Vol 18 No 6, June 2009
1674-1056/2009/18(06)/2610-05

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

The effect of annealing on structural, optical and electrical properties of ZnS/porous silicon composites*

Wang Cai-Feng(王彩凤)[a)†], Li Qing-Shan(李清山)[b)], Hu Bo(胡 波)[c)], and Li Wei-Bing(李卫兵)[a)]

[a)] *Department of Physics and Electronic Science, Binzhou University, Binzhou* 256603, *China*
[b)] *Physics Department, Ludong University, Yantai* 264025, *China*
[c)] *Flying College, Binzhou University, Binzhou* 256603, *China*

(Received 23 August 2008; revised manuscript received 10 December 2008)

ZnS films were prepared by pulsed laser deposition (PLD) on porous silicon (PS) substrates. This paper investigates the effect of annealing temperature on the structural, morphological, optical and electrical properties of ZnS/PS composites by x-ray diffraction (XRD), scanning electron microscope (SEM), photoluminescence (PL) and I–V characteristics. It is found that the ZnS films deposited on PS substrates were grown in preferred orientation along β-ZnS (111) direction, and the intensity of diffraction peak increases with increasing annealing temperature, which is attributed to the grain growth and the enhancement of crystallinity of ZnS films. The smooth and uniform surface of the as-prepared ZnS/PS composite becomes rougher through annealing treatment, which is related to grain growth at the higher annealing temperature. With the increase of annealing temperature, the intensity of self-activated luminescence of ZnS increases, while the luminescence intensity of PS decreases, and a new green emission located around 550 nm appeared in the PL spectra of ZnS/PS composites which is ascribed to the defect-center luminescence of ZnS. The I–V characteristics of ZnS/PS heterojunctions exhibited rectifying behavior, and the forward current increases with increasing annealing temperature.

Keywords: photoluminescence, I–V characteristics, annealing
PACC: 7855, 7865, 8115I

1. Introduction

The ZnS is an n-type II–VI group semiconductor material,[1] which has recently been extensively investigated due to its optoelectronic properties and high potential for various applications such as n-window layers for solar cells, blue-light diodes, electroluminescent displays, photoluminescence devices, etc.[2,3] It has a wide band gap of 3.5–3.7 eV and 3.7–3.8 eV for zinc blende and wurtzite ZnS, respectively. It can crystallize in two allotropic forms: a cubic form (β-ZnS) with sphalerite structure and a hexagonal form (α-ZnS) with wurtzite structure.[4] The light transmittance of ZnS film is high in the visible region, and its luminescence includes defect-center luminescence and self-activated luminescence.[5] The ZnS is now widely used to fabricate semiconductor light-emitting diode (LED), laser diode and displays of high brightness such as field-emission displays and cathode-ray displays. The ZnS has been widely investigated on various substrates,[6,7] while ZnS films grown on porous silicon (PS) substrates have not been studied much.

The PS has been intensively studied since the discovery of its efficient photoluminescence (PL) at room temperature.[8,9] This makes it very promising to integrate the very well-established silicon technology to the field of optoelectronic system where the indirect-band gap bulk Si materials can now find applications.[10] Its open structure and large surface area, combined with unique optical and electrical properties, make PS a good option for substrates.[11−13]

In this paper, we combine PS which has particular properties with ZnS which has potential application prospects in the aspect of optoelectronics to investigate the influence of annealing at 200 °C, 300 °C and 400 °C on the structural, morphological, optical and electrical properties of ZnS/PS composites.

2. Experimental

The preparation of the samples involved two steps: first, the preparation of the PS substrate with strong visible photoluminescence by electrochem-

