

# Refractory doped titanium nitride nanoscale field emitters

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Refractory materials exhibit high damage tolerance, which is attractive for the creation of nanoscale field-emission electronics and optoelectronics applications that require operation at high peak current densities and optical intensities. Recent results have demonstrated that the optical properties of titanium nitride, a refractory and CMOS-compatible plasmonic material, can be tuned by adding silicon and oxygen dopants.<sup>1</sup> However, to fully leverage the potential of titanium (silicon oxy)nitride, a reliable and scalable fabrication process with few-nm precision is needed.

In this work,<sup>2</sup> we developed a fabrication process for producing engineered nanostructures with gaps between 10 and 15 nm, aspect ratios larger than 5 with almost 90° steep sidewalls. The nanostructures were patterned by electron beam lithography and then etched with a dry etching procedure using an Al/Cr bilayer hard mask (see Figure 1(a)). Fabrication results are shown in Figure 2(b-c). Using this process, we fabricated large-scale arrays of electrically-connected bow-tie nanoantennas with few-nm free-space gaps. We measured a typical variation of 4 nm in the average gap size. Using applied DC voltages and optical illumination, we tested the electronic and optoelectronic response of the devices, demonstrating sub-10-V tunneling operation across the free-space gaps, and quantum efficiency of up to  $1 \times 10^{-3}$  at 1.2  $\mu\text{m}$ , which is comparable to a bulk silicon photodiode at the same wavelength and three orders of magnitude higher than with nearly identical gold devices.<sup>3</sup> The results of both optical and electrical characterizations are shown in Figure 2(a-b).

Our tests demonstrated that the titanium silicon oxynitride nanostructures did not significantly degrade, exhibiting less than 5 nm of shrinking of the average gap dimensions over few- $\mu\text{m}^2$  areas after roughly 6 hours of operation (see Figure 3). Our results will be useful for developing the next generation of robust and CMOS-compatible nanoscale devices for high-speed and low-power field-emission electronics and optoelectronics applications.

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<sup>1</sup> W. A. Britton et al. *Optical Material Express*, 9, 878–891 (2019).

<sup>2</sup> A. Nardi et al. *arXiv:2011.06157* (2020).

<sup>3</sup> Y. Yang et al. *Nature Communications*, 11, 3407 (2020).

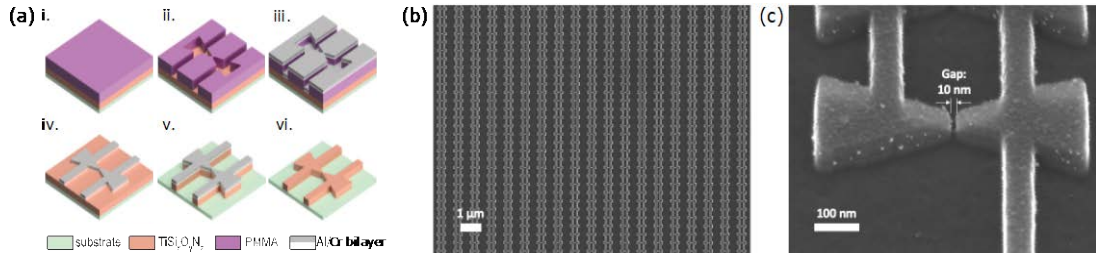


Figure 1: (a) Fabrication process for patterning doped titanium nitride nanostructures. (a.i) Spin of e-beam positive resist. (a.ii) Electron beam exposure and development. (a.iii) Evaporation of an Al/Cr bilayer hard mask. (a.iv) Resist lift-off. (a.v) Reactive ion etching of doped titanium nitride. (a.vi) Hard mask removal by wet etching. (b) Top-down scanning electron micrograph of a bow-tie nanoantenna array. (c) 45°-tilted scanning electron micrograph of a fabricated bow-tie nanoantenna.

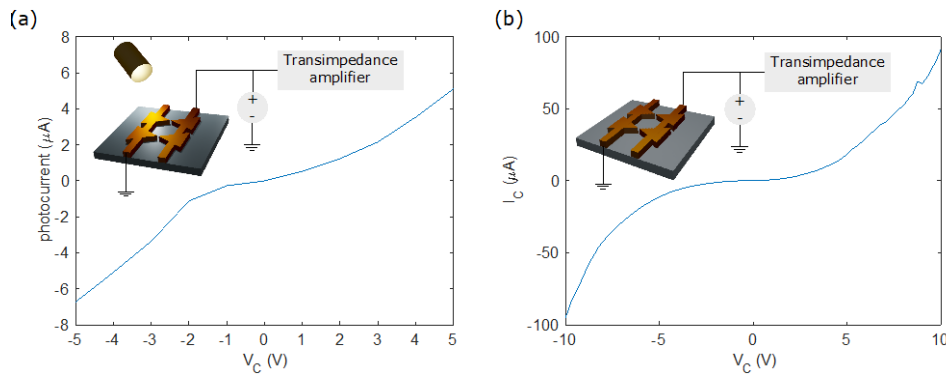


Figure 2: Optical and electrical characterization for a fabricated array composed of 2016 bow-tie nanoantennas with an average gap of 14 nm. (a) Optical I-V curve with 13 mW laser power optical excitation. The voltage sweep ranges from -5 V up to 5 V. The elliptical laser spot was roughly  $2.4 \mu\text{m} \times 5 \mu\text{m}$  full-width at half maximum at the point of interaction with the device array. Inset: experimental setup composed of a supercontinuum broadband laser, a bias voltage source, a transimpedance amplifier. (b) Electrical I-V curve. The voltage sweep ranges from -10 V up to 10 V. Inset: experimental setup composed of a bias voltage source and a transimpedance amplifier.

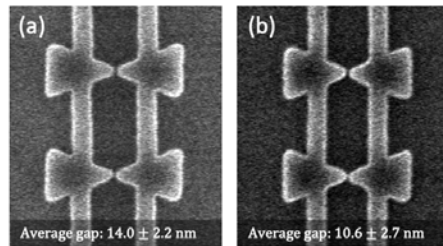


Figure 3: SEM images of the fabricated bow-tie nanostructures. Measured gap sizes were: (a) 14 nm before testing and (b) 10.6 nm after testing.

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