Study of white light emission from ZnS/PS composite system

Caifeng Wang (王彩凤)[1,2], Qingshan Li (李清山)[1,3], Lei Lü (吕 磊)[1], Lichun Zhang (张立春)[1], and Hongxia Qi (齐红霞)[1]

[1] *College of Physics and Engineering, Qufu Normal University, Qufu 273165*

[2] *Department of Physics and Electronics Science, Binzhou University, Binzhou 256600*

[3] *Ludong University, Yantai 264025*

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ZnS films were deposited by pulsed laser deposition (PLD) on porous silicon (PS) substrates formed by electrochemical anodization of p-type (100) silicon wafer. The photoluminescence (PL) spectra of ZnS/PS composites were measured at room temperature. Under different excitation wavelengths, the relative integrated intensities of the red light emission from PS layers and the blue-green emission from ZnS films had different values. After samples were annealed in vacuum at different temperatures (200, 300, and 400 °C) for 30 min respectively, a new green emission located at around 550 nm appeared in the PL spectra of all ZnS/PS samples, and all of the ZnS/PS composites had a broad PL band ($450-700$ nm) in the visible region, exhibiting intensively white light emission.

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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 is of interest because it can be used for full-color flat-panel displays with color filters and as an alternative lighting source[1−3]. Generally, there are two methods to produce white light from light-emitting diodes (LEDs): combining three LED chips (red, green, and blue) in one discrete package or as a cluster LED chips, and coating blue indium-gallium-nitride (InGaN) LED chips with phosphorous. The combination of white light emission and color filters should simplify the fabrication process of fine-pixel large-screen displays[3].

Porous silicon (PS) has been intensively studied since the discovery of its efficient photoluminescence at room temperature[4]. This makes it very promising to integrate the very well-established silicon technology to the field of optoelectronic system[5−9]. The emitting wavelength in PS could be changed by adjusting the erosion process[10]. Red, green, and blue emitting PSs were reported and the red one can be easily obtained[11]. 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, photoluminescence devices, etc.[12−16]. ZnS films are transparent in the visible region, and its luminescence includes defect-center luminescence and self-activated luminescence[17]. In our previous work[15], we had studied the structural, optical and electrical properties of ZnS/porous silicon heterostructures, and acquired that combining the luminescence of ZnS and the luminescence of PS, an intensively white light emission could be obtained. In this experiment, we regulated the excitation wavelength and got the composites annealed to study the photoluminescence properties of ZnS/PS composites, and we found that a new green emission located at around 550 nm appeared in the photoluminescence (PL) spectra of ZnS/PS composites which had been annealed, and an intensively white light emission ranging from 450 to 700 nm in the visible region was also obtained.

The preparation processes of PS and ZnS films were the same as those in our previous work[15]. The growth temperature of ZnS films was 200 °C. After deposition, the ZnS/PS sample was cut into three pieces, and annealed in vacuum at 200, 300, and 400 °C for 30 min, respectively. The measurement of the samples was also taken on the same apparatus as that in our previous work[15].

Figure 1 shows the X-ray diffraction (XRD) pattern of ZnS films prepared on the PS substrate before annealing. The diffraction peak is observed at about 28.7° corresponding to β-ZnS (111) direction[16], which indicates that ZnS films have been grown in the preferred orientation. The large full-width at half-maximum (FWHM) is ascribed to the structure of the PS substrate. Because of the frangibility of PS, the PS substrate was only rinsed in de-ionized water and dried in air before ZnS films were deposited, so there might be some impurities on the PS

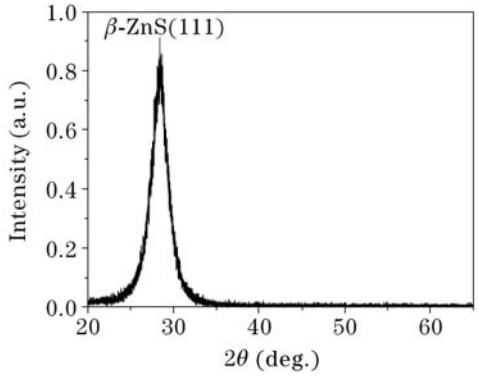

Fig. 1. XRD pattern of ZnS films grown on PS substrate before annealing.

