Supplementary Information for

Exploiting Native Al$_2$O$_3$ for Multispectral Aluminum Plasmonics

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This document consists of 11 pages including the cover page and has 11 figures.

Fabrication of NO-MIM structures using e-beam lithography
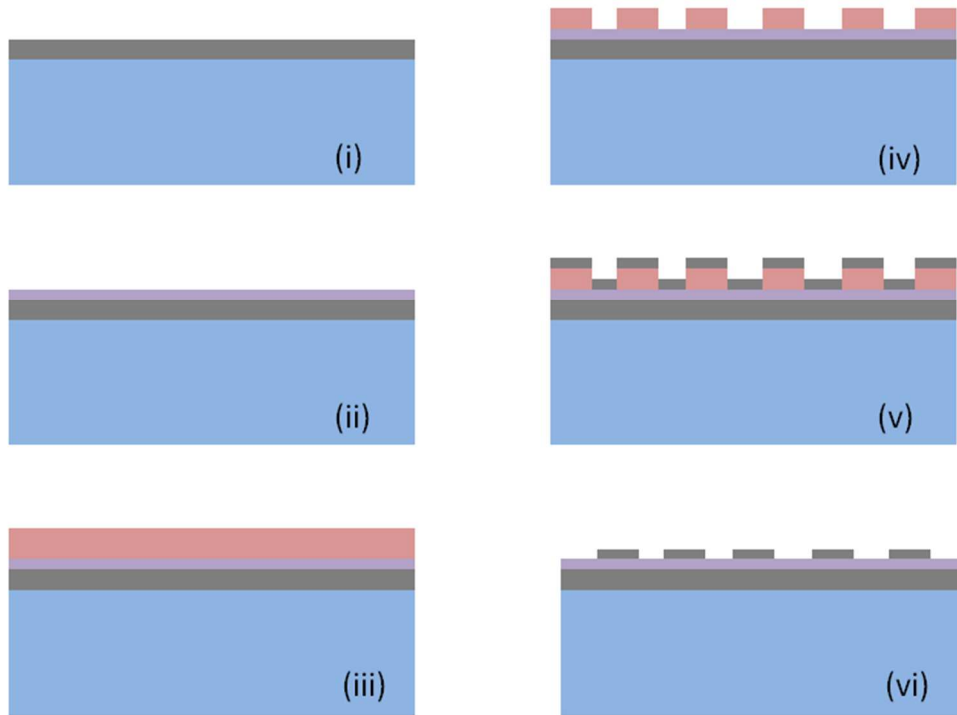

Figure S1. (i) Thermal evaporation of Al on silicon substrates. 3nm germanium is evaporated as an adhesion layer prior to Al deposition. (ii) Formation of a thin aluminum oxide (Al_2O_3) layer upon exposing the Al films to air for e-beam lithography. (iii) ~100nm PMMA is spin coated and annealed at 180˚C for 120 seconds. (iv) Patterns are formed using e-beam lithography. (v) 50nm of Al or Ag is evaporated. (vi) Lift-off process to form the final structures.

Characterization of the Native Oxide Layer Using XPS

We measured the samples immediately after Al deposition (in 15min) to minimize the samples exposure to air. Native oxide thickness is calculated using [1]:

$$d_{oxide} = \lambda_0 \sin\theta \ln\left(\frac{N_m \lambda_m I_0}{N_0 \lambda_0 I_m} + 1\right)$$

