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Growth of ZnSe films on ZnO–Si templates

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Abstract

We report the growth and characterization of ZnSe films prepared on ZnO–Si(1 1 1) templates. It was found that the as-deposited ZnSe films were highly oriented with zinc blende structure and a preferred (1 1 1) crystal orientation. It was also found that quality of ZnSe epitaxial layers depends on the ZnO annealing conditions. With a 1 h 1000 °C ZnO annealing, we could achieve a ZnSe/ZnO–Si(1 1 1) sample with a 53 meV room temperature (room temperature) photoluminescence (PL) full-width-half-maximum (FWHM).

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1. Introduction

Wide bandgap ZnSe-based II–VI materials have received increased attention owing to their promising optoelectronic application as light emitters such as light emitting diodes (LEDs) and laser diodes (LDs). ZnSe-based II–VI materials could also be used in visible-blind ultraviolet (UV) photodetectors. Since lattice constant of ZnSe is very close to that of GaAs, conventional ZnSe epitaxial layers were grown on GaAs substrates. Compared with GaAs, Si is a much more mature material. Commercially available Si substrates are also much larger. Thus, if we could epitaxially grow high quality ZnSe layers on Si substrates, we should be able to significantly reduce the cost of the fabricated devices. We should also be able to integrate ZnSe-based optical devices with Si-based electronic devices by growing ZnSe layers on Si substrates. Recently, various ZnSe/Si-based devices such as electroluminescent cells [1], photoelectric cells- [2] and visible sensitive emitter bipolar transistors [3] have all been demonstrated. Although we can indeed grow ZnSe-based epitaxial layers on Si substrates, large mismatches of lattice constant and thermal expansion coefficient between ZnSe and Si will always result in a defective epitaxial layer [4]. The poor wetting of polar ZnSe on non-polar Si substrates also impedes the direct nucleation and consequently results in poor quality; and morphology of the ZnSe epitaxial layers. To overcome these problems, various methods have been proposed, such as nitrogen treated Si substrates [5], hydrogen-terminated Si substrates [6], and the insertion of an intermediate layer between ZnSe and the underneath Si substrates [7].

In this work, we choose ZnO as the intermediate layer due to the following reasons. ZnO is a hard and chemically stable material, which has already been used as the intermediate layer between GaN epitaxial layers and SiC and/or sapphire substrates [8,9]. Furthermore, it is known that the surface of Si substrates is normally covered by a thin SiO_x film [10]. This thin SiO_x film should have good wetting

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properties with ZnO. Physical properties of ZnSe and ZnO are also similar. Therefore, we should be able to achieve a reasonably good ZnSe/ZnO interface. It should be noted that the thermal expansion coefficients of ZnSe, ZnO and Si are 7.5×10^{-6}, 5.5×10^{-6} and $2.44 \times 10^{-6}\,K^{-1}$, respectively. In other words, the thermal expansion coefficient of ZnO is close to the mean value of the thermal expansion coefficients of ZnSe and Si. Thus, we should be able to effectively reduce the thermal stress between ZnSe epitaxial layers and Si substrates by inserting a ZnO layer. In this paper, we report the deposition of ZnSe epitaxial layers on Si substrates with a ZnO intermediate layer. It was found that the quality of ZnSe epitaxial layers depends on the ZnO annealing conditions. The physical and optical properties of the as-prepared ZnSe/ZnO–Si samples will be reported.

