Supporting Information: Designing Two-Dimensional Temperature Profiles Using Tunable Thermoplasmonics

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A calibration plot based on the temperature-dependent Raman shift

Due to thermal (Boltzmann) pumping of excited vibrational levels, the lattice spacing and the lifetime of optical phonons are sensitive to temperature. This allows us to introduce intensity-, shift- and linewidth-based probes, respectively. The intensity (anti-Stokes/Stokes ratio) based probe features the most sensitive performance. However, this approach suffers from non-Boltzmann heating known as vibrational pumping.[1,2] This effect basically impacts resonant nanostructures. In the regime of vibrational pumping, the anti-Stokes/Stokes ratio

exhibits a linear dependence of the pump power for different Si pillar heights, as shown in Fig. S1, and, as a result, this leads to overestimating the temperature. The linewidth-based probe is less sensitive to temperature compared to the others, but this provides more robust results for materials under stress. Here, we will utilize the shift-based probe. For most materials, the specific Stokes peaks are red-shifted with increasing temperature. The Stokes peak shift $\Delta(T)$ as a function of T is determined as follows[3,4]

$$\Delta(T) = \Omega(T) - \Omega(T_0) = A\left(1 + \frac{2}{e^{\frac{\hbar\omega_0}{2kT}} - 1}\right) + B\left(1 + \frac{3}{e^{\frac{\hbar\omega_0}{3kT}} - 1} + \frac{3}{(e^{\frac{\hbar\omega_0}{3kT}} - 1)^2}\right) \quad \text{(S1)}$$

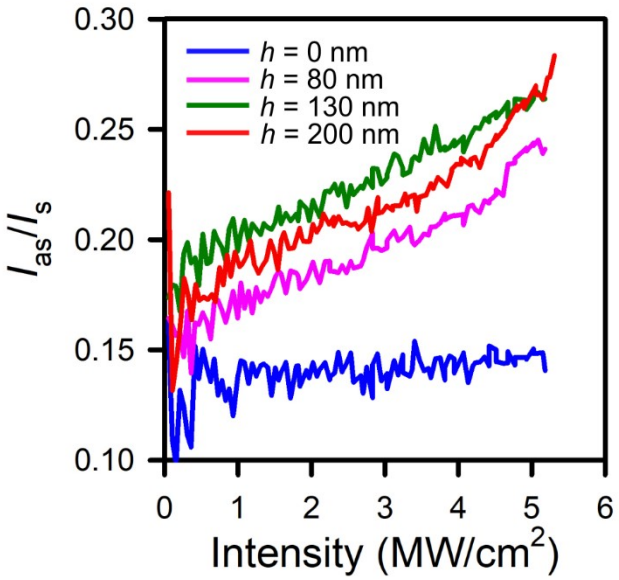

Figure S1. Dependence of an anti-Stokes and Stokes intensities ratio vs the pumping intensity for different Si pillar heights.

where A and B are constants specific to materials, ω_0 is the incident photon frequency, Ω is a phonon frequency, $\hbar$ is the Plank's constant, k_B is the Boltzmann's coefficient, T is the absolute temperature of a sample in unit of K, T_0 is equal to 0 K. For silicon, we found the

following values $A = -4.391\,\mathrm{cm}^{-1}$ and $B = -0.042\,\mathrm{cm}^{-1}$ using temperature-dependent Raman measurements in the range from 25°C to 600°C (see Fig. S2). As seen from the figure, the experimental data can be reliably fitted by a linear function within the range from 25°C to 200°C (dashed blue curve). For larger temperatures, these should be extrapolated by using Eq. S1 (solid blue curve).

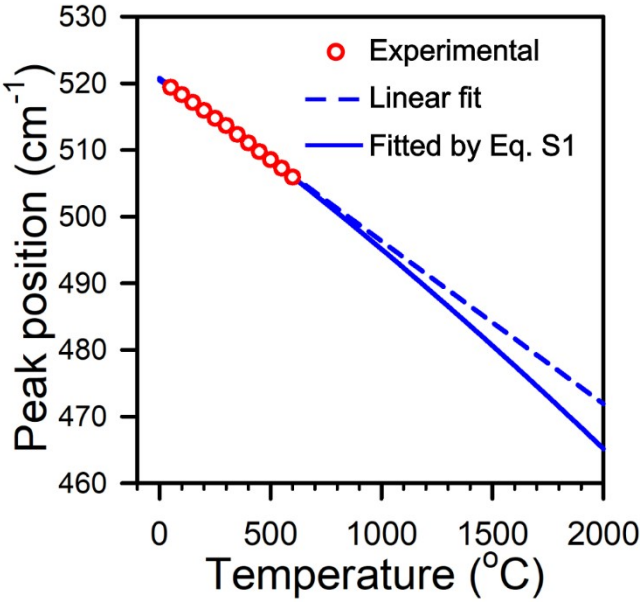

Figure S2. A plot of the peak position vs the temperature for pure silicon.

