Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

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 TiO2, a small rutile peak is observed, which is not observed in the nitrided samples, suggesting the conversion of both, anatase and rutile phases to TiN.

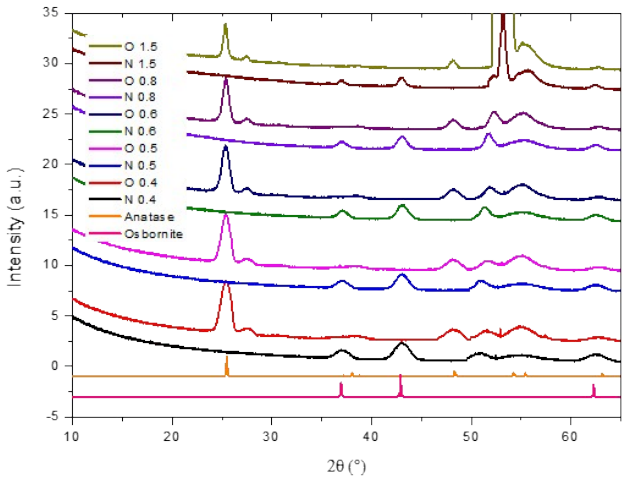

Figure S1. XRD patterns from low incidence angle scans. Un-nitrided (O) and nitrided (N) patterns are compared at angles from 0.4 to 1.5°.

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.

$$f_v = \frac{C - A}{B - A}$$

Where, $A = \frac{n_A^2 - 1}{n_A^2 + 2}$, $B = \frac{n_B^2 - 1}{n_B^2 + 2}$, and $C = \frac{n_C^2 - 1}{n_C^2 + 2}$.

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-Lorenz 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.

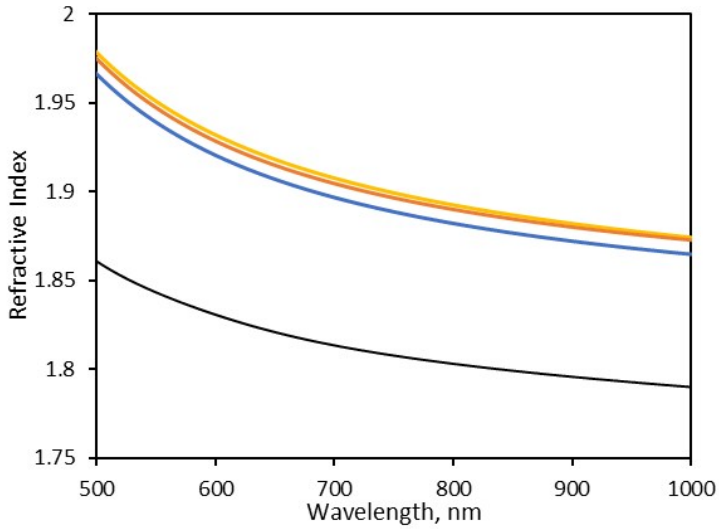

Figure S2. Elliposometric data of annealed TiO_2 films using the Cauchy model.

Table S1. Heat treatments and porosity of TiO_2 films

Temperature, ^oC	time (hr)	n(628.2)	porosity, %
RT	-	1.82	29.85
475	1	1.92	23.86
475 2hr	2	1.91	24.44
475 4hr	4	1.92	23.86

Porosity of Nitrided TiO2 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.