N is the volume density, λ is the inelastic mean free path of electrons and I is the intensity of fit curves to the experimental results. Subscripts "m" and "o" refer to metal and oxide, respectively. θ is the takeoff angle of photoelectrons from the surface. For our XPS system θ=90. For Al, $\frac{N_m}{N_0} = 1.5$ and λ_m=2.8, λ_0=2.6. The evolution of oxide thickness over 24 days is shown in Figure S2. The high energy shoulder which corresponds to the oxide peak increases over time. The native oxide thickness is found to be 2.4nm 15min after deposition and increases to 3nm after 24 days of exposure to air.
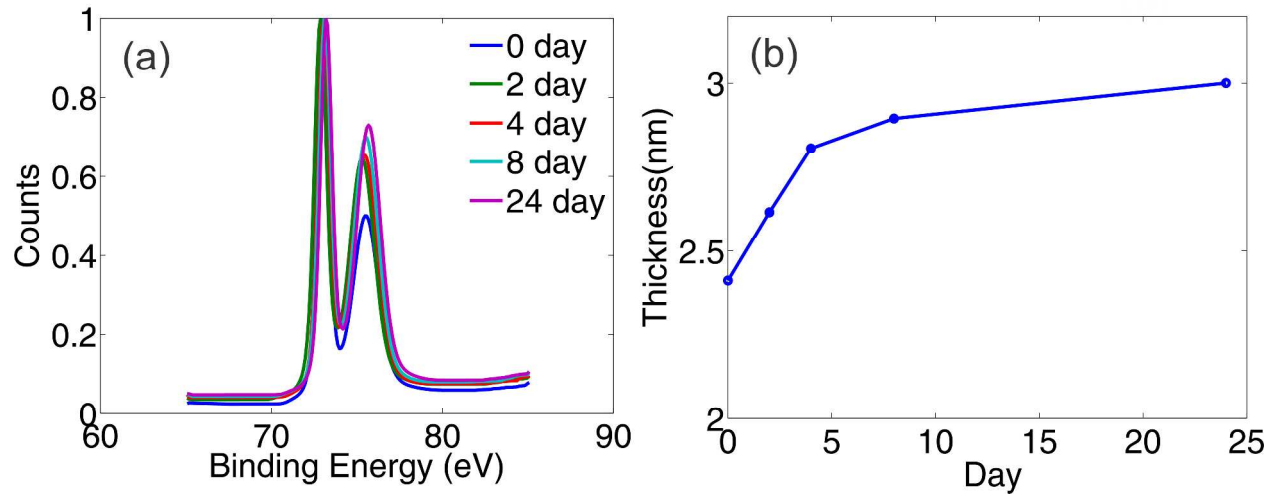