An atomic force microscopy of a 2D array of TiN:Si voxels

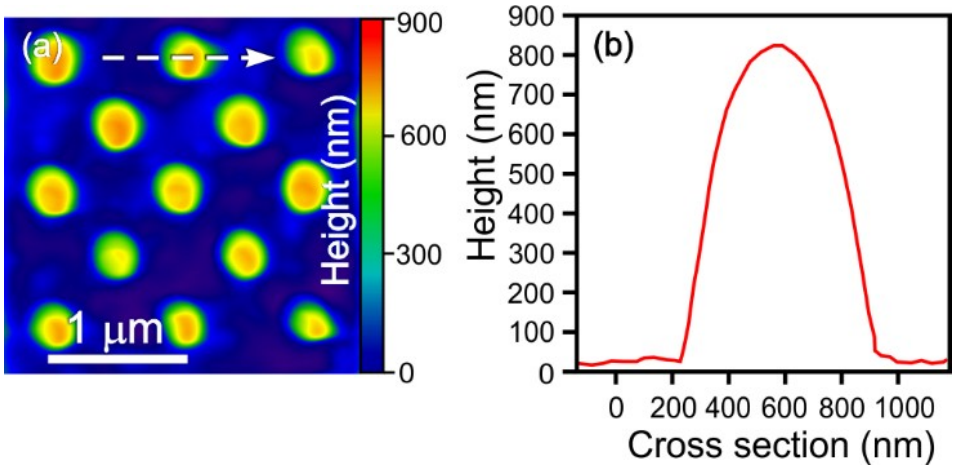

Figure S3. (a) AFM image of a 2D array of TiN:Si voxels shown in Fig. 2 (a2), and (b) its cross section along the dashed white arrow.

A truncated square-shaped TiN:Si voxel

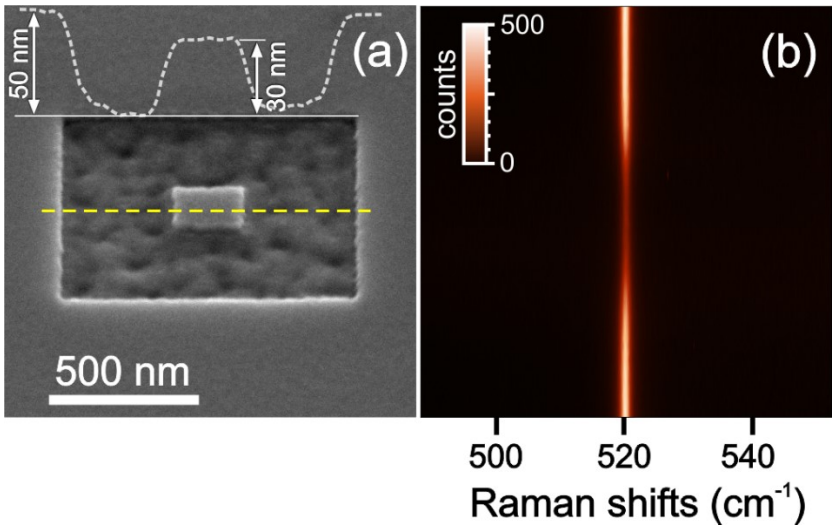

Figure S4. (a) A 52° tilted SEM image of the truncated square-shaped Si microstructure. The top inset shows an AFM cross section along the yellow dashed straight line. (b) a Raman waterfall of the microstructure along the yellow dashed straight line marked in Fig. S4 (a).

Deconvolution of a composite Raman band

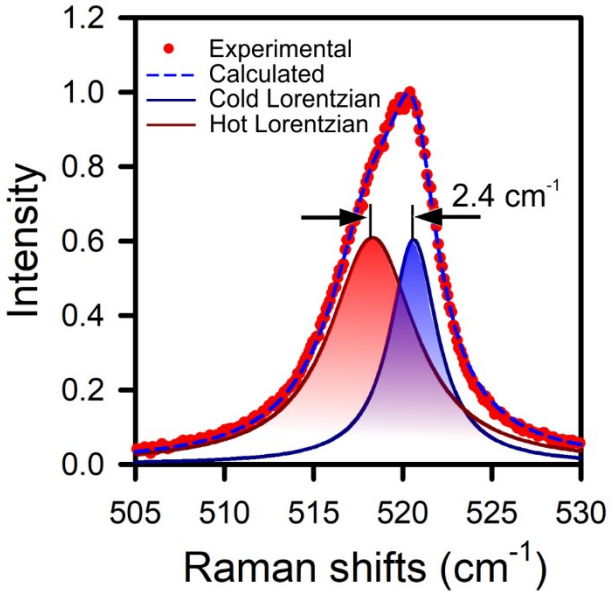

Figure S5. Deconvolution of a composite Raman band coming from a TiN:Si voxel into "hot" and "cold" Lorentzians.

