

# Thermowetting embossing nanoimprinting of the organic–inorganic hybrid materials

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## Abstract

A new UV-based soft-lithographic technique for submicron patterns via thermowetting of organic–inorganic hybrid materials is described. Specifically, 300-nm scale patterns were replicated utilising this coating-free fabrication method. With thermowetting embossing nanoimprinting technique, a poly(dimethyl siloxane) (PDMS) mold with a submicron-scale relief was placed on a thermally wetted organic–inorganic hybrid material, which was then polymerized with UV light. The thermowetting embossing nanoimprinting technique can be applied universally to patternable organic–inorganic hybrid materials, such as methacrylic and vinylic organic–inorganic hybrid materials. Fabricated submicron patterns can also be applied to the nanoscale patterning, e.g., arrayed photonic band gap materials.

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## 1. Introduction

Several techniques for the submicron scale patterning, especially those using flexible organic materials, have been investigated in the last few years [1–4]. In particular, soft lithography [5], which is based on conformal contact between a UV and thermally patternable material and a stamp, offers increasing potential as a lower cost and quicker replacement for expensive lithography techniques. Typically, the stamp is fabricated from transparent quartz or poly(dimethyl siloxane) (PDMS) polymer. PDMS polymer can cover large areas and have very low reactivity, and interfacial energy, toward organic materials and is sufficiently elastic to allow its removal from patterned organic materials without destruction or distortion of the replicated patterns [6]. Among soft lithography techniques, soft

molding is one of the main candidate for soft and nanoimprint lithographies [7]. One particular advantage of UV-based soft lithography over other fabrication methods, such as hot embossing, is that it is a low-temperature and low-pressure process. The organic–inorganic hybrid materials made by sol–gel processes can be applied to these soft lithographic methods, with curing by UV irradiation and heat [8].

In this communication, a coating-free soft lithographic method assisted by the thermal wettability of organic–inorganic hybrid materials, which is termed thermowetting embossing nanoimprinting, is described. This process makes possible the direct patterning of organic–inorganic hybrid materials with features in the submicron range. The proposed technique uses an elastomeric PDMS polymer stamp and does not require either the cycling of temperature or high pressure during the imprinting process. The thermowetting embossing nanoimprinting is suitable for patterning of solution type materials, like organic–inorganic hybrid materials. These have attracted great interest due to

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their physical and chemical properties, which arise from their hybrid nature [9]. Organic–inorganic hybrid materials are synthesized by sol–gel processing and offer the flexibility for one to tailor his properties to a particular application [10,11]. In this report, the fabrication of a representative organic–inorganic hybrid material containing both an organically methacrylic functionality and a silica inorganic network is described.

## 2. Experimental details

For obtaining the organic–inorganic sol–gel hybrid resin, 3-(trimethoxysilyl)propyl methacrylate (Aldrich) and diphenylsilanediol (TCI) were used as precursor molecules without further purification, and barium hydroxide monohydrate ( $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ; Aldrich) was used as a catalyst to promote the condensation reaction between the two precursors. 3-(trimethoxysilyl)propyl methacrylate and  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$  were mixed, and diphenylsilanediol was added continuously at 80 °C for 2 h to prevent self-condensation of diphenylsilanediol and phase separation. The solution was kept at 80 °C for additional 2 h for complete condensation reaction. After finishing the reaction, methanol, which is the by-product of the condensation reaction between the two precursors, was extracted by vacuum heating. The solution was cooled to room temperature and filtered through 0.45- $\mu\text{m}$  filter to remove remaining  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ . Finally, the methacrylic organic–inorganic hybrid resin was obtained.

The thermowetting embossing nanoimprinting process is schematically illustrated in Fig. 1, which shows a typical experiment, to fabricate a periodically arranged submicron pattern. First, an original master structure is fabricated on a silicon wafer by electron beam lithography using a Leica Lion-LV1 pattern generator working at 20 keV. After that, an elastomeric stamp mold is fabricated with PDMS (Sylgard 184, Dow corning). Because PDMS is homogeneous, isotropic, and optically transparent down to 300 nm, it is suitable for UV curing. Then, the methacrylic functionalized organic–inorganic hybrid material synthesized by a non-hydrolytic sol–gel process is dispensed onto the silicon substrate [12]. In this process, a predetermined amount of organic–inorganic hybrid material for precalculated volumes of patterns should be dispensed accurately. In these experiments, a Mushashi SMP-III nanodispenser was used to ensure this accuracy. The methacrylic organic–inorganic hybrid material used contained 1 wt.% of photo-initiator (Irgacure369, Ciba Geigy) to ensure polymerization during UV curing. The dispensed substrate was heated at 100 °C for 3 min to be fully wetted around the expected structuring region on the substrate. After applying the PDMS mold onto the wetted substrate, UV curing was carried out for 30 s with a UV lamp (Mercury arc spare lamp, Oriel) to allow for absorption of consumed photo-initiator. In the methacrylic organic–inorganic hybrid material, methacrylic moieties

