Reflectance and photoluminescence characterization of CdS and CdSe heteroepitaxial films deposited by laser ablation technique

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Abstract

Optical properties of CdSe and CdS films, deposited on sapphire substrate by means of pulsed laser ablation technique, have been investigated in order to study the effect of such a transparent substrate on the photoluminescence efficiency of the deposited epilayers. CdSe and CdS films present intrinsic (excitonic) emission at low temperature, differently from the same films deposited on quartz. The temperature dependence of the excitonic energy has been analyzed taking into account the contribution of both the thermal dilatation and electron–phonon interaction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Semiconductors; Thin films; Optical properties; Luminescence; Electron–phonon interaction

1. Introduction

The pulsed laser ablation technique is commonly used for epitaxial deposition of wide bandgap semiconductor films, because of the simplicity and low cost of such a technique with respect to other growth methods [1], and the good optical properties of the deposited films. The importance of wide bandgap materials is related to the possibility of fabricating light emitting diodes (LEDs) or laser heterostructures for emission in the visible spectral range. These devices are important for many applications. For example, they are useful in medical diagnosis and for fabricating red-green-blue displays [2]. Recently, several works have been concerned with the growth of II-VI laser ablated compounds, having large photoluminescence (PL) efficiency [3,4]. In particular, our group has previously studied the optical characterization of CdSe and CdS compounds deposited on different substrates like silicon [5], GaAs [6] and quartz [3]. Optical properties of a semiconduc-

tor film can be influenced by the substrate on which it is deposited. In fact, the substrate affects the epitaxy process by directly determining strains due to lattice and thermal expansion mismatch.

In this work, we study the optical properties of CdSe and CdS films deposited on sapphire substrate by means of laser ablation technique. Comparison of the PL properties of the CdSe and CdS deposited on different substrates is interesting in order to select the substrate for useful devices based on CdS_xSe_{1-x} structures. PL and reflectance spectra present excitonic structures in the absorption edge region; the spectral energy of the exciton line has been analyzed as a function of the temperature (T).

2. Experimental

The CdSe and CdS films were deposited on sapphire substrates at 400°C by laser ablation of a cold pressed target (99.999%) of CdSe and CdS powder, respectively. A pulsed Kr–F laser operating at 248 nm, repetition rate of 10 Hz and pulse width of 18 ns, was used for the ablation process. The target–substrate distance was fixed at 3 cm. The laser fluence was optimized at

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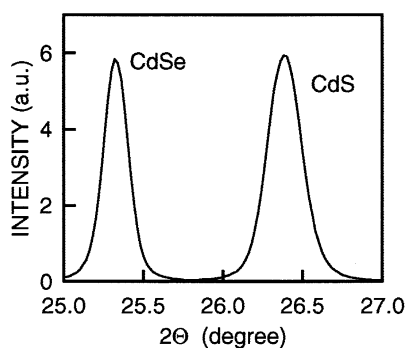*E-mail address:* capozzi@ba.infn.it (V. Capozzi).

Fig. 1. X-Ray spectra of the CdSe and CdS films deposited on sapphire substrate.

approximately 10 J/cm^2. The deposition chamber was pumped at a pressure of approximately 10^{-6} mbar before starting the deposition process.

X-Ray diffraction (XRD) measurements were performed by using the CuKα radiation ($\lambda = 1.5406$ Å) of the θ-2θ diffractometer. Reflectance measurements at low temperature were performed by a 100-W tungsten lamp light source. The sample was 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, using the photon counting technique. For the PL measurements, the line 458 nm of an Ar ion laser was used for excitation. Standard PL backscattering geometry was used. The light emitted from the sample surface was analyzed and detected by the same spectrometer and photomultiplier used for the reflectance measurements.

