

The Studies of Quantum Size Effects in CdS Thin Film

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CdS thin films with various thicknesses ($50 \text{ \AA} \sim 3500 \text{ \AA}$) are fabricated by laser evaporating technique at room temperature. Using Nd: YAG laser as the light source, p-type silicon as the substrate and 99.999 % CdS powder as the target, we can manufacture high orientation CdS thin films with different thicknesses. These films were used to investigate the thickness dependence of the longitudinal optical (LO) phonon modes. The phenomena of LO phonon frequency redshift and luminescence peak blueshift might be attributed to the small size, the lower-dimensional, and mechanical stress.

1.Introduction

Cadmium sulfide is a member of the II-VI group semiconductor compounds formed by alloying one element from group II of the periodic table with another from group VI. The energy gap of cadmium sulfide between the valence and conduction band is about 2.42 eV at room temperature. The cadmium sulfide has been studied extensively in past 40 years. This is because that the cadmium sulfide is very important in the optical application due to its energy gap falling in the visible region of the spectrum. Its absorption edge is at about 5100 Å at room temperature. The hexagonal wurtzite structure (α -phase $a=4.16$ Å, $c=6.756$ Å) of the cadmium sulfides is found in the naturally occurring mineral greenockite, artificially grown crystals, and most vacuum deposited films. The β -phase in a cubic zinc-blende structure ($a=5.832$ Å) of CdS can be obtained by hydrogen sulfide precipitation from cadmium sulfate solution.

Applications of CdS are mainly in the form of thin films. Thin films of CdS are of practical interests as photoconductors[1], piezoelectric transducers[2], as laser materials[3], and solar cells[4]. Recently, CdS and CdSe have also been explored actively as materials for nonlinear optical processing. Optital switching and bistability were demonstrated in CdS with femto-joule energy[5]. The basic requirements of these CdS thin films in these applications are high optical transparency, low electrical resistivity, good crystalline structure and low deposited substrate temperature. Particularly, it is necessary to prepare CdS films on low-temperature substrates when they are used as the top electrode of various optoelectronic devices[5] and are applied in heterojunction solar cells[4]. This low-temperature growing property is also very improtant in depositing films on organic film substrates[6]. Therefore, how to grow the highly oriented CdS films at room substrate temperature without post-annealing is one of the improtant challenge in these applications.

CdS thin films have been grown by thermal evaporation[7], chemical va-

por deposition(CVD)[8], rf sputtering[9], and laser evaporation[10] with varying degrees of crystallinity and optical quality. The undoped CdS films with low-resistivity and high transparency properties prepared by thermal evaporation[7,8], have in general two major drawbacks: first, crystallinity—amorphous CdS films are formed at low substrate temperature ; second, stoichiometry—in thermal evaporation the starting powder of CdS has to be rendered deficient in sulphur for the purpose of keeping the films with the same stoichiometry. Although the films crystallinity can be improved with higher temperature substrate. Nevertheless, higher substrate temperature will cause the interdiffusion effects and thus alter the stoichiometry.

In the past decades, many authors have devoted to the growing of CdS thin films at low substrate temperature. One of the feasible ways is the laser evaporation techniques[10]. The use of laser radiation as an external energy source to vaporize materials and to deposit thin films in a vacuum chamber was first reported by Smith and Turner[11]. Thereafter, research work in this area was sporadic with a lack of continuous and in-depth studies. Systematic investigations began to emerge in the late 1970s to provide a better understanding in the fundamental physics of laser–solid interaction and its relationship to deposition mechanism and thin–film quality. Recently, excimer lasers at lower power densities have been used to deposit semiconducting and high- T_c superconducting thin film from bulk targets[10,12].

One of current research interests in material studies is to investigate the physical properties of materials while their physical dimensions are very small. Microcrystallites of several semiconductor materials have attracted many extensive investigations recently [13,14]. Most of these works were carried out with respect to their electronic and vibrational structures of semiconductor materials both experimentally and theoretically. Studies on the Raman scattering is one of the most convenient optical diagnostic techniques for probing the vibrational

structures of microcrystallites, hence several investigations on Raman scattering from microcrystallites have been published [15,16].

Quantum size effects in semiconductors have attracted much attention in recent years. 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 latter becomes comparable to the de Broglie wavelength of the charge carriers. As the film thickness which is measured along the z direction is much less than the two in-plane dimension which is measured in the x-y plane and is comparable to the de Broglie wavelength of the carrier, quantization of the carrier motion in perpendicular direction to the film plane occurs, although the carrier motion is still particle-like in the other two dimensions. Quantum size effects are usually attributed to the following factors: the small size of microcrystallites in the films[17-25], the lower-dimensional thin film structure [26,27,28,29] , and the effect of mechanical stress[29,30,31]. 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[26,27,28,29]. Meanwhile, some authors studied the relationship between the Raman line shift and the film thickness[26,27,28,29]. Ekimov, Efros, and Onushchenko[24] developed a growth technique of the semiconductor microcrystals in 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 that a considerable short-wavelength shift of the exciton lines was observed as the micro-

crystal size decreased. Ramsteiner et. al. [26,27] 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 et. al.[31] studied the thickness dependence of the band gap by measuring the resistivity in the intrinsic region. Brüesch et. al.[29] 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 existed for a layer thickness thinner than ~ 500 Å.

