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Enhanced semiconductor optical absorption via surface plasmon excitation in metal nanoparticles

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Surface plasmon resonances in metallic nanoparticles are of interest for a variety of applications due to the large electromagnetic field enhancement that occurs in the vicinity of the metal surface, and the dependence of the resonance wavelength on the nanoparticle's size, shape, and local dielectric environment. Here we report an engineered enhancement of optical absorption and photocurrent in a semiconductor via the excitation of surface plasmon resonances in spherical Au nanoparticles deposited on the semiconductor surface. The enhancement in absorption within the semiconductor results in increased photocurrent response in Si *pn* junction diodes over wavelength ranges that correspond closely to the nanoparticle plasmon resonance wavelengths as determined by measurements of extinction spectra. These observations suggest a variety of approaches for improving the performance of devices such as photodetectors, imaging arrays, and photovoltaics. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1855423]

Surface plasmon resonances in metallic nanoparticles are currently being exploited for a variety of applications including molecular sensing[1–3] and tagging,[4,5] focusing of light,[6] near-field optical microscopy,[7] and subwavelength photonics.[8] The appeal of surface plasmon excitations for such applications typically arises from the large electromagnetic field enhancement near the metal surface, and the dependence of the resonance wavelength on the nanoparticle's size, shape, and local dielectric environment. Because of the localized field amplification that occurs, excitation of surface plasmons in metal nanoparticles placed on a semiconductor might be expected to enhance optical absorption of incident photons within the semiconductor region near each nanoparticle. In this letter, we report such an engineered enhancement of absorption and photocurrent in a semiconductor via excitation of surface plasmon resonances in Au nanoparticles deposited on a semiconductor surface.

The basic device structure is shown schematically in Fig. 1. Si *pn* junction diodes were fabricated by diffusion of B at 900 °C for 30 min into an *n*-type Si (001) wafer with resistivity $\rho \approx 10^{-2}\ \Omega$ cm. Based on the diffusion conditions employed, the B depth profile was computed analytically[9] and yielded a *pn* junction depth of 80 nm, with the B concentration at the wafer surface estimated to be $\sim 1.1 \times 10^{20}$ cm^{-3}. Ohmic contacts to the *p*-type surface were formed by optical lithography followed by thermal evaporation of ~150 nm Al. A large-area Ohmic contact to the *n*-type underside of the wafer was formed by a second thermal evaporation of ~150 nm Al. Au nanoparticles were deposited as illustrated in Fig. 1 by placing a drop of Au colloidal solution containing Au particles of uniform size onto the surfaces of fabricated devices that had been subjected to prior exposure to a poly-L-lysine solution to facilitate immobilization of the Au nanoparticles on the device surface. Figure 2 shows scanning electron microscope images of Au nanoparticles with diameters of 50, 80, and 100 nm, which have been deposited onto the surfaces of Si *pn* junction diodes. Nanoparticle densities on the Si surfaces were approximately 6.6×10^8, 1.6×10^8, and 7.7×10^7 cm^{-2} for, respectively, 50-, 80-, and 100-nm-diam particles. These densities correspond to surface coverages of 0.6%–1.3%. The Au nanoparticles are present predominantly as isolated single particles; fewer than 1% appear to be present within multiparticle clusters, for which the plasmon resonance behavior may be altered compared to that for a single isolated particle.[10]

Photocurrent and extinction spectra were measured using a 100 W tungsten-halogen lamp as an illumination source and a grating monochromator with a 1200 groove/mm grating, providing monochromatic light at wavelengths of 400–1300 nm. For measurements at wavelengths of 600 nm and longer, a red filter was employed to eliminate illumination from the second-order diffraction line. Illumination was incident normal to the sample surface and chopped at 338 Hz. A lock-in amplifier was used to isolate the signal component arising specifically from the incident illumination. For pho-

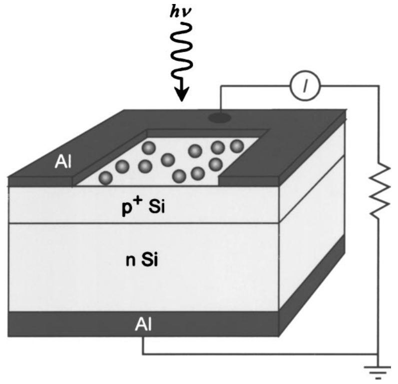

FIG. 1. Schematic diagram of Si *pn* junction diode device structure with metallic nanoparticles. Illumination and measurement geometry employed to obtain photocurrent response data are also shown.