A temperature kinetics of a TiN:Si voxel under cw illumination

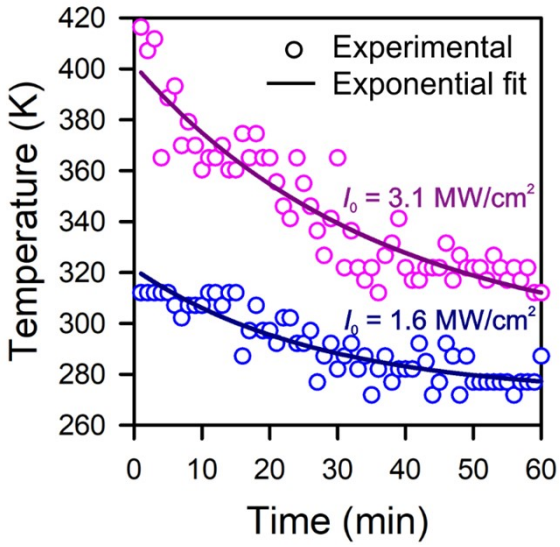

Figure S6. A temperature kinetics of a TiN:Si voxel under 633 nm laser illumination with different pump power.

Light-induced oxidation of the central TiN:Si voxel

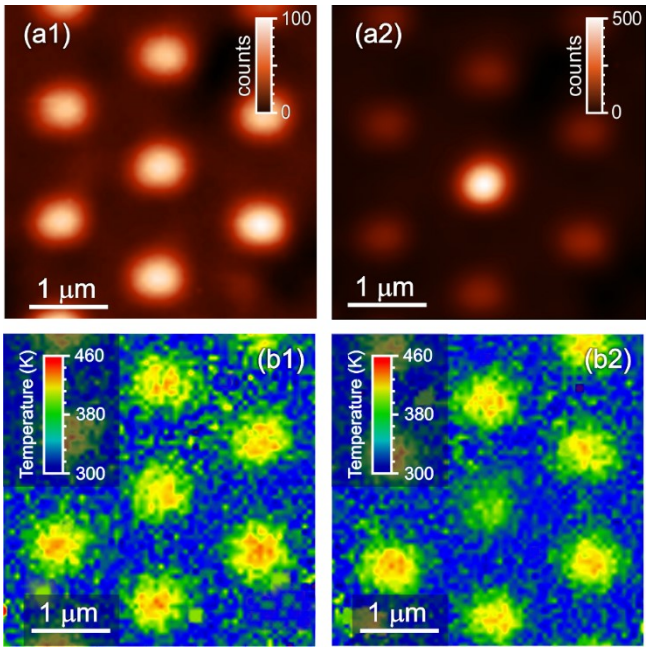

Figure S7. (a) Raman maps at 521 cm^{-1} and (b) temperatures profiles before (1) and after (2) light-assisted annealing of the central TiN:Si voxel during 2 hours at the intensity of 5 MW/cm^2.

Light-induced oxidation of a 2D array of TiN:Si voxels

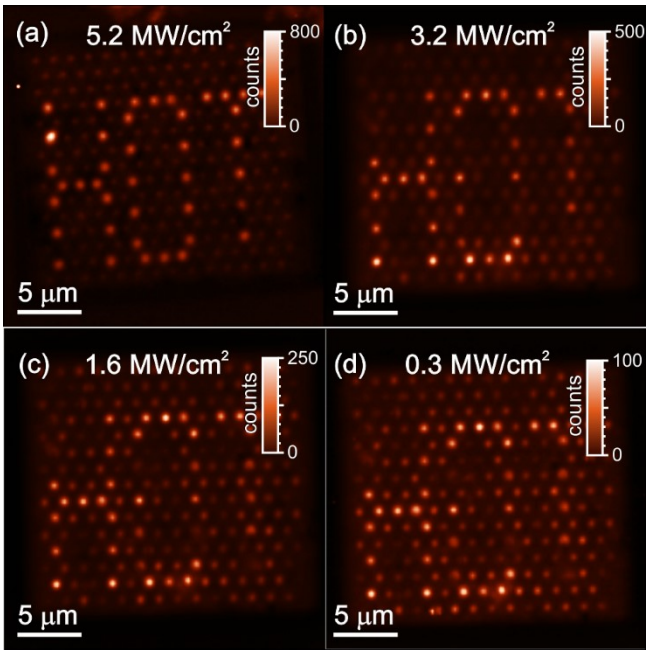

Figure S8. Raman maps of a 2D array of TiN:Si voxels with the engraved word "HOT" at different intensities.

1. H. Kang, G. H. Lee, H. Jung, J. W. Lee and Y. Nam, *ACS Nano*, 2018, **12**, 1128–1138.

NOTES AND REFERENCES

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