Electronic Supplementary Information (ESI)

Polymer Blend-Filled Nanoparticle Films via Monomer-Driven Infiltration of Polymers and Photopolymerization

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Spectroscopic Ellipsometry Data Fitting and Modeling

**Step 1.** The optical constants (A, B, and C) of pure PS film and pure SiO₂ NP film are measured using a spectroscopic ellipsometry under ambient conditions. The thickness of a SiO₂ NP/PS bilayer is determined using a two-layer Cauchy model with measured optical constants of the pure PS and SiO₂ NP films as inputs as shown in Figure S1. The refractive index (n) of each Cauchy layer as a function of wavelength (λ) is described by:

\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (S1)
\]

where A, B and C are optical constants of the Cauchy Model.

![Figure S1](image1)

**Figure S1** Measurement of the thickness of a bilayer consisting of a SiO₂ NP layer atop a PS layer, using a two-layer Cauchy model.

**Step 2.** We perform *in situ* spectroscopic ellipsometry to monitor PS infiltration into the SiO₂ NP packing and the photopolymerization of MMA. The bilayer sample is placed in an ellipsometry cell that have small aliquots of MMA and HMP. Then the cell is sealed and the collection of the change in amplitude ratio (ψ) and the phase difference (Δ) starts within a few seconds. To fit *in situ* data during solvent annealing and UV exposure, we use a two-layer Cauchy model with

![Figure S2](image2)

**Figure S2** Fitting of the refractive index of composite layer and the thickness of PS layer undergoing monomer-driven infiltration of polymers and subsequent photopolymerization using a two-layer Cauchy model.
measured optical constants of the pure PS and the thickness of the SiO$_2$ NP film fixed. The optical constants of the composite layer and the thickness of PS layer are set as variables (Figure S2).

**Step 3.** To determine the refractive index of polymer blend-filled SiO$_2$ NP film and the thickness of residual PS layer, the film is measured with ellipsometry again after 12 hrs drying. With the optical constants of the pure PS layer and the thickness of the composite layer fixed, the data is fitted using a two-layer Cauchy model.

### Calculating Volume Fraction of Each Component in Composite Films

**Volume Fraction-Weighted Mixing Rule for Refractive Index**

1. SiO$_2$ NP layer (before annealing or photopolymerization):

\[ n = \phi_{\text{void}} n_{\text{void}} + \phi_{\text{SiO}_2} n_{\text{SiO}_2} \quad (S2) \]

\[ \phi_{\text{void}} + \phi_{\text{SiO}_2} = 1 \quad (S3) \]

\[ \therefore \phi_{\text{void}} = \frac{n_{\text{SiO}_2} - n}{n_{\text{SiO}_2} - 1} \quad (S4) \]

2. Top layer of SiO$_2$ NP/PS bilayer after monomer-driven infiltration of polymers and drying

\[ n_{\text{comp}} = \phi_{\text{void}}' n_{\text{void}} + \phi_{\text{SiO}_2} n_{\text{SiO}_2} + \phi_{\text{PS}} n_{\text{PS}} \quad (S5) \]

\[ \phi_{\text{void}}' + \phi_{\text{SiO}_2} + \phi_{\text{PS}} = 1 \quad (S6) \]

\[ \phi_{\text{void}}' + \phi_{\text{PS}} = \phi_{\text{void}} \quad (S7) \]
\[ \phi_{PS} = \frac{\Delta h_{PS}}{h_{SiO_2}} \] (S8)

3. SiO\textsubscript{2} NP film after MMA condensation, photopolymerization and drying

\[ n_{comp} = \phi_{void} n_{void} + \phi_{SiO_2} n_{SiO_2} + \phi_{PMMA} n_{PMMA} \] (S9)

\[ \phi_{void} + \phi_{SiO_2} + \phi_{PMMA} = 1 \] (S10)

\[ \phi_{void} + \phi_{PMMA} = \phi_{void} \] (S11)

4. PS/PMMA/SiO\textsubscript{2} NP Composite Film:

\[ n_{comp} = \phi_{void} n_{void} + \phi_{SiO_2} n_{SiO_2} + \phi_{PS} n_{PS} + \phi_{PMMA} n_{PMMA} \] (S12)

\[ \phi_{void} + \phi_{SiO_2} + \phi_{PMMA} + \phi_{PS} = 1 \] (S13)

\[ \phi_{void} + \phi_{PMMA} + \phi_{PS} = \phi_{void} \] (S14)

\[ \phi_{PS} = \frac{\Delta h_{PS}}{h_{SiO_2}} \] (S15)

where \( n_{comp}, n_{void}, n_{SiO_2}, n_{PS} \) and \( n_{PMMA} \) refer to the refractive indices of the polymer filled composite, void (air), SiO\textsubscript{2}, PS, PMMA respectively, whereas \( \phi_{void}, \phi_{SiO_2}, \phi_{PS} \) and \( \phi_{PMMA} \) refer to the volume fraction of each component. The values for \( n_{void} \) and \( n_{SiO_2} \) are taken as 1 and 1.45, respectively.\(^3\)
\( \Phi_{\text{void}} \) which refers to the original void fraction of densely-packed SiO\(_2\) NP film prepared by spin-coating can be determined by Equations S3 where \( n \) is obtained by characterizing the SiO\(_2\) NP layer (pure SiO\(_2\) NP film or SiO\(_2\) NP/PS bilayer before annealing) with spectroscopic ellipsometry. Thus, \( \Phi_{\text{SiO}_2} \) can be calculated based on Equation S3.

\( \Phi_{PS} \) can be calculated from Equation S15 where \( \Delta h_{PS} \) is the change in the thickness of the PS layer and \( h_{\text{SiO}_2} \) is the thickness of the SiO\(_2\) NP layer before annealing (see Figure. S1).

