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Analysis of optical spectra of CdS and CdSe films deposited on a sapphire substrate by laser ablation technique

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Abstract. CdSe and CdS films, deposited on a sapphire substrate by means of pulsed laser ablation technique, have been investigated by means of reflectivity and photoluminescence measurements in order to study the effect of such a transparent substrate on the optical properties of the deposited epilayers. The reflectivity spectra at low temperature have been studied by means of an analytical model which permits one to obtain the energies of the excitonic resonances. The photoluminescence spectra show that our CdSe and CdS films present excitonic emission at low temperature, differently from the same films deposited on quartz. The temperature dependence of the excitonic energy has been analysed by taking into account the contribution of both the thermal expansion and electron-phonon interaction. The exciton linewidth has been analysed according to well known phenomenological models.

PACS. 52.38.Mf Laser ablation – 78.55.-m Photoluminescence – 78.55.Et II-VI semiconductors

1 Introduction

Pulsed laser ablation technique is commonly used for epitaxial deposition of wide bandgap semiconductor films, because of the simplicity and the low cost of such a technique with respect to other growth methods [1] and the good optical properties of the deposited films. The interest in 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 diagnostic and for fabricating red-green-blue displays [2]. Optical properties of a semiconductor film can be deeply influenced by the substrate on which it is deposited: in fact, the substrate affects the epitaxy process by directly determining the strains due to the lattice mismatch and thermal expansion mismatch. Recently, several works have been concerned with the growth of II-VI laser ablated compounds, having large photoluminescence (PL) efficiency [3–5]. In particular, our group has previously studied the optical characterisation of CdSe and CdS compounds deposited on different substrates, both opaque to the visible light, like silicon [6] and GaAs [7], and transparent to it, like quartz [3]. In particular, we found that CdS and CdSe films deposited on silicon and GaAs substrate present intrinsic (excitonic) luminescence, whereas the films deposited on quartz substrates do not show intrinsic luminescence. Therefore, in order to obtain a film whose intrinsic emission can pass through the substrate, we have deposited CdS and CdSe films on a sapphire substrate. In fact, sapphire single crystals present a lattice and thermal expansion match to CdS and CdSe which are similar to those of quartz [8]. For optoelectronic applications, it is very important to have a transparent substrate to the intrinsic light emitted by the active area of epitaxial films.

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 $\mathrm{CdS}_x\mathrm{Se}_{1-x}$ structures. Reflectance spectra present excitonic structures in the absorption edge region. Moreover, PL spectra present excitonic emission, contrary to the films deposited on quartz. This property is interesting for application in optoelectronic devices. The spectral energy and broadening of the exciton line in the PL spectra have been analysed as a function of the temperature (T), because of the necessity to control the emission energy under various operating conditions, as required for device applications.

2 Experimental

The CdSe and CdS films were deposited on a sapphire substrate 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, with a repetition

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rate of 10 Hz and pulse width of 18 ns, was used as the source for the ablation process. The target-substrate distance was fixed at 3 cm. The laser fluence was optimized at about 10 J/cm^2. The deposition chamber was pumped at a pressure of about 10^{-6} mbar before starting the deposition process. The sample thickness was measured with an "Alphastep" profilometer and the obtained thickness values are 0.55 μm for CdSe and 0.24 μm for CdS.

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. Reflectivity spectra were derived from the ratio of the reflected signal measured from the sample and from an aluminium mirror: the spectra were then scaled with respect to the reflectivity of aluminium (assumed to be 92% in the spectral range considered [9]). 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

Structural study of the CdSe and CdS films was performed by means of XRD measurements, which are compared in Figure 1 with the XRD patterns of CdSe and CdS films deposited on a quartz substrate [3]. All the deposited films present a preferential orientation, as can be deduced by the dominant peak at 25.3° for CdSe and 26.4° for CdS: these lines refer to the (002) orientation of the film, corresponding to the hexagonal phase, with the c-axis perpendicular to the film surface. The XRD patterns permit one to obtain information about the crystallinity of the films. In fact, the CdSe films grow in a highly oriented way on both substrates, but the presence of several XRD reflections in the spectrum of CdS film deposited on the quartz substrate indicates the polycrystalline nature of such a film, with the crystalline grains oriented according different directions. On the contrary, the CdS film deposited on sapphire substrate grows oriented in the (002) direction. The better structural quality of the films deposited on sapphire with respect to the films deposited on quartz can be deduced from the lower full width at half maximum (FWHM) of the diffraction peaks of the former (0.182 degrees for CdSe and 0.254 degrees for CdS) with respect to the latter ones (0.193 degrees for CdSe and 0.307 degrees for CdS). An estimate of the crystalline grain size D can be performed according to the Debye-Scherrer relationship [10] $D = 0.9\lambda/(\mathrm{FWHM}\cos\theta)$, where λ is the X-ray wavelength and θ is the Bragg angle. The D values obtained for the crystalline grains oriented according to the (002) direction are the following: 44.7 nm and 42.6 nm for CdSe films deposited on sapphire and quartz, respectively; 32.2 nm and 30.4 nm for CdS films deposited on sapphire and quartz, respectively.

