Capturing by self-assembled block copolymer thin films: transfer printing of metal nanostructures on textured surfaces

Hidenori Mizuno,* Isao Sakata, and Koji Matsubara

Research Center for Photovoltaic Technologies, National Institute of Advanced Industrial Science and Technology
Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568 Japan
E-mail: h-mizuno@aist.go.jp

1. Experimental Procedures

General. The nanoimprinted plastic film used as a stamp mold was purchased from Scivax Corp. (product ID: FLH-230/500). Two kinds of poly(dimethysiloxane) (PDMS), termed hard- and soft-PDMS, were used in this study. The prepolymers of hard-PDMS (VDT-731, HMS-301, and SIP6831.1) were purchased from Gelest Corp., and those of soft-PDMS (Sylgard 184) were purchased from Dow Corning. 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane was purchased from Sigma-Aldrich. Polystyrene-*block*-poly-2-vinylpyridine (PS-*b*-P2VP) with molecular weights of 133 and 132 kg/mol (for PS and P2VP, respectively, PDI = 1.15) was purchased from Polymer Source, Inc. The textured F-doped SnO_2 (SnO_2:F) film on glass was purchased from Asahi Glass Company.

Stamp Fabrication. The surface of the nanoimprinted plastic film was spin-coated with hard-PDMS [a mixture of VDT-731 (0.38 g), SIP6831.1 (2 μL), 2,4,6,8-tetramethyltetra-vinylcyclotetrasiloxane (12 μL), and HMS-301 (0.12 mL)] at 1000 rpm for 40 s, and then cured at 65 ^{o}C for 30 min. Subsequently, soft-PDMS (a 10:1 mixture of Sylgard 184 polymer kit) was poured onto the hard-PDMS-coated nanoimprinted film, degassed, and cured again at 80 ^{o}C at least for 3 h. After the second curing, the whole sample was allowed to cool to room temperature, and then the composite PDMS was carefully separated from the plastic film and used as a stamp.

Transfer Printing. A metal (Au, Ag, or Cu) film was deposited on the composite PDMS stamp using an electron beam evaporation apparatus at the rate of ~1 nm/s. A cleaned Si wafer or SnO_2:F/glass substrate was spin-coated with a 0.3 mg/mL o-xylene solution of PS-*b*-P2VP at 5000 rpm for 40 s. The metal-coated PDMS stamp was manually placed on the PS-*b*-P2VP coated substrate whose surface was wet with ethanol. The whole samples was transferred into a desiccator and dried under a reduced pressure (~10 torr) to remove the ethanol from the metal/polymer interface. After 5-10 min, the sample was taken out from the desiccator, and the PDMS stamp was released from the substrate.

Characterization. Atomic force microscopy was taken with SII Nanotechnology Nanonavi II (tapping mode) using Si cantilevers under ambient conditions. Scanning electron microscopy (SEM) was performed with Hitachi S-4300 using an electron energy of 10k eV. UV-visible spectroscopy was taken with PerkinElmer Lambda 950.

2. Supporting Figures

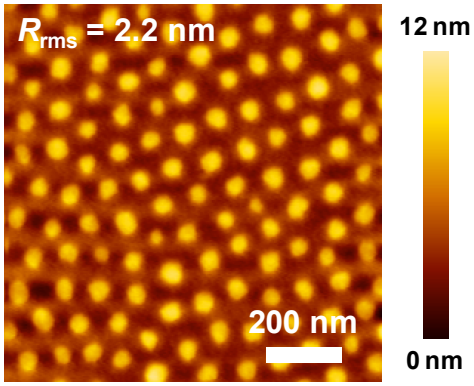

Figure S1. The AFM image of a self-assembled PS-*b*-P2VP thin film on a flat Si surface. A pseudohexagonal arrangement of P2VP domains surrounded by a continuous PS network was observed. The R_{rms} here was 2.2 nm.