In our work, the undoped CdS thin films were prepared at room temperature on p-type (100) silicon by pulse laser evaporation(PLE). The properties of the as-deposited thin films were analyzed by X-ray diffraction(XRD) pattern and Raman spectra. The XRD is used to determine the crystal structure and composition of these films. The energies of optical phonon modes can be observed by the Raman shift in the Raman scattering study. An increase in phonon scattering efficiencies was predicted for the laser energy slightly less than the direct gap[32]. Because CdS has a direct gap which is very close to the photon energy of the high-power cw 4880 Å line of argon laser. Therefore, CdS was made itself to be an obviously suitable material to study the effect of the measurement in photon scattering efficiencies when the 4880 Å line of Ar^+ laser was used as the excitation source for Raman experiment. From the Raman spectra, we also observed that the grain sizes varied as the film thickness varied. Furthermore, the LO vibrational mode softening and the blue shift of the energy gap of CdS thin films depend also on film thickness. We also observed silicon O_T peak upshifts due to the increase of the interface stress. The thickness of the films is measured by an ellipsometer and Dektak 3030 surface profile measuring system. The thicknesses of the films were found from ~ 50 Å to ~ 3570 Å.

2. Experimental

The laser deposition setup is shown in fig-1. This system is evacuated by a turbo-molecular pump. There are two gauges to measure the total pressure of the vacuum chamber, pirani gauge and cold cathode gauge. The useful range of the pirani gauge is from atmosphere to 1×10^{-3} Torr, cold cathode gauge is from 1×10^{-3} to 1×10^{-7} Torr. The base pressure was less than 1×10^{-5} Torr. The target holder is connected with rotary motor. The distance between target and substrate is about 30 mm. The target is formed by pressing pure(99.999%) CdS powders into pellet. The substrate is p-type (100) silicon wafer. For our experiments we used a Nd:YAG laser with 532 nm wavelength, a repetition rate of 5 Hz, a duration time of 8×10^{-9} sec, and a pulse energy of 10 mJ. The laser beam was focused on a rotating, CdS pellet in a vacuum chamber. The material, which was evaporated perpendicularly to the target surface. The deposition rate was about 100 Å/min. The substrate temperature remained at room temperature. The films are smooth. The surface morphology was thicker in the center and thinner in the edge. So that we could get different thickness easily. The thickness of the CdS sample was obtained from ~ 50 Å to ~ 3570 Å.

3. Results and Discussions

3.1 High orientation CdS thin films

The structure of the as-deposited films were analyzed by X-ray diffraction(XRD) with Cu K_{α} source ($\lambda=1.5418$ Å). Fig-2 showed the XRD results of the films deposited by PLE technique at room temperature and (b) was the XRD spectrum for the CdS powder. The pattern of powder agrees well with the previous result for the wurtzite structure of CdS. All the films have highly orientation in (002) direction.

3.2 Surface phonon peak shift in Raman spectra

Figs-3 -4 showed that the surface phonon Raman line shift was extended from 298 cm^{-1} to 295 cm^{-1} for different thicknesses. For the view point of magnitude of Raman line shift, the 1LO phonon shift of CdS crystal was given in the literatures[33,34] as 305 cm^{-1} (bulk), while the values measured by Dai et.al. were 300 cm^{-1} and 297 cm^{-1} in PLE and TE films [35]. The different shift between the PLE and TE films was attributed to the grain size effect. The Raman shift of the surface modes of the microcrystallites in CdS film, reported by Scott and Damen[18] is 296 cm^{-1} . The discrepancies of the Raman line shift among the results obtained by Scott, Dai and us might be attributed to the size effect.

The Raman spectra of our measurements showed in figs-5(a) (b), have a shoulder extending to about 228 cm^{-1} . This data is similar to the result obtained by Scott and Damen[18]: the spectral envelope extends from about $\omega_{TO}=228\text{ cm}^{-1}$ to $\omega_{LO}=305\text{ cm}^{-1}$.

3.3 Blue-shift of luminescence spectra in CdS thin film

From the Raman spectra as showed in figs-6(a) (b) (c), we could get the luminescence peaks. As the CdS thickness is not too thick, the 2TO mode of p-type silicon substrate was also to be observable at $\sim 960\text{ cm}^{-1}$. The dependence of the luminescence peak energy on the film thickness is shown in fig-7. It can be noted that if the thickness of CdS films increase, then the energy-gap decreases. The energy-gap of films can be determined as 2.462 and 2.453 eV for thickness of 50 and 3570 Å, respectively. The value of blue-shift of films are about 0.042 and 0.033 eV (i.e. compared to energy-gap of the bulk CdS (2.42 eV)) for thickness of 50 and 3570 Å, respectively. Quantum size effects on electron-hole systems confined in semiconductor microcrystals have recently been an intensive subject either in experimental or theoretical studies. Various types of microcrystalline samples such as colloidal particles [36,37], gas-evaporated parti-

cles[38,39] and particles embedded in solid matrices (glass or crystal)[24,40,41,42], have been prepared. The absorption and luminescence spectra of these samples were investigated. The effects of three-dimensional confinement normally result in obserable high-energy shift of the absorption, transmittance, and luminescence peaks, which are in good agreement at least qualitatively with theoretical results [43,44]. In addition to the absorption, transmittance and luminescence measurements, the observation of the resonant Raman scattering (RRS) is also important for the study of the quantum size effect. Since the resonant intermediate states in semiconductors are usually the exciton states[17,34,35,45], the resonant behavior of Raman lines will be very sensitive to the change of the exciton states.