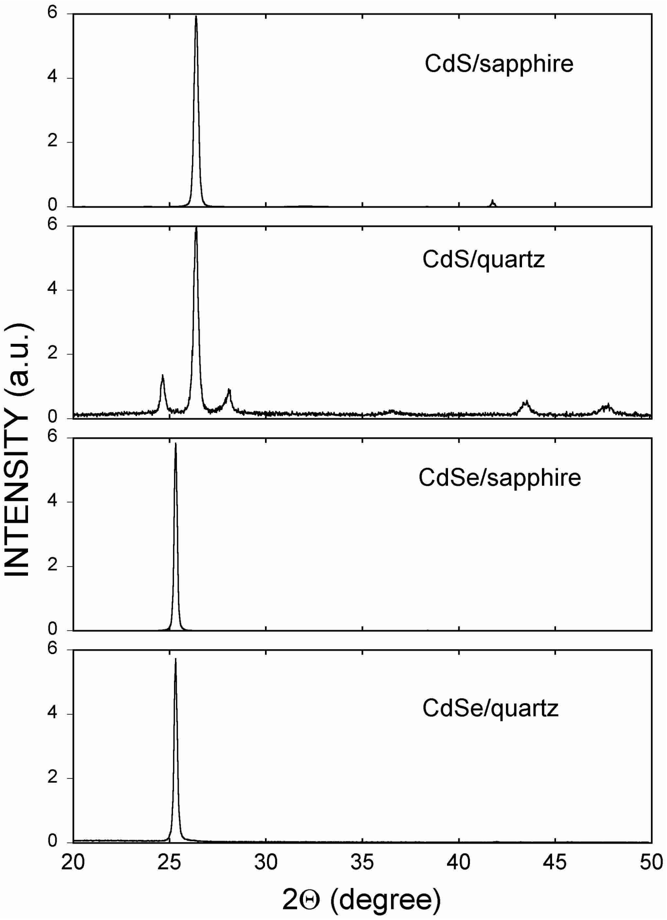

Fig. 1. X-ray diffraction measurements of the CdS and CdSe films deposited on sapphire and quartz substrates.

The reflectivity spectra of CdS and CdSe at $T = 10$ K are shown in Figure 2 (dots). A deep structure (indicated by arrows) characterises the reflectivity spectrum of both samples in the respective absorption edge region. Such a structure is due to the excitonic resonance associated with the fundamental energy gap. In order to determine the energetic position $\hbar\omega_X$ of the excitons we have analysed the reflectivity spectrum $R(\hbar\omega)$ by means of the following model [11]:

$$R(\hbar\omega) = R_0 + A_X \ \mathrm{Re}\left[\frac{1}{\hbar\omega_X - \hbar\omega - \mathrm{i}\hbar\Gamma_X}\exp(\mathrm{i}\theta)\right] \quad (1)$$

where R_0 is a background reflectance, A_X is an amplitude, Γ_X a broadening parameter and θ is a phase factor which takes into account absorption effects in the surface layer. Expression (1) is based on a simplified procedure for analysing the reflectivity spectra, consisting in approximating the excitonic contribution to the dielectric constant by using a complex Lorentz function [11]. The results of least squares fits of the experimental data to