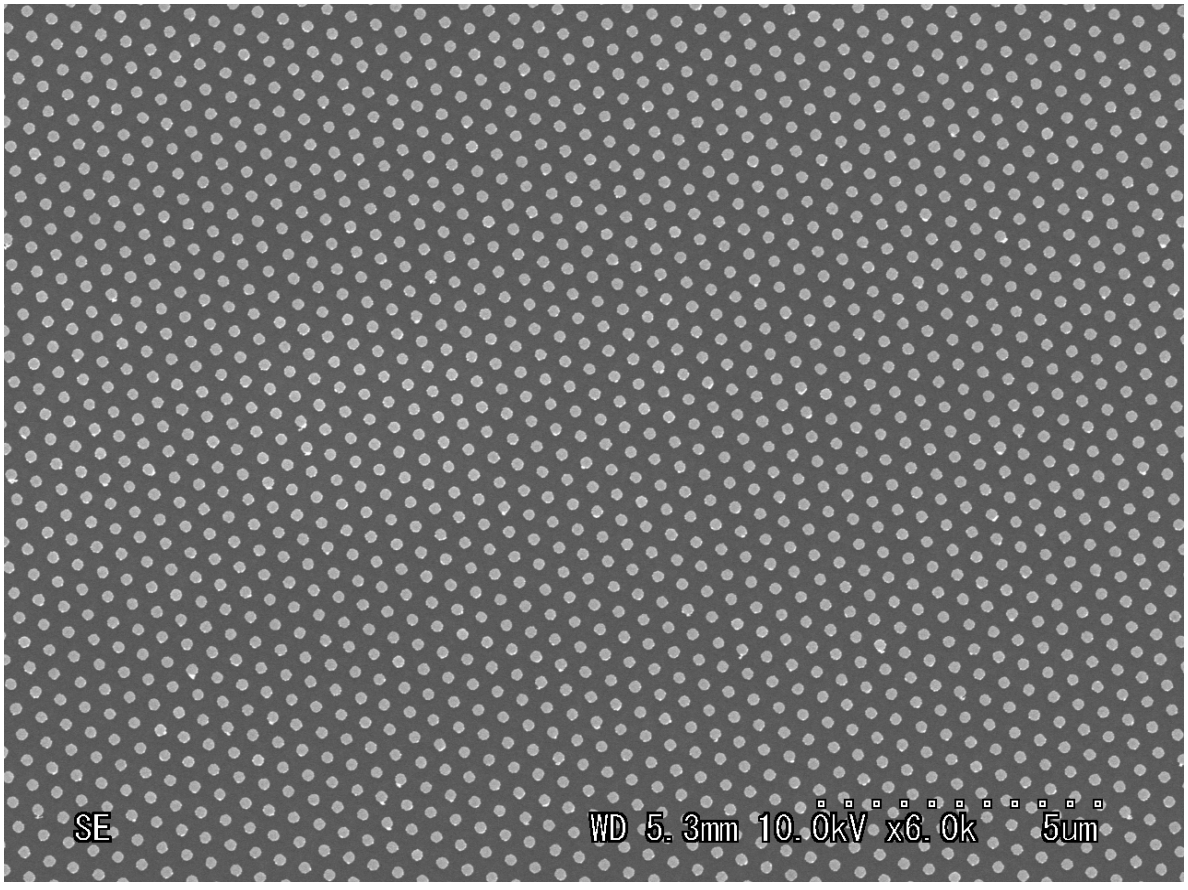

Figure S2. The SEM image of transfer-printed Ag nanodisks on a flat Si surface, with a lower magnification compared to Figure 2b in the main text.

