PHYSICAL REVIEW B VOLUME 45, NUMBER 20 15 MAY 1992-II

Quantum size effects in CdS thin films

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(Received 2 October 1991; revised manuscript received 17 December 1991)

Resonant Raman spectroscopy is used to study quantum size effects in CdS films. The lattice softening of the CdS LO-phonon mode in a CdS film with a thickness less than 800 Å is observed. As the thickness is less than 410 Å, the TO-phonon mode is observed at 4880 Å excitation wavelength, which is above the band gap of bulk CdS (2.42 eV) at room temperature. These phenomena are attributed to the size quantization effects of the grain size and the low-dimensional thin-film structure. The quantum size effects cause a blueshift of the band gap in the as-deposited CdS thin film. The peak of the TO-phonon-mode Raman line of the CdS film is observed around 220 cm^{-1}, which has a shift of 8 cm^{-1} from the Raman line of the most active TO-phonon mode of bulk CdS. The magnitude of softening energy of the TO-phonon mode is observed to be independent of the film thickness.

I. INTRODUCTION

Quantum size effects in semiconductors have attracted much attention in recent years.[1-16] In these investigations, vibrational spectroscopy has played an important role. The quantum size effect is usually defined as the dependence of certain physical properties of a solid on its characteristic geometric dimensions when the latter becomes comparable to the de Broglie wavelength of the charge carriers. As the film thickness (measured along the z direction) is much less than the two in-plane dimensions (measured in the x-y plane) and is comparable to the de Broglie wavelength of the carriers, quantization of the carrier motion in the perpendicular direction to the film plane occurs, although the carrier motion is particlelike in the other two dimensions. Quantum size effects are usually attributed to the small size of microcrystallites in the films,[1-10] the lower-dimensional thin-film structure,[11-14] and the effect of mechanical stress.[14-16] In the last few years, the studies of quantum size effects were mainly focused on the observation of the shift of Raman peaks. This is because Raman spectroscopy can probe the local vibrational environment and thus can determine the presence of semiconductor microcrystallites in the films.

To date, several works have discussed the size effects of small CdS crystallites with a diameter ranging from 30 to 1000 Å. Meanwhile, some authors studied the relationship between the Raman shift and the film thickness.[11-14] Ekimov, Efros, and Onushchenko[8] developed a growth technique of the semiconductor microcrystals in a glassy dielectric matrix which permitted one to vary the size of the grown microcrystals in a controlled manner from some tens to thousands of angstroms and thus to study the size dependence of absorption spectra of a number of semiconductors. Their results showed a considerable short-wavelength shift of the exciton lines was observed as the microcrystal size decreased. Ramsteiner *et al.*[11,12] studied the hard hydrogenated amorphous carbon films on Si by using Raman spectroscopy. They observed that the frequency of the main Raman peak decreased for layers thinner than 100 Å and applied the term "mode softening" to describe the result. Tu, Wong and Ketterson[16] studied the thickness dependence of the band gap by measuring the resistivity in the intrinsic region. Brüesch *et al.*[14] studied the vibrational properties of thin Al_2O_3 films sputtered onto Au, Al, and Si substrates by using infrared reflection and absorption spectroscopy. They found a softening of the longitudinal-optical Al-O stretching mode for a layer thickness less than ~500 Å.

In this paper we report that the thickness dependence of the LO vibrational mode softening of the CdS thin films can be observed as for film thicknesses less than 800 Å. Furthermore, the TO-phonon mode of CdS film can be observed at 4880 Å excitation wavelength, which is above the band gap of bulk CdS (2.42 eV) at room temperature as for film thicknesses less than 410 Å.

