Vol 17 No 8, August 2008
1674-1056/2008/17(08)/3103-05

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Trap induced slow photoresponse of single CdS nanoribbons*

Wang Fei-Fei(王菲菲)[a)b)†], Wang Chong(王 翀)[c)],
Cheng Ke(程 轲)[b)], and Zou Bing-Suo(邹炳锁)[b)d)]

[a)] *School of Physics and Electronic Engineering, Ludong University, Yantai* 264025, *China*
[b)] *Institute of Physics, Chinese Academy of Sciences, Beijing* 100080, *China*
[c)] *Institute of Opto-Electronic Information Technology, Yantai University, Yantai* 264005, *China*
[d)] *Micro-Nano Technologies Research Center and National Key Laboratory of CBSC, Hunan University, Changsha* 410082, *China*

(Received 14 March 2008; revised manuscript received 25 March 2008)

Wurtzite CdS nanoribbons are prepared by using a simple thermal evaporation method. Electron microscopy shows that the ribbons are smooth in surface and uniform in size. Besides the intrinsic emission, the photoluminescence spectrum of a CdS nanoribbon shows a peak at about 580 nm, which may arise from the defect- and the trap- related transitions. The photoresponse of single CdS nanoribbons is researched. When these nanoribbons are exposed to a laser with a wavelength of 400 nm, their conductivity is enhanced greatly. The conductivity of CdS nanoribbons cannot be restored to a value without any illumination even at 5 minutes after the illumination. A model is proposed to explain this phenomenon, which may be due to a slow photoresponse induced by the trap.

Keywords: CdS, photoresponse
PACC: 7865K, 7960

1. Introduction

Recently, the growing interest has focused on the construction and the integration of functional nanodevices based on the one-dimensional semiconductor materials. Electrically driven lasers,[1] transistors,[2] light emission diodes,[3−5] and gas sensors[6] have been reported and demonstrated well their electronic, optical, photoconducting, and sensor properties. Photodetector is also one of the most important applications of semiconductor materials. The first single nanowire photodetectors and optical switches were reported by Yang *et al*[7] and the conductivity of the ZnO nanowires was extremely sensitive to ultraviolet exposure. After that, a lot of coherent work has been proceeded. So far, the photoconducting properties of one-dimensional semiconductor materials such as carbon,[8,9] ZnO,[7,10] SnO_2,[11,12] GaN,[13,14] and CdS[15−17] have been investigated. Among these materials, CdS is the most suitable for detecting visible light due to its band gap (2.47 eV) and high sensibility. However, the defects and the trapping states in samples may strongly affect carrier dynamics and are deleterious for device applications. Up to now, persistent photoconductivity has been observed in ZnO[18−23] and GaN,[24−26] and this phenomenon is attributed to the defects and the trapping states. In the persistent photoconductivity effect, the carrier concentration increases gradually when exposed to the light and the photocurrent lasts for a long period of time after illumination. So, studying the effects of defects and trapping states on photoconductivity may help us understand the metastable properties of defects and optimize the properties of devices by improving the sample quality.

In this paper, CdS nanoribbons are prepared by using a simple method and the optical and photoresponse properties are studied. A model is proposed to illustrate the slow decay of carriers after illumination.

2. Experiment

The CdS nanoribbons were synthesized by using the physical evaporation of CdS powder in the presence of Au catalyst. Several silicon wafers were ultra-

*Project supported by the National Natural Science Foundation of China (Grant No 20173073), the State Key Development Program for Basic Research of China (Grant No 2002CB713802), the Nano- and Bio-device Key Project of Chinese Academy of Sciences, China, and the 985 Project of Hunan University, China.
†E-mail: fyfyforever@163.com

sonically cleaned in acetone and then a thin Au film of 10 nm in thickness was coated on each of them by sputtering. CdS powder was placed in a ceramic boat. The boat was located in the middle of a quartz tube of the horizontal tube furnace. Next to the ceramic boat, several clean silicon wafers coated each with an Au film were placed downstream of the gas flow. Prior to heating, high-purity He gas was flown through the quartz tube to eliminate O_2 and avoid any sort of oxidization. After about one hour, the gas flow rate was reduced. The furnace was rapidly heated to 900°C and maintained this temperature for one hour. The power was then switched off, and the quartz tube was cooled down to room temperature naturally. After vapour deposition, a yellow product was formed on the surface of Au-coated silicon wafers, which were placed in the downstream end about 9 cm away from the CdS source material.

