ZnS/Si composite nano-structured thin films and their photoluminescence

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Abstract: Thin films of ZnS/Si composite were prepared using pulsed laser deposition by alternately ablating ZnS and Si materials on a rotary target holder onto an ultra-clean glass substrate in vacuum. The film structure consisted of a mixture of Si and ZnS nanocrystals with some segregation of S and Zn. Most of the particles in the film were found to be less than 15 nm in diameter even after annealing for 6 hours at 500°C in air. With excitation wavelengths of 280 nm and 380 nm, the composite film yielded largely independent photoluminescent (PL) emission peaks originating from the Si and ZnS nanoparticles. There is a slight difference in the Si and ZnS PL results compared with those obtained from thin films of Si nanocrystals and ZnS nanoparticles embedded in SiO₂ matrices. This difference is attributed to the different segregation and oxidation behaviors of the materials in different neighborhood environments. Our results open up the possibility of modifying the PL of ZnS/Si composite films for potential applications in multiple-function optoelectronic devices.

1. Introduction

In recent years, low-dimensional semiconductors, especially composites, have attracted much interest because of their valuable photoluminescent (PL) properties [1-3], especially visible PL at room temperature of nanometer-sized Si [4-7] and II-VI materials such as ZnS [8-18]. Much research was focused on light-emitting materials, modification of their optical properties [17], and their potential applications in devices in electronics, optoelectronics and sensors. ZnS has a wide band gap of 3.5-3.8 eV at room temperature, and the band gap can be tuned in the UV region. However, hitherto, tuning in the visible region was possible only by employing appropriate dopants [10, 11]. This limitation, together with the small Bohr exciton radius of ZnS (2.5 nm), has attracted much interest in the study of ZnS nanoparticles [12-14]. Results from Kanemoto’s work [17] indicated that the defect levels play an important role in determining the luminescence characteristics of the ZnS nanoparticles. The PL efficiency was found to be grossly affected by the presence of intrinsic surface states of the nanoparticles, and the nature of the chemical treatment employed in their fabrication [11, 16].

In this paper, we report PL investigations of ZnS/Si thin films prepared by using a variation of the pulsed laser deposition method. The PL emission of the ZnS/Si composite film produced from excitation by the 280 nm wavelength line was similar, but not identical, to that of pure Si nanoparticles, or Si nanoparticles in thin films of Si/C, Si/Ge and Si/Al₂O₃ [19-23]; while that caused by excitation by the 380 nm line was similar to that of ZnS nanoparticles embedded in SiO₂ matrices [24]. The slight variation in the PL of the ZnS/Si composite film is attributed to its different neighboring compositions and structures, and their different segregation and oxidation behaviors. These results open up possibilities of modifying the PL characteristics of ZnS/Si films for the multiplexing of their optical functions in optoelectronic devices.

2. Experimental
Details of the target and sample preparation are similar to those for the fabrication of thin films of Si nanocrystals [20-22] or ZnS nanoparticles embedded in SiO₂ matrices as described elsewhere [24]. The laser deposition was carried out for 40 minutes with the target rotating at about 0.8 round/minute, and the substrate at room temperature. From the ablated circles marked on the target surface, the exposed area ratio of ZnS:Si under the laser ablation was evaluated to be about 1:2 in our present experiments. The total thickness of the film deposited on the substrate was found to be about 250 nm.

A set of five different samples was prepared for the film structure and the PL study. These were the as-deposited sample and the samples annealed at 300°C, 400°C, 500°C for 1 hour, and at 500°C for 6 hours in the open but clean atmosphere. They are referred as samples (a)-(e) respectively. In order to ensure uniformity, all the samples to be annealed were cut from the same as-deposited sample. The film structures were investigated by secondary ion mass spectroscopy (SIMS), atomic force microscopy (AFM), X-ray diffraction (XRD), and Raman spectrometry. The PL measurements were carried out with a fluorescent spectrophotometer (Perkin Elmer, LS 50B) using two excitation light wavelengths of 280 nm and 380 nm respectively. A 300W Xe lamp was used as the excitation source. In order to compare the results meaningfully, all measurements were taken under the same conditions unless otherwise specified.

