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The enhancement of ZnO nanowalls photoconductivity induced by CdS nanoparticle modification

F. Fang,[1,2] D. X. Zhao,[1,a)] B. H. Li,[1] Z. Z. Zhang,[1] J. Y. Zhang,[1] and D. Z. Shen[1]
[1]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 East Nan-Hu Road, Open Economic Zone, Changchun 130033, People's Republic of China*
[2]*Graduate School of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

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10 nm sized hexagonal CdS nanoparticles were decorated on the surface of well-aligned ZnO nanowall through a facile hydrothermal approach. The effects of CdS-cap layer on the optical and photoelectrical properties of ZnO nanowalls have been studied. It was found the CdS acted not only as a passivation layer to suppress the detrimental surface states of ZnO nanowalls, which reduced the deep-level emissions, but also as an interfacial carrier transport layer to reduce the probability of carrier recombination. Due to this effect a significant enhancement in ultraviolet photoconductivity of ZnO nanowalls was observed by the surface modification with CdS nanoparticles. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3045952]

The applications of nanostructured materials in microelectronic and optoelectronic devices are one of the major focuses in recent nanoscience researches.[1–3] As a wide-band-gap semiconductor ZnO nanostructures have attracted particular attention because of their unique properties and diverse nanostructures. In order to increase the performance of devices, how to suppress or eliminate the detrimental surface defect states becomes very important. For example, concerning the UV detection, higher surface recombination velocity reduces the photocurrent generation and lowers the sensitivity.[4] Therefore, it is necessary to develop an appropriate method to effectively passivate the unwanted surface states.

Surface modification has been recognized as one of the most advanced and intriguing methods to build tailored nanomaterials, which has been studied to improve the performance of photodetectors.[5,6] For example, AlO_x, GaAs, and Si were used as cap layers to passivate the surface states.[7,8] In this letter we report the effect of CdS nanoparticles coating on the photoconductivity of ZnO nanowalls. A UV photoconductivity enhancement was observed with the CdS surface modification of ZnO nanowalls.

The ZnO nanowalls were fabricated via a simple vapor-phase transport process in a horizontal tube furnace. A mixture of commercial ZnO and graphite powders with a certain weight ratio (1:1) was loaded in a quartz boat serving as the source material. The highly *c*-axis-oriented ZnO template layer (100 nm thick) was deposited on the Si substrate surface by electron beam evaporation at 400 °C. The substrates (ZnO/Si) were laid above the source material with a vertical distance of 4 mm. The whole experiment was in the protection of a constant flow of Ar (99.99%) with a flow rate of 100 SCCM (SCCM denotes cubic centimeter per minute at STP). Once the temperature was raised to 990 °C, oxygen was introduced into the furnace with a flow rate of 10 SCCM. After the growth of 30 min, the substrate was cooled down to room temperature under the mixture gas. Then, gray-colored product was found on the substrate. The CdS coating layer was formed by using a hydrothermal synthesis method on ZnO nanowalls.[9] 1 mmol $CdCl_2 \cdot 2.5H_2O$, 3 mmol $SC(NH_2)_2$, and required amount of polyethylene glycol were dissolved in aqueous solution. Then, 15 ml solution was transferred to a Teflon-lined stainless autoclave with a capacity of 30 ml. The as-grown ZnO nanowall/Si and a quartz substrate were put on the bottom. The reaction was carried out at 90 °C for 1.5 h. After reaction, buff-colored product was washed by de-ionized water and dried in air at 60 °C for several hours.

The x-ray diffraction (XRD) patterns of the as-synthesized ZnO/CdS composites were measured with an x-ray diffractometer with the Cu *Ka* radiation ($\lambda = 0.1542$ nm). The morphology of as-grown samples was investigated by field-emission scanning electron microscopy (FESEM). A standard lock-in amplifier technique was employed for the spectral response measurements, where a 150 W Xe lamp was used. Photoluminescence (PL) was performed by using a He–Cd laser line of 325 nm as the excitation source and a micro-Raman spectrometer in a back-scattering geometry configuration to detect the emission spectra. Moreover, in order to make the PL intensity data comparable, the position of the samples, the intensity of the laser, and the area of laser facula were kept almost the same for the samples.

Figure 1 shows the typical top view SEM micrographs of the pure ZnO nanowalls and CdS modified ZnO nanowalls, respectively. Two-dimensional ZnO nanowalls interconnect with each other forming a random honeycomblike template [shown in Figs. 1(a) and 1(b) at different magnification], which are serpentine with random curvature on the substrate. The nanowalls are about 200–300 nm thick and 1 μm high, whereon some stripes stand upright (because they are higher than other parts, they look bright in SEM image). Figure 1(c) shows the image of the ZnO nanowall/CdS composites. Compared with Fig. 1(b), it can be clearly seen that the surface of ZnO nanowalls becomes rough, and CdS nanoparticles could be observed covering the whole ZnO nanowalls surface. The CdS nanoparticles are nearly spherical in shape and show some aggregation. Because of

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[a)] Author to whom correspondence should be addressed. Electronic mail: dxzhao2000@yahoo.com.cn. Tel.: +86-431-86176322. FAX: +86-431-84627031.