The sample morphology was characterized by using a field-emission scanning electron microscope (SEM, Hitachi S-4200), and the sample composition was analysed by using an energy dispersive x-ray spectrum (EDS). X-ray powder diffraction (XRD) data were obtained from a Japan Rigaku D/MAX-2400 type diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ=1.54178Å). Micro-Raman experiments were conducted by using a Raman scattering spectrometer (LABRAM-HR, JY, Horiba), with a 514.5 nm line of an Ar+ laser used as an excitation source. The photoluminescence spectrum (PL) was taken on a PTI-C-700 fluorescence spectrometer, in which a He–Cd laser line (325 nm) was used as an excitation source.

3. Results and discussion

Figures 1(a) and 1(b) are the typical SEM images of the as-synthesized product collected from the silicon wafers. The product is composed of a large quantity of ribbon-like structures with lengths in a range of tens of micrometres. The high magnification SEM image shows that the nanoribbons each have a width of about 300 nm and a thickness of about 80 nm. The nanoribbons are uniform in width and thickness along their length direction. The yellow product deposited on the Au-coated silicon surface was identified as CdS by the XRD. Figure 1(c) shows the XRD patterns of the product. All the peaks correspond to the hexagonal wurtzite phase of CdS with lattice constants a=0.414 nm and c=0.672 nm. The peaks match well

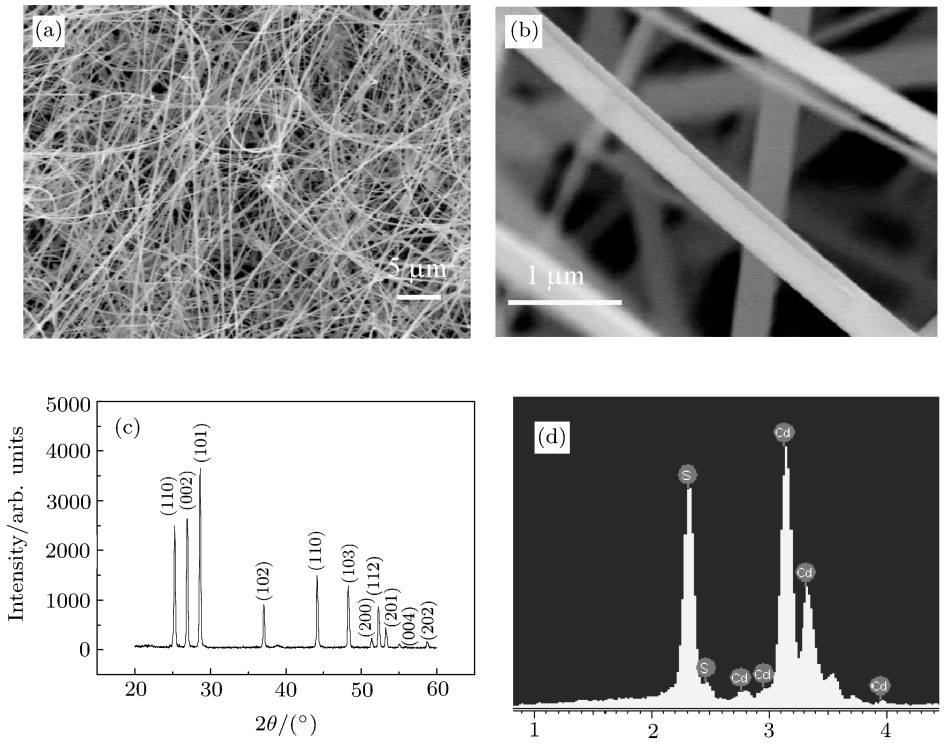


Fig.1. SEM images of the CdS nanoribbons at a low (a) and high (b) magnification power; and XRD patterns (c) and EDS (d) of CdS nanoribbons.

with those in the JCPDS card (Joint Committee on Powder Diffraction Standard, card no. 41–1049). The elemental compositions of these ribbons were investigated by using an in-situ EDX spectrum. Figure 1(d) shows the EDX spectrum of the sample, revealing the chemical purity of the sample with only cadmium and sulfur elements.

Figure 2(a) shows the microscopic confocal Raman spectrum recorded from a typical CdS nanoribbon. The characteristic Raman peaks of the nanoribbon is similar to those of a pure crystalline CdS.[27] These peaks at 300.52 cm^{-1} and 602.94 cm^{-1} correspond to the first-order and second-order longitudinal optical phonon bands of CdS, respectively. The PL was excited by a 325 nm line of a He–Cd laser. The PL spectrum of the sample is shown in Fig.2(b). The samples show an emission band at around 506 nm, which corresponds to the near band gap emission (2.47 eV). Besides the intrinsic emission, another emission at about 580 nm can be found, which may arise from the defect- and the trap- related transitions.[28] The defects and the trap states are unfavourable to the optical and electronic properties of semiconductor, and will affect the photoelectric property as well.