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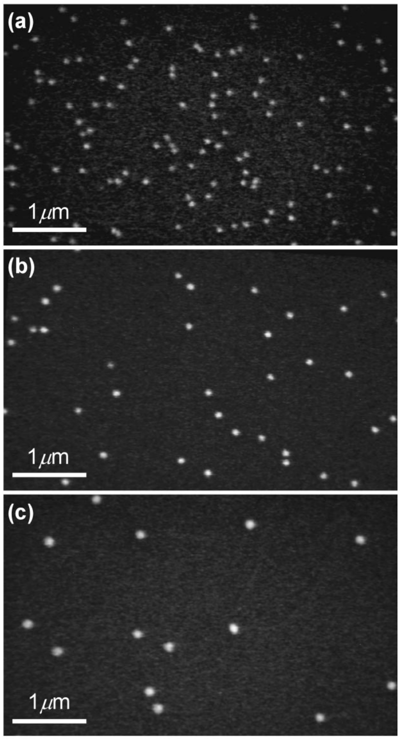

FIG. 2. Scanning electron micrographs of Au nanoparticles deposited on Si *pn* junction diode surfaces. Images are shown for devices with particles (a) 50 nm, (b) 80 nm, and (c) 100 nm in diameter.

tocurrent measurements the input to the lock-in amplifier consisted of the *pn* junction diode current measured under monochromatic illumination. For measurements of extinction spectra, monochromatic light transmitted through the sample was incident on a Si photodetector, from which the current signal was directed to the lock-in amplifier.

Extinction spectra for Au nanoparticles 50, 80, and 100 nm in diameter suspended in aqueous solution are shown in Fig. 3. The spectra have been normalized to account for the extinction response of the aqueous environment and the rectangular optical glass cell containing the solution. The extinction efficiency is defined as $\log(T_c/T_{\mathrm{Au}})$, where T_c and T_{Au} are the light intensities transmitted through cells containing de-ionized water and the colloidal Au solution, respectively. Maxima in the extinction spectra are clearly visible at wavelengths corresponding to plasmon excitations in the Au nanoparticles,[11] with negligible extinction activity at wavelengths above 800 nm. As expected, the plasmon resonance peak increases in wavelength and broadens with increasing particle size.[12]

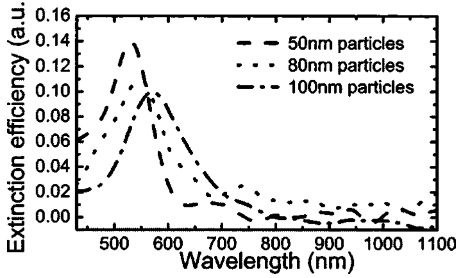

FIG. 3. Extinction efficiency as a function of wavelength for Au nanoparticles 50, 80, and 100 nm in diameter suspended in aqueous solution. Peaks corresponding to excitation of plasmon resonances are clearly visible in each spectrum.

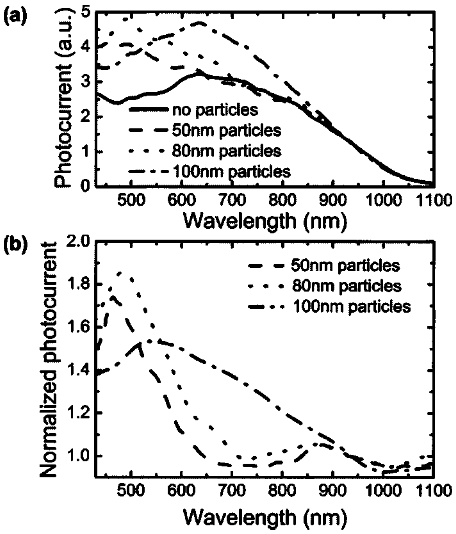

FIG. 4. (a) Photocurrent response as a function of illumination wavelength for Si *pn* junction diodes in the absence of nanoparticles, and with Au nanoparticles 50, 80, and 100 nm in diameter. (b) Photocurrent response spectra for diodes with Au nanoparticles 50, 80, and 100 nm in diameter from part (a), normalized to the photocurrent response measured in the absence of nanoparticles, revealing the increased response arising from the presence of the nanoparticles.

In a purely semiconductor-based device structure, electromagnetic radiation incident on the semiconductor gives rise to an optical transition rate that is proportional to the square of the electric field amplitude E_0; furthermore, the probability that a photon traversing a semiconductor volume element is absorbed, resulting in creation of an electron–hole pair, is proportional to n/c, where n is the index of refraction of the semiconductor and c is the speed of light in vacuum.[13] This factor can be understood as representing the duration of the interaction between the photon and the semiconductor, given by the transit time of the photon per unit thickness of the semiconductor. In comparison, for an electromagnetic field in a semiconductor arising from a surface plasmon excitation in a proximate metal nanoparticle, the duration of the interaction between the field and the semiconductor will be determined by the lifetime of the surface plasmon excitation. Experimental observations of the lifetime and dephasing of nanoparticle surface plasmon resonances have typically yielded values of $\sim 5-10$ fs,[14,15] which compare favorably with the photon transit time across the semiconductor region within which the surface plasmon field would be present—typically ~100 nm—of ~1 fs. Furthermore, the peak amplitude of the surface plasmon-induced electromagnetic field is expected to be much greater than that of the incident electromagnetic field.[16] Thus, the increased field amplitude and increased interaction time between the field and the semiconductor would be expected to increase absorption of incident electromagnetic energy near the nanoparticle.