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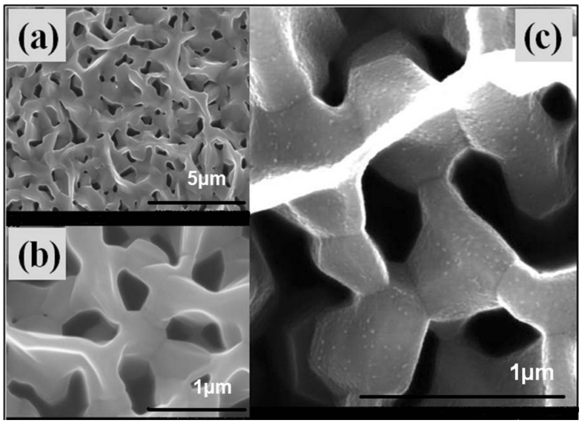

FIG. 1. FESEM images of [(a) and (b)] pure ZnO nanowalls at different magnification and (c) ZnO nanowall/CdS composites.

the impact of precision of the apparatus, we can only estimate that the diameter of CdS nanoparticles is about 10 nm. However, due to a strong tendency of aggregation, many of the individual CdS nanoparticles seem to be attached to each other to form clusters with bigger sizes (20–50 nm).

Figure 2 shows the XRD spectra of the pure ZnO nanowalls and the ZnO nanowall/CdS composites. As can be seen in Fig. 2(a), only hexagonal ZnO (002) diffractive peak could be observed, which suggests that ZnO nanowalls have the *c*-axis orientation. After the hydrothermal reaction, some additional diffraction peaks corresponding to the hexagonally structured CdS phase appear [as shown in Fig. 2(b)]. From the inset of Fig. 2, the broad nature of the CdS XRD peaks means the sizes of the CdS nanoparticles are very small. According to the Debye–Scherrer formula $D = 0.94\lambda / B \cos \theta_B$, the diameters of the CdS particles could be calculated at about 8 nm, which is in agreement with the SEM results.

Figure 3 shows the room temperature PL spectra of pure ZnO nanowalls, ZnO nanowall/CdS composites, and CdS nanoparticles, respectively (PL measurements were made several times and the phenomena were the same). The amplified emission spectrum of the CdS nanoparticles (inset of Fig. 3) shows two emission bands centered at 470 and 600 nm, which can be attributed to the near band emission and defect states related emission band (such as cadmium interstitials or sulfur vacancies in CdS nanoparticles).[10,11] Compared with the bulk CdS, the blueshift (from 510 to 470 nm) is clearly observed due to the quantum confinement effect.[12] The PL spectrum of the ZnO nanowalls is composed of two main parts. The UV emission band is attributed to the near-band-edge exciton emission. The visible emission band at around 2.43 eV (510 nm) is commonly believed to have originated from the singly ionized oxygen vacancy[13] or surface states.[14] For the ZnO nanowall/CdS composites, no emission band from CdS was observed. Compared with pure ZnO nanowalls, the peak position of the UV emission is the same, but the intensity is reduced, and the defect-related deep level emission is almost suppressed. It is understandable that the captured sulfur atoms or CdS nanoparticles could greatly change the surface structures of the ZnO nanowalls. For example, the oxygen vacancies or surface states (such as dangling bonds) in the surface area of ZnO nanowalls will be annihilated with the absorption of sulfur atoms or CdS nanoparticles, which decreases the deep-level emission of the ZnO nanowalls significantly. We suggest that both the reduced PL in the UV region of ZnO and the absence of CdS luminescence could be attributed to the quenching by interfacial charge transfer. It is generally accepted that the chemical properties of oxygen and sulfur are similar to each other. Consequently, the sulfur anions generated in the solution would have a tendency to be captured by the oxygen vacancies located mainly on the surface of ZnO nanostructures.[15,16] The absorbed sulfur anions on the ZnO nanostructures provide the initial nucleation sites for the surface growth of CdS nanoparticles, which make ZnO and CdS have the close contact. This close proximity makes possible the charge carrier transport through the interface between ZnO nanowalls and CdS nanoparticles. When high energy photons are absorbed, electrons are excited to the conducting band of the ZnO and holes are left in the valance band. The excited electrons will return from the conduction band back to the valance band through a radiative process. In the system of as prepared ZnO nanowall/CdS composites, holes from ZnO migrate favorably to CdS. This possibility is illustrated by the relative energy levels of ZnO and CdS,[17] as shown in Fig. 4. Because the conducting band of CdS is higher than that of ZnO, the photon generated electrons in CdS could migrate from CdS nanoparticles to the ZnO nanowalls. Such an interfacial charge transfer brings down the direct transition probability from conducting band to val-

