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Energy harvesting in semiconductor-insulator-semiconductor junctions through excitation of surface plasmon polaritons

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We have demonstrated a simple approach for developing a photovoltaic device consisting of semiconductor-insulator-semiconductor (SIS) heterojunction using surface plasmon polaritons (SPPs) generated in one of the semiconductors (Al:ZnO) and propagated through the dielectric barrier (SiO₂) to other (Si). This robust architecture based on surface plasmon excitation within an SIS device that produces power based on spatial confinement of electron excitation through plasmon absorption in Al:ZnO in a broad spectrum of visible to infrared wavelengths enhancing the photovoltaic activities. This finding suggests a range of applications for photovoltaics, sensing, waveguides, and others using SPPs enhancement on semiconductors without using noble metals.

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The field of photovoltaics, the conversion of sunlight to electricity, is emerging as a promising technology that can make a considerable contribution to solving the next generation energy problem. While the technology for semiconductor-based thin-film solar cells such as amorphous and polycrystalline Si, GaAs, CdTe, and CuInSe₂ and organic semiconductors is pushing continuously for improving their efficiency, the limitation is imposed due to the small absorbance of near-band gap light. Among several nanostructures, metallic nanostructures are used for light trapping in thin-film solar cells, supporting the phenomena of surface plasmons: excitations of the conduction electrons at the interface between a metal and a dielectric. Localized surface plasmons excited in metal nanoparticles as well as surface plasmon polaritons (SPPs) propagating at the metal/semiconductor interface are of great interest.¹ Surface plasmon excitation within a metal-insulator-metal device has been observed due to spatial confinement of electron excitation through plasmon absorption: plasmons excited in the upper metal are absorbed, creating a high concentration of hot electrons which can inject above or tunnel through the thin insulating barrier, producing current.² The enhanced photocurrents have been demonstrated in several systems owing to the plasmonic near-field coupling, for example, in ultrathin-film organic solar cells doped with very small, such as 5 nm diameter of Ag nanoparticles,^{3,4} inorganic solar cells have shown increased photocurrents owing to near-field effects, such as CdSe/Si hetero-structures⁵ and other systems.^{6,7}

It is known that losses due to interband transitions are highly undesirable and severely limit potential applications of plasmonic metals, Ag and Au. However, it was recently found that wide band gap semiconductor such as Ga or Al doped ZnO (AZO) and other transparent conductive oxides (TCOs) are potential candidates to replace silver and gold in plasmonic applications.⁸⁻¹⁰ We have demonstrated that the doped degenerate wide-band-gap semiconductors can be efficient nanoplasmonic materials in the near-infrared spectral

range because of strong confinement of SPPs, low loss, and metallic behavior.^{8,11,12} Because semiconductors do not have bound-state absorption transitions in their band-gaps, their SPP losses can be even smaller in the near infrared (NIR) region than those in conventional plasmonic materials at corresponding visible wavelengths.¹³ On the other hand, the carrier density and the refractive index in these materials can also be tuned in a broad range by an applied electric field.¹⁴

In this paper, robust semiconductor-insulator-semiconductor (SIS) junctions have been used to fabricate plasmonic-based solar cell, in which the top TCO layer is a degenerate semiconductor, such as AZO. We have demonstrated the enhancement of photocurrent due to plasmonic effects of the AZO layer. The SPP wave generated from the AZO layer can transmit through 5 nm of insulating SiO₂ layer to p-Si. AZO layer not only allows wide spectrum of light from the ultra-violet range but also absorbs the source from the NIR range as it coincides with AZO's plasma frequency.

