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Light-Controlled Selective Metal Deposition on a Photochromic Diarylethene Film
—Toward New Applications in Electronics and Photonics—

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Selective metal deposition controlled by light irradiation was achieved for Zn, Mg, and Mn on a photochromic diarylethene (DAE) film; metal vapor atoms were deposited only on the colored film but not on the uncolored film. The deposition properties of the metals were strongly dependent on the deposition rates. Fine metal patterns were produced by laser scanning and a conventional vacuum-evaporation method without a shadow mask. Multiple-metal pattern preparation of Zn, Mg, and Mn via a maskless evaporation in a single vacuum process was also demonstrated.

Organic electronic devices, which have advantages for various applications due to low cost, light weight, and flexibility, have been studied widely.[1–6] A vacuum-evaporation method with a shadow mask[7] or an ink-jet-printing process with metal nanoparticles[8] is generally used to prepare electrodes or wiring for the devices. However, it is difficult to further improve their resolution due to the complexity of the setup with a shadow mask system, or of thermal damage to the organic layer during heat treatment in an ink-jet-printing method.

We have reported light-controllable selective Mg deposition on photochromic diarylethene (DAE) surfaces, where metal Mg atoms are deposited on a colored DAE surface but not on an uncolored surface by a vacuum-evaporation method.[9,10] Photochromism is defined as a reversible change in color induced by light irradiation.[11] The selective Mg deposition originates from large glass-transition temperature (T_g) change in the amorphous organic film in response to photoreaction.[9,12] An essential factor of the selective Mg deposition is desorption of Mg atoms from the uncolored surface due to active surface-molecular motion caused by the low T_g. Mg is an important cathode material in organic electronics,[13–15] and therefore the selective Mg deposition can be applied to fine cathode preparation for organic devices.[16,17]

For a variety of industrial applications containing electronics and optics, the selective deposition of various metal species is desirable. We report here the selective deposition of Zn and Mn as well as Mg, and demonstrate metal pattering controlled by light irradiation with maskless vapor deposition.

Results and Discussion

Selective Metal Deposition. Interaction of Metals and Deposition Rate Dependence: Figure 1 shows a photoisomerization of DAE. Selective Mg deposition means that an Mg film is formed on the colored DAE surface while not at all formed on the uncolored DAE surface by vacuum evaporation. Selectivity in Mg deposition is correlated with the difference in the T_g of the DAE in its colored and uncolored states. The colored amorphous state has a T_g of 95 °C, whereas the uncolored state 32 °C. Because the interaction between Mg atoms and DAE surface molecules such as van der Waals' force is weak, Mg is desorbed from the uncolored surface by thermal energy even at ambient temperature.[9] Therefore, we tested the selective deposition for other metals such as Ca, Al, Mn, and Ag, simply by evaporating those metals to the colored and the uncolored surfaces. Our first try to extend the selective deposition to other metals, however, was unsuccessful; metal vapor atoms were deposited on both the colored and the uncolored surfaces.

The first breakthrough was suggested when the deposition rate dependence of selective Mg deposition was investigated. The deposition of Mg on the DAE film strongly depends on the deposition rate; Mg was deposited on the uncolored surface at a high rate ($10\,\mathrm{nm\,s^{-1}}$), and was not deposited even on the

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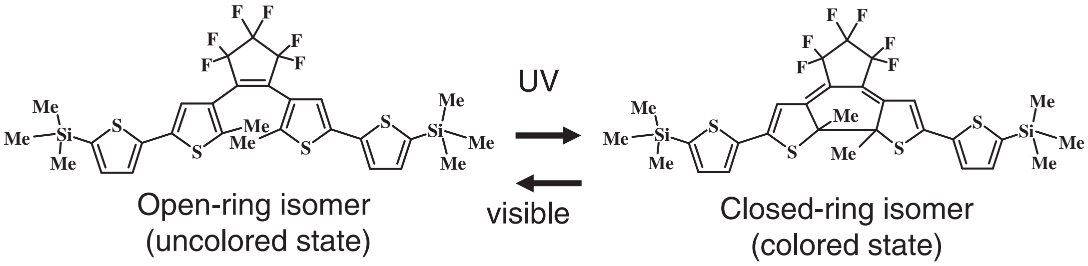

Figure 1. Photoisomerization of diarylethene.

