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Light-Harvesting in *n*-ZnO/*p*-Silicon Heterojunctions

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Zinc oxide (ZnO) films were deposited onto Si to form *n*-ZnO/*p*-Si heterojunctions. Under the illumination of by both ultraviolet (UV) light and sunlight, obvious photovoltaic behavior was observed. It was found that the conversion efficiency of the heterojunctions increased significantly with increasing thickness of the ZnO film, and the mechanism for light-harvesting in the heterojunctions is discussed. The results suggest that ZnO films may be helpful to increasing the harvesting of UV photons, thus decreasing the thermalization loss of UV energy in Si-based solar cells.

Key words: Zinc oxide, ultraviolet light, photovoltaic

INTRODUCTION

Silicon-based solar cells have witnessed a number of milestone improvements in the past decades.[1–7] Improving conversion efficiency is one of the most important issues for solar cells. Shockley and Queisser[8] found that one of the important factors that limit the conversion efficiency of a solar cell is that photovoltaic semiconductor materials usually have a relatively high photoresponse only when the photon energy approaches their bandgap, while when the photon energy is higher than the bandgap, the extra energy is lost as heat in the solar cells. Since the bandgap of Si is 1.12 eV, the majority of energy in the ultraviolet (UV) region will be consumed by thermalization loss,[9,10] which adversely affects the conversion efficiency of Si solar cells. Meanwhile, thermalization loss caused by excess photon energy will increase the temperature of silicon solar cells, thus degrading their performance.[11] It has been demonstrated that the portion of UV light (with wavelength shorter than 380 nm) that is usable by silicon solar cells is less than 30%.[12] It is rational to speculate that, if a semiconductor that has a relatively high photoresponse in the UV region can be employed as an UV absorber, it will be of great help in improving the conversion efficiency and reducing the thermalization loss of Si solar cells. Zinc oxide (ZnO) has a bandgap of about 3.37 eV,[13] which corresponds to around 380 nm. It has a very high photoresponse in the UV range but is almost transparent in the visible and near-infrared regions.[14] Furthermore, ZnO is abundant, inexpensive, and environmentally friendly. The above characteristics make ZnO a suitable candidate UV absorber for use in Si solar cells. Nevertheless, a fundamental step in the combination of ZnO and Si solar cells is to study the UV light-harvesting properties and carrier transportation process in ZnO/Si heterojunctions. However, such reports are still very limited.[15–24]

In this work, *n*-ZnO/*p*-Si heterojunctions were constructed, in which the *n*-ZnO film served as an UV absorber, and Si as a visible and near-infrared absorber. The photogenerated carriers are separated at the *n*-ZnO/*p*-Si interface. It was found that the conversion efficiency of the heterojunctions increased with increasing thickness of the ZnO film under illumination by both UV (365 nm, 8 mW/cm^2) and solar irradiation (AM1.5G, 100 mW/cm^2), which suggests that, as an UV absorber, ZnO films are of help in increasing harvesting of UV light and reducing the thermalization loss of Si solar cells.

EXPERIMENTAL PROCEDURES

The *n*-ZnO/*p*-Si heterojunctions studied in this paper were obtained by depositing *n*-ZnO films onto

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p-Si substrates using a plasma-assisted molecular beam epitaxy (MBE) technique. The detailed growth conditions can be found elsewhere.[25] Briefly, the substrate temperature was kept at 600°C, the O_2 flow at 0.80 sccm (sccm denotes standard cubic centimeter per minute), and the pressure in the MBE chamber was maintained at 1.5×10^{-5} mbar during the growth process. By keeping other parameters constant except the growth duration, three n-ZnO/p-Si heterojunctions with different ZnO thickness were fabricated. The structural properties of the ZnO film were characterized by a Rigaku D/max-RA x-ray diffractometer (XRD) using the Cu K_α line as the irradiation source. Both optical transmission and absorption spectra of the films were recorded using a Shimadzu UV-3101PC scanning spectrophotometer. Current–voltage (I–V) characteristics of the heterojunctions were obtained by using a source meter (Keithley, 2400). The photocurrent was measured under illumination from a ThermoOriel 150-W solar simulator with AM1.5G filters with an intensity of 100 mW/cm^2 or 365-nm UV light with a power intensity of 8 mW/cm^2.

