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Resonant Raman scattering and photoluminescence in $SiO_x/CdSe$ multiple quantum wells

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Raman scattering, photoluminescence, and x-ray diffraction measurements have been carried out in $SiO_x/CdSe$ multilayers with varying CdSe sublayer thickness d_w (2.5, 3.5, 4.0, 5.0, and 10.0 nm). The x-ray data have revealed that after annealing at 673 K in air, CdSe wurtzite type nanocrystals are formed having an average size smaller than the CdSe sublayer thickness. A strong increase in the intensity of 1 LO phonon Raman band of CdSe at room temperature has been observed for samples with d_w 3.5 and 4.0 nm when excited by the 647.1 nm Kr^+ laser line. This increase is attributed to resonant conditions for Raman scattering brought about by an increase of the optical band-gap energy E_g of CdSe layers with decreasing sublayer thickness. It is argued that this E_g increase is not an internal strain-related, but a quantum-size effect manifested by one-dimensional carrier confinement. Assuming such a confinement and taking into consideration electrical and optical measurements, a band diagram is produced for the $SiO_x/CdSe$ system, from which the E_g values for each multilayer material is calculated. It is found that the calculated E_g values corresponding to $d_w = 3.5$ and 4.0 nm differ by 59 and 19 meV, respectively, from the quantum energy of the 647.1 nm (1.916 eV) laser line, thus supporting the above arguments and the idea that these structures constitute multiquantum wells. Two photoluminescence bands of CdSe layers have been observed in all multilayers. The peak of the main band shifts from 1.76 to 1.95 eV for multilayers with d_w from 10 to 2.5 nm. This shift provides further evidence that the E_g increase with decreasing d_w is due to quantum-size effect. [S0163-1829(98)06836-2]

I. INTRODUCTION

Semiconductors with reduced dimensions down to the nanometer regime have attracted great scientific and technological interest over the past decade because of their applications as optoelectronic and nonlinear optical materials.[1,2] Particular attention has been given to nanocrystals of $CdS_{1-x}Se_x$, Si, Ge, GaAs, CuCl(Br), etc. embedded in a large band-gap matrix, such as glasses, polymers, zeolites or liquids.[3,4] On the other hand, since intense photoluminescence has been observed[5] in superlattices, there have recently been combined efforts to prepare and characterize amorphous/nanocrystalline semiconductor multiquantum wells[6–9] (MQW). It is expected that nanocrystals of a given average-size and narrow-size distribution can be produced in such multilayer structures, as counterparts to nanocrystals embedded in a large band-gap matrix.

Raman and luminescence spectroscopies are among the techniques most widely employed for studying low-dimensional materials. Compared to CdSe single crystal, a shift to lower frequencies (red shift) and an asymmetric broadening of the Raman bands have been predicted by the phonon localization model[10] and observed in previous studies.[10–13] On the other hand, a shift to higher frequencies (blue shift) has also been reported[14] and attributed to compressive strain related changes of lattice parameters. Usually, both these opposing effects are present in low-dimensional materials and a net red or blue shift of Raman bands will be observed depending on whether the phonon confinement or the internal strain is the dominant effect. Moreover, photoluminescence studies can provide, apart from practical benefits, very important information concerning changes in the electronic structure of semiconductors caused by the quantum-size effect.[15,16]

In this article we report on the preparation and characterisation of a-$SiO_x/CdSe$ multilayer structures ($x \approx 1.5$) for which we have obtained strong evidence for the existence of CdSe nanocrystals. We have combined Raman scattering, photoluminescence and x-ray diffraction techniques in order to assess both the electronic and space structures of the CdSe layers. Resonant Raman scattering conditions have been observed in samples corresponding to the lower sublayer thickness side, indicating an increase of the optical band gap of CdSe with decreasing layer thickness, and this has been attributed to one-dimensional carrier confinement. Like the Raman scattering intensity, a similar enhancement of the photoluminescence intensity at room temperature has been observed with decreasing CdSe layer thickness. Because of these quantum-size effects, we shall, from now on, refer to these multilayer structures as multiquantum wells.

II. EXPERIMENT

Multilayers of $SiO_x/CdSe$ having CdSe sublayer thickness $d_w = 2.5$, 3.5, 4.0, 5.0, and 10 nm and total CdSe thickness of about 75, 145, 80, 150, and 155 nm, respectively, were prepared by thermal evaporation in vacuum (10^{-3} Pa) of SiO and CdSe from two independent Tantalum crucibles. The step-by-step deposition technique described elsewhere[17] was used. The thickness and deposition rate were controlled by a quartz monitor type MIKI-FFV. The ratio of SiO_x to CdSe sublayer thicknesses was about 1.5 in all samples.