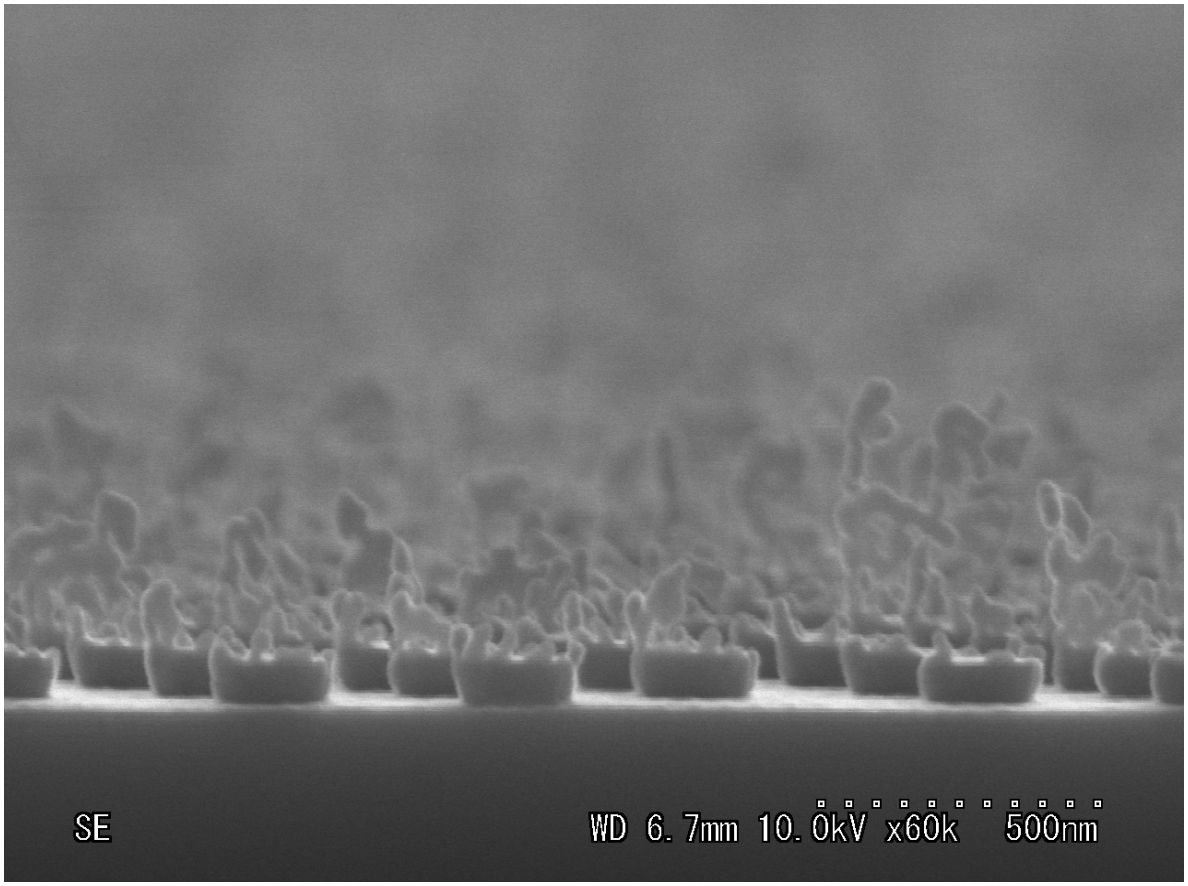

Figure S3. The cross-sectional SEM image of transfer-printed Ag nanodisks on a flat Si surface. The thickness of the Ag was 100 nm when evaporated on the PDMS stamp. Burr formations along the disk edges were clearly observed (an extreme case).