Figure S2. Characterization of the native oxide thickness over a time span of 24 days using XPS. (a) XPS spectrum of an aluminum film. High energy shoulder corresponds to the aluminum oxide peak. (b) Evolution of the calculated native oxide thicknesses.
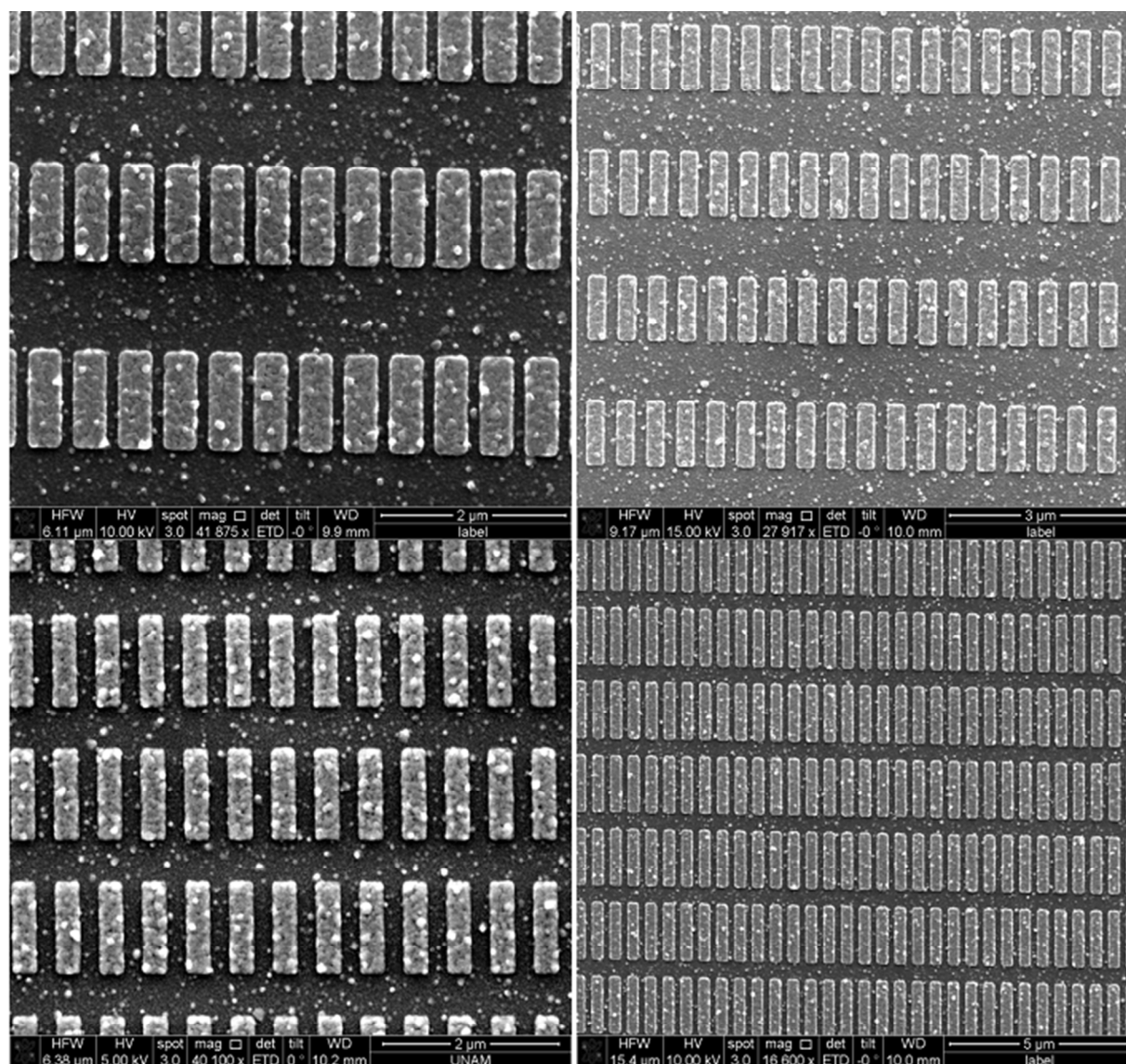
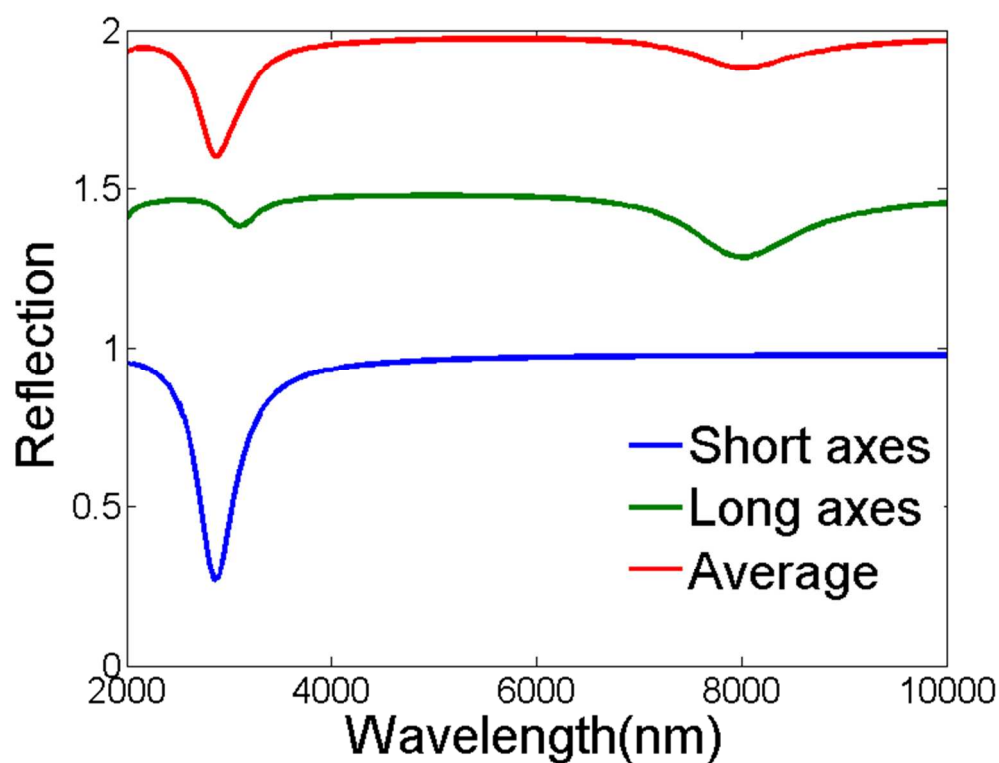Figure S3. SEM images of 2D NO-MIM structures with periods in x and y directions: P_x=500nm and P_y=2000nm.

