Supporting Information

Direct nanoimprinting of metal oxides by \textit{in situ} thermal co-polymerization of their methacrylates

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Supplementary material (ESI) for Journal of Materials Chemistry
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**Fe$_2$O$_3$ Resin**

![Cross-sectional SEM images of (a) as-imprinted and (b) heat-treated patterns of Fe$_2$O$_3$ resin using 250 nm line/space grating mold. The spin-coating speed of the resin was 3000 rpm. Notice the lack of cracking of the residual layer of thickness ~600 nm.](image)

**Figure S1.** Cross-sectional SEM images of (a) as-imprinted and (b) heat-treated patterns of Fe$_2$O$_3$ resin using 250 nm line/space grating mold. The spin-coating speed of the resin was 3000 rpm. Notice the lack of cracking of the residual layer of thickness ~600 nm.

One of the interesting characteristics of Fe$_2$O$_3$ resin is its ability to give crack-free residual layer at large film thickness [Figure S1].

XRD studies of heat-treated Fe$_2$O$_3$ resin show that crystallization starts around 450 °C with sharp peaks of hematite phase appearing at 600 °C [Figure S2].
Figure S2. XRD data of Fe₂O₃ resin heat-treated at various temperatures for 1 hour showing the formation of hematite phase (JCPDS Card No. 33-664).

ZrO₂ Resin

Figure S3. SEM images of (a) as-imprinted and (b) heat-treated patterns of ZrO₂ resin using 200 nm dimple mold. The spin-coating speed of the resin was 6000 rpm.

The SEM images above [Figure S3] shows an array of dots imprinted using ZrO₂ resin without diluting it in n-butanol in 1:1 volumetric ratio. It is interesting to note that although the as-prepared imprint looks neat and devoid of cracks, its heat-treatment resulted in the appearance of cracks around the dots.

Figure S4. SEM image of heat-treated patterns of ZrO₂ resin (spin-coated at 6000 rpm) using 100 nm line/space mold.

Similar observation was also made when line gratings were imprinted using a 100 nm mold. While no cracking was observed in the imprinted sample, the residual layer showed cracking after heat-treatment at 450 °C for 1 hour [Figure S4].

These observations necessitated further reduction of residual layer by diluting the ZrO₂ resin in n-butanol in 1:1 volumetric ratio in order to obtain high quality imprints.
This brings us to the issue of how the residual layer in cross-section looks like for ZrO$_2$ resin spin-coated at 3000 and 6000 rpms. The cross-section of the residual layer at these two spin speeds is shown in Figure S5. Notice the enormously thick residual layer obtained when the resist was spun at 3000 rpm.

**Figure S5.** Cross-sectional SEM images of as-imprinted patterns of ZrO$_2$ resin using 250 nm line/space grating mold. The spin-coating speed of the resin was (a) 3000 rpm and (b) 6000 rpm. Notice the residual layer thicknesses of ~1800 nm and ~900 nm for the imprinted resin spin-coated at 3000 rpm and 6000 rpm, respectively.
**Figure S6.** Cross-sectional SEM image of as-imprinted patterns of TiO$_2$ resin using 100 nm line/space grating mold. The spin-coating speed of the resin was 3000 rpm. A residual layer thickness of ~1200 nm was observed in this case.
Figure S7. SEM images of (a) as-imprinted and (b) heat-treated patterns of optimized Nb$_2$O$_5$ resin composition with the molar ratio Nb(OEt)$_5$: EDMA:MMA = 1:1:2 using 250 nm line/space grating mold. The spin-coating speed of the resin was 3000 rpm.

Optimizing the composition of Nb$_2$O$_5$ resin does not mean good quality lines after heat-treatment at 550 °C for 1 hour as seen in Figure S7. Here reduction of residual layer thickness by increasing the spin-speed to 6000 rpm eliminates cracking completely after heat-treatment.
Ta$_2$O$_5$ Resin

Effect of Ta$_2$O$_5$ resin composition on imprintability

In case of Ta$_2$O$_5$ resin, a composition of Ta(OBu)$_5$:EDMA=1:2.5, was studied for its imprintability [Figure S8]. As observed for the similar composition of Nb$_2$O$_5$ resin, Ta$_2$O$_5$ resin composition also showed excessive cracking in the residual layer. Since tantalum too is a pentavalent metal, this phenomenon may be attributed to the polymerization-induced shrinkage along five directions.

![Figure S8. SEM images of (a) as-imprinted and (b) heat-treated patterns of Ta(OBu)$_5$:EDMA= 1:2.5 resin using 250 nm line/space grating mold. The resin was spin-coated at a speed of 3000 rpm.](image)

Reduction in residual layer thickness by spinning at 6000 rpm does not seem to change the cracking characteristics of the imprints.

![Figure S9. SEM images of (a) as-imprinted and (b) heat-treated patterns of Ta(OBu)$_5$:EDMA:MMA = 1:1.0:2 resin using 100 nm line/space grating mold. The resin spin-coating speed was 6000 rpm.](image)
However, optimizing Ta$_2$O$_5$ resin in conjunction with lower residual layer thickness gave crack-free imprints after heat-treatment [Figure S9].