White light photoluminescence from ZnS films on porous Si substrates*

Wang Caifeng(王彩凤)[1,†], Li Qingshan(李清山)[2], Hu Bo(胡波)[3], and Li Weibing(李卫兵)[1]

(1 Department of Physics and Electronic Science, Binzhou University, Binzhou 256603, China)
(2 School of Physics and Electronic Engineering, Ludong University, Yantai 264025, China)
(3 Flying College, Binzhou University, Binzhou 256603, China)

Abstract: ZnS films were deposited on porous Si (PS) substrates using a pulsed laser deposition (PLD) technique. White light emission is observed in photoluminescence (PL) spectra, and the white light is the combination of blue and green emission from ZnS and red emission from PS. The white PL spectra are broad, intense in a visible band ranging from 450 to 700 nm. The effects of the excitation wavelength, growth temperature of ZnS films, PS porosity and annealing temperature on the PL spectra of ZnS/PS were also investigated.

Key words: white light emission; photoluminescence; ZnS films; porous Si
DOI: 10.1088/1674-4926/31/3/033002 **PACC:** 7855; 7865; 8115I

1. Introduction

The achievement of Si-based white light emission is one of the challenging goals in the field of display and lighting technologies. White light emission from light-emitting devices has attracted significant research interests due to its applications to a full color display combined with a color filter, a backlight for liquid crystal displays, or other various lightings[1−3]. It is expected that conventional white light sources will soon be replaced by the new generation of Si-based semiconductor white light emitting sources. White light emission is obtained by combining two complementary colors (e.g., blue and orange) or three primary colors (red, green and blue) from different emitting molecules. This can be done either using a multilayer structure with two or more emitting layers or doping an active host material with several fluorescent dyes[4]. Various methods and challenges for generating white light have been reported[5, 6].

ZnS is a Ⅱ−Ⅵ group semiconductor material with a wide band gap of about 3.7 eV, 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, and photoluminescence devices[7−9]. ZnS films generally display a self-activated PL band centered at about 480 nm; some groups also reported an additional green PL band centered at about 550 nm besides the self-activated blue band, and this green band has been ascribed to originate from some defect states[10]. Porous silicon (PS) has been intensively studied since the discovery of its efficient PL at room temperature[11]. This makes it very promising to integrate the very well-established silicon technology to the field of optoelectronic system[12]. The emitting wavelength in PS could be changed by adjusting the erosion process[13]. Red, green, and blue PS were reported and the red emitting PS can be easily obtained[14].

In this article, we discuss white color photoluminescence (PL) from ZnS/PS devices consisting of the two emitting layers: ZnS and PS. The effects of the excitation wavelength, growth temperature of ZnS films, PS porosity and annealing temperature on the PL spectra of ZnS/PS are studied in detail. The intense white light emission is obtained by the combination of blue and green emission from ZnS and the red emission from PS, and it consists of two broad PL bands at about 480 nm (ZnS), 625 nm (PS) or three broad PL bands around 480 nm (ZnS), 550 nm (ZnS) and 615 nm (PS), which may be suitable for some applications, e.g., in thin film electroluminescence for flat full color display applications. It simplifies the fabrication process of fine-pixel large-screen displays.

2. Experimental

The sample preparation involved two steps: first, the preparation of PS substrates with strong visible PL by electrochemical anodization; and second, pulsed laser deposition (PLD) of ZnS films on the PS substrates. The PS samples were formed by electrochemical anodization of (100)-oriented p-type single-crystal Si wafer with resistivity of 7.5–11.5 Ω·cm. The Si wafers were irradiated 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 different current densities of 8, 5, 10, and 12 mA/cm^2 for 20 min. After anodization, the samples were rinsed in de-ionized water and dried in air. The as-prepared PS sample with a current density of 8 mA/cm^2 was cut into three pieces, and ZnS films were deposited on the three PS samples at different temperatures 200, 300, and 400 °C by PLD. The PLD chamber was first vacuumed to a base pressure of 10^{-8} Torr. 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 pulse energy of 250 mJ and a repetition rate of 2 Hz, then 5 Hz, so that the crystalline grains can be deposited into the pores of PS

