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Light-controlled selective metal deposition on photopolymer films

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Fine metal patterning was performed by selective Mg deposition on photopolymers. Mg patterns with a minimum width of 5 μm were obtained by using maskless vacuum evaporation. The selective deposition originates in the difference of glass transition temperature, microscopically, of surface molecular motion between polymerized and nonpolymerized photopolymer surfaces. The difference between photoreactive small molecules and polymers was also discussed. The selective metal deposition method would be applied to a wide range of organic surfaces; this method showed great potential for the preparation of fine wiring for various organic electronic devices. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3064138]

Organic electronic devices such as light-emitting devices, thin-film transistors, solar cells, and memories have recently been attracting interest.[1–7] Organic devices require metal electrodes or wiring for their operation. To prepare patterned metal films or wires on an organic layer, a vacuum evaporation method with a shadow mask[8,9] or an inkjet printing method involving conducting nanoparticles[10–13] is generally used. However, these methods have potential difficulties: The low-resolution limit in the vacuum evaporation method is related to the complexity of the setup with a shadow mask or thermal damages occur in the organic layer after the heat treatment for the inkjet printing method. Such difficulties restrict the integration of circuits using organic materials.

Recently, we developed a method to prepare fine metal patterns by using a vacuum evaporation method without a shadow mask; in this method, it is possible to set the resolution limit of metal patterning to the diffraction limit of light. This method is based on selective metal deposition on a photochromic diarylethene (DAE) surface.[14,15] In this paper, we report the possibility of performing selective metal deposition and fine metal patterning without a shadow mask on other photoreactive organic materials such as photopolymers.

The selective metal deposition of photochromic DAEs signifies that Mg vapor atoms are deposited on the colored DAE film and not on the uncolored DAE film.[14] It has been understood that elective deposition, which does not relate a contact angle of a water droplet, is strongly correlated with a change in the glass transition temperature T_g of the film: T_g is 32 °C for the amorphous DAE film in the uncolored state, while it is 95 °C for films in the colored state. Selective deposition is affected by surface molecular motion, which is characterized as surface T_g and related to T_g as a bulk property. When Mg atoms are evaporated onto a low T_g surface, the weak interaction between the uncolored molecules and the Mg atoms and the active molecular motion related to the low T_g causes the desorption of Mg atoms from the uncolored surface. On the basis of the above-mentioned principle for selective deposition, we suggest the possibility of a large T_g change in other photoreactive materials.

Figure 1 shows the procedure of selective Mg deposition on photopolymer samples as typical photoreactive materials. A photopolymer (UV-curable resin TESK A-1445, purchased from TESK Co., Ltd.) was dissolved in acetone (20 wt %) and the solution was spin coated on a glass substrate. The films were then dried at a temperature of 60 °C for 30 min. One sample was polymerized by UV irradiation ($\lambda = 365$ nm; power: 700 mW/cm^2). Thus, polymerized and nonpolymerized samples were prepared. The T_g of the nonpolymerized film was −7.2 °C, whereas that of the polymerized film was 144 °C. (T_g was measured by using Rigaku DSC8230.) Finally, Mg was evaporated onto these samples at a deposition rate of 0.5 nm/s. Thereby, Mg was deposited only on the polymerized film. (In Fig. 1, the films were observed by using transmitted white light; thus, the area where Mg was deposited appears black.) The selective deposition effect was also observed in the case of another photopolymer (TESK A-1408).

By using the selective deposition method, we can easily obtain any fine metal pattern, as shown in Fig. 2. (i) An UV laser spot with a wavelength of 375 nm, laser power of 1 mW, and diameter of 3 μm was then scanned on the nonpolymerized films with a thickness of 3 μm at a speed of 100–200 μm/s, and various polymerized patterns were obtained. (ii) Subsequently, Mg was evaporated onto the entire surface area without a shadow mask. (iii) Thus, fine Mg pat-

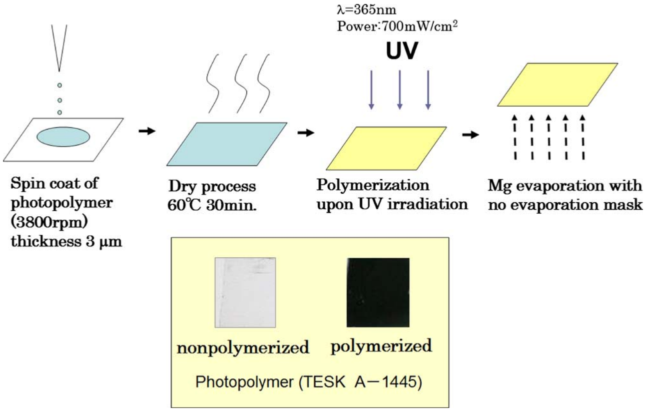

FIG. 1. (Color online) Selective metal Mg deposition based on a photopolymer film.