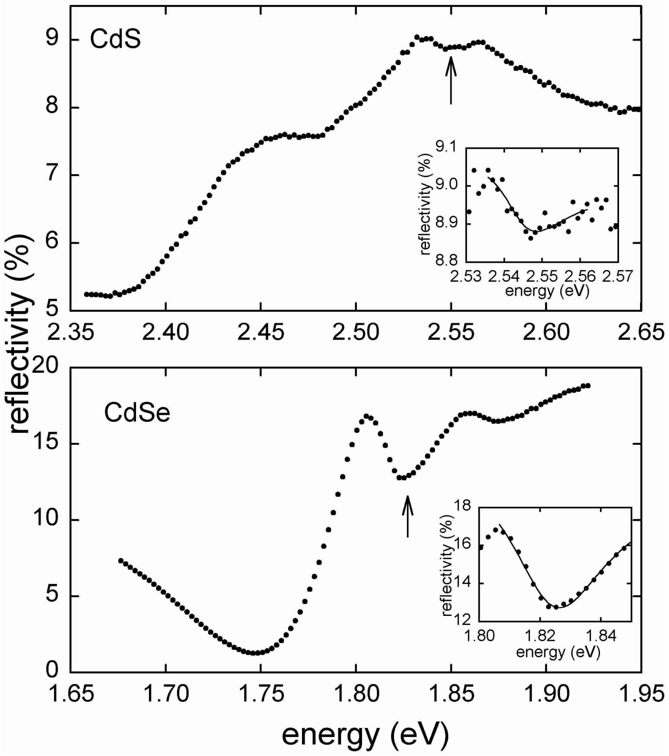

Fig. 2. Reflectance spectra at $T = 10$ K for CdS and CdSe films deposited on a sapphire substrate by means of laser ablation technique (dots). The spectral resolution is 1 meV. The best fit of the experimental data to equation (1) is represented in the inset (continuous line).

equation (1) are reported as continuous lines in the inset of Figure 2. The experimental data fit equation (1) only in the excitonic spectral region because the model is based on an harmonic oscillator which simulates the excitonic resonance. The energies obtained for excitons are 2.544 ± 0.001 eV and 1.822 ± 0.001 eV for CdS and CdSe, respectively. These values are in good agreement with the literature values of the free exciton energy, *i.e.* 2.554 eV and 1.825 eV found for CdS and CdSe single crystals, respectively [8]. The small red-shift is related to the mismatch between the epilayers and the sapphire substrate. At lower energies, the reflectivity spectral shape is due to interference effects of light by the interfaces of the film.

The temperature dependence of the PL spectrum is shown in Figures 3a and b for CdSe and CdS, respectively. Each PL spectrum at low T is characterised by two main emission bands: the band X_A, centred at 1.815 eV for CdSe and 2.541 eV for CdS, and the emission B_1, centred at about 1.75 eV for CdSe and 2.50 eV for CdS. The X_A linewidth is narrower than that of the B_1 band in both films. The X_A line is attributed to excitonic recombination [8,12]. In fact, its spectral position is slightly lower than the excitonic resonance energy found by the reflectivity measurements. This Stokes-shift is due to the presence of lattice defects and impurities in the films. The B_1 bands are due to radiative recombinations involving extrinsic levels, due to radiative impurities and structural defects, located in the energy gap of the CdSe and CdS films.

The total PL intensity decreases with increasing T in both semiconductors, due to the increasing role of the non radiative processes. The main difference between the thermal behaviour of the PL spectrum of the two samples is that the PL efficiency of CdS persists up to room T, whereas the PL features of the CdSe film disappear at $T > 150$ K. The larger PL quenching with T in CdSe with respect to the CdS can be due to the larger density of impurities and defects (which may cause both radiative and non radiative recombination paths for the carriers) in the former with respect to the latter: in fact, the extrinsic emission in CdSe is dominant with respect to the excitonic emission from low to high T. On the contrary, the excitonic line X_A in CdS becomes dominant with increasing T. This result supports the free excitonic nature of this line rather than a bound excitonic origin, whose intensity, as is well known, bleaches when T increases. The PL spectra of both samples show a red-shift on raising T, due to the thermal shrinkage of the energy gap. At energies lower than the X_A line, the PL spectra are dominated by extrinsic recombinations: in particular, two broad bands B_1 at about 1.74 eV and B_2 at about 1.56 eV characterise the PL spectrum of the CdSe at low T, whereas only the B_1 emission is present in the low T spectrum of CdS. The B_1 band rapidly quenches on increasing T in both samples: such a behaviour suggests to assign the B_1 band to donor-acceptor pairs recombinations involving shallow impurity levels: in fact, the rapid thermal quenching is caused by the thermal ionization of the related intragap levels. In particular, the B_1 emission in CdSe consists of two bands in Figure 3a, where a band B_1' becomes more resolved at a sufficiently high T ($T \approx 70$ K); indeed, the B_1' has an ionization energy higher than the B_1 band and, consequently, it is thermally quenched at larger temperatures with respect to that of the B_1 band. On the contrary, the broader and more intense band B_2 in CdSe is present from low to high T: it is related to extrinsic recombinations involving deep impurity levels, whose ionization energies are so large that the B_2 band is not thermally quenched even up to 150 K. Moreover, the sharp lines LO in the PL spectra of the CdS in Figure 3a (at energies of 2.593 eV, 2.554 eV, 2.516 eV, 2.477 eV) are separated from each other by 38 meV: this energy corresponds to that of the LO phonon in the CdS single crystals. The thermal behaviour of the LO lines (whose energies are T-independent) suggests their explanation in terms of resonant Raman peaks: in fact, the laser energy is very close to the band gap energy of CdS at low T and, therefore, the intensity of the Raman peaks can become very large [13]. The LO peaks disappear with increasing T because the thermal shrinkage of the fundamental gap weakens the resonance effect between the CdS band gap and the laser energy.