* Project supported by the Natural Science Foundation of Shandong Province of China (No. Y2002A09) and the Research Foundation for Young Scientists in Innovation Engineering of Binzhou University, China (No. BZXYQNLG200703).
† Corresponding author. Email: cfwang_2004@163.com
Received 23 August 2009, revised manuscript received 12 October 2009

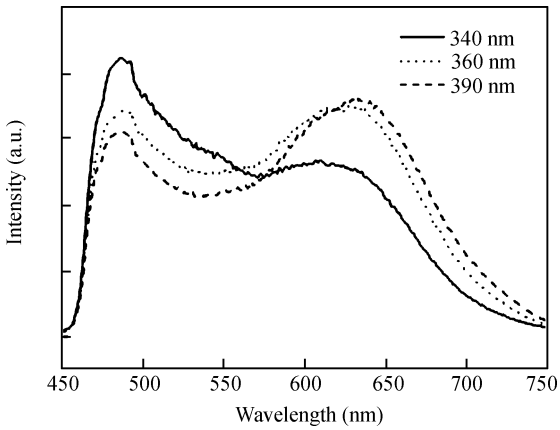

Fig. 1. PL spectra of sample A excited at a wavelength of 340, 360, and 390 nm.

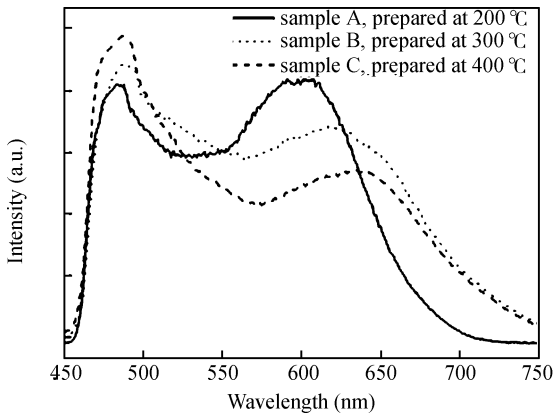

Fig. 2. PL spectra of samples A, B and C.

and made the ZnS films pinning in the PS substrates, increasing the adherence of the films. The laser was focused on the target with an area of 4 mm^2, producing an energy density of 6 J/cm^2. The obtained samples prepared at different temperatures were marked A, B and C respectively. ZnS films deposited on PS samples with current density of 5, 10 and 12 mA/cm^2 at 200 °C were labelled as a, b and c respectively. Take the sample c cut into three pieces and annealed in vacuum at different temperatures 200, 300, and 400 °C for 30 min respectively, and the annealed samples were marked c1, c2 and c3 respectively.

The measurement of the samples was taken on the same apparatus as that in our previous work[15]. The prepared ZnS films were obtained in the cubic phase along β-ZnS (111) orientation, which showed a perfect match with the earlier report.

3. Results and discussion

Figure 1 shows the PL spectra of sample A excited at a wavelength of 340, 360, and 390 nm. It is observed that the PL spectra are composed of two intense luminescence bands: the blue emission band located around 480 nm at the high-energy side, which is ascribed to the self-activated luminescence of ZnS[16], and the red emission band of PS located around 625 nm at the low-energy side. The absolute integrated intensity of the two peaks at 480 nm and 625 nm has different values at different excitation wavelengths. The relative (blue/red) integrated intensities are 1.58, 0.97, and 0.85 for the sample excited by 340 nm, 360 nm, and 390 nm excitation wavelengths, respectively. With the increase of excitation wavelength, the relative (blue/red) integrated intensity decreases. This phenomenon indicates that the longer wavelengths' excitation light can excite the luminescence of PS more effectively. That is to say, if the excitation wavelength is shorter, it may be absorbed heavily by ZnS films, and only a small part can transmit ZnS films and excite the luminescence of PS, so the relative (blue/red) integrated intensity is larger. With the increase of excitation wavelength, more excitation light can transmit ZnS films and the luminescence intensity of PS increases, so the relative (blue/red) integrated intensity decreases. The blue emission from ZnS films combining with the red emission from PS layers, a broad PL band from 450 to 700 nm in the visible region is obtained, exhibiting light emission that is close to white light.