II. EXPERIMENT

The pulsed laser evaporation (PLE) technique was used to produce the CdS thin film on a p-type (100) silicon wafer.[2] In general, the Raman signal is quite sensitive to crystal orientation due to selection rules. As shown in a previous paper,[2] the PLE technique could easily produce the high-quality thin films that yielded sharp Raman peaks. The CdS thin films were grown by a PLE system which contains a homemade Xe-ion laser[17] ($\lambda=495$ nm) operating at about 1 pulse per second with maximum pulsed energy of 10 mJ. The laser beam was focused onto a target at about 20° from the surface normal of the target. The laser fluence was about 1 J/cm^2 and the target was moved slightly after hundreds of shots to prevent causing a sunken spot. A clean vacuum chamber, which was pumped by a 25 liter/sec ion pump, having a base pressure of 3×10^{-6} Torr was used. CdS thin films were deposited on the p-type (100) silicon wafers at 150 °C substrate temperature. The temperature was controlled to fix at 150 °C with the aid of a temperature controller. The deposition rate was about 0.07 Å/pulse. CdS powder of 99.999% purity was pressed into a pellet which was deliberately left rough so that the coupling of the laser beam into the target was quite efficient.

The crystallinity and surface morphology were identified by x-ray diffraction (XRD) and scanning electron microscopy (SEM). These high-orientation films were prepared with a thickness ranging from ~80 to ~800 Å. The thickness of film was measured by using an ellipsometer which has a resolution of ±10 Å. The Raman spectra were recorded by using the unpolarized line of 4880 Å of an Ar^+ laser. Spectra were recorded at room temperature in 45° reflection geometry with samples being placed under the micrometer stage of a triple-grating spectrograph (Spex 1877C) equipped with a liquid-nitrogen-cooled charge coupled devices detector array (Photometrics CC200). The incident power on the sample was about 100 mW. The emission spectra of Ne and Xe lamps were used for frequency calibration. The slit width (100 μm) used in the experiment led to an accuracy of 3-cm^{-1} resolution.

III. RESULTS AND DISCUSSIONS

The structure and crystallinity were analyzed by XRD with a Cu $K\alpha$ source ($\lambda=1.54$ Å). Figure 1 shows the XRD spectrum of as-deposited CdS film on a p-type (100) silicon wafer at room temperature. One can see that the film has wurtzite structure and high orientation in (002) direction even when the substrate is at room temperature. This result manifests itself in that the clusters in the films have a columnar structure in the normal direction to the film surface. Figure 2 shows the SEM photographs of the films at substrate temperatures 30 °C and 150 °C. The results reveal that the surfaces of the as-deposited CdS films are smooth and uniform. The crystallite sizes of the CdS films can be either estimated from the SEM photograph or calculated by the Scherrer equation: $d=k\lambda/D\cos\vartheta$, where k is taken to be 1 for hexagonal CdS, λ is the x-ray wavelength, D is the angular linewidth for half-maximum intensity (in radians), and ϑ is the Bragg angle. These results obtained are ~290 Å for 30 °C and ~380 Å for 150 °C. These are very close to the results estimated from the transmission electron microscopy photographs.

Figure 3 shows the Raman spectra of the as-deposited CdS thin films with film thicknesses ranging from 85 to 800 Å. These Raman spectra were excited by the 4880-Å line of an Ar^+ laser. The spectra show a main CdS Raman peak (1LO) around 300 cm^{-1} as well as the intrinsic Raman scattering (O_Γ) of p-type (100) silicon substrate around 520 cm^{-1}. The 1LO phonon frequency for a single crystal of CdS was given[18] as 305 cm^{-1}, while the values measured by us were around 300 cm^{-1}. This low-frequency shift of the 1LO Raman peak in CdS thin film