P-Si substrate (boron doped) wafers corresponding to a resistivity 4-8 Ω-cm, a thickness of 275 μm, an orientation of (100) were cut and cleaned. Cleaned and H-terminated surface of p-Si substrates were oxidized to form SiO₂ layers of thickness varying from 5 to 20 nm. Typically, 70-80 nm thick AZO layer was deposited on the top of the barrier layer by either rf magnetron sputtering technique typically at 350 °C to form AZO/SiO₂/p-Si heterostructure without any further annealing. The junction was illuminated under the halogen lamp with 1 Watt/cm² on 1 cm² area with the SIS structure, ranging wavelength from UV to IR, in order to observe the photovoltaic effect. The junction was also irradiated at various wavelength of light to study the effects of SPP effect. The transmittance $T(\lambda)$ and reflectance $R(\lambda)$ spectra of the AZO/glass samples have been recorded with the Lambda 950 UV-Vis-IR spectrophotometer. It is noted that AZO film is highly transparent ($T > 90\%$)^{11,12} in the visible region and that allows the visible light passes through AZO film.

The current density (J) Vs voltage characteristics for AZO/SiO₂/p-Si are shown for two SiO₂ barrier thicknesses, (a) 5 and (b) 20 nm. It is very interesting to note that the

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current-voltage characteristics are surprisingly different for two different barrier thickness. Although, the voltage between the emitter and collector can change the barrier profile that changes the transmission probability of photocurrent by tuning the physical barrier height, Φ_p , which also modifies the photocurrent behavior as shown in Fig. 1. The current SIS device configuration corresponds to a *pin* photodiode, where AZO is an n-type semiconductor. The photocurrent decreases linearly with negative bias. However, when the bias V is equal to $[(E_{ph} - \Phi_c)/e]$, where E_{ph} is the photon energy, photocurrent decreases exponentially (not shown in Fig. 1(a)), indicating the crossover to the tunneling behavior. In case of positive bias, the maximum barrier height remains Φ_c at the interface resulting constant injection current. Although the positive bias reduces the effective barrier thickness for tunneling, this only results in a small additional current. The additional photocurrent observed at zero-bias voltage is due to the SPPs from AZO and will be discussed in later section. Similar behavior is recently observed in the context of plasmonic energy collection through hot carrier extraction using two metal electrodes (Au) separated by an insulator. On the other hand, when the physical barrier height Φ_p increases to 20 nm, the pin junction acts like a regular photovoltaic diode as shown in Fig. 1(b).

In order to investigate the SPP induced photovoltaic activities, we performed the reflectivity measurements. The optimized angle of incidence was selected to be 45° . The

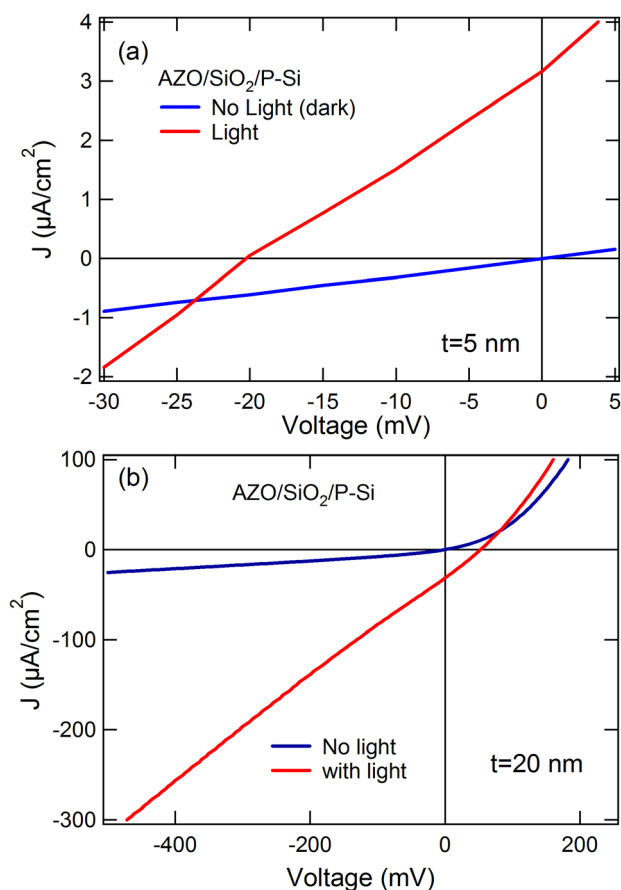


FIG. 1. (Color online) Current density Vs. bias voltage of AZO/SiO₂/p-Si heterostructure with and without light illumination, (a) for SiO₂ of 5 and (b) 20 nm.