From the theoretical point of view, the ground state property of an electron and a hole confined in the microcrystal possesses a fundamental problem of quantum mechanics: the competition between the attractive two-body force and the one-body force exerted on the well boundary. As noted by Efros et.al.[46], it can be readily infered that there are two limited situations according to the amount of the ratio of the characteristic length "R", which indicates the size of the microcrystal, to the effective Bohr radius a_0^* of the exciton in bulk material. In the limit of $R/a_0^* \gg 1$ (i.e. the regime of exciton or weak confinement), the character of the exciton as a quasiparticle is well conserved while the translational degrees of freedom are confined with little energy increment. In another limit of $R/a_0^* \ll 1$ (the regime of the individual particle or strong confinement), the electron and the hole should occupy primarily the relatively little spatial correlation. As it is known, the limit of the strong confinement is relatively easy to handle. However, the analysis of the weak confinement limit is rather difficult because one does not know how to chose the zeroth-order approximation for the wave function which satisfies the boundary conditions.

The pronounced feature of the band-gap blue-shift was observed in our result. This phenomenon can be ascribed to the quantum size effects which includes

two mechanisms, namely, the confinement of electron or hole in small volume microcrystallites and effect of reducing dimension as the thickness decreases.

3.4 Interface stress of CdS/Si

Raman spectroscopy was used to determine built-in stresses in silicon on sapphire(SOS) device[47,48]. If the interface has compression stress then the Raman peak will shift to the higher frequency region[48]. If the interface has tensile stress, the Raman peak will shift down to the lower frequency region[47,49]. The Raman O_{Γ} peak shift of p-type silicon is about 520 cm^{-1} (bulk). It was found that the Raman peak of silicon(substrate) may depend on the CdS film thickness[50]. Fig-3 also manifests that silicon substrate Raman peak shifts while CdS film thickness changes. Fig-8 showed that as the film thickness increases then the peak shifts to the higher frequency region. The Raman spectra for different thickness CdS films showed that the intensity of silicon decreases as the thickness of CdS increases. Because in the thick films the active volume of Si with incident photon was very small. Namely, only the Si surface near the interface could act with photon. So the interface stress was important to the silicon in the thick films that the silicon O_{Γ} peak upshifts from 520 cm^{-1} to 524 cm^{-1} (CdS film thickness = 2337 \AA). As the CdS thickness was thicker than 2337 \AA , signal of the Si- O_{Γ} can be observed.

4. Conclusion

We have constructed a PLE system, manufactured the CdS thin films on p-type (100) silicon substrate at room temperature and studied the Raman effect of the as-deposited films. The result of XRD showed that the films obtained are highly orientation in (002) direction. Our results also show that small physical dimension of the scattering crystals lead to a broadening of the first order Raman line through a relaxation of the $q \cong 0$ selection rule. The increase in the width

of Raman signal was observed when the size of grain decreases. This is in good agreement with the previous theoretical results. According to the electromagnetic theories, the Raman peak due to the surface phonon mode should locate between the bulk TO and LO phonon frequencies. The obtained Raman spectra have a shoulder extending from the main peak to about $228 \text{ cm}^{-1}(\omega_{TO})$. The phenomenon was due to a wide distribution of grain sizes in our CdS films. The spectra intensity distribution in this frequency region describes the distribution of particle sizes.

In Raman spectra of different thickness films, we also observed that the main peak of surface mode shifts from 298 cm^{-1} to 295 cm^{-1} . This shift in frequency might be attributed to the grain size effect or lower dimension.

The blue shift of luminescence peak was observed in Raman spectra. This pronounced feature of band gap blue-shift is interpreted by combining the quantum size effects due to confinement of electron or hole in small volume microcrystallites and thickness effects due to lower dimension as the thickness decreases. We could observe five overtones in our Raman spectra due to the fact that the 4880 \AA line of Ar^+ laser is very close to the energy gap of CdS.

For the Raman spectra of different thickness CdS films, we observed that the intensity of silicon decreases as the thickness of CdS increases. Because in the thicker films the active volume of Si with incident photon was very small. Namely, only the Si adjacent to the interface could interact with photons. So the interface stress was important to the silicon in the thicker films in which the silicon O_{Γ} peak can upshift from 520 cm^{-1} to 524 cm^{-1} (CdS film thickness = 2337 \AA).