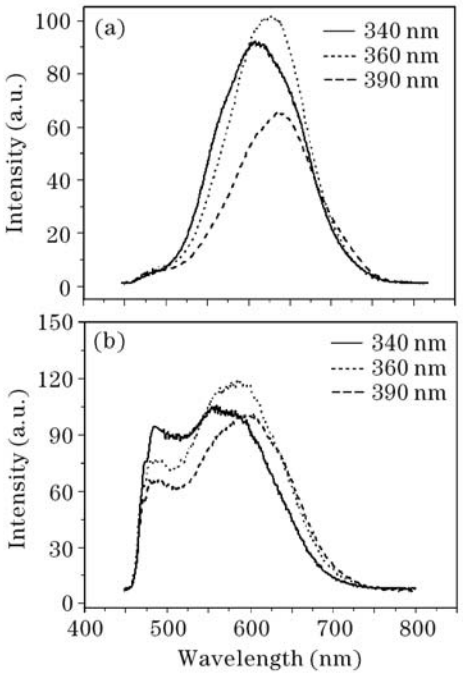

Fig. 2. PL spectra of (a) as-prepared PS and (b) ZnS/PS composite before annealing.

surface influencing the quality of the ZnS films. Additionally, the roughness of the PS surface also leads to the poor crystalline quality of the ZnS films.

PL spectra were obtained at room temperature by different excitation wavelengths. Figures 2(a) and (b) show the PL spectra of the as-prepared PS and ZnS/PS composite before annealing, respectively. In Fig. 2(a), the red emission band of PS is located at around 625 nm, and with the increase of excitation wavelength, the peak position of PS has a redshift. After ZnS films were deposited, in Fig. 2(b), a blueshift of the red emission occurs, and this may be ascribed to the covering of ZnS films. A blue-green emission band centered at 480 nm appears in Fig. 2(b), which is ascribed to the self-activated luminescence of ZnS[17]. In Fig. 2(b), there are two intense visible PL bands that provide white light emission at proper excitation wavelength. The absolute integrated intensities of the two peaks at 480 and 600 nm have different values at different excitation wavelengths. The relative (blue/red) integrated intensities are 0.92, 0.66, and 0.65 for the sample excited by 340, 360, and 390-nm excitation wavelengths, respectively. With the increase of excitation wavelength, the relative (blue/red) integrated intensity decreases, and this phenomenon indicates that, 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 by ZnS films mostly, and only a small part transmits the ZnS films and excites 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-green 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.

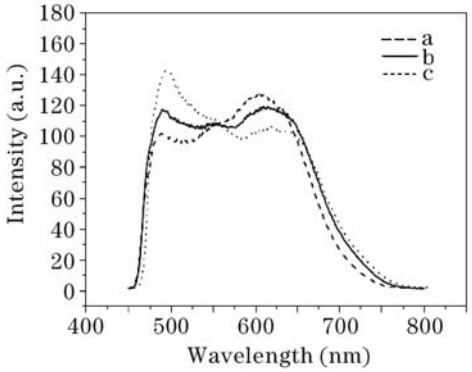

Fig. 3. PL spectra of ZnS/PS composites annealed in vacuum at (a) 200, (b) 300, and (c) 400 °C for 30 min.

Figure 3 shows the PL spectra of ZnS/PS composites annealed in vacuum at 200, 300, and 400 °C for 30 min respectively. The excitation wavelength is 360 nm. In Fig. 3, besides the blue emission of ZnS located at around 480 nm at high-energy side and the red emission of PS located at around 610 nm at low-energy side, a new green emission at around 550 nm is observed which is attributed to the defect-center luminescence of ZnS[17]. The appearance of the green emission may be ascribed to the defects formation 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. When the electron was excited by the light, it dropped into the luminescence center, as the electron transmitted to the valence band, the light was emitted. In the spectrum of the sample annealed at 200 °C, the relative (blue:green:red) integrated intensity is 1:1.04:1.25, the blue and green emission from ZnS films combining with the red emission from PS layers form a broad PL band (450−700 nm) in the visible region, and the ZnS/PS composite exhibits intensively white light emission. With the increase of annealing temperature, the intensity of blue emission from ZnS increases but the red emission intensity of PS decreases along with the redshift of the red peak position. This phenomenon may be ascribed to the crystalline grain of ZnS films growing larger and optical band gap shrinking of a-Si:H as a function of hydrogen loss during annealing[18]. The relative (blue:green:red) integrated intensity is 1:0.94:1.01 and 1:0.78:0.74 for samples annealed at 300 and 400 °C, respectively. According to the principle of tricolor overlay, the ZnS/PS composites exhibit intensive white light emission.