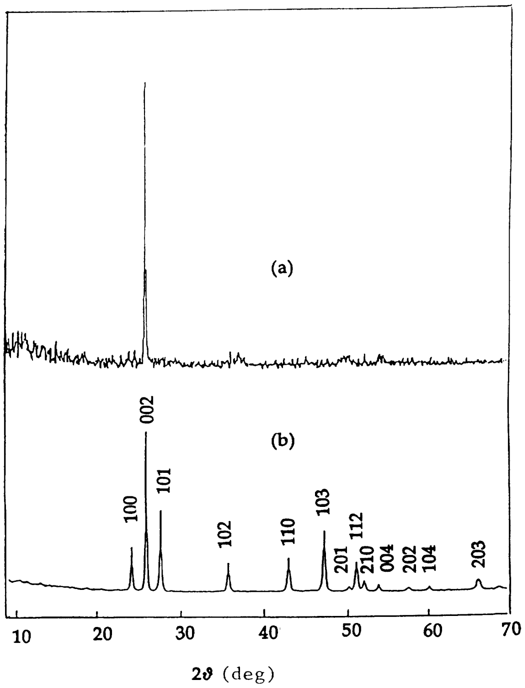

FIG. 1. (a) The XRD spectrum of the as-deposited CdS films on silicon substrate at room temperature. (b) The pattern of CdS powders.

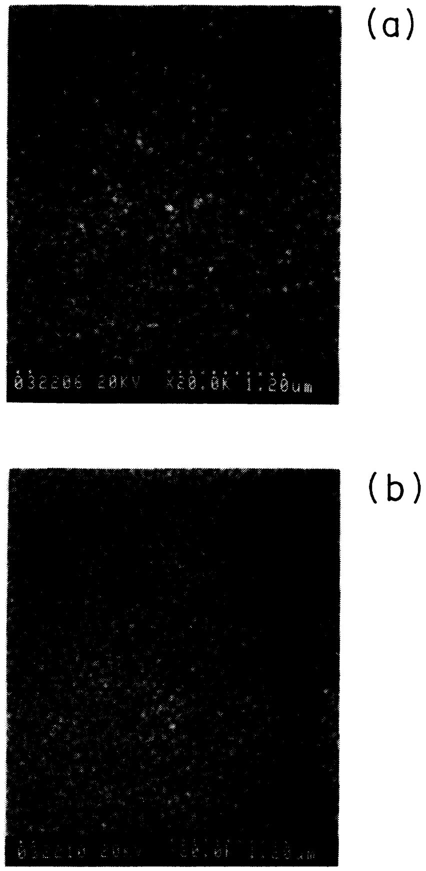

FIG. 2. The SEM photographs for the films grown on silicon substrates at temperature (a) 30 °C and (b) 100 °C.

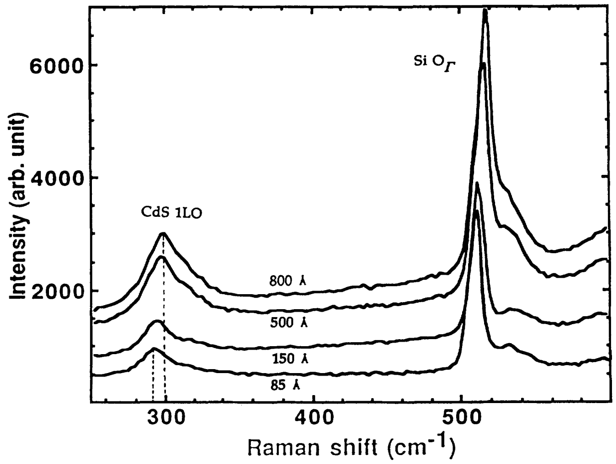

FIG. 3. Thickness dependence of the 1LO phonon energies. These RRS spectra of CdS films deposited on a p-type silicon wafer were excited at 4880 Å and were detected at room temperature. CdS film thickness is indicated in the figure. The dashed line marks the frequency of the main Raman peak (300 cm^{-1}) for a thick (800 Å) film.

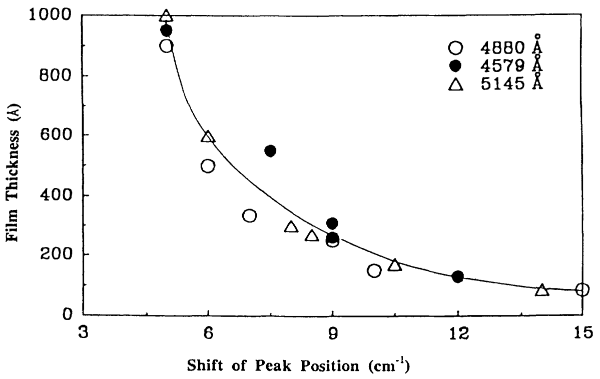

FIG. 4. Frequency downshifts of the 1LO Raman peaks relative to its position for bulk CdS as a function of film thicknesses. The full curve is drawn to guide the eye. The Raman spectra were excited at 4579, 4880, and 5145 Å.

