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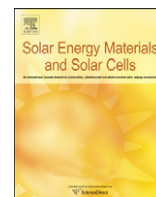
ZnO/ZnSe type II core–shell nanowire array solar cell

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ABSTRACT

We report the realization of a prototype solar cell based on a ZnO/ZnSe core/shell nanowire array. The ZnO/ZnSe core/shell nanowire forms a type II heterojunction that can have an effective bandgap much below that of either component. The nanowire array architecture offers strong enhancement in light absorption through increasing the junction area and light trapping. The device shows a photo-response threshold of ~ 1.6 eV and a large open circuit voltage of 0.7 V. Type II optical transition at the ZnO/ZnSe interface is further confirmed by transmission, photoluminescence and time-resolved photoluminescence. This result opens up new options in selecting the absorber material for a solar cell.

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1. Introduction

The premise of a sensitized solar cell (SSC) is that a semiconductor with a large bandgap (e.g., TiO_2 or ZnO) on its own cannot efficiently absorb light to be practically useful for making a solar cell, thus, needs to be "sensitized" by an appropriate "sensitizer" (e.g., dye molecules or quantum dots) [1]. In the SSC, on the one one hand, the sensitizer plays the primary role of light absorption and carrier generation; on the other hand, the sensitizer and the high bandgap material form a type II heterojunction (T2HJ) that facilitates charge separation, a key step for the formation of the photocurrent, and the large bandgap material further serves the role of carrier transporter. It has been recently suggested that when two large bandgap semiconductors (e.g., ZnO and ZnSe), which on their own neither of can be an efficient light absorber, forms a T2HJ, by working together they can absorb a much broad spectrum of light as though the T2HJ has a much lower bandgap than any of the components. Therefore, an array of such T2HJs, core-shell nanowires in particular, can make an efficient solar cell [2]. Conceptually, this is a major departure from the general idea of the SSC where the light absorption is almost entirely relying on the work of the "sensitizer". One could perhaps view the proposed approach as two large bandgap semiconductors mutually sensitizing each other. And in fact, on this regard, it is closer to the genuine sense of sensitization, because the high bandgap materials are now actively involved in the carrier generation process. Previous attempts along this line have shown some success, for instance, the synthesis of ZnO/ZnSe core/shell nanowire array, [3] and the demonstration of a PV device based on the ZnO/ZnS core/shell nanowire array [4]. However, the key feature, photo-response associated with the T2HJ in the spectral region well below both bandgaps of the components, was not demonstrated. In this paper, we report the first demonstration of this key effect in a solar cell based on the ZnO/ZnSe core/shell nanowire array, where the threshold of the photo-response is found to be at around 1.6 eV, much below the bandgap of either component (3.3 and 2.7 eV, respectively) [5]. In addition, we report the results of optical measurements, including transmission, photoluminescence (PL), and time-resolved PL, to characterize the type II transition that occurs at the ZnO/ZnSe interface.

2. Approach and techniques

The growth of well-aligned ZnO/ZnSe nanowire arrays (NWAs) was carried out in a horizontal quartz tube furnace in two steps (ZnO followed by ZnSe) on a glass substrate that was first coated with a 1-μm-thick ZnO film by MBE at room temperature. Morphologies of the as-grown ZnO and ZnO/ZnSe NWAs were characterized by a FE-SEM. The structures and compositions were analyzed by XRD at grazing angle mode, as well as TEM, and EDS. Details for the growth and structural characterizations have been reported elsewhere [5]. An UV/Vis/NIR spectrophotometer was used to measure the transmission spectra. Room temperature PL

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Fig. 1. Device structure.