*Project supported by the Research Foundation for Young Scientists in Innovation Engineering of Binzhou University (Grant No BZXYQNLG200703)
†Corresponding author. E-mail: cfwang_2004@163.com

ical anodization; and second, pulsed laser deposition (PLD) of ZnS films on the PS substrate. The PS sample was formed by electrochemical anodization of (100)-oriented p-type single-crystal Si wafer with resistivity 7.5–11.5 $\Omega \cdot$cm. The Si wafer was irradiated by using a 200 W white light from a distance of 20 cm above the electrochemical cell. The etching was carried out in 49% HF-ethanol solution ($HF : C_2H_5OH = 1 : 1$) at the current density of 10 mA/cm^2 for 20 min. After anodization, the sample was rinsed in de-ionized water and dried in air. The as-made PS sample was put into the vacuum chamber immediately, and the deposition of ZnS films was carried out by PLD. The PLD chamber was first vacuumed to a base pressure of 10^{-8} Torr (1 Torr = 133 Pa). The distance between the target and the substrate was 5 cm. The ZnS target (99.99%) was a sintered ceramic disc. A KrF excimer laser (Tuilaser) operating at 248 nm was used to ablate the ZnS target. Throughout the experiment, the excimer laser was set at a pulse energy of 250 mJ and a repetition rate of 2 Hz, then 5 Hz, so that the crystalline grains could be deposited into the pores of PS. The laser was focused on the target with an area of 4 mm^2, producing an energy density of 6 J/cm^2. The growth temperature was 200 °C. After deposition, the ZnS/PS sample was cut into three pieces and annealed in vacuum at different temperatures 200 °C, 300 °C and 400 °C for 30 min respectively. A 100 nm-thick indium tin oxide thin film was deposited also by pulsed laser on ZnS as n-type contact layer. An Ohmic contact was formed by a thin Al film about 200 nm on the back side using an electron beam evaporation (EB-500) system.

The crystallinity of the ZnS/PS composites was investigated by x-ray diffraction (XRD) utilizing D/max-2500PC x-ray diffractometer in the 2θ range of 20–65. The surface morphology was characterized by using a JSF6100 scanning electron microscope (SEM). The PL spectra were measured at room temperature on RF-5301PC fluorophotometer. The electrical source of measuring I–V characteristics was provided by DH1722 direct current voltage-stabilizing source.

3. Results and discussion

Figure 1 displays the XRD patterns of the as-prepared ZnS/PS composite and the ZnS/PS composites annealed at different temperatures in vacuum. For all the samples, a single diffraction peak at $2\theta = 28.5°$ can be observed in the XRD patterns, corresponding to β-ZnS (111) orientation.[14] The full width at half maximum (FWHM) of all the peaks is large, which may be attributed to the roughness of PS surface.[15] The XRD patterns also show that the intensity of the diffraction peak is markedly increased after annealing, that illuminates the enhancement of crystallinity and grain size of ZnS films. With the increase of annealing temperature, the intensity of the diffraction peak increases.

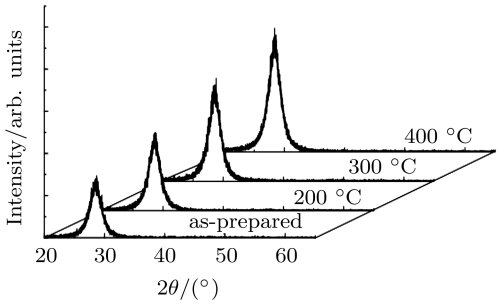


Fig.1. The XRD patterns of as-prepared ZnS/PS and ZnS/PS annealed at different temperatures.

Figure 2 shows SEM images of as-prepared ZnS/PS composite and the ZnS/PS composites annealed at different temperatures. It can be seen that the surface of the as-prepared ZnS/PS composite is relatively smooth and uniform, which indicates that the ZnS films have been well covered onto the PS surface, while the surface of the ZnS/PS composites annealed becomes rougher by annealing. The result may be related to the grain growth of ZnS films during annealing. The grain size increased from 60 nm to 100 nm when the annealing temperature increased from 200 °C to 400 °C.

Figure 3 shows the PL spectra of as-prepared ZnS/PS composite and the ZnS/PS composites annealed at 200 °C, 300 °C and 400 °C in vacuum, respectively. The excitation wavelength is 360 nm. It can be seen that there are two luminescence bands in the as-prepared ZnS/PS composite: the blue emission band around 480 nm at high energy side which is attributed to the self-activated luminescence of ZnS[5] and the red emission band of PS at low energy side, while there is a new green emission band at about 550 nm appeared at the three annealed ZnS/PS composites, which is attributed to the defect-center luminescence of ZnS.[5] The appearance of the green emission may be ascribed to the formation of defects in ZnS films during annealing, and furthermore, the corresponding defect energy level was formed in the forbidden band of ZnS films, and these defects furthermore became the luminescence center.

