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Enhanced photoresponse in ZnO nanowires decorated with CdTe quantum dot

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The photoresponse of ZnO nanowires irradiated with photons having energies below the band gap of ZnO (3.4 eV) was studied before and after deposition of CdTe quantum dots via a pulsed electron-beam technique. The small amount of deposited CdTe did not increase the dark current of the samples. However, a substantial increase in the steady state photocurrent was observed after CdTe deposition suggesting a clear photosensitization effect. Results revealed that CdTe influences the photoconductivity transients of ZnO by minimizing its interaction with oxygen in air as well as by providing additional traps that serve to increase the photocurrent time constant. © 2007 American Institute of Physics. [DOI: 10.1063/1.2822896]

Recently, ZnO nanowires (ZnO NWs) have been employed in dye-sensitized1 and hybrid solar cells (PVs).2 Nanowires provide direct conduction pathways for the electrons from the point of injection to the collection electrode. Thus, it can significantly improve the charge transport efficiency, which is arguably the bottleneck for nanocomposite PVs. In addition, it is a key challenge to harness most of the photons in the solar spectrum, where about 60% of them have wavelengths longer than 700 nm. One attractive concept to realize this is to employ narrow band gap quantum dots (QDs) to photosensitize a wide band gap semiconductor, which serves as the host material. In the late 1990s, this concept was demonstrated on TiO2 electrodes by using QDs dispersed in solution3,4 and recently, it has been reported on ZnO NWs.5 However, reports of other potential photosensitizers for ZnO are still limited. In fact, most reported QD-photosensitized PVs utilize solution-processed QDs. In these systems, surface contaminants produced during solution synthesis may result in a poor interface between the QDs and the host materials, thus limiting the charge transfer efficiency. It is therefore important to explore other materials as well as alternative techniques in depositing QDs directly on the host material for PVs. In this report, it is demonstrated that CdTe, whose band gap energy is 1.5 eV (bulk), is a promising photosensitizer for ZnO. It can be directly deposited on ZnO NWs as QDs via pulsed electron-beam deposition (PED) technique.

The samples were prepared by growing ZnO NWs on 8 × 16 mm2 glass substrates via a modified low temperature method.6 For characterization, the sample was pressed on a custom-made holder by spring-loaded clips, as shown Fig. 1(a). The Cu contacts on the holder with separation of ~7 mm, facilitate two-point probe I-V measurement. A window with dimension of 4 × 7 mm2 was created between the Cu contacts to expose the middle region of the sample to the light source for photoresponse studies. The light source was a halogen lamp equipped with a long-wave pass filter with a cutoff wavelength of 450 nm. Near the sample surface, the power density was ~10 mW/cm2. The photoresponse was measured by recording the current versus time at a constant bias of 2 V while illumination was turned on and off by a shutter. To deposit CdTe on the exposed region of the sample, the whole assembly was transferred into the PED

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**FIG. 1.** Experimental details. (a) Mounting of ZnO nanowire sample on the holder during characterization and (b) CdTe deposition. The exposed ZnO nanowires are facing directly the light source and the CdTe target, respectively. (c) Representative scanning electron micrograph and (d) photoluminescence spectra of ZnO nanowires used in this study.

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chamber [Fig. 1(b)]. Commercially available CdTe was used as the ablation target with a target-to-substrate distance of \( \sim 50 \) mm. Deposition was performed with a background gas pressure of 12 mtorr (Ar), an average electron energy of 15 keV, and a pulse width of 100 ns at 2 Hz repetition rate. The whole assembly was then removed from the PED chamber and was left in the dark in order for the sample to reach dark equilibrium. Afterwards, the photoresponse of the sample was characterized again using the same conditions employed prior to the CdTe deposition. By not removing the sample from the holder during the whole experiment, it eliminated possible variation in the contact resistance. Overall, the ZnO NWs featured a weblike morphology with evident interwire connectivity [Fig. 1(c)]. The nanowire diameter has a broad distribution and most of them have lengths exceeding 1 \( \mu \)m. All the samples used in this study displayed good stoichiometric composition and crystallinity. Figure 1(d) depicts a typical photoluminescence spectrum showing a sharp excitonic emission at 384 nm with intensity of two orders of magnitude stronger than the visible emission associated with defects such as oxygen vacancies. From \( I-V \) measurement in the dark, a slightly non-Ohmic conduction of the samples was observed even after the deposition of CdTe. This may be due to the electron hopping between defect states. The samples had an average dark resistance in the order of 10\(^9\) \( \Omega \) from fitting a line roughly to the nonlinear \( I-V \) curves. Under UV light with power density of \( \sim 7 \) mW/cm\(^2\), the observed \( I-V \) characteristics were linear and their resistance dropped by about four orders of magnitude.