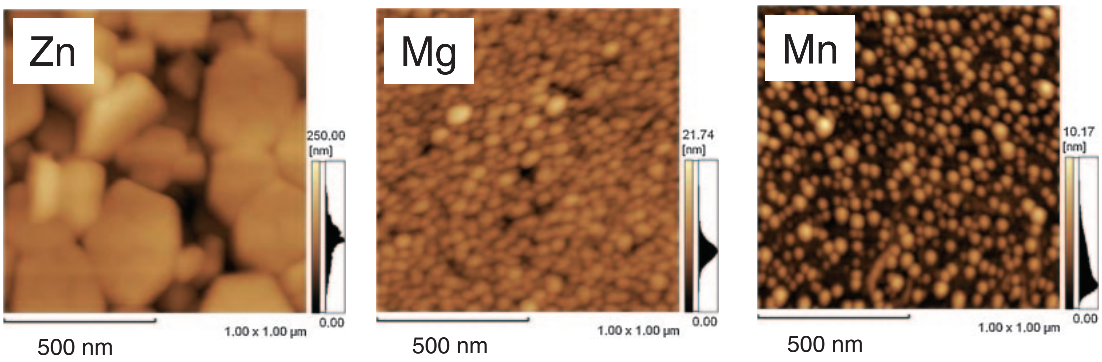

Figure 2. AFM images of metal crystals on a glass substrate prepared by vacuum evaporation.

colored surface at a very low rate (0.03 nm s^{-1}).[10] Thus, the selective Mg deposition is possible only within a restricted range of the deposition rate (around 1 nm s^{-1}). This indicated that it might be possible to achieve selective metal deposition for other metals by adjusting their deposition rate.

The deposition rate dependence of Mg deposition further indicates that the nucleation for film formation is due to a collision between Mg atoms themselves during migration on the surface. When Mg is evaporated onto the DAE film, Mg atoms are adsorbed and migrate on the surface. If the density of Mg atoms on the surface is high, the collision and nucleation for film formation occurs easily. The pre-existing nucleation sites such as defects on the surface are not essential in this case, because Mg film is not formed at the low rate; the atoms that did not collide desorb from the surface. From this viewpoint, it is expected that the interaction between metal atoms and substrate is also very important because it affects the migration and desorption.

To investigate the interaction of metals, metal films on glass substrates were prepared by vacuum evaporation and atomic force microscopy (AFM) images were recorded of their fine crystals. This is because crystal size reflects migration length of metal atoms, and therefore, the strength of the interaction. Various metals such as Au, Ag, Al, Zn, Mg, and Mn were tested. Each metal was deposited on the glass substrate by using conventional vacuum evaporation. The average film thicknesses and deposition rate of metals were set to be 10–30 and 0.2 nm s^{-1}, respectively.

Figure 2 shows the AFM images of metal crystals for Zn, Mg, and Mn on the glass substrates. The crystal size of Zn was around 300 nm, which was much bigger than that of Mg (several tens of nanometers). The size of Mn was around 10 nm and was slightly smaller than that of Mg. Other metal crystals were much smaller than that of Mg. This indicates that the interaction between Zn (Mn) atoms is weaker (stronger) than the interaction between Mg atoms. It suggests the selective deposition of Zn (Mn) is possible if the deposition rate is faster (slower) than the selective Mg deposition rate. The deposition of other metals forms much smaller crystals, suggesting much lower deposition rate for the selective deposition.