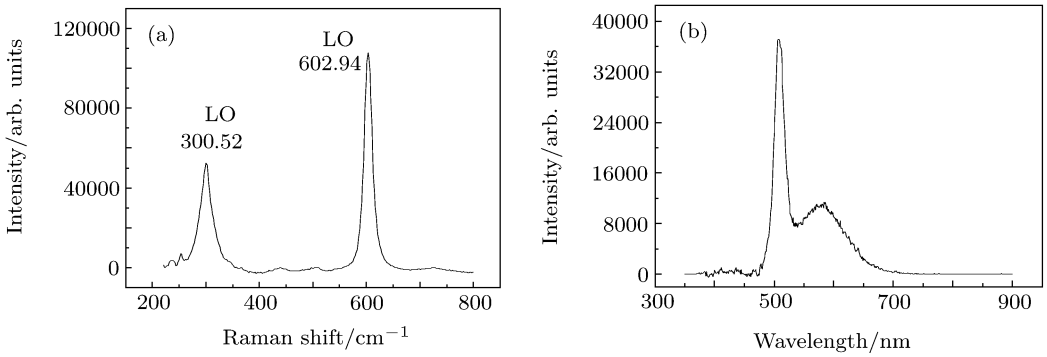


Fig.2. The room-temperature micro-Raman spectrum of a single CdS nanoribbon (a) and the photoluminescence of CdS nanoribbons at room temperature (b).

Figure 3 illustrates single-nanoribbon electrical characterization by using an atomic force microscope (AFM). Conductive atomic force microscope (C-AFM) is one of the most successful apparatus, which can provide us with abundant information of both the morphological and electronic properties of the material. The conductivity of the nanorribon was measured by applying a small voltage to the conductive AFM tip (Au plating) positioned directly on the nanoribbon. For the fabrication of single nanoribbon devices, CdS nanoribbons were dispersed on a silicon substrate (600 nm oxide) with two pre-fabricated Au electrodes. A frequency-doubled Ti:sapphire laser (400 nm) was used to provide the monochromatic light, which was focused and guided on the nanoribbons perpendicularly. We measured ten nanoribbons and the typical curves were presented. The current-voltage (I–V) curves of sample with and without light irradiation at two and five minutes after illumination were measured and shown in Fig.3, in which the upper-left and the lower-right insets are an SEM image of the device and the measurement setup diagram in our experiment, respectively. The applied voltage ranged from –3.0 V to +3.0 V. It is found from the I–V curves that the current increases nonlinearly with applied bias. The curve is symmetrical between the positive and negative regions of the bias voltage under the above conditions. It is found that the conductance of individual CdS nanoribbons is poor without any illumination. When these nanoribbons are exposed to a laser with a wavelength of 400 nm, their conductivity is enhanced greatly. The enhancement of conductivity under UV light illumination is due to the photo-generated carriers in the semiconducting nanoribbon as observed from the optical properties of both bulk and nanoscale CdS.[29,30] A larger photoresponse was detected at a higher bias. Unlike any usual photodetector, the current cannot be restored to a value without illumination, even at five minutes after the illumination.

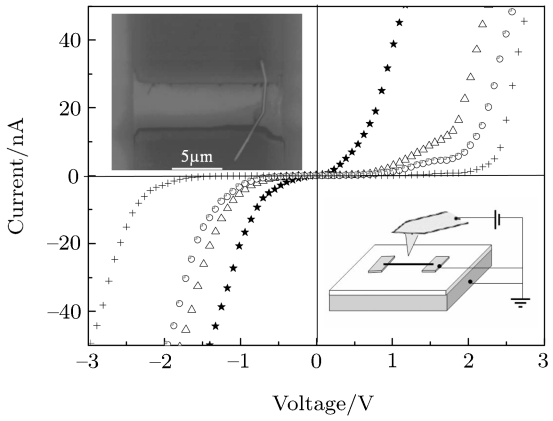


Fig.3. *I–V* curves of a CdS nanoribbon measured without any illumination (+), and with an exposure to UV light at a wavelength of 400 nm (⋆) at two (△) and five (○) minutes after turning off the UV light. The inset in the upper-left corner shows an SEM image of the nanoribbon bridging two Au electrodes. The inset in the lower-right corner shows a schematic diagram of the configuration for the photoconductive measurement.