RESULTS AND DISCUSSION

Figure 1 shows a typical XRD pattern of the ZnO films grown on p-Si substrates. Besides diffraction from the Si substrate, only a sharp peak located at around 34.46° is visible in the pattern. The full-width at half-maximum of this peak is about 0.23°. According to its position, this peak can be indexed to diffraction from the (0002) facet of wurtzite ZnO. The XRD result indicates that the ZnO films are of wurtzite structure with their c-axis perpendicular to the substrate.

The absorption and transmission spectra of the n-ZnO films are shown in Fig. 2. Note that the films for the absorption measurements were prepared on sapphire under the same growth conditions as those grown on Si. It is clear from the transmission spectrum that the ZnO film has an average transmittance of over 85% in the visible region, while it has a relatively high absorption in the UV region. The transmission and absorption data indicate that, under illumination by sunlight, photons with a wavelength shorter than 380 nm will be absorbed by the ZnO layer, while those with a wavelength greater than 380 nm will be transmitted through the n-ZnO film and reach silicon in the n-ZnO/p-Si heterojunctions. Since silicon has a relatively high absorption in the visible and near-infrared regions, most of the transmitted light will be absorbed by the silicon. Light irradiation will therefore result in the generation of electron–hole pairs in both the ZnO and Si layers. By proper adjustment of the band alignment, electrons and holes may be separated at the n-ZnO/p-Si interface.

Figure 3 shows current density–voltage (J–V) curves of the n-ZnO/p-Si heterojunction for a ZnO thickness of 550 nm in the dark and under illumination by AM1.5G (100 mW/cm^2) sunlight. As evidenced from the figure, photovoltaic effect is clearly observed under AM1.5G (100 mW/cm^2) sunlight illumination. The open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) for the device are 131 mV, 6.7 mA/cm^2, and 22.8%, respectively. A conversion efficiency (η_p) of about 0.206% has been achieved in this heterojunction. Typical I–V curves of the heterojunction in the dark and under AM1.5G (100 mW/cm^2) sunlight illumination are shown in the inset of Fig. 3. Note that the reverse current of the device under simulated AM1.5G (100 mW/cm^2) sunlight illumination is larger than that under dark conditions, while the current under forward bias for the two conditions is almost the same. The above phenomenon can be understood as follows: A large number of electron–hole pairs will be generated under the simulated sunlight illumination, and the electrons and holes will be driven toward opposite electrodes with little barrier. As a result, the current for the device under illumination is larger than that under dark. Under forward bias, the electrons and holes will drift to the

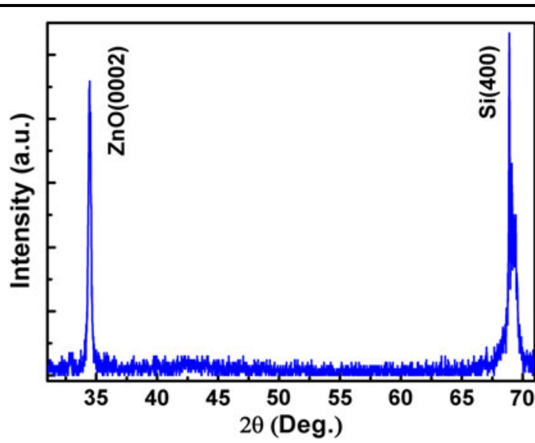

Fig. 1. Typical XRD pattern of the ZnO films grown on Si substrate.

