Metal atom behavior on photochromic diarylethene surfaces—deposition rate dependence of selective Mg deposition

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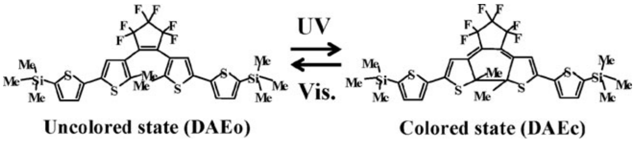
Selective Mg metal deposition based on the isomerization of a photochromic diarylethene (DAE) showed a threshold in the isomerization ratio. The deposition threshold was shifted to the uncolored side with an increase in the rate of Mg deposition. The size of the Mg crystals at the threshold, which reflect the migration length of the Mg atoms on the surface, changed, depending on the deposition rate. Relatively small crystals were formed on the uncolored surface at the threshold obtained by an increasing deposition rate, indicating a short migration length. The occurrence of selective deposition was determined by the concentration and migration of Mg atoms, which were found to be the most important factors affecting the formation of the Mg film on the DAE surface, and therefore determining the occurrence of selective metal deposition.

Organic electronic devices such as light-emitting devices, thin film transistors, solar cells and memories have recently attracted considerable interest.[1] Organic electronic devices require metal electrodes or wiring for their operation. Vacuum evaporation methods with a shadow mask[2] or inkjet printing involving conducting nanoparticles[3] are generally used to prepare patterned metal films on organic layers. However, several difficulties are encountered with these methods. The low resolution limit of vacuum evaporation methods is due to the complexity of the setup with the shadow mask. The organic layer suffers thermal damage after heat treatment in the inkjet printing method. Such difficulties restrict the integration of circuits using organic materials. Recently, we have developed a new method based on photochromism for forming fine metal patterns by using vacuum evaporation without a shadow mask. Photochromism is generally defined as a change in the color of certain substances when they are exposed to light of a particular wavelength. [4] In this method, we could 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 (1,2-bis[2-methyl-5-(5-trimethylsilylthien-2-yl)-thien-3-yl]-perfluorocyclopentene, DAE) surface.[5]

In selective metal deposition on photochromic DAE (Scheme 1) by vacuum evaporation, Mg vapor atoms are found to be deposited on colored DAE (DAEc) film and not on uncolored DAE (DAEo) film. Selective deposition is strongly correlated with changes in the glass transition temperature T_g of the film: T_g is 32 °C for the amorphous DAE film in the uncolored state and 95 °C for the film in the colored state. 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, cause desorption of the Mg atoms from the uncolored DAE surface.[5]

Fig. 1 shows the deposition threshold property in the isomerization ratio of DAE. The areas indicated by the word "Photochromism" were colored into four levels upon UV irradiation, as shown in Fig. 1(i). The numbers 1–5 indicate the degrees of the film color and the corresponding absorption spectra obtained by adjusting the UV irradiation (shown in Fig. 1(iii)). The area indicated by the number 1 is a photostationary state consisting of more than 90% closed-ring isomers, and area number 5 surrounding the word "Photochromism" is completely uncolored (open-ring). Fig. 1(ii) shows the degree of Mg deposition arising on the surface at a rate of 1.4 nm s^{-1}. Since the sample was observed under transmitted white light, Mg-deposited areas appeared shaded black. Mg atoms were deposited on the DAE film in the area numbers 1, 2 and 3, which contained more than 60% of the closed-ring isomer. On the other hand, Mg films were not formed in area numbers 4 and 5.