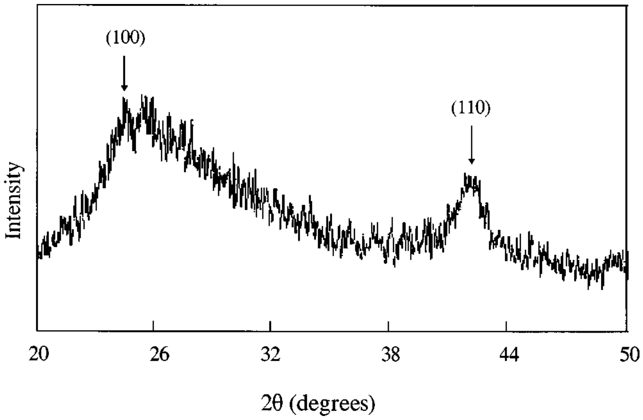

FIG. 1. X-ray diffraction pattern of a SiO_x/CdSe multiquantum well having CdSe sublayer thickness $d_w = 10$ nm.

Corning 7059 glass substrates were used and kept at room temperature throughout the deposition process. In order to crystallize the CdSe sublayers and reduce the internal strain in the SiO_x sublayers, the samples were annealed in air at 673 K for 1 h. A small-angle x-ray diffraction test has shown[18] that a-SiO_x/CdSe multilayers maintain good periodicity after annealing.

X-ray diffraction patterns were obtained in the region $2\Theta = 20-50°$ (at a step of 0.01°) using an automated Siemens D-500 diffractometer and the Cu K_α line ($\lambda = 0.154$ nm). The Raman and photoluminescence spectra were recorded (at steps of 1 cm^{-1} and 5 cm^{-1}, respectively), at room temperature using a SPEX model 1403 double monochromator in connection with photon counting equipment. The spectral resolution for the Raman spectra was ~3.5 cm^{-1}. The 530.9 and 647.1 nm lines of a Kr^+ laser were used for the excitation with the laser beam focused by a cylindrical lens. In the Raman scattering and photoluminescence experiments, the laser beam power density used was in most cases out 170 mW/mm^2 and 420 mW/mm^2, respectively.

III. RESULTS AND DISCUSSION

A. CdSe sublayer structure

The x-ray diffraction pattern of a SiO_x/CdSe multiquantum well (MQW) having CdSe well thickness $d_w = 10$ nm is presented in Fig. 1. Two broad bands related to diffraction from CdSe are observed in this pattern. The band at smaller angles (~25°) appears to consist of three peaks at about 23.9, 25.4, and 27°, which coincide with the (100), (002), and (101) diffraction peaks of hexagonal wurtzite CdSe.[19] This observation is in agreement with the report[19] that thin films of cubic (polycrystalline) CdSe become hexagonal upon annealing. It is reminded that all our samples were annealed at 673 K. The second band at ~42° is assigned to diffraction from the (110) planes. Similar patterns have been recorded for the other MQWs of the series, showing the same, but increasingly wider (with decreasing d_w) diffraction bands. The peak position of the (110) band in our MQWs practically coincides with the diffraction peak of single crystal wurtzite CdSe and its large width reflects primarily the small size of the crystalline grains, but also the existence of a wide distribution of grain sizes.

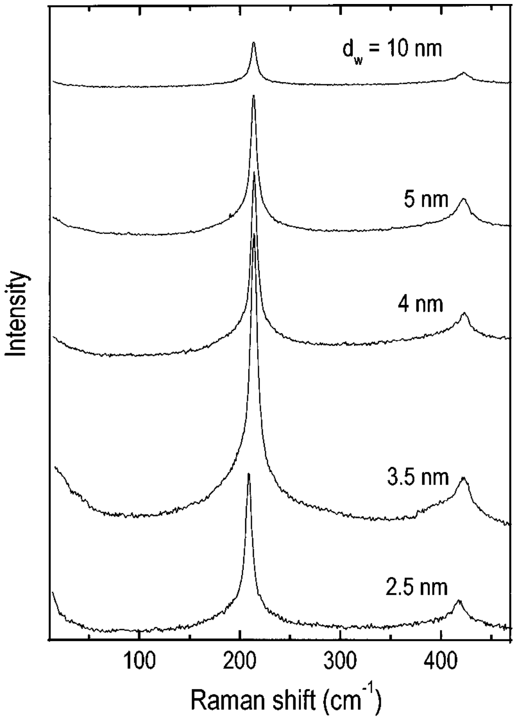

FIG. 2. Raman spectra of SiO_x/CdSe multiquantum wells of various CdSe layer thicknesses excited by the 647.1 nm Kr^+ laser line, showing the 1 LO at 210 cm^{-1} and 2 LO at 418 cm^{-1} phonon peaks. All spectra, recorded at identical experimental conditions, correspond to the same intensity scale with the top four of them vertically displaced for clarity. The Raman intensity becomes maximum for samples with $d_w = 3.5-4.0$ nm, implying resonant absorption for these d_ws (see text for details).

