Electronic Supplementary Material

Molecular Sentinel-on-Chip for SERS-Based Biosensing†

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SUPPLEMENTARY NOTE 1: FINITE DIFFERENCE TIME DOMAIN (FDTD) CALCULATIONS

Numerical electromagnetic (EM) field calculations - using the Finite Difference Time Domain (FDTD) method - were performed in order to determine enhancement of the EM fields in the narrow nano-gaps between the triangle shaped nanowires. In our FDTD calculations, continuous plane waves (having polarization of the electric field being in the TM and TE directions) were incident normally on the gold nanowire structures. The nanostructures that we simulated were similar to the nanowire structures that were experimentally fabricated by us (See TEM cross-sections of the fabricated nanowire structures in Fig. 2 of the main paper). FDTD software called Fullwave 6.0 was employed for carrying out the Finite Difference Time Domain (FDTD). In the two dimensional FDTD calculations performed by us, we employed an extended Debye dispersion relation model for determining the dielectric constant for gold and silver (*S1-S4*):

$$\varepsilon(\omega) = 1 + \sum_{k=1}^{6} \frac{\Delta\varepsilon_k}{-a_k\omega^2 - ib_k\omega + c_k} \qquad (1)$$

where $\Delta\varepsilon_k$, a_k, b_k *and* c_k are constants. The following values of $\Delta\varepsilon_k$, a_k, b_k, and c_k for gold were employed in our work - $\Delta\varepsilon_1$: 1589.516, $\Delta\varepsilon_2$: 50.19525, $\Delta\varepsilon_3$: 20.91469, $\Delta\varepsilon_4$: 148.4943, $\Delta\varepsilon_5$: 1256.973, $\Delta\varepsilon_6$: 9169; a_1: 1, a_2: 1, a_3: 1, a_4: 1, a_5: 1, a_6: 1; b_1: 0.268419, b_2: 1.220548, b_3: 1.747258, b_4: 4.406129, b_5: 12.63, b_6: 11.21284; c_1: 0, c_2: 4.417455, c_3: 17.66982, c_4: 226.0978, c_5: 475.1387, c_6: 4550.765. We employed perfectly matched layers (PML) having a reflection coefficient $\Gamma=10^{-8}$ and a grid size of 1nm were employed in our calculations. Each

FDTD simulation was run for long enough time duration to ensure that the system reached a steady state while employing a simulation time step $c\Delta t$ = 1nm ('c' being the speed of light) to satisfy the Courant stability criterion (*S2*) at this resolution.

SUPPLEMENTARY NOTE 2: REFLECTANCE SPECTRA OF PERIODIC GOLD-COATED NANOWIRES

We employed the software DiffractMOD 3.2 to carry out Rigorous Coupled Wave Analysis (RCWA) calculations in order to obtain the reflection spectra from the plasmonics-active nanowires (TNWs). In the RCWA calculations, the dispersion relation of plasmonics-active metals such as gold and silver was modeled using an extended Debye model. In these simulations, the height '*H*' of gold-coated inverted triangle-shaped nanowires was taken as ~ 475 nm and the periodicity was varied between 200 nm and 300 nm.

By selecting the correct dimensional parameters – the periodicity 'P' as well as the height 'H' of the TNWs – one can match the plasmon resonance wavelengths in the reflection spectra of the nanowires with the wavelength (633 nm) of the incident laser employed (indicated by the dashed red line in Fig. 3C of the main paper) in our SERS measurements. One can observe that as we change the periodicity 'P' from 240 nm to 260 nm, the plasmon resonance dip in the reflection spectrum around 635 nm shifts slightly, although there are more significant shifts in the peak located around 780 nm. Hence, employing a periodicity in the range of 240-260 nm allows coupling the incident radiation at 633 nm (laser line wavelength) into plasmons. Moreover, the multiple dips in the reflection spectra indicate that the different structures (with different periodicities) can be employed for SERS measurements using excitation lasers at different wavelengths. In both FDTD and RCWA simulations, the height '*H*' of gold-coated inverted triangle-shaped nanowires was taken as ~ 475 nm. The effect of varying the refractive index of the medium surrounding the gold-coated nanowires is shown in Fig. 3D of the main paper. The Rigorous Coupled Wave Analysis (RCWA) simulations in Fig. 3D of the main paper show that the dips in the reflectance spectra have a red-shift on increasing the refractive index *n* of the media surrounding the gold-coated inverted triangle-shaped nanowires, indicating that these dips in the reflectance spectra are due to excitation of surface plasmons in the gold-coated triangle-shaped nanowires (when TM polarized light is incident on the nanowires). Moreover, there is no dip in the reflectance spectra when TE polarized light is incident on the periodic gold-coated nanowires, for the different periodicities P and refractive indices *n*.