The rectified *I–V* relation confirms the formation of Schottky junction between a high work-function metal (Au) and an n-type semiconductor (CdS). The metal-semiconductor-metal (M-S-M) structure may be modelled as being composed of two back-to-back Schottky barriers formed between CdS and Au electrode, in series with a semiconductor having a resistance *R*. And the curve shape is consistent with the structure.[31] The current increases nonlinearly with the bias voltage increasing, which may be concerned with the barrier formed at the interface between electrode and CdS. Usually, the energy band of CdS bends upwards near the surface, which may be caused by two factors. First, the difference in work function between Au (5.1 eV) and CdS (4.5 eV) leads to the formation of energy barrier at the interface between metal and semiconductor, thereby blocking the electrons moving to the metal and resulting in a high contact resistance with respect to the semiconductor. Second, when the CdS is exposed to the ambient air, oxygen is adsorbed on its surface. The adsorbed oxygen will capture electrons from the CdS and form negatively charged ions on the CdS surface. This process also leads to the band bending upward near the semiconductor surface. After illumination, the adsorbed oxygen is partially released, which results in the lowering of barrier height and the enhancing of carrier mobility. So, both the lowering of barrier height and the increasing of carrier concentration may lead to a higher conductivity after illumination.

In the previous reports, the one-dimensional CdS showed a good photoconductor characteristic of rapid response time.[15−17] While in our experiment, it is found that after removing the illumination, the current is higher than that without any illumination even at five minutes after the illumination. Why does there exist a persistent current? We believe that the persistent current observed may be concerned with the crystalline quality of the sample and due to the capture of holes by deep trap levels formed in the bandgap as shown schematically in Fig.4. Generally, for an n-type semiconductor, the intrinsic photoconductivity is mainly caused by photoexcited electrons. There may exist a small quantity of impurities and the defects in the material, and the impurities and defects form recombination centres and trapping centres in the energy gap according to their property. Though the numbers of photoexcited electrons and holes are equal, the holes are trapped by the recombination centres and trapping centres and so cannot move freely before their recombination with the electrons. Several processes may occur in the production and recombination processes of carriers. An electron is transitioned from a valence band to a conduction band by absorbing light with an energy equal to or greater than the band gap of the material, which leaves a hole in the valence band (1). The photoexcited holes can be captured by the recombination centre (2) and trapping centre (3). How are the non-equilibrium carries are recombed? Usually, there are two kinds of the recombination process. One is the direct recombination. The transition of electrons from a conduction band to a valence band leads to the direct recombination of electrons with holes (4). The other is the indirect recombination. Capture of a photoexcited electron by a recombination centre, which has previously captured a photoexcited hole (2), leads to the recombination of carriers (5). However, the holes in the trapping centre cannot recombined directly with the electrons in the conduction band, because the trapping centre, which has trapped holes, cannot trap electrons any more. The holes in the trapping centre may be thermally free from the valence band (6), trapped by the recombination centre (2), and then recombination with the electrons in the recombination centre (5). The holes may follow a series of capture and emission processes before they are recombined with electrons. Because the photoexcited holes are mainly captured by the trapping centre, the recombination rate is reduced. At the same time, the complicated recombination process of the holes in the trapping centre with the electron leads to

a slow decay process of photoconductivity along with a quick decay process by the recombination centre. So, the trapping, emission, and recombination of photogenerated holes in a CdS photoresponse device may cause the persistent photoconductance in this structure as have been observed for GaN.[24−26] The poorer crystalline quality of sample is correlated with an increased trapping density and a slow photoresponse to illumination.

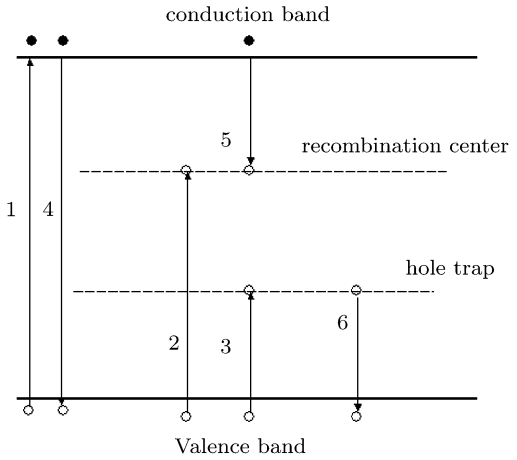


Fig.4. Schematic illustration of the possible processes that occur during photoconductivity experiments.

