Pre-hardening Ultraviolet nanoimprint lithography using opaque mold

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Ultraviolet (UV) nanoimprint lithography (NIL) is very useful for fabrication of fine pattern. However, silicon mold cannot use for mold when opaque materials are substrates. This problem is solved by UV light from the side region method[1]. This method is UV exposures from the side region which is a UV curable resin layer between mold and substrate. This process is effective for relatively thick UV curable resin, but transfer of thin resin takes a long time because UV light does not expose efficiently. In order to improve this issue, pre-hardening UV-NIL has been developed. The key point of this method is control of Martens hardness by pre-hardening, and mold press deforms resin layer and proper Martens hardness keeps transfer pattern. After the mold removal, main cure is carried out by UV exposure.

Figure 1 shows process of pre-hardening UV-NIL. In this experiment, UV curable resin of epoxy polymer and cation type curing system was used because this type resin can cure in the air (without oxygen inhibition). The substrate was silicon. The mold was also silicon with 200 nm diameter pillar patterns. This mold was coated with the fluorinated silane coupling agent (Optool DSX, Daikin Co.). UV dose of pre-hardening was 514 J/cm^2, and then mold pressed this resin with 1MPa pressure and 120 s keeping time. After the mold removal, main cure was carried out with 1530 J/cm^2. After the curing, pattern transfer was completed. Hardness of pre-hardening resin and completely cured resin was measured with nano-indentator (Shimadzu, DUH-211). Optical microscope and scanning electron microscope (SEM) were used for observation of patterns.

Figure 2 shows the relationship between transit time and indentation shape. With pre-hardening, shape remained up to 10 min. On the other hand, without pre-hardening, shape faded at 4 min. Thus, pre-hardening process can keep the resist shape which caused by pressure. We measured force curves and Martens hardness of pre-hardening and complete cured resin layer. The force curve shows pre-hardening resin was elasticity and Martens hardness was 14.4 N/mm^2. The complete cured resin was 78.9 N/mm^2. The value of 14.4 N/mm^2 (18 % of complete cured resin) was suitable for patterning, when weaker Martens hardness resin (see Fig.2 non-pre-hardening shape), the shape could not keep. On the other hand, harder Martens hardness resin, more pressure would require.

Figure 3 shows the transferred result using pre-hardening UV-NIL. The 200 nm holes patterns were obtained. In addition, whole area was transferred without resist adhesion on mold.

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[1]R. Kirchner, A. Finn, L. Teng, M. Ploetner, A. Jahn, L. Nueske, W.-J. Fischer, Microelectronic Engineering **88** (2011) 2004-2008.

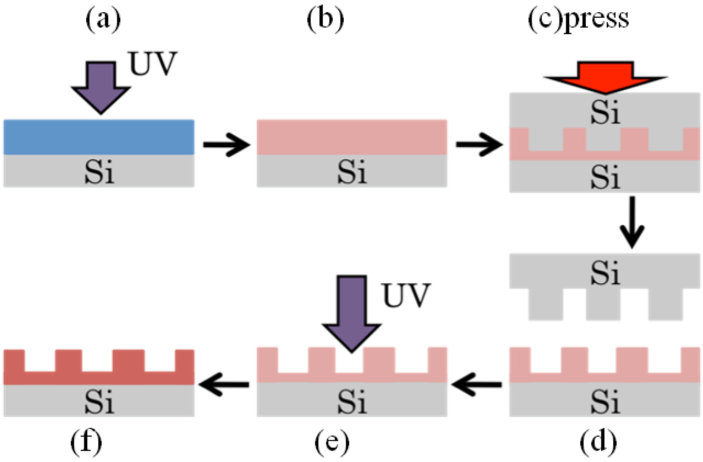

Figure 1: Process of pre-hardening UV-NIL. (a) Ultraviolet exposure, (b) Pre-hardened resin, (c) Mold press, (d) Release the mold, (e) Ultraviolet exposure (main cure), (f) Complete hardening.

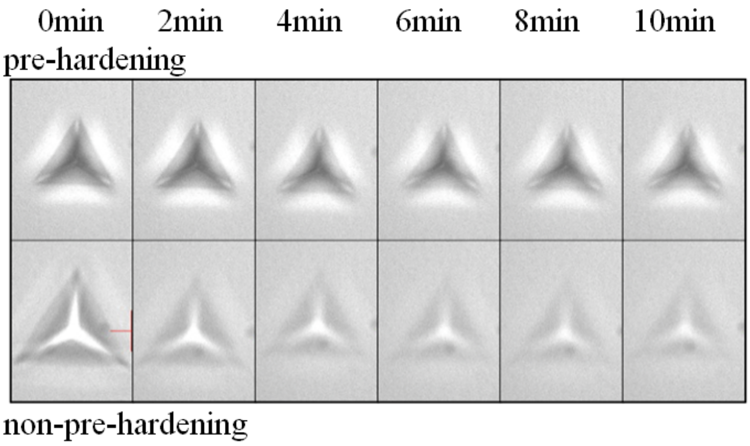

Figure 2: Shape keeping time using nanoindentor.

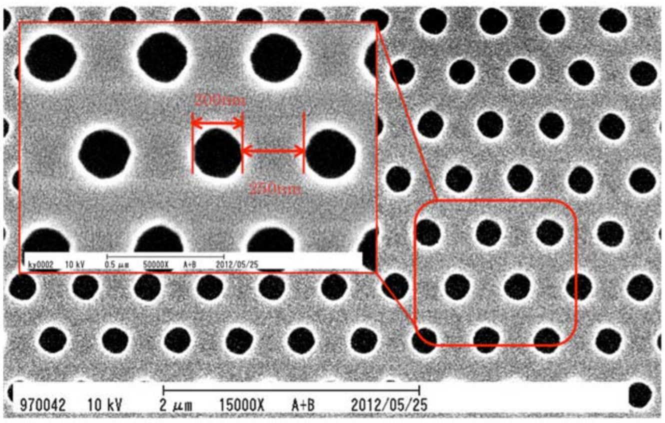

Figure 3: Transferred holes alley for pre-hardening UV-NIL (using pillar mold).