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Metal Deposition Selectivity Based on Photochromism of Diarylethene Film in Intermediate Vacuum

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We report on metal deposition selectivity on a photochromic diarylethene (DAE) surface in intermediate vacuum. Selective deposition means that metal vapor is deposited on colored DAE but not on uncolored. Mg was evaporated on the DAE surfaces at various pressures with the introduction of inert gas. Mg was easy to deposit on the uncolored DAE surface in intermediate vacuum (2×10^{-1} Torr). The easy-deposition effect in intermediate vacuum was explained by the re-adsorption of Mg atoms desorbed from the DAE surface. Mg cathode patterning of an organic light emitting device on the basis of selective deposition in the intermediate vacuum was successfully demonstrated.

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1. Introduction

Organic electronics has become a hot topic recently in terms of its light weight, flexibility, and low-cost production processes.¹⁻³⁾ In particular, organic light emitting devices (OLEDs) have been developed as high-performance displays.⁴⁾ Organic transistors,⁵⁾ organic solar cells⁶⁻⁸⁾ and organic memories⁹⁻¹³⁾ have also been studied for future organic electronics. These organic devices require metal electrodes/interconnections for their electrical operation. Inkjet printing is a promising method for interconnections,^{14,15)} but a vacuum evaporation method is indispensable because reactive metal species such as Mg, Ca, and Al are used for cathode preparation on an organic layer.^{3,16)}

Photochromism is defined as a reversible interconversion of molecular structure upon light irradiation. Photochromic diarylethenes (DAEs) have thermal stability in two isomers and fatigue resistance, and have been studied as a promising material for future optical memories and switches.¹⁷⁾ Recently, various novel functions of photochromic molecules have been developed: the mechanical change of crystal shape,^{18,19)} the photoreversible water-repelling property,^{20,21)} surface relief gratings,^{22,23)} and photocontrolled current switching.²⁴⁻²⁶⁾ One such new function is selective metal deposition.^{27,28)} Mg is deposited by vacuum evaporation onto the colored surface of an amorphous DAE film but not on the uncolored surface. Selective Mg deposition is due to a change in the glass transition temperature (T_g) as a result of photoreaction.^{27,29)} T_g is 32 °C for the uncolored state and 95 °C for the colored state. Active molecular motion of the low- T_g surface enhances the desorption of Mg atoms from the surface. Several kinds of metal, including Zn, Mg, and Mn, are applicable in selective metal deposition.³⁰⁾ Selective metal deposition on the DAE surface would be a promising method of preparing metal-cathode patterns or interconnections on organic surfaces by vacuum evaporation without a shadow mask.³¹⁻³³⁾

In this paper, we report a pressure dependence of selective metal deposition on the DAE surface. We found the Mg-deposition property to be dramatically changed depending on pressure. Mg was easy to deposit on the DAE surface in intermediate vacuum with the introduction of inert gas. We also report Mg cathode patterning for the OLED by maskless evaporation in intermediate vacuum.

2. Metal Deposition Property on DAE Surface in Intermediate Vacuum

2.1 Selective Mg deposition on DAE surface

First, we tested selective Mg deposition on the DAE surface in high and intermediate vacuums. Figure 1 shows the photochromism of DAE1 with a selective deposition capability. The open-ring molecule DAE1o is in the uncolored state and converts to the closed-ring molecule DAE1c (blue color) upon UV irradiation. The colored molecule DAE1c is return to the uncolored state DAE1o upon visible light irradiation.

Figure 2 shows selective Mg deposition on the DAE1 surface in high and intermediate vacuums. (i) The amorphous uncolored DAE1 film was formed on a glass substrate, which had been cleaned by ultrasonication in acetone and using UV-ozone cleaner, by conventional vacuum evaporation (pressure: 1×10^{-5} Torr, deposition rate: 1 nm/s, thickness of DAE1: 50 nm). (ii) The film surface was colored upon UV irradiation ($\lambda = 365$ nm, light power: $200 \mu\text{W}/\text{cm}^2$, irradiation time: 10 min) with a photomask, and (iii) a partially colored area was obtained. Then, Mg was evaporated on the surface in high vacuum (1×10^{-5} Torr) or in intermediate vacuum (5×10^{-2} Torr) at room temperature. The intermediate vacuum was prepared by introducing inert gas (Ar) during vacuum exhaust. The thickness and deposition rate of Mg were controlled using a quartz thickness monitor during Mg evaporation and were set to be 100 nm and 1 nm/s, respectively. Figures 2(iv) and 2(v) show the deposited Mg patterns. These samples were observed with transmitted white light, and black areas indicate Mg-deposited areas. This result indicates selective deposition is possible in intermediate vacuum. However, we found a difference in the Mg deposition property between high and intermediate vacuums. Although the colored areas formed by UV irradiation are the same, the Mg-deposited area on the corresponding colored area prepared in intermediate vacuum became larger than that in high vacuum. This means that the Mg deposition property on the DAE1 surface depends not only on the isomerization state but also on a pressure.

