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Phase Transition from the Cubic to the Hexagonal Modification in Thin CdS Films on InP(110)

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CdS films were prepared by molecular beam epitaxial growth on clean cleaved InP(110) substrates. Films with thicknesses in the 200 nm range were studied by optical techniques: spectroscopic ellipsometry, reflection and photoluminescence. The film thickness and the dielectric function of the films are evaluated from the ellipsometry data. The feature in the imaginary part of the film dielectric function which is induced by the E_1 interband transition in CdS is found to be extremely sensitive to the crystal modification. A splitting of this feature occurring at approximately 200 nm indicates a phase transition in the thin films from the cubic to the hexagonal modification. This is confirmed by reflection measurements which show two series of reflection loops for both modifications for film thickness exceeding 200 nm. The energy positions of the free excitons of the hexagonal and cubic modifications are derived. In addition, the band gap for the cubic modification is determined for the first time. The photoluminescence spectra also reveal cubic and hexagonal contributions of donor–acceptor pair recombinations. From the excitonic transitions attempts are made to identify the main impurities in the layers.

KEYWORDS Heteroepitaxy CdS Crystal structure Photoluminescence Reflection Thin films

INTRODUCTION

Recently, the molecular beam epitaxial growth of CdS on clean cleaved InP(110) was investigated using *in situ* Raman and photoluminescence spectroscopies as well as *ex situ* spectroscopic ellipsometry.[1,2] The results have shown that CdS grows in the metastable cubic zincblende modification. These studies were limited to very thin layers with maximum thicknesses in the 20 nm range. One interesting question arising from this previous work was how long the CdS would continue to grow in its metastable modification or whether it will return to its preferred wurtzite structure at larger coverages. In this paper a study using different non-destructive optical probes was carried out to characterize CdS layers in a thickness range where a phase transition occurs.

EXPERIMENTAL

CdS films were grown by molecular beam epitaxy using a single Knudsen cell containing high-purity (5N) polycrystalline CdS powder. The base pressure in the ultrahigh-vacuum (UHV) chamber was better than 2×10^{-10} mbar and the evaporation rate was approximately $40\ \mathrm{nm\,h^{-1}}$ using a cell temperature of 590 °C. UHV-cleaved InP(110) crystals were used as substrates. They were kept at 200 °C during CdS deposition. All samples under investigation were prepared in one run, i.e., without breaking the vacuum or refilling the CdS source. Immediately after breaking the vacuum, the samples were investigated by spectroscopic ellipsometry (SE) and thereafter by reflection and photoluminescence (PL).

Ellipsometry spectra were recorded at room temperature in the spectral range from 2 to 5.5 eV

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using a rotating analyser type of instrument. A xenon high-pressure arc lamp served as a light source. After passing a 0.1 m focal length monochromator equipped with a spherical holographic grating, the light was polarised by a quartz Rochon prism. Light reflected from the sample was analysed by the rotating prism analyser and finally detected by a photomultiplier with an S20 cathode. The signal was digitized in real time and then Fourier transformed and processed by a microcomputer.

A halogen lamp (100 W) was employed for the reflection measurements, while the ultraviolet lines of an Ar^+ ion laser were used for recording the PL spectra. For these experiments the samples were cooled to $T = 1.6$ K in a suprafluid helium cryostat. The light reflected or emitted from the samples was analysed using a double-grating monochromator and detected by a bialkali photomultiplier.

