NANO LETTERS

LETTER

pubs.acs.org/NanoLett

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

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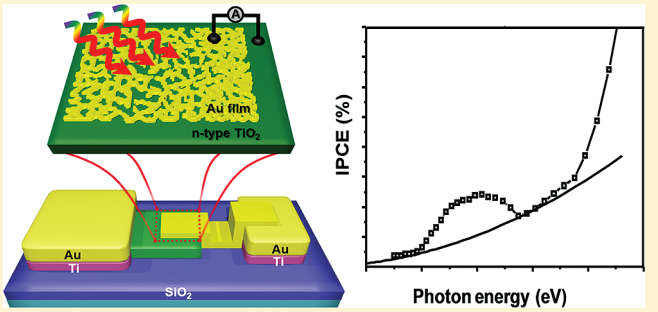
Supporting Information

ABSTRACT: A continuous flow of hot electrons that are not at thermal equilibrium with the surrounding metal atoms is generated by the absorption of photons. Here we show that hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) is amplified by localized surface plasmon resonance. This was achieved by direct measurement of photocurrent on a chemically modified gold thin film of metal-semiconductor (TiO_2) Schottky diodes. The short-circuit photocurrent obtained with low-energy photons is consistent with Fowler's law, confirming the presence of hot electron flows. The morphology of the metal thin film was modified to a connected gold island structure after heating such that it exhibits surface plasmon. Photocurrent and optical measurements on the connected island structures revealed the presence of a localized surface plasmon at 550 ± 20 nm. The results indicate an intrinsic correlation between the hot electron flow generated by internal photoemission and localized surface plasmon resonance.



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

It is known that a pulse of electrons of high kinetic energy (1−3 eV) in metals can be generated with the deposition of external energy to the surface, such as in the absorption of light or in exothermic chemical processes.[1−7] These energetic electrons are not in thermal equilibrium with the metal atoms and are called "hot electrons". Pump−probe experiments carried out on femtosecond time scales detect the presence of hot electrons that have elastic mean free paths of approximately 10 nm in metal.[8,9] The concept of photon energy conversion to hot electron flow was suggested by McFarland and Tang.[10] In this scheme, photons are harvested by dye molecules adsorbed on a Schottky diode composed of a thin gold layer on titanium dioxide (TiO_2) via internal photoemission. When light falls on the dye layer, electrons are released from the dye molecules and injected into the conduction band of the metal layer. The disadvantage of this scheme is the ineffectiveness of the adsorbed dye molecules in producing photocurrents. One reason for this is that electrons injected by the dye layer into the metal can be immediately recaptured through reverse charge transfer from filled electronic states of the metal into the dye, resulting in no net current flow.[11]

One scheme to overcome this issue with dye molecules involves enhanced light absorption with localized surface plasmon resonance. It has been suggested that surface plasmon induces electron transfer between noble metal nanoclusters and the semiconductor.[12−14] Tian and Tatsuma observed a plasmon-induced photocurrent in a gold−TiO_2 nanocomposite system by utilizing $Fe^{2+/3+}$ as an electron mediator.[15−17] Furube et al. observed plasmon-induced electron transfer from 10 nm gold nanodots to TiO_2 nanoparticles by using femtosecond transient absorption spectroscopy with an IR probe.[18] Knight et al.[19] observed hot electron flows generated by photons in the infrared range with Au/Si diodes.

Here, we measured steady-state current from the continuous flow of ballistic charge carriers generated by absorption of photons in the visible range.[20] The energy band diagram of the photovoltaic device is described in Figure 1a. To generate electric current through the device, these electrons need enough energy to travel over the Schottky barrier and into the TiO_2 conduction band. We describe a scheme for enhanced light absorption with localized surface plasmon resonance and, therefore, for enhanced hot electron generation by utilizing Au/TiO_2 Schottky diodes with no dye layers, as illustrated in Figure 1b. The morphology of the metal thin film was modified to a connected gold island structure that exhibits surface plasmon. The nanometer-scale domains in the connected gold island structure were electrically connected to the ohmic pad, ensuring measurement of the

