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Supplementary Information

Selective metal deposition on photosensitive organic crystal surfaces

*Tsuyoshi Tsujioka
Osaka Kyoiku University, Asahigaoka 4-698-1, Kashiwara, Osaka 582-8582, Japan
*Email: tsujioka@cc.osaka-kyoiku.ac.jp
Phone/Fax: +81-72-978-3633

1. Absorption spectra and force curve (FC) characterization of the amorphous diarylethene (DAE) films prepared by vacuum evaporation

It is difficult to know the isomerization ratio of DAE crystal-film surfaces within a several-tens-nm depth when the crystal surface was irradiated upon UV light, because of their irregular shapes of the polycrystalline films and isomerization distribution in depth. To estimate the isomerization ratio of DAE crystal surfaces, we investigated absorption spectra of the amorphous DAE films with a thickness of 50 nm, which were UV-irradiated under the same conditions with the crystal-film samples. Their absorption spectra are shown in Fig. S1. The 900-s sample (photostationary state, PSS) contained the colored (closed-ring) isomers of 90%. FC characterization of the amorphous DAE films with a thickness of 500 nm was carried out (Fig. S2). Each slope was determined within a sample displacement of 10 nm from the surface, and reflects the surface-softness within the 10-nm-depth. The slope for the uncolored film (0-s sample) was 22 nN/nm, and was gradually increased with UV irradiation. The PSS film (900-s sample) showed 36 nN/nm. This means the surface became harder gradually, and is corresponding to a change of T_g (T_g=32^{o}C for the uncolored state and 90^{o}C for the PSS). (The slope for a glass surface, a perfectly hard surface, is 42 nN/nm.)

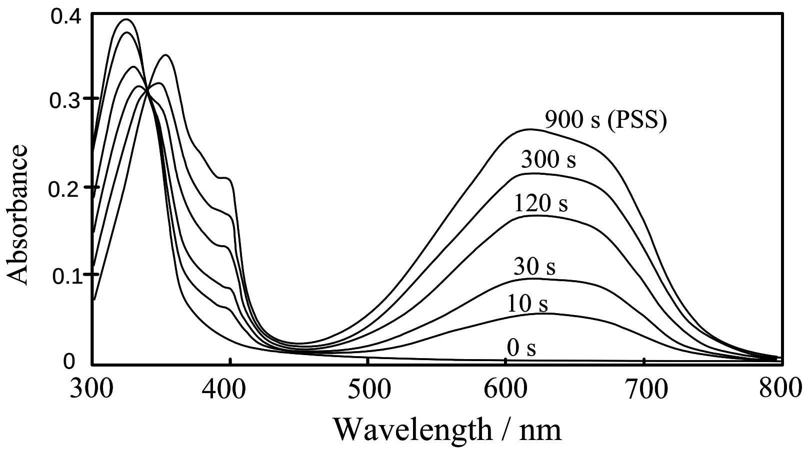


Fig. S1 Absorption spectra of the amorphous DAE films (thickness 50 nm) with various isomerization ratios. The samples were prepared by adjusting the irradiation of UV light (λ=365 nm).