To obtain \( \Phi_{PMMA} \) and \( \Phi_{\text{void}} \) by combining Equations S12-S15, it is important to determine \( n_{PS} \) and \( n_{PMMA} \) in the interstices of NP packing. It has been well established that the refractive index of one polymer is the result of several factors, including polarization, chain flexibility, orientation in the backbone, etc.\(^4\) Large shifts in the refractive index of a polymer from its bulk value are known to occur when polymer chains are mechanically rubbered.\(^5\) Confinement in the interstices could result in a shift in polymer’s refractive index from its bulk value.

Thus, to determine the refractive indices of PS and PMMA in the interstices, we prepare SiO\(_2\) NP/PS and SiO\(_2\) NP/PMMA bilayers by first spin-coating polymer solution (in toluene) on Si wafer at a rotation speed of 2250 rpm for 1.5 min, followed by coating NP layer on the polymer layer at a rotation speed of 2500 rpm for 2 min. Then the bilayers are annealed with MMA in ellipsometry cell for a certain period. Take the PS/SiO\(_2\) NP bilayer as an example, as the thickness change of the polymer layer reflects the actual amount of polymer that infiltrates into the NP packing, \( \Phi_{PS} \) can be calculated according to Equation S8. Then \( n_{PS} \) can be derived from Equation S5-S6. \( n_{PMMA} \) can be determined similarly using SiO\(_2\) NP/PMMA bilayers. The value of
$n_{PS}$ is determined to be 1.74±0.06 by averaging the values calculated from 5 SiO$_2$ NP/PS bilayers while values of $n_{PMMA}$ is determined to be 1.50±0.04 by averaging 4 SiO$_2$ NP/PMMA bilayers.


**Refractive Index Profile of a SiO$_2$ NP film exposing to HMP**

![Figure S3](image)

*Figure S3* Refractive index profile of a 264 nm SiO$_2$ NP film as a function of annealing time, obtained using *in situ* spectroscopic ellipsometry. The SiO$_2$ NP film is annealed with HMP for 140 mins and then exposed to air for 10 mins.
Table S1 The refractive index of a SiO$_2$ NP film before exposing to MMA and after exposing to MMA for 30 mins

<table>
<thead>
<tr>
<th>Solvent</th>
<th>RI of NP layer before annealing</th>
<th>RI of NP layer after 30 mins</th>
<th>$\phi_{\text{void}}$</th>
<th>$\phi_{\text{MMA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>1.308</td>
<td>1.439</td>
<td>0.318</td>
<td>0.316</td>
</tr>
</tbody>
</table>

This result shows that the interstices of the NP packing are completely flooded with MMA after 30 mins exposure to MMA vapour.

Table S2 Volume Fractions of PS in the nanoparticle layer after annealing a SiO$_2$ NP/PS bilayer with MMA

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PS layer thickness before annealing (nm)</th>
<th>PS layer thickness after annealing (nm)</th>
<th>SiO$_2$ NPs thickness (nm)</th>
<th>Annealing time (mins)</th>
<th>$\phi_{PS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>222.4</td>
<td>173.7</td>
<td>246.8</td>
<td>40</td>
<td>0.197</td>
</tr>
<tr>
<td></td>
<td>226.1</td>
<td>175.2</td>
<td>252.2</td>
<td>120</td>
<td>0.202</td>
</tr>
<tr>
<td></td>
<td>220.7</td>
<td>168.5</td>
<td>233.6</td>
<td>150</td>
<td>0.224</td>
</tr>
</tbody>
</table>

$\phi_{PS}$ in this table is calculated according to equation S7.
Table S3 Volume fraction of PS, PMMA and void in composite films which are fabricated by being exposed to UV light for 30 mins

<table>
<thead>
<tr>
<th>UV exposure duration (mins)</th>
<th>$\frac{h_{PS}}{h_{SiO_2}}$ Average</th>
<th>$\phi_{PS}$</th>
<th>$\phi_{PMMA}$</th>
<th>$\phi_{void}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.079</td>
<td>0.065±0.002</td>
<td>0.059±0.018</td>
<td>0.213±0.011</td>
</tr>
<tr>
<td></td>
<td>0.121</td>
<td>0.108±0.006</td>
<td>0.071±0.030</td>
<td>0.149±0.022</td>
</tr>
<tr>
<td></td>
<td>0.195</td>
<td>0.179±0.002</td>
<td>0.057±0.005</td>
<td>0.094±0.003</td>
</tr>
<tr>
<td></td>
<td>0.240</td>
<td>0.205±0.018</td>
<td>0.047±0.032</td>
<td>0.075±0.008</td>
</tr>
</tbody>
</table>

Table S4 Volume fraction of PS, PMMA and void in composite films which are fabricated by being exposed to UV for different duration

<table>
<thead>
<tr>
<th>$\frac{h_{PS}}{h_{SiO_2}}$ Average</th>
<th>UV exposure duration (mins)</th>
<th>$\phi_{PS}$</th>
<th>$\phi_{PMMA}$</th>
<th>$\phi_{void}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.123</td>
<td>0</td>
<td>0.105±0.001</td>
<td>0.009±0.0004</td>
<td>0.209±0.001</td>
</tr>
<tr>
<td>0.128</td>
<td>10</td>
<td>0.109±0.005</td>
<td>0.032±0.017</td>
<td>0.181±0.014</td>
</tr>
<tr>
<td>0.121</td>
<td>30</td>
<td>0.108±0.006</td>
<td>0.071±0.030</td>
<td>0.149±0.022</td>
</tr>
<tr>
<td>0.134</td>
<td>50</td>
<td>0.119±0.002</td>
<td>0.091±0.007</td>
<td>0.118±0.009</td>
</tr>
</tbody>
</table>