Fig. 2. Transmission spectrum of a ZnO/ZnSe nanowire array. (a) Transmission spectrum, (b) derivative spectrum.
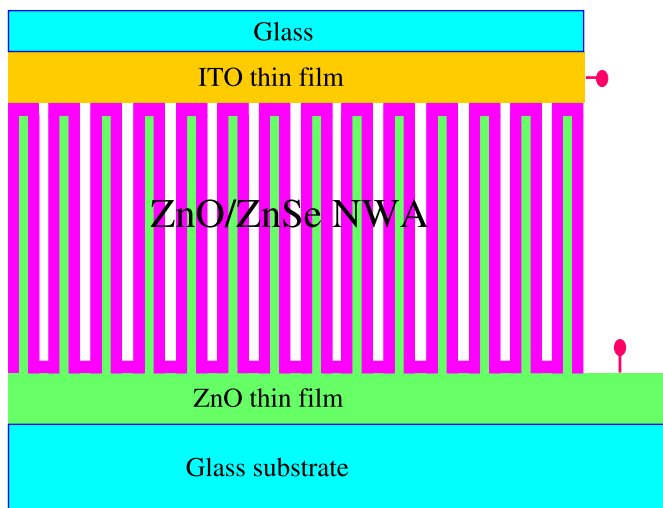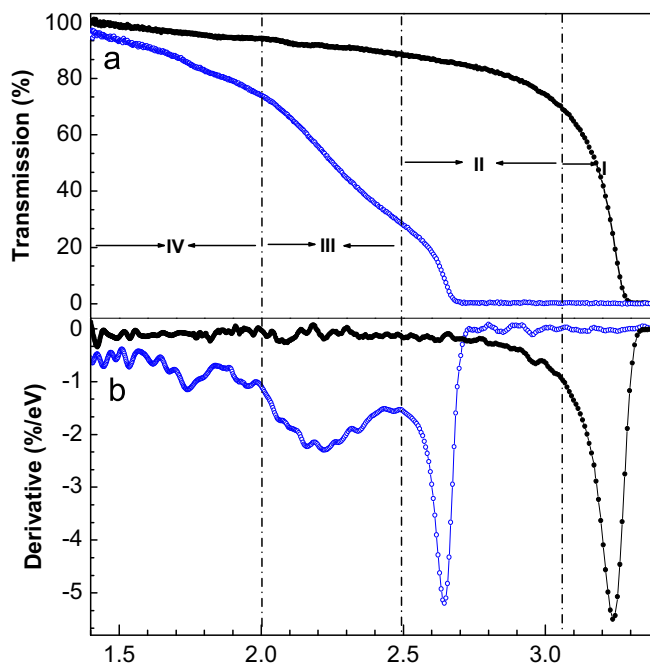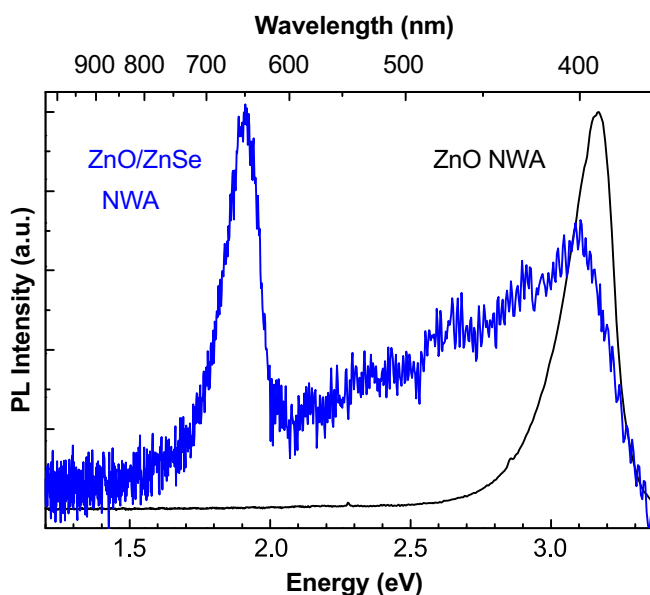

Fig. 3. Photoluminescence spectra (room temperature).

