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ZnSe films deposited on crystalline GaAs and amorphous quartz substrates by means of pulsed laser ablation technique

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Abstract. ZnSe films were deposited by pulsed laser ablation on a crystalline GaAs substrate and on an amorphous quartz substrate. The deposition process was performed with the same growth parameters. The films were investigated by means of X-ray diffraction, reflectance and photoluminescence spectroscopy. The X-ray diffraction spectra have demonstrated that the films grow in a highly oriented way but having different orientations, *i.e.* the films deposited on GaAs grow (100)-oriented and the films deposited on quartz grow (111)-oriented. Reflectance spectra as a function of the temperature have been analysed by means of the classical oscillator model, in order to obtain the temperature dependence of the band gap energy. This gives results comparable to those of ZnSe single crystals for ZnSe on GaAs, but it is red-shifted for ZnSe on quartz, because of lattice and thermal strains. The photoluminescence measurements at $T = 10$ K confirm the better quality of ZnSe deposited on GaAs and show that pulsed laser ablation is a promising technique to grow films having intrinsic luminescence even on an amorphous substrate.

PACS. 61.10.Eq X-ray scattering – 78.40.Fy Semiconductors – 78.55.Et II-VI semiconductors

1 Introduction

II-VI wide band gap semiconductors are promising materials for optoelectronic applications. Some of these compounds exhibit efficient luminescent emission which make them suitable for the fabrication of light emitting diodes and semiconductor lasers. In particular, ZnSe, with a band gap of about 2.7 eV at room temperature, has an emission light in the blue-green spectral region. Thin films of ZnSe are usually deposited by molecular beam epitaxy [1], metal-organic vapour phase epitaxy [2] and electrodeposition techniques [3]. Recently, there have been a number of papers on the growth of ZnSe films by pulsed laser ablation (PLA) technique [4–7]. One of the major advantages of PLA is congruent evaporation, so that multicomponent compounds (semiconductors, magnetic materials, high temperature superconductors) can be stoichiometrically grown as thin films.

One important aspect in thin film deposition is the substrate selection, because it determines the lattice mismatch and thermal expansion mismatch. Usually, ZnSe films are deposited on a GaAs substrate, because of the low lattice mismatch between ZnSe and GaAs (0.27%); such films have a very good crystallinity and high photoluminescence (PL) efficiency. However, it is important to study how the structural and optical properties of ZnSe films change when the deposition occurs on other commonly available substrates, in view of ZnSe-based device fabrication. In particular, growth processes on optical windows and inexpensive substrates are becoming of great interest.

Our interest is to compare the structural and optical properties of the ZnSe films deposited on different kinds of substrate. Therefore, we present experimental results on the X-ray diffraction (XRD), reflectance and PL properties of ZnSe films deposited by PLA on GaAs (100)-oriented and amorphous quartz in the identical growth conditions. In fact, the XRD spectra have shown that all the films are highly oriented but the film orientation is different in the two cases. In addition, the crystalline quality strongly depends on the substrate type: in fact, the films grown on amorphous quartz have a smaller grain size with respect to those deposited on GaAs single crystals. The reflectance measurements show that the energy gap of the ZnSe films on GaAs substrates is comparable to that of ZnSe single crystals, whereas the energy gap of ZnSe epilayers on quartz substrates present a red-shift, due to the lattice and thermal expansion coefficient mismatch. We

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have observed PL emission in the near band gap region, due to excitonic and impurity levels, and in the red-yellow region, which is known to originate from deep centres. The luminescence data have been found to be consistent with the reflectance data.

2 Experimental

ZnSe epilayers were grown on GaAs(100) and amorphous quartz substrates by laser ablation of a ZnSe solid target. A frequency doubled Nd:Yag laser having a wavelength of 532 nm, a pulse width of 10 ns, a laser fluence of about $10\,J/cm^{-2}$ and a repetition rate of 10 Hz was used as the pulsed laser source. The GaAs and quartz substrates were mounted on a rotating and heated holder, positioned 3 cm from the target. The substrates were degreased in trichloroethylene, acetone and methanol before starting the deposition process; in addition, the GaAs substrates were chemically etched in a H_2SO_4:H_2O_2:H_2O (5:1:1) solution and finally rinsed in deionized water. Film deposition was performed in a evacuated stainless-steel chamber (residual pressure of 10^{-6} mbar). During the growth, the substrate temperature was kept at 400 °C and the deposition time was 30 minutes. The ZnSe samples appeared shining and adhered to the substrates. The thickness of each film was measured by using an "Alphastep" profilometer: it resulted to be about 300 nm for both the samples.