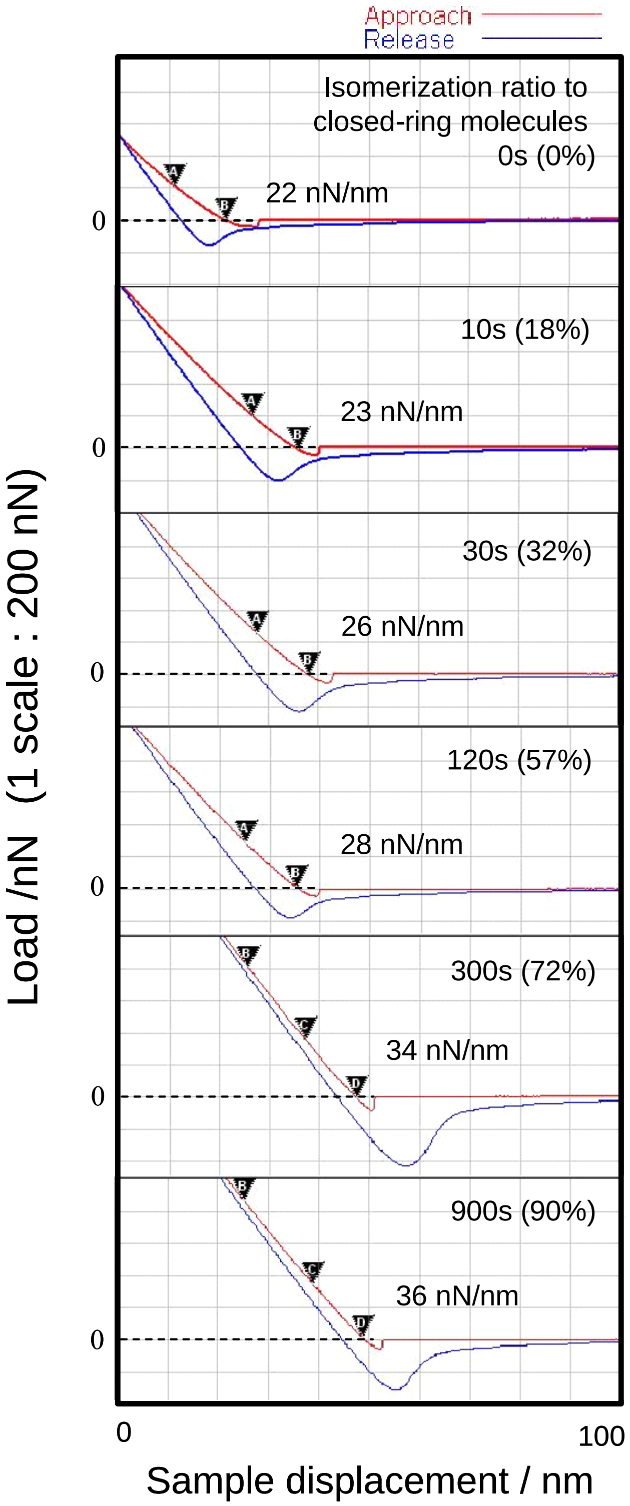


Fig. S2 Force curves of the amorphous DAE films with a thickness of 500 nm.

2. Force per unit-indent-distance into the crystal and amorphous surface

A slope in FC indicates the force on cantilever per unit sample-displacement. To get more objective values on the surface, the force per unit-indent-depth was adopted in Fig. 3. The force per unit-indent-depth was evaluated by a following procedure. In Fig. S3, a slope α of FC for a hard surface (no indent into the surface) is set to be *F/a*, while a slope β for a sample is *F/b*. The values of α and β can be obtained by FC characterization of the samples. The real indent-depth into the sample surface is *x*=*b*-*a*. The force per unit-indent-depth *F/x*, therefore, is given by the following equation.

$$\frac{F}{x} = \frac{\alpha\beta}{\alpha - \beta}$$

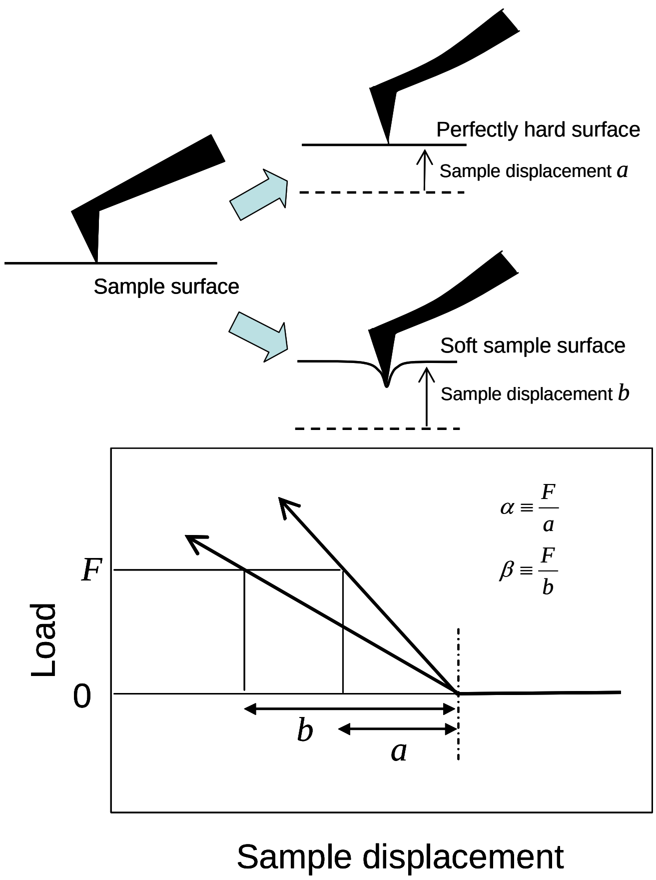
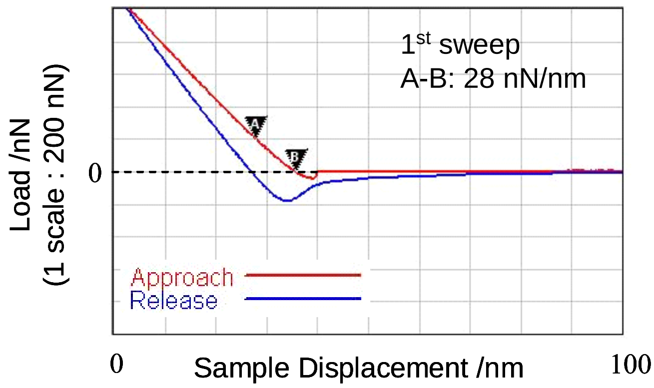


Fig. S3 Illustrations of FCs for obtaining the force per unit-indent-depth.