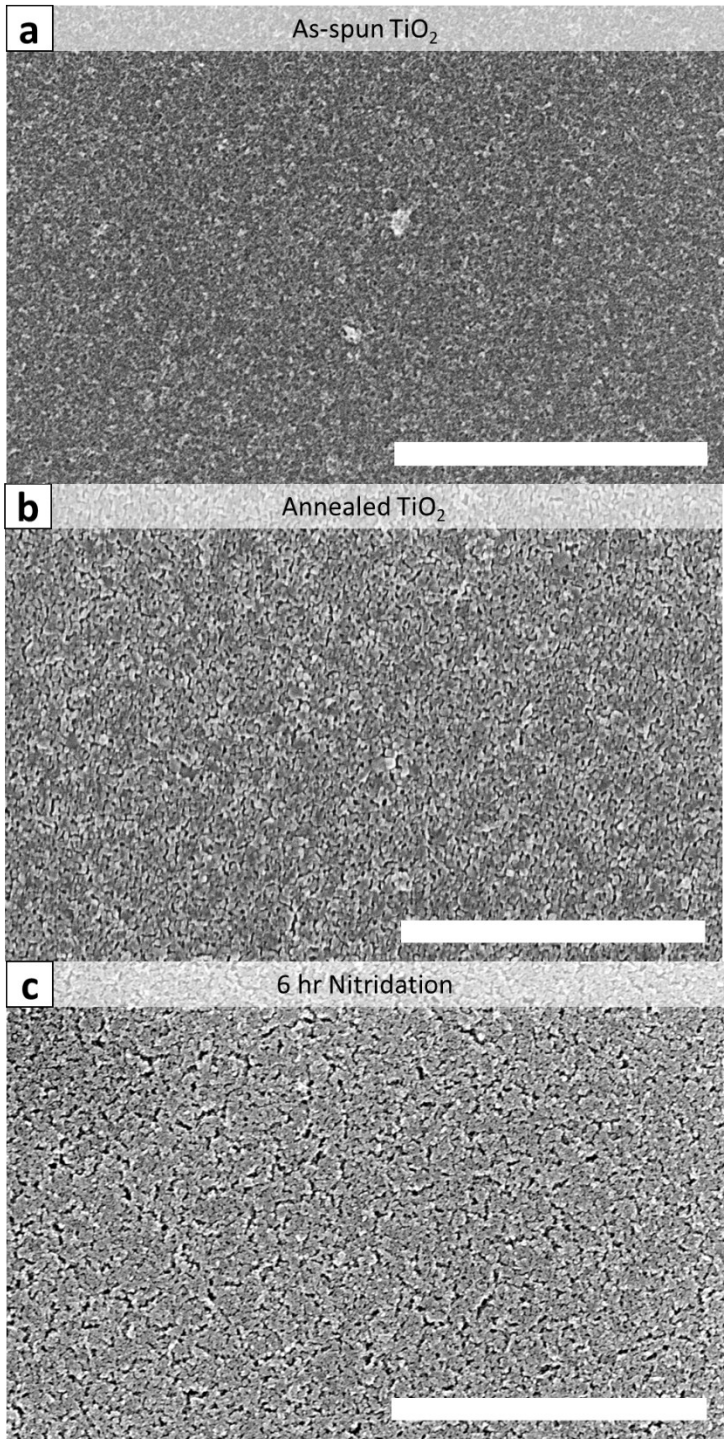

Figure S3. a) TiO_2 as spin coated b) TiO_2 heated at 475°C for 4 hrs in air and c) after 6 hour nitridation treatment (NH3, 1000°C). Scale bars are 1 um.

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.

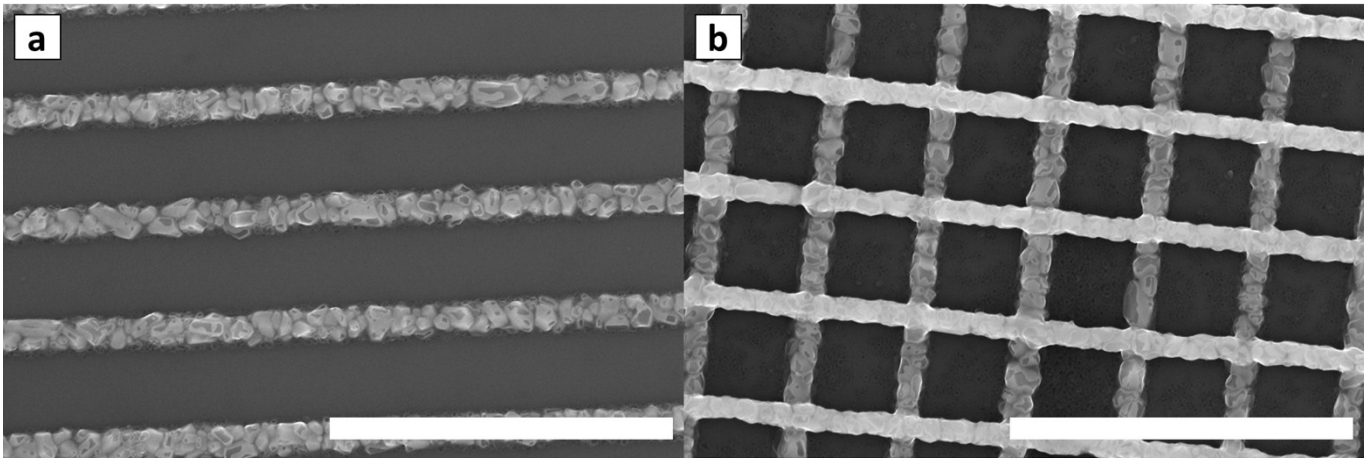

Figure S4. SEM images of a) single layer lines and b) double layer lines of TiO_2. Samples heated for 6 hours at 1000°C. Scale bars 3 µm.

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.

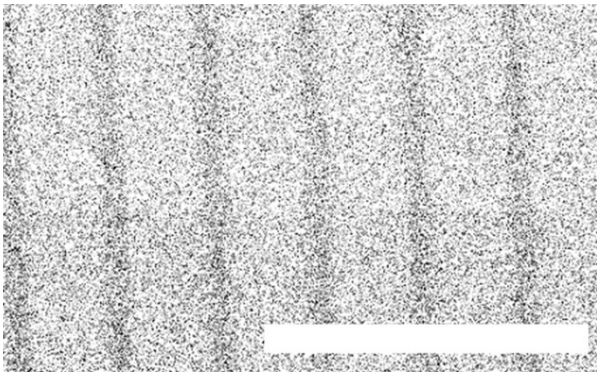

Figure S5. Mapping of Si on untreated TiO_2 patterned lines. Scale bar is 3 µm.

AFM height of gratings

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

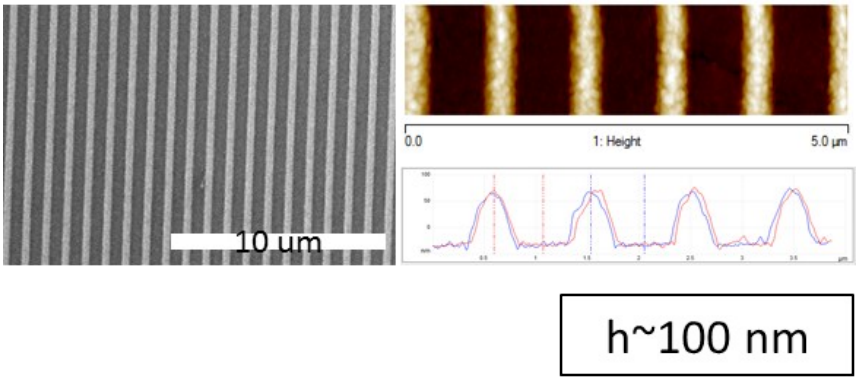

Figure S6. AFM height information of nitrided lines