Figure S4. Simulations of 2D NO-MIM structures. 2D simulations are performed for electric field polarization along the short period axis (P_x=500nm) (blue curve) and the long period axis (P_y=2000nm) (green curve). Overall reflection is calculated by averaging these two curves (red curve).
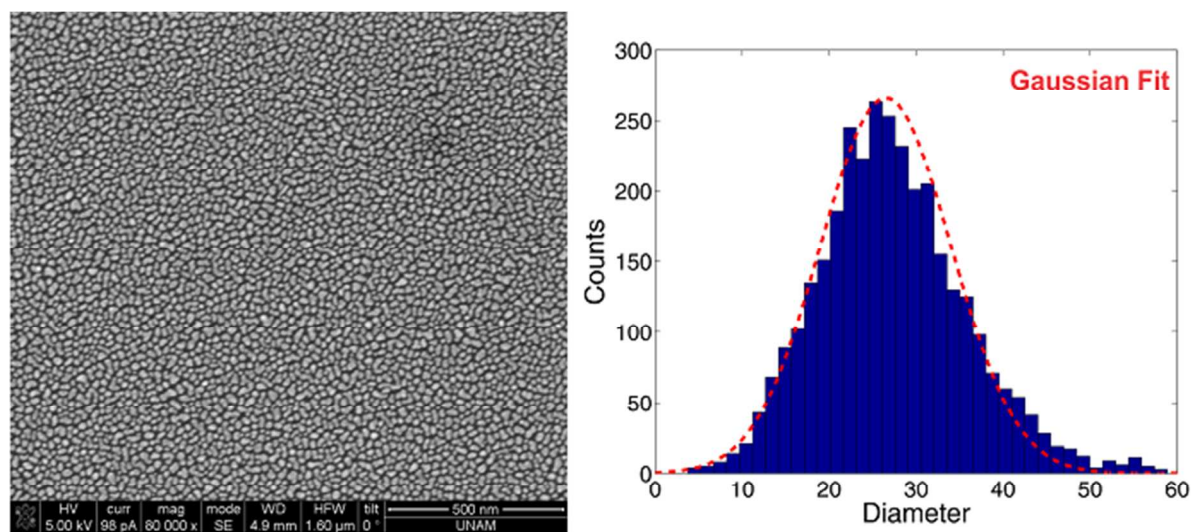

Figure S5. SEM images of Ag nanoparticles on silicon and their size distribution.
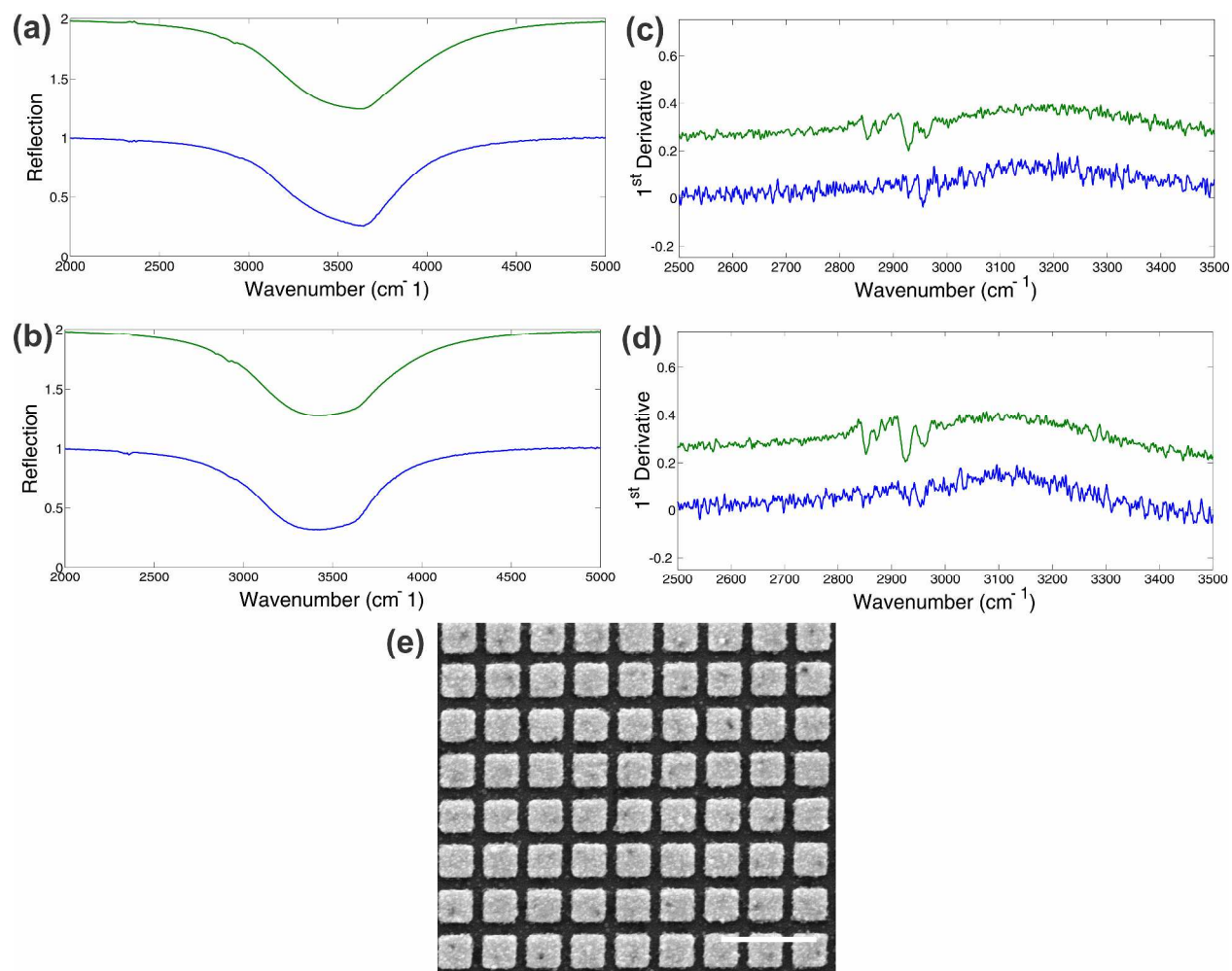
Figure S6. SEIRA on NO-MIM structures with patterned Ag top layer fabricated by e-beam lithography. Reflection spectra of these structures before (blue) and after (green) DDT monolayer formation for (a) $W_{x,y}$=300nm and (b) $W_{x,y}$=350nm. Periods along x and y directions are the same (P_x=P_y=50nm). (c) and (d) First derivative of the reflection spectra in (a) and (b), respectively. Molecular signatures of PMMA and DDT are more visible in the first derivative curves in (c) and (d) compared to the reflection spectra in (a) and (b). (e) An SEM image of the fabricated structures (Scale bar: 1 μm).