The X-ray diffraction analysis was performed by using the CuKα radiation ($\lambda = 1.5406$ Å) from a conventional $\theta - 2\theta$ diffractometer (D5000 Siemens). Reflectance measurements were performed by using as light source a 100 W tungsten lamp. The samples were mounted in a He-closed cycle refrigerator thermoregulated from 10 to 300 K. The light reflected from the sample was analyzed by means of a double grating spectrometer (1 meV/mm of dispersion) and detected by a GaAs cooled (−20 °C) photomultiplier. Photon counting technique was used to record the spectra. For the PL measurements, the 325 nm line of a He-Cd laser was used for exciting the sample in the standard backscattering geometry. The light emitted from the sample surface was analyzed and detected by the same apparatus used for the reflectance measurements.

3 Results and discussion

3.1 XRD measurements

The XRD spectra of the ZnSe films deposited on GaAs and quartz substrates are shown in Figure 1. Although the deposition parameters were identical in the growth experiment, significant differences appear between the films. In fact, the XRD spectrum of the ZnSe films deposited on GaAs consists of three different peaks, which can be resolved after a deconvolution procedure by means of Voigt functions [8] (shown in the inset). In particular, the peak

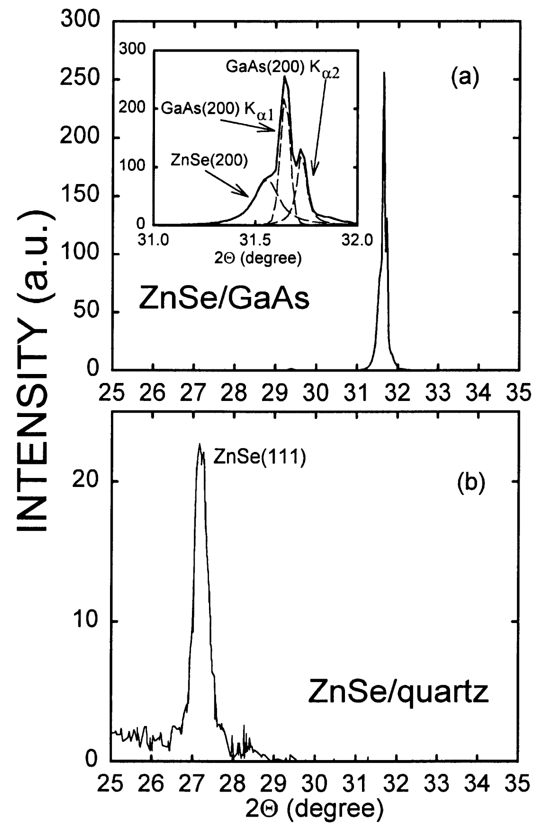

Fig. 1. XRD spectra of a ZnSe film deposited on GaAs (100)-oriented (a) and amorphous quartz (b) substrates. The Miller indexes of the reflection planes from the ZnSe and GaAs are indicated. In the inset of Figure 1a a deconvolution of the ZnSe and GaAs peaks by means of Voigt function [8] is illustrated.

at 31.58 degrees can be identified with the (200) cubic reflection from the ZnSe film, whereas the peaks at 31.65 and 31.73 degrees are the (200) reflections from the GaAs substrate ($K_{\alpha1}$ and $K_{\alpha2}$ lines, respectively). Therefore, the ZnSe films deposited on (100) oriented GaAs grow with the same orientation of the substrate. On the contrary, the XRD pattern of ZnSe deposited on quartz consists of a single peak at 27.20 degrees, assigned to the (111) cubic reflection.