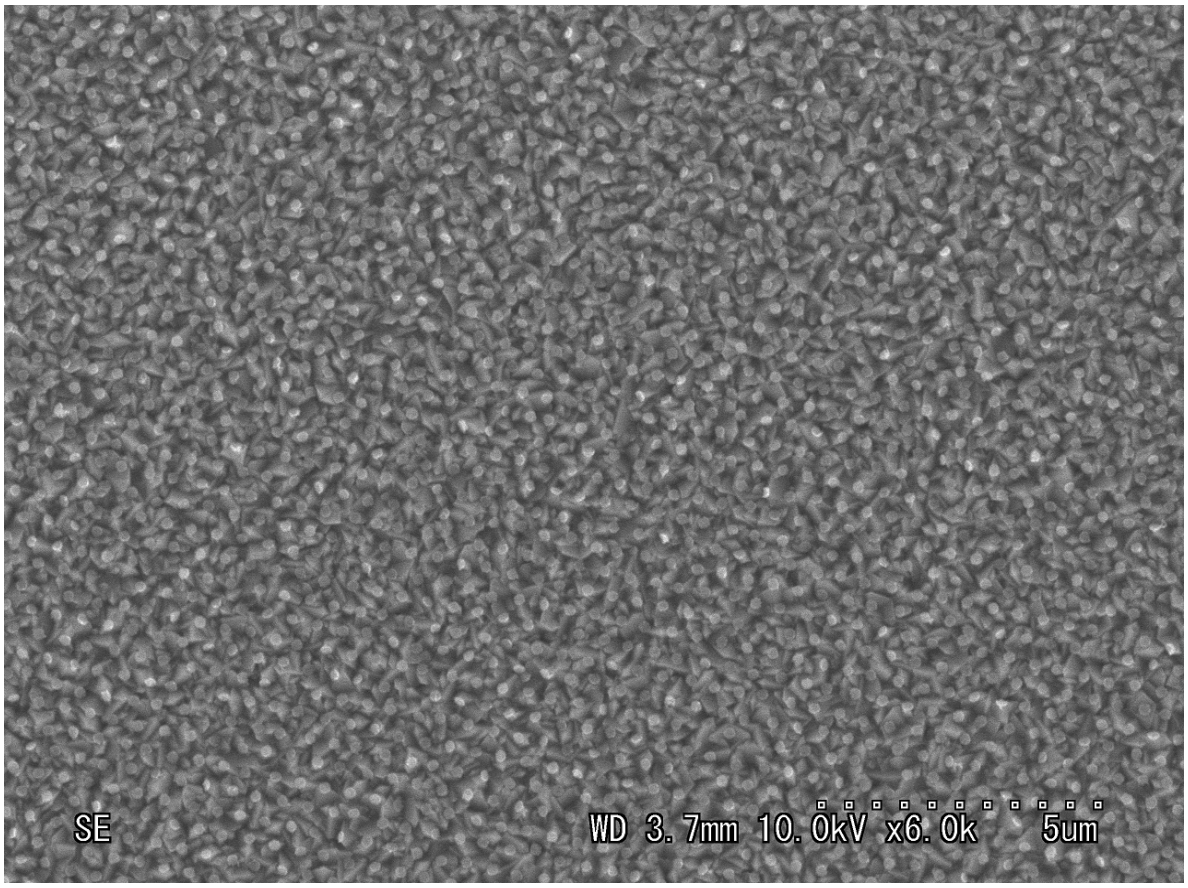

Figure S4. The SEM image of transfer-printed Ag nanodisks on a textured SnO_2:F surface, with a lower magnification compared to Figure 3b in the main text.