Calculation the SEIRA enhancement factor

Although calculation of the number molecules that contribute to the SEIRA signal for hierarchical NO-MIM structures is challenging; it is easier for NO-MIM structures with patterned Ag top layer due to the selective binding of DDT to Ag. We assume that only the molecules on the sidewall of Ag patches contribute to SEIRA signal. Assuming closely packed DDT molecules with $0.2nm^2$ coverage area, the total number of molecules per resonator which contribute to the SEIRA signal is calculated as 70000. The total measurement area of the NO-MIM structures is 100x100 μm^2 and the periods along both axes are 500nm. Hence, the total number of resonators used per measurement is 40000. Therefore, the total number of contributing DDT molecules is calculated as $2.8x10^9$ which is $\sim 4.610^{-15}$ moles (4.6 femtomoles). Reference measurements are performed on a bare Ag mirror under grazing angle illumination using a grazing angle objective. SEIRA enhancement is defined as the ratio of the average absorption signal per molecule absorbed on the NO-MIM surface to the average absorption signal per molecule on the bare Ag mirror [2]. The area measured with the grazing angle objective is ellipsoidal with 450μm short and 1800μm long axes. The reflection spectrum of the monolayer DDT is shown in Figure S7a. After background subtraction the reflection spectrum of the NO-MIM structures with Ag top layer, we obtained the reflection spectrum of the monolayer DDT as shown in Figure S7b. We choose C-H stretching at 2930cm^{-1} to calculate the SEIRA enhancement factor which is estimated to be ~2200.
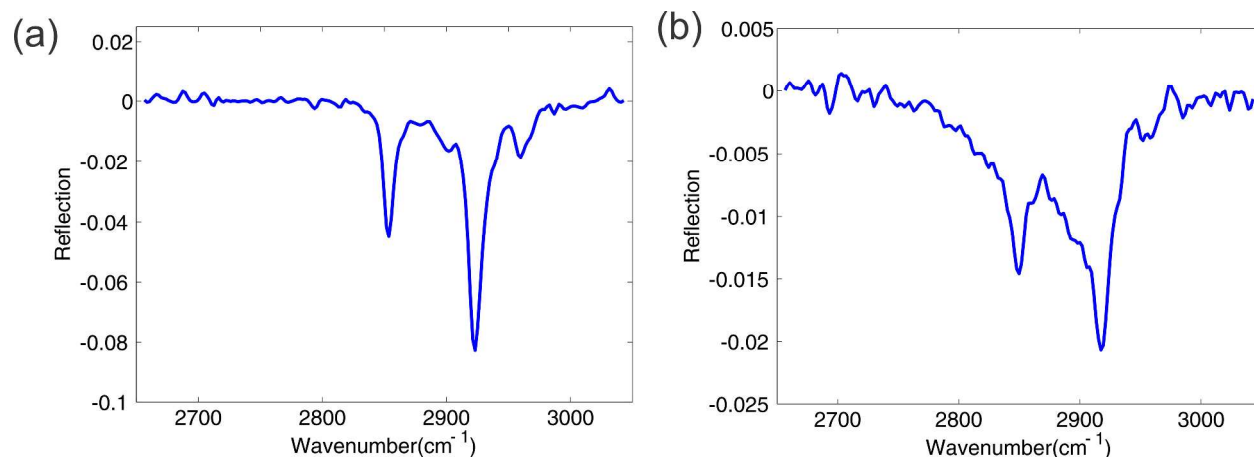

Figure S7. (a) Infrared reflection spectrum of the monolayer DDT on bare Ag mirror measured under Grazing Angle Illumination after background subtraction. (b) Infrared reflection of the monolayer DDT on the NO-MIM structures with Ag top layer after background subtraction.