5. references

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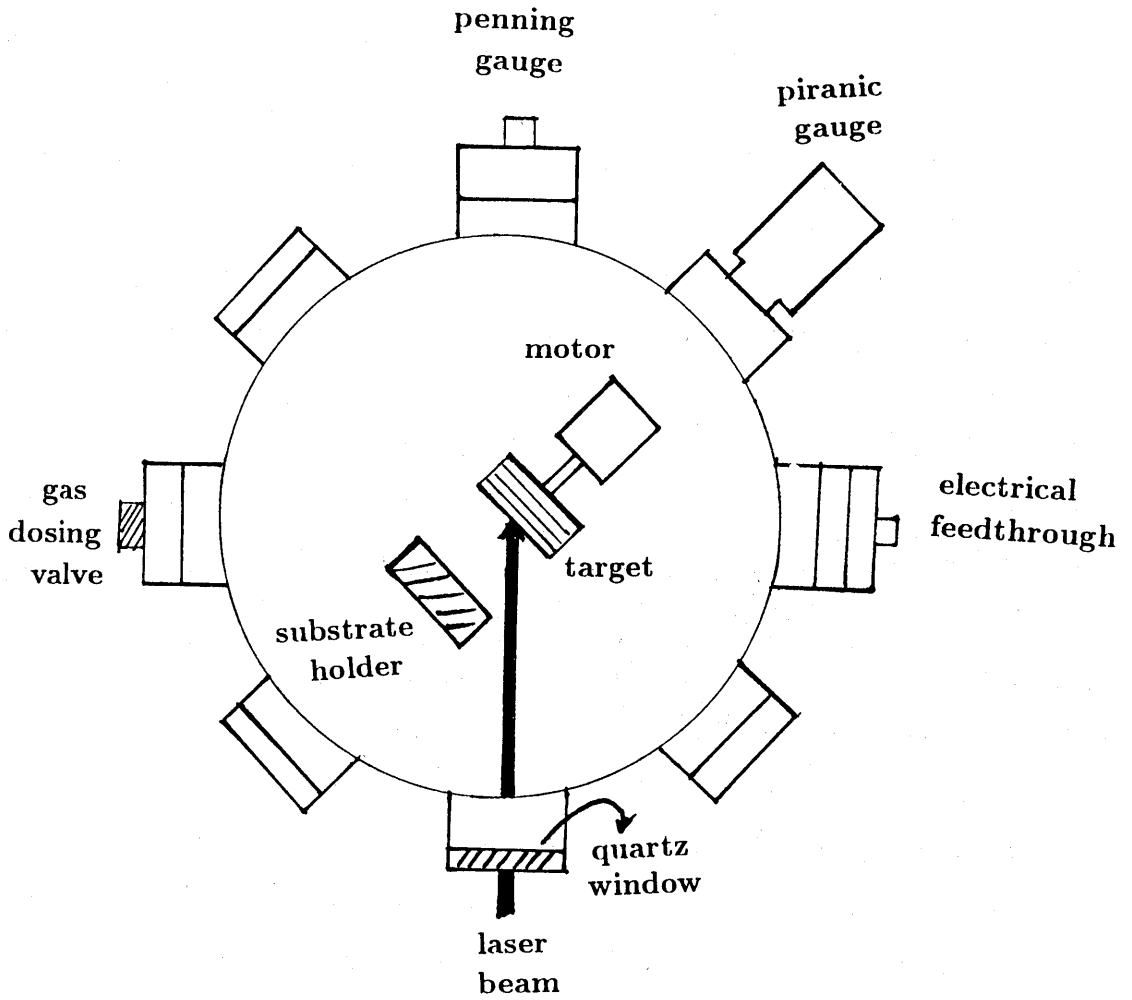


Fig-1: The vacuum system used for laser evaporation deposition.