We have used the formula[20,21] $d = \lambda/\Delta 2\Theta \cos\Theta$ in order to determine the average size of CdSe crystallites forming after annealing; in this formula Θ and $\Delta 2\Theta$ correspond to the position and full width at half maximum (FWHM) of the (110) band and $\lambda = 0.154$ nm is the wavelength of the x-ray beam. In this way, the average CdSe grain size along the ⟨110⟩ direction in our MQWs having $d_w = 3.5$ and 10 nm has been estimated equal to 1.8 and 4.8 nm, respectively, values that are two times lower than the CdSe well thicknesses; the same result has been obtained for the MQWs with $d_w = 4.0$ and 5.0 nm. Chen *et al.*[22] reported the formation of Si nanocrystals in a-Si:H/a-SiN_x:H MQWs in which crystallization was carried out by Ar^+ laser annealing. They estimated[22] the Si grain size along the MQW axis and found it roughly equal to the well thickness, which implied that the crystallization process was constrained by the stable a-SiN_x:H layers. It is possible that longer annealing or annealing at a higher temperature may result in an increase of CdSe grain size up to the well thickness in the MQWs of this work.

B. Raman scattering

The Raman spectra of all SiO_x/CdSe MQWs measured with the $\lambda = 647.1$ nm Kr^+ laser line are shown in Fig. 2. All deconvoluted Raman spectra (Fig. 3) correspond to excitation with the red Kr^+ line. Before deconvolution, the under-

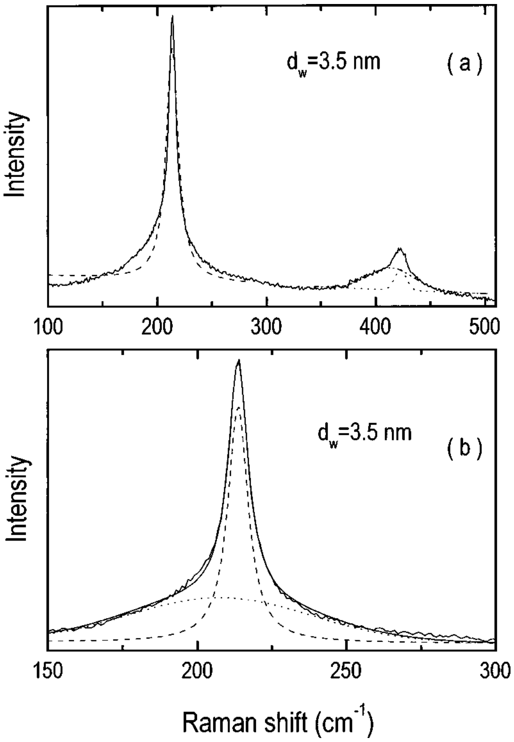

FIG. 3. Raman spectrum of a $SiO_x/CdSe$ multiquantum well with CdSe sublayer thickness $d_w = 3.5$ nm excited by the 647.1 nm Kr^+ laser line and two different fittings of the spectrum. (a) Fitting of the 1 LO band to one Lorentzian (dashed line) is not satisfactory, but it reveals an asymmetry of the band in the low-frequency side; the 2 LO band has been successfully fitted to two Gaussians. (b) A good fitting of the 1 LO band is obtained using a Lorentzian and a broad Gaussian, showing that there is another contribution to this band particularly on the low-frequency side.

lying luminescence background was subtracted from the overall spectrum of luminescence and Raman scattering by approximating it to a linear baseline connecting the minimum intensity points on both sides of the Raman band (see also Fig. 7).

Two bands at 210 cm^{-1} and 418 cm^{-1} are observed and attributed to scattering by the 1 LO (first order) and 2 LO (second order) phonons of CdSe, respectively. The band at 210 cm^{-1} in our spectra consists of two unresolved peaks corresponding to A_1 (209 cm^{-1}) and E_1 (211 cm^{-1}) LO symmetry phonons.[23,24] A first sight comparison of the spectra of the three MQWs having similar CdSe total thickness ($d_w = 3.5$, 5.0, and 10 nm) shows clearly that the Raman intensity of both bands strongly increases with decreasing CdSe thickness. Comparison of the spectra of MQWs with $d_w = 3.5$ and 4.0 nm indicates that their intensities should be comparable given that the total thickness of the former is almost twice that of the latter. Finally, if we compare the spectra of MQWs with $d_w = 2.5$ and 4 nm (having nearly the same CdSe total thickness), we conclude that the intensity of Raman scattering is much lower in the former. All these observations point out that the scattering intensity becomes maximum for a well thickness $d_w = 3.5 - 4.0$ nm.

Particular attention was paid to make sure that the above-mentioned intensity comparisons were reliable, i.e. that the spectra from different samples were recorded at identical experimental conditions. First, we mention that the top layer in all samples was SiO_x and hence all samples had the same surface reflectance. The laser beam and the scattered light were precisely focused on the sample and spectrometer slit respectively by mounting the respective lenses on micrometer translation units. The Raman signal was maximized for each sample through fine transverse, longitudinal, and vertical adjustments of these units. The Raman spectrum of each sample was recorded several times (on different spots of the sample) using the 647.1 nm line and the alignment procedures described above, and in each occasion the pattern of the intensity variation from one sample to the other was almost the same, that is, showing maximum scattering intensity for $d_w = 3.5 - 4.0$ nm. When these Raman measurements were repeated using the 530.9 nm Kr^+ laser line for the excitation, the (normalized to total MQW thickness) scattering intensity was (within the margins of error) the same for all samples. This result confirms first that the intensity comparisons between different samples are reliable and that the scattering intensity variations observed among different samples when excited by the 647.1 nm line are due to resonance effects that are discussed below in detail.