Received: July 2, 2011
Revised: September 8, 2011
Published: September 14, 2011

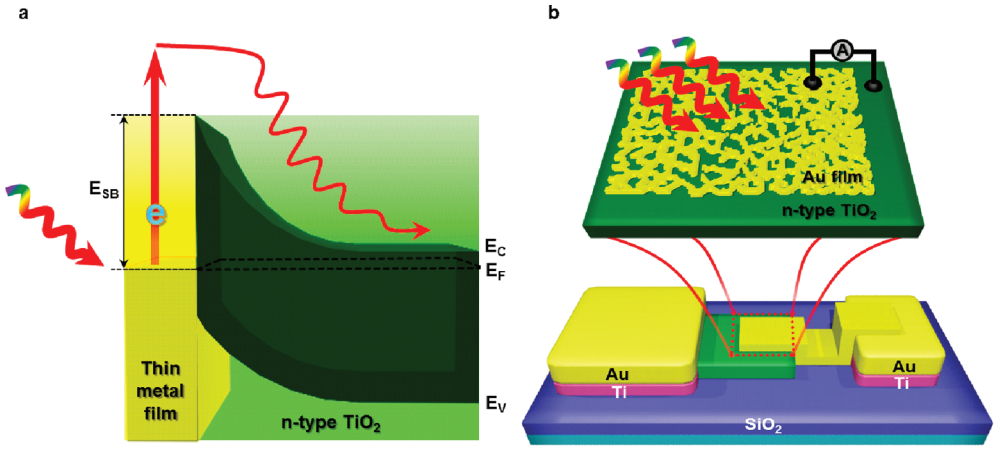


Figure 1. (a) The energy band diagram for Schottky diode-based hot electron detection. (b) Schemes for hot electron flow detection from photon absorption and surface plasmon driven hot electrons on the modified Au/TiO_2 diode.

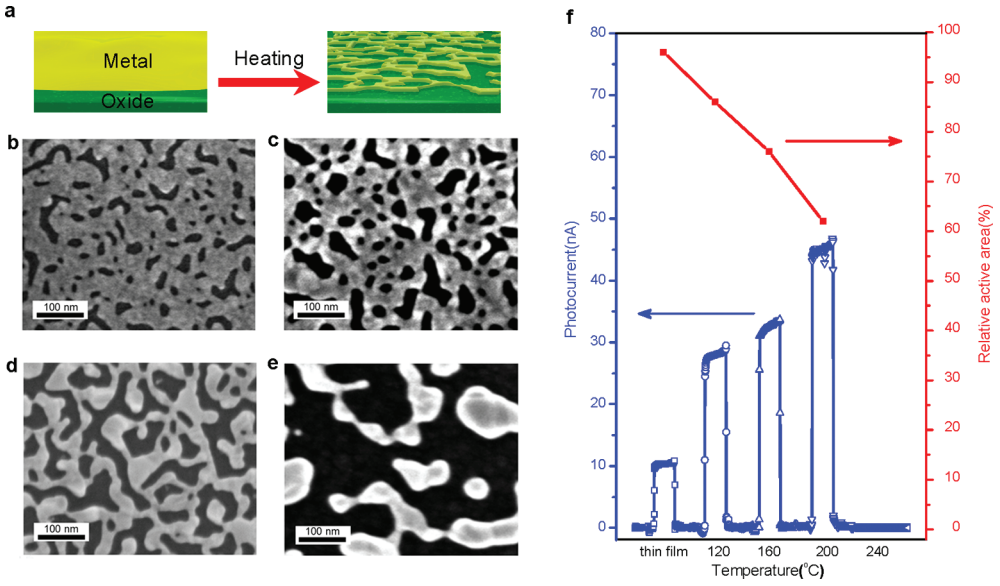


Figure 2. Scanning electron microscopy images of a surface-treated gold thin film (10 nm thickness) in a Au/TiO_2 diode, revealing the evolution of film morphology. (a) The formation of the metallic nanoscale domains is illustrated. Surface modification was performed by heating the diode for 1 h at (b) 120, (c) 160, (d) 200, and (e) 240 °C. The scale bar represents 100 nm. The surface exhibits connected island structures with an irregular shape after heating at 120∼200 °C and isolated island structures at the highest temperature (240 °C). (f) Plot of a short-circuit photocurrent (blue line) and relative active area (red line) measured on Au/TiO_2 diodes treated at several different temperatures under illumination of a tungsten-halogen lamp.

flow of hot electrons. The photocurrent was measured to determine the correlation between the surface plasmon and hot electron flows on the modified Au/TiO_2 Schottky diodes.