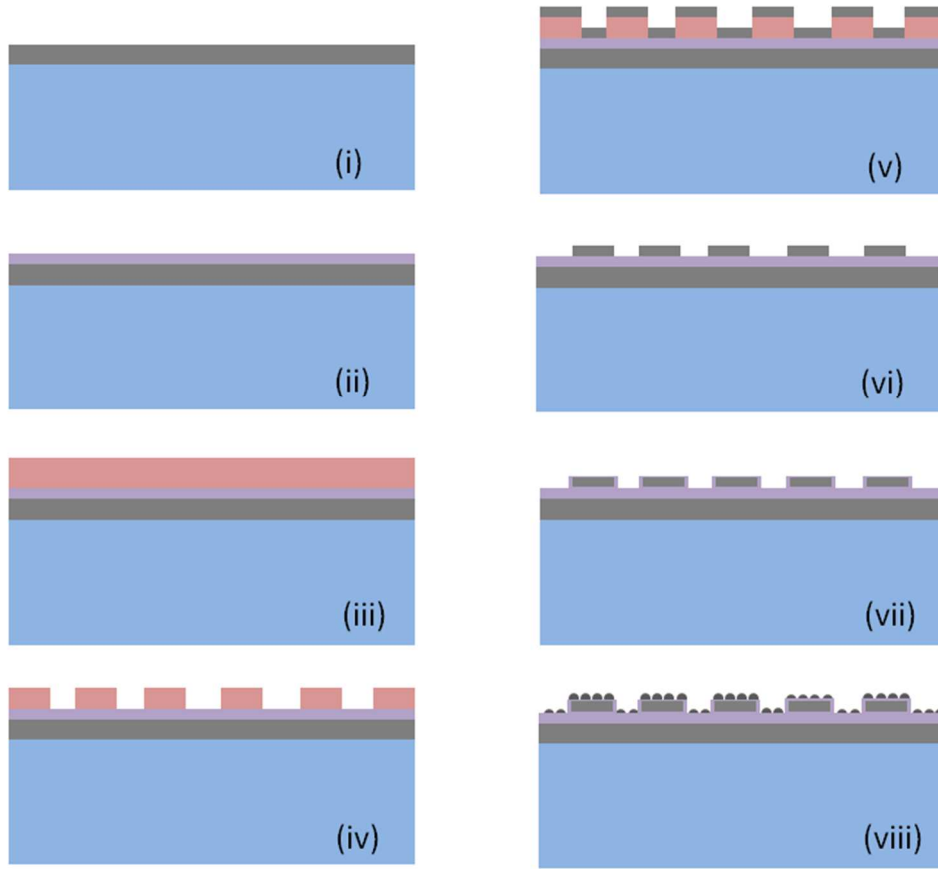**Fabrication of the hierarchical NO-MIM structures**