4. Conclusions

CdS nanoribbons are prepared by using a simple thermal evaporation method. Scanning electron microscopy shows that the ribbons are uniform in size and smooth in surface. The XRD patterns show that the as-prepared product is wurtzite CdS. The PL spectrum of CdS nanoribbon shows two peaks. One is at around 506 nm, which corresponds to the near band gap emission (2.47 eV). The other is at about 580 nm, which may arise from the defect- and the trap- related transitions. The photoresponse of single CdS nanoribbons were researched without any illumination and with an illumination, and at a few minutes after the illumination, separately. The conductivity of these nanoribbons is enhanced greatly when exposed to a laser with a wavelength of 400 nm, and it cannot be restored to a value without any illumination, even at 5 minutes after the illumination. A model is proposed to explain this phenomenon. The persistent photoconductivity may be due to the trapping states in the sample, which cause a slow response to illumination.

References

[1] Duan X, Huang Y, Agarwal R and Lieber C M 2003 *Nature* **421** 241

[2] Zheng G F, Lu W, Jin S and Lieber C M 2004 *Adv. Mater.* **21** 1890

[3] Huang Y, Duan X F and Lieber C M 2005 *Small* **1** 142

[4] Wang F F, Cao L, Liu R B, Pan A L and Zou B S 2007 *Chin. Phys.* **16** 1790

[5] Yao Z T, Sun X R, Xu H J and Li X J 2007 *Chin. Phys.* **16** 3108

[6] Wan Q, Li Q H, Chen Y J, Wang T H, He X L, Li J P and Lin C L 2004 *Appl. Phys. Lett.* **84** 3654

[7] Kind H, Yan H, Messer B, Law M and Yang P 2002 *Adv. Mater.* **14** 158

[8] Chen R J, Franklin N R, Kong J, Cao J, Tombler T W, Zhang Y and Dai H 2001 *Appl. Phys. Lett.* **79** 2258

[9] Freitag M, Martin Y, Misewich J A, Martel R and Avouris Ph 2003 *Nano Lett.* **3** 1067

[10] Fan Z, Chang P C, Lu J G, Walter E C, Penner R M, Lin C H and Lee H P 2004 *Appl. Phys. Lett.* **85** 6128

[11] Law M, Kind H, Kim F, Messer B and Yang P 2002 *Angew. Chem. Int. Ed.* **41** 2405

[12] Mathur S, Barth S, Shen H, Pyun J C and Werner U 2005 *Small* **1** 713

[13] Han S, Jin W, Zhang D, Tang T, Li C, Liu X, Liu Z, Lei B and Zhou C 2004 *Chem. Phys. Lett.* **389** 176

[14] Calarco R, Marso M, Richter T, Aykanat A I, Meijers R, Hart A v d, Stoica T and Lüth H 2005 *Nano Lett.* **5** 981

[15] Gao T, Li Q H and Wang T H 2005 *Appl. Phys. Lett.* **86** 173105

[16] Li Q H, Gao T and Wang T H 2005 *Appl. Phys. Lett.* **86** 193109

[17] Jie J S, Zhang W J, Jiang Y, Meng X M, Li Y Q and Lee S T 2006 *Nano Lett.* **6** 1887

[18] Sharma P, Sreenivas K and Rao K V 2003 *J. Appl. Phys.* **93** 3963

[19] Jimenez Gonzalez A E and Soto Urueta J A 1998 *Sol. Energ. Mat. Sol.* C **52** 345

[20] Liu M and Kim H K 2004 *Appl. Phys. Lett.* **84** 173

[21] Studenikin S A, Golego N and Cocivera M 1998 *J. Appl. Phys.* **84** 5001

[22] Studenikin S A, Golego N and Cocivera M 2000 *J. Appl. Phys.* **87** 2413

[23] Moazzami K, Murphy T E, Phillips J D, Cheung M C-K and Cartwright A N 2006 *Semicond. Sci. Technol.* **21** 717

[24] Chung S J, Cha O H, Kim Y S, Hong C-H, Lee H J, Jeong M S, White J O and Suh E K 2001 *J. Appl. Phys.* **89** 5454

[25] Lin B 2001 *J. Electrochem. Soc.* **148** G110

[26] Salis M, Anedda A, Quarati F, Blue A J and Cunningham W 2005 *J. Appl. Phys.* **97** 033709

[27] Leite R C C and Porto S P S 1966 *Phys. Rev. Lett.* **17** 10

[28] Maity R and Chattopadhyay K K 2006 *J. Nanopart. Res.* **8** 125

[29] Wu C and Bude R H 1974 *J. Appl. Phys.* **45** 648

[30] Orton J W, Goldsmith B J, Chapman J A and Powell M J 1982 *J. Appl. Phys.* **53** 1602

[31] Soole J B D and Schumacher H 1991 *J. Quantum Electron.* **27** 73