on the magnification of the objective lens. Figure 4 shows the Ag micropatterns obtained by using the objective lens of 5 magnifications, where the linewidths are larger than 10 μm. The height of the wiring after the development process under the condition (b) was determined to be ca. 60 nm by using an electromechanical stylus instrument (Dektak, ULVAC). Further large Ag patterns can be prepared with a lens of the lower

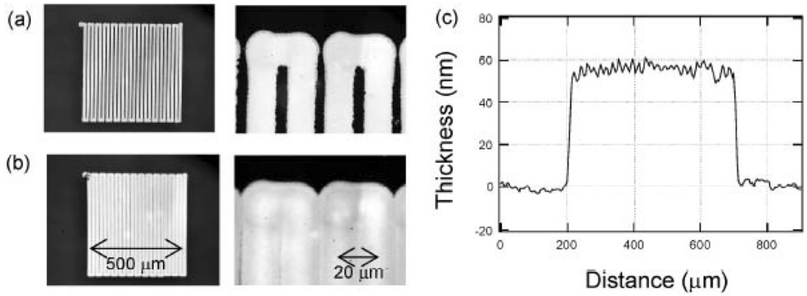

FIGURE 4 Optical micrographs of the Ag micropatterns. The Ar-ion laser beam (multiline) was scanned under the following conditions: objective lens magnification = 5×, scanning length along the x- and y- axes = 500 μm, interval between the x-axis scanning lines = 20 μm, and scanning speed = 100 μm/s. Laser intensity: (a) 0.334 MW/cm^2, (b) 0.491 MW/cm^2. (c) Surface roughness of the Ag micropattern (b).

magnifications. Figure 5 shows the Ag micropattern fabricated using an objective lens with 5× magnification, where the laser beam spot size was increased by shifting the focusing point upward from the top of the spin-coated film. A smooth Ag film with about 100 μm line-width was drawn by the LIP method. These features enable the improvement of wiring speed and productivity.

The resistances of an Ag pattern were measured by two-point method changing the distance of probes under the microscope. From the slope of the line obtained by least-squares fitting, the resistivity of the Ag thin film was determined to be $1.9 \times 10^{-6}\,\Omega$ cm, which is comparable to that of bulk Ag ($1.6 \times 10^{-6}\,\Omega$ cm).

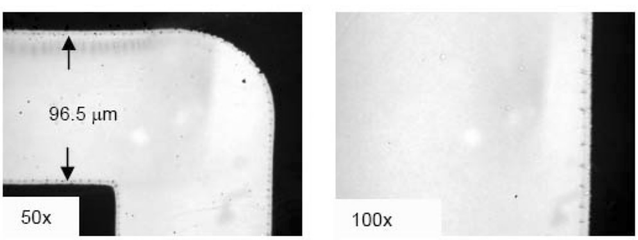

FIGURE 5 Optical micrographs of the Ag micropatterns. The Ar-ion laser beam was scanned under the following conditions: objective lens magnification = 5×, scanning length along the x-axis = 1000 μm, interval between the x-axis scanning lines = 200 μm and scanning speed = 200 μm/s. Laser intensity: 2.08 KW/cm^2. The spot size of the laser beam was increased by shifting the focusing point upward from the top of the spin-coated film.

In conclusions, we first succeed in direst-drawing of a submicron wiring using LIP (Laser-Induced Pyrolysis) method. LIP method is maskless and wet process with a high resolution and flexibility in controlling the drawing size in the comparison with inkjet technique. The LIP method is expected to be applicable to the preparation of various taylor-made micro-devices.

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