spectra were measured with excitation of a KrF excimer laser (248 nm). To investigate the photo-response of the ZnO/ZnSe core/shell NWA, the nanowire wafer was bonded to a 200 nm-thick indium tin oxide (ITO) coated quartz glass, and the ZnO film was contacted with an indium probe. The solar cell device structure is shown schematically in Fig. 1. The effective device area is about 1.0 cm^2. The external quantum efficiency (EQE) was measured on a broadband spectroscopy system consisting of a grating monochromator, a 200 W bromine-tungsten lamp, and a locked-in amplifier, by comparing with a reference Si cell. To further study the photo-response of the photovoltaic device, the open-circuit voltage V_{oc} of the device was measured under the radiation of a defocused 10 mW He-Ne laser, and compared with the reference Si cell. Time-resolved PL and the time-integrated PL spectrum were measured at low temperature ($\sim$8 K), excited by a femtosecond laser at 365 nm with a 76 MHz repetition rate (an average power 120 μW or density $\sim$5 kW/cm^2) and detected by APD detectors.

3. Results

The SEM measurement showed that well-aligned ZnO nanowires with a length of about 1.4 μm were grown vertically from the ZnO film substrate, with nanowire sizes varying from 40 to 80 nm. The ZnSe shell was found to cover uniformly over the ZnO nanowire core. The structures of ZnO and ZnO/ZnSe NWAs were determined by XRD: for the former only the wurtzite (WZ) (0 0 2) was observed, for the latter three additional peaks were found corresponding to the Zinc-blende (ZB) (1 1 1), (2 2 0), and (3 1 1) peaks of ZnSe. TEM and EDS data confirmed the epitaxial growth of the ZnSe shell on the ZnO core. A thin transitional ZnSe layer of WZ phase was found between the ZnO core and the ZB ZnSe shell.

Fig. 2(a) and (b) show the transmission spectra of ZnO and ZnO/ZnSe core/shell NWA and their derivative curves, respectively, measured at room temperature. For the core/shell NWA, the absorption was found to extend into to NIR. The spectrum is qualitatively and approximately divided into four spectral ranges that correspond to four different optical transition processes: I – the interband transition of ZnO, II – the interband transition of ZnSe, III – Interfacial transition between ZnO and ZB-ZnSe (the WZ-ZnSe layer could be very thin for certain portion of a NW or

some NWs), and IV – the interfacial transition between ZnO and WZ-ZnSe. The spectral range of the process III and IV are expected to overlap significantly in the spectrum. Fig. 3 shows the PL spectra for ZnO and ZnO/ZnSe NWAs, also measured at room temperature. For the latter, a distinct peak emerges in the region from 1.7 to 2.0 eV, corresponding to the near infrared absorption shown in Fig. 2. The optical transition below the bandgap of ZnSe was attributed to the interfacial transition at the interface of ZnO and ZnSe [5]. In the simple type II heterojunction picture, the transition should result from the free electron in ZnO and free hole in ZnSe, perhaps with some small Coulomb
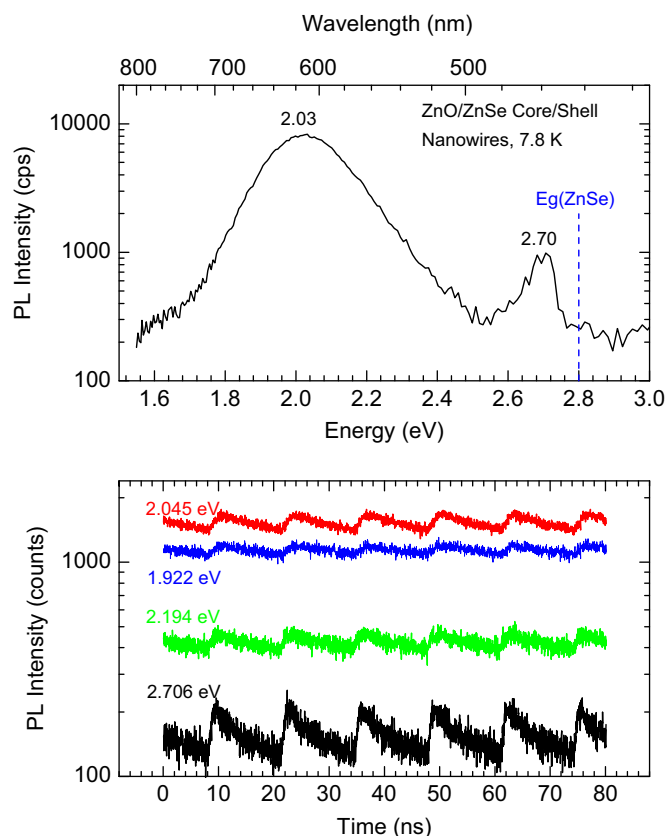
Fig. 4. Time-resolved photoluminescence measured at low temperature. (top) Time averaged spectrum, (bottom) decay curves monitored at different emission energies.