2.2 Pressure dependence of metal deposition property on DAE1 surface

In order to reveal the origin of the difference between Mg deposition properties shown in Figs. 2(iv) and 2(v), we

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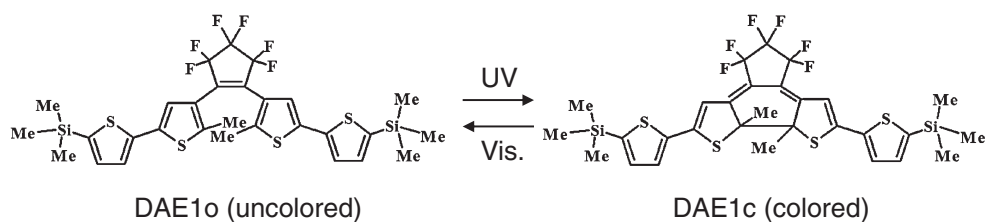


Fig. 1. Photochromism of diarylethene molecule (DAE1).

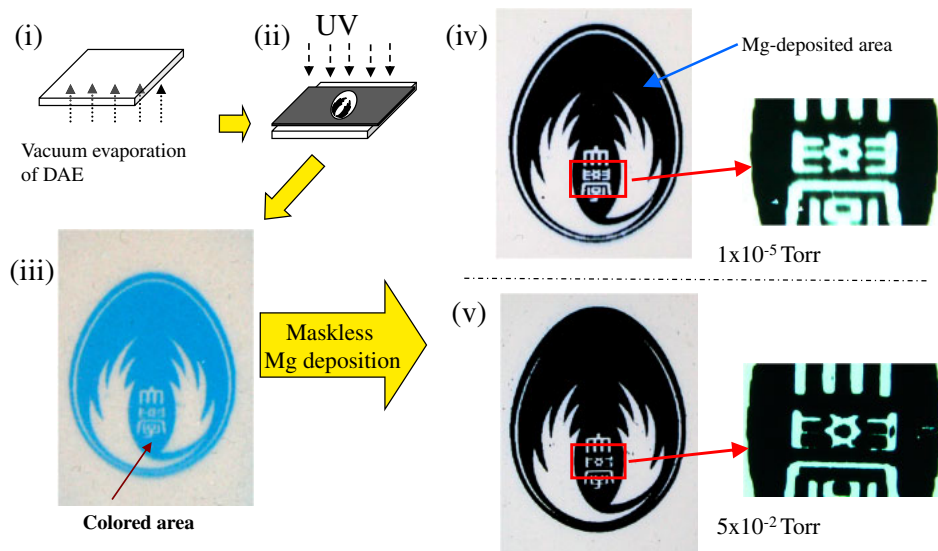


Fig. 2. (Color online) Mg patterning by high and intermediate vacuum processes with selective deposition on the DAE1 surface. The pattern is our university logo. (i) Amorphous DAE1 film prepared by vacuum evaporation. (ii) UV irradiation with a photomask. (iii) Colored mark obtained by UV irradiation. (iv) Mg-deposited areas by vacuum evaporation in high vacuum (1×10^{-5} Torr). (v) Mg-deposited areas by vacuum evaporation in intermediate vacuum (5×10^{-2} Torr). The samples were observed with transmitted white light and, therefore, Mg-deposited areas appear black.