3. Results and discussion

XRD results established that both the Si and ZnS nanoparticles in the ZnS/Si composite films possessed crystalline structures. The average sizes of the nanoparticles obtained from the Debye-Scherrer formula agree well with AFM results for samples (a)-(d) with sizes of about 8 nm for the as-deposited sample. However, the formula gave a value smaller than that estimated from AFM results for sample (e) in which the nanoparticles have an average size of 15 nm. This difference arose because the AFM results show the particles size while the XRD results show the crystal size. However, it shows that the films were composed of Si and ZnS nanocrystals with the possibility of some Zn and S segregation which reaffirmed by SIMS results.

Raman spectra (produced from excitation by the 632.8nm line) in the Raman shift region 500-550 cm⁻¹ of sample (d) and (e) are shown in Figure 1. The broad peak at 521 cm⁻¹ is the Raman peak of crystalline Si. The peak is broad because the sizes of the particles in the film are in nanometers. The peak intensity of sample (e) is much lower than that of sample (d), because Si nanoparticles in sample (e) were extensively oxidized due to the high temperature and long annealing duration.

![Figure 1 Raman spectra of samples (d) sample annealed at 500°C for 1 hour; and (e) sample annealed at 500°C for 6 hours] in the Raman shift region of 500-550 cm⁻¹.

![Figure 2 PL results with 280 nm excitation wavelength for (a) as-deposited sample; (b) sample annealed at 300°C for 1 hour; (c) sample annealed at 400°C for 1 hour; (d) sample annealed at 500°C for 1 hour; and (e) sample annealed at 500°C for 6 hours. The new fine-structure is indicated by a vertical arrow.]

![Figure 3 PL results for the samples (a) — (e), as defined in Fig.3, with excitation light wavelength of 380 nm.]

300 400 500 600 700 800 900 1000
Wavelength (nm)

PL Intensity (a.u.)

600 620 640 660 680 700
PL Intensity (a.u.)

Wavelength (nm)
Figures 2 and 3 show the PL results of the ZnS/Si film using excitation light wavelengths of 280 and 380 nm respectively. In order to avoid overlapping, the spectra are arbitrarily shifted vertically. The 280 nm excitation line yielded a PL spectrum over the wavelength region of 300-800 nm as shown in Fig. 3. They are similar to those of Si nanoparticles in thin films of Si/C, Si/Ge, Si/Al$_2$O$_3$ or pure Si nanoparticles; including the broad peak in the region of 550-800 nm, and they originated from the silicon nanoparticles in the films [20-23]. However, for the present samples, the FWHM of the peak is broader and there also exists a side peak in the shoulder of the main peak at about 412 nm. Similar fine-structure peaks are observed and their positions remained unchanged, regardless of the intensity of annealing applied to the sample. In the case of the Si/Al$_2$O$_3$ thin film, the PL intensity first increased, and then decreased, with increasing annealing temperature. In the present ZnS/Si film, the PL intensity increases gradually with annealing [samples (a)-(c)], and finally reaches saturation with further annealing [samples (d) and (e)].

The PL of Si was explained in refs. [19-23]. Since it was established that this emission came from the silicon nanoparticles, the existence of the silicon nanoparticles in our films is reaffirmed. Furthermore, as quantum confinement is known to determine the wavelengths of the PL of the Si nanoparticles, a small variation in the confinement effect in the present ZnS/Si films is expected, because here, the Si nanoparticles are surrounded by neighboring ZnS, Zn or S nanoparticles, instead of SiO$_2$, Al$_2$O$_3$, C or Ge [19-23]. Due to the different neighborhood, the FWHMs of the peaks in the ZnS/Si film were found to be much larger. However, the main PL peak position of the Si nanoparticles did not change even after the samples were annealed. This indicates that the size of the Si nanoparticles did not change much during annealing. This was because the as-deposited film surfaces were covered by S and Zn segregation materials (as established by the SIMS results), so that although residual oxygen could diffuse into the film and interact with the Si particles thereby causing the PL intensity to increase, it did not affect the particle size much. Therefore, the PL peak position shifted very little. The oxygen diffusion was fast at first even with a low sample annealing temperature because the surface and sub-surface layers of the films were in fairly low oxidation states. With increasing annealing temperature and/or time applied to the sample, the surface and sub-surface layers of the films became more intensively oxidized, thereby increasingly obstructing further oxygen diffusion into the film. Thus, the increase of the Si PL intensity slowed down, and eventually almost halted.