Figure S-1 shows the RCWA simulated reflectance spectra for TE polarization (Fig. S-1a), TM polarization (Fig. S-1b), and the ratio of the reflectances for TM and TE polarizations respectively (Fig. S-1c) when the refractive index of the media surrounding the gold-coated triangular-shaped nanowires was 1.33. Similarly, Figs. S-2 and S-3 show the reflectance spectra for the TE, TM, and the ratio of the TM and TE polarizations when the refractive indices of the media surrounding the nanowires are 1.36 (Fig. S-2) and 1.40 (Fig. S-3). One can observe from Figs. S-1, S-2, and S-3 that the dips in the reflectance spectra are present only when TM polarized light is incident on the periodic gold-coated nanowires and not when TE polarized light is incident on the nanowires. Figure S-4 shows that the dips in the reflectance spectra have a red-shift on increasing the refractive index 'n' of the media surrounding the gold-coated inverted triangle-shaped nanowires for TM polarization (Fig. S-4a) and ratio of TM and TE polarizations (Fig. S-4b). Figure S-5 shows the effect of varying the periodicity of Au-coated silicon nanowires on the reflectance spectra for TM polarization of the incident radiation (Fig. S-5a) and the ratio of TM and TE polarizations (Fig. S-5b). In both Fig. S-4b and Fig. S-5b, one can observe very distinct plasmon resonance related dips in the reflection spectra when the ratio of the reflectance spectra for the TM and TE polarizations is taken as compared to the reflection spectra for only TM polarization of the incident radiation.

SUPPLEMENTARY NOTE 3: TEM IMAGES OF THE NANOWIRES

We obtained TEM cross-sectional images of the Au-coated nanowires by employing a Hitachi HF2000 is a 200kV Cold Field Emission Transmission Electron microscope (TEM). The TEM cross-sections were prepared by employing Focused ion beam (FIB) milling (using FEI Quanta 3D FEG). Figures S-6A, S-6B and S-6C show TEM images of one-dimensional arrays of Au-coated silicon nanowires for 120 nm electron beam deposition of gold on top of the nanowires.