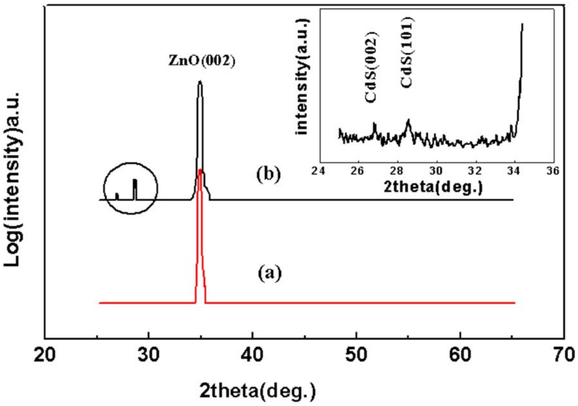

FIG. 2. (Color online) XRD results of (a) pure ZnO nanowalls and (b) ZnO nanowall/CdS composites. The inset shows the amplified spectrum, which is marked in (b).

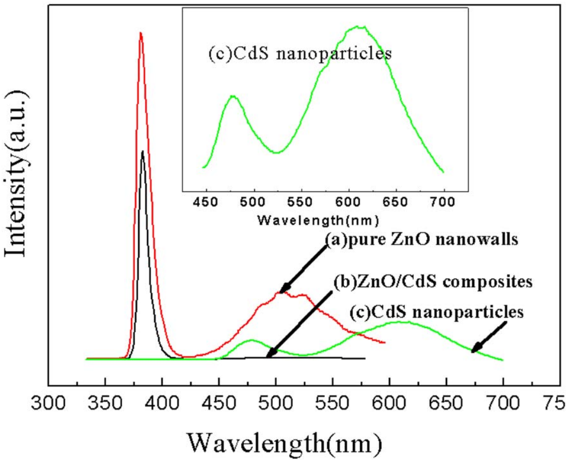

FIG. 3. (Color online) Room temperature PL spectra of (a) pure ZnO nanowalls, (b) ZnO nanowall/CdS composites, and (c) CdS nanoparticles. The inset shows the amplified emission spectrum of the CdS nanoparticles.

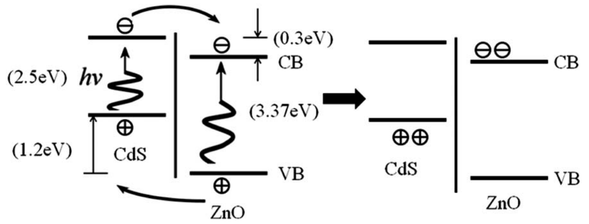

FIG. 4. The schematic of the interfacial charge generation, transfer, and separation between ZnO and CdS in the ZnO nanowall/CdS composites.

ance band in CdS. Moreover, the large extent of the ZnO nanowalls means that electrons and holes can diffuse far from the interfaces during their recombination time and some holes will not get trapped into CdS nanoparticles (thus some ZnO band-edge PL survives), while the smaller CdS particles mean that electrons generated in CdS almost all reach a ZnO nanowall/CdS interface during their recombination time and get trapped in ZnO, and the CdS band-edge PL is completely quenched.

To further investigate the effect of the CdS nanoparticles on the ZnO nanowalls, we examined the photoconductivity of pure ZnO nanowalls and ZnO nanowall/CdS composites using indium as electrodes [as shown in the inset of Fig. 5]. Figure 5 illustrates the photocurrent spectra of the pure ZnO nanowalls and ZnO nanowall/CdS composites, which shows after the surface modification by the CdS nanoparticles that the photocurrent efficiency of ZnO nanowalls is enhanced by one order of magnitudes. Meanwhile, the photon response peak shifts to a longer wavelength by 10–12 nm with a long tail. The appearance of the long tail is induced by the photoabsorption of the CdS nanoparticles (the PL emission peak at 470 nm). As for the redshift, we suggest that some new defect or surface states could be formed in the interface region with the absorption of sulfur atoms or CdS nanoparticles.[18] These defects may work as nonradiation recombination centers, which do not appear in PL spectrum, but they can also absorb photons to generate carriers, which corresponds to the 390 nm photoresponse. The above results show that the CdS nanoparticles have broadened the spectral range of the photocurrent response and improved the photoconductivity of ZnO nanowalls.