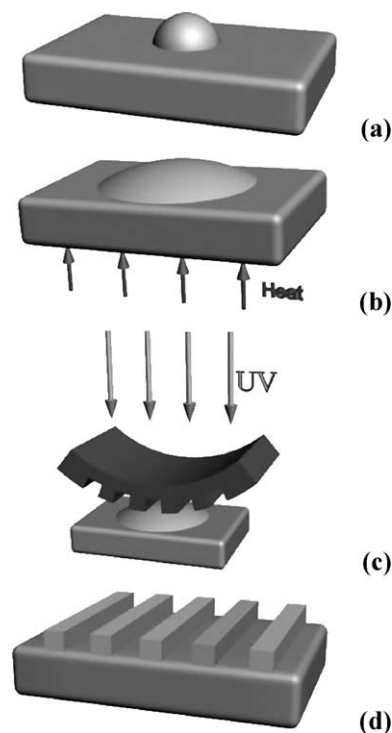


Fig. 1. Schematic diagrams of the thermowetting embossing nanoimprinting technique. (a) Dispensing of organic–inorganic hybrid material, (b) thermowetting by increasing temperature, (c) soft embossing with stamp, (d) UV-cured final replica after demolding.

were attached to the inorganic–oxidic units to facilitate photochemical cross-linking during UV curing. Because of the soft lithographic contact between the PDMS stamp and the organic–inorganic hybrid material, an oxygen inhibition reaction between the methacrylic functionality and the oxygen was not observed [13]. The methacrylic organic–inorganic hybrid material is highly compatible with the silicon wafer substrate as well as the PDMS replica mold. Removing the PDMS mold from the final pattern required no further intervention. After removal of the PDMS stamp, an organic–inorganic hybrid material gel nanostructure that replicated closely the original master was fabricated.

The photographs of dispensed organic–inorganic hybrid material drop and thermowetted organic–inorganic hybrid material drop were obtained with the “Olympus PM-30 optical microscope.” The viscosity of methacrylic organic–inorganic hybrid material was checked by “Brookfield DV-III viscometer” with varying temperature of resin. Finally, the pictures of arrayed line and the hole arrays for photonic crystal application were obtained by “Philips XL30SFEG scanning electron microscope.”

## 3. Results and discussions

The thermowetting embossing nanoimprinting process, a simple soft lithographic technique, was enhanced by moderately increasing the temperature of the substrate. The enhancement of wetting used in this process, which drove the

fluid organic–inorganic hybrid materials into the recessed structure of the replica, arose from the effect of temperature on the viscosity of the applied solution [14] as well as the surface tension of the substrate [15]. The viscosity of organic–inorganic hybrid materials decreased, and the surface tension of the silicon substrate was lowered as the temperature increased to around 100 °C. Thus, the dispensed organic–inorganic hybrid materials fully wetted and filled the entire PDMS mold. Fig. 2 shows separately each dispensing and thermowetting step. In Fig. 2(a), a droplet of organic–inorganic hybrid material is dispensed by nano-dispenser (20  $\mu\text{l}$ ) onto the silicon substrate. The contact angle of dispensed organic–inorganic hybrid material was 39.45°, and that of the thermowetted organic–inorganic hybrid material was 16.55°. The diameter of a dispensed organic–inorganic hybrid material droplet on the substrate was 2.09 mm, whereas that of a thermowetted organic–inorganic hybrid material droplet was 3.89 mm. Because the surface tension decreased and the viscosity of the fluid organic–inorganic hybrid material was lowered during the thermowetting process, the dispensed organic–inorganic hybrid material was widely wetted for 3 min. As the pressure of molding in the thermowetting embossing nanoimprinting process was low, the capillary effect, which drove the organic–inorganic hybrid material to penetrate into the recessed structure of the PDMS stamp, was significant. The relationship between the processing time of thermowetting and the surface tension, viscosity, and capillary force can be written as [16]

$$t \propto \frac{2\eta}{\gamma \cos\theta}$$

where  $\eta$  is the organic–inorganic hybrid material viscosity, and  $\gamma$  and  $\theta$  indicate the fluid–air surface tension and the