Fig. 5. External quantum efficiency of a ZnO/ZnSe nanowire array PV device.

interaction between the electron and hole. Nevertheless, we do recognize the possibility that such transition could be related to the defects associated with the highly strained and complicated interface.

To gain more insight into the origin of the below bandgap transition, we have performed time-resolved PL at low temperature, because one of the key fingerprint of the type II transition is that the radiative recombination typically has a long decay time. Fig. 4 shows the time dependence of the PL intensity at various energies, together with a time-averaged PL. Although not measured from the same sample, the peak energy of type II transition is found to be around 2.03 eV at 8 K, which is consistent with the room temperature value of $\sim$1.9 eV, if one takes into account the temperature dependence of the bandgap change (typically $\sim$100 meV between 0 K and 300 K). The time dependent data show periodic modulations with very little decay within each period with its length of 13.16 ns determined by the repetition rate of the laser. The time dependent data clearly indicate long PL decay times for various optical transitions in the whole broad spectral range. Fitting the curve of 2.045 eV (near the peak of the broad band, we obtain an estimated decay time of $\sim$64 ns. This value is two orders of magnitude longer than the typical radiative decay time in a direct bandgap semiconductor at low temperature. In the future, more accurate measurements should be performed using a substantially lower laser repletion rate. The weak peak at $\sim$2.70 eV, which is below the bandgap energy of 2.80 eV for ZnSe, [6] also exhibits relatively slow decay with a fitting result of $\sim$20 ns for the decay time. We tentatively suggest this transition is related to the interfacial transition of WZ-ZnSe/ZB-ZnSe that is expected to also have a type II band-alignment [5].
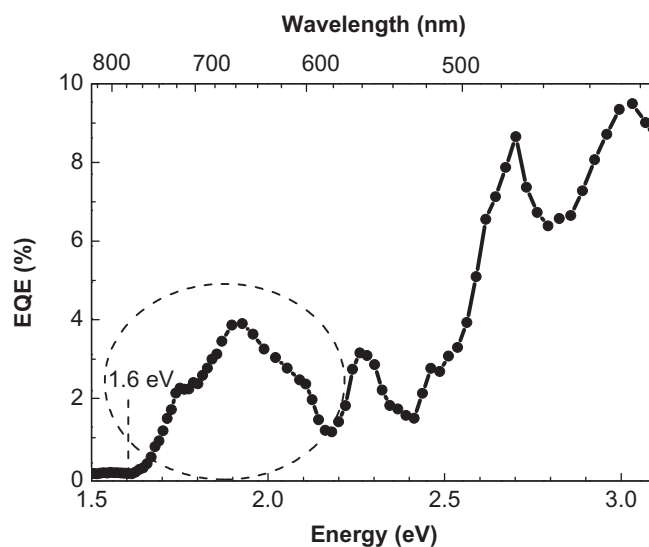
Fig. 5 shows the external quantum efficiency (EQE) of the coaxial nanowire cell under different light wavelengths. A photo-response band associated with the type-II interfacial transition appears in the energy range well below the bandgap of ZnSe, with a peak energy at $\sim$1.9 eV and a threshold at $\sim$1.6 eV. This result offers the ultimate confirmation that the type II transition can indeed be useful for the photovoltaic application. The EQE in the red spectrum reaches about 4%, which is comparable to the maximum of about 9.5% in the violet spectral range. The relatively low absolute efficiency, resulting from the small photocurrent, is likely due to the fact that both electrical contacts are not of high quality: the ZnO buffer layer being highly resistive and the ZnSe/ITO contact being merely pressed against each other. However, the comparable efficiencies between the NIR and UV spectral ranges shown in Fig. 5 suggest that such a device could potentially achieve much higher efficiency, because the EQE of the ZnO spectral range can be expected to be much higher than the result achieved on this preliminary device. In Fig. 6, we show the power density dependence of the open-circuit voltage V_{oc} of the device. For the NWA device, V_{oc} reaches as high as 0.70 V at 660 μW/cm^2 (a fairly low power density compared to the AM 1.5 solar spectrum, $\sim$100 mW/cm^2), compared to 0.37 V for the Si cell. We further note that on one hand, based on Fig.6(a), the power dependence of the NWA device is very different from that of the Si cell, the typical behavior of a p–n junction cell (showing a "saturating" V_{oc}), which indicates that the V_{OC} of the NWA device could potentially grow to a significantly even higher value; on the other hand, based on the semi-log plot of Fig.6(b), the NWA device shows more apparent deviation than the Si cell from the ideal model of Shockley–Queisser (i.e., a slope of kT/q), indicating that defects are playing more significant role in the NWA devices.