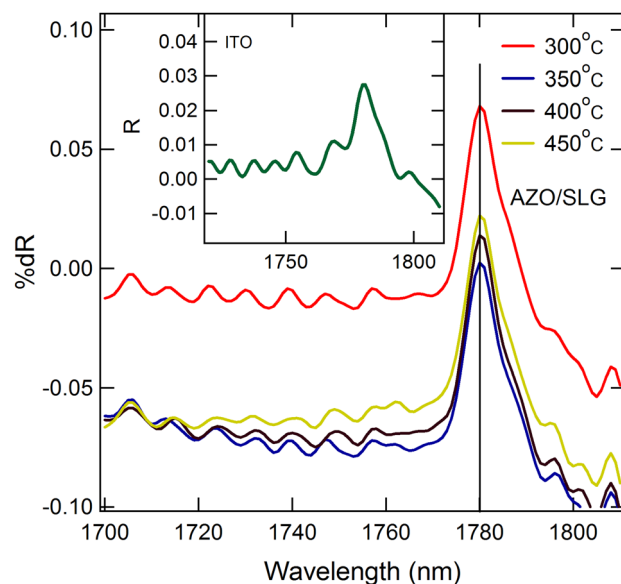


FIG. 2. (Color online) Wavelength dependence of differential reflectance of AZO/glass films grown at different temperatures. The inset shows the reflectance Vs. wavelength of ITO/glass.

SPP is an electronic oscillation with an in-plane charge motion at the interface and can only occur within the skin depth of a conducting film. When the appropriate condition is met the induced dipole gives rise to extinction at its plasma frequency. Figure 2 shows the percentage of differential reflectivity of AZO films on glass as a function of frequency. The films were synthesized at different temperatures as mentioned. The reflectivity of ITO is shown in the inset as a reference. It is very clear that the extinction is around 1780 nm wavelength for the specified angle above. This is also consistent with our earlier report for Indium Tin Oxide (ITO).⁸ Note that the corresponding plasma frequency, which depend on target compositions, substrate

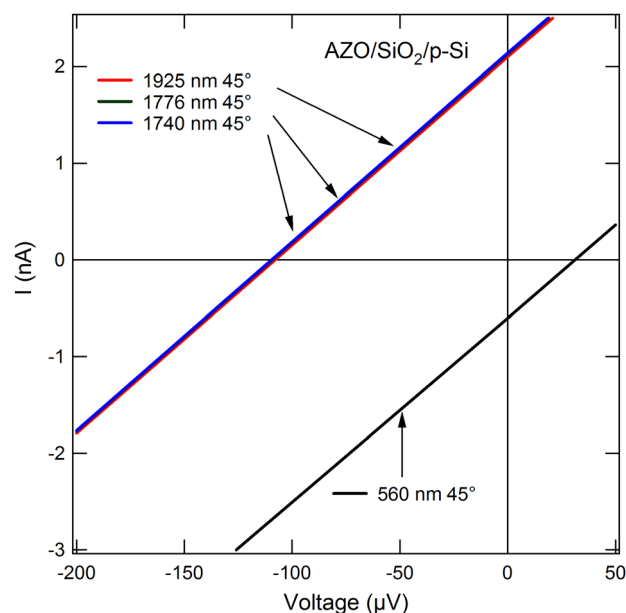


FIG. 3. (Color online) Current Vs. bias voltage of AZO/SiO₂/p-Si heterostructure with illumination of light at NIR and visible wavelengths for SiO₂ barrier of 5 nm.

