Supplemental Information for

Surface Plasmon-Driven Hot Electron Flow Probed with Metal-Semiconductor Nanodiodes

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KEYWORDS: surface plasmon, hot electron, Schottky diode, photon, Fowler's law, internal photoemission

Electrical measurement of Au/TiO2 diodes after surface modification

Figure S1 shows I-V curves for Au/TiO₂ diodes after heating at various temperatures. After surface modification, the I-V curves show slight changes, but the rectifying behavior of each diode was well preserved, except after 240 °C because of the discontinuity of the active layers.

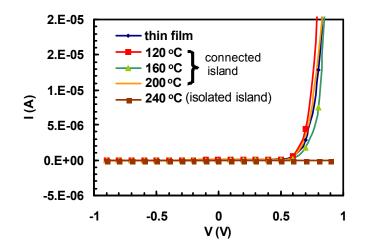


Figure S1. I-V curves of Au/TiO_2 diodes after surface modification, showing that the rectifying behaviors of the diodes were well maintained.

Characterization of the morphology of the connected islands with atomic force microscopy (AFM)

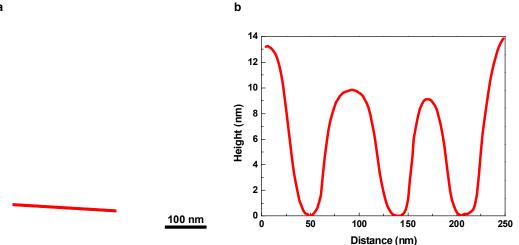


Figure S2. (a) AFM image (500 nm x 500 nm) of connected islands of Au/TiO2 diodes that were heated at 200 $^{\circ}$ C. (b) The height profile across the line in (a).

The morphology and heights of the connected islands have been characterized with AFM. Figure S2 shows (a) the AFM image and (b) height profile. Multiple measurements of height profiles reveal that the average height of the islands is 12 ± 2 nm.

UV-vis characterization of localized surface plasmon on modified gold and Pt layers

Surface plasmon resonance is responsible for enhanced light scattering, absorption, and large local field enhancement near the surface of the metal nanostructure. The surface plasmon absorption is strongly dependent on the size, shape, and arrangement of nanostructures ¹⁻². Figures S3(a)-(d) show SEM images of gold layers on quartz after the surface was treated at various temperatures. Gold layers after surface treatment exhibit nanometer scale domains similar to the surface of Au/TiO₂ diodes. Figure S3e shows UV/Vis spectra of the gold film that changed according to the annealing temperature. The absorption below 490 nm is related to interband transitions from the d-band to the sp-band of gold. It is evident that the resonance wavelength changes with annealing temperature and can be tuned to the visible ³. Absorbance spectra exhibit a long tail in the low energy regime (after ~ 600 nm), while the plasmon peaks only appeared in IPCE at 2.0 eV and 2.7 eV. The morphological changes of

the Au thin film on diodes upon heating at certain temperatures are slightly different from that of the Au layer on quartz because of different metal film-substrate interactions, even though the general trend is similar. In addition, the hot electron flux decreases with decreasing photon energy due to the transport nature of hot electrons. The low flux of internal photoemission by low energy photons can cause the absence of the tail feature in IPCE.

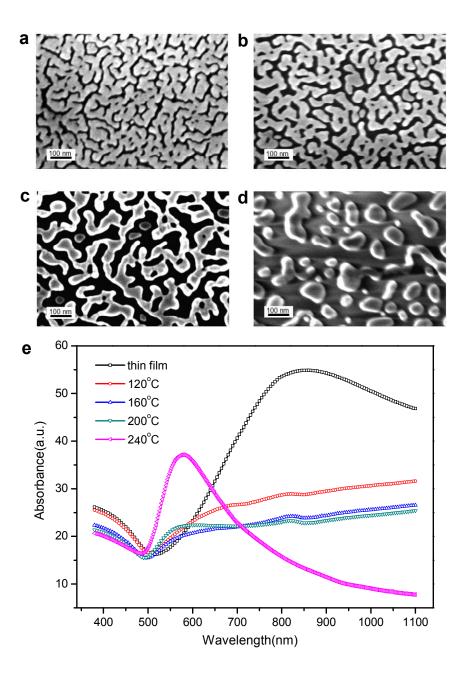


Figure S3. SEM images of gold layers on quartz after the surface was treated at (a) 120 °C, (b) 160 °C, (c) 200 °C, and (d) 240 °C. The scale bar represents 100 nm. The surfaces exhibit

nanometer-scale domains after heating, similar to the surface of Au/TiO₂ diodes. (e) UV/Vis spectra of the gold film after different thermal treatments. The spectra of 200 $^{\circ}$ C and 240 $^{\circ}$ C treated surfaces exhibit surface plasmon peaks at 550 nm and 570 nm, respectively.

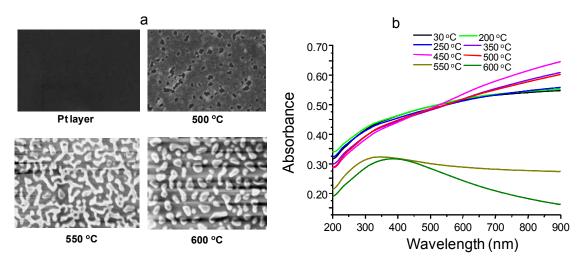


Figure S4. (a) SEM images of Pt layers on quartz and modified Pt layers by heating the surface at 500 °C, 550 °C, and 600 °C. (b) UV/Vis spectra of the Pt film after different thermal treatments.

Figure S4 shows SEM images and absorbance spectra of modified Pt layers on quartz. Unlike Au, the Pt layer does not exhibit any distinct feature associated with surface plasmon on the island structures.

References

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