The deconvolution of the PL spectra has been performed by means of a least squares fit of Lorentzian and Gaussian functions to the experimental excitonic and impurity bands, respectively. This detailed analysis permits

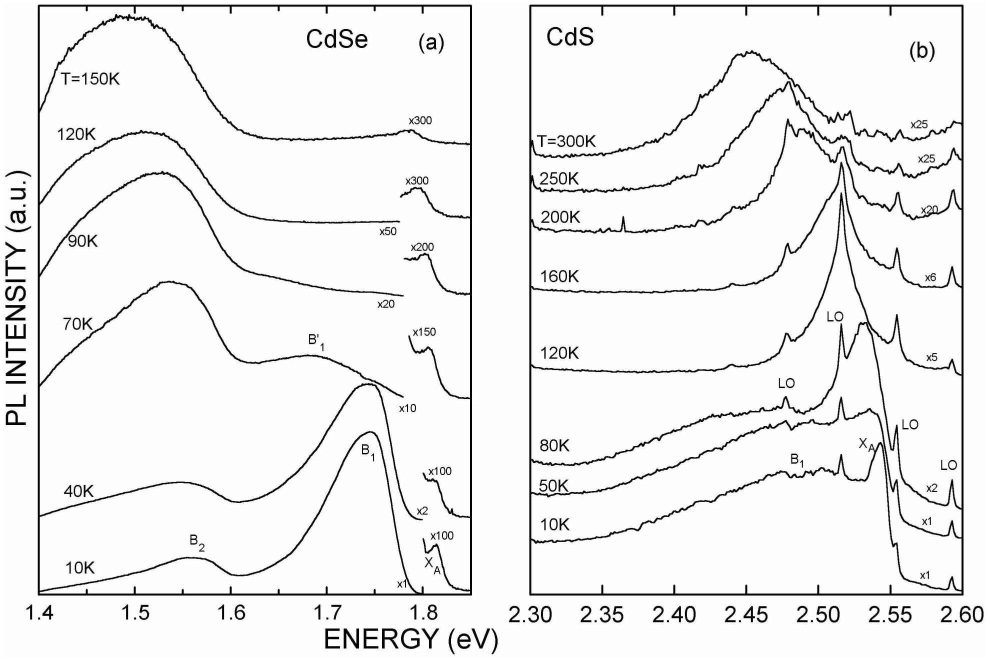

Fig. 3. Photoluminescence spectra measured at different temperatures of a CdSe (a) and CdS (b) film deposited on a sapphire substrate. The spectra were measured by the line 458 nm of an Ar ion laser with an exciting intensity of 80 W/cm^2. For each spectrum, the relative scale factor is indicated on the right-hand side. The spectral resolution is 1 meV. The attribution of the spectral features involving A-type exciton (X_{A}) and impurity related bands (B_1, B_2, B_1') are indicated.