2. Experiments

Prior to the growth, Si(1 1 1) wafers were first chemically degreased in three different kinds of organic solvents: 2-1 trichlorothylene, acetone and methanol. These Si(1 1 1) wafers were then oxidized in HNO_3, etched in dilute aqueous HF, and finally treated in a mixed solution of HCl, H_2O_2 and H_2O to grow a thin protective oxide layer on wafer surface. Subsequently, these chemically cleaned Si(1 1 1) wafers were transferred into a rf magnetron sputter deposition system to grow a ZnO layer. During RF sputtering, a 99.99% metallic Zn pellet was used as the target material while a mixture of 75% Ar and 25% O_2 was used as the sputtenng gas and the deposition temperature was kept at 150 °C. To improve the quality of the deposited ZnO layer, we then furnace annealed the samples in oxygen ambient at 600–1000 °C for 1–4 h. These ZnO–Si(1 1 1) templates were then transferred into a horizontal-type low-pressure metal-organic vapor phase epitaxy (LP-MOVPE) system to grow the 1 μm-thick ZnSe epitaxial layer. During MOVPE growth, dimethylzinc (DMZn) and hydrogen selenide (H_2Se) were used as the source materials of Zn and Se, respectively, hydrogen was used as the carrier gas, growth temperature was controlled at 350 °C, flow rates of DMZn and H_2Se were fixed at 5.6×10^{-6} and 8×10^{-5} mol/min, respectively, total flow rate was kept at 2 l/min, and the growth pressure was kept at 3×10^4 Pa. The physical and optical properties of the as-prepared ZnSe/ZnO/Si(1 1 1) samples were then evaluated by photoluminescence (PL) and X-ray diffraction (XRD). For PL measurements, a He–Cd laser operated at 325 nm was used as the excitation source while a UV Labran Infinity spectrophotometer and a charge coupled device camera with a resolution of 0.04 nm were used for signal detection.

3. Results and discussion

Fig. 1(a) shows normalized XRD spectrum of the fabricated ZnSe/Si(1 1 1). It was found that we could observe an extremely strong ZnSe(1 1 1) peak and much weaker ZnSe(2 2 0), ZnSe(3 1 1) and ZnSe(4 0 0) peaks in this XRD spectrum. It can be seen that the ZnSe film was highly oriented with zinc blende structure, and the preferred (1 1 1) orientation is the same as that of the underneath Si substrate.

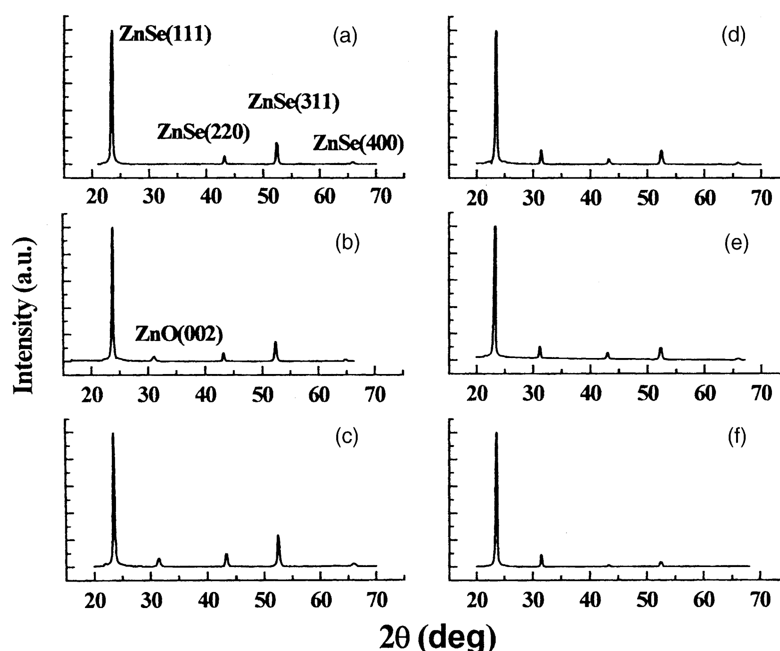

Fig. 1. Normalized XRD spectra of (a) the fabricated ZnSe/Si(1 1 1), and ZnSe/ZnO–Si(1 1 1) with ZnO annealed at (b) 600; (c) 700; (d) 800; (e) 900; and (f) 1000 °C.