3. Results and discussion

A structural study of the CdSe and CdS films was performed by means of XRD measurements, which are shown in Fig. 1. The diffraction peaks refer to the (002) orientation of the film, corresponding to the hexagonal phase, with the c-axis perpendicular to the film layer. A comparison of the XRD spectra with those of CdSe and CdS deposited on quartz substrates (reported in Fig. 1 of [3]) reveals better structural quality in films deposited on sapphire compared with those films deposited on quartz. This can be deduced from the lower full width at half maximum (FWHM) of the diffraction peaks of the former ($0.182°$ for CdSe and $0.254°$ for CdS) with respect to the latter ones ($0.193°$ for CdSe and $0.207°$ for CdS). Consequently, the average grain dimension, D, of the films according to the Debye–Scherrer relationship [7], is larger for films deposited on sapphire ($D = 44.7$ nm for CdSe and $D = 32.2$ nm for CdS) with respect to films deposited on quartz ($D = 42.6$ nm for CdSe and $D = 30.4$ nm for CdS).

Fig. 2 shows PL and reflectivity spectra in the band edge region for CdSe (Fig. 1a) and CdS (Fig. 1b), both measured at $T = 10$ K. Each PL spectrum is characterized by two main emission bands; the narrow line X_A, centered at 1.815 eV for CdSe and 2.541 eV for CdS, and the broad band I_1, centered at approximately 1.75 eV for CdSe and 2.50 eV for CdS. The spectral position of the X_A line corresponds to the ground state of the A-type exciton for the hexagonal phase, as reported by Madeluung et al. [8]. In fact, the valence band of CdSe and CdS at the center of the Brillouin zone splits into three sub-bands, conveniently named A, B and C [8], as a result of the crystal field and spin-orbit coupling. The I_1 bands are due to radiative recombinations involving extrinsic levels, due to radiative impurities and/or structural defects.

The reflectivity spectrum of the CdSe film present two well-resolved excitonic resonances X_A and X_B, associated with the A and B states of the threefold split valence band: in fact, the energy gap values which are commonly reported [8] for the A-type and B-type sub-bands in CdSe at low T are 1.841 eV and 1.866 eV, respectively. Such values correspond (by taking into account 15 meV of the exciton binding energy of CdSe) to the two reflectivity dips. Moreover, the spectral position of the X_A reflectivity resonance corresponds
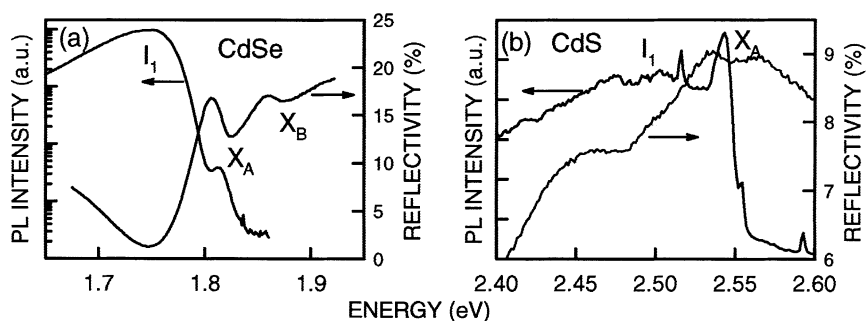

Fig. 2. Photoluminescence and reflectance spectra at $T = 10$ K for CdSe (a) and CdS (b) films deposited on sapphire substrate. The PL spectra were measured with an exciting intensity of 80 W/cm^2. The attribution of the spectral features involving A-type (X_A) and B-type (X_B) excitons, and extrinsic recombinations (I_1) are indicated. The spectral resolution is 1 meV.

to the energy of the PL band X_A. On the contrary, only the *A*-type line is visible, as a weaker dip, in the reflectivity spectrum of the CdS film; its spectral position corresponds approximately to that of the X_A peak in the PL spectrum.