investigate the details of the Mg deposition property on the DAE1 surface at various pressures with Ar gas introduction. Figure 3(a) shows the Ar pressure and isomerization dependences of Mg deposition. The horizontal axis indicates the isomerization ratio (concentration of closed-ring molecules), and the vertical axis is the pressure. The DAE1 films, which were obtained in the same manner as described in the previous section, with various isomerization ratios were prepared by adjusting the duration of UV ($\lambda = 365$ nm) irradiation. Absorption spectra of the DAE1 films corresponding to isomerization ratios 1 (DAE1c: 0%), 2 (20%), 3 (50%), 4 (70%), and 5 (90%) are shown in Fig. 3(b). Sample 1 is a completely uncolored state (no DAE1c) and sample 5 is a photostationary state obtained by 365-nm-wavelength irradiation. The Mg thickness and deposition rate were the same as those given in the previous subsection. The samples after Mg evaporation were observed by transmitted white light and, therefore, Mg-deposited areas look black color.

Mg was not deposited on surfaces with an isomerization ratio below 50% (samples 1 and 2) at 1×10^{-5} (high vacuum), 1×10^{-4} , and 1×10^{-3} Torr. The Mg deposition threshold, in which a thin layer of Mg was deposited, was between 50–70%. The Mg deposition threshold, however, was shifted to the uncolored side with increasing pressure. Mg was deposited even on the uncolored surface at 2×10^{-1}

Torr. This indicates that the Mg deposition selectivity on the DAE1 surface depends on the pressure during Mg evaporation; Mg was easy to deposit on the surface in intermediate vacuum. The cause of the enlargement of the Mg-deposited area in Fig. 2(v), therefore, is Mg deposition on the half-colored areas surrounding the deep-colored area.

The desorption of Mg atoms and nucleation caused by collision between the atoms on the DAE1 surface are essential processes in selective deposition in high vacuum.²⁷⁾ High substrate temperature, which might occur in an intermediate vacuum process, causes the enhanced desorption of Mg. We, therefore, compared the change in substrate-surface temperatures in the high and intermediate vacuum processes (1×10^{-5} and 2×10^{-1} Torr) during Mg evaporation. The temperature was measured using a thermocouple attached to the sample surface. The change in temperature was $+3$ °C from room temperature for the high vacuum process and $+10$ °C for the intermediate vacuum process. On the basis of our previous result,²⁷⁾ the temperature increase of 10 °C negligibly influences Mg-atomic desorption. Furthermore, the result in Fig. 3 means the suppression of desorption in the intermediate vacuum process. Therefore, we can conclude that the dominant factor in the change of the Mg-deposition property is a change in the nucleation rate on the surface. A high deposition rate of Mg, that is, a high concentration of Mg atoms on the surface,

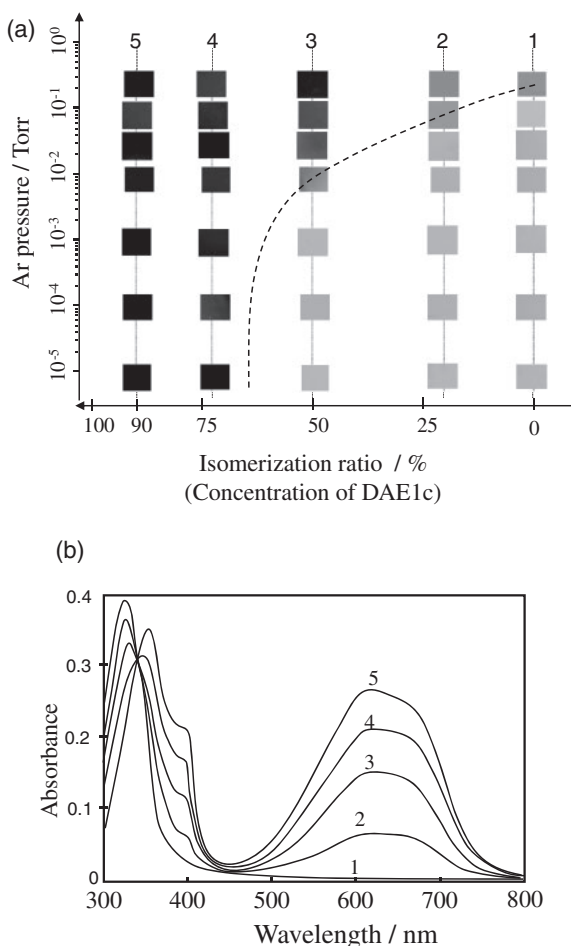


Fig. 3. (a) Ar pressure dependence of Mg deposition on the DAE1 surface. Broken line indicates the deposition threshold of Mg. (b) Absorption spectra of DAE1 films with various isomerization ratios.