It is known[19] that the 210 cm^{-1} Raman band of single crystals of CdSe is symmetric and can be well approximated by a Lorentzian of a FWHM of ~4 cm^{-1}. In the $SiO_x/CdSe$ MQWs, this band is slightly asymmetric [Fig. 3(a)] to the low-frequency side with the asymmetry becoming increasingly noticeable with decreasing well thickness. This band fits better to two curves: a Lorentzian with FWHM varying from 6 to 8 cm^{-1} for $d_w = 10$ and 2.5 nm, respectively, and a broad Gaussian of a FWHM of ~60 cm^{-1} [Fig. 3(b)]. The Lorentzian curve peaks at 210 cm^{-1} in all MQWs, while the Gaussian appears to vary from 206.5 cm^{-1} for $d_w = 10$ nm to 204 cm^{-1} for $d_w = 2.5$ nm [Fig. 3(b)]. It has been found that the ratio of the integrated intensity of the Lorentzian to the Gaussian band decreases with decreasing well thickness. The 2 LO band at 418 cm^{-1} can also be fitted to two Gaussians, one at 418 cm^{-1} for all MQWs studied and another whose peak position varies from 408 cm^{-1} for $d_w = 10$ nm to 410 cm^{-1} for $d_w = 2.5$ nm.

A redshift of the 1 LO Raman band of CdSe nanocrystals embedded in a glassy matrix has been reported by Saviot *et al.*[12] and attributed to the effect of three-dimensional phonon confinement.[10] As was mentioned in Sec. III A, the x-ray diffraction measurements have indicated that CdSe layers in $SiO_x/CdSe$ MQWs are built of nanocrystals with an average size smaller than the CdSe sublayer thickness. Hence, one would have expected to observe a redshift of at least 4 cm^{-1} (see Ref. 12) for MQWs of small d_w (2.5, 3.5, and 4.0 nm). In the present work, the position of the Lorentzian component of the 1 LO band is fixed at 210 cm^{-1} in all MQWs studied, while the broad Gaussian component [Fig. 3(b)] has a tendency to shift to lower frequencies with decreasing CdSe well thickness. Bearing in mind the large width of the Gaussian component, this redshift may be considered to be within the error bars; however, the redshift trends and the overall influence of this component in the spectral profile of the 1 LO band are further supported by an apparent increase of its relative (to the Lorentzian component) intensity with decreasing d_w. The fixed position of the Lorentzian component in all MQWs indicates that an overall three-dimensional phonon confinement does not exist, but such a confinement probably exists in some nanocrystals and this effect, we believe, is demonstrated by the presence of the Gaussian band and its variable position and intensity with well thickness. A calculation by Campbell and Fauchet[10] of the red Raman shift due to phonon confinement in the case of a thin film of variable thickness (3–10 nm) has shown that this shift cannot exceed the value of 1 cm^{-1}, a result that is compatible with our observations. Cardeira *et al.*,[19] have also reported that in chemically deposited CdSe films having an average grain size of 4.2 nm, the frequency of the 1 LO band coincides with that of the single crystal.

From the above, the following picture emerges regarding the microstructure of the MQWs studied: if we assume the presence of nanocrystallites in the CdSe layers, then the lack of an overall three-dimensional phonon confinement indicates that phonon propagation is, in fact, restricted only along the direction of the MQW axis; therefore, it appears that in the MQW planes, the potential barriers at the grain boundaries are relatively low to cause appreciable phonon confinement. This qualitative picture is in agreement with the low potential barrier height (~0.2 eV) at the grain boundaries of SiO_x/CdSe MQWs determined by electrical measurements[25,26] and based on Kazmerski's idea[27] of potential barriers on such boundaries. We must bear in mind that the grain boundaries between CdSe nanocrystals are of a different nature compared to those in Ge, Si or GaAs nanocrystal layers in which an oxide shell surrounds practically every crystalline grain.[10,28] Finally, we comment on the spectral characteristics of the Gaussian component of the 1 LO band. The large FWHM of this component can be attributed to a wide size distribution of CdSe nanocrystals, as well as to a possible existence of small regions of amorphous CdSe that sustain strong lattice deformation by the surrounding crystallites. The increase of the relative intensity of the Gaussian to the Lorentzian component with decreasing well thickness may be a consequence of the fact[13,29,30] that the thinner the sublayer, the higher the resistance to crystallization of amorphous multilayer systems.