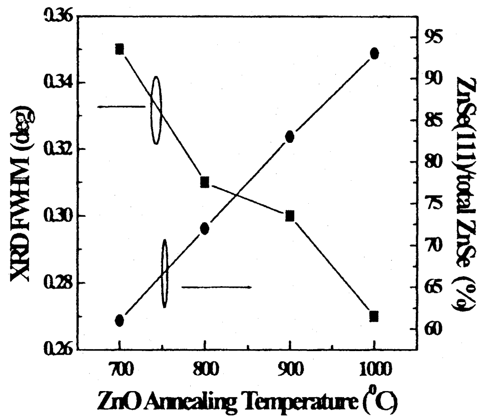

Fig. 2. Integrated XRD intensity ratio of ZnSe(1 1 1) peak to total ZnSe peaks (i.e. ZnSe(1 1 1) + ZnSe(2 2 0) + ZnSe(3 1 1) + ZnSe(4 0 0)) and the observed ZnSe(1 1 1) XRD FWHM as functions of ZnO annealing temperature.

Fig. 1(b)-(f) show normalized XRD spectra of ZnSe/ZnO–Si with ZnO annealed for 1 h at 600, 700, 800, 900 and 1000 °C, respectively. It was found that we could still observe the ZnSe(2 2 0), ZnSe(3 1 1) and ZnSe(4 0 0) peaks. However, it was also found that these ZnSe films were still highly oriented with the same preferred (1 1 1) orientation even though we had inserted a ZnO layer in between ZnSe epitaxial layers and Si(1 1 1) substrates. Furthermore, it was found that we could also observe a ZnO(0 0 2) XRD peak from the ZnSe/ZnO–Si(1 1 1) samples, as shown in Fig. 1(b)-(f). Fig. 2 shows integrated XRD intensity ratio of ZnSe(1 1 1) peak to total ZnSe peaks (i.e. ZnSe(1 1 1) + ZnSe(2 2 0) + ZnSe(3 1 1) + ZnSe(4 0 0)) and the observed ZnSe(1 1 1) XRD full-width-half-maximum (FWHM) as functions of ZnO annealing temperature. As shown in Fig. 2, it was found that the integrated XRD intensity ratio of ZnSe(1 1 1) peak to total ZnSe peaks increases monotonically while the ZnSe(1 1 1) XRD FWHM decreases monotonically as we increased the ZnO annealing temperature from 600 to 1000 °C for 1 h. Furthermore, it was found that the ZnSe(1 1 1) XRD FWHMs observed from the five ZnSe/ZnO–Si(1 1 1) samples were all smaller than that observed from ZnSe/Si(1 1 1) sample (i.e. 0.39°). These results suggest that we could indeed improve the ZnSe epitaxial layer quality by the insertion of a ZnO intermediate layer, and a post-deposition annealing of ZnO at 1000 °C could further improve the crystal quality of the subsequently grown ZnSe epitaxial layer. Previously, Zhu et al. [11] have shown that high temperature annealing could improve the surface structure of ZnO films, which agrees well with our XRD results shown in Fig. 2.

Fig. 3(a) shows room temperature (RT) PL spectrum of the fabricated ZnSe/Si(1 1 1), while Fig. 3(b)-(f) show RT PL spectra of ZnSe/ZnO–Si(1 1 1) with ZnO annealed at 600, 700, 800, 900 and 1000 °C for 1 h, respectively. Compared with the ZnSe/ZnO–Si(1 1 1) samples, it can be seen very clearly that the absolute PL peak intensity of ZnSe/Si(1 1 1) was much weaker. For the ZnSe/ZnO–Si(1 1 1) samples, it was also found that the PL peak intensity seems to increase as the ZnO annealing temperature increases. The PL peak positions and their FWHMs were also indicated in each PL spectrum. It can be seen that the smallest PL FWHM (i.e. 53 meV) was observed from the ZnSe/ZnO–Si(1 1 1) sample with the ZnO intermediate layer annealed at 1000 °C. Furthermore, it was found that PL peak position seems to red shift toward lower energy side as we increased the ZnO