Results from two samples, labeled as S1 and S2, are presented in this report. These results fairly represent the overall finding from several samples. The difference between S1 and S2 was the number of pulses used in the deposition of CdTe. S1 and S2 received 25 and 50 pulses, respectively. Based on prior calibration, the average deposition rate as measured from 3000 pulses was 0.06 nm/pulse. This suggests that the distribution of CdTe was sparse and that they did not form a continuous network on top of ZnO NWs. This is strongly supported by the fact that the dark resistance for both samples did not change after deposition. To examine the optical property of the CdTe deposited on S1 and S2, a CdTe film was prepared separately on glass substrate using the same PED parameters. The thickness of the film was around 180 nm. Results from optical transmission measurement revealed that the transmission onset of this film was blue shifted from 800 nm (bulk) to around 600 nm indicating that the CdTe deposited on ZnO NWs indeed consisted of QDs. However, further high-resolution electron microscopy study will be necessary to verify this. Figures 2(a) and 2(b) plot the change in photocurrent (\( \Delta I \)) versus time when illumination was turned on at time \( t=0.5 \) min, as marked by the dashed line. The dark current was subtracted from the data so that \( \Delta I \sim 0 \) before illumination. Prior to CdTe deposition, both samples have consistent \( \Delta I \) (black curve) when illumination was turned on. This is the well-observed sub-band-gap photocconductivity in ZnO, which corresponds to the generation of electron-hole pairs via optical transitions between defect states and the band edge. After CdTe deposition, \( \Delta I \) was enhanced for both samples (red curve) suggesting that when CdTe was illuminated, it contributed to the transport current in ZnO NWs. This behavior is attributed to the transfer of photoexcited electrons from the conduction band of CdTe to that of ZnO, which is favorable because for CdTe, the position of the lowest unoccupied energy level is just above the lowest unoccupied energy level of ZnO. This is a strong evidence of a photosensitization effect. CdTe provides additional electrons, which the ZnO cannot generate under visible illumination. It is worthwhile to mention that for comparison, another sample was subjected to the same PED process but the CdTe target was replaced with ZnO. Hence, it was assumed that ZnO nanoparticles were deposited on the ZnO NWs. For this sample, the photoresponse before and after CdTe deposition strongly overlapped. This result further supports that the CdTe QDs deposited on ZnO NWs were responsible for the photosensitization effect. In addition, S2 had the higher \( \Delta I \) after CdTe deposition because it received 50 pulses, which is twice the number received by S1.

To quantify the enhancement of \( \Delta I \), the transient photocurrent of the samples was analyzed. In the analysis, time \( t=0 \) was set as the time the illumination was turned on and \( \Delta I \) was measured up to \( t=30 \) s in order to capture the relevant curve. It can be seen in Figs. 2(a) and 2(b) (red curves) that \( \Delta I \) rises rapidly after illumination and reaches a steady state then starts to decrease gradually. For S1 and S2, the steady state photocurrent started to decrease gradually after roughly 30 s of illumination. This phenomenon is mostly observed when ZnO is in air due to surface related photocurrent, which is primarily governed by desorption and adsorption of oxygen. The rise in \( \Delta I \) when illumination is turned on can be described by a stretched exponential function of the form

\[
\Delta I = I_s [1 - e^{-(t/\tau)^\delta}]
\]