3. FCs of the half-colored amorphous DAE film

Figure S4 shows FCs of the half-colored (57%) amorphous DAE surface. The slope of FC in the 1st sweep was 28 nN/nm, while that in the 2nd sweep at the same position was reduced to 17 nN/nm. Because the 2nd sweep showed lower value and large hysteresis, the soft surface of the DAE film was not elastic but viscous.



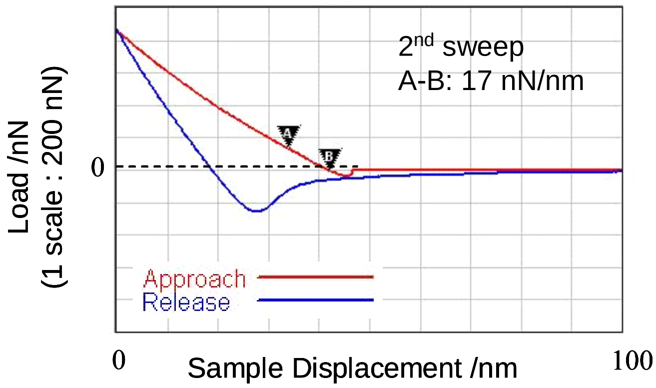


Fig. S4 FCs in the 1st and 2nd sweeps of the half-colored (57%) amorphous DAE film.

4. Laser power dependence of Mg deposition property on the DAE crystal film

Figure S5 shows the laser power dependence of Mg deposition. Mg-deposited and -undeposited grid patterns were obtained for 375-nm and 410-nm laser scanning, respectively, with laser power of 0.5 mW, as reported in main text. For the case of 375-nm laser scanning, Mg-deposited areas were enlarged with laser power increase, and Mg was deposited on the whole area at 0.8 mW. On the other hand, Mg-undeposited areas were enlarged with laser power increase for 410-nm laser scanning. These results indicate the existence of optimum laser power for obtaining good Mg patterns.

On the basis of the result in Fig. 4(b), we expected that Mg-deposited lines at the center of Mg-undeposited area should be formed for the sample scanned by high-power 410-nm laser. However, we could not observe the Mg-lines on the surface of 410-nm laser (2.0 mW) scanned sample; instead, the melted lines were observed in the center areas. This is attributed to large absorption of closed-ring molecule at 410nm (See Fig. S1). When the 410nm-laser is irradiated to the uncolored crystal surface, the photoisomerized closed-ring molecules absorb the laser light more and generate heat because of large absorption. This is a reason of the melted lines.