As was mentioned above, the intensity of the 210 cm^{-1} band becomes maximum for a CdSe well thickness between 3.5 and 4.0 nm. We attribute this intensity variation to resonant Raman scattering that comes into effect as a result of an optical band gap increase of CdSe with decreasing well thickness. In such a case, the optical band gap energy E_g of CdSe wells with $d_w = 3.5-4.0$ nm should be close to the quantum energy of the 647.1 nm Kr^+ laser line (=1.916 eV).

Often in resonant Raman scattering, maximum intensity is not attained at the peak of resonance, but for slightly off-resonance conditions (mainly because of the small sampling volume due to strong absorption). If we assume a typical value for the absorption coefficient $\alpha = 5.000\ cm^{-1}$ at the band-gap energy of a semiconductor and consider the MQW with the largest total CdSe thickness $d = 155$ nm, then from the expression $T = T_0 \exp[-\alpha \times d]$ we find that the incident or scattered beam intensity is reduced, at most, by about 7%. Therefore, in the present study, the $E_g \cong 1.92$ eV value for the optical band gap of CdSe wells with $d_w = 3.5-4.0$ nm obtained from conditions of maximum Raman intensity is fairly accurate and, as will be discussed below, very close to the corresponding E_g value estimated from the band diagram of SiO_x/CdSe MQWs (Fig. 4). This energy is considerably higher than the optical band gap energy of CdSe single crystals ($E_g = 1.75$ eV at room temperature).

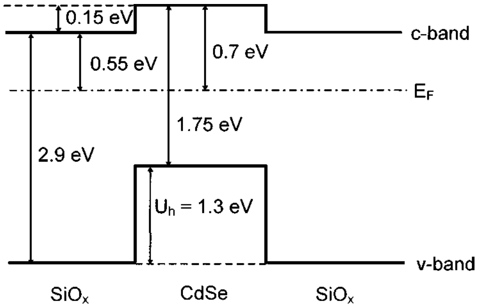

FIG. 4. Schematic band diagram of SiO_x/CdSe multilayers; E_f corresponds to the Fermi-level and U_h is the energy depth of the potential well for holes in CdSe sublayers; all other energy differences have resulted from electrical and optical measurements (Refs. 26 and 25).

The increase of the optical band gap energy can be caused: (i) by the existence of strong internal strain in the CdSe layers, (ii) or/and a quantum size effect. It is known[31,32] that the optical band gap decreases with increasing pressure and, therefore, since we assume an optical bandgap increase of CdSe with decreasing d_w, if this were an internal strain-related effect, the strain would be tensile. In such a case, one would have observed substantial changes in the lattice parameters, accompanied by a considerable redshift of the 1 LO phonon peak. As was mentioned above, the x-ray diffraction pattern shows that there are no appreciable changes in the lattice parameters of CdSe in the MQWs compared with the single crystal parameters. On the other hand, taking into account the pressure coefficient[33] $dE_g/dP = 4.5$ meV/kbar and slope[33] $d\omega/dP = 0.43\ cm^{-1}$/kbar for the 1 LO phonon frequency of CdSe, we estimate that the redshift would have been of the order of 15 cm^{-1}; such a large redshift has not been observed. Consequently, the estimated increase of the optical band gap of CdSe wells in thin sublayer MQWs should be related primarily to a quantum size effect but without excluding some contribution due to an internal strain effect. The assumed value of $E_g \approx 1.92$ eV for MQWs with $d_w = 3.5-4.0$ nm, (which results from resonance conditions for Raman scattering) is considerably lower than the value of ~2.2 eV calculated[15] for CdSe nanocrystals with an average diameter of 3.5 nm and assuming that electrons and holes in CdSe are confined in deep potential wells; it is also substantially lower than the experimentally determined values of E_g for CdSe nanocrystals in glassy or organic matrix.[3,34,35] Therefore, the estimated lower value of E_g for the CdSe wells of this study provides further support for the suggestion made above that the potential barriers at the grain boundaries of CdSe nanocrystals are not high enough for an effective three-dimensional phonon and carrier confinement.

In order to obtain an approximate estimation of the optical band-gap increase of CdSe layers induced by the carrier confinement, we have made a schematic band diagram (Fig. 4) of SiO_x/CdSe MQWs assuming room temperature E_g values of 1.75 eV for single layers of CdSe,[36] (that is, equal to the E_g of CdSe single crystals) and 2.9 eV for single layers of SiO_x,[35] ($x \approx 1.5$). We have defined the Fermi-level energies of SiO_x and CdSe sublayers by measuring the dark current