The PL spectra at different temperatures have been analyzed by means of a least squares fit of Lorentzian and Gaussian functions to the experimental excitonic and impurity bands, respectively. This detailed analysis permits us to obtain the *T*-dependence of the excitonic energy, as shown in Fig. 3. The excitonic energy shows a red-shift when *T* increases; this is due to the thermal shrinkage of the energy gap as a consequence of the thermal expansion of the lattice and the *T*-dependence of the electron–phonon interaction. An empirical model describing the thermal shrinkage of a semiconductor band gap (and related excitonic levels) was introduced in [9], according to:

$$X(T) = X(0) - 2a_B n_B \qquad (1)$$

where a_B is the strength of the electron–phonon interaction, $n_B = [\exp(\theta/T) - 1]^{-1}$ 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. This model (continuous line in Fig. 3) fits very well the $X_A(T)$ data of each sample. The parameters obtained by the fitting (Table 1) give information about the electron–phonon interaction in the films. The obtained $X(0)$ value in CdSe is lower than that in the literature (1.825 eV for the free exciton in CdSe single crystals [8] and CdSe films deposited on silicon [10]). This discrepancy may be due to the presence of a residual strain in the deposition of CdSe films on the sapphire substrate or to the fact that the X_A emission is due to a bound exciton instead of a free exciton. Similar considerations are valid for the CdS film, where the $X(0)$ value of

Table 1
The second, third and fourth columns report the values of the parameters $X(0)$, a_B and θ obtained by fitting Eq. (1) to the exciton energy $X_A(T)$

	$X(0)$ (eV)	a_B (meV)	θ (K)
CdSe	1.8138 ± 0.0056	38.6 ± 4.1	187 ± 11
CdS	2.5400 ± 0.0055	36.8 ± 4.2	184 ± 16

2.540 eV results are lower than that in the literature (2.554 eV) for CdS single crystals but comparable to the value obtained for CdS films deposited on silicon [6]. The values of the parameter $\theta = 187$ K for CdSe and $\theta = 184$ K for CdS indicate that acoustic, as well as optical phonons, contribute to the energy gap shrinkage. Indeed, the LO-phonon energy of E_1 mode corresponds to a temperature of approximately 300 K for CdSe and 440 K for CdS [8], well above the average θ value obtained for the two compounds. In particular, the contribution of acoustic phonon results is larger in CdS with respect to the CdSe.

4. Conclusion

A detailed study of the optical spectra of CdSe and CdS films deposited on a sapphire substrate by the laser ablation technique has been performed. The good optical properties of the CdSe and CdS films are demonstrated by the presence of excitonic features in the reflectance and PL spectra. The CdS PL efficiency persists up to room temperature, whereas the CdSe one is scarcely visible for $T > 150$ K. Although this latter result make our CdSe ablated films unsuitable for optoelectronique applications, we find that the sapphire substrate is more suitable than other transparent substrates, like quartz. In fact, laser-ablated films deposited on quartz do not present intrinsic PL emission [3]. Our next goal is to study the growth parameters in order to deposit on a transparent substrate CdS_xSe_{1-x} system having an intrinsic PL efficiency up to room temperature.

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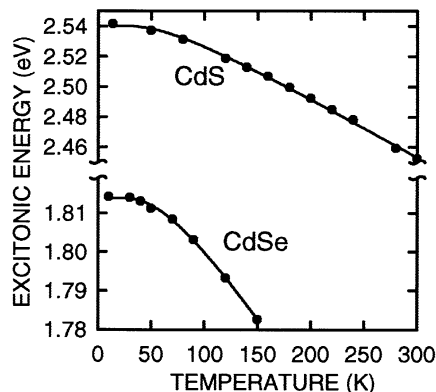[5] G. Perna, S. Pagliara, V. Capozzi, M. Ambrico, M. Pallara, Solid State Commun. 114 (2000) 161.

Fig. 3. Temperature dependence of the excitonic energy (dots) of the CdSe and CdS films deposited on sapphire substrate. The continuous line represents the best fit of Eq. (1) to the experimental data. The fitting parameters are reported in Table 1.

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