RESULTS AND DISCUSSION

Considering SE, the dielectric function of the CdS films was derived from the measured effective dielectric functions using a three-phase (ambient–film–substrate) model. The procedure used also yields the film thickness to an accuracy of

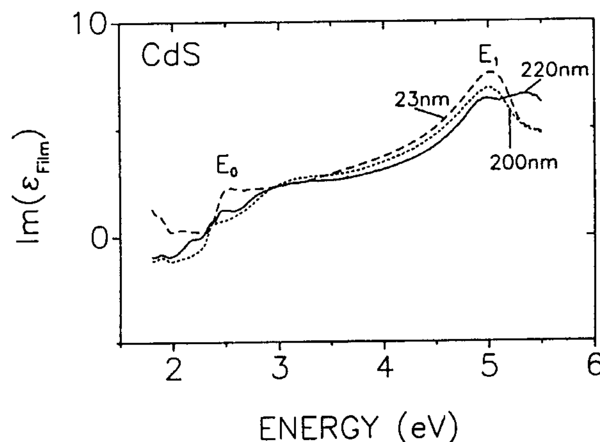

Fig. 1. Imaginary part of the CdS film dielectric function derived from a three-phase model, showing results for samples of thickness 23, 200 and 220 nm. The discrepancies near 2 eV may be attributed to the presence of reacted layers at the interface between CdS and InP

approximately 0.5 nm and was previously applied successfully to the ZnSe/GaAs system.[3] Figure 1 shows the imaginary parts of the film dielectric function for three different samples. The film thicknesses given in Fig. 1 are derived from the SE data. As a standard for the dielectric function of a thin cubic CdS film, the result for a 23 nm thick sample is included. In this thickness range CdS films were shown to be cubic according to Refs. 1 and 2. The apparent features of this film dielectric function are clearly due to the direct gap E_0 of cubic CdS near 2.41 eV and the E_1 optical transition near 5 eV. In particular, this E_1 feature is entirely different for hexagonal CdS. As pointed out by Cardona *et al.*,[4] this peak should clearly split into two components for the hexagonal modification. However, up to 200 nm of CdS film thickness this is not the case, indicating that this sample is still predominantly cubic. For the somewhat thicker film of 220 nm, on the other hand, a clear splitting is observable and therefore it can be concluded that a phase transition from the cubic to the hexagonal phase takes place in this thickness range. The presence of hexagonal CdS also induces the second step in the direct gap energy range of the dielectric function, which is in agreement with a room temperature band gap of the hexagonal modification of close to 2.5 eV.[5] In this photon energy range contributions of both modifications can be seen. Consequently, the film is most likely to be composed of a top layer of hexagonal CdS and underlying cubic CdS. In the same spectral region the dielectric function for the slightly thinner 200 nm film also differs somewhat from that of the cubic standard 23 nm film. This could well be due to a minor contribution of the hexagonal phase in this film.

In order to confirm the phase transitions, reflection experiments were performed. The results are shown for the above-mentioned samples ((a) 200 and (c) 220 nm) in Fig. 2. Clearly, the thinner film is cubic only exhibiting the strain-split free exciton loops X_{lh} (light hole) and X_{hh} (heavy hole) in the 2.45 eV energy range. As a result, the energy positions of the free excitons from the cubic modification can be determined for the first time. Additional exciton loops A and B shifted by approximately 100 meV towards higher energy appear for the thicker film. These two features can be assigned unambiguously to the hexagonal phase and are correlated with the A and B valence bands.[6] For decreasing energy the onset of Fabry–Perot interferences becomes apparent.

Table 1. Energy positions (eV) of the free excitons in the hexagonal and cubic modifications

CdS ($T = 1.6$ K)	Hexagonal			Cubic	
	A	B	C	X_{lh}	X_{hh}
Bulk[6]	2.553	2.569	2.630		
CdS on InP	2.5547	2.5734	—	2.4602	2.4509

