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MOVPE 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 are highly oriented with zinc blende structure, and the preferred crystal orientation is (1 1 1). The small X-ray diffraction (XRD) full-wide-half-maximum (FWHM) also suggests that the crystal quality of the deposited ZnSe films is reasonably good. From temperature dependent photoluminescence (PL) measurements, it was found that exciton binding energy, E_B, equals 25.6 meV for the as-prepared ZnSe/ZnO/Si(1 1 1) samples.

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Keywords: PL; Si substrate; MOVPE; ZnSe

1. Introduction

ZnSe is a II–VI compound semiconductor with a room temperature direct bandgap energy of 2.7 eV. Such a property makes ZnSe potentially useful as optical modulator and light emitters in the blue spectra region [1-3]. Conventional ZnSe epitaxial layers were grown on GaAs substrates since lattice constants of these two materials are nearly matched [4]. Compared with GaAs, Si is a much more matured materials. Commercially available Si substrates are also much larger. Thus, if high quality ZnSe layers can be epitaxially grown on Si substrates, the cost of the fabricated devices will besignificantly reduced,and also, it will bring promise for the integration of ZnSe-based optical devices with Si-based electronic. However, it is difficult to grow high quality ZnSe layers directly on Si substrates due to the large lattice mismatch and the large thermal expansion coefficient mismatch between the two materials. 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. One possible way to solve these problems is to insert an intermediate layer between ZnSe and the underneath Si substrates [5]. 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 [6,7]. Furthermore, it is known that surface of Si substrate is normally covered by a thin SiO_x film [8]. This thin SiO_x film should have good wetting properties with ZnO. Physical properties of ZnSe and ZnO are also similar that we should be able to achieve a reasonably good ZnSe/ZnO interface. More importantly, thermal expansion coefficients of ZnSe, ZnO and Si are 7.5 $\times 10^{-6}$, 5.5 $\times 10^{-6}$ 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

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ZnSe and Si. Thus, by inserting a ZnO intermediate layer, the thermal stress between ZnSe layers and Si substrates should be effectively reduced. In this paper, we report the deposition of ZnSe epitaxial layers on Si substrates with a ZnO intermediate layer. The physical and optical properties of the as-prepared ZnSe/ZnO/Si samples will be reported.

2. Experimental

Prior to deposition, Si(1 1 1) wafers were first chemically cleaned using the method described previously [9]. A ZnO layer was subsequently deposited onto the cleaned Si(1 1 1) substrates by RF sputtering at 150. 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 sputtering gas. To improve the quality of deposited ZnO layer, we then furnace annealed the samples in oxygen ambient at 1000 °C for one hour. An about 1 μm-thick ZnSe layer was then grown on the ZnO/Si(1 1 1) templates in a horizontal-type low-pressure metal-organic vapor phase epitaxy (LP-MOVPE). 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^{-1}, respectively, the total flow rate of the carrier hydrogen was kept at 2l min^{-1}, 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 shows XRD spectrum of the as-prepared ZnSe/ZnO/Si(1 1 1) samples. It was found that an extremely strong peak and a much weaker peak appear at 27.29° and 34.72° in the XRD spectrum, and they can be indexed as the differaction peak from the ZnSe(1 1 1) and ZnO(0 0 2) indices, respectively. A peak at about 28.5° can be seen in larger magnification, which is corresponding to the diffraction peak of Si(1 1 1). From the XRD spectrum, one can conclude that the ZnSe film is highly oriented with zinc blende structure, and the preferred ZnSe(1 1 1) orientation is the same as that of the underneath Si substrate. The small 0.25° full-width-half-maximum (FWHM) of the observed ZnSe(1 1 1) XRD peak indicates that quality of our ZnSe epitaxial layer is reasonably good.

Fig. 2 shows the PL spectra of the as-prepared ZnSe/ZnO/Si(1 1 1) samples measured at various temperatures. It can be seen that the PL spectra exhibited a strong and dominant emission peak at 2.77 eV at low temperatures, which may be related to free exciton emission of ZnSe (labeled as E_X) [10]. The peak at 2.69 eV is presumably due to the emission from donor–acceptor pairs (DAP) [11] (labeled as E_{DA}). As the temperature increases, it was found that E_X peak shifts toward small energy side while its intensity decreases. Similar behaviors were also observed from E_{DA} peak. The red-shifts of these two peaks could both be attributed to the decrease in ZnSe bandgap energy as the temperature is increased. Fig. 3 shows the integrate PL intensity of E_X as a function of temperature. It was found that the integrated PL intensity could be fitted by [12]:

$$I = \frac{I_0}{1 + C\exp(-E_B/k_BT)} \quad (1)$$

where I_0 is a constant, C the ratio of non-radiative transition probability P_{nr0} at infinite temperature to radiative transition probability P_r (i.e. $C = P_{nr0}/P_r$), k_B is the Bolzmann's constant, and E_B is the exciton binding energy. By curve fitting the experimental data in Fig. 3, we found that the exciton binding energy, E_B, equals to 25.6 meV. Fig. 4 shows the peak energy of E_X as a function of temperature. It was found

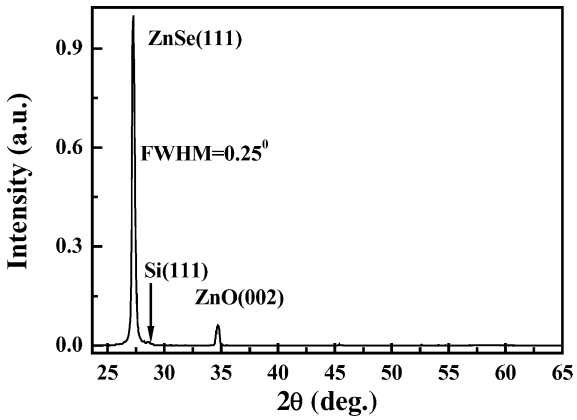

Fig. 1. X-ray spectrum for the ZnSe/ZnO/Si(1 1 1) samples used in this study.