The XRD spectra reveal also that the films grow highly oriented: in fact, no other XRD peak is clearly evident in the scanned angular range. Information about the structural quality of the films can be obtained by evaluating the full width at half maximum (FWHM) of the main peak. In fact, the FWHM of the ZnSe films deposited on GaAs (0.15°) gives results comparable to that obtained by other authors [4,7,9]. In contrast, the FWHM of the ZnSe film grown on quartz (0.38°) is large with respect to that of the film deposited on GaAs, because of the amorphous substrate, but comparable to that reported in literature [5,10].

Moreover, the FWHM gives an estimate of the crystalline grain size D, according to the Debye-Scherrer

relationship [11] D=0.9λ/(FWHM$\cdot\cos\theta$), where λ is the X-ray wavelength and θ is the Bragg angle. The obtained average D values are 57 ± 4 nm and 21 ± 2 nm for the films deposited on GaAs and quartz, respectively.

3.2 Reflectance measurements

In order to compare the influence of the substrate type on the optical properties of the ZnSe layers, reflectance (R) measurements at normal incidence have been carried out in the excitonic region. Figure 2 shows the R spectra (dots) at $T = 10$ K for the ZnSe films deposited on the two different substrates. The R spectrum of a thin film is usually different from that of a single crystal, because optical interference effects strongly influence the film reflectance in the transparent and lightly absorbing (if the film is sufficiently thin) spectral regions. However, a dispersion line is evident in Figure 2 for both the samples: it can be assigned to the free excitonic resonance, in agreement with the analysis performed in reference [2]. In order to compare the energy gap E_g values of the ZnSe films with the E_g value of ZnSe single crystals as reported in literature, we have calculated the $R(\hbar\omega)$ spectra taking into account the interference in the "dead layer" [12] (a near-surface layer depleted of excitons), according to the model described in reference [13]:

$$R(\hbar\omega) = r \cdot r^*, \qquad r = \frac{r_{12} + r_{23}\mathrm{e}^{2\mathrm{i}\theta}}{1 + r_{12} \cdot r_{23}\mathrm{e}^{2\mathrm{i}\theta}} \tag{1}$$

with $\theta = 2\pi d/\lambda_{\mathrm{m}}$, where λ_{m} is the light wavelength within the medium, d is the thickness of the dead layer, $r_{12} = (1-\varepsilon_s^{1/2})/(1+\varepsilon_s^{1/2})$ is the reflection coefficient at the air-dead layer boundary, $r_{23} = \left(\varepsilon_s^{1/2} - \tilde{n}\right) / \left(\varepsilon_s^{1/2} + \tilde{n}\right)$ is the reflection coefficient at the dead layer-bulk boundary, ε_s is the background dielectric constant ($\varepsilon_s = 8.3$ for ZnSe [14]), $\tilde{n} = n + \mathrm{i}k$ is the complex refractive index, whose real (n) and imaginary (k) parts are related to the real (ε_1) and imaginary (ε_2) parts of the dielectric function $\varepsilon = \varepsilon_1 + \mathrm{i}\varepsilon_2$ by the following equations:

$$n(\omega) = \left\{ \frac{1}{2} \left[\varepsilon_1(\omega) + \left(\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) \right)^{1/2} \right] \right\}^{1/2} \tag{2a}$$

$$k(\omega) = \left\{ \frac{1}{2} \left[-\varepsilon_1(\omega) + \left(\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) \right)^{1/2} \right] \right\}^{1/2}. \tag{2b}$$

The dielectric function $\varepsilon = \varepsilon_1 + \mathrm{i}\varepsilon_2$ can be represented, in the damped harmonic oscillator model [15], by the expression:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{A\omega_0^2}{\omega_0^2 - \omega^2 - \mathrm{i}\omega\Gamma} \tag{3}$$

where ε_∞ is the background dielectric constant for $\omega \to \infty$ ($\varepsilon_\infty = 5.6$ for ZnSe [14]), A is the polarizability, Γ the broadening and $\omega_0 = E_0/\hbar$ the circular frequency corresponding to the exciton energy E_0.