The deposition behavior also depends on the deposition rate of the Mg atoms. When the deposition rate is increased, the Mg film is formed, even on the uncolored surface.[5] This indicates that the Mg atoms do not rebound elastically from the uncolored surface because elastic rebounding is independent of the deposition rate; once adsorbed, the Mg atoms migrate on the DAE surface, after which they are desorbed from it. On the other hand, if the concentration of Mg atoms on the surface is high, collisions between the atoms during migration will result in a nucleus of Mg



Scheme 1

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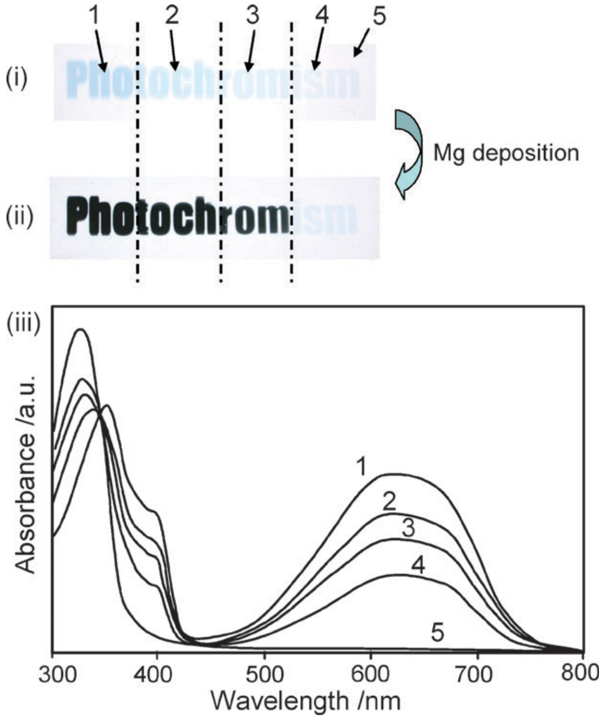

Fig. 1 Deposition threshold behavior for the isomerization ratio of DAE. (i) Four-level colored areas in the word "Photochromism". (ii) The corresponding Mg-deposited areas. (iii) The absorption spectra of areas 1–5.

crystal growth leading to film formation. This result suggests that the deposition threshold with the isomerization, indicated above, changes with the Mg deposition rate.

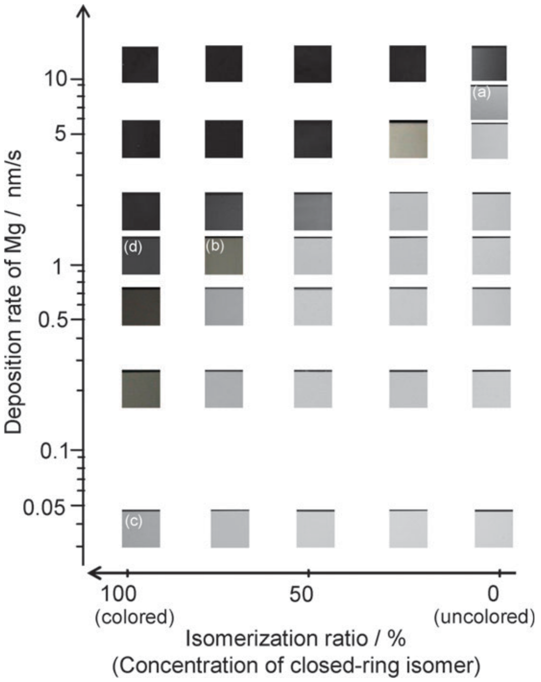

Fig. 2 The dependence of isomerization ratio on Mg deposition rate. Areas in black indicate the Mg-deposited areas.

Fig. 2 shows the changes in Mg deposition with isomerization ratio and deposition rate. The thickness of the DAE layer was 20–30 nm. The areas in black denote the Mg-deposited areas and those in white denote the areas lacking deposition. The color of the sample was gray at the threshold, at a rate of 1.2 nm s^{-1} (labelled (a)), at which the Mg was deposited in a thin layer, corresponding to around 70% of the closed-ring isomers. The threshold, however, was shifted to the uncolored state when the deposition rate was increased. Mg was deposited in a thin layer at a very high deposition rate (7 nm s^{-1}) (labelled (b)), even in the completely uncolored state where there was no closed-ring isomer. On the other hand, the threshold was shifted to the colored side when the rate of Mg deposition was decreased (as indicated by (c)). These results indicate that the deposition rate of the metal is as important as the surface molecular motion (or T_g) for efficient selective deposition behavior. This suggests that selective deposition of a variety of metals can be undertaken by adjusting the deposition conditions.