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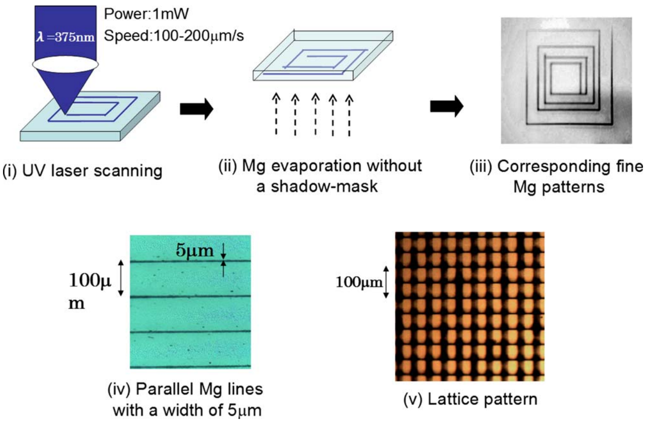

(i) UV laser scanning (ii) Mg evaporation without a shadow-mask (iii) Corresponding fine Mg patterns

(iv) Parallel Mg lines with a width of 5μm (v) Lattice pattern

FIG. 2. (Color online) Preparing process and obtained various fine Mg patterns obtained by using selective deposition method with no evaporation mask. Black color indicates Mg deposited areas.

terns corresponding to the polymerized patterns were easily obtained. (iv) The minimum Mg line obtained by the method was 5 μm. The resolution limit of metal patterning is to be restricted to the diffraction limit of light. (v) Furthermore, closed metal patterns such as the lattice pattern could also be obtained; it is impossible to obtain such patterns in a conventional evaporation process using a shadow mask. This shows the wide possibility of the selective deposition method for future applications in organic electronics.

In order to prepare wires with the Mg metal pattern for organic devices, the conductivity of Mg metal film obtained by the selective deposition method is important. The electrical resistivity of the Mg film deposited on the polymerized photopolymer film was determined to be 8.7×10^{-6} mΩ. On the other hand, the resistivity of the Mg film deposited on glass substrate was 2.6×10^{-6} mΩ. No significant difference was observed.

In order to understand the mechanism of selective deposition, we investigated the Mg atom behaviors on the surface. Figure 3 shows the UV irradiation time (corresponding to the change in T_g) dependence and substrate temperature dependence of Mg deposition on photopolymer films. T_g of the photopolymer film was increased from −7.2 to 144 °C upon UV irradiation. A thick Mg film was formed on the polymerized film with a T_g of 144 °C at room temperature. On the other hand, Mg was not deposited on the nonpolymerized film with a T_g of −7.2 °C; however, very thin Mg films were formed on the semipolymerized films with T_g values of 2 and 6 °C. Furthermore, the thickness of Mg films deposited on the polymerized film with a T_g of 144 °C decreased at high substrate temperatures.

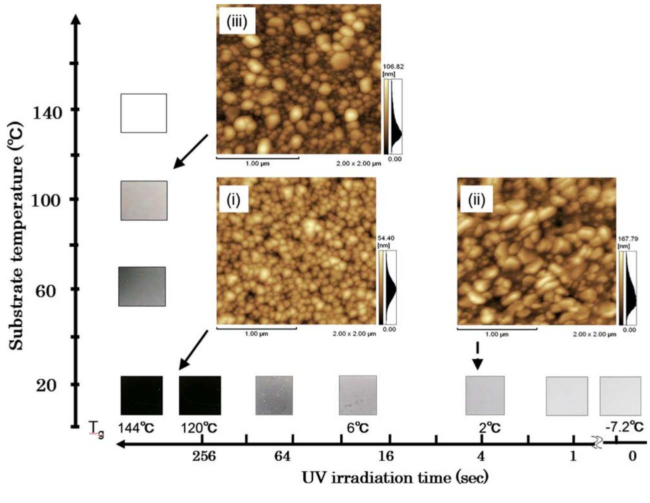

FIG. 3. (Color online) Substrate temperature and UV irradiation time dependences of Mg deposition. AFM images of Mg crystals on polymerized and semipolymerized film surfaces after Mg evaporation are also displayed.