On the basis of the above, we investigated the rate dependence of deposition on the colored and uncolored DAE films for Zn, Mg, and Mn. (Figure 3a). The amorphous DAE films were formed on glass substrates by conventional vacuum evaporation. The initial sample was in the uncolored state. The colored state (photostationary state containing closed-ring isomers of 90%) was obtained upon UV irradiation. Each metal was evaporated to the samples. The samples shown in Figure 3a were observed by using transmitted white light, and the black color indicates metal deposited areas. We found that the selective deposition was achieved at the rates of 7 nm s^{-1} for Zn, and of 0.05 nm s^{-1} for Mn, which were higher and lower rates than that for Mg. We can conclude that the strength of the interaction between metal atom and the diarylethene surface determine the nucleation rate and consequently the deposition rate dependence of the metal deposition.

Figure 3b shows energy dispersive X-ray spectroscopy (EDS) characterization of colored and uncolored samples after metal deposition at the deposition rate, in which the selective deposition was possible. Existence of each metal species was determined on the colored samples (Zn at 1.015, 8.635, and 9.575 keV, Mg at 1.255 keV, or Mn at 5.895 keV) In contrast, it was revealed that there is no metal that was evaporated on the uncolored samples. The other peaks of Si (at 1.745 keV), K (at 3.315 keV), Na (at 1.045 keV), and Ca (at 3.695 keV) were attributed to the atoms in the glass substrate.