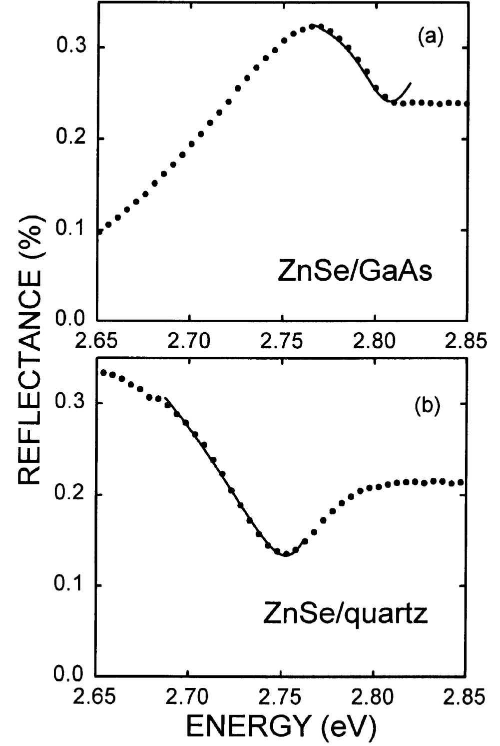

Fig. 2. Reflectance spectra of a ZnSe film deposited on GaAs (a) and quartz (b) substrates, measured at $T = 10$ K in the excitonic resonance region. The experimental spectra (dots) have been fitted according to equation (1) (continuous lines).

A fit of the experimental measurements to the $R(\hbar\omega)$ expression has been performed, by varying the following parameters: the excitonic frequency ω_0, the broadening parameter Γ, the dead layer thickness d and the polarizability A. The shapes of the reflectance spectra are in good agreement with equation (1), as illustrated by the continuous lines in Figure 2. Furthermore, the energy gap of the ZnSe films can be estimated: in fact, Eg is given by $Eg = E_0 + E_{\mathrm{b}}$, where E_{b} is the exciton binding energy (20 meV for ZnSe [14]). The obtained Eg values at $T = 10$ K are 2.820 eV and 2.767 eV for ZnSe deposited on GaAs and quartz, respectively. These values have to be compared to the values of $Eg = 2.820$ eV for ZnSe single crystals [14]. The Eg value obtained for films grown on GaAs corresponds to that of single crystals, as expected because of the negligible lattice mismatch. Unlike the ZnSe films on GaAs, there is no mismatch estimate between the ZnSe thin film and the amorphous quartz substrate. The Eg value obtained for the films deposited on quartz shows that they experience a tensile strain that results in a shrinkage of the band gap of about 53 meV. In addition to the lattice mismatch, strains are usually developed due to the difference in the thermal expansion coefficient between the substrate and the film (thermal strain). The thermal expansion coefficient of ZnSe (6.82×10^{-6} K^{-1} at room temperature) is considerably larger than that of amorphous quartz (5.5×10^{-7} K^{-1} at room temperature).

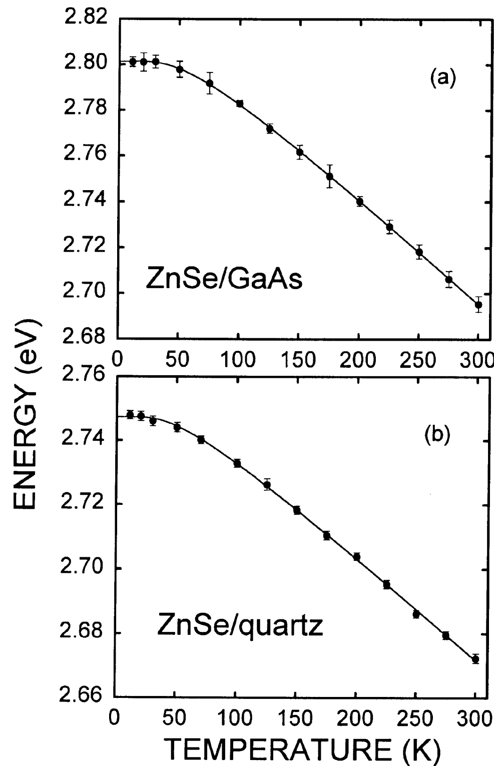

Fig. 3. Temperature dependence of the excitonic energy (dots) for a ZnSe film deposited on GaAs (a) and quartz (b) substrate. The excitonic energies have been obtained from the fitting procedure of the experimental reflectance spectra to equation (1), as illustrated in Figure 2. The continuous lines are the best fit of the experimental data to equation (4).