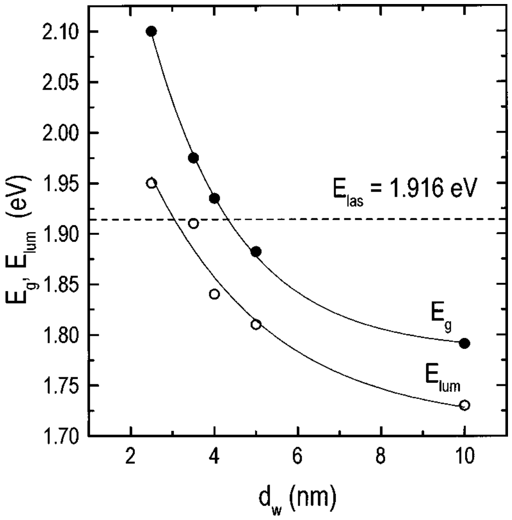

FIG. 5. Thickness dependence of the calculated [Eq. (1)] band gap energy E_g (full circles) and the measured peak position energy E_{lum} (open circles) of the photoluminescence main band of SiO_x/CdSe multiquantum wells; the dashed line denotes the quantum energy level of 647.1 nm Kr^+ laser line. The E_g values have been calculated assuming conditions of one-dimensional carrier confinement.

activation energies of SiO_x single layers and SiO_x/CdSe MQWs, respectively. It has been assumed that the activation energy of the MQWs effectively corresponds to the Fermi-level position of CdSe sublayers because the electron mobility of thermally evaporated SiO_x layers is very low (as a result of the large number of defects in them) and, for this reason, the parallel (to the layer plane) carrier transport in these MQWs should be considered almost exclusively through the CdSe sublayers. It is evident from the band diagram that, in the CdSe sublayers, only the holes are confined in a potential well $U_h \approx 1.3$ eV. Then the optical band gap increase E, due to the hole confinement, can be calculated by solving the transcendent equation[37]

$$\cos[d_w(2m_h^*E)^{1/2}/2\hbar]=(E/U_h)^{1/2}, \tag{1}$$

where $m_h^*=0.45m_e$ is the effective mass of light holes in CdSe and m_e is the mass of the free electron.[32] The calculated $E_g=E_0+E(E_0=1.75\ \mathrm{eV})$ values from Eq. (1) have been plotted against d_w and shown in Fig. 5, which also shows the peak position of the luminescence band (see next section for details). We notice that the calculated values of E_g for MQWs with well thicknesses of 3.5 and 4.0 nm differ only by 59 and 19 meV from the quantum energy of the 647.1 nm laser line (=1.916 eV) at which we have observed resonant Raman scattering for these well thicknesses. Bearing in mind the uncertainty of the optical band gap value of microcrystalline CdSe (it was assumed 1.75 eV, equal to the E_g of the single crystal), we believe that these calculations confirm, on the whole, the idea of resonance conditions for Raman scattering in the MQWs with thin wells.

C. Photoluminescence

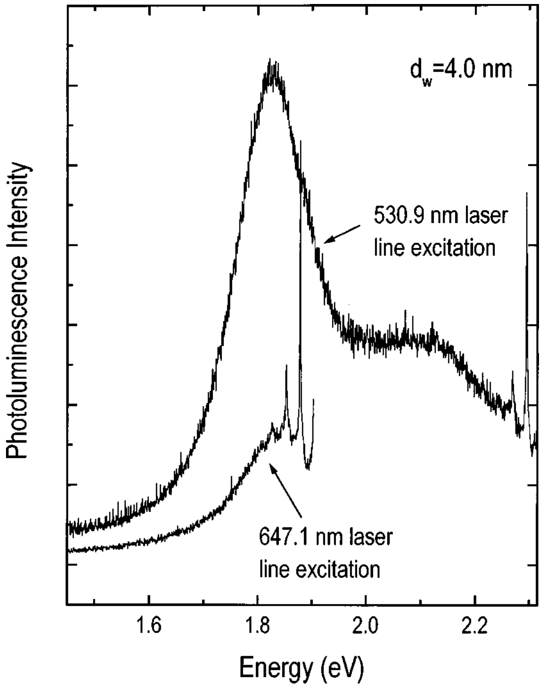

FIG. 6. Photoluminescence spectra of a SiO_x/CdSe multiquantum well with CdSe sublayer thickness $d_w=4.0$ nm excited by the 530.9 nm (50 mW) and 647.1 nm (10 mW) Kr^+ laser lines. The sharp peaks superimposed on the luminescence spectra correspond to various orders of Raman scattering by the 1 LO phonon of CdSe. The intensity scale is the same for the two spectra.

The photoluminescence spectra of the SiO_x/CdSe MQW with $d_w=4.0$ nm excited by the 647.1 (10 mW) and 530.9 (50 mW) nm Kr^+ laser lines are shown in Fig. 6. Notice that excitation by the red line gives only half of the spectrum, starting from about the main band position. The sharp superimposed peaks correspond to various orders of Raman scattering by LO phonons (up to the 3th and 4th order for the green and red line excitations, respectively). The Raman peaks of Fig. 6 confirm further the idea of resonant Raman scattering in thin wells since the actual Raman intensity obtained with the red line is nearly an order of magnitude higher that that obtained with the green line after normalization by the ratio of the incident powers of the green to the red line (=5) and by the factor $(\lambda_r/\lambda_g)^4$, where λ_r and λ_g are the wavelengths of the red and green excitation lines.