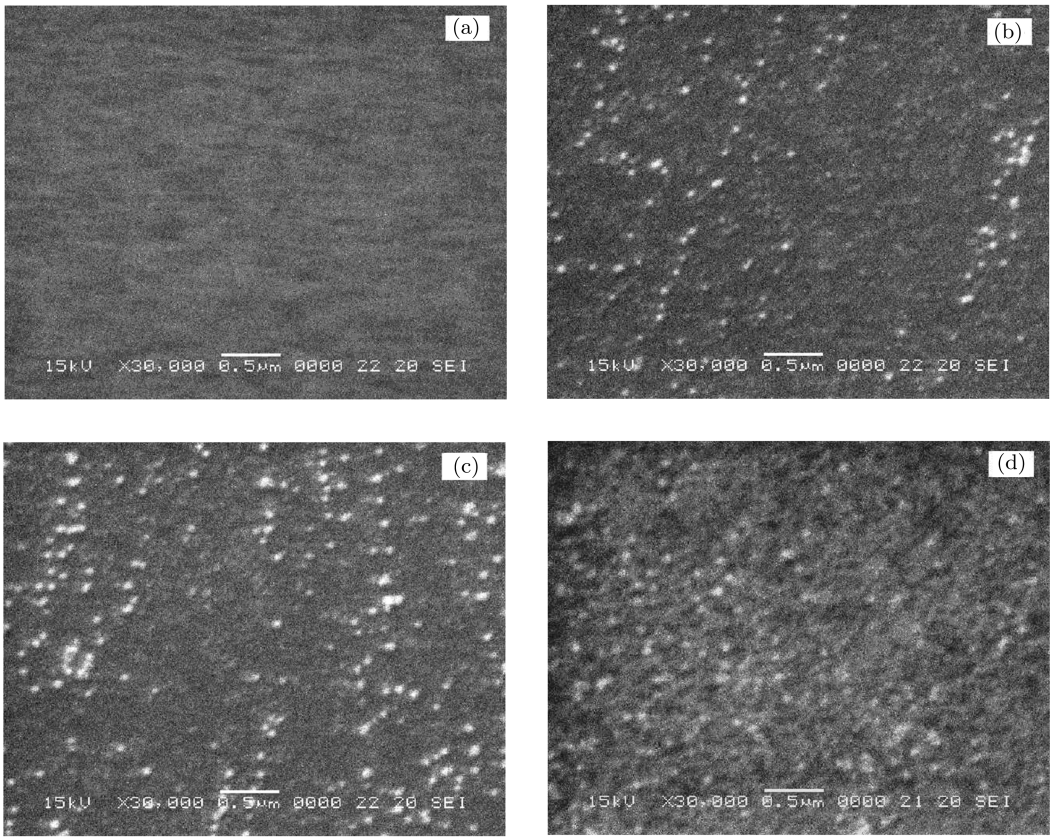


Fig.2. The SEM images of as-prepared ZnS/PS and ZnS/PS annealed at different temperatures: (a) as-prepared; (b) annealed at 200 °C; (c) annealed at 300 °C; (d) annealed at 400 °C.

When the electron was excited by the light energy, it dropped into the luminescence center, as the electron transited to the valence energy band, the light was emitted.[16] In the spectrum of the ZnS/PS composite annealed at 200 °C, the relative (blue: green: red) integrated intensity is 1 : 1.04 : 1.25, the blue, green emission from ZnS films combining with the red emission from PS layers, a broad PL band (450 nm∼700 nm) in the visible region is formed, and the ZnS/PS composite exhibits intensively white light emission. With the increase of annealing temperature, the intensity of blue emission from ZnS increases due to the crystalline grain growth of ZnS films during annealing, but the red emission intensity of PS decreases along with the redshift of the red peak position, and this phenomenon may be ascribed to the optical band gap shrinking of a-Si : H as a function of hydrogen loss during annealing.[17] In the hydride model, the peak energy of the luminescence in PS can be related to the type of hydride presented, and the intensity is a function of the number of hydrides. Also, the presence of hydrogen complexes [SiH, SiH_2, SiH_3, or $(SiH_2)_n$] is very closely related to the luminescence of PS.[17] With higher H content, such as SiH_3, even deeper states occur, expanding the optical band gap even more, but with lower H content, the optical band gap shrinks. So, during the increase of annealing temperature, the hydrogen content decreased, and the shrinking of the optical band gap of a-Si:H occurred, thus, the red emission intensity of PS decreases along with the redshift of the red peak position. The relative (blue : green : red) integrated intensity is 1 : 0.94 : 1.01 and 1 : 0.78 : 0.74 for ZnS/PS composites annealed at 300 °C and 400 °C, respectively. According to the principle of tricolor overlay, the annealed ZnS/PS composites exhibit intensively white light emission.