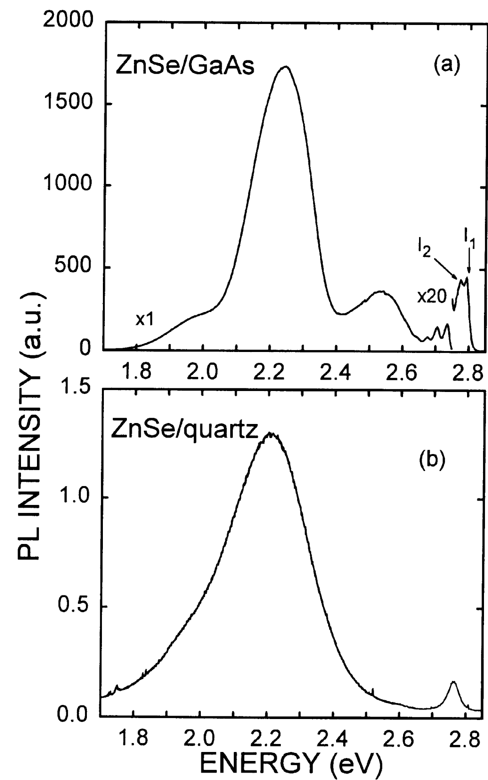

Fig. 4. PL spectra of a ZnSe film deposited on GaAs (a) and quartz (b) substrates, measured at $T = 10$ K. The ZnSe films were photoexcited by means of the 325 nm line of a He-Cd laser. The sensitivity factors relative to the near band gap and deep levels regions are indicated.

Therefore, after the ZnSe film is cooled down from the growth temperature to the measurement temperature, it suffers tensile stress, which lowers the energy gap. The thermal expansion coefficient of ZnSe is also larger than that of GaAs (5.7×10^{-6} K^{-1} at room temperature), but the tensile stress is compensated by the compressive stress due to the larger lattice constant of ZnSe (5.6683 Å at room temperature) with respect to GaAs (5.6533 Å at room temperature).

The reflectance measurements have been performed at different temperatures from 10 K to 300 K. The analysis of these measurements by means of the equation (1) permits us to obtain the temperature dependence of the excitonic energy, which is shown in Figure 3 (dots). The data in Figure 3 have been fitted by a Bose-Einstein type expression (continuous line in Fig. 3), usually used to describe the thermal red shift of excitonic levels $X(T)$ in semiconductors due to electron-phonon interactions [16]:

$$X(T) = X(0) - 2a_{\mathrm{B}}n_{\mathrm{B}} \quad (4)$$

where a_{B} represents the strength of the exciton-phonon interaction, $n_{\mathrm{B}} = [\exp(\theta/T) - 1]^{-1}$ is the Bose-Einstein statistical factor for phonon emission and absorption, θ is a temperature corresponding to the average energy of the phonons involved in the process. The good agreement between experimental data and the model described by equation (4) confirms the crystalline nature of the ZnSe lattice in each deposited film: in fact, equation (4) describes the band gap shrinkage of semiconductors having a crystalline nature, because it is mainly based on the electron-phonon interaction theory. In particular, the values obtained for the θ parameter (160 ± 3 K for ZnSe deposited on GaAs and 143 ± 7 K for ZnSe deposited on quartz) are lower than the θ value corresponding to LO phonons (about 30 meV $\rightarrow$ 350 K). This suggests that acoustic as well as optical phonons are responsible for the thermal band gap shrinkage. The contribution of acoustic phonons is larger in ZnSe films deposited on quartz substrates.