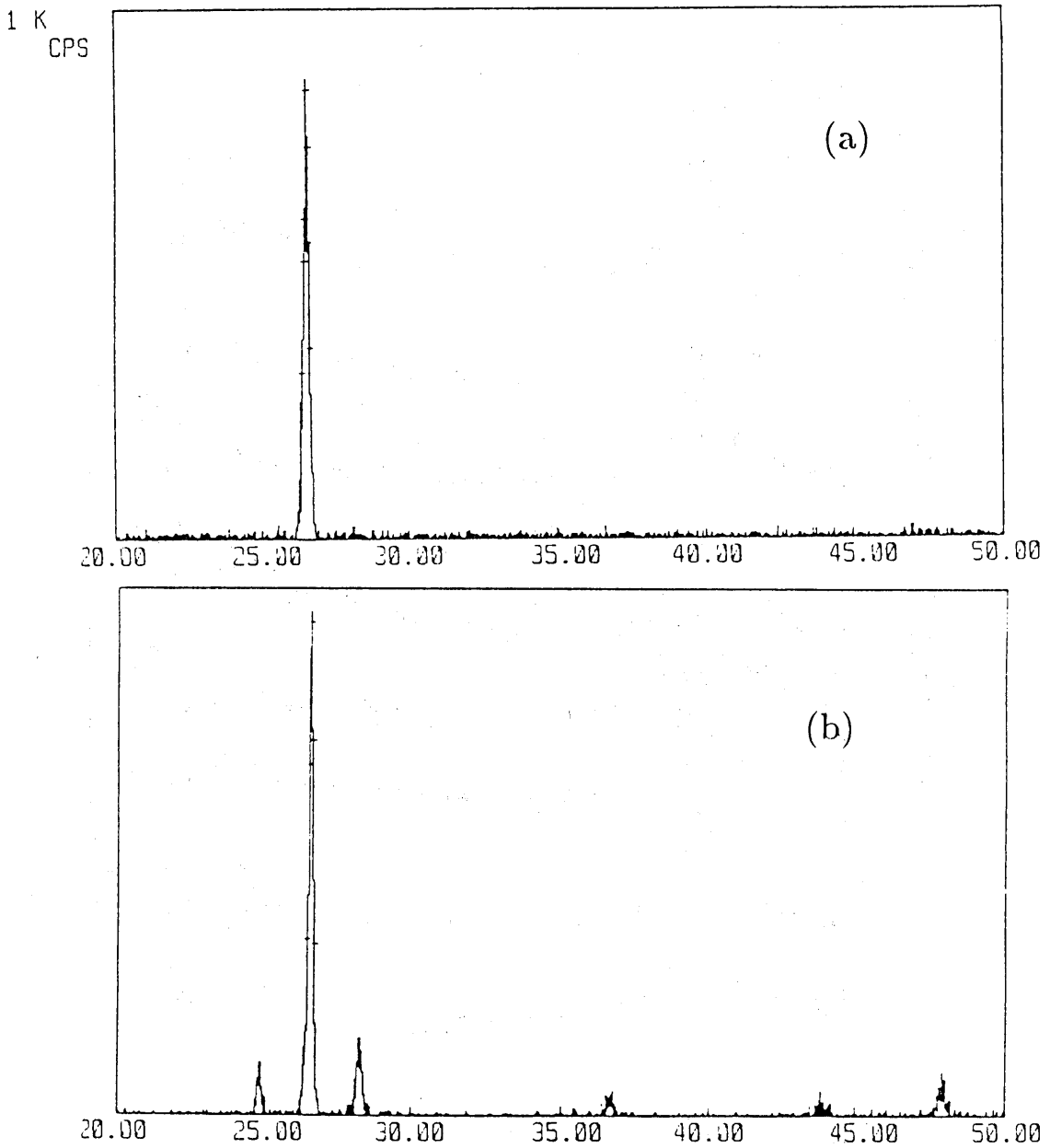


Fig-2: (a) The XRD spectrum of the as-deposited CdS films on silicon structure at room temperature (b) The pattern of CdS powders.

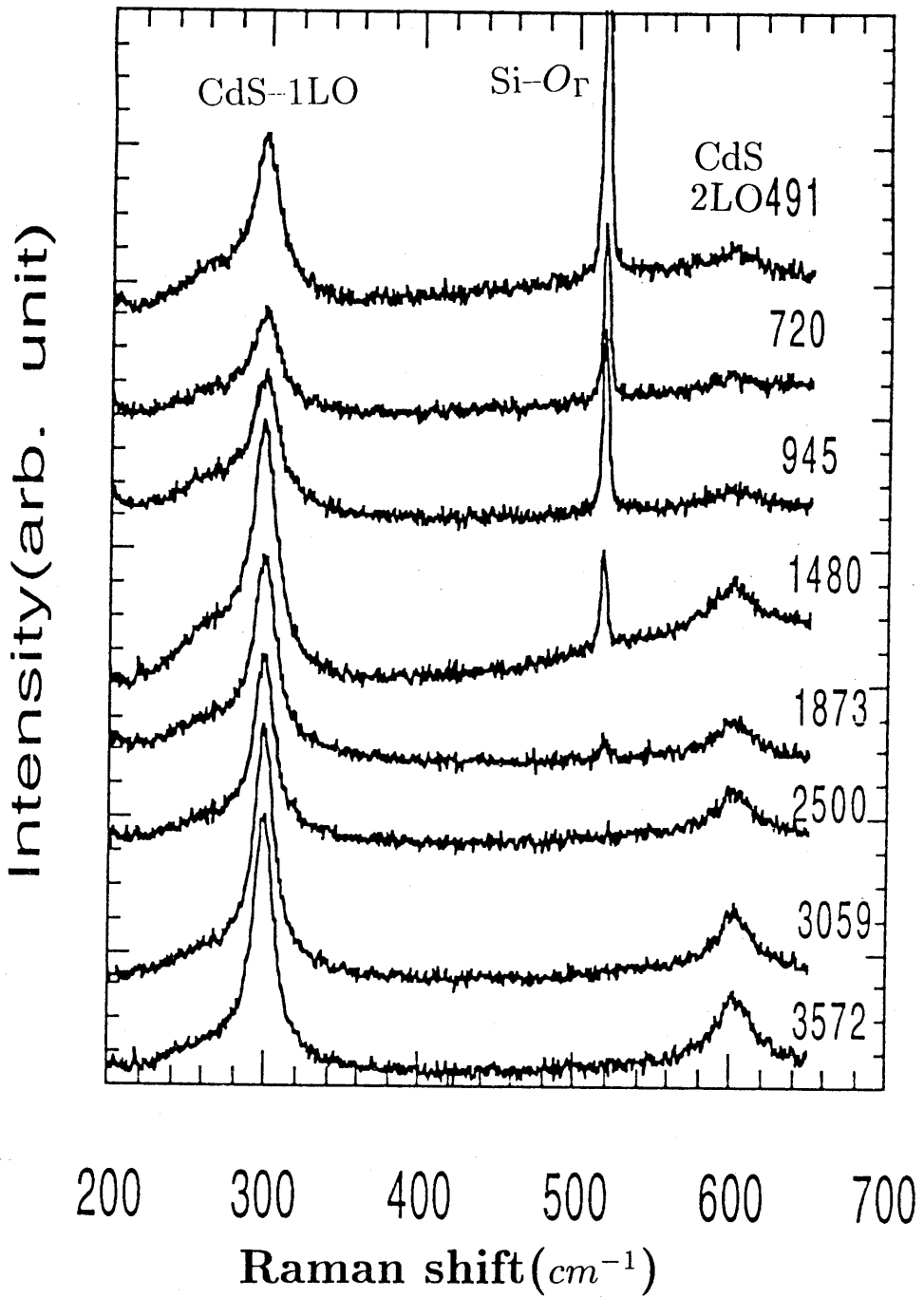


Fig-3: Thickness dependence of the CdS 1LO phonon energies and Si-Or peak. These RRS spectra of CdS films deposited on p-type silicon wafer were detected at room temperature. The spectra were excited at 4880Å. The various thickness of the CdS films are indicated in the figure.