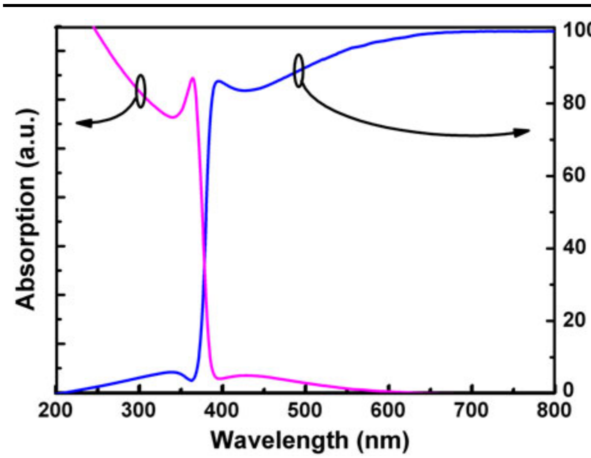

Fig. 2. Absorption and transmission spectra of the ZnO films.

depletion area and recombine there, so the current is almost the same for the device under sunlight illumination or under dark conditions, as shown in the inset of Fig. 3.

The mechanism for light-harvesting in the heterojunction can be understood well in terms of the band alignment. The equilibrium band diagram of the heterojunction derived from the Anderson model is shown in Fig. 4. The bandgap (E_g) and electron affinity (χ) values used are E_g(Si) = 1.12 eV and χ(Si) = 4.05 eV,[26] E_g(ZnO) = 3.37 eV, and χ(ZnO) = 4.35 eV.[27] The carrier concentration in the n-ZnO and p-Si layers measured by Hall measurement is 2×10^{18} cm^{-3} and 1×10^{19} cm^{-3}, respectively. Based on the carrier concentration data, the Fermi level in ZnO lies 81 meV below its conduction band, while the Fermi level in Si lies 1.5 meV above its valence band. According to the Anderson model, the conduction band and valence band offsets in the n-ZnO/p-Si heterojunction are 0.3 eV and 2.55 eV, respectively. When the heterojunction is illuminated by sunlight, the majority of the UV photons [with energy $E > E_g$(ZnO)] of the sunlight will be absorbed by the ZnO film due to its large absorption coefficient in this spectral region, and electron–hole pairs will be generated in the ZnO layer. Meanwhile, most of the photons with energy $E < E_g$(ZnO) will be transmitted through the n-ZnO film due to its high transparency in the visible and near-infrared regions. These transmitted photons will be absorbed by the p-Si, and electron–hole pairs will be generated therein. The built-in electric field in the n-ZnO/p-Si interface will drive the photogenerated holes in the ZnO layer toward the Si side, while the electrons generated in the Si layer will be driven to the ZnO side. As shown in Fig. 4, the barrier that hinders holes in ZnO from moving toward Si is negligible; simultaneously the barrier that hinders electrons in Si from moving toward ZnO is also negligible. Consequently, electrons and holes are separated at the heterojunction interface, and a photovoltaic effect results.

It is noted that the conversion efficiency is dependent on the thickness of the ZnO film. The conversion efficiency of heterojunctions with different ZnO film thicknesses under irradiation of 365 nm (8 mW/cm^2) and solar irradiation (AM1.5G, 100 mW/cm^2) is summarized in Table I. One can see that, under UV irradiation (365 nm), the conversion efficiency of the heterojunction with a ZnO film thickness of 150 nm is 0.000288%, but when the thickness of the ZnO film increases to 320 nm,

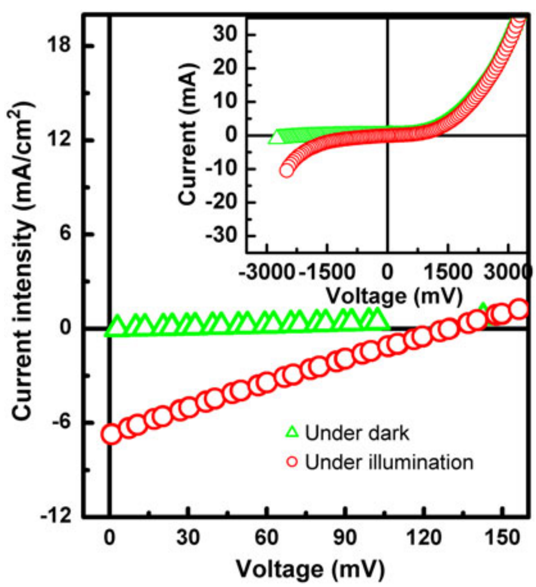

Fig. 3. J–V curve of the heterojunction in the dark and under AM1.5G (100 mW/cm^2) simulated sunlight. The *inset* shows the I–V curve of the heterojunction in the dark and under AM1.5G (100 mW/cm^2) simulated sunlight.

