

Metal patterning using maskless vacuum evaporation process based on selective deposition of photochromic diarylethene

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We developed an electrode/wiring patterning method that does not employ evaporation shadow masks; this method is based on selective metal deposition of photochromic diarylethene (DAE). In the selective Mg deposition based on the photoisomerization of DAE, Mg vapor atoms are deposited only on colored DAE film obtained upon UV irradiation, but not on uncolored film. We demonstrated fine metal Mg patterning with a minimum width of 3 μm and the preparation of a patterned cathode. The selective metal deposition method has significant potential for preparing fine electrodes/wiring for various organic electronic devices. © 2008 American Institute of Physics. [DOI: 10.1063/1.3028650]

Organic electronic devices such as organic light-emitting devices (OLEDs), organic thin-film transistors, and organic memories have recently been attracting interest.^{1–5} Organic devices, in general, require metal electrodes or wiring for their electronic operation. To prepare patterned metal films or wires on an organic layer, a vacuum evaporation method with a shadow mask^{6,7} or an inkjet printing method involving conducting nanoparticles^{8–11} is generally used. These methods, however, involve potential difficulties: the low-resolution limit is related to the complexity of the setup in the vacuum evaporation method or thermal damages occur in the organic layer after heat treatment. In this paper, we report a method to prepare fine metal wiring or a patterned electrode by using a maskless vacuum evaporation method.

The method proposed here utilizes the selective metal deposition¹² of photochromic diarylethenes (DAEs);^{13–17} Mg vapor atoms are deposited on the colored DAE film, but not on the uncolored DAE film. The selective deposition occurs as a result of the interaction forces and molecular motion dynamics being different for each DAE isomerization state. When Mg atoms are evaporated onto the uncolored DAE surface, the weak interaction between the uncolored DAE molecule and the Mg atoms and the active molecular motion causes the desorption of Mg atoms from the uncolored surface.

We demonstrated “grating” formation by using the method. Figure 1(a) shows a process to prepare a grating comprising parallel Mg microlines. The uncolored DAE film had a thickness of 10 nm, and it was prepared on a glass substrate by a vacuum evaporation method. (i) A UV laser spot on the film surface with a wavelength of 375 nm, laser power of 0.4 mW, and diameter of 5 μm was then scanned with a speed of 1 mm/s, and parallel colored DAE lines with a length of 2 mm and pitch of 50 μm were obtained. (ii) Subsequently, Mg was evaporated onto the entire surface area without a shadow mask. (iii) Thus, a grating pattern with fine and parallel Mg lines corresponding to the colored lines was obtained.

Figure 1(b) shows the laser power dependence of the Mg line width. The Mg lines are indicated by the bright regions. The width of the Mg lines was 25 μm for 0.8 mW of laser power and it decreased to 15 μm when the power weakened to 0.4 mW. This observation shows that the deposited Mg linewidth can be controlled by regulating the power and scan speed as well as spot shape and spot diameter. The observation also suggests that the isomerization ratio has a threshold value for the Mg deposition because the light intensity distribution of the laser spot and, therefore, the distribution of

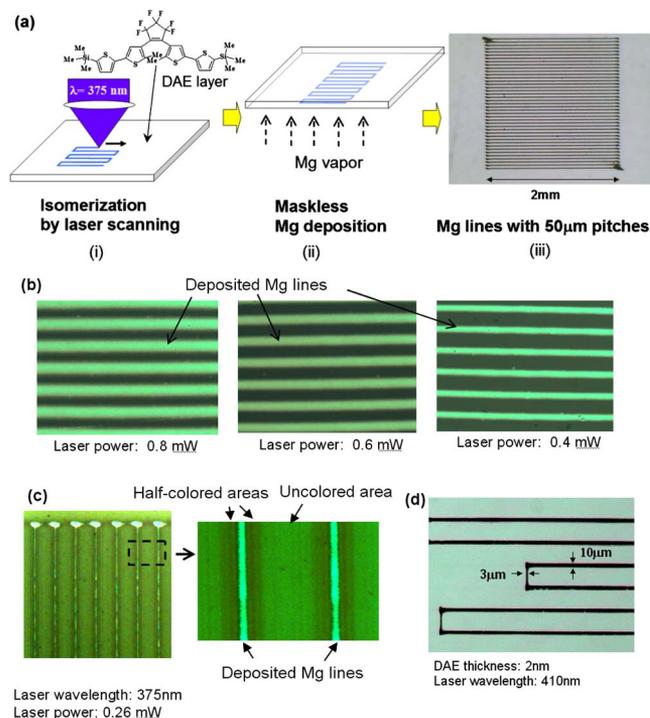


FIG. 1. (Color online) (a) Generation of fine Mg patterns via maskless metal deposition using DAE thin films. (i) UV laser (λ : 375 nm; power: 0.4 mW; scan speed: 1 mm/s) scanning on uncolored DAE film generated parallel colored lines with a pitch of 50 μm . (ii) Mg vapor deposition without a shadow mask. (iii) Obtained metal Mg grating corresponding to the colored line patterns.