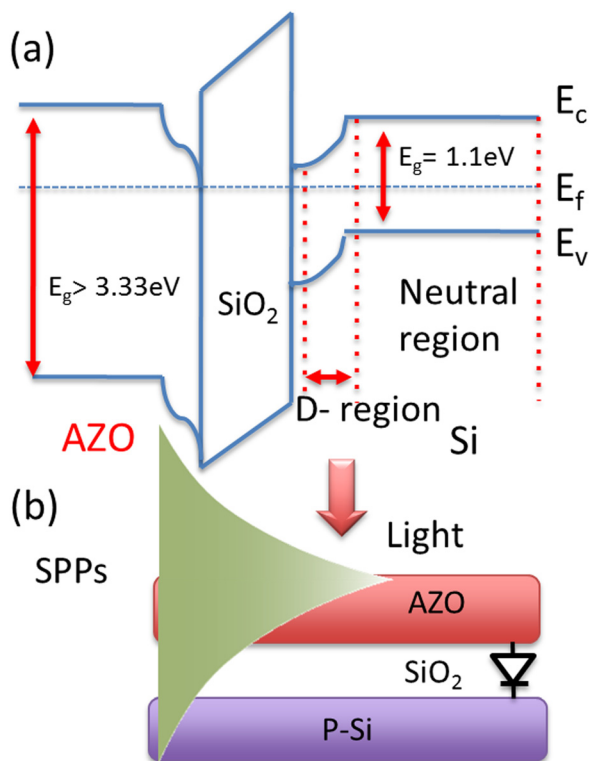


FIG. 4. (Color online) (a) Schematic of simple equilibrium energy-band diagram of the AZO/SiO₂/p-Si heterostructure and (b) Schematic profile diagram of the SPPs propagation on illumination.

temperatures, atmosphere in a chamber, and annealing, are within the range of reported values.¹⁵

Taking into account the above NIR frequency range, the AZO/SiO₂/p-Si diode device was illuminated with light in the range of NIR frequencies using the above configuration and the current and voltage characteristics are shown in Fig. 3. Two separate frequency ranges were selected, one in the region of NIR and the other in the visible range. It is remarkable to note that the enhanced photocurrent behavior is shown while the device is illuminated with NIR light compared to that of light with visible wavelength.

Figure 4(a) shows the energy band diagram of the AZO/SiO₂/Si heterostructure diode in equilibrium state. A SiO₂ insulating barrier with barrier height Φ_b is formed to integrate the two Fermi levels by energy band bending. Energy is mainly absorbed in Si substrate by generating electron-hole pairs when white light illuminates the AZO film. The photo-generated electrons tunnel through SiO₂ into AZO layer, while the holes are left in Si substrate. SPPs produced from the AZO layer propagate at the boundary between two media, metal (m) and dielectric (d), with positive $\text{Re}(\epsilon_d)$ and negative $\text{Re}(\epsilon_m)$ real parts of electric permittivity. Both electric and magnetic fields decay exponentially with an increase of the distance from the interface¹⁶ as shown in

Fig. 4(b). SPPs can pass through 5 nm SiO₂ layer to Si and enhances the photocurrent, however for SPPs decays for higher thickness.

The output photocurrent could be further improved by using more effective coupling methods for SPPs that can minimize the interface recombination and optimizing semiconductor as well as barrier thicknesses. In addition, our measurements indicated an alternative way to harvest light. Although the efficiency of these devices is currently much low, the process of surface recombination can be minimized for remarkable enhancement in energy conversion devices.

In Summary, we have demonstrated a simple approach for photovoltaic device comprising of SIS heterojunctions using surface plasmon polaritons generated in one of the semiconductor (AZO) and propagated through the dielectric barrier (SiO₂) to the other semiconductor (Si). AZO produces SPPs in the NIR range and enhanced the photovoltaic activities in the junction. The findings also suggest a range of new applications, since the IR plasmonic activity of semiconductor oxides semiconductor makes them suitable for SPR sensing, plasmonic waveguides, and electromagnetic surface enhancement on Si-based microelectronics/micro-photonics applications without using noble metals, Ag or Au.

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