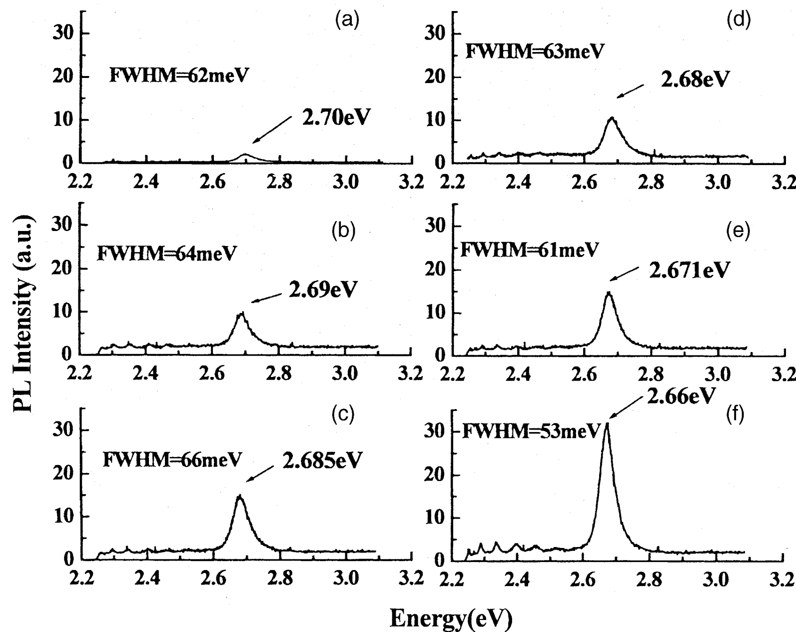

Fig. 3. Room temperature PL spectra of (a) the fabricated ZnSe/Si(1 1 1), and ZnSe/ZnO–Si(1 1 1) with ZnO annealed at (b) 600; (c) 700; (d) 800; (e) 900; and (f) 1000 °C.

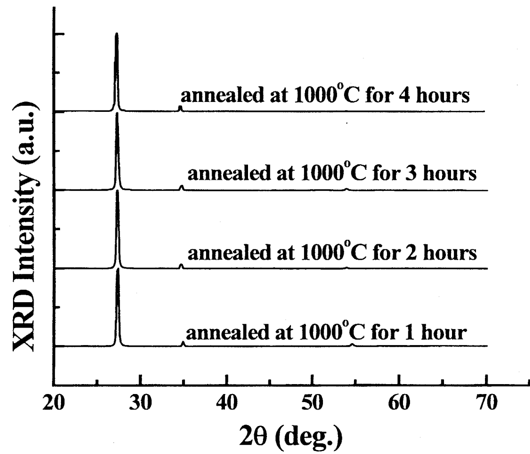

Fig. 4. Normalized XRD spectra of ZnSe/ZnO–Si(1 1 1) samples with ZnO annealed at 1000 °C for 1–4 h.

annealing temperature. This may be due to the increase of grain size of ZnO buffer layer [12]. As a result, we could achieve a better crystal quality of ZnSe epitaxial layers and thus a narrower PL FWHM.

Fig. 4 shows normalized XRD spectra of ZnSe/ZnO–Si(1 1 1) samples with ZnO annealed at 1000 °C for 1 to 4 h. It can be seen that these four XRD spectra were almost identical with similar XRD FWHM. With a high ZnO annealing temperature of 1000 °C, such a result indicates that we cannot further improve the crystal quality of ZnSe epitaxial layers by using a long ZnO annealing time. Fig. 5(a)-5(d) show RT PL spectra of ZnSe/ZnO–Si(1 1 1) with ZnO annealed at 1000 °C for 1, 2, 3 and 4 h, respectively. Again, we observed a ZnSe-related PL peak at around 460 nm from all four samples. Furthermore, it was found that PL peak intensity and FWHM of the samples with 1–3 h ZnO annealing were about the same. In contrast, PL peak intensity decreased significantly while the PL FWHM became much