We can explain this improvement in the photoresponse from two sides. On one hand, any detrimental recombinations that occur at the surface will reduce the magnitude of photocurrent.[4] Such CdS cap layer suppresses the surface states effectively. On the other hand, photoconductivity is a convolution of photoinduced charge generation and charge transport. CdS can serve as hole traps in interface of ZnO/CdS composites by judging from their band structures (Fig. 4). After electrons and holes are generated by photoabsorption in ZnO nanowalls, the holes move to CdS and could be accumulated in the valance band of CdS. Such an interfacial charge transfer brings down the recombination probability of electrons and holes and increases the lifetime of the electrons in the conducting band of ZnO, which means the electrons in the conducting band of ZnO have more chances to migrate. In addition, the CdS nanoparticles can absorb photons with energy $E > 2.5$ eV and create carriers. The photon generated electrons in the conduction band of CdS have higher energy level than that of ZnO, which will intend to move to ZnO and be accumulated in the conducting band of ZnO. Thus, the UV photoconductivity of ZnO is enhanced effectively.

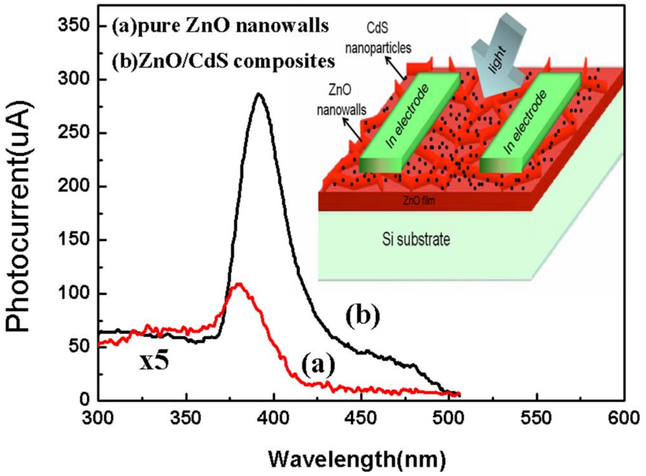

FIG. 5. (Color online) Photoconductivity spectra of pure ZnO nanowalls and ZnO nanowall/CdS composites. The inset shown the schematic of the ZnO nanowall/CdS composites photoconductor.

In conclusion, we synthesized CdS nanoparticles on ZnO nanowalls by a hydrothermal method. Significant photoconductivity enhancement of ZnO nanowalls has been demonstrated due to the surface modification with CdS nanoparticles. PL and photoconductivity results indicate that the surface states of ZnO nanowalls were passivated and an interfacial electron transfer occurred between the CdS nanoparticles and the ZnO nanowalls.

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[1] Y. Cui, Q. Q. Wei, H. K. Park, and C. M. Lieber, Science **293**, 1289 (2001).
[2] C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, and H. J. Lee, Appl. Phys. Lett. **81**, 3648 (2002).
[3] Z. L. Wang, Adv. Mater. (Weinheim, Ger.) **15**, 432 (2003).
[4] V. Adivarahan, G. Simin, J. W. Yang, A. Lunev, N. Pala, M. Shur, and R. Gaska, Appl. Phys. Lett. **77**, 863 (2000).
[5] F. Caruso, Adv. Mater. (Weinheim, Ger.) **13**, 11 (2001).
[6] R. A. Caruso and M. Antonietti, Chem. Mater. **13**, 3272 (2001).
[7] K. C. Hui, H. C. Ong, P. F. Lee, and J. Y. Dai, Appl. Phys. Lett. **86**, 152116 (2005).
[8] M. Passlack, M. Hong, J. P. Mannaerts, J. R. Kwo, and L. W. Tu, Appl. Phys. Lett. **68**, 3605 (1996).
[9] W. Qingqing, X. Gang, and H. Gaorong, Cryst. Growth Des. **6**, 1776 (2006).
[10] M. Agata, H. Kurase, and S. Hayashi, Solid State Commun. **76**, 1061 (1990).
[11] N. A. Arul Dhas and A. Gedanken, Appl. Phys. Lett. **72**, 2514 (1998).
[12] L. Spanhel, M. Haase, H. Weller, and A. Henglein, J. Am. Ceram. Soc. **106**, 5649 (1987).
[13] K. Vanheusden, W. L. Warren, C. H. Sesger, D. R. Tallant, J. A. Voigt, and B. E. Gnage, J. Appl. Phys. **79**, 7983 (1996).
[14] B. D. Yao, Y. F. Chan, and N. Wang, Appl. Phys. Lett. **81**, 757 (2002).
[15] P. D. Yang, H. Q. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, and H.-J. Choi, Adv. Funct. Mater. **12**, 323 (2002).
[16] Y. B. Li, Y. Bando, and D. Golberg, Appl. Phys. Lett. **84**, 3603 (2004).
[17] M. Ruckh, D. Schmid, and H. W. Schock, J. Appl. Phys. **76**, 5945 (1994).
[18] T. Gao and Q. H. Wang, Chem. Mater. **17**, 887 (2005).