Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

Direct nanoimprinting of metal oxides by *in situ* thermal co-polymerization of their methacrylates

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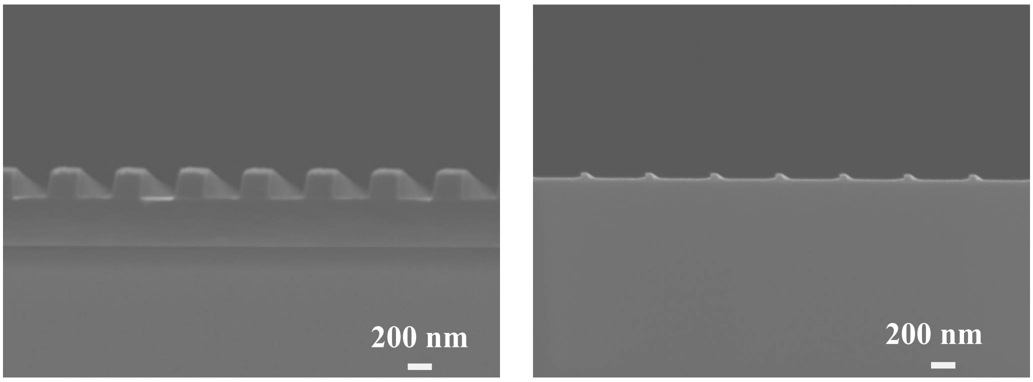
Supplementary material (ESI) for Journal of Materials Chemistry

Fe_2O_3 Resin



(a) (b)

Figure S1. Cross-sectional SEM images of (a) as-imprinted and (b) heat-treated patterns of Fe_2O_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_2O_3 resin is its ability to give crack-free residual layer at large film thickness [Figure S1].

XRD studies of heat-treated Fe_2O_3 resin show that crystallization starts around 450 °C with sharp peaks of hematite phase appearing at 600 °C [Figure S2].

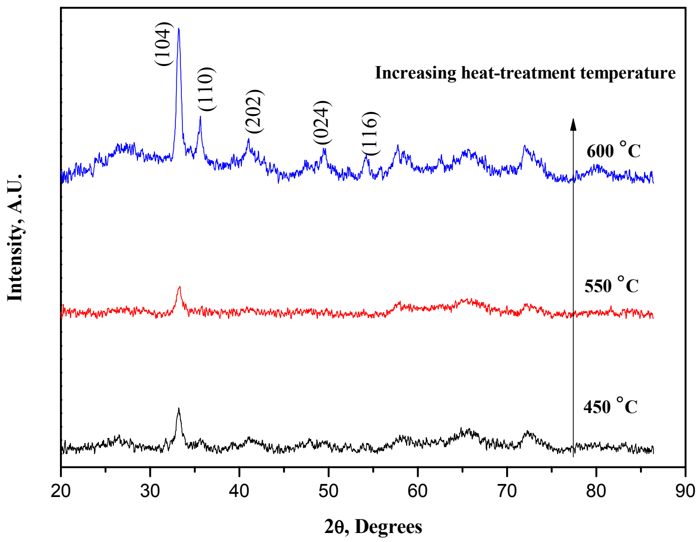


Figure S2. XRD data of Fe_2O_3 resin heat-treated at various temperatures for 1 hour showing the formation of hematite phase (JCPDS Card No. 33-664).

ZrO_2 Resin

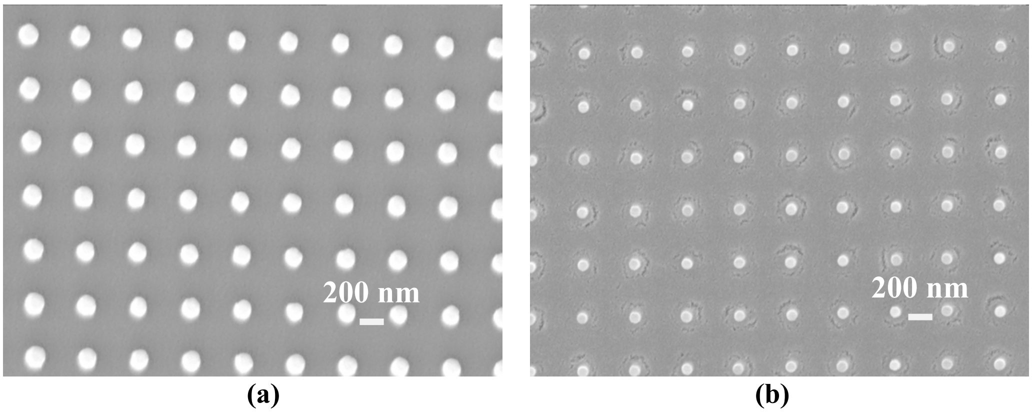


Figure S3. SEM images of (a) as-imprinted and (b) heat-treated patterns of ZrO_2 resin using 200 nm dimple mold. The spin-coating speed of the resin was 6000 rpm.