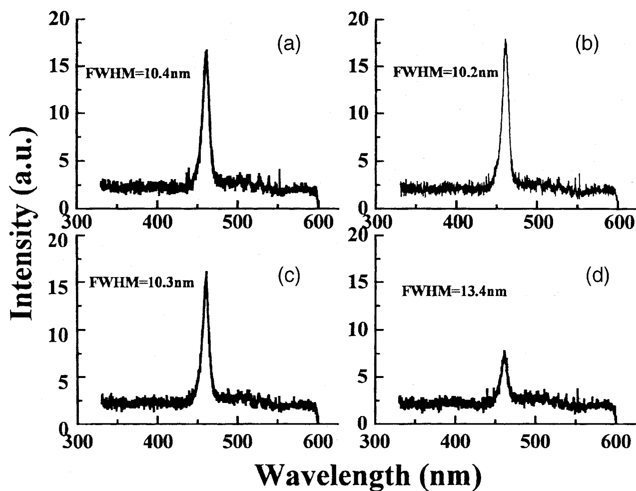

Fig. 5. Room temperature PL spectra of ZnSe/ZnO–Si(1 1 1) with ZnO annealed at 1000 °C for (a) 1; (b) 2; (c) 3; and (d) 4 h.

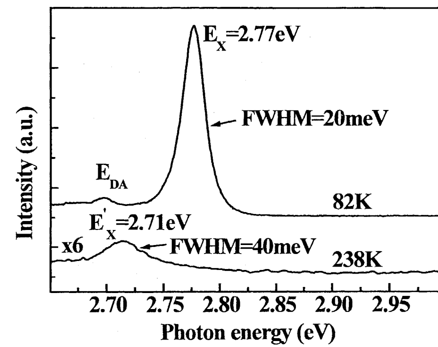

Fig. 6. 82 and 238 K PL spectra of ZnSe/ZnO–Si(1 1 1) with ZnO annealed at 1000 °C for 1 h.

broader as the ZnO annealing temperature was increased to 4 h. To further study the ZnSe/ZnO–Si(1 1 1) sample with ZnO annealed at 1000 °C for 1 h, we measured its PL spectra at two different temperatures (i.e. 82 and 238 K), as shown in Fig. 6. At 238 K, it was found that we could only observe a weak near-band-edge emission (NBE) peak from the ZnSe epitaxial layer (labeled as E'_x) at 2.71 eV. In contrast, the PL intensity of this NBE peak increased significantly when the temperature was reduced to 82 K. A blue shift of this PL peak to 2.77 eV was also observed. Such a blue shift could be attributed to the change of bandgap energy as temperature was decreased. At 82 K, it was found that we could also observe a small PL peak at 2.69 eV. This small PL peak is presumably due to the emission from donor–acceptor pairs (DAP) [13] (labeled as E_{DA}), which can only be observed from certain ZnSe/ZnO–Si(1 1 1) samples at low temperatures. It should be noted that PL intensity of ZnSe/Si(1 1 1) sample was much smaller and no DAP peak could be observed even at low temperatures. Such an observation again indicates that we could improve the quality of ZnSe epitaxial layers on Si(1 1 1) substrates by the insertion of a ZnO intermediate layer.

4. Conclusions

In summary, high quality ZnSe films were grown on Si(1 1 1) substrates by LP-MOCVD with ZnO as an intermediate layer. It was found that the as-deposited ZnSe films were highly oriented with zinc blende structure and a preferred (1 1 1) crystal orientation. It was also found that quality of ZnSe epitaxial layers depends on the ZnO annealing conditions. With a 1 h 1000 °C ZnO annealing, we could achieve a ZnSe/ZnO–Si(1 1 1) sample with a 53 meV RT PL FWHM.

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