Figure S8. (i) Thermal evaporation of Al on silicon substrates. 3nm germanium is evaporated as an adhesion layer prior to Al deposition. (ii) Formation of a thin aluminum oxide (Al_2O_3) layer upon exposing the Al films to air for e-beam lithography. (iii) ~100nm PMMA is spin coated and annealed at 180˚C for 120 seconds. (iv) Patterns are formed using e-beam lithography. (v) 50nm of Al is evaporated. (vi) Lift-off process to form all Al MIM structures. (vii) O_2 plasma cleaning for PMMA residue removal and formation of a thin oxide film on the top Al structures. (viii) Formation of Ag nanoparticles through evaporation of 3nm Ag film.
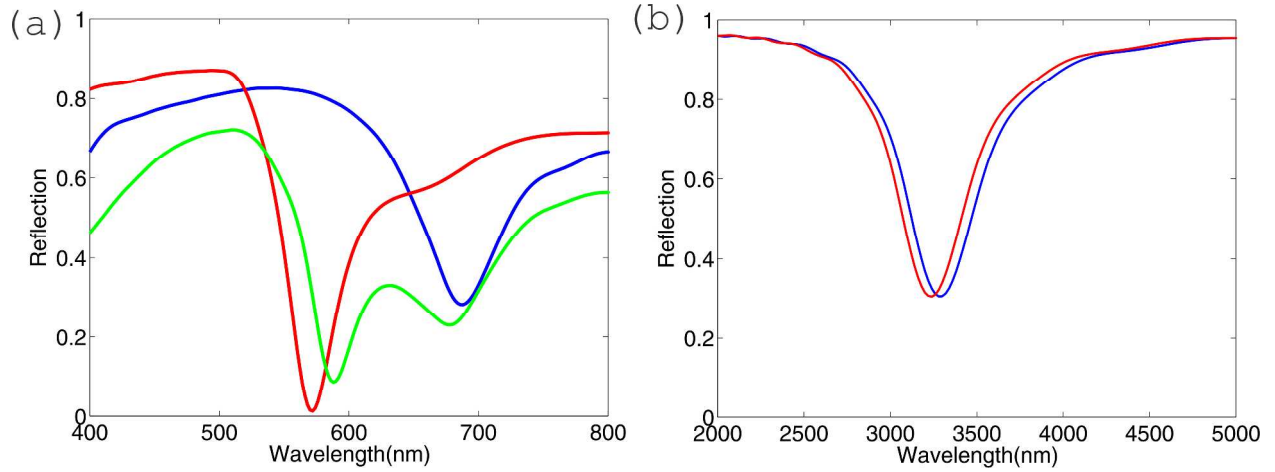
Figure S9. (a) Reflectance spectra for the Ag nanoparticles-based NO-MIM (blue), all Al NO-MIM (red) and hierarchical NO-MIM (green) surfaces in the visible regime. (b) Reflectance spectra for the all Al NO-MIM and hierarchical NO-MIM (red) surfaces in the MIR regime.
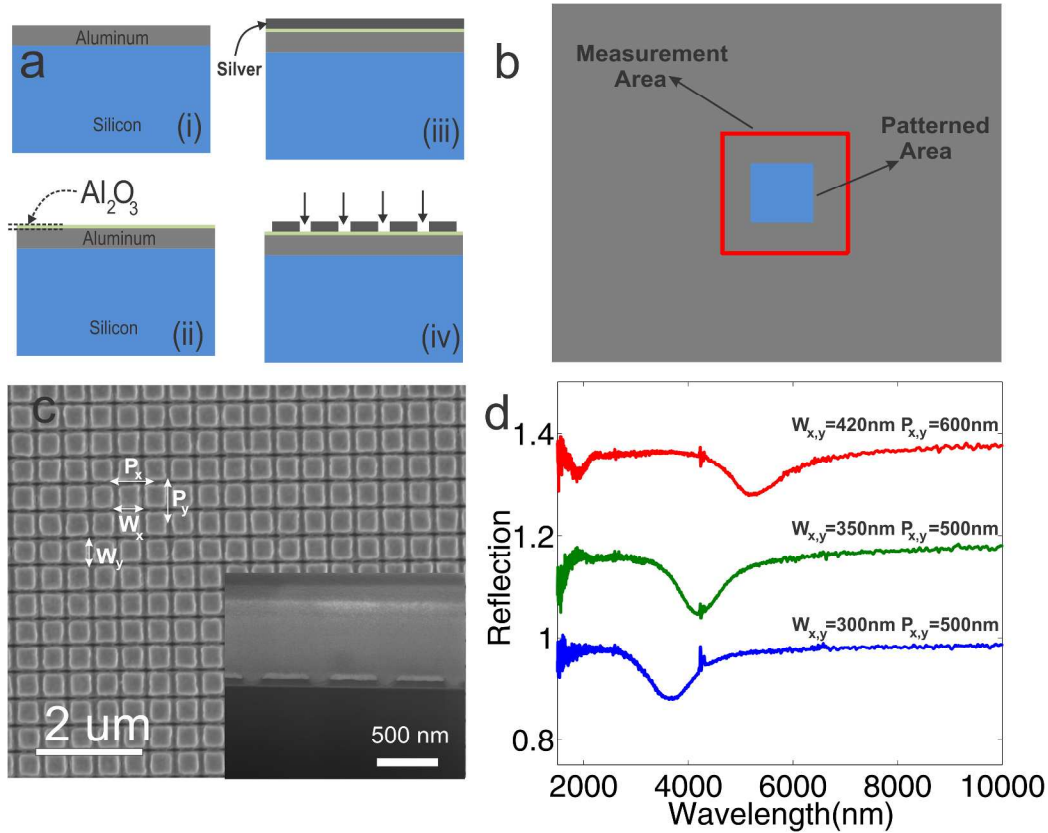