has been studied before[2] and is mainly ascribed to the grain-size effect. In Fig. 3 the spectra reveal as decreasing the thickness of the CdS films, the silicon Raman peak shifts to the low-frequency region although the amount of shift is not very evident (around 6 cm^{-1} for 85-Å-thick film). The low-frequency shift of the silicon Raman peak as the film thickness is less than 800 Å might be ascribed to the stress effect caused by the coupling of the CdS film and the silicon substrate at the interface. As the film thickness of CdS increases, the coupling effect between the CdS film and the silicon substrate at the interface becomes less prominent. Hence, for CdS films thicker than 800 Å, the optical zone center of the Raman line of silicon resumes eventually to the value of 520 cm^{-1} of a p-type (100) silicon substrate.

From Fig. 3 it is also found that the main CdS 1LO Raman peak shows an increasing shift to the lower-frequency region with decreasing layer thickness. The shifts of the Raman peak of the 1LO phonon mode as a function of the film thicknesses at three excitation energies, 4579, 4880, and 5145 Å, are shown in Fig. 4. One can note that these shifts are independent of the photon excitation energies and are consistent with the previous works.[11,12] From Fig. 4 it can be seen that the Raman shifts of the 1LO phonon peak of CdS films are saturated to the value of 5 cm^{-1} when the films are thicker than 800 Å and the 1LO Raman peak has a shift $\sim 15\ \text{cm}^{-1}$ for a thin film with 85 Å thickness. The saturation of 1LO Raman shift as film thickness exceeds 800 Å is due to the grain-size effect, as mentioned above. The low-frequency shift of the 1LO Raman peak of CdS films as the film is thinner than 800 Å might be attributed to the combination of (1) the size effect,[3,5,10] i.e., the effect of size on the vibrational properties in small crystallites and the low-dimensional thin-film structure, and (2) the stress effect induced by the film-substrate interface on the vibrational spectrum. It is also known that the vibrational mode frequencies vary with increasing temperature. Thus, the Raman shift might be caused by the higher temperature due to the higher absorption of the probe energy in the thicker films. However, this possibility can be ruled out because as we will show later (see Fig. 6) a significant difference in the absorption cannot happen for the films having a thickness difference within only an order of several hundred angstroms. Thus, the thickness variations of the films cannot make a meaningful difference in temperature.

The vibrational properties of the Al_2O_3 thin films on Si and Au have been studied by Brüesch *et al.*[14] They found a softening of the longitudinal-optical Al-O stretching mode for a layer thickness less than ~ 100 Å. For a 10-Å-thick Al_2O_3 film a relative mode softening of $\sim 3\%$ with respect to the mode of the bulk crystal was reported. Ramsteiner *et al.*[11,12] studied *a*-C:H on Si using Raman spectroscopy. They reported that the relative softening of a 10-Å *a*-C:H film on Si is $\sim 4.5\%$. They also found a clear substrate dependence of the softening. Our present results yield a relative softening of $\sim 4.4\%$ (with respect to the mode of bulk CdS) for a 100-Å CdS film on Si wafer. The discrepancy between our results and previous work might be caused by the following. (1) The lattice mismatch in CdS/Si system (23.8%, lattice constant of CdS, a axis $=4.136$ Å; for Si, 5.43 Å) is larger than those in *a*-C:H/Si or Al_2O_3/Si systems. The energy of the LO-phonon mode contains a higher contribution from the lattice mismatch. (2) The grain-size effect was combined with the thickness effect in our work which was not considered by the previous works.[11-14]