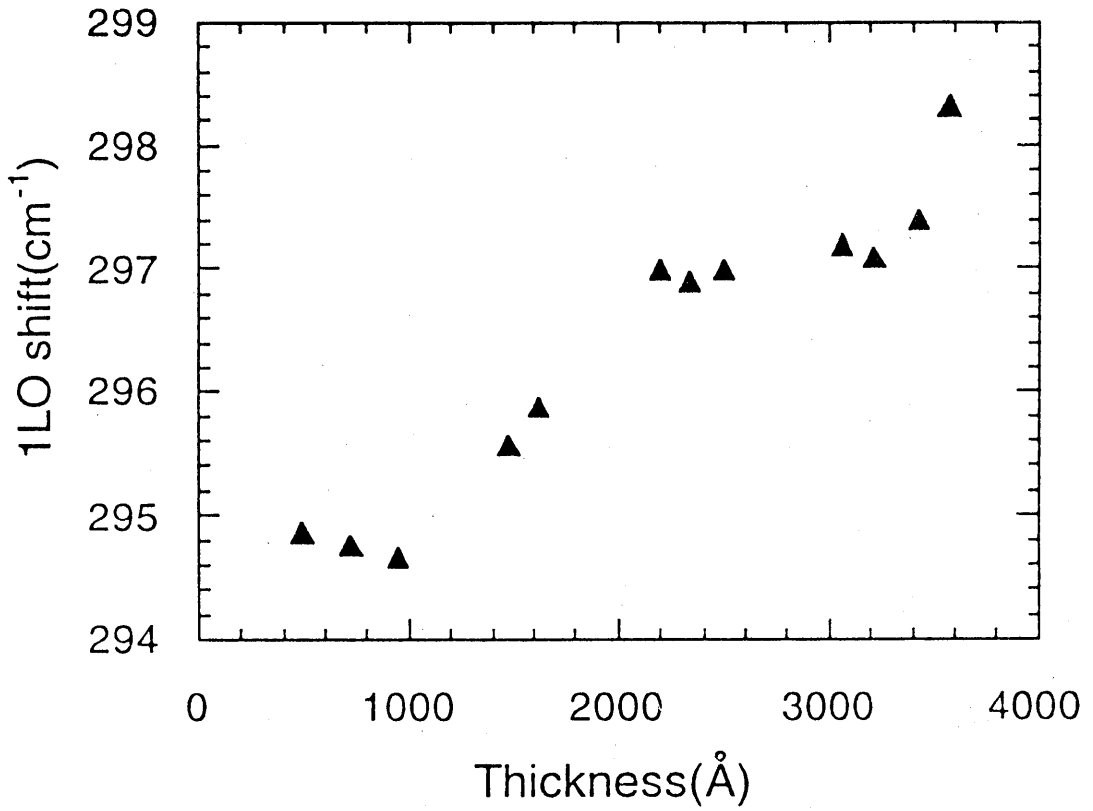


Fig-4: Frequency of the CdS 1LO Raman peak as a function of film thickness.