enables efficient Mg atom collision on the surface and makes the nucleation rate high. For example, an increase in the Mg-deposition rate from 1 to 2 nm/s changes the threshold of Mg deposition from 60 to 40–50% in the isomerization ratio.²⁸⁾ The nucleation effect with a high Mg-atom concentration can be the cause of the easy deposition in intermediate vacuum. Figure 4 illustrates a model of nucleation for Mg film formation on the DAE1 film. When Mg is evaporated onto the uncolored DAE1 surface in high vacuum, adsorbed Mg atoms diffuse over the surface and are desorbed, as shown in Fig. 4(a). The desorbed atoms do not return to the surface because of their long mean free path. On the other hand, in the case of Mg evaporation in intermediate vacuum, desorbed Mg atoms are adsorbed into the DAE1 surface again via Ar scattering. The deposition rate of Mg is controlled using the quartz thickness monitor, and is defined as the incident Mg flux to the quartz monitor surface; Mg desorption from the monitor surface does not occur. Mg desorption, however, occurs on the DAE1 surface, and the readsorption of desorbed Mg atoms via Ar-gas scattering is possible because of the short mean free path. The readsorption causes the high concentration of Mg atoms on the surface, resulting in a high nucleation rate.

The pressure dependence of other metal-species deposition or in other inert gas was also investigated. Figure 5

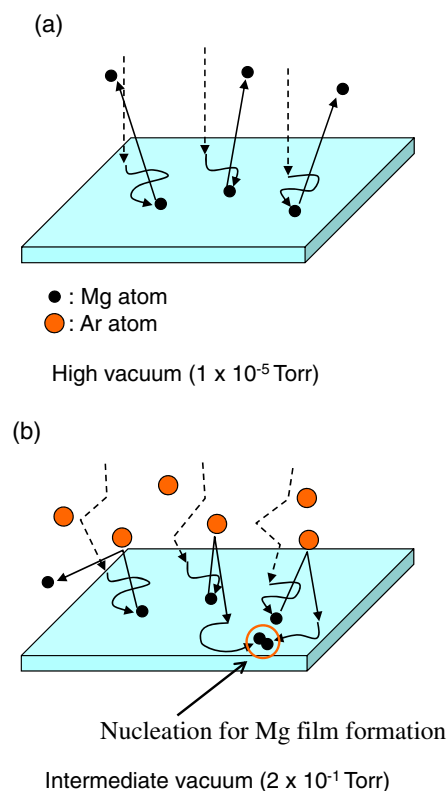


Fig. 4. (Color online) Model of Mg nucleation on DAE1 surface in high and intermediate vacuums.

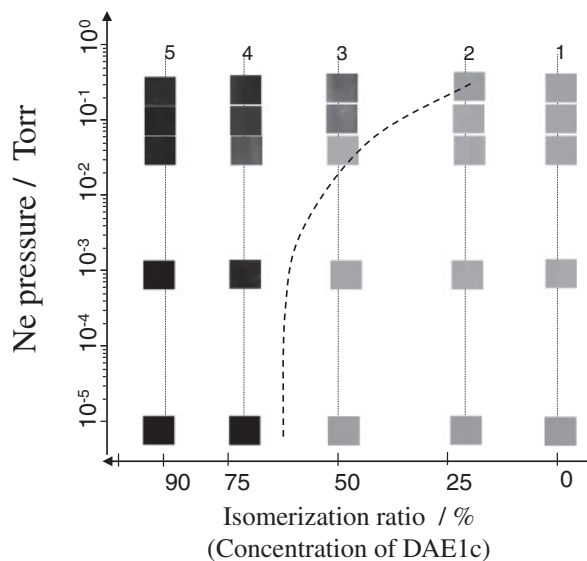


Fig. 5. Ne pressure dependence of Mg deposition on DAE1 surface.

shows the Ne pressure dependence. The experiment was carried out in the same manner with that in the case of Fig. 3, changing the inert gas species. Analogous tendencies were observed; Mg was easily deposited in intermediate vacuum by introducing Ne gas. Selective deposition of Zn on the DAE1 surface is also possible.³⁰⁾ Figure 6 shows the Ar pressure dependence of Zn deposition; the same result was obtained. These results indicate that the easy-deposition effect in intermediate vacuum is a general phenomenon.