The photoluminescence spectra of all MQWs of this work excited by the red line are shown together for comparisons in Fig. 7. The position of the main luminescence band shifts towards the higher energies with decreasing CdSe sublayer thickness. These results were confirmed when the spectra were excited by the green line. Apart from the main band, a second broad luminescence band exists in the high energy side of the spectra. The position of both luminescence bands and their FWHM values have been determined after deconvolution of the spectra excited by the green line. A best fit has been achieved by adopting a Lorentzian lineshape for the main band and a Gaussian one for the high energy band. As an example, the result of such a fitting is illustrated in Fig. 8 for the luminescence spectrum of the MQW with $d_w=3.5$ nm. The complete results of the fittings for all MQWs studied are compiled in Table I, which gives the peak position and FWHM of both bands, as well as the Stokes shift of the main band from the calculated value of the optical band

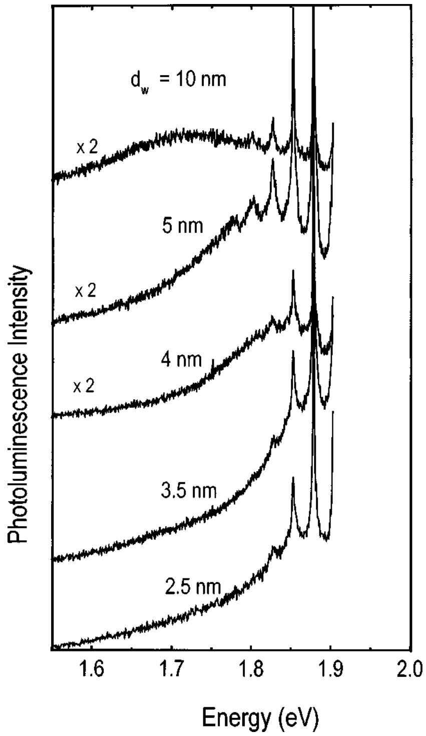

FIG. 7. Photoluminescence spectra of all $SiO_x/CdSe$ multiquantum wells excited by the 647.1 nm Kr^+ laser line, showing a gradual shift of peak position towards the higher energies with decreasing CdSe layer thickness d_w. The excitation power was 50 mW for all MQWs, except that with $d_w = 4.0$ nm for which the power was 10 mW. The photoluminescence intensity becomes maximum for $d_w = 3.5$ nm. The sharp peaks correspond to Raman scattering of various orders by the 1 LO phonon of CdSe. The top four spectra are vertically displaced for clarity.

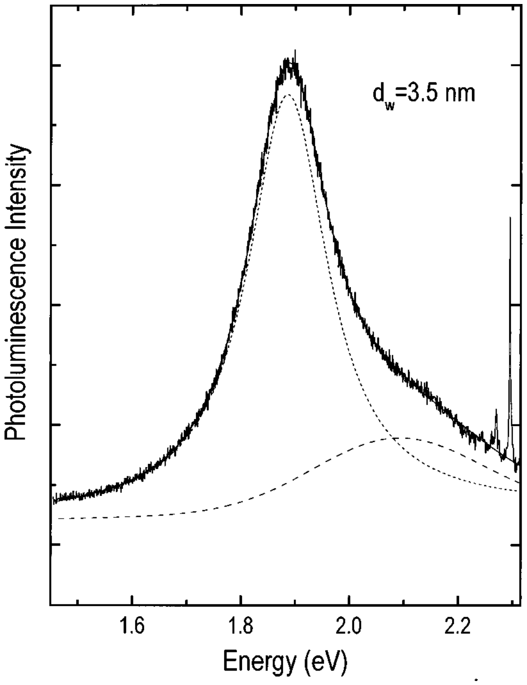

FIG. 8. Photoluminescence spectrum of a $SiO_x/CdSe$ multiquantum well with CdSe sublayer thickness $d_w = 3.5$ nm excited by the 530.9 nm Kr^+ laser line and fitting (solid line) by a Lorentzian (dotted line) and a Gaussian (dashed line). The sharp peaks correspond to Raman scattering by the 1 LO (intense line) and 2 LO (weak line) phonons of CdSe.

gap (see also Fig. 5). The FWHM values corresponding to the main luminescence band are less than 250 meV for MQWs having $d_w \leqslant 5$ nm, these values are close to those reported[19] in a photoluminescence study (at $T = 100$ K) of nanocrystalline CdSe layers prepared by chemical deposition, as well as to those observed in room temperature photoluminescence of CdSe (Refs. 21, 34, and 38) and CdS (Ref. 39) nanocrystals in glassy or polymeric matrix. The FWHM corresponding to MQW with $d_w = 10$ nm is quite large (~400 meV), but this is most likely due to the low intensity of the luminescence spectrum of this sample. The FWHM values observed in most MQWs of this work are considerably lower than those (~400 meV) observed in crystallized a-Si:H/a-SiN_x:H MQWs,[8] and in c-Si/SiO_2 superlattices.[9]