To understand the behavior of Mg atoms on the DAE surface during deposition, we investigated the growth of Mg nanocrystals on DAE surfaces using atomic force microscopy (AFM). Fig. 3 shows AFM images of the Mg nanocrystals; each image labelled with a lower case letter corresponds to an identically-labelled sample in Fig. 2. Relatively larger crystals were observed at the deposition threshold state in (b) than the colored state in (d), which had a high concentration of the closed-ring isomer. On the other hand, smaller Mg crystals were formed at the threshold in (a) at a high deposition rate of 7 nm s^{-1}. Large crystals, over 100 nm in diameter, were formed at the threshold in (c) at a very low deposition rate of 0.04 nm s^{-1}.

Fig. 4 shows the results of a particle size analysis of images (a), (b) and (c) in Fig. 3. Small crystals with an average radius

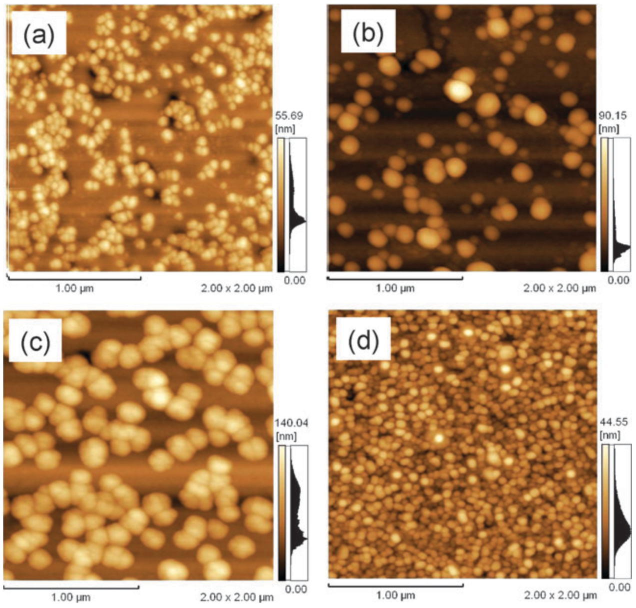

Fig. 3 AFM images of the samples obtained in Fig. 2. Each image labelled with a lower case letter corresponds to an identically-labelled sample in Fig. 2.