The SEM images above [Figure S3) shows an array of dots imprinted using ZrO_2 resin *without* diluting it in *n*-butanol in 1:1 volumertic 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.

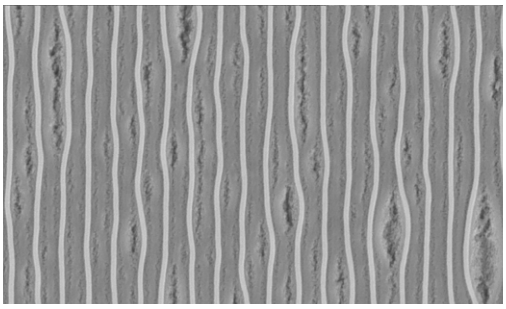
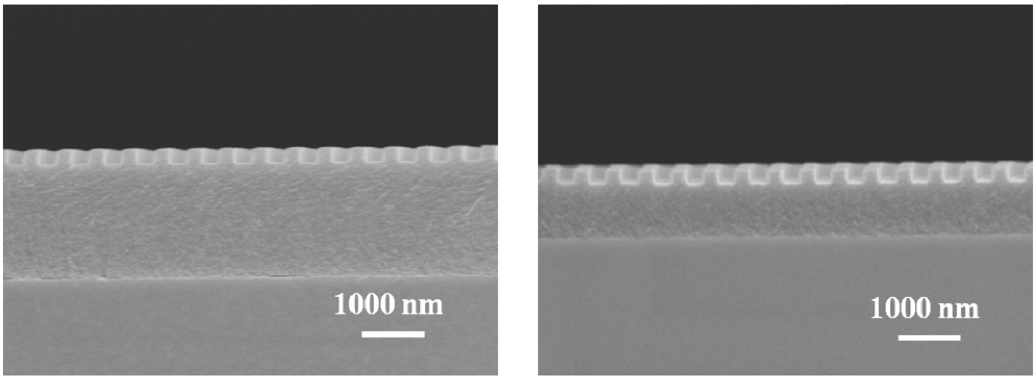


Figure S4. SEM image of heat-treated patterns of ZrO_2 resin (spin-coated at 6000 rpm) using 100 nm line/space mold.

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 ZrO_2 resin in *n*-butanol in 1:1 volumertic 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.



(a) (b)

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.

TiO_2 Resin

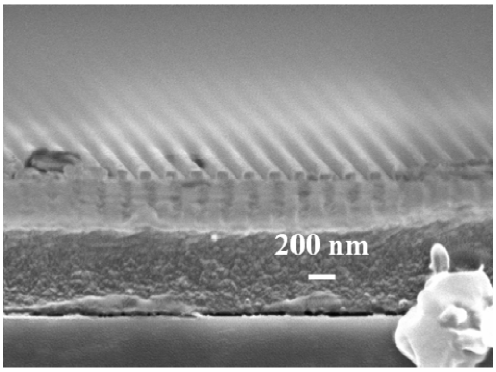
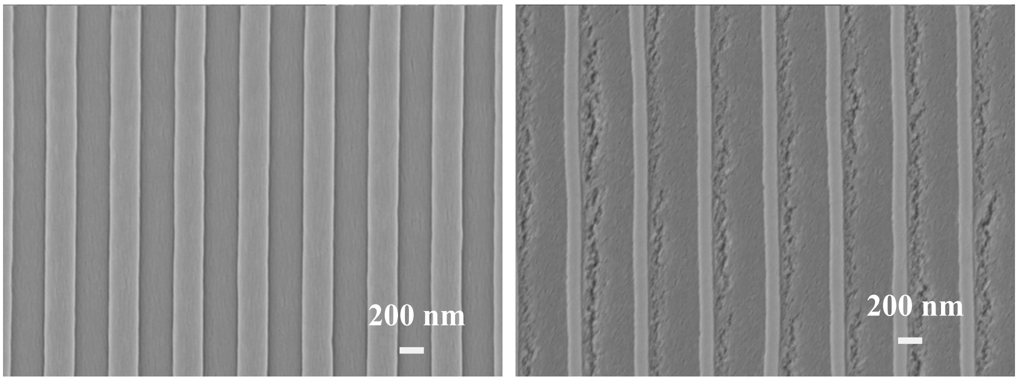