The main luminescence band in CdSe has been ascribed to various mechanisms in the literature:[32,34,40] free-exciton recombination, recombination of excitons coupled with ionized (donor or acceptor) or neutral defect, recombination of electron-hole pairs captured in shallow donor and acceptor states, and recombination through surface defects. The photoluminescence observed in CdSe nanocrystals showing an average Stokes shift of about 85 meV (Ref. 34) was related to transitions from the top of the valence band to the bottom of the conduction band ($1S_{3/2}-1S_e$ transition). It has been reported[34,40] that the luminescence band related to surface states in CdSe nanocrystals is shifted to energies considerably below (by 200–500 meV) the optical band gap, although in another report[4] this shift has been measured ~75 meV. In our MQWs, the main luminescence band shows a relative Stokes shift from the calculated optical band gap energy E_g, which varies (fluctuates) between 60 and 150 meV (Table I). These results are similar to those reported[34] for CdSe nanocrystals in a glassy matrix for which an unambiguous thickness dependence of this Stokes shift has not also been observed. On the other hand, the almost symmetrical profile of the main luminescence band on the low-energy side (Fig. 8) implies that the process of radiative recombination through the surface states is negligible in the MQWs of this work. Therefore, we suggest that the origin of the main band is due to the $1S_{3/2}-1S_e$ transition. The intensity of this band increases with decreasing CdSe well thickness (Fig. 7), most likely because of an increase of the absorbed power of the red laser light by the MQWs with thin sublayers.

Finally, we would like to comment on the broad luminescence band that appears in all MQWs at higher energies (position of the broad peak at ~2.1 eV, Figs. 6 and 8). This band could be attributed to: (i) luminescence from Si nanoclusters in the SiO_x sublayers[41] or/and (ii) photoluminescence from the recombination of three-dimensionally confined carriers in several CdSe nanocrystals, namely those nanocrystals that are responsible for the Gaussian component of the 1 LO Raman band of CdSe. The existence of Si clusters in our SiO_x layers has been assumed on the basis of x-ray diffraction and transmission studies of CdSe nanocrystals in a SiO_x matrix.[35] Moreover, visible room temperature photoluminescence has been reported[41] in sputtered SiO_x films having a composition similar to that of our SiO_x sub-

TABLE I. Spectral characteristics of room temperature photoluminescence of SiO_x/CdSe multiquantum wells; apart from the first column all other quantities are in units of eV.

d_w, (nm)	Main band position	FWHM of the main band	High-energy band position	FWHM of the high-energy band	Stokes shift of the main band
10	1.73	0.40	2.09	0.50	0.060
5.0	1.81	0.20	2.11	0.50	0.070
4.0	1.84	0.15	2.11	0.37	0.095
3.5	1.91	0.18	2.11	0.45	0.075
2.5	1.95	0.25	2.13	0.13	0.150

layers and related to Si nanocluster formation. However, we have not observed appreciable photoluminescence around 2.1 eV in single layers of SiO_x deposited and treated by identical procedures as those applied to SiO_x/CdSe MQWs. Consequently, this broad luminescence band is most likely due to emission from CdSe nanocrystals. The large FWHM of the band should be attributed to a wide distribution of nanocrystal sizes.

IV. CONCLUSIONS

X-ray diffraction measurements in SiO_x/CdSe multilayers have provided evidence for the existence of CdSe nanocrystals whose average size has been estimated to be half of the sublayer thickness d_w.

A strong enhancement of the intensity of the 1 LO Raman band of CdSe observed in multilayers having small sublayer thicknesses (3.5–4.0 nm) indicates that resonant Raman scattering takes place in these samples when excited by the 647.1 nm Kr^+ laser line. This result leads to the conclusion that the optical band-gap energy E_g of CdSe layers increases with decreasing sublayer thickness and becomes equal to the quantum energy of the red laser line for multilayers of $d_w = 3.5-4.0$ nm. Should this E_g increase be the result of strong internal tensile strain only, one would expect to observe a large redshift of the 1 LO Raman band of CdSe. In the absence of such a large shift, we conclude that the E_g increase with decreasing d_w is caused mainly by a quantum-size effect with only a small (if any) contribution to this increase resulting from an internal strain effect. Based on electrical and optical measurements, as well as on the assumption of one-dimensional carrier confinement, we have produced the band diagram for these MQWs from which we have calculated the optical band-gap energy for each MQW. The calculated values of E_g for the MQWs with $d_w = 3.5$ and 4.0 nm have been found to deviate from the quantum energy of the red laser line by only 59 and 19 meV, respectively.

An intense luminescence spectrum is observed consisting of a main band shifting from 1.76 to 1.95 eV for MQWs with d_w from 10 to 2.5 nm and a broad band at higher energies. The main peak position shift is directly related to the E_g change, thus providing further evidence that the E_g increase with decreasing d_w is a quantum-size effect. Finally, it has been evident that these materials have the potential for utilizing them in light-emitting devices in the visible.

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