Figure 2 reveals the PL spectra of samples A, B and C. The excitation wavelength is 360 nm. The PL spectra also consist of blue emission from ZnS and red emission from PS. When the growth temperature of ZnS films increases, the intensity of the blue emission from ZnS increases, which is attributed to the crystalline grain of ZnS films growing larger and the crystalline quality becoming better with the increase of growth temperature. While the red emission intensity of PS decreases along with the redshift of the red peak position (The PS peak position of sample A located at 600 nm redshifting to 635 nm of sample C), which is ascribed to the optical band gap shrinking of a-Si:H as a function of hydrogen loss during the increase of growth temperature[17]. In the hydride model, the peak energy of the luminescence in PS can be related to the type of hydride present, 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 growth 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/red) integrated intensities are 0.98, 1.30 and 1.80 for the samples A, B and C, respectively. White light emission is obtained by combination of the two intense, visible PL bands of ZnS and PS.

Figure 3 gives the PL spectra of samples a, b and c. The excitation wavelength is 360 nm. From the emission spectrum of sample a, two obvious emission bands can be observed: the red emission band from PS layer located at 635 nm, and the blue emission band from ZnS at about 480 nm. The integrated intensity of blue emission is stronger than that of red emission (blue : red = 1 : 0.72), and this is related to the small porosity of the PS substrate which contributes to the good crystalline quality of ZnS films, so the self-activated luminescence of ZnS films is predominant in the PL spectrum of ZnS/PS. With an increase in PS porosity, the red emission intensity increases along with the blueshift of the red peak position, but the intensity of blue emission decreases in the PL spectrum of sample b. Meanwhile, another emission band located around 550 nm in

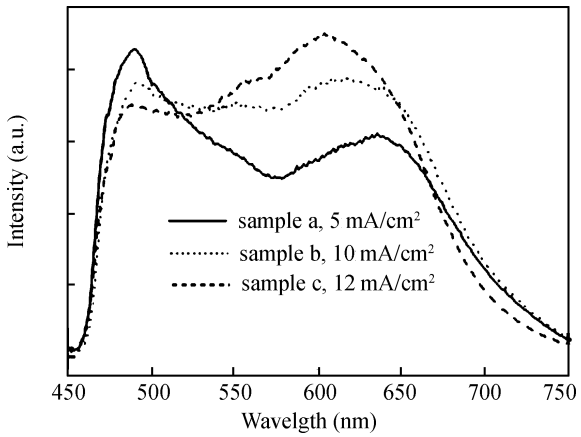

Fig. 3. PL spectra of samples a, b and c.

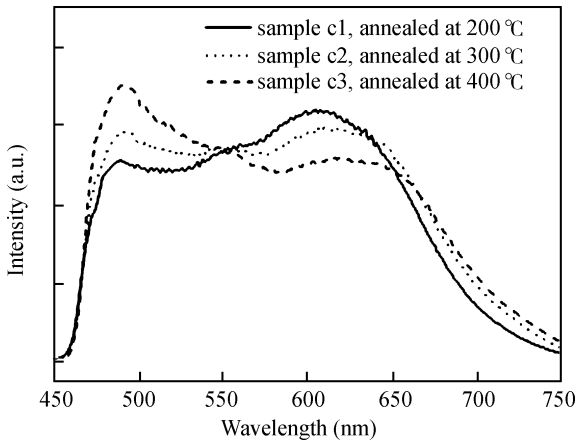

Fig. 4. PL spectra of samples c1, c2 and c3.

the green region is observed, which is ascribed to defect-center luminescence of ZnS[16]. The appearance of defect-center luminescence of ZnS films is attributed to the defect formation in ZnS films during the increase of PS porosity, and furthermore, the corresponding defect energy level was formed in the forbidden band of ZnS films, and these defects furthermore became the luminescence center. 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[18]. The relative (blue : green : red) integrated intensity is 1 : 0.92 : 1.01. With a continuing increase of PS porosity, the intensity of the red emission still increases, and the same with the intensity of the green emission, while the intensity of the blue emission still decreases. These contribute to the relative (blue : green : red) integrated intensity being 1 : 1.08 : 1.28 in the PL spectrum of sample c. Combining the blue, green emission of ZnS and the red emission of PS, an intensively white light emission is obtained.