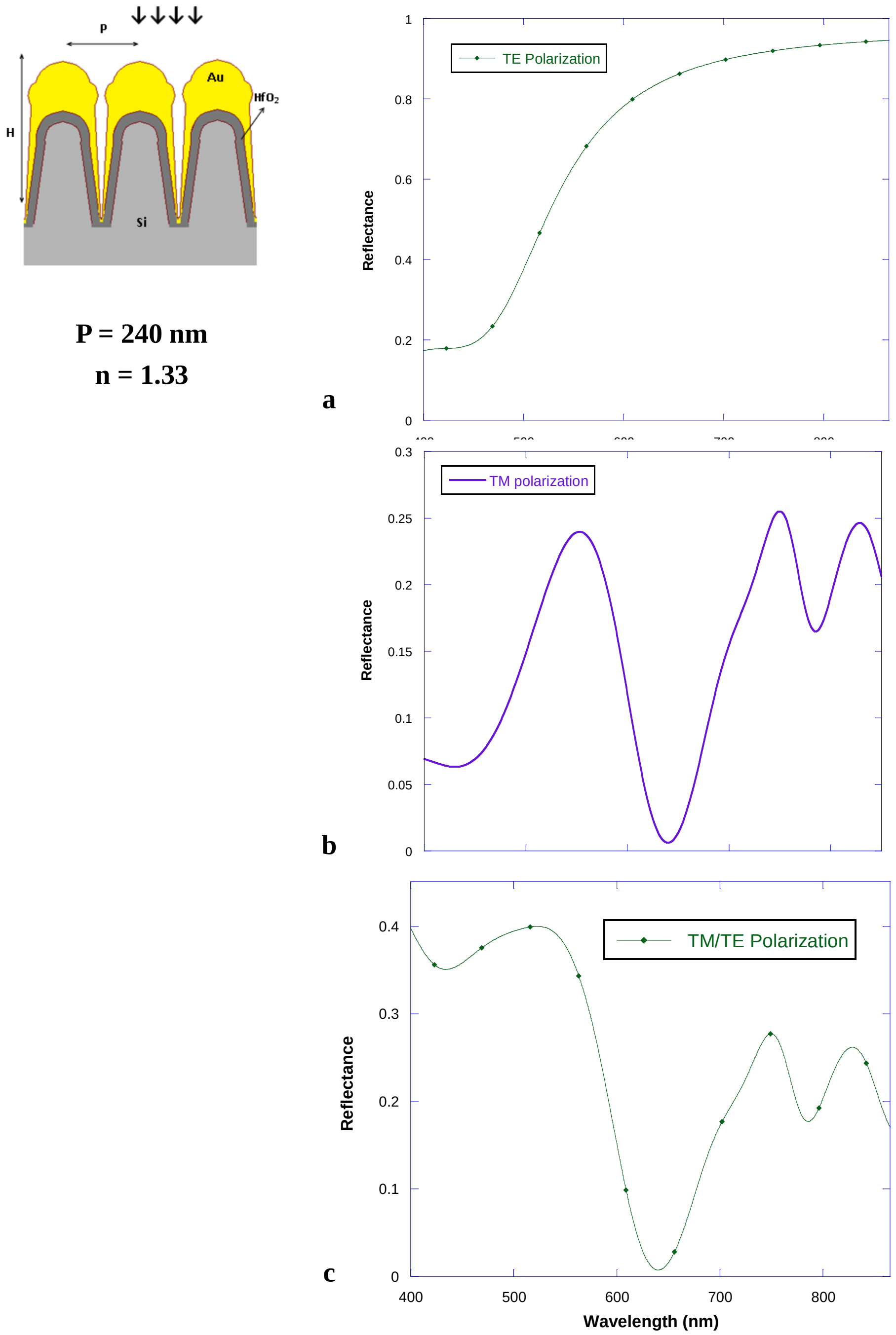


Figure S-1. Gold-coated triangular shaped nanowires with 120 nm gold deposited on top of the nanowires for (a) TE polarization, (b) TM polarization, and (c) ratio of TM and TE polarizations. The Refractive index of the surrounding media (n) was taken as 1.33.