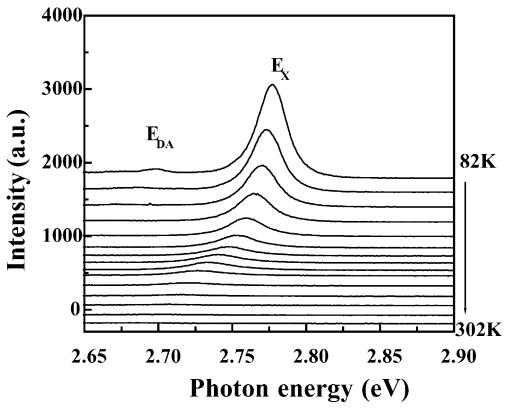

Fig. 2. Temperature dependent PL spectra for the ZnSe/ZnO/Si(1 1 1) samples used in this study.

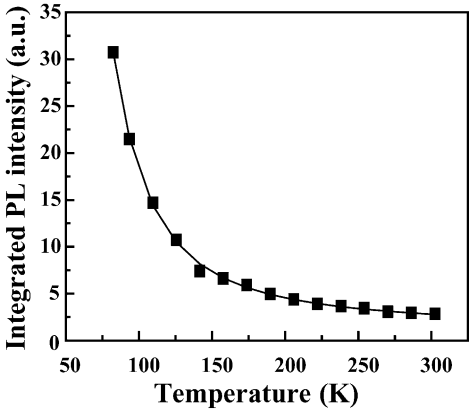

Fig. 3. Integrate PL intensity of E_X as a function of temperature for the ZnSe/ZnO/Si(1 1 1) samples used in this study.

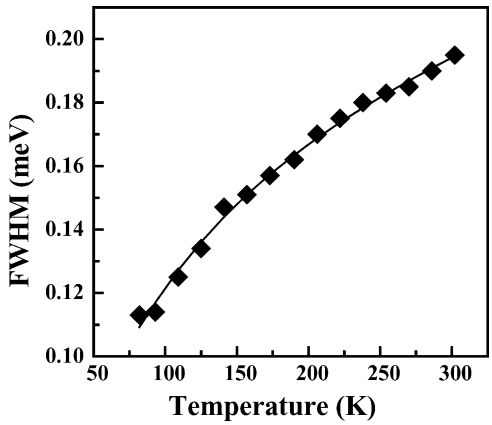

Fig. 5. FWHM(Γ) of peak E_X as a function of temperature for the ZnSe/ZnO/Si(1 1 1) samples used in this study.

that the experimental data could be fitted well by the Varshni semi-empirical relationship [13]:

$$E(T) = E(0) - \frac{\alpha T^2}{(T+\beta)} - \frac{\sigma^2}{k_B T} \quad (2)$$

where $E(0)$ is the ZnSe bandgap energy at 0 K; α and β are the Varshni's fitting parameters, and σ indicates the degree of confinement. In other words, a large value of σ means a strong confinement effect. By curve fitting the experimental data in Fig. 4, we found that $E(0)$ = 2.78 eV and σ = 4 meV. The 2.78 eV (0 K ZnSe bandgap energy) is consistent with the previously reported value. Such an agreement also indicates that E_X is indeed originated from free exciton emission. On the other hand, the large σ (i.e. 4 meV) suggests a strong confinement effect, which is probably due to the large 25.6 meV exciton binding energy of our ZnSe/ZnO/Si samples. FWHM(Γ) of peak E_X as a function of temperature is shown in Fig. 5. It was found that FWHM(Γ) of peak E_X could be fitted by [14]:

$$\Gamma(T) = \Gamma_{inh} + \Gamma_{LA} T + \frac{\Gamma_{LO}}{\exp(E_{LO}/k_B T) - 1} \quad (3)$$

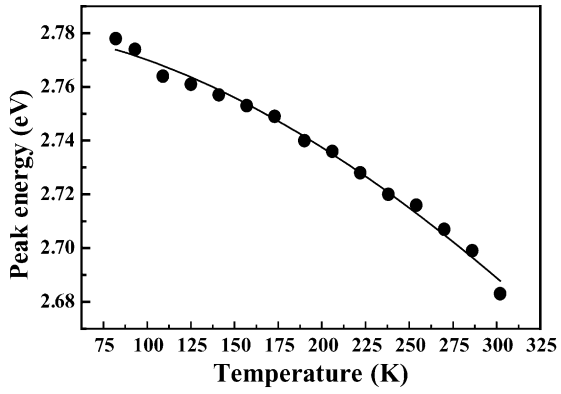

Fig. 4. The observed peak energy of E_X as a function of temperature for the ZnSe/ZnO/Si(1 1 1) samples used in this study.

where Γ_{inh} is the inhomogeneous broadening factor, Γ_{LA}, Γ_{LO} are the measured weightings of LA, LO phonons, respectively, and E_{LO} is the energy of LO phonons. By curve fitting the experimental data in Fig. 5, we found that the energy of LO phonons, E_{LO}, equals 31 meV. Such a value is in well agreement with the previously reported value of 31.7 meV [15]. Such a result again indicates that E_X is indeed the ZnSe related free exciton related PL peak.

4. Conclusions

High quality ZnSe film has been deposited onto ZnO/Si(1 1 1) templates by LP-MOVPE. It was found that the as-deposited ZnSe films are highly oriented with zinc blende structure, and the preferred crystal orientation is (1 1 1). The small XRD FWHM also suggests that the crystal quality of the deposited ZnSe films is reasonably good.

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