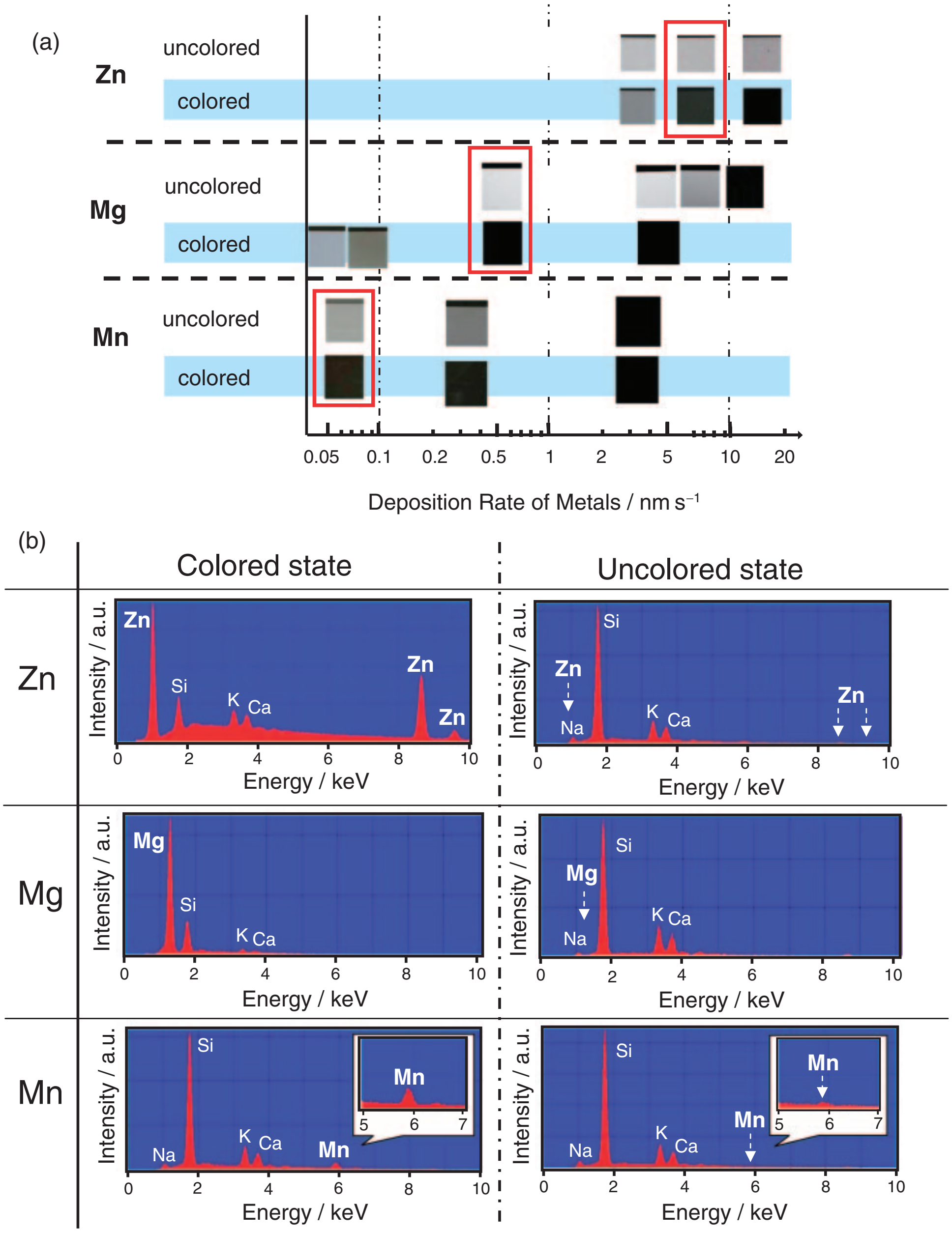

Figure 3. (a) Deposition rate dependence for the selective deposition of Zn, Mg, and Mn. (b) Energy dispersive X-ray spectroscopy (EDS) characterization of colored and uncolored samples after metal deposition.

How the Metal Film Formation Depends on the Isomerization Ratio and the Deposition Rate: To study the detailed metal-deposition properties on the DAE films, we investigated the dependence of metal film formation on the isomerization ratio and the deposition rate. The isomerization ratio of DAE films was estimated from the absorption spectra of the films (Figure 4a). The labels 1, 2, 3, 4, and 5 correspond to isomerization ratios of DAE films, in which the concentrations of the closed-ring isomers are 90%, 70%, 50%, 25%, and 0%, respectively.

Figure 4b shows the deposition-rate dependence for the formation of Zn films on DAE films at various isomerization ratios. The horizontal and vertical axes show the isomerization ratio of the DAE film and the deposition rate of Zn, respectively. At a deposition rate of 13 nm s^{-1} at room temperature (25 °C), a Zn film was formed on the colored film but not on the uncolored film. The deposition threshold, in which the metal-deposition properties changed, was at the isomerization ratio of 50%. The threshold shifted to the uncolored side with increasing deposition rate and to the colored side with decreasing rate.

To understand the behavior of Zn atoms on the DAE surfaces, Zn crystals on the films at the deposition threshold were investigated by AFM. Figure 4c shows that large Zn crystals with a diameter of 100–500 nm (i) were formed on the colored film at a low deposition rate, whereas quite small crystals with a diameter of several tens nanometers (ii) were formed on the uncolored film at a high deposition rate. We have previously reported[9,10] that the collision between the metal and the surface is non-elastic, therefore in general, adsorbed atoms