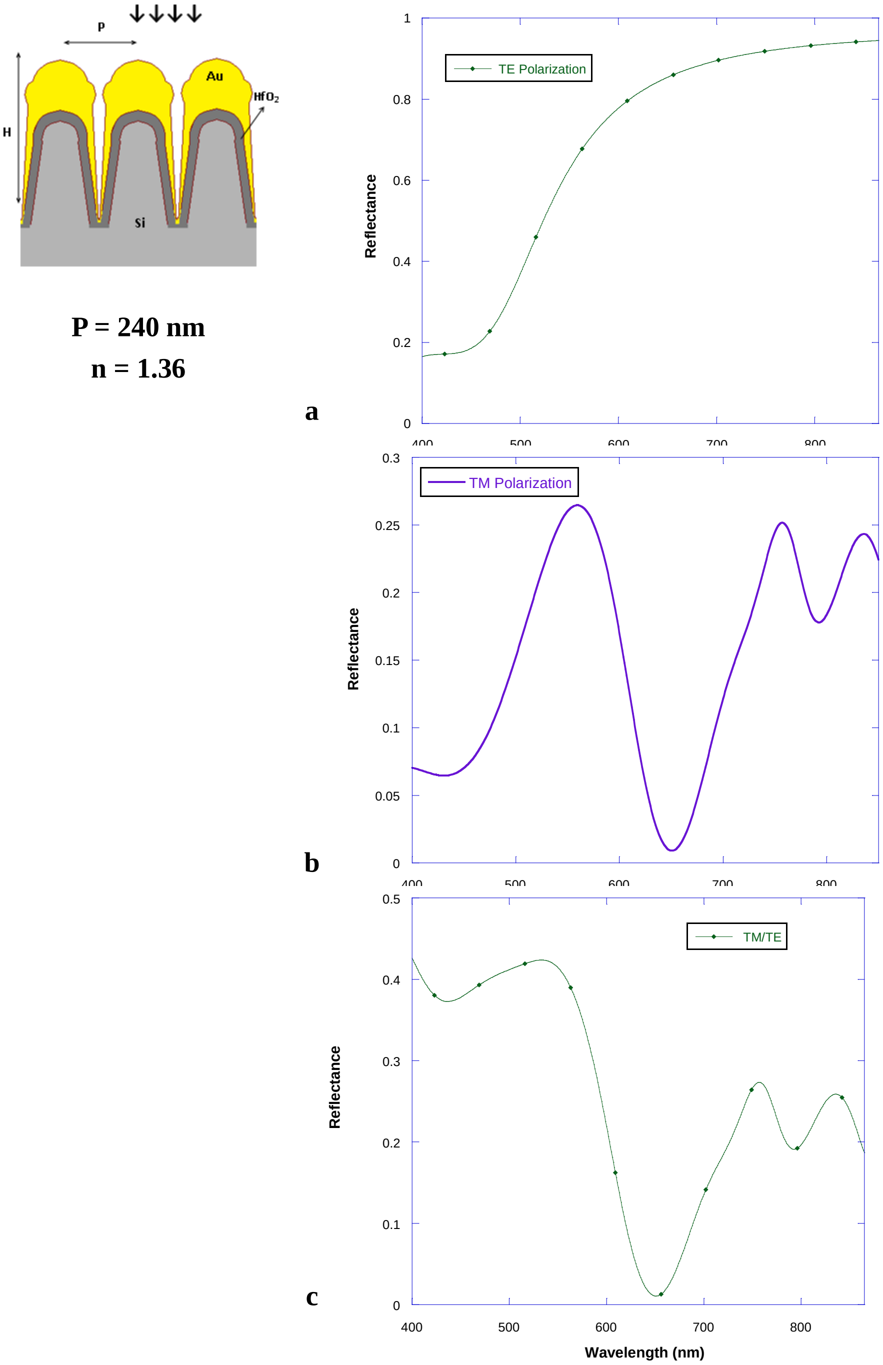


Figure S-2. Gold-coated triangular shaped nanowires with 120 nm gold deposited on top of the nanowires for (a) TE polarization, (b) TM polarization, and (c) ratio of TM and TE polarizations. The Refractive index of the surrounding media (n) was taken as 1.36.