Figure S6. Cross-sectional SEM image of as-imprinted patterns of TiO_2 resin using 100 nm line/space grating mold. The spin-coating speed of the resin was 3000 rpm. A residual layer thickness of ~1200 nm was observed in this case.

Nb_2O_5 Resin



(a) (b)

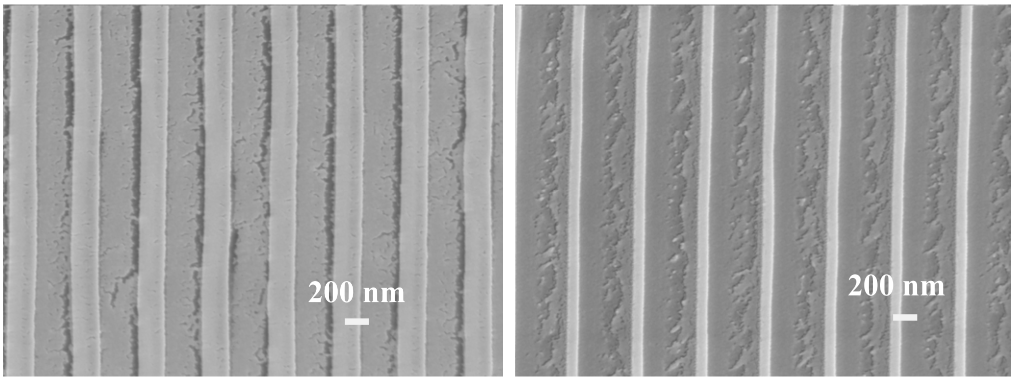
Figure S7. SEM images of (a) as-imprinted and (b) heat-treated patterns of optimized Nb_2O_5 resin composition with the molar ratio $Nb(OEt)_5$: EDMA:MMA = 1:1:2 using 250 nm line/space grating mold. The spin-coating speed of the resin was 3000 rpm.

Optimizing the composition of Nb_2O_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_2O_5 Resin

<u>Effect of Ta_2O_5 resin composition on imprintability</u>

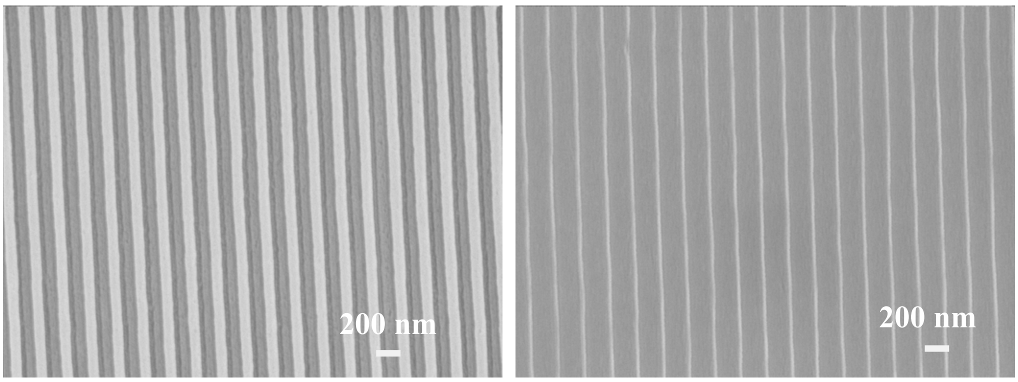
In case of Ta_2O_5 resin, a composition of $Ta(OBu)_5$:EDMA=1:2.5, was studied for its imprintability [Figure S8]. As observed for the similar composition of Nb_2O_5 resin, Ta_2O_5 resin composition also showed excessive cracking in the residual layer. Since tantalum too is a pentavalent metal, this phenomenon may be attributed to the polymerization-induced shrinkage along five directions.



(a) (b)

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.

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



(a) (b)

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.

However, optimizing Ta_2O_5 resin in conjunction with lower residual layer thickness gave crack-free imprints after heat-treatment [Figure S9].