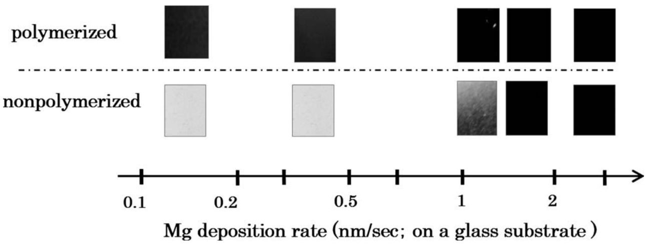

FIG. 4. Deposition rate dependence of selective Mg deposition on photopolymer films.

Three representative samples [(i) the thick Mg film deposited on the polymerized film with a T_g of 144 °C, (ii) the thin Mg film deposited on the semipolymerized film with a T_g of 2 °C at room temperature, and (iii) the thin Mg film deposited on the polymerized film with a T_g of 144 °C at a temperature of 100 °C] were investigated by using atomic force microscopy (AFM). Small Mg crystals with diameters of 10–100 nm filled the polymerized surface for sample (i). In contrast, significantly larger Mg crystals with diameters over 100 nm are formed on the second and third samples, as shown in Fig. 3 (ii) and (iii), respectively. It is well known that crystal growth is enhanced when the temperature is increased. At higher temperatures and/or in a lower polymerization state, molecular motion on the surface is greater. As molecular motion on the surface increases, the surface migration among the deposited Mg atoms also increases. The existence of large Mg crystals demonstrates that molecular motion on the surface is the dominant determining factor in the selectivity of Mg deposition. The result obtained here indicates that the selectivity of Mg deposition on the photopolymer surface is basically the same for the DAE surface.[14]

In order to determine the undeposition effect on the photopolymer, we investigate the deposition rate dependence of Mg atoms on the surfaces (Fig. 4). The deposition rate was defined by the rate on a glass substrate. When the deposition rate increased to over 1 nm/s, the Mg film was formed even on the nonpolymerized surface. This result signifies that Mg atoms did not rebound elastically from the surface because such a rebound does not directly depend on the deposition rate. The Mg atoms are adsorbed once on the surface; they then migrate and are desorbed from the surface at a low deposition rate that is below 1 nm/s. This result also indicates that the surface adsorption energy for Mg atoms on the nonpolymerized surface is small compared to that on the polymerized surface and, therefore, Mg atoms are easily desorbed by thermal energy at room temperature.

Figure 5 shows thickness dependence of selective Mg deposition on the photopolymer. Selective deposition occurred for a film thicker than 1 μm; however, Mg was deposited even on the nonpolymerized film whose thickness was below 1 μm. In the case of DAE, Mg was not deposited on the uncolored DAE film with a thickness of 1 nm.[14] Furthermore, in Fig. 3, thin films of Mg were deposited on the photopolymer film with a T_g of 2 °C, but Mg was not de-

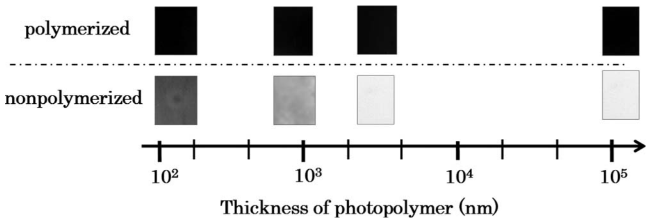

FIG. 5. Thickness dependence of selective Mg deposition on photopolymer film.

posited at all on the uncolored DAE film with a T_g of 32 °C. Such differences between DAE and the photopolymer could be important because the difference between surface molecular motions in the two materials would be considerable. The surface molecular motion of polymers is strictly restricted by a polymer chain and by the substrate compared with small molecules. The degree of freedom of molecular motion on the surface would affect the occurrence of selective deposition. Many studies on the surface property (or surface T_g) of polymers have been reported,[16–18] but there are no reports that clearly discuss the difference between the surface T_g of polymers and that of small molecules. Unfortunately, we are at present unable to perform experiments for investigating the surface T_g, and thus leave it for a future study. However, it has not escaped our result that the selectivity of Mg deposition on organic surfaces immediately suggests a possible estimation for surface T_g itself.

In conclusion, we have demonstrated fine metal patterning using selective Mg deposition based on polymerization of photopolymers. Fine metal Mg patterns with a minimum width of 5 μm were obtained by using maskless vacuum evaporation. Selective deposition originated from the difference of surface molecular motion between polymerized and nonpolymerized photopolymer surfaces. This result shows great potential for the preparation of fine metal wiring for various organic electronic devices.

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