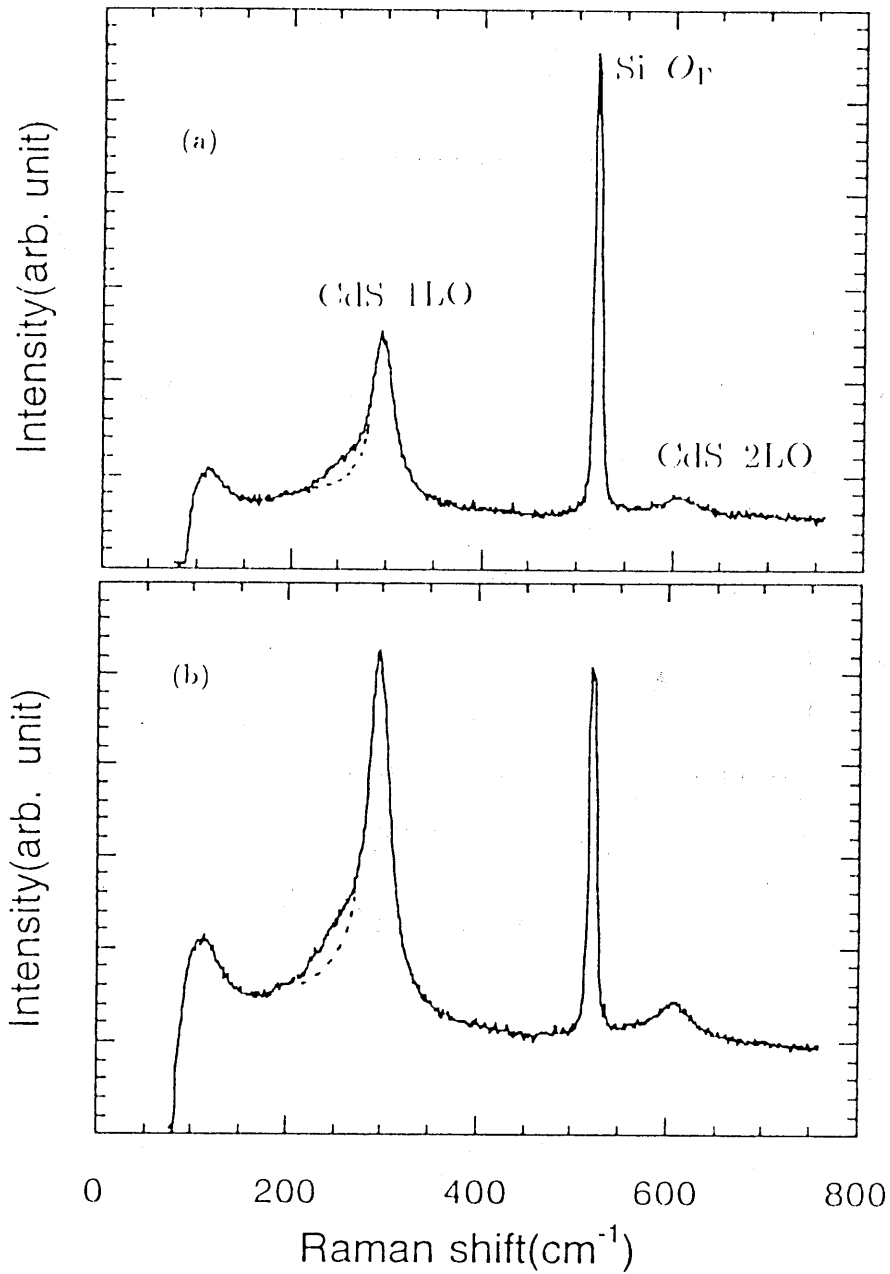


Fig-5: Raman spectra for (a) 720 Å, (b) 1630 Å CdS films. The dashed line is a guide to the eyes for the symmetry of 1LO peak.

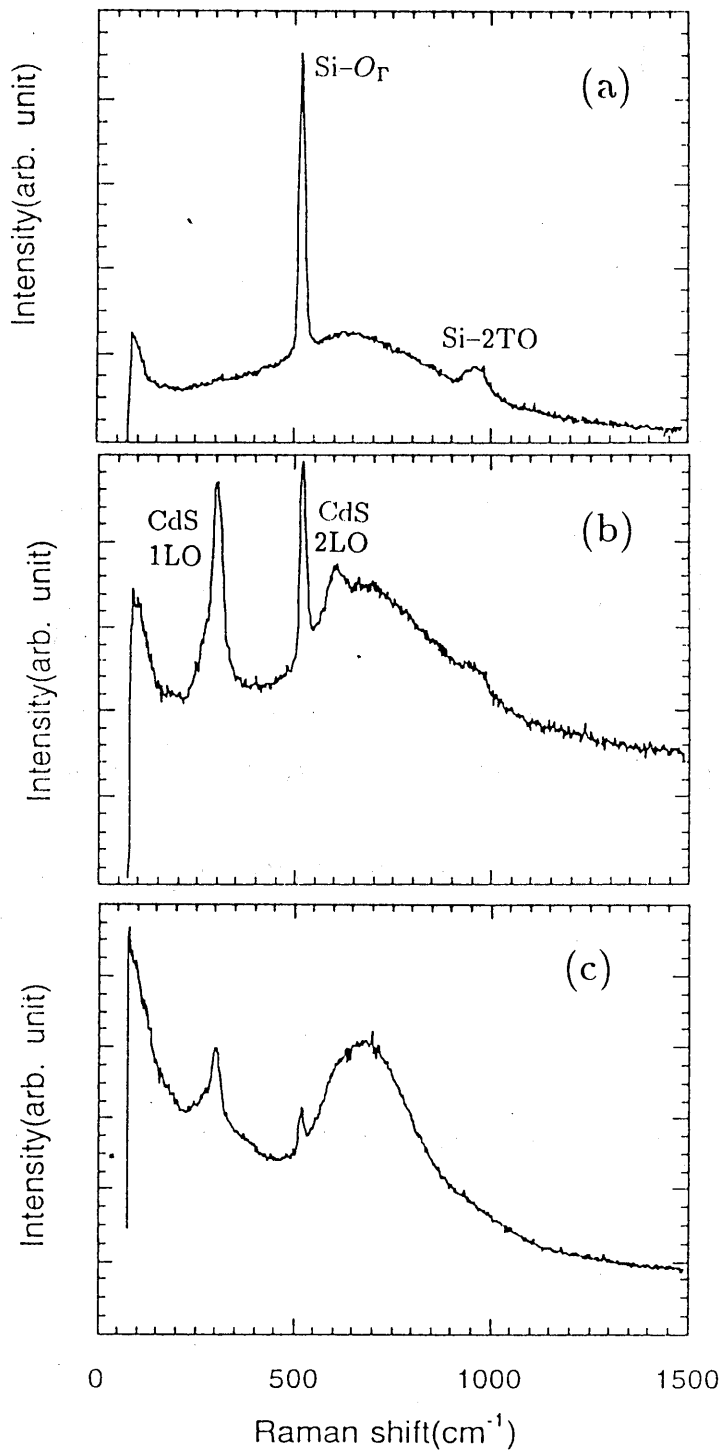


Fig-6: Raman spectra for (a) 50 Å, (b) 490 Å, (c) 950 Å CdS films. The wide peak is luminescence emission of CdS.