The parameter \( \delta \), which reflects the relaxation mechanism, is an exponent between 0 and 1. The steady state photocurrent and its time constant are represented by \( I_s \) and \( \tau \), respectively. Figures 2(c) and 2(d) show the transient \( \Delta I \) (symbols) and the best fit of the stretched exponential function (red curve). For S1, \( I_s \) markedly increased from 0.42 to 3.8 nA and \( \tau \) changed from 0.6 to 2.3 s after CdTe deposition. How-
ever, $d$ stayed the same at 0.4, which implies that the underlying relaxation mechanism is the same with or without CdTe. A similar trend was observed for S2. The quantity $I_0$ increased from 0.43 to 12 nA, and $\tau$ from 1.4 to 4.7 s. The value of $d$ for S2 (0.6) was slightly different than for S1 but it also remained unchanged after CdTe deposition. The increase in $\tau$ after CdTe deposition may be explained in terms of the effect of electron trapping in achieving steady state current after illumination. In the ZnO nanowire network, the number of electrons reaching the electrode determines the measured current under a constant bias voltage. However, conducting electrons can be captured at trap centers. As a result, the photocurrent onset is slowed because steady state current will be reached only after all the traps are filled. Under this condition, an equilibrium between multiple electron trapping and detrapping events is observed. In the samples, the CdTe QDs provided additional electron traps, causing $\tau$ to increase. After the illumination is turned on, the CdTe traps must be filled before they can inject photoelectrons into the ZnO. The photocurrent onset is then determined by the filling times of ZnO and CdTe QDs. Since only the number of traps changed and not the underlying mechanism of trap filling, only $\tau$ was affected but not the value of $d$. Such traps in CdTe have already been documented. Similar traps have been identified from samples prepared by different methods and varying postannealing treatment. Hence, they are believed to be due to native defects and they are likely to be the traps present in the QDs deposited by PED. The filling times of most traps observed in CdTe are in the submillisecond range.

The photocurrent decay from the steady state value to dark current value was also investigated and it was normalized for S1 and S2 (Fig. 3). The slow decay, which suggests persistent photoconductivity, can be described by a sum of two exponentially decaying functions given by

$$I_n = A_1 e^{-(t/\tau_1)} + A_2 e^{-(t/\tau_2)}.$$

This equation reflects two different relaxation mechanisms with time constants $\tau_1$ and $\tau_2$. The condition $\tau_1 < \tau_2$ can be assigned so that the first term corresponds to the faster process. The values of $A_1$ and $A_2$, where $A_1 + A_2 = 1$, represent weighing factors that quantify the relative contribution of each mechanism to the decay process. It can be seen in Fig. 3 that the model equation (red curve) fits fairly well with the experimental data. For S1 and S2 before CdTe, the values of $A_1$ are 0.75 and 0.7, respectively, while $\tau_1 = 2.4$ s for both. They have $A_2$ values of 0.25 and 0.3, respectively, and $\tau_2$ values of 152 s and 136 s, respectively. These results show that the first term, which can be attributed to bulk related processes, dominates the decay process. They are characterized by shorter time scale. The second term is likely to be related to surface photocurrent, which is known to be a slower process. After CdTe deposition, $\tau_1$ remained the same for both samples indicating that the CdTe did not contribute to the number of hole traps that could reduce electron-hole recombination rate. This interpretation is further supported by the photocurrent onset data where the mechanism was unaltered after CdTe deposition as indicated by the unchanged value of $d$ in the stretched exponential model. However, $\tau_2$ decreased from 152 to 71 s for S1 and from 136 to 100 s for S2 after CdTe deposition. The reduction in $\tau_2$ implies that CdTe plays a significant role in the surface photocurrent by providing partial passivation that minimizes the interaction of oxygen with ZnO surface. This is consistent with what has been previously reported. ZnO films passivated with SiO$_2$ exhibits faster photocurrent decay than the unpassivated. The influence of CdTe on surface related photoconductivity is also reflected in the increase of $A_2$.

For S1, $A_2$ value changed from 0.25 to 0.35 while for S2, it changed from 0.3 to 0.4 after CdTe deposition. This indicates that the CdTe enhanced the contribution of surface photoconductivity to the photocurrent decay.

In summary, CdTe QDs have been deposited on ZnO NWs via PED technique resulting in a photosensitization effect. This effect is due to the photoinduced charge transfer from CdTe to the ZnO. The efficiency of ZnO nanowire-based PVs decorated with CdTe QDs is under investigation.

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