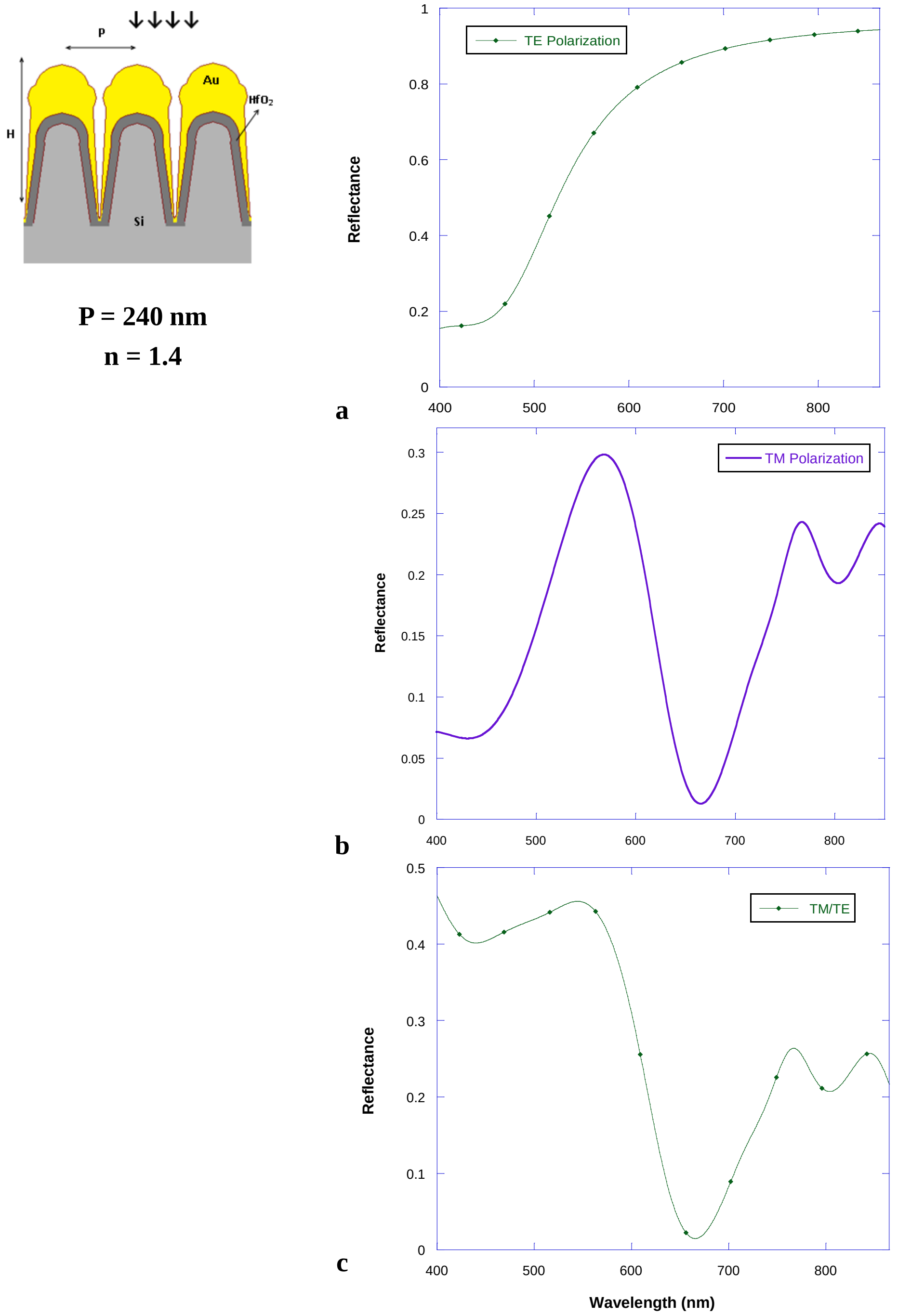
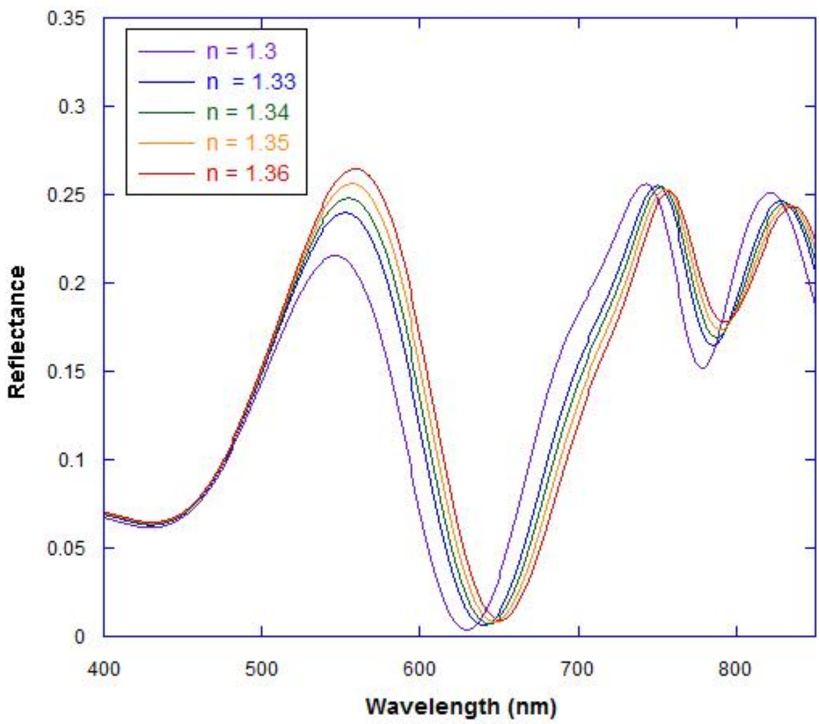