Figure 5 shows the Raman spectra of as-deposited CdS thin films with film thicknesses ranging from 700 to 100 Å. These Raman spectra were also excited by the 4880-Å line of an Ar^+ laser. The spectra reveal that there is a TO mode accompanying the main CdS Raman peak (1LO) around 300 cm^{-1} when the film thickness is less than 410 Å. This TO Raman line of the CdS thin film shifts from 228 cm^{-1}, the most active TO mode of bulk CdS, to 220 cm^{-1} and is independent of the film thickness. Since the deformation potential is the main mechanism of the TO Raman scattering, the TO phonon line can be degraded only by the grain-size and stress effects. Therefore, the softening of the TO mode (shift from 228 cm^{-1} of the most active TO mode of bulk CdS to 220 cm^{-1} for a film thinner than 800 Å) shown in Fig. 5 might be ascribed to the combined effect of the stress and the grain size. It is well known that the resonant Raman scattering (RRS) cross section of the TO mode has the highest efficiency when the resonant condition is satisfied.[19–21] As the photon energy approaches the band gap of cadmium sulfide, the pronounced decrease in the Raman scattering efficiency of the TO mode will be observed prior to the onset of resonant enhancement.[19–21] The observed decrease in the TO mode as the photon energy approaches the band gap of CdS can be interpreted by extending the Loudon theory[20–22] to include in the Raman-scattering amplitude the destructive interference term between resonant and nonresonant contributions. To date, TO mode scattering was observed[19–26] for photon energy of a laser beam larger than the band-gap energy. Although the phenomenon of the disappearance of the scattering intensity of the TO mode for photon energy larger than the band-gap energy is well known, however, the real mechanism still remains unknown. Since the band-gap energy of bulk CdS at room temperature (i.e., 25 °C) is 2.42 eV, the TO mode of the bulk CdS single crystal cannot be observed by using 4880-Å (2.54-eV) excitation. The abnormal occurrence of the TO mode at 4880-Å excitation in this work might be ascribed to the blueshift of the band gap of a CdS film when the film thickness is less than 700 Å. The effect of reducing film thickness will normally result in the observable high-energy shifts of the absorption and transmittance. As shown in Fig. 6, the transmittance properties of CdS thin films deposited on the glasses with various thicknesses ranging from 1000 to 4000 Å were investigated. We can note from the figure that the absorption edge of thinner film is shifted to the smaller-wavelength region (blueshift). One can also note that the transmittance curves below absorption edges are highly thickness dependent, and the features of these curves agree with the work of El-Nahass *et al.*[27]

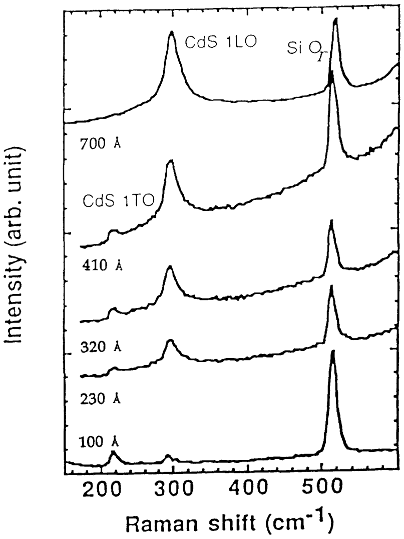

FIG. 5. Thickness dependence of the 1TO phonon intensities and energies. The RRS spectra of CdS films deposited on the *p*-type (100) silicon wafer were detected at room temperature. The spectra were excited at 4880 Å.

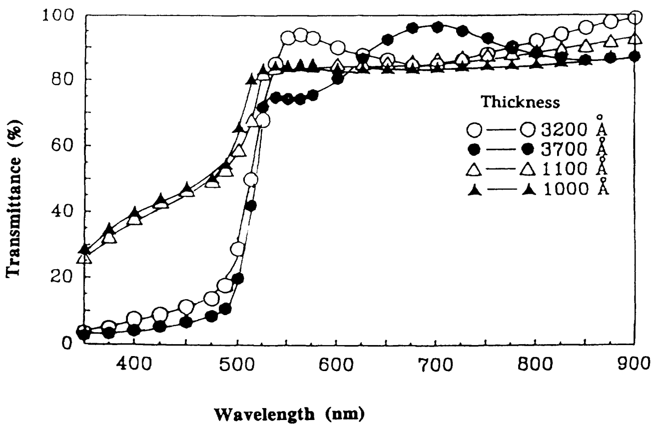

FIG. 6. Spectral dependence of the transmittance for the as-deposited films deposited on glass substrate at different thickness.