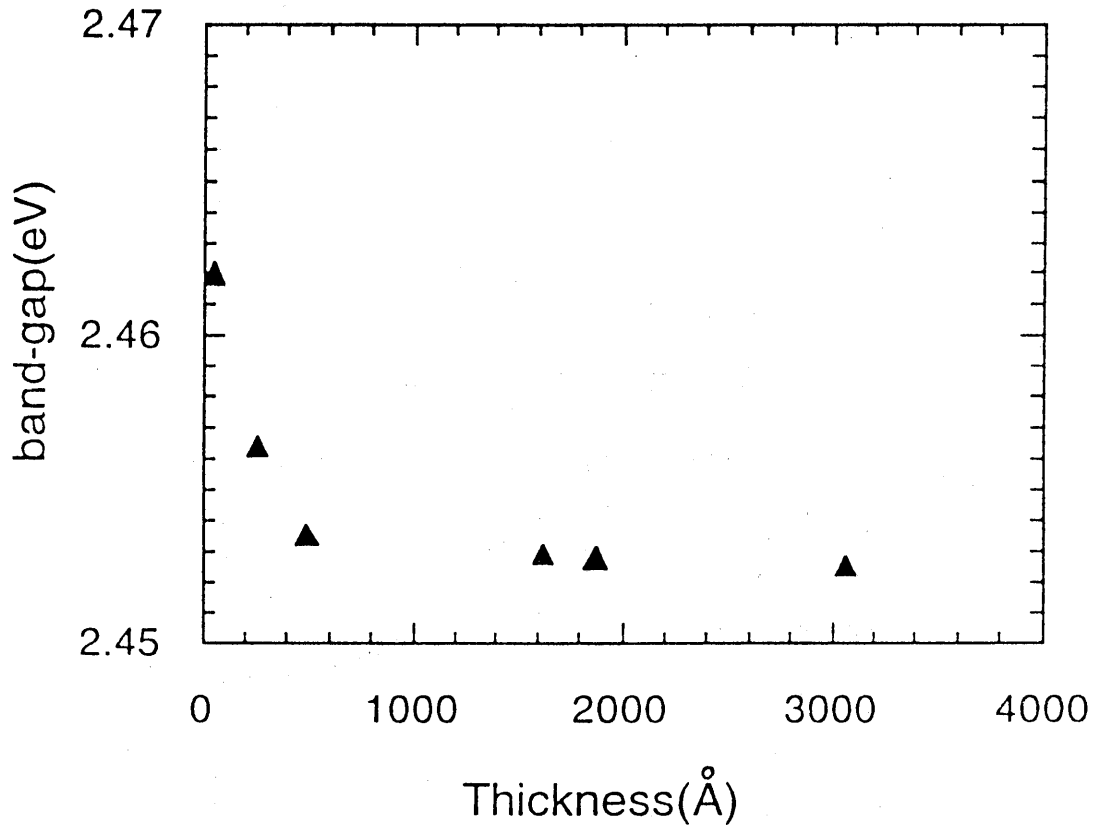


Fig-7: Optical band energy of CdS films versus the thickness of films.

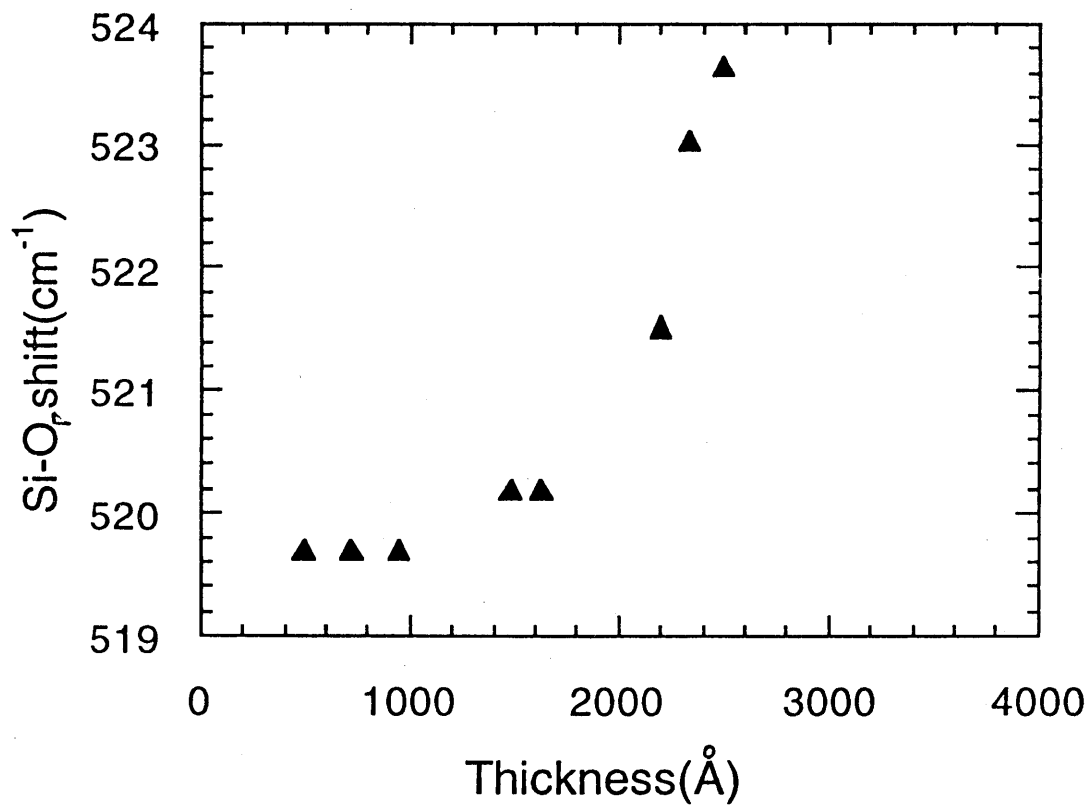


Fig-8: Frequency of Si-O_r Raman peak as a function of CdS film thickness.