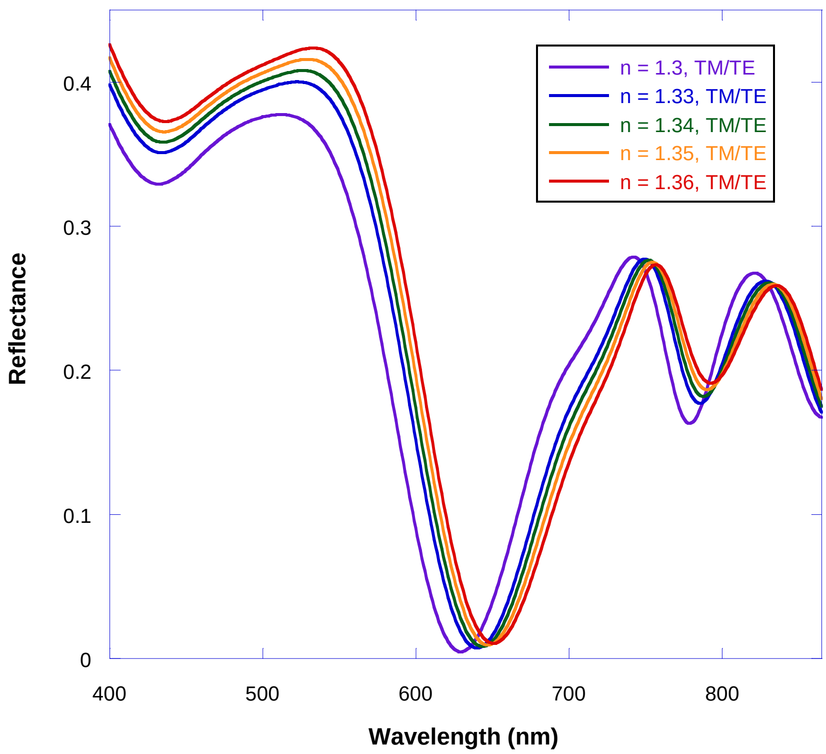