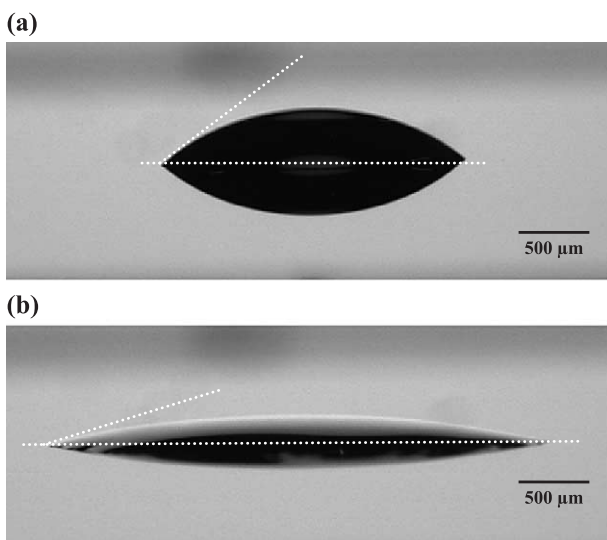


Fig. 2. Pictures of the dispensed organic–inorganic hybrid material drop and thermowetted organic–inorganic hybrid material drop. (a) Contact angle of dispensed organic–inorganic hybrid material on the silicon substrate=39.45°, (b) contact angle of thermowetted organic–inorganic hybrid material on the silicon substrate=16.55°.

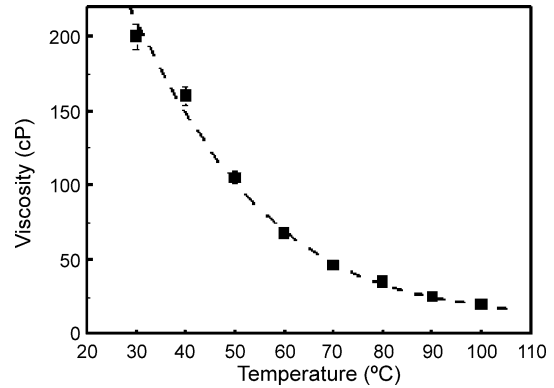


Fig. 3. Methacrylic organic–inorganic hybrid material viscosity change as a function of temperature.

contact angle between the liquid and the surface of the capillary, respectively. Although  $\gamma$  is reduced with increasing temperature, the  $\eta$  and  $\theta$  of dispensed organic–inorganic hybrid material are also lowered. According to the above equation, the processing time of equilibrium thermowetting was minimised with increasing temperature. The thermowetting temperature was determined from the region of reduced viscosity of methacrylic organic–inorganic hybrid material around 100 °C (Fig. 3, as measured by a Brookfield viscometer). It was also selected so as to reduce evaporation of the photo-initiator in the

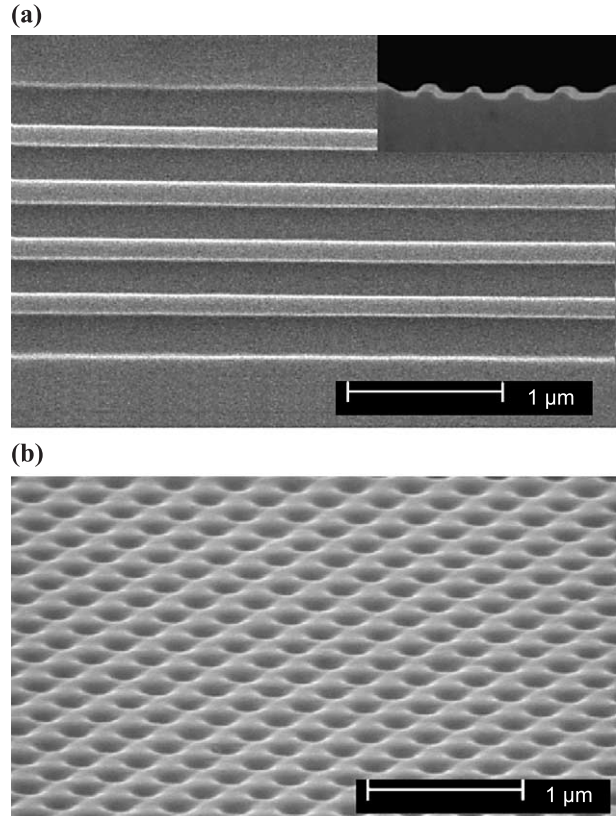


Fig. 4. Scanning electron micrograph of patterned organic–inorganic hybrid material structure. (a) Line direction and cleaved edge image of 300-nm lines, (b) 300-nm hole array structure for photonic crystal application.

methacrylic organic–inorganic hybrid material. Due to the close dependence on temperature of the structural dynamics of organic–inorganic hybrid material patterning, the thermowetting embossing nanoimprinting process was enhanced by thermowetting.