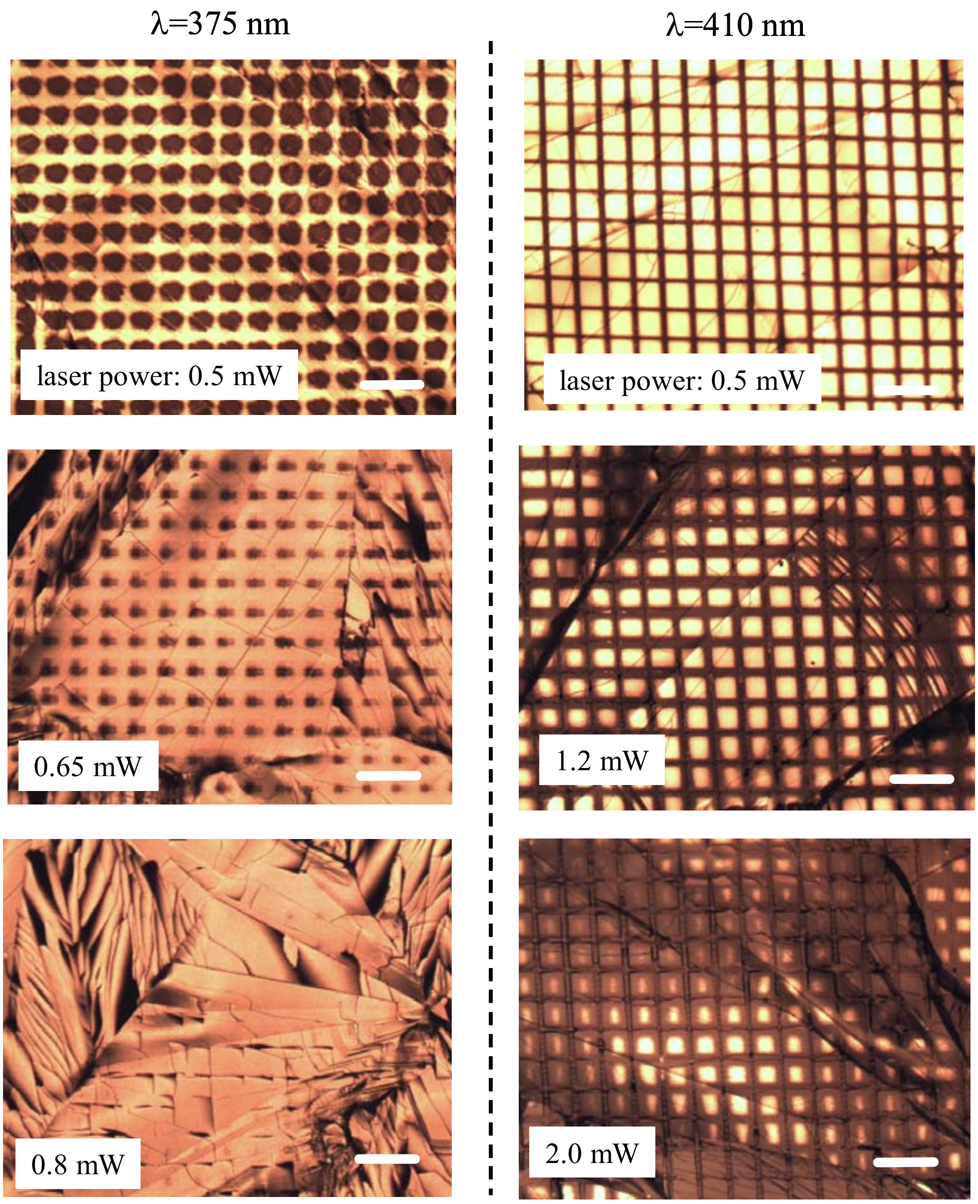


Fig. S5 Laser power dependence of Mg-deposition patterns on the DAE crystal surface. Laser scan speed: 2 mm/s. Bright areas show Mg deposited. Scale bar: 100 μm.

5. Excessive UV irradiation to DAE crystal film

As described in the main text, moderate UV irradiation softened the crystal film surface. However, excessive UV irradiation to the film for obtaining the whole colored film destroyed the film as shown in Fig. S6. The uncolored film (i) was changed to the (surface) half-colored state, which showed the Mg-undeposition, upon moderate UV (□=375 nm) irradiation. The half-colored surface had no cracks or defects. The excessive UV irradiation generated many cracks and at last the crystal film was destroyed (iii).This result means that the softening effect occurs only at the surface, not in the whole crystal film.

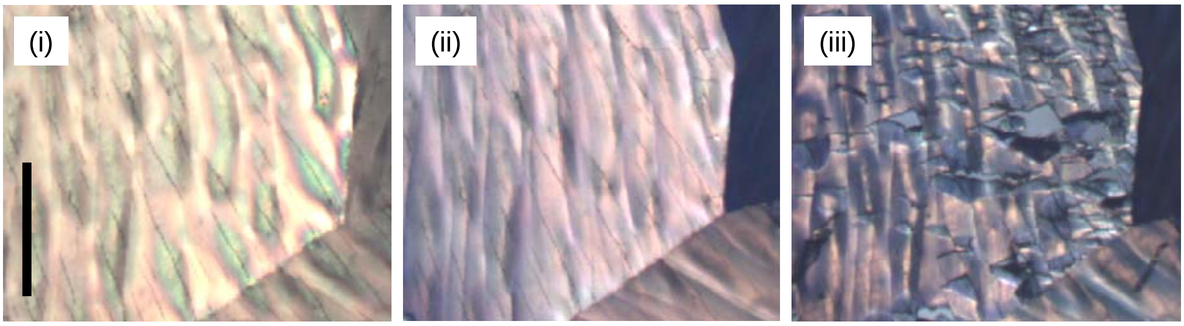


Fig. S6 Change of the DAE crystal film by excessive UV (λ=375 nm) irradiation. (i) Unolored film. (ii) Half-colored (surface) state. (ii) After excessive UV irradiation. Scale bar: 200 μm.