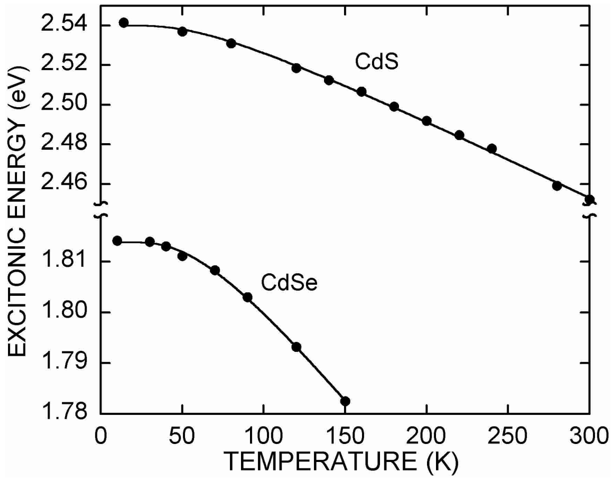

Fig. 4. Temperature dependence of the excitonic energy (dots) of the CdSe (a) and CdS (b) films deposited on a sapphire substrate. The continuous line represents the best fit of equation (2) to the experimental data. The fitting parameters are reported in Table 1.

one to obtain the dependence of the $X_{\mathrm{A}}(T)$ emission line position on temperature, as shown in Figure 4 for CdSe and CdS. The excitonic energy of both lines 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 [14], according to:

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

where a_{B} is the strength of the electron-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 an average energy of the phonons involved in the process. This model (continuous line in Fig. 4) fits very well the $X(T)$ data of each semiconductor. The parameters obtained by the fitting (Tab. 1) give information about the electron-phonon interaction in the films. The obtained $X(0)$ value in CdSe is lower than the literature one (1.825 eV for the free exciton in CdSe single crystals [8] and CdSe films deposited on silicon [15]): this discrepancy may be due to the presence of strain in the deposition of CdSe films on the sapphire substrate, as discussed above. Similar considerations are valid for the CdS film, where the $X(0)$ value of 2.540 eV is lower than the literature one (2.554 eV) for CdS single crystals but comparable to the value obtained for CdS films deposited on silicon [6]. The θ value indicates how large the contribution of acoustic phonons to the red-shift of the band gap is: the lower the θ value with respect to the LO-phonon temperature, the larger the contribution of acoustic phonons to the band gap shrinkage due to the electron-phonon interaction. 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 about 300 K for CdSe and 440 K for CdS [8], well above the average θ value obtained for the

Table 1. Values of the parameters $X(0)$, a_B and θ obtained by fitting the equation (2) to the exciton energy $X_A(T)$. In the last four columns, the values of the broadening parameters Γ_0, Γ_{LO}, Γ_I and the binding energy E_I obtained by fitting the equation (4) to the experimental full width at half maximum (FWHM) of the exciton line are reported.

	$X(0)$ (Ev)	a_B (meV)	θ (K)	Γ_0 (meV)	Γ_{LO} (meV)	Γ_I (meV)	E_I(meV)
CdSe	1.814 ± 0.001	38.6 ± 4.1	187 ± 11	10.2 ± 1.7	89.6 ± 8.1	13.4 ± 1.3	3.5 ± 1.4
CdS	2.540 ± 0.001	36.8 ± 4.2	184 ± 16	14.8 ± 1.1	101.8 ± 13.7	45.7 ± 8.6	11.6 ± 2.2

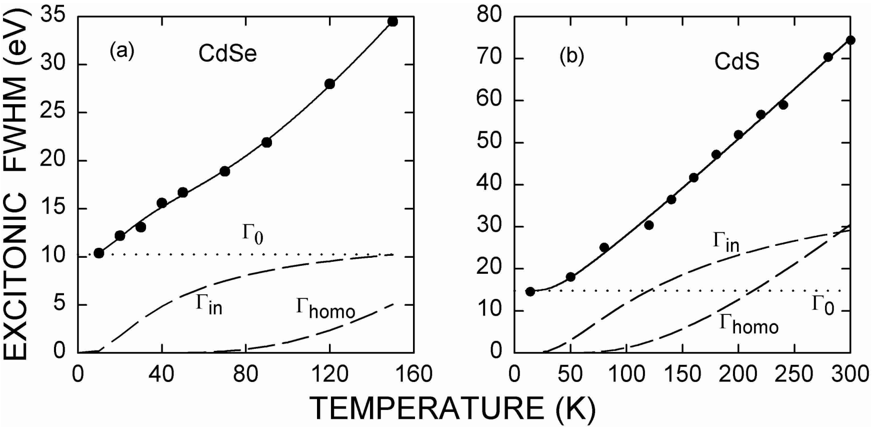

Fig. 5. Temperature dependence of the full width at half maximum (FWHM) (dots) of the excitonic band X_A of the CdSe (a) and CdS (b) films deposited on a sapphire substrate. The continuous line represent the best fit of equation (4) to the experimental points. The fitting parameters are reported in Table 1.

two compounds. In particular, the contribution of acoustic phonons is larger in CdS with respect to CdSe, although the contribution of the acoustic phonons in CdSe may be overestimated, because of the fitting performed in a limited T-range at low T, between 10 K and 150 K, where the LO-phonons are not completely activated.