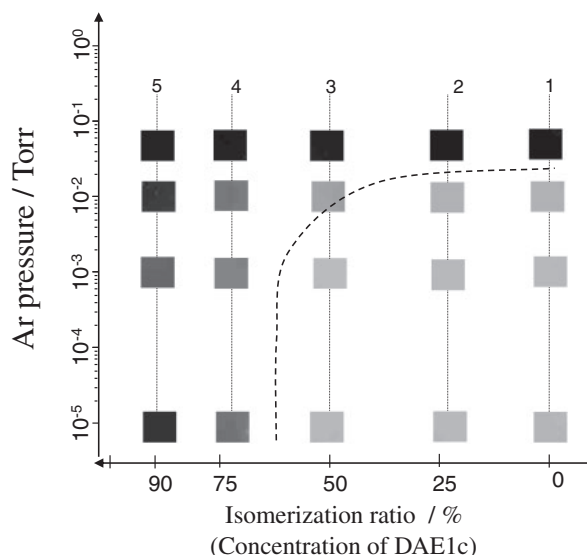


Fig. 6. Ar pressure dependence of Zn deposition on DAE1 surface.

3. Fine Mg Patterning Based on Selective Deposition in Intermediate Vacuum

In general, cathode patterning in organic devices requires a high vacuum process. If the selective deposition method is applicable in intermediate vacuum, a more efficient process would be possible; fine cathode patterning with short exhaust time and maskless metal evaporation. On the basis of the enlarging effect of the Mg deposition area shown in Figs. 2(iv) and 2(v), however, we are concerned that the fine pattern formation based on selective deposition become difficult, that is, the resolution of selective deposition is reduced. Then, we attempted fine metal patterning based on selective deposition with laser scanning in intermediate vacuum as follows.

Figure 7(a) shows the process for preparing fine Mg patterns by selective deposition. The uncolored DAE1 film was prepared on a glass substrate in the same manner as in the case of Fig. 2. A UV laser spot ($\lambda = 375 \text{ nm}$) scanned over the uncolored DAE1 surface at a speed of 1 mm/s with a laser power of 0.20, 0.30, or 0.45 mW, and colored lines on the surface were obtained. Finally, Mg was evaporated onto the surface in high ($1 \times 10^{-5} \text{ Torr}$) or intermediate (Ar introduction, $5 \times 10^{-2} \text{ Torr}$) vacuum. Upper figures in Fig. 7(b) show Mg patterns obtained in high vacuum, and lower figures show in intermediate vacuum. Mg was deposited on the colored lines in intermediate vacuum as well as in high vacuum. A difference in the width of Mg lines, however, was observed; the wider Mg line was formed in the intermediate vacuum process. This reflects the change in the deposition property shown in Fig. 3. We, however, found that the Mg line became thinner, even in intermediate vacuum, upon lowering laser power, as shown in the lower figures in Fig. 7(b). The same Mg linewidth for the 0.30 mW sample in intermediate vacuum as that for 0.45 mW sample in high vacuum was obtained. This result indicates that the enlarging effect of the metal deposition area can be overcome by adjusting the irradiation laser power.

Finally, we demonstrated the Mg cathode patterning of OLED in intermediate vacuum. We adopted the device