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colored molecules in the DAE film are not steep.

To clarify the threshold property of the selective deposition on a micron scale, laser scan isomerization of a 30-nm-thick DAE film was investigated for a low power. Figure 1(c) shows the Mg lines deposited with a width below 10 μm . Half-colored areas and wide uncolored areas were observed around and between the Mg lines, respectively. This observation indicates that Mg was deposited only in the dense colored regions at the center of the lines that were formed by irradiation with the intensity peak of the laser spot. Mg was not deposited on the half-colored area in which the concentration of the colored isomer was below a certain value. This observation indicates the existence of a threshold concentration for selective deposition on a micron scale.

The result obtained above indicates that the resolution limit of the Mg patterns depends on not only the diffraction limit of the laser light but also the laser power, scanning speed, and photosensitivity of DAE. Figure 1(d) shows Mg lines formed by using a violet laser with a wavelength of 410 nm; this wavelength corresponds to a low sensitivity of DAE since the absorption is low at this wavelength. A minimum linewidth of 3 μm was achieved.

Magnesium is one of the widely used cathode materials in organic electronic devices.^{18–21} Therefore, the method for the formation of metal patterns has considerable potential for obtaining a fine cathode pattern in organic electronic devices. Hereafter, we discuss the potentiality for using selective Mg deposition for cathode pattern formation.

To apply the selective deposition method to the fabrication of cathodes for organic devices, it is essential to know the electronic characteristics of the colored DAE layer. Therefore, the current-voltage characteristics of the DAE layer were investigated by using the device structure shown in Fig. 2(a). The device consisted of an anode [indium tin oxide (ITO)] on a glass substrate, a carrier transport layer (CTL), a colored DAE layer with a thickness of 1 nm, and a Mg cathode. The organic layers were deposited on the ITO substrate by a vacuum evaporation method. Devices with an *N,N*-di(1-naphthyl)-*N',N'*-diphenylbiphenyl-4,4'-diamine (NPB) (a typical hole transport material) layer or tris(8-hydroxyquinoline)aluminum (Alq3, a typical electron transport material) layer as the CTL were investigated. When CTL was composed of NPB, no major difference was observed between the devices (i) without and (ii) with the DAE layer, as shown Fig. 1(b). This indicates that the DAE layer did not affect the hole transportation because the current in the NPB devices is dominated by holes.

On the other hand, the current was dramatically suppressed in the Alq3 devices (iv) with the DAE layer in comparison with the device (iii) without the DAE layer, as shown in Fig. 2(c). The current in the Alq3 devices was dominated by electrons. The suppression of the electron current is, therefore, caused due to the existence of the thin DAE layer between the Alq3 layer and the Mg cathode. These observations indicate that the DAE layer presents a large potential barrier for electron injection or low electron mobility. This is a problem when the selective deposition method is employed to prepare a patterned Mg cathode.

In order to enhance electron injection into the thin DAE layer, a device that had an additional Alq3 intermediate layer between DAE and the Mg cathode was investigated. The intermediate Alq3 layer had a thickness of 1 nm and was formed on the colored DAE layer on the Alq3 CTL. Plot (v)

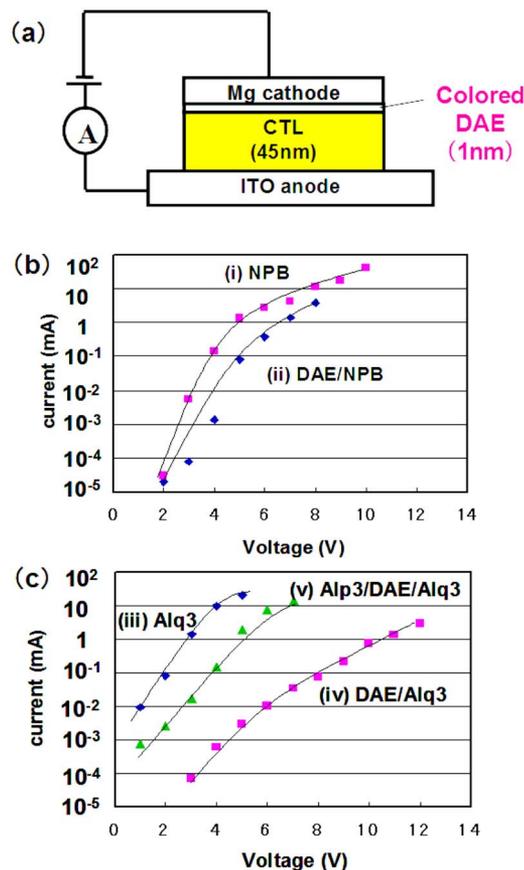


FIG. 2. (Color online) Electronic characteristics of the device with a thin DAE layer. (a) Device structure. (b) Current-voltage characteristics for the NPB device. (c) Current-voltage characteristics for the Alq3 device.