Furthermore, the analysis of the PL spectra permits study of the T-dependence of the broadening of the exciton line, that can yield important information about exciton-phonon and impurity scattering occurring in semiconductors. In general, the total linewidth of the exciton line in a semiconductor has one T-independent contribution and two T-dependent contributions: the homogeneous and inhomogeneous ones [16,17]. The main mechanism producing the homogeneous broadening of the exciton line is the phonon scattering process: both acoustic and optical phonons are involved in the process, each one with a contribution proportional to the respective population density. Therefore, the T-dependence of the total homogeneous linewidth (Γ_{homo}) is given by [17]:

$$\Gamma_{homo} = \Gamma_{AC}T + \Gamma_{LO}/\left[\exp\left(\theta_{LO}/T\right) - 1\right] \tag{3}$$

where the first term represents the acoustic phonons contribution and the second term is the optical phonons contribution and it is proportional to the Bose-Einstein occupation factor for LO-phonons, $\Gamma_{AC}(\Gamma_{LO})$ is the acoustic (optical) phonon coupling constant, θ_{LO} is the temperature corresponding to the average energy of the LO optical phonons involved in the scattering process. The inhomogeneous broadening (Γ_{in}) depends mainly on the scattering of excitons by impurities and it is proportional to the number of ionized scattering centres, according to the form: $\Gamma_{in} = \Gamma_I \exp(-E_I/kT)$, where Γ_I is the linewidth due to the fully ionized impurities scattering, E_I is the average binding energy of the impurities and k is the Boltzmann constant. So, the T-dependence of the exciton linewidth in a semiconductor is given by:

$$\begin{aligned}\Gamma(T) &= \Gamma_0 + \Gamma_{homo}(T) + \Gamma_{in}(T)\\ &= \Gamma_0 + \Gamma_{AC}T + \Gamma_{LO}/[\exp(\theta_{LO}/T - 1] + \Gamma_I \exp(-E_I/kT).\end{aligned} \tag{4}$$

Figures 5a and b show the T-dependence of $\Gamma(T)$ of the X_A line (dots) for the CdSe and CdS films, respectively. The continuous line is a four parameter (Γ_0, Γ_{LO}, Γ_I and E_I) least squares fit of the equation (3) to the experimental data. The fit was performed by fixing the value of θ_{LO} and Γ_{AC}: θ_{LO} was fixed at 300 K (corresponding to the LO phonon energy of 26 meV) for CdSe and 440 K (LO phonon energy of 38 meV) for CdS; Γ_{AC} was fixed to the literature value of 6×10^{-5} eV/K and 1.8×10^{-4} eV/K for CdSe and CdS, respectively [18]. The parameters obtained by the fitting are reported in Table 1. As can be seen in Figure 5, equation (3) (continuous line) fits well the experimental linewidths (dots). The homogeneous contribution becomes important for T larger than about 60 K, as commonly reported for semiconductor compounds [17], whereas the broadening due to the scattering of excitons with ionized impurities tends to a saturation value (given by the Γ_I value) at a sufficiently high T, because of the finite number of the related impurities.

4 Conclusion

A detailed study of the optical spectra of CdSe and CdS films deposited on sapphire substrates by the laser ablation technique has been performed. The good optical properties of the CdSe and CdS films is 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 makes our CdSe ablated films unsuitable for potential optoelectronic applications, we retain the sapphire substrate as a better choice with respect to other transparent substrates, like quartz. In fact, laser ablated films deposited on quartz do not present intrinsic PL emission [3]. Our next goal is the study of the growth parameters in order to deposit on a transparent substrate $\mathrm{CdS}_x\mathrm{Se}_{1-x}$ system having an intrinsic PL efficiency up to room temperature.

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