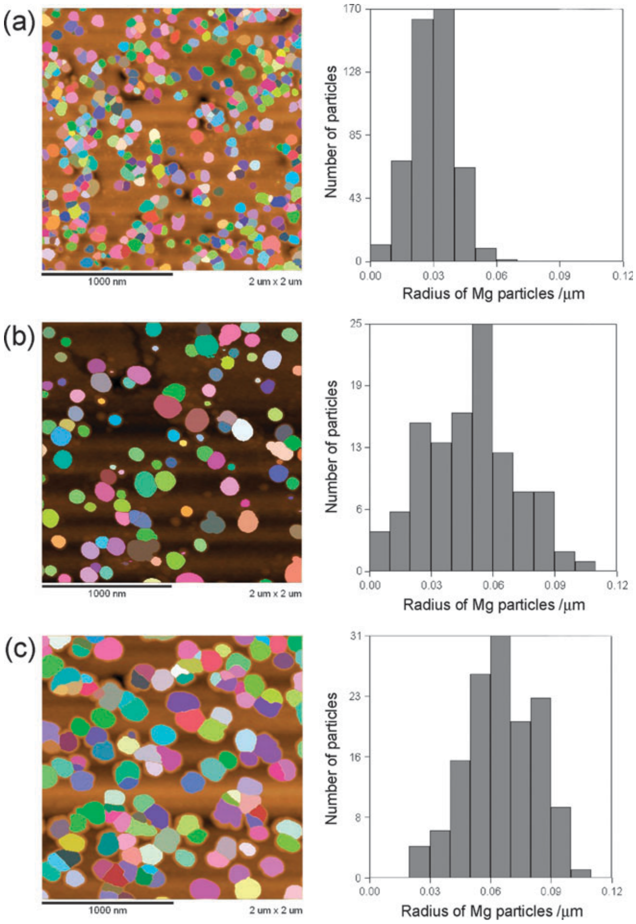

Fig. 4 Analytical results of Mg crystal size distributions for (a), (b) and (c) in Fig. 3.

of 30 nm were seen in (a), but the average radius of the crystals increased to 70 nm in (c). Such differences in Mg crystal size at the deposition threshold are attributed to the migration behavior of Mg atoms on the DAE surface.

The dominant factors that affect the formation of the Mg film are considered to be the concentration of Mg atoms, migration length, desorption rate and density of nucleation sites on the surface. In general, crystals are grown under equilibrium conditions, for example, from a saturated solution by the supply of source atoms/molecules from the surroundings to the nuclear crystals. Vacuum evaporation, however, is a non-equilibrium process, and crystal growth is achieved when source atoms that are adhere to the surface migrate and finally gather on the nucleus crystal.[6] The difference in size between Mg crystals (b) and (d) suggests that the migration of Mg atoms on the surface is more effective and occurs over greater distances at threshold (b) than in colored state (d). This is because active molecular motion leads to active migration of the Mg atoms, and hence the crystal growth is enhanced, as in the case of high substrate temperatures.[6] This is consistent with the result reported in our previous paper.[5]

On the other hand, the observations in Fig. 3 and Fig. 4 also show that the crystals formed in samples (a) and (c) are smaller and larger, respectively, than those formed in (b). The small crystals in (a) result from the short migration length, which results from the high concentration of Mg atoms on the DAE surface. Furthermore, the enhanced crystal growth in (c) at a very low deposition rate is indicative of the long migration length of Mg atoms on the colored surface. These results indicate that nucleation for film formation is caused mainly by collisions among Mg atoms and is not caused by the presence of nucleation sites on the surface. In general, it is considered that nucleation for film formation in vacuum evaporation occurs at specific sites on the surface (see ref. 6), the sites being surface defects, crystal steps and/or other irregular places. Such sites exist on the surface before Mg evaporation, so if the relatively strong interactions between the colored molecules and the Mg atoms result in a high density of nucleation sites on the surface, many small crystals are expected to be formed, even at a low deposition rate. Nevertheless, our observations contradict this prediction, indicating that nucleation of Mg on the organic surface is achieved by the collision of Mg atoms on the surface, which is strong correlated to the density (or deposition rate) and migration (or isomerization ratio) of Mg. On the basis of the above interpretation, we conclude that the concentration and migration length of the Mg atoms are the most essential factors in Mg nanocrystal formation on the DAE surface, and therefore it is these factors, as well as the desorption, that govern the selective metal deposition process.

The deposition threshold for selective deposition was found to shift with the deposition rate. The size of the Mg nanocrystals at the deposition threshold was dependent on the deposition rate. The dominant factors determining the growth of Mg crystals and the formation of the Mg film were determined to be the concentration and migration length of the Mg atoms on the DAE surface.

Experimental

Glass substrates for DAE film formation were pre-cleaned by an ultrasonic treatment in acetone and by a UV–ozone cleaner. DAE and metals were deposited on substrates using the conventional vacuum evaporation method. All evaporation experiments were carried out at pressures of less than 6×10^{-4} Pa. The film thickness was controlled using a quartz thickness monitor during evaporation, and was directly measured by a monochromatic light interference method. The thickness of all Mg films, which were deposited on a glass substrate as a template, were set to 30–50 nm. All AFM images and particle distributions were obtained using AFM and a particle analyzer (Shimadzu, SPM 9600).

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