4. Conclusions

This work demonstrates a promising new PV technology based on the type II heterojunction in the architecture of core/shell nanowire array, involving only the large bandgap materials that are generally considered not useful as absorber. For the specific combination of ZnO/ZnSe and the device tested, the effective bandgap is approximately 1.6 eV, which corresponds to a Shockley–Queisser efficiency limit 30% under AM 1.5. The device
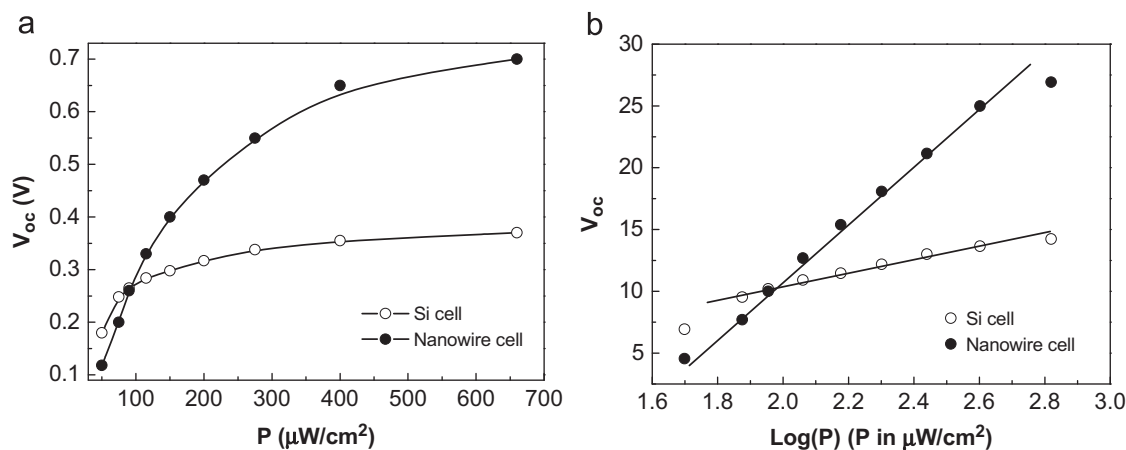
Fig. 6. Open-circuit voltage vs. power density. (a) P (μW/cm^2) and (b) Log(P) (V_{oc} in kT/q and P in μ/W/cm^2).

can be further optimized in terms of the geometrical parameters, structural uniformity, electrical contacts, etc.

Acknowledgment

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