In summary, ZnS films were successfully deposited on PS substrates by pulsed laser deposition (PLD). XRD pattern showed that ZnS films were grown in the preferred orientation along β-ZnS (111) direction. The photoluminescence properties of ZnS/PS composites were studied experimentally. At different excitation wavelengths, the relative (blue/red) integrated intensities were different. After samples were annealed at different temperatures, a green light emission appeared in the PL spectra of ZnS/PS composites which is ascribed to the defect-center luminescence of ZnS films. The blue and green emissions from ZnS films combining with the red

emission from PS layers form a broad PL band in the visible region, so an intensive white light emission is obtained.

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References

1. J. Kido, M. Kimura, and K. Nagai, Science **267,** 1332 (1995).
2. C. W. Ko and Y. T. Tao, Appl. Phys. Lett. **79,** 4234 (2001).
3. S. Tokito, T. Lijima, T. Tsuzuki, and F. Sato, Appl. Phys. Lett. **83,** 2459 (2003).
4. L. T. Canham, Appl. Phys. Lett. **57,** 1046 (1990).
5. Y. Yang, Q. Li, and X. Liu, Chin. Opt. Lett. **4,** 297 (2006).
6. A. Gokarna, S. V. Bhoraskar, N. R. Pavaskar, and S. D. Sathaye, Phys. Stat. Sol. (a) **182,** 175 (2000).
7. A. Gokarna, N. R. Pavaskar, S. D. Sathaye, V. Ganesan, and S. V. Bhoraskar, J. Appl. Phys. **92,** 2118 (2002).
8. L. Wang, Y. Xia, J. Ju, Y. Fan, W. Zhang, Y. Mo, W. Shi, and W. Sang, Acta Opt. Sin. (in Chinese) **21,** 753 (2001).
9. Y. Bai, Y. Lan, H. Zhu, and Y. Mo, Acta Opt. Sin. (in Chinese) **25,** 1712 (2005).
10. Q. Chen, D. Zhu, C. Zhu, J. Wang, and Y. Zhang, Appl. Phys. Lett. **82,** 1018 (2003).
11. Y. Liu, Y. Liu, H. Yang, W. Wang, J. Ma, J. Zhang, Y. Lu, D. Shen, and X. Fan, J. Phys. D **36,** 2705 (2003).
12. S. Yano, R. Schroeder, H. Sakai, and B. Ullrich, Appl. Phys. Lett. **82,** 2026 (2003).
13. S. Velumani and J. A. Ascencio, Appl. Phys. A **79,** 153 (2004).
14. M. McLaughlin, H. F. Sakeek, P. Maguire, W. G. Graham, J. Molloy, T. Morrow, S. Laverty, and J. Anderson, Appl. Phys. Lett. **63,** 1865 (1993).
15. C. Wang, Q. Li, L. Lü, L. Zhang, H. Qi, and H. Chen, Chin. Phys. Lett. **24,** 825 (2007).
16. T. B. Nasrallah, M. Amlouk, J. C. Bernede, and S. Belgacem, Phys. Stat. Sol. (a) **201,** 3070 (2004).
17. N. K. Morozova, I. A. Karetnikov, V. G. Plotnichenko, E. M. Gavrishchuk, E. V. Yashina, and V. B. Ikonnikov, Semiconductors **38,** 36 (2004).
18. S. M. Prokes, J. A. Freitas, Jr., and P. C. Searson. Appl. Phys. Lett. **60,** 3295 (1992).