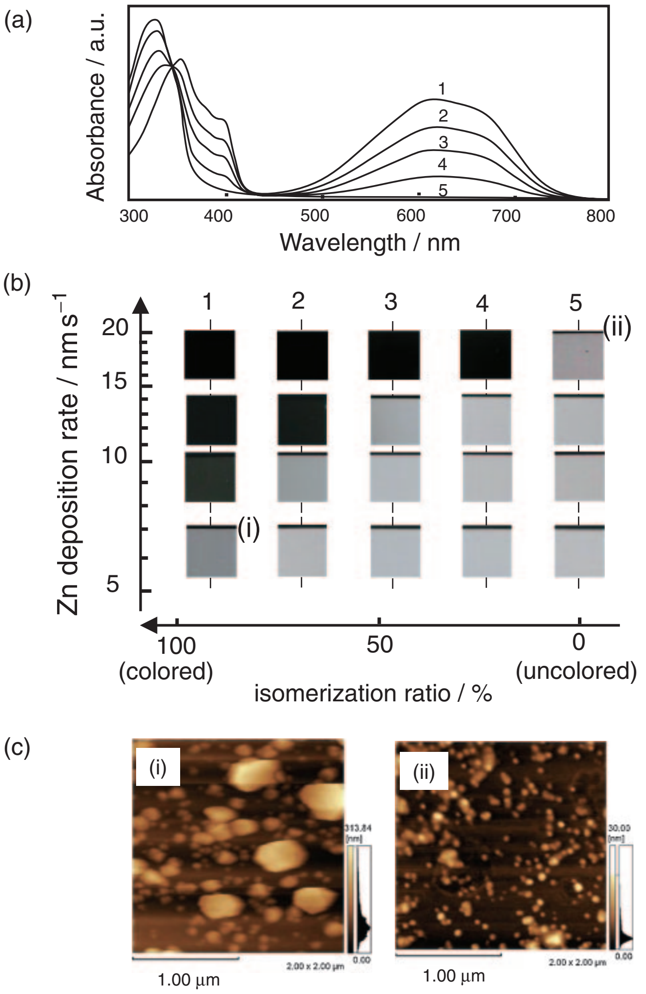

Figure 4. (a) Absorption spectra of the DAE amorphous films. (b) Deposition rate dependences of Zn deposition on the DAE films with various isomerization ratios. (c) AFM images of Zn crystals at the threshold (i) and (ii).

migrate on the surfaces of the films, and a collision between the metal atoms during migration results in nucleation to form crystals. The crystal size therefore, reflects the migration length and the density of the atoms at the surfaces. Small crystals at a high deposition rate in Figure 4c(ii) indicate frequent nucleation and short Zn atom migration. Although active migration of Zn atoms on the uncolored surface enhances crystal growth, the very high atom density on the surface causes the formation of a large number of small crystals. This result for Zn is consistent with that for Mg qualitatively.[10]

The deposition of Mn was also investigated by changing the deposition rate and the isomerization ratio of the DAE films. A similar profile with Zn and Mg was observed apart from the absolute value of deposition rate, as shown in Figure 5a; the deposition threshold was at the isomerization of 50% at a rate of 0.2 nm s^{-1} (i) and shifted to the uncolored side with increasing rate (ii). Mn crystal size showed the same tendency as well; smaller crystals were observed on the uncolored threshold sample at the high deposition rate (ii) than those on the half-colored threshold sample (i), as shown in Figure 5b.

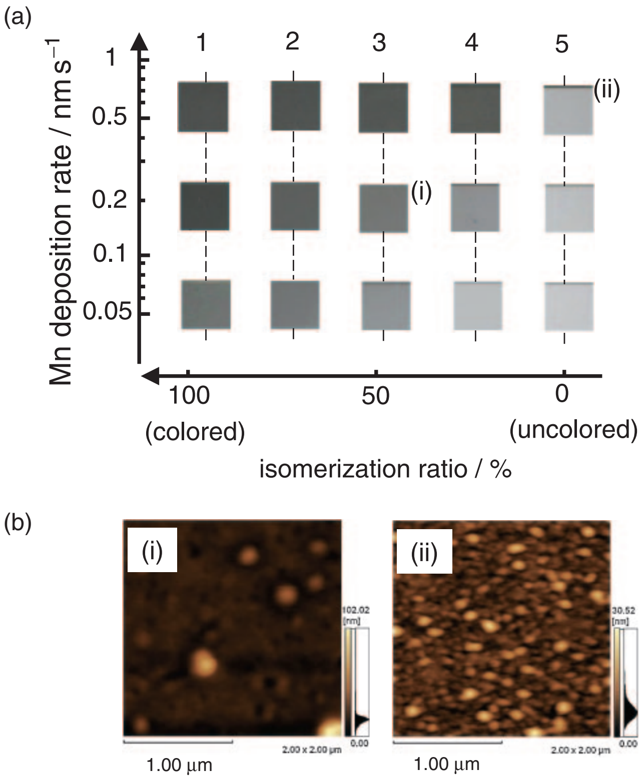

Figure 5. (a) Deposition rate dependences of Mn deposition on the DAE films with various isomerization ratios. (b) AFM images of Mn crystals at the threshold (i) and (ii).