Nanometer-sized metallic particles are interesting candidates to increase the absorption of photon energy because they possess very large and easily tunable optical cross sections associated with their localized surface plasmon resonance.[13,14] Energy transfer between metal particles and the photoactive region of a solar cell may occur via the strongly enhanced electromagnetic field near the particle dimensions' length scale.[18] In order to utilize this process, modification of the flat thin film is required.[21,22] Another challenging aspect of this approach is making adequate electrical contact to the nanoscale structures to ensure a back supply of low-energy electrons to the metal nanostructures. We found that the surface morphology can be modified by annealing the Au/TiO_2 diode in air. The change in morphology by heating can be tuned by changing the annealing temperature, as shown in Figure 2. These changes in surface morphology are due to the higher surface energy of the metallic layers, as compared to oxide layers. The diffusion rate of metal atoms increases at high temperature, causing the thin film to ball up into an island structure. Figure 2a shows an illustration of the formation of metal islands on oxide substrates. We found that the morphology of the thin film starts to change after heating at 120 °C for 1 h, developing voids on the surface (as shown in Figure 2b). The surface heated at 160 or 200 °C exhibits connected island structures, as shown in Figure 2c and d, respectively. The Schottky diode remains functional after this treatment. At a higher temperature (240 °C), however, the connected island structures turn into isolated island structures, which are electrically separated from one another (Figure 2e), resulting in the loss of electrical contact to the nanostructures and the failure of the Schottky diodes.

dx.doi.org/10.1021/nl2022459 |*Nano Lett.* 2011, 11, 4251–4255

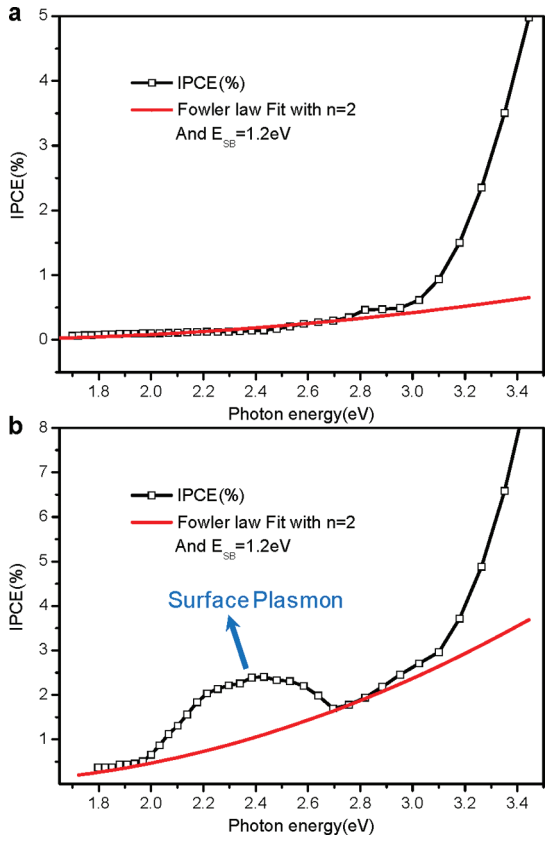


Figure 3. (a) IPCE as a function of photon measured on a Au/TiO_2 diode with a 10 nm thick continuous metal film. The red line represents the Fowler's law fit with fitting parameters of $n = 2$ and $E_{SB} = 1.2$ eV. (b) IPCE measured as a function of photons on a Au/TiO_2 diode after heating at 160 °C to obtain Au island structures.

Figure 2f shows a plot of the short-circuit photocurrent measured on the Au/TiO_2 diodes treated at several different temperatures. Heating the diodes in air was carried out first, followed by measurement of the short-circuit current in air at room temperature. The diodes were exposed to a tungsten-halogen lamp with a normal incidence angle for the photocurrent measurement. It was observed that the short-circuit photocurrent of the modified surfaces with the connected islands is significantly higher than that of the untreated Au/TiO_2 diode. For example, the current measured on a 200 °C treated sample is 4.5 times higher than that of the gold thin film. The current density of the treated diode, considering the reduction of the active area (the area of the interface between the Au islands and the TiO_2 surface), can be 7.5 times higher than that of an untreated diode. The photocurrent measured on Au/TiO_2 that was treated at 240 °C is lower than the error of the detection limit, which suggests that the photocurrent diminished due to the loss of electrical contact. The slope shown in Figure 2f is associated with the temporal change of the photocurrent due to thermal drift.