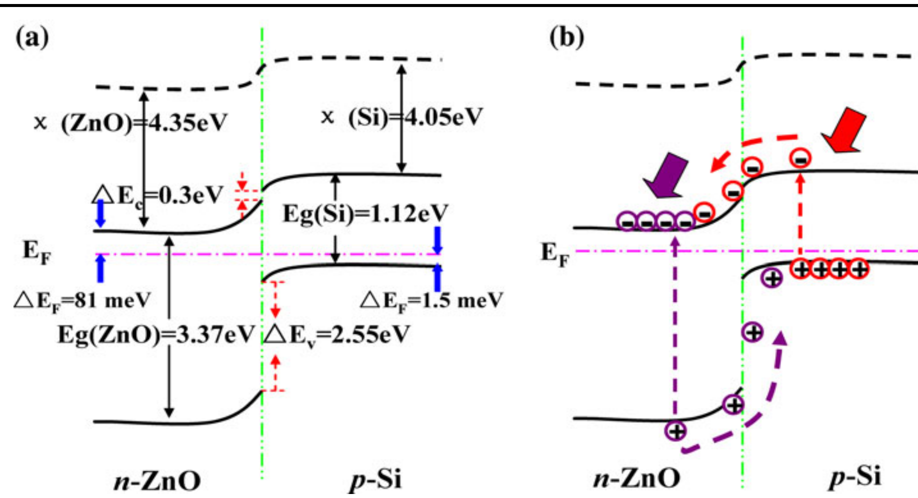

Fig. 4. Band diagrams of the n-ZnO/p-Si heterojunction in the dark (a) and under solar illumination (b).

Table I. Conversion efficiency of heterojunctions with different ZnO film thicknesses under UV or solar illumination

Solar Cell	Thickness of ZnO (nm)	Light Irradiation	Power Conversion Efficiency (%)
A	150	UV (8 mW/cm^2)	0.000288
		Sunlight AM1.5G (100 mW/cm^2)	0.00158
B	320	UV (8 mW/cm^2)	0.00358
		Sunlight AM1.5G (100 mW/cm^2)	0.00474
C	550	UV (8 mW/cm^2)	0.887
		Sunlight AM1.5G (100 mW/cm^2)	0.206

the efficiency increases to 0.00358%, and it increases to 0.887% when the thickness of the ZnO film is 550 nm. A similar trend was observed for heterojunctions illuminated by sunlight. As shown in the table, under solar irradiation, with increasing thickness of the ZnO film from 150 nm to 550 nm, the conversion efficiency of the heterojunctions increases gradually from 0.00158% to 0.206%. The above variation of conversion efficiency of the heterojunctions with ZnO thickness can be understood as follows: With increasing thickness of the ZnO film, the UV light absorbed by the ZnO film increases. Thus, more carriers that are generated by the illumination can reach the ZnO/Si interface and be separated by the heterojunction, assuming that the mean free path of the carriers is beyond the investigated thickness. As a result, higher efficiency is recorded. The above facts confirm that the *n*-ZnO/*p*-Si heterojunction can increase UV light-harvesting and decrease the thermalization loss of UV energy in Si-based solar cells.

CONCLUSIONS

n-ZnO/*p*-Si heterojunctions have been fabricated. With increasing the thickness of the ZnO film, the conversion efficiency of the heterojunctions increases significantly under the illumination of both UV and sunlight, which suggests that, as an UVs absorber and converter, ZnO films can effectively harvest UV photons. One can speculate from the above results that, by depositing a ZnO films onto Si solar cells, the thermalization loss that adversely affects performance could be effectively reduced, and the efficiency of Si solar cells may be increased due to increased harvesting of UV light by the ZnO film.

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