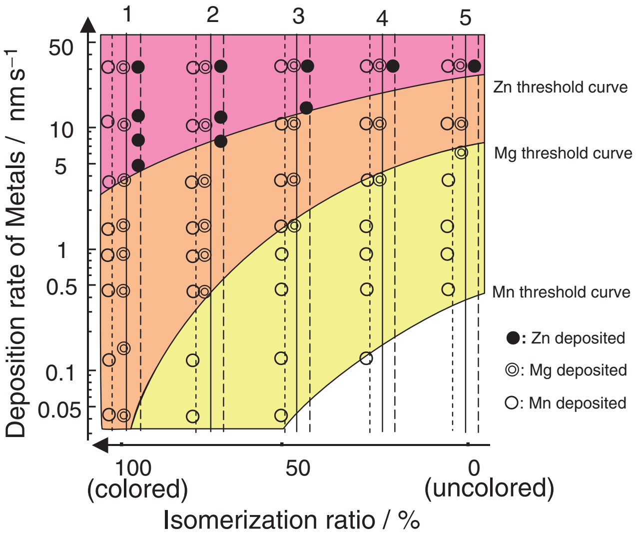

Figure 6. Deposition properties of Zn, Mg, and Mn on the DAE films with various isomerization ratios.

These deposition properties of Zn, Mg, and Mn are summarized in Figure 6. The deposition properties of Zn, Mg, and Mn showed analogous tendencies apart from the absolute values of a deposition rate. The metal deposition thresholds shifted to the uncolored side with increasing deposition rate, but the absolute values of the threshold curves were different from each other. These data indicate that there is the same mechanism of film formation.

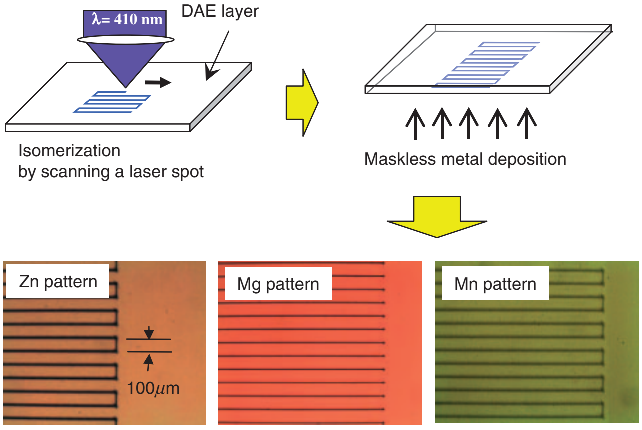

Figure 7. Fine metal patterning of the metals on DAE surface.

In the present case, the selective metal deposition is possible for metal species of Zn, Mg, and Mn. A discussion on the extension to other metals however is helpful for applying the selective deposition to electronics and photonics, because a variety of metals such as Ca and Al have been used in the field.[18–21] Desorption of metal atoms from a DAE surface is an important factor in selective metal deposition. Among the metal species such as Zn, Mg, Li, Ca, Mn, Ag, Al, and Au we tested, Zn, Mg, Li, and Ca have relatively high vapor pressure at low temperatures compared with other metals. High vapor pressure indicates the weak interaction between metals and also between the atom and the surface, indicating easy desorption. However, Li and Ca have very high chemical reactivity and, therefore, easily form nucleation due to chemical reaction with an organic surface. Ag, Al, and Au do not have large chemical reactivity, but Au and Ag have very large atomic weight compared with Zn, Mg, and Mn. This discussion suggests that Al is promising rather than Ag and Au for selective deposition. Al is an important metals as an electrode material in organic electronics as well as Mg.[20]

Metal Patterning Based on Selective Metal Deposition. The selective metal deposition would be a promising method to prepare fine metal patterns with maskless vacuum evaporation for electronic/optical devices.[16] Figure 7 shows a fine metal patterning process based on selective deposition. An uncolored DAE film was prepared on a glass substrate by using conventional vacuum evaporation and fine colored lines were drawn by scanning a violet laser spot (λ: 410 nm, power: 4.5 mW, scan speed: 1 mm s^{-1}, line pitch: 100 µm). Metal vapor of Zn, Mg, or Mn was then directed to the substrate without a shadow mask at a deposition rate of 7, 0.5, or 0.05 nm s^{-1}, respectively. Such a rate corresponds to the deposition rate necessary to achieve selective deposition, as shown in Figure 6. As a result, fine Zn, Mg, or Mn patterns corresponding to the photoisomerization patterns were produced successfully.