After heating the diodes in air, the $I-V$ curves of the diodes show slight changes, but the rectifying behavior of each diode was well preserved, except the diode treated at 240 °C, due to the loss of electrical contact across the device (Figure S1, Supporting Information). The thickness of the Au layer was characterized with atomic force microscopy (AFM). The line profile of the AFM images of the connected islands after heating at 200 °C shows that the height of the Au layers is 12 ± 2 nm, a slight increase compared to the thin film, suggesting that the influence of the thickness change on hot electron transport through the metal is not significant. The AFM data and height profile are shown in Figure S2, Supporting Information.

The interface area between gold and TiO_2 gets smaller as surface modification takes place. It was expected that the photocurrent would be proportional to the interface area. The measured photocurrent, however, increases when the interface area decreases, as shown in Figure 2f. We attribute the increase of photocurrent after formation of connected gold islands to a localized surface plasmon resonance (the collective oscillation of conduction band electrons induced by interaction with an electromagnetic field).

The short-circuit photocurrent was measured as a function of the wavelength of light on the metal-semiconductor Schottky diodes. The incident photon to current conversion efficiency (IPCE, flux of collected electrons per flux of incident photons) was evaluated from the short-circuit photocurrent. Figure 3a shows a plot of IPCE as a function of photon energy measured on a Au/TiO_2 diode with a 10 nm thick continuous metal film. IPCE increases with increasing photon energy. In order to verify the relationship between hot electron flux and photon energy in the internal photoemission process, we fit the IPCE to Fowler's law.[23,24] According to Fowler's law, the photoelectric threshold occurs when $h\nu$ equals the work function of the sample, ϕ. In this case, only electrons at the Fermi level can be excited outside of the solid. As the photon energy increases above ϕ, there is an increase in the fraction of valence electrons with energy below the Fermi level that can be excited above the vacuum level. The range of angles that can result in escape increases (increase in escape cone based on thermionic emission). The effect of these two factors makes the photoelectric current I:

$$I = c(h\nu\text{-}\varphi)^n/h\nu$$

where c is a constant. For most metals, $n = 2$;[25,26] other exponents apply to semiconductors. Figure 3a also shows the fit of IPCE to Fowler's law with the fitting parameters of $n = 2$ and ϕ (in our case, E_{SB}, the Schottky barrier height) of 1.2 eV. The Schottky barrier height of Au/TiO_2 is determined by the difference between the work function of Au and the electron affinity for TiO_2. Because the work function of Au is 5 eV and the electron affinity for TiO_2 is approximately 3.9 eV,[27] the Schottky barrier should be 1.1 eV, which is consistent with the value we obtained from fitting to Fowler's law. The fitting result shows that the measured IPCE is in good agreement with Fowler's law for the low-energy photon ($h\nu < 3.0$ eV). This result confirms that the measured photocurrent is mainly attributed to hot electron flow, assuming that the contribution by defect states localized in the bandgap of TiO_2 is negligible. At high photon energy (>3.1 eV), the IPCE increases significantly, showing a departure from the Fowler's law fit and indicating a significant contribution of electron−hole excitation from TiO_2 for the high-energy photon in addition to internal photoemission. The presence of a localized surface plasmon resonance is also confirmed in IPCE measurements on a modified Au/TiO_2 diode with Au island structures. Figure 3b shows the plot of IPCE of the surface heated at 160 °C. As shown in Figure 3b, there is a peak at around 2.3 eV (~540 nm), deviating from the Fowler's law fit.

To confirm the presence of localized surface plasmon resonance, absorbance was measured on thin films of gold on quartz

dx.doi.org/10.1021/nl2022459 |Nano Lett. 2011, 11, 4251–4255

after similar surface treatment, as shown in Figure S3, Supporting Information. Indeed, the plasmon resonance band of the surface plasmon was observed at 550 nm after heating at 200 °C. The spectrum of the surface heated at 240 °C exhibits a strong plasmon resonance band in the range of visible light (peak position at 570 nm). The energy level of this peak lies in the same range as the surface plasmon detected with IPCE, as shown in Figure 3b. However, the IPCE spectra were measured on Au/TiO_2 Schottky diodes, while absorption spectra were measured on Au layers on quartz. 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.

