A Comparative Study of the Effect of Metallic Au and ReO₃ Nanoparticles on the Performance of Silicon Solar Cells

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The influence of gold (~35 nm diameter) as well as ReO₃ (~17 nm diameter) nanoparticles placed atop silicon photovoltaic devices on absorption and photocurrent generation has been investigated. The nanoparticles improve the power transmission into the semiconductor and consequently, the photocurrent response at wavelengths corresponding to plasmon absorption. An increase in short circuit current up to 4.5% under simulated solar irradiation was observed with the ReO₃ nanoparticles, while the gold nanoparticles showed enhancements up to 6.5%. The increase in photocurrent is observed at wavelengths corresponding to the maxima in the surface plasmon resonance absorption spectra.

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Commercially available crystalline Si solar cells, which dominate the photovoltaics market, typically possess power conversion efficiencies in the range of 10–20%. As potential routes to improve the performance of photovoltaic devices, there is considerable interest in light trapping and manipulation techniques such as antireflection coatings (ARCs), surface texturing, and increasing the optical path length for photovoltaic films.¹⁾ Surface plasmon resonance in metallic nanoparticles is currently being exploited for a variety of applications employing the large electromagnetic field enhancement near the surface of the nanoparticle. Excitation of surface plasmons in metal nanoparticles placed on a semiconductor may enhance the optical absorption of incident photons within the semiconductor region near each nanoparticle. Optical absorption enhancement via scattering from metallic nanoparticles has been employed as a light-trapping technique for semiconductor devices such as solar cells.^{2–7)} There are studies showing measurable photocurrent enhancement for silicon on insulator photodiode structures,^{2,3)} hydrogenated amorphous Si thin-film cells,^{5,8)} crystalline Si p–n photodiodes,^{4,7)} organic bulk heterojunction solar cells,⁹⁾ and dye-sensitized solar cells^{10–12)} using gold or silver metal nanostructures. Design principles for plasmonic solar cells with broad band absorption enhancement are being developed.^{13–15)}

ReO₃ is a unique oxide metal, which looks like copper and conducts like copper.^{16,17)} Metallic ReO₃ nanoparticles, exhibiting the plasmon absorbance like that of gold at around 520 nm in the visible region, have been shown to be SERS active.¹⁸⁾ Here, we present a comparative study of the effect of metallic ReO₃ and Au nanoparticles on the photocurrent generation in silicon solar cells.

The solar cell devices used in our experiments consisted of a crystalline Si p–n junction with front side surface texturing and without antireflection coating, obtained from Bharat Electronics. A 100-nm-thick gold layer was coated on the top as the contact by thermal evaporation. Aqueous solutions of colloidal Au nanoparticles with an average diameter of 35 nm (see inset in Fig. 1) were synthesized following the reported procedure.¹⁹⁾ These Au nanoparticles show surface plasmon resonance absorption at 525 nm. ReO₃ nanoparticles with an average diameter of 17 nm (see

Fig. 1. Absorption spectrum of gold nanoparticles. Inset shows the transmission electron microscopy image of the nanoparticles along with the size distribution histogram.

Fig. 2. Absorption spectrum of ReO₃ nanoparticles. Inset shows the transmission electron microscopy image of the nanoparticles along with the size distribution histogram.

inset in Fig. 2) were prepared by the decomposition of the Re₂O₇–dioxane complex under solvothermal conditions²⁰⁾ and ultrasonically dispersed in toluene. The ReO₃ nanoparticles show a broad surface plasmon resonance absorption

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Fig. 3. Schematic diagram of the Si p-n junction solar cell with metallic nanoparticles deposited on the device surface.

Fig. 4. Field emission scanning electron micrographs of (a) Au and (b) ReO_3 nanoparticles deposited on Si solar cell surfaces.

peak at 520 nm. The solution of Au or ReO_3 colloidal particles was drop coated onto the sample and then blown dry with nitrogen. The device structure with deposited metallic nanoparticles is shown schematically in Fig. 3. Field emission scanning electron microscopy (FESEM) images were recorded with an FEI NOVA NANOSEM 600, to observe the nanoparticles deposited onto the devices. To measure the photocurrent response, samples were illuminated at normal incidence using a xenon lamp through a monochromator (Jobin Yvon TRIAX 180). For measurements at wavelengths of 600 nm and longer, a red filter was employed to eliminate illumination from the second-order diffraction line. Current-voltage (I - V) characteristics were obtained, either in the dark or under illumination from a 300 W Newport Solar Simulator with a global AM 1.5 direct filter using a Keithley 236 source measure unit.

Figures 4(a) and 4(b) show respectively the FESEM images of the Au nanoparticles and ReO_3 nanoparticles deposited onto the devices. The density of the Au nanoparticles was approximately $4.1 \times 10^8 \text{ cm}^{-2}$ as estimated from the FESEM image. The Au nanoparticles are present predominantly as isolated single particles, but the ReO_3 nanoparticles show some clustering. The density of the ReO_3 nanoparticles on the device surface is estimated to be 10^9 cm^{-2} from the FESEM images. Figure 5 shows the I - V characteristics under AM 1.5 illumination for devices with and without the ReO_3 nanoparticles. The inset in Fig. 5 shows the I - V characteristics for devices with and without the Au nanoparticles. A clear increase in I_{sc} is observed in the presence of the nanoparticles with the increase being 6.5 and 4.5% for the Au and ReO_3 nanoparticles, respectively.

Fig. 5. I - V characteristics, under AM 1.5 illumination, of Si solar cell before and after deposition of ReO_3 or Au (inset) nanoparticles.

Fig. 6. Photocurrent response of Si solar cell as a function of illumination wavelength in the absence of nanoparticles and with ReO_3 or Au (inset) nanoparticles.

Figure 6 shows the experimentally observed photocurrent response spectrum for the device with the ReO_3 nanoparticles along with that of the same device without the nanoparticles. The inset in Fig. 6 shows the photocurrent response spectra in the case of the Au nanoparticles. The correspondence between the plasmon absorption band and the photocurrent response maxima clearly demonstrates the role of the nanoparticle plasmon resonance in the observed photocurrent response. At the plasmon resonance wavelengths, the increase in the photocurrent response relative to that of the Si solar cell is ~ 8.5 and 14% for the ReO_3 and Au nanoparticles, respectively.

The observed enhancement in I_{sc} of the Si p-n junction device for the gold nanoparticles is higher than the value reported in the literature (1–3%).⁷⁾ In the case of the ReO_3 nanoparticles, the enhancement is comparable to that due

to the Au nanoparticles. Further increases in I_{sc} may be possible by avoiding the clustering of the ReO_3 nanoparticles. However, the reported values for the enhancement of photocurrent in plasmonic solar cells vary significantly and are smaller than those achievable with conventional ARC technologies for crystalline silicon solar cells.¹³ The nanoparticle-based scattering for light trapping may be beneficial in the case of organic semiconductor devices^{7,9} as well as dye-sensitized solar cells,^{10–12} where it is difficult to employ traditional antireflection coatings.

In conclusion, an enhancement in short circuit current up to 4.5% has been obtained for crystalline Si photovoltaic devices by making use of ReO_3 nanoparticle-based scattering, compared with the 6.5% enhancement in the case of Au nanoparticles. Increased photocurrent generation is observed at wavelengths corresponding to the plasmon absorption of the metallic nanoparticles.

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