in Fig. 2(c) shows the voltage-current characteristics of the Alq3/DAE/Alq3 device. The current characteristics were dramatically improved in comparison with the DAE/Alq3 device.

The selective deposition was also investigated for the structure of the abovementioned device with the Alq3 intermediate layer with various thicknesses. As a result, it was observed that the selective deposition was performed despite the existence of the thin intermediate layer with a thickness below 3 nm. The atomic force microscopy characterization indicates the mesh growth of Alq3 on the colored DAE film, but large islands of Alq3 on the uncolored DAE film for the samples with the 3-nm-thick intermediate layer of Alq3 on a 6-nm-thick DAE layer three days after the evaporation of Alq3. The development of mesh and island structures is known to take place at the beginning of a film growth process. These observations indicate that the deposited Alq3 molecules move more easily on the uncolored DAE surface than on the colored DAE and migrate to form island structures in the former. This results in the existence of DAE molecules on the surface. This is the mechanism of the selective deposition in the device with the intermediate layer.

On the basis of the above results, we employed the selective deposition method for the preparation of the cathode pattern for an OLED. The widely used organic materials 4,4',4''-Tris(*N*-3-methylphenyl-*N*-phenyl-amino)-triphenylamine, NPB, and Alq3 were used as the hole injection layer, hole transport layer, and emitting layer, respectively. After the selective deposition of the DAE layer with a

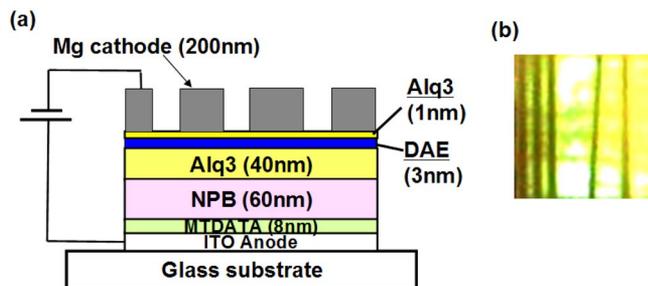


FIG. 3. (Color online) (a) OLED structure with a Mg cathode patterned by using the selective deposition method. (b) An emission pattern corresponding to the cathode pattern. (c) Laser power dependence of the Mg line width. The pitch of the Mg lines is $50\ \mu\text{m}$. (d) Threshold property of Mg deposition with DAE isomerization. The pitch of the Mg lines is $100\ \mu\text{m}$, and the DAE thickness is $30\ \text{nm}$. (e) Microscale Mg lines obtained by the selective deposition method.

thickness of $3\ \text{nm}$ on the Alq3 emitting layer, the entire DAE layer was colored upon UV irradiation. The Alq3 intermediate layer with a thickness of $1\ \text{nm}$ was then deposited. Subsequently, a red laser spot on the sample surface with a wavelength of $630\ \text{nm}$, diameter of $2\ \mu\text{m}$, and laser power of $1\ \text{mW}$ was scanned. As a result, discoloration lines were formed on the DAE layer. Finally, a Mg cathode was formed by vacuum evaporation without any shadow mask. Thus, an OLED with a line-patterned Mg cathode corresponding to the isomerization line pattern of the DAE layer was obtained; the device structure is shown in Fig. 3(a). Figure 3(b) shows the light-emission pattern corresponding to the cathode pattern. (The width of the cathode line is $100\ \mu\text{m}$.) The cathode patterning demonstrated here is not restricted to OLEDs, but can be applied to various other devices in organic electronics.

In conclusion, we have demonstrated fine metal patterning using selective Mg deposition based on DAE isomerization. Fine metal Mg pattern with a minimum width of $3\ \mu\text{m}$ was achieved by using maskless vacuum evaporation. Electron injection into the DAE layer was greatly improved by inserting an Alq3 intermediate layer with a thickness of $1\ \text{nm}$ between the Mg and the DAE layers with keeping the selective deposition. The preparation of a cathode pattern and the

resulting light emission was demonstrated for an OLED. The selective deposition shows considerable potential for the preparation of fine electrodes/wiring for various organic electronic devices.

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