Figure S10. Characterization of NO-MIM structures fabricated using Focused Ion Beam (FIB) milling. (a) Fabrication steps for NOMIM structures: (i) Thermal evaporation of 100nm of Al on silicon substrates, (ii) formation of a thin aluminum oxide (Al_2O_3) layer upon exposing the Al films to air, (iii) thermal evaporation of 50nm of Ag, (iv) FIB patterning of the top Ag layer. (b) The measured (100μm x 100μm) area with respect to the fabricated area (50μm x 50μm). (c) Top-view and cross-section (inset) SEM images of the FIB fabricated surfaces. (d) Reflectance spectra for the FIB fabricated surfaces with shown widths and periods. Reflection spectra is shifted in y-axis direction.
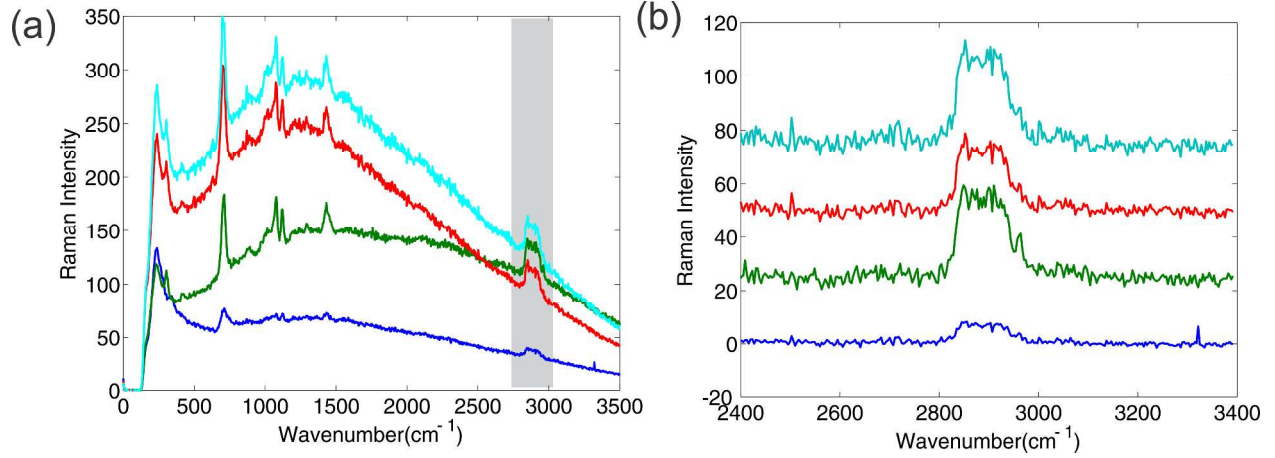
Figure S11. (a) Raman spectra of monolayer DDT on bare Ag (blue), on Ag nanoparticles on glass (green), on Ag nanoparticles-based NO-MIM (red) and hierarchical NO-MIM (cyan) surfaces. C-H stretching band that is used for the calculation of the SERS enhancement factor is shaded. (b) Raman spectra after background subtraction from the shaded region in (a). Raman intensities are shifted in y-axis direction for better visualization.

Calculating the SERS Enhancement Factor

The SERS enhancement factor is given by $EF = \frac{I_{SERS}/N_{SERS}}{I_{REF}/N_{REF}}$. I_{SERS} and I_{REF} are the Raman intensities corresponding to SERS and reference Raman experiments, respectively. N_{SERS} and N_{REF} are the number of molecules contributing to SERS and reference Raman experiments, respectively. We used the same intensities and integration time for both experiments. We used 20x objective with a spot size of 800nm. To find the enhancement factor we used the broad C-H stretching around 2900 cm^{-1}. N_{REF} can be calculated using the formula $N_{REF} = \frac{\pi R_{spot}^2}{A_{DDT}}$ where A_{DDT}=0.2nm^2 and R_{spot} =400nm. Hence, N_{REF} is estimated to be 2.5x10^6. To calculate N_{SERS} , we assume only one Ag nanoparticle contributes to the SERS signal. To calculate the number of molecules per nanoparticle, Ag nanoparticles are assumed to be cylinders with 15nm height and 25nm diameter which results in 8.3x10^3 for the number of molecules per Ag nanoparticle. After background subtraction, the signal intensities for SERS and reference Raman experiments are found as $I_{SERS} \cong 40$ and $I_{REF} \cong 8$ as shown in Figure S11b. Thus, we estimate the SERS enhancement factor to be EF =1000.

References

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3. Jan Kischkat, Sven Peters, Bernd Gruska, Mykhaylo Semtsiv, Mikaela Chashnikova, Matthias Klinkmüller, Oliana Fedosenko, Stephan Machulik, Anna Aleksandrova, Gregorii Monastyrskyi, Yuri Flores, and W. Ted Masselink, "Mid-infrared optical properties of thin films of aluminum oxide, titanium dioxide, silicon dioxide, aluminum nitride, and silicon nitride," Appl. Opt. **51**, 6789-6798 (2012)