The fine structures of the PL spectra are also consistent with our previous suggestion [19-23]. However, for the present ZnS/Si films, there is a new fine structure appearing in all the Si PL curves at about 310 nm wavelength (indicated by an arrow in Fig.2), which was not observed in the Si/Al$_2$O$_3$ film. This possibly arose from a broken ZnS bond or from the formation of a Si-Zn alloy bond in the interface between the Si and ZnS nanoparticles, and the new interfacial states then coupled with the electronic transitions of the silicon nanoparticles to produce the new PL fine structure.

In Fig. 3, the PL results in the wavelength region of 600-700 nm were obtained with excitation light wavelength of 380 nm. Overall, the results are similar to those of the ZnS/SiO$_2$ films in ref. [24]. The intensity of the PL similarly increased with increasing annealing temperature and/or time. However, there are significant shifts in the PL peak positions. In ZnS/SiO$_2$ films, a shallow peak started to appear in sample (c), centered at the wavelength of about 655 nm, which became more pronounced and increasingly blue-shifted with higher annealing intensity. In the present results, a low shallow peak appeared in the as-deposited sample, sample (a), at about 626 nm. Upon gentle annealing, the peak intensity increased slightly without any shift in position, as shown in sample (b). With further annealing, both the intensity and the red shift occurred with increasing magnitude, as seen in samples (c) and (d), but this increase eventually became saturated as observed in sample (e). The peak position for sample (c) is at about 637 nm, while that for samples (d) and (e) is at 644 nm and 647 nm respectively.

As the PL spectra in Fig.3 are similar to those in ref. [24], and the PL in this region could not have originated from S or Zn or Si, it could only be from ZnS. The origin of the PL was attributed to the S vacancies in the films, which were formed partly during the laser ablation film preparation stage, and partly from the S-bond disruption at the ZnS particle surfaces during the film annealing stage. However, the behavior of the PL in the present ZnS/Si film is a little different from that in the ZnS/SiO$_2$ film. As observed previously, the different neighboring materials of the nanoparticles in the film have an effect on their PL [19-21]. The difference caused by the different neighboring materials would lead to a different oxidation
behavior of the nanoparticles in the films. As ZnS was neighbored by Si, both Si and ZnS (as well as some segregated S and Zn) interacted with the residual oxygen particles when the sample was annealed. Since the crystal structure of Si is not as compact as that of SiO₂, both S and Zn can segregate to the surface or subsurface even during the preparation process. In the ZnS/SiO₂ films, the amount of S segregating to the surface increased with increasing annealing temperature. In the ZnS/Si films, this S segregation did not change much. Therefore, the nature and intensities of defects of the ZnS particles in the two different types of films were a little different from each other.

The ZnS particles in the ZnS/Si film could diffuse and aggregate together more easily than those in the ZnS/SiO₂ film. Firstly, this was due to the difference in Zn and S segregation behavior; secondly, the ZnS particles in the ZnS/Si film were generally smaller than those in the ZnS/SiO₂ film; and thirdly, the matrix base Si was not as compact (and dense) as SiO₂. Hence there was an increase in the effective size of the ZnS particles in the ZnS/Si films when the film was annealed. This accounts for the red shift of PL in the films.

4. Conclusion

In conclusion, we have prepared ZnS/Si thin films by using a modified version of the PLD method. The films consisted of co-existing Si and ZnS nanocrystals with a significant segregation of S and Zn. The sizes of the nanoparticles were generally smaller than 15 nm in diameter even after intensive annealing. With different excitation light of wavelengths 280 nm and 380 nm, the composite films yielded independent photoluminescent emissions originating separately from the Si and ZnS nanoparticles. These PL emissions were modified by the neighboring materials of the nanoparticles in the film, and the modification is attributed to the different oxidation and segregation behavior. This possibility of modifying the PL of the nanoparticles in the film with different matrix compositions enhances the possibility of exploiting such tailor-built composite films in optoelectronic devices.

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