The thermowetting step of the thermowetting embossing nanoimprinting process constitutes an advanced coating-free technique, enhancing wettability between the substrate and the structured pattern so as not to be pulled off from the substrate. This step improved the uniformity of the replicated sample. Further, the total processing time was rapid due to the ready attaining of wetting equilibrium. Thus, the thermowetting step was essential to the process and obviated the use of spin-coating on the replicated sample.

Fig. 4 shows (a) scanning electron micrograms of arrayed line and the end-face of the fabricated nanopatterns and (b) hole arrays for photonic crystal application. The fabricated patterns of the original master were replicated; their line widths were 300 nm, and their height was 100 nm (Fig. 4a), their hole diameter was 300 nm, and their depth was 100 nm (Fig. 4b). This well-defined quality pattern showed that the expected resolution attained from the thermowetting embossing nanoimprinting process could be varied depending upon the master. Although the thermowetting embossing nanoimprinting process is a form of modified and heat-assisted UV-based soft lithography, use of well-structured organic–inorganic hybrid materials means that the technique can be applied without degrading the organic functionality of the organic–inorganic hybrid material.

#### 4. Conclusion

In conclusion, the thermowetting embossing nanoimprinting process is a modified, UV-based soft lithography, promising a synergistic approach to the patterning of sol–gel organic–inorganic hybrid materials with low temperature heating for submicron applications. Although 300-nm patterns were replicated in these experiments using a methacrylic organic–inorganic hybrid material, thermowetting of solution-type organic-based materials can be universally applied to nanometer scale patterns by a coating-free thermowetting embossing nanoimprinting process.

A lower resolution of patterns can be achieved depending on the original master. This process is simple, cheap, reproducible, and avoids the difficulties associated with spin-coating. A more detailed and systematic investigation of the various parameters is necessary to further optimize the thermowetting embossing nanoimprinting process.

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#### References

- [1] S.Y. Chou, P.R. Krauss, P.J. Rennstrom, *J. Vac. Sci. Technol.*, B 14 (1996) 4129.
- [2] S.Y. Chou, P.R. Krauss, W. Zhang, L. Guo, L. Zhang, *J. Vac. Sci. Technol.*, B 15 (1997) 2897.
- [3] T. Bailey, B.J. Choi, M. Colburn, M. Meissl, S. Shaya, J.G. Ekerdt, S.V. Sreenivasan, C.G. Willson, *J. Vac. Sci. Technol.*, B 18 (2000) 3572.
- [4] C. Park, J. Yoon, E.L. Thomas, *Polymer* 44 (2003) 6725.
- [5] Y. Xia, G.M. Whitesides, *Angew. Chem., Int. Ed.* 37 (1998) 550.
- [6] Y. Xia, N. Venkateswaran, D. Qin, J. Tien, G.M. Whitesides, *Langmuir* 14 (1998) 363.
- [7] L. Malaquin, F. Carcenac, C. Vieu, M. Mauzac, *Microelectron. Eng.* 61 (2002) 379.
- [8] H. Schmidt, *Macromol. Symp.* 159 (2000) 43.
- [9] M. Popall, A. Dabek, M.E. Robertsson, G. Gustafsson, O.J. Hagel, B. Olswski, R. Buestrich, L. Cergel, M. Leby, P. Kiely, J. Joly, D. Lambert, M. Schaub, H. Reichl, *IEEE Electron. Com. Technol. Conf.* (1998) 1018.
- [10] J.I. Jung, O.H. Park, B.S. Bae, *J. Sol–Gel Sci. Technol.* 26 (2003) 897.
- [11] J.U. Park, W.S. Kim, B.S. Bae, *J. Mater. Chem.* 13 (2003) 738.
- [12] R. Buestrich, F. Kahlenberg, M. Popall, P. Dannberg, R. Mueller-Friedler, O. Roesch, *J. Sol–Gel Sci. Technol.* 20 (2001) 181.
- [13] G. Odian, *Principles of Polymerization*, J. Wiley and Sons, New York, 1981, p. 249.
- [14] J.J. Aklonis, W.J. Macknight, *Introduction to Polymer Viscosity*, J. Wiley and Sons, New York, 1982, p. 47.
- [15] J.C. Berg, *Wettability*, Marcel Dekker, New York, 1993, p. 467.
- [16] D. Myers, *Surfaces, Interfaces and Colloids*, Wiley, New York, 1999.