For a *pn* junction diode, increased optical absorption due to the presence of metal nanoparticles will be manifested as an increase in photocurrent response at wavelengths corresponding to those of the nanoparticle surface plasmon resonances. Figure 4(a) shows photocurrent response as a function of wavelength for a reference Si *pn* junction diode with no Au nanoparticles present, and for diodes upon which Au nanoparticles 50, 80, or 100 nm in diameter were deposited.

The photocurrent spectra have been normalized to account for the measured source illumination spectrum, and scaled to yield identical response for wavelengths of 950–1100 nm to account for variations in external factors such as contact resistance and illumination area. Over this range of wavelengths, the nanoparticles are, based on the extinction spectra shown in Fig. 3, not expected to contribute to the diode photocurrent response; the similarity of the spectra (within a scaling factor) for all devices over this wavelength range supports this assertion.

Enhanced photocurrent response is observed at wavelengths of approximately 900 nm and shorter for devices upon which Au nanoparticles have been deposited. The degree and wavelength range of this enhancement are dependent on the Au nanoparticle size. Due to the relatively high dopant concentrations in the diode, the region within which photoexcited carriers are collected by drift and diffusion is substantially smaller than the photon absorption depths, which at these wavelengths are $\sim 0.5\ \mu$m or more. Thus, improvement of quantum efficiency and hence photocurrent is expected if carrier generation is increased specifically in the vicinity of the *pn* junction. However, it would not be beneficial for the increased generation to be confined solely to a region within several nanometers of the surface, where surface recombination effects play a prominent role—as evidenced by the decrease in photocurrent response observed below ~630 nm for the reference Si diode.[17]

Figure 4(b) shows photocurrent response spectra for diodes upon which Au nanoparticles have been deposited, normalized to the measured photocurrent response of the diode itself. The close correspondence between the plasmon peaks in the extinction spectra and the diode photocurrent response peaks is clear evidence of the role of the nanoparticle plasmon resonances in the observed photocurrent response. The shift to slightly shorter wavelengths in the diode response is a consequence of the change in local dielectric environment. At or near the plasmon resonance wavelengths, increases in photocurrent response of 50%–80% or more relative to that of the Si *pn* junction diode itself are observed; considerably larger increases may be possible at greater nanoparticle densities.

In previous studies, increased photocurrent has also been observed for incorporation of metal clusters into organic semiconductor devices, and variously attributed to a combination of interband transitions in the metal clusters and surface plasmon resonance excitation,[18,19] or electron–hole pair excitation in the metal mediated by surface plasmons.[20] However, increased electron–hole pair creation within the semiconductor via surface plasmon excitations was not demonstrated, nor were correlations among nanoparticle size, surface plasmon resonance wavelength, and the resulting absorption in the semiconductor evident.

Alternate mechanisms that might be proposed for the enhancement in photocurrent response observed here include (i) photoexcitation of carriers within an Au nanoparticle and subsequent carrier injection into the semiconductor, as in a conventional metal–semiconductor photodetector; or (ii) excitation of an electron–hole pair in an Au nanoparticle via plasmon decay followed by carrier injection into adjacent semiconductor and metal contact layers.[20] Mechanism (i) can be eliminated due to the observation of enhanced photocurrent only at the surface plasmon resonance wavelengths. Mechanism (ii) will not yield a contribution to steady-state photocurrent in our device geometry as this would result in charging of the nanoparticles, which are electrically isolated from the diode contacts. In this respect our results and proposed mechanism for increased photocurrent response differ fundamentally from those in Ref. 20.

In summary, we have demonstrated a mechanism for localized enhancement of semiconductor optical absorption via excitation of surface plasmon resonances in proximate metal nanoparticles. Our observations suggest a number of approaches for improving the functionality or performance of photodetectors and related optoelectronic devices. For example, increased sensitivity and color selectivity could be achieved in photodetectors and photodetector arrays for imaging applications. Efficiency of thin-film photovoltaic devices could be increased by enhancing absorption at wavelengths corresponding to the solar radiation spectrum. Extension of these concepts to longer wavelengths could enable their use in applications in optical communications or infrared imaging. Molecular sensing applications based on the dependence of surface plasmon resonance wavelength on local dielectric environment could also be envisioned. More generally, the coupling of dielectric and electromagnetic behavior in the optical regime in nanostructured metals and semiconductors is likely to enable or extend a variety of new and emerging approaches to the engineering of photonic and optoelectronic devices.

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