3.3 PL measurements

Figure 4 shows the PL spectra at $T = 10$ K of ZnSe films deposited on GaAs (Fig. 4a) and quartz (Fig. 4b) wafers. The films show PL emission both in the green-blue region (energy larger than 2.65 eV) and in the red-yellow region (energy between 1.80 eV and 2.65 eV). The near band gap emission of the ZnSe film deposited on a GaAs substrate consists of several structures, whereas a single band characterizes the near band gap emission of the ZnSe deposited on a quartz substrate. In particular, the I_1 and I_2 peaks at 2.795 eV and 2.775 eV in ZnSe/GaAs epilayers can be assigned to bound exciton recombination,

which dominates the near band gap PL spectra at low temperature [2,17]: the energy red shift of these peaks with respect to the free exciton energy as obtained from the reflectance spectra confirms such an attribution. In particular, the I_1 peak involves donor bound excitons and the I_2 peak involves acceptor bound excitons, with binding energies of 5 meV and 25 meV respectively, as commonly seen in undoped ZnSe [18]. The excitons are bounded to a number of possible impurities due to contamination of the deposition chamber. Moreover, the peak at 2.735 eV can be attributed to donor-acceptor pairs (DAP) recombination, with clear phonon replica at 2.705 eV, 2.675 eV and 2.645 eV. On the contrary, the broad PL band at 2.765 eV in the PL spectrum of the ZnSe deposited on quartz can be attributed to band-band recombination: in fact, the structural disorder present in ZnSe films on quartz originates electric fields which dissociate the excitonic complexes, so excitonic recombination is negligible in such a film.

PL spectra of both ZnSe samples are dominated by the red-yellow luminescence band centred at about 2.2 eV. However, the lineshape and intensity of this broad emission band are different for the two types of films. The broad PL emission mainly originates from deep centres due to vacancies and intersites. In particular, the bands at 2.22 eV and 2.53 eV in ZnSe deposited on GaAs can be identified as due to Ga atoms in ZnSe films [14,19] and excess of Zn in ZnSe [14,20], whereas the band at 1.95 eV is commonly attributed to Cu impurities [14,21]. The band at 2.2 eV in ZnSe deposited on quartz seems higher than that related to Zn vacancies in ZnSe (2.03 eV [6]), so further investigations are needed to understand the origin of this deep level.

The PL intensity of ZnSe films deposited on quartz is almost three orders of magnitude lower than the PL intensity of the ZnSe film on GaAs. This is expected for the large number of non radiative recombination centres in ZnSe on quartz, because of the more disordered deposition process due to the mismatched substrate.

4 Conclusion

In conclusion, we have reported the structural and optical properties of ZnSe films grown on GaAs and amorphous quartz substrates, by means of laser ablation with identical deposition parameters. The properties of the films depend significantly on the substrate nature. XRD, reflectance and PL measurements have shown better crystalline and optical qualities of ZnSe/GaAs epilayers with respect to the ZnSe films deposited on quartz. This result was expected because of the low lattice mismatch between ZnSe and GaAs. However, the XRD measurements have shown that crystalline quality ZnSe is obtained on amorphous quartz, too. The reflectance measurements confirm such a result, but the excitonic energy is red-shifted with respect to that of ZnSe deposited on GaAs, because of lattice and thermal strains. The PL intensity of ZnSe grown on quartz is about three orders of magnitude lower with respect to ZnSe grown on GaAs. However, the presence of intrinsic emission in both heterostructures confirms that pulsed laser ablation is a suitable technique to fabricate high quality films both on crystalline and amorphous substrates.

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$$I_{\mathrm{VOIGT}}(hv) = \frac{a_0}{\sqrt{\pi}a_2}\int_{-\infty}^{+\infty}\frac{\exp(-t^2)\mathrm{d}t}{a_3^2 + \left(\frac{hv-a_1}{a_2} - t\right)^2}$$
where the fitting parameters $a_{0,1,2,3}$ have the following meaning: a_0 is an amplitude factor, a_1 is the degree corresponding to the function peak, a_2 is the Gaussian width and a_3 is proportional to the ratio of Lorentzian and Gaussian width
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