Figure 4 shows the I–V characteristics of the diodes consisting of as-prepared ZnS/PS and the ZnS/PS annealed at different temperatures. The rectifying behavior as seen from the plots indicates the

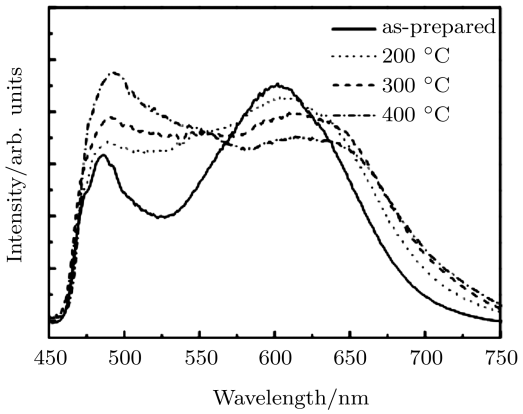


Fig.3. The PL spectra of as-prepared ZnS/PS and ZnS/PS annealed at different temperatures.

formation of heterojunctions as a result of the deposition of the ZnS films on PS substrates. The I–V characteristics show an increase in the forward current after annealing, and with the increase of annealing temperature, the forward current increases. The change in the I–V characteristics for higher annealing temperature of ZnS/PS composites indicates the change in the forward resistance of the diodes. Increase of the current density for the higher annealing temperature of the samples is expected because the crystallinity of ZnS films and the adhesion between ZnS and PS are improved as the annealing temperature of the samples is increased, so the forward current would increase.

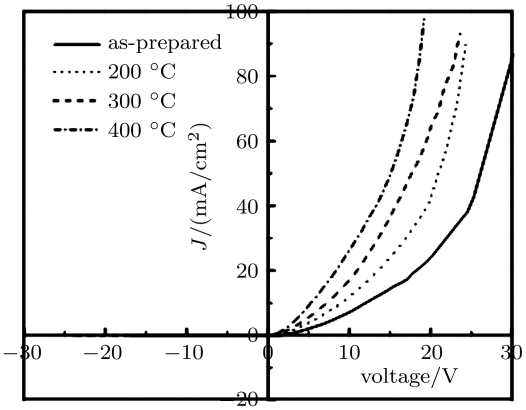


Fig.4. The I–V characteristics of as-prepared ZnS/PS and ZnS/PS annealed at different temperatures.

A few other parameters are determined from the I–V characteristics. The rectification factor defined by the ratio of forward current to reverse current, varies with the annealing temperature of ZnS/PS composites. The onset of forward current is seen to be around +1.2 V for ZnS/PS, although there is a small variation with the increase of annealing temperature of the samples. Under reverse bias conditions, the current density is significantly low, possibly even zero (The error limit when measuring the current density is about ±2%). For all the diodes the forward resistance is low (a few tens of Ω/cm^2), and the reverse resistance is considerably high. The resistance for the different diodes is different. The difference can be expected because of the different interfaces formed between ZnS and PS during annealing of ZnS/PS composites at different temperatures. Another useful parameter, namely the ideality factor n, is calculated from the I–V plots. The ideality factor gives the deviation of the diode characteristics from that of the ideal diode. It is defined as[18]

$$n = \frac{q}{kT}\frac{\partial V}{\partial \ln J}, \tag{1}$$

where q is the electron charge, J is the current density, V is the applied voltage, k is the Boltzmann's constant, and T is the absolute temperature. The ideality factor is calculated from the I–V plot and its value for ZnS/PS annealed at 200 °C is 81 ($T = 300$ K, 2∼4 V). The large value of the ideality factor indicates a high density of trap states.[18] A high density of trap states is commonly observed in heterojunctions formed from the materials with large lattice mismatch, as also between PS and ZnS. Additionally, the roughness of the PS surface is also the reason for the large value of the ideality factor.