Figure 8 shows the multiple-metal patterning with maskless evaporation via a single vacuum process by using degrees of freedom in the deposition rate and the isomerization ratio. The blue-colored letters "Zn," "Mg," and "Mn" were drawn on a DAE film by UV irradiation through a photomask. The isomerization ratios to colored state for the domains of the letters "Zn," "Mg," and "Mn" were adjusted to 90%, 70%, and 50%, respectively, by controlling UV irradiation. Zn, Mg, and Mn metals were successively evaporated to the substrate without a shadow mask at deposition rates of 7, 0.3, and 0.03 nm s^{-1}, respectively. At first evaporation of Zn, Zn was deposited only on the colored pattern of "Zn." Mg was evaporated following the Zn evaporation, and was deposited on the colored pattern of "Mg." Finally, Mn was deposited on the colored pattern of "Mn" as well. As a result, metal patterning of these metals on the organic layer was successfully demonstrated.

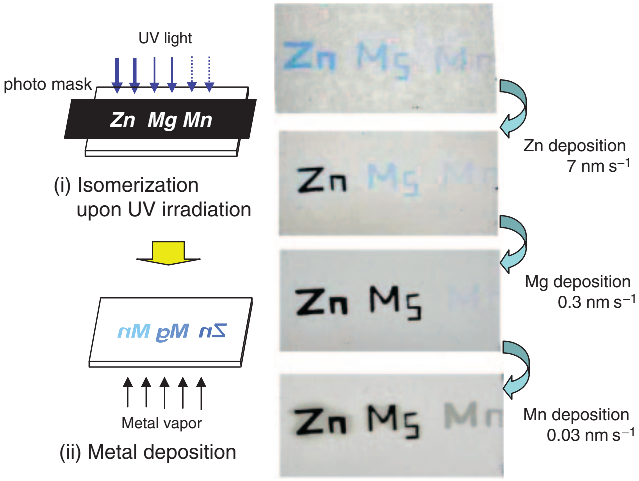

Figure 8. Multiple-metal patterning with maskless evaporation via a single vacuum process based on the selective deposition of the DAE film.

In the present case, metal patterning is being restricted to Zn, Mg, and Mn. The discussion in the previous section however, suggests the possibility of extension of the selective deposition to other metals by adjusting evaporation conditions such as a deposition rate. The selective deposition and fine metal patterning with maskless vacuum evaporation for various metals reported here would contribute to large-scale integration of a variety of organic electronics circuits.

Conclusion

Zn, Mg, and Mn were selectively deposited on a photochromic DAE surface by adjusting deposition rate and controlling light irradiation. The deposition properties such as the deposition threshold of Zn, Mg, and Mn showed analogous tendencies depending on an isomerization ratio and a deposition rate apart from the absolute values of the deposition rate. Fine Zn, Mg, and Mn patterns were produced by laser scanning and maskless deposition. The multiple-metal patterning with maskless evaporation via a single vacuum process was also successfully produced. The metal-patterning method based on selective metal deposition would be a promising technique for obtaining large-scale integration of organic electronic/optical devices.

Experimental

The diarylethene derivative used in the experiment has been reported in Ref. 22. Glass substrates were cleaned by ultrasonication in acetone for 10 min and were followed by treatment with a UV–ozone cleaner. DAE and the metals were deposited on a substrate using conventional vacuum-evaporation. All evaporation experiments were carried out at pressures of less than 6×10^{-4} Pa. The film thickness and deposition rate were controlled using a quartz thickness monitor during evaporation. Film thicknesses were also directly measured by monochromatic light interference. The deposition rate of metal films was defined as the rate on a glass substrate as a template, because the metal deposition on the DAE surface depended on the rate itself. All AFM images and EDS data were obtained by using atomic force microscopy SPM9600 (Shimadzu Corp.) and TinyEDXSII (Technex Lab Co., Ltd.), respectively.

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