Figure 7 shows the curves of the square of the absorption coefficient α versus the photon energy $h\nu$ by using the results in Fig. 6. As shown in Fig. 7, α^2 varies linearly with $h\nu$, and thus the interband transition can be interpreted[28] by the relation $\alpha^2 = A(h\nu - E_g)$. To obtain the value of the optical band gap we extrapolated the straight lines in Fig. 7 to zero absorption. Results showed that the band-gap energy E_g decreases as the thickness of the CdS film increases. The blueshifts of E_g of CdS films were estimated at about 0.06 and 0.16 eV for thicknesses of 3700 and ~1000 Å, respectively (comparing with the band gap of 2.42 eV of bulk CdS). Recently, the blueshift ΔE_g caused by the quantum size effects of CdS crystallites was measured by Tanahashi *et al.*[29] They reported that the blueshifts ΔE_g are 0.13 eV for 76-Å and ~0.05 eV for 313-Å microcrystallites embedded in the SiO_2 matrix. Since the grain size of our CdS films for different

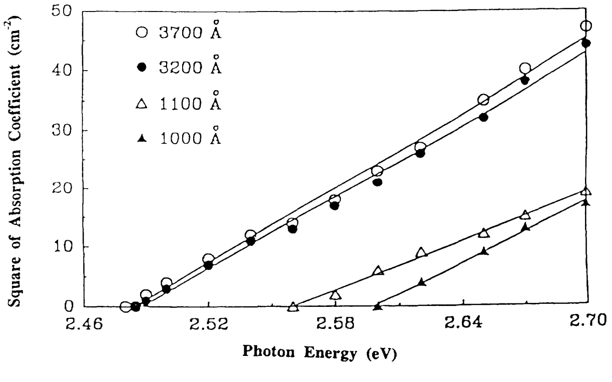

FIG. 7. Square of the absorption coefficient of CdS thin films plotted against the photon energy.

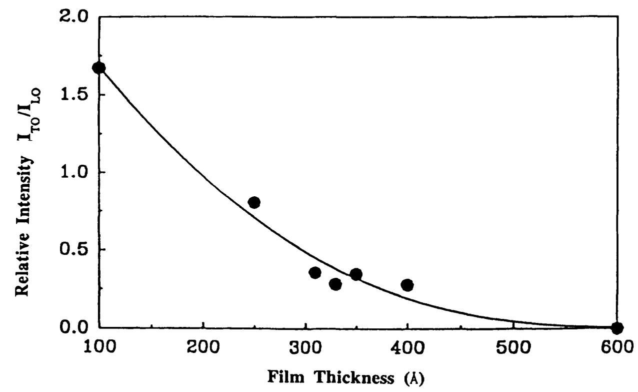

FIG. 8. Thickness dependence of the ratio of the 1TO intensity to the 1LO intensity. The solid line is only a guide to the eyes.

thicknesses are in the range of ~300 Å, therefore, we conclude that the blueshift of 0.06 eV for film thickness 3700 Å might be caused by the grain-size effect of the polycrystalline CdS film. Another blueshift of ~0.1 eV between the band gaps of films with thicknesses 3700 and ~1000 Å can be attributed to the thickness effect of the CdS films. Therefore, as the thickness is less than 700 Å, the quantum size effect due to the low-dimensional thin-film structure becomes dominant and the band gap of the film will blueshift to the range of ≥2.58 eV. Under this circumstance, the photon energy of 2.54 eV (4880 Å) lying below the band edge of the film becomes sufficient for satisfying the necessary resonance condition of the TO mode of CdS films.