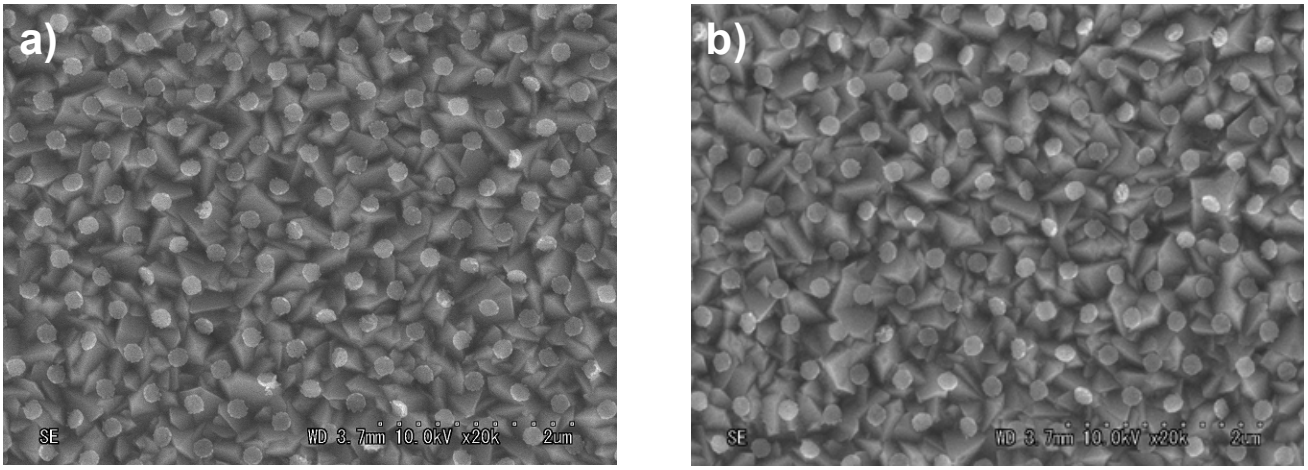

Figure S5. The SEM images of transfer-printed Ag nanodisks on textured SnO_2:F surfaces. (a) Before and (b) after the ultrasonication treatment in H_2O for 15 min. No significant difference was observed.

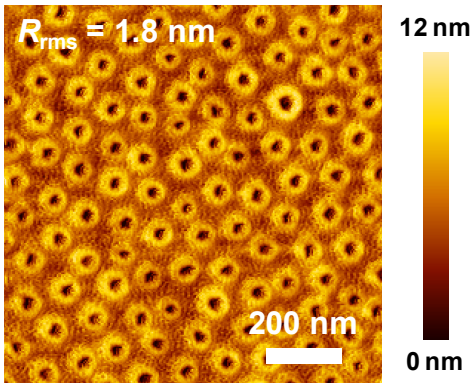

Figure S6. The AFM image of a self-assembled PS-*b*-P2VP thin film on a flat Si surface, reconstructed by an ethanol treatment. The R_{rms} here was 1.8 nm.

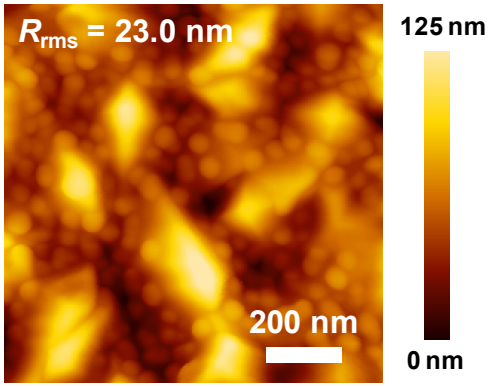

Figure S7. The AFM image of a self-assembled PS-*b*-P2VP thin film on a textured SnO_2:F surface. The R_{rms} here was 23.0 nm.

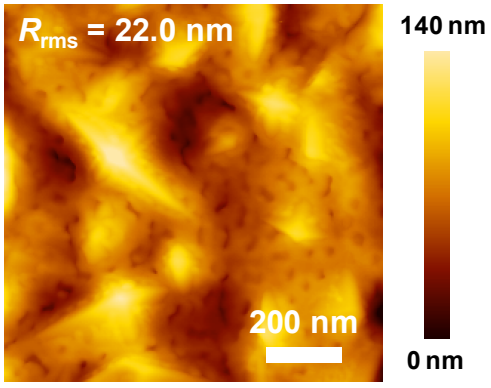

Figure S8. The AFM image of a self-assembled PS-*b*-P2VP thin film on a textured SnO_2:F surface, reconstructed by an ethanol treatment. The R_{rms} here was 22.0 nm.