We carried out UV−vis on Pt islands on quartz (presented in Figure S4, Supporting Information), which shows that surface plasmon on Pt islands is diminished, unlike Au islands. We could not obtain Pt/TiO_2 with Pt islands because surface modification of Pt/TiO_2 to obtain the islands structure required a higher temperature (∼500 °C), which resulted in the loss of rectifying behavior of the diodes. Earlier studies on Pt/TiO_2 and Au/TiO_2 diodes show that hot electron flows are generated and detected during exothermic chemical reactions[6,28,29] or photon adsorption.[10,20] The enhancement of hot electron flows by the presence of connected islands takes place only on Au/TiO_2. Furthermore, the peak observed in Figure 3b shows the signature of internal photoemission enhanced by surface plasmon resonance on Au/TiO_2. The results imply an intrinsic correlation between hot electron generation and surface plasmon. Possible future research involves improving the energy conversion efficiency by tailoring the structures and materials of Schottky diodes. A different method for formation of metal islands on the diode will be employed, for example, using photolithography or nanopatterning with self-assembled silica nanosphere structures. Photoreceptor layers, such as organic dyes, can be deposited on the ultrathin metallic layers to increase the photon absorption on the metallic layer. Tandem structures created by combining diodes with high Schottky barriers with diodes with lower barriers may increase photon energy conversion efficiency. Enhancement of internal photoemission via localized surface plasmon resonance can have intriguing possible applications, including more efficient light harvesting with thinner photoactive layers and hot electron-based photodetectors.

CONCLUSION

The steady-state flow of hot electrons generated from photon absorption was probed with metal-semiconductor Schottky diodes. An enhancement of internal photoemission was observed by changing the surface morphology in such a way that the surface exhibits nanoscale domains with a strong localized surface plasmon resonance. The absorption through the gold layers deposited on quartz was measured separately using UV−vis spectroscopy, which revealed a strong plasmon mode in the modified gold layers. The photocurrent on these modified surfaces increased by a factor of 7 compared to the thin film surface, considering the loss of active area. The results suggest that plasmon resonance is responsible for the large increase in photocurrent signal and the enhancement of internal photoemission.

METHODS

For this approach, a metal-semiconductor Schottky diode of Au/TiO_2 has been fabricated. Details on the device fabrication are described elsewhere.[7,29,30] Briefly, vertically oriented Au/TiO_2 Schottky diodes were fabricated on an insulating n-type (100) silicon wafer covered by 200 nm SiO_2 using plasma-enhanced chemical vapor deposition. The first step consists of depositing a 4 × 6 mm, 150 nm thick film of titanium oxide onto the silicon oxide, through an aluminum shadow mask using multitarget sputtering. The wafer is then annealed in air at 200 °C for 3 h to control the sheet resistance of the titanium oxide film. A 50 nm film of titanium is then deposited through a second mask using electron beam evaporation. A 150 nm film of gold, which constitutes the nanodiode's two ohmic electrodes, is then deposited through the same mask. Finally, a thin gold film (10 ± 2 nm thick) is deposited through a third mask. By fitting the current−voltage ($I-V$) curves of the diodes to the thermionic emission equation, the barrier heights and ideality factors for the nanodiodes are obtained.[31] Typical barrier height and ideality factors for the $Au-TiO_2$ nanodiodes are 1.1−1.2 and 1.5−2.0 eV, respectively.

The short-circuit photocurrent was measured with a sourcemeter (Keithley Instrumentation, 2400) under illumination from light sources. For electrical characterization of the diodes, current−voltage measurements were performed by sweeping the voltage between two electrodes and measuring the resulting current. The optical properties of the gold films were characterized by using a UV−vis spectrophotometer (U-4001, Hitachi). The spectral range capability of the instrument is from 300 to 1100 nm. For measurement of the gold films, a gold layer was deposited on a (1/16 inch thick) quartz window, and the instrument was used in standard setup mode. A clean quartz window was used as a reference.

ASSOCIATED CONTENT

Supporting Information. $I-V$ curves of the diodes. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work was supported by World Class University (WCU) program through the National Research Foundation of Korea (R31-2008-000-10055-0) and KRF-2011-0015387. This work was partly supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences, and Engineering of the U.S. Department of Energy under contract no. DE-AC02-05CH11231.

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