Figure S-3. Gold-coated triangular shaped nanowires with 120 nm gold deposited on top of the nanowires for (a) TE polarization, (b) TM polarization, and (c) ratio of TM and TE polarizations. The Refractive index of the surrounding media (n) was taken as 1.40.



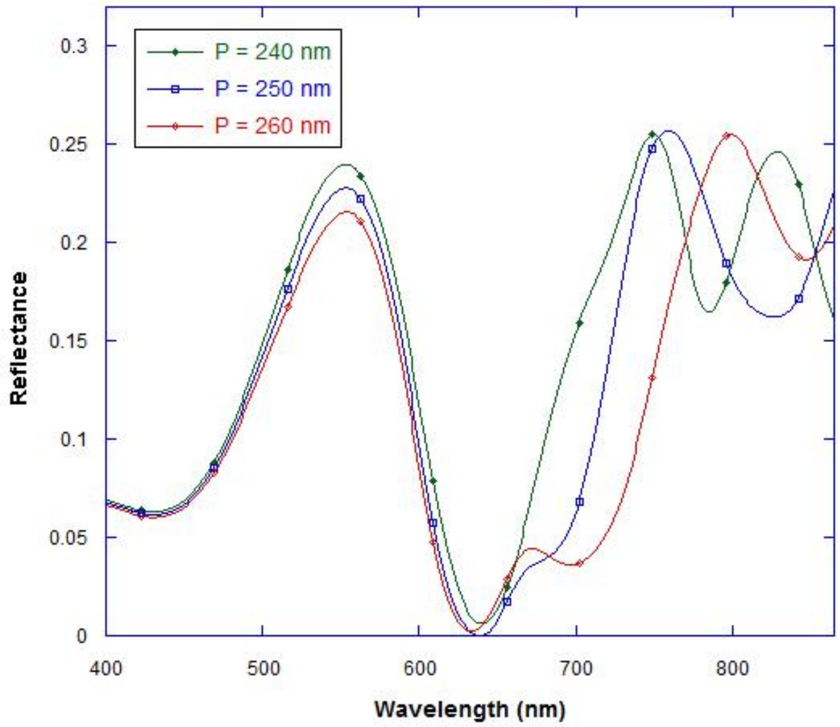
a



b

Figure S-4. Effect of refractive index of the media surrounding gold-coated triangular shaped nanowires, with 120 nm gold deposited on top of the nanowires for (a) TM polarization and (b) ratio of TM and TE polarizations.

a



b

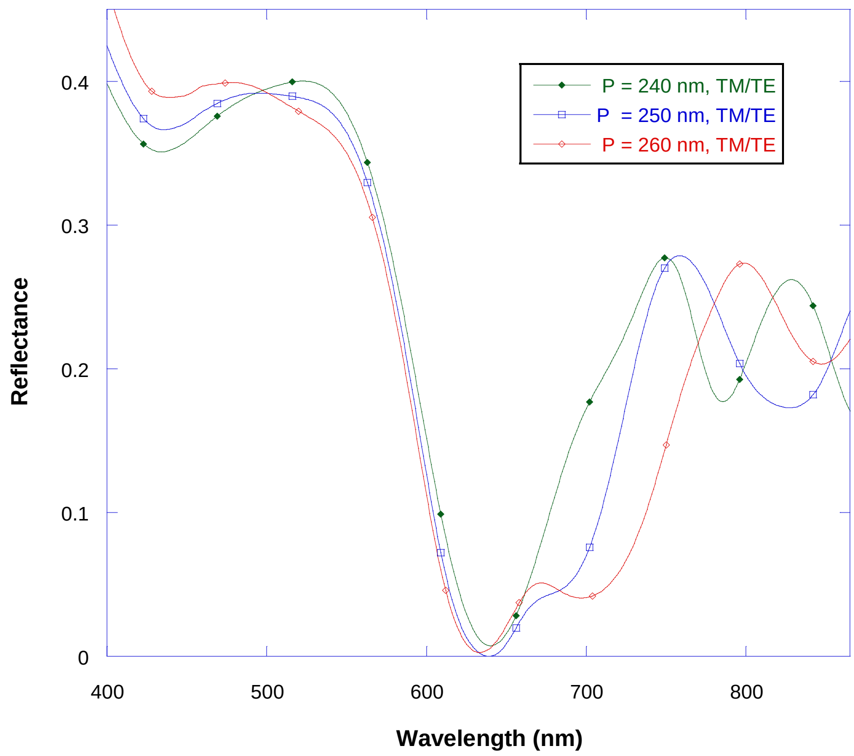


Figure S-5. Effect of periodicity of the gold-coated triangular shaped nanowires having 120 nm gold deposited on top of the nanowires for (a) TM polarization and (b) ratio of TM and TE polarizations.