In order to see the thickness effect more clearly, the relative intensity ratio $I_{\text{TO}}/I_{1\text{LO}}$ as a function of film thickness is plotted in Fig. 8. We can see that the ratio decreases when the film thickness increases. One can also note that the Raman signal of the TO mode is insufficient for observing as film thickness is larger than 410 Å. This might be due to (1) the intrinsic thermal broadening of the LO Raman peak at room temperature; (2) the intensity of the LO peak becomes stronger as the film thickness increases and finally the Raman signal of the TO mode is masked by the envelope of the LO signal; and (3) the scattering efficiency of the LO mode is larger than the TO mode in the resonant Raman-scattering condition. It is worth noting that the scattering efficiency of the TO mode overshadows that of the LO mode when thickness is less than 150 Å. It is evidence that the Fröhlich interaction is weak for very thin films, so that LO-mode scattering is mainly caused by the deformation potential.

IV. CONCLUSION

In conclusion, the shift of the 1LO mode Raman peak to the lower-frequency region as the thicknesses of as-deposited CdS films vary from 800 to 85 Å is ascribed to the size effect (including the lower-dimensional thin-film structure and the grain-size effect of the thin films) and the stress effect. For films thicker than 800 Å, the peak of the 1LO phonon line is at 300 cm^{-1} instead of 305 cm^{-1} for the bulk CdS. This saturation of the shift of 1LO Raman peak for films thicker than 800 Å is attributed to the effect of the grain size. For thicknesses less than 410 Å, the TO-phonon mode around 220 cm^{-1} in the CdS thin film can be observed by using 4880-Å photon excitation energy which is above the band-gap energy of bulk CdS. The occurrence of the TO-phonon mode is attributed to the quantum size effect because the size quantization of free carriers in the lower-dimensional thin-film structure will cause the blueshift of the band gap in thin films. The size quantization of free carriers is caused by either small-volume microcrystallities or low-dimensional thin-film structure as the film thickness decreases. The Raman shift of the TO mode of CdS films is about 8 cm^{-1} from the Raman peak of the most active TO mode of bulk CdS. The magnitude of this softened energy is found to be independent of the film thickness.

ACKNOWLEDGMENTS

One of the authors (D.S.C.) is grateful to Professor Y. C. Lee at SUNY at Buffalo for his helpful comments. We also thank Professor M. C. Lee and Professor W. F. Hsieh for their helpful discussions. This work has been partially supported by the National Council of Science, ROC under Grant No. NSC 80-0208-M-009-25.

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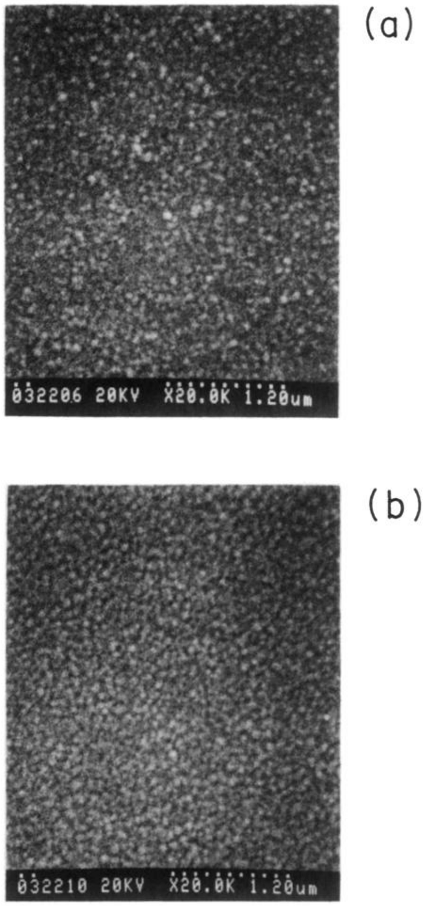

FIG. 2. The SEM photographs for the films grown on silicon substrates at temperature (a) 30 °C and (b) 100 °C.