Fabrication of Plasmonic TiN Nanostructures by Nitridation of Nanoimprinted TiO$_2$ Nanoparticles

Supporting Information

XRD patterns at glancing angles from 0.4 to 1.5 of untreated (O) and treated (N) films. Reference patterns of anatase TiO$_2$ and osbornite TiN are shown at the bottom. In the glancing angle scans of un-nitried TiO$_2$, a small rutile peak is observed, which is not observed in the nitried samples, suggesting the conversion of both, anatase and rutile phases to TiN.

![Figure S1](image_url)

**Figure S1.** XRD patterns from low incidence angle scans. Un-nitried (O) and nitried (N) patterns are compared at angles from 0.4 to 1.5°.

**TiO$_2$ nanoparticle film porosity**

To estimate the porosity of imprinted TiO$_2$ nanoparticle samples, we measured the refractive indices of planar TiO$_2$ nanoparticle films, heated them under various conditions, and measured the refractive indices again. We used the Lorenz-Lorentz equation (shown below), where $n_A$ corresponds to TiO$_2$ and $n_B$ to air. $n_D$ for bulk TiO$_2$ is reported as 2.43 (628 nm) and for air is assumed to be 1.

\[
f_v = \frac{C - A}{B - A}
\]

\[
A = \frac{n_A^2 - 1}{n_A^2 + 2}
\]

\[
B = \frac{n_B^2 - 1}{n_B^2 + 2}
\]

\[
C = \frac{n_D^2 - 1}{n_D^2 + 2}
\]

Where, $n_A$, $n_B$, and $n_D$ are the refractive indices of TiO$_2$, air, and bulk TiO$_2$, respectively.

Figure S2 shows refractive indices for films heated at 475°C for 0, 1, 2 and 4 hours, and Table S1 shows the calculated porosity based on the Lorentz-Lorentz equation. It is possible that some...
conversion of anatase to rutile TiO$_2$ may occur during extended heating times, in which case the calculated porosity would be lower than actual porosity due to the higher refractive index of rutile TiO$_2$. We assume that these phase transitions are negligible in these calculations.

Figure S2. Ellipsometric data of annealed TiO$_2$ films using the Cauchy model.

Table S1. Heat treatments and porosity of TiO$_2$ films

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>time (hr)</th>
<th>n(628.2)</th>
<th>Porosity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>-</td>
<td>1.82</td>
<td>29.85</td>
</tr>
<tr>
<td>475</td>
<td>1</td>
<td>1.92</td>
<td>23.86</td>
</tr>
<tr>
<td>475 2hr</td>
<td>2</td>
<td>1.91</td>
<td>24.44</td>
</tr>
<tr>
<td>475 4hr</td>
<td>4</td>
<td>1.92</td>
<td>23.86</td>
</tr>
</tbody>
</table>

Porosity of Nitrided TiO$_2$ films

The remaining oxygen concentration seen in the XPS sputtering data may be a result of the nature of nanoparticle-based films. As seen in Figure S3, porosity persists in the films even after nitridation treatment.
Figure S3. a) TiO$_2$ as spin coated b) TiO$_2$ heated at 475°C for 4 hrs in air and c) after 6 hour nitridation treatment (NH$_3$, 1000°C). Scale bars are 1 um.

*TiO$_2$ heated in air*

When TiO$_2$ is heated in air, the grain growth/transition to the rutile phase is evident in the SEM images. This behavior is not observed when heated under ammonia.
Figure S4. SEM images of a) single layer lines and b) double layer lines of TiO$_2$. Samples heated for 6 hours at 1000°C. Scale bars 3 µm.

**Discretely patterned TiO$_2$**

EDS was used to determine the elemental presence of treated and untreated TiO$_2$ samples. The TiO$_2$ lines were printed discretely, as demonstrated by the strong silicon presence in between the TiO$_2$ lines. The bright white areas in Figure S4 indicate the presence of silicon, which appears between the TiO$_2$ regions.

Figure S5. Mapping of Si on untreated TiO$_2$ patterned lines. Scale bar is 3 µm.

**AFM height of gratings**

AFM data was collected on nitrided lines, showing a height of 100 nm, as shown in Figure S6.
Figure S6. AFM height information of nitried lines