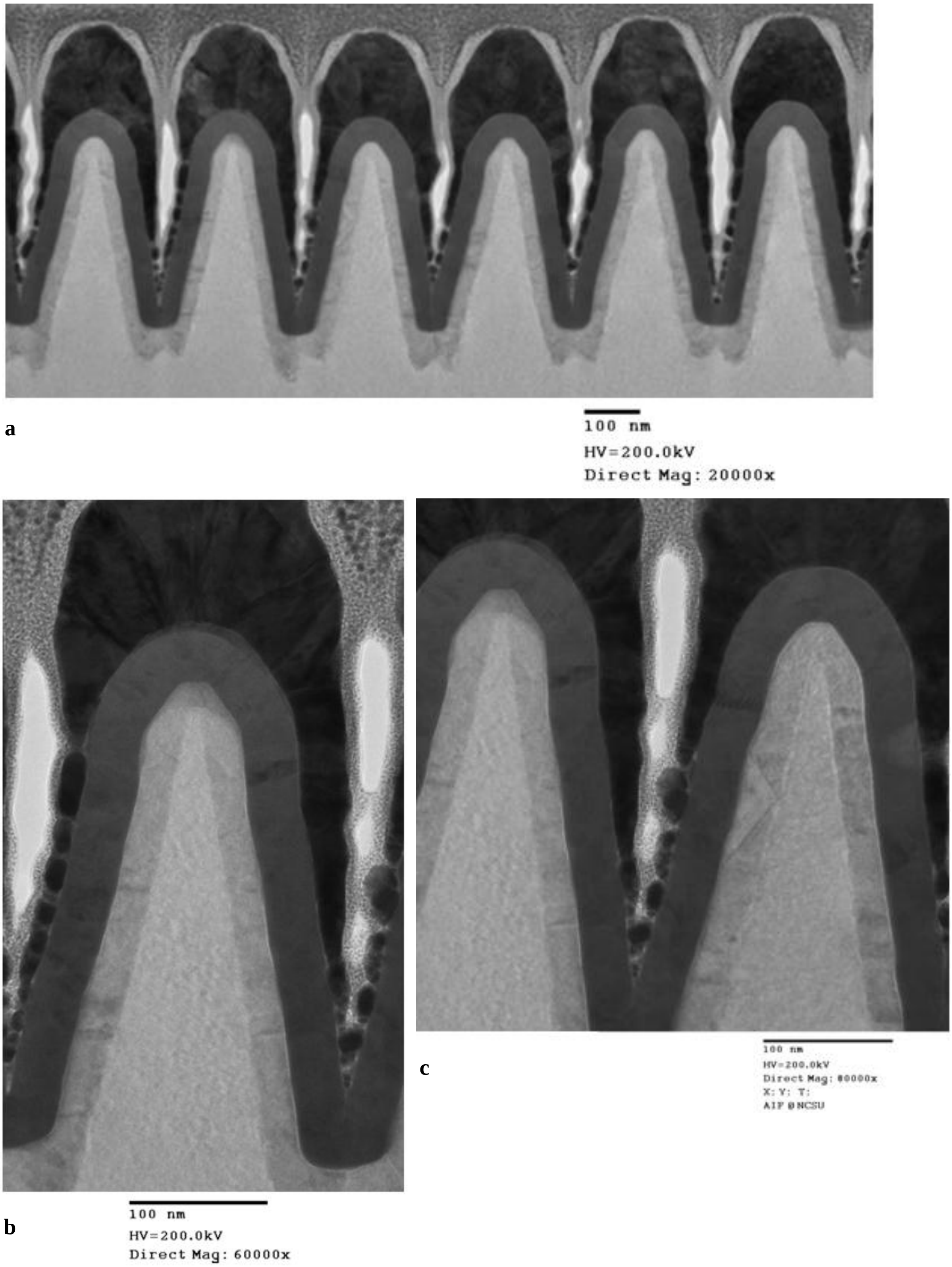


Fig. S6. TEM images showing gold-coated triangular shaped silicon nanowires (in white color), coated with a silicon germanium layer (in light grey color) employing ultra high vacuum rapid thermal chemical vapor deposition and further coated with hafnium oxide (in dark grey color) employing atomic layer deposition. The nanowires were further coated with a 120 nm gold (in black color) using electron beam evaporation.