Figure 4 illustrates the PL spectra of samples c1, c2 and c3. The excitation wavelength is 360 nm. It is observed that, the PL spectra of the three annealed samples all consist of three luminescence bands: the blue, green emission band of ZnS and the red emission band of PS. The green emission band is attributed to the defect-center luminescence of ZnS. The appearance of the defect-center luminescence of ZnS in the three PL spectra is ascribed to the defects formation in ZnS films which is due to the large PS porosity and annealing treatment. In the spectrum of sample c1, 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 (450–700 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, which is ascribed to the optical band gap shrinking of a-Si:H as a function of hydrogen loss during annealing. This phenomenon shows a perfect match with the aforementioned in Fig. 2. The relative (blue : green : red) integrated intensity is 1 : 0.94 : 1.01 and 1 : 0.78 : 0.74 for samples c2 and c3, respectively. According to the principle of tricolor overlay, ZnS/PS composites exhibit intensively white light emission.

4. Conclusions

In summary, white light emission can be obtained from ZnS/PS composites by the combination of blue and green emissions from ZnS and red emission from PS. The white light PL spectra ranging from 450 to 700 nm consist of two broad peaks at about 480 nm (ZnS) and 625 nm (PS) or three broad peaks around 480 nm (ZnS), 550 nm (ZnS) and 615 nm (PS), although the PL spectra slightly changed with the excitation wavelength, growth temperature of ZnS films, PS porosity and annealing temperature.

References

[1] Kido J, Kimura M, Nagai K. Multilayer white light-emitting organic electroluminescent device. Science, 1995, 267: 1332
[2] Xie Zhiyuan, Li Chuannan, Huang Jinsong, et al. Organic multilayer white LEDs. Chinese Journal of Semiconductors, 2000, 21(2): 184
[3] Tokito S, lijima T, Tsuzuki T, et al. High-efficiency white phosphorescent organic light-emitting devices with greenish-blue and red-emitting layers. Appl Phys Lett, 2003, 83(12): 2459
[4] Lim J T, Lee M J, Lee N H, et al. Efficient white light emitting devices with a blue emitting layer doped with a red dye. Current Applied Physic, 2004, (4): 327
[5] Xiao Jing, Deng Zhenbo, Liang Chunjun, et al. An efficient and bright organic white-light-emitting device. Displays, 2005, 26: 129
[6] Shen W C, Su Y K, Ji L W. High bright white organic light-emitting diode based on mixing orange and blue emission. J Cryst Growth, 2006, 293: 48
[7] Yano S, Schroeder R, Sakai H, et al. High-electric-field photocurrent in thin-film ZnS formed by pulsed laser deposition. Appl Phys Lett, 2003, 82(13): 2026
[8] Velumani S, Ascencio J A. Formation of ZnS nanorods by simple evaporation technique. Appl Phys A, 2004, 79: 153
[9] Du Yuanyuan, Jie Wanqi, Li Huanyong. Synthesis of ZnS whiskers and their photoluminescence properties. Journal of Semiconductors, 2009, 30(8): 083005
[10] Ye Changhui, Fang Xiaosheng, Li Guanghai, et al. Origin of the green photoluminescence from zinc sulfide nanobelts. Appl Phys Lett, 2004, 85(15): 3035
[11] Canham L T. Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers. Appl Phys Lett,

1990, 57(10): 1046
[12] Long Yongfu, Ge Jin, Ding Xunmin, et al. Temperature: a critical parameter affecting the optical properties of porous silicon. Journal of Semiconductors, 2009, 30(6): 063002
[13] Chen Q W, Zhu D L, Zhu C, et al. A way to obtain visible blue light emission in porous silicon. Appl Phys Lett, 2003, 82(7): 1018
[14] Liu Y L, Liu Y C, Yang H, et al. The optical properties of ZnO films grown on porous Si templates. J Phys D: Appl Phys, 2003, 36: 2705
[15] Wang Caifeng, Li Qingshan, Hu Bo. Optoelectronic characterization of ZnS/PS systems. Chinese Optics Letters, 2009, 7(5): 432
[16] Morozova N K, Karetnikov I A, Plotnichenko V G, et al. Transformation of luminescence centers in CVD ZnS films subjected to a high hydrostatic pressure. Semiconductors, 2004, 38(1): 36
[17] Prokes S M, Freitas J A Jr, Searson P C. Microluminescence depth profiles and annealing effects in porous silicon. Appl Phys Lett, 1992, 60(26): 3295
[18] Peng Yingcai, He Yuliang. The research development on light emitting properties of Si-based nanometer materials. Chinese Journal of Quantum Electronics, 1999, 16(1): 1