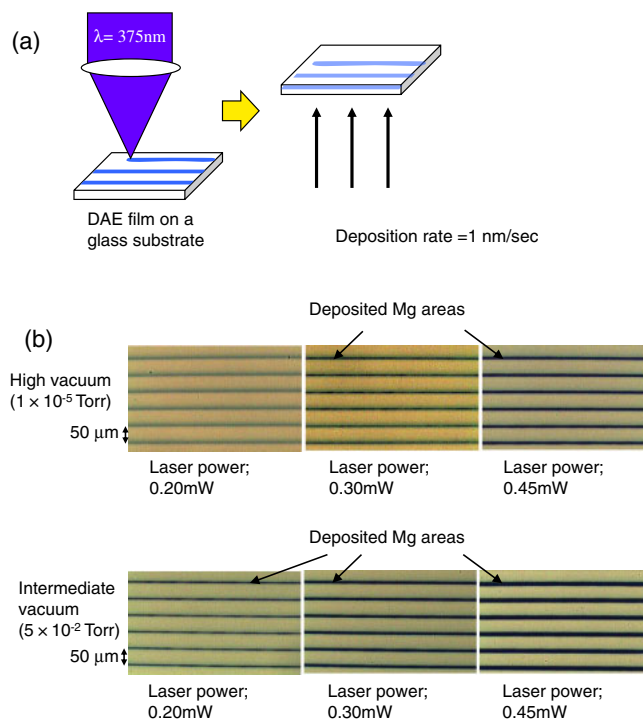


Fig. 7. (Color online) Fine Mg pattern formation based on selective deposition. (a) UV Laser spot was scanned over the uncolored DAE1 film (λ : 375 nm; scan speed: 1 mm/s; pitch: 50 μm). Then, Mg was evaporated onto the DAE1 surface without a shadow mask. (b) Laser power and pressure dependences of Mg lines obtained by selective deposition.

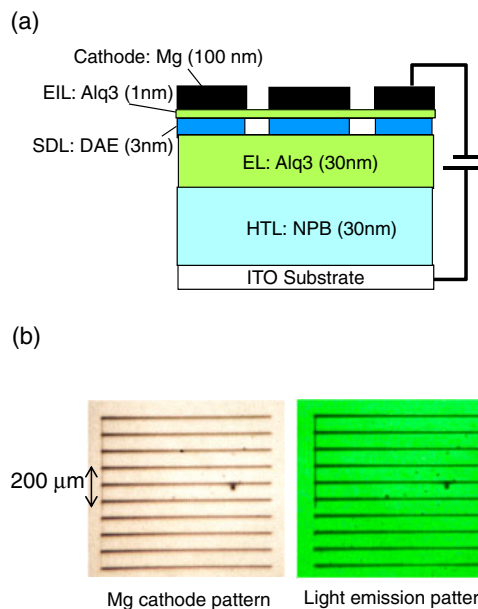


Fig. 8. (Color online) (a) OLED structure with Mg cathode patterns prepared by selective Mg deposition under intermediate vacuum condition. (b) Cathode pattern (white color areas) and green-light emission pattern corresponding to the isomerization pattern (applied voltage: 15 V, current density: 50 mA/cm²).

structure shown in Fig. 8.³²⁾ The hole transport layer (HTL) and emission layer (EL) consisted of *N,N*-di(1-naphthyl)-*N',N'*-diphenylbiphenyl-4,4'-diamine (NPB) and tris(8-hydroxyquinoline)aluminum (Alq3), respectively and were formed by a conventional vacuum evaporation method

on an indium tin oxide (ITO) substrate in turn. The DAE1 layer with a thickness of 3 nm was prepared as a selective deposition layer (SDL) on the EL. An additional Alq3 layer with a thickness of 1 nm, which is an electron injection layer (EIL), was formed on the DAE1 layer to improve electron injection. Selective Mg deposition is possible despite the existence of the additional thin EIL by adopting the following process.³¹⁾ First, the whole SDL layer was colored upon UV irradiation. Then, a red laser spot with a wavelength of 630 nm and power of 2.0 mW was scanned over the surface, resulting in uncolored patterns in the SDL. Alq3 molecules in the EIL aggregated into islands on the uncolored SDL because of the thermal effect of laser irradiation, and the uncolored SDL surface appeared. Finally, Mg was deposited onto the surface without an evaporation shadow mask under the intermediate vacuum condition (Ar: 5×10^{-2} Torr). As a result, Mg was deposited only on the remaining colored areas and not on the uncolored areas, and Mg cathode patterns corresponding to the isomerization pattern were obtained. Figure 8(b) shows the Mg cathode patterns with a pitch of 100 μm . The emission patterns corresponding to the cathode patterns were successfully demonstrated.

4. Conclusion

We reported the deposition selectivity of metal vapor resulting from the photochromism of DAE1 in intermediate vacuum. The metal deposition property on the DAE1 surface was affected by the pressure of inert gas; metal vapor was easily deposited on the DAE1 surface, and the deposition threshold was shifted to the uncolored side in intermediate vacuum. Mg cathode patterning was successfully demonstrated by selective deposition in intermediate vacuum.

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