4. Conclusions

The aim of the present work is to investigate the effect of annealing temperature on the properties of ZnS/PS composites. It is concluded as follows.

The XRD, SEM, optical and electrical properties of the ZnS/PS composites are sensitive to the annealing temperature in vacuum.

a) The intensity of the diffraction peak is markedly increased after annealing, which illuminates the enhancement of crystallinity and grain size of ZnS films. With the increase of annealing temperature, the intensity of the diffraction peak increases.

b) The smooth and uniform surface of as-prepared ZnS/PS becomes rougher with increasing annealing temperature due to the grain growth of ZnS films during annealing.

c) After annealing, besides the blue emission of ZnS and the red emission of PS, a new green emis-

sion band at about 550 nm appeared in the PL spectra in comparison with as-prepared ZnS/PS, which is attributed to the defect-center luminescence of ZnS. According to the principle of tricolor overlay, the annealed ZnS/PS composites exhibit intensively white light emission.

d) The rectifying behavior as seen from the I–V plots indicated the formation of ZnS/PS heterojunctions, and the I–V characteristics showed an increase in the forward current with the increase of annealing temperature, which may be attributed to the improvement of crystallinity of ZnS films and the adhesion between ZnS and PS as the annealing temperature of the samples increases.

References

[1] Du P, Zhang X Q, Sun X B, Yao Z G and Wang Y S 2006 *Chin. Phys.* **15** 1370

[2] Yano S, Schroeder R, Sakai H and Ullrich B 2003 *Appl. Phys. Lett.* **82** 2026

[3] Velumani S and Ascencio J A 2004 *Appl. Phys.* A **79** 153

[4] Hu C E, Zeng Z Y, Cheng Y, Chen X R and Cai L C 2008 *Chin. Phys.* B **17** 3867

[5] Morozova N K, Karetnikov I A, Plotnichenko V G, Gavrishchuk E M, Yashina E V and Ikonnikov V B 2004 *Semiconductors* **38** 36

[6] Bandic Z Z, Piquette E C, McCaldin J O and McGill T C 1998 *Appl. Phys. Lett.* **72** 2862

[7] McCamy J W, Lowndes Douglas H, Budai J D, Zuhr R A and Zhang X 1993 *J. Appl. Phys.* **73** 7818

[8] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046

[9] Bai Y, Lan Y N and Mo Y J 2005 *Acta Phys. Sin.* **54** 4654 (in Chinese)

[10] Liu G Y, Tan X W, Wang Z, Yao J C and Xiong Z H 2008 *Acta Phys. Sin.* **57** 5302 (in Chinese)

[11] Xu D S, Guo G L, Gui L L, Tang Y Q, Shi Z J, Jin Z X, Gu Z N, Liu W M, Li X L and Zhang G H 1999 *Appl. Phys. Lett.* **75** 481

[12] Zhang P, Kim P S and Sham T K 2002 *J. Appl. Phys.* **91** 6038

[13] Gokarna A, Bhoraskar S V, Pavaskar N R and Sathaye S D 2000 *Phys. Stat. Sol.* (a) **182** 175

[14] Nasrallah T Ben, Amlouk M, Bernede J C and Belgacem S 2004 *Phys. Stat. Sol.* **201** 3070

[15] Wang C F, Li Q S, Zhang L C, Lü L and Qi H X 2007 *Optoelectron. Lett.* **3** 0169

[16] Peng Y C and He Y L 1999 *Chin. J. Quantum Electron.* **16** 1 (in Chinese)

[17] Prokes S M, Freitas Jr. J A and Searson P C 1992 *Appl. Phys. Lett.* **60** 3295

[18] Gokarna A, Pavaskar N R, Sathaye S D, Ganesan V and Bhoraskar S V 2002 *J. Appl. Phys.* **92** 2118