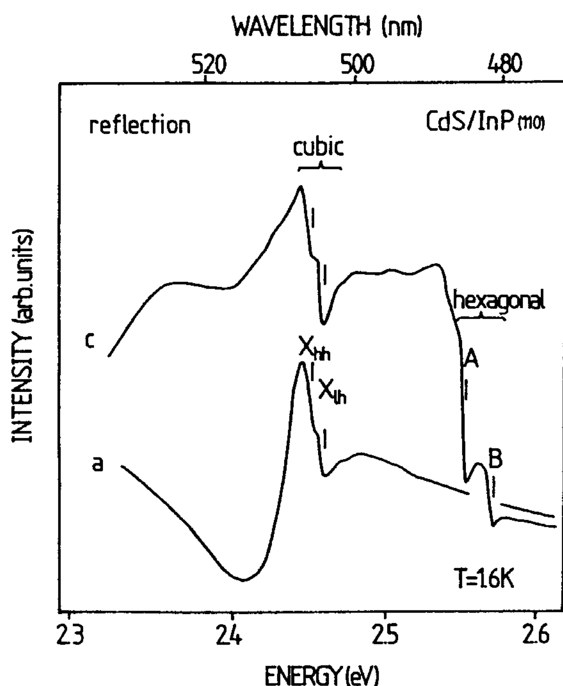

Fig. 2. Reflection spectra for samples of thickness (a) 200 and (c) 220 nm in the excitonic energy range

In addition, polarization-dependent reflection measurements were performed. They did not reveal any significant changes in the intensity of the hexagonal reflection loops. Consequently, it can be excluded that the *c*-axis of the hexagonal modification lies in the (110) plane and it may be expected that it lies along a [111] direction of the substrate, i.e. at an angle to the (110) plane.

The energy positions of all free excitons are given in Table 1. Owing to the strain effects between the film and the substrate, the energy positions for the hexagonal A and B excitons are slightly higher than the well-known bulk values. According to the lattice mismatch of 0.74% between CdS and InP, one may expect an energy

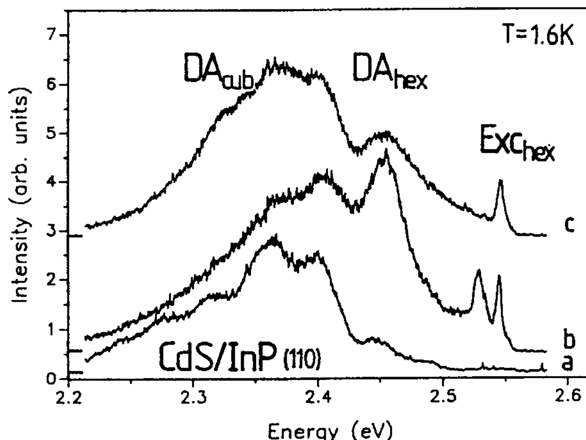

Fig. 3. Photoluminescence spectra for samples of thickness (a) 200, (b) 220 and (c) 220 nm in the near-band gap energy range

difference of 39 meV between the 'lh' and 'hh' components of the cubic valence band for layer thicknesses below the critical thickness. In a previous work[1] the critical thickness was calculated to be 25 nm, in good agreement with experiment (21 nm). Since the layers investigated here are far beyond the critical thickness, the strain is most likely reduced due to partial relaxation of the layer. Consequently, the energy difference between the strain-split free excitons is lower, approximately 10 meV in this case.

The PL spectra recorded in the near-band-gap energy region for three different samples (a)–(c) are plotted in Fig. 3. Besides transitions from excitons of the hexagonal modification (samples (b) and (c)), donor–acceptor pair (DAP) recombinations from both the hexagonal and cubic modifications are observable. While for the thinnest sample (a) the cubic DAP contribution is dominant, samples (b) and (c) show DAP contributions of comparable intensity from both modifications. The difference in samples (b) and (c), although nominally of equal thickness, may be attributed to minor inhomogeneities observed in the thickness across the individual samples. Owing to the diffusion of photoexcited carriers in the layer, the PL light can originate from regions much deeper than that probed in a reflection measurement, for which the probing depth is limited by the penetration depth of light. As a result, the underlying cubic parts of the CdS layers contribute intensely to the spectral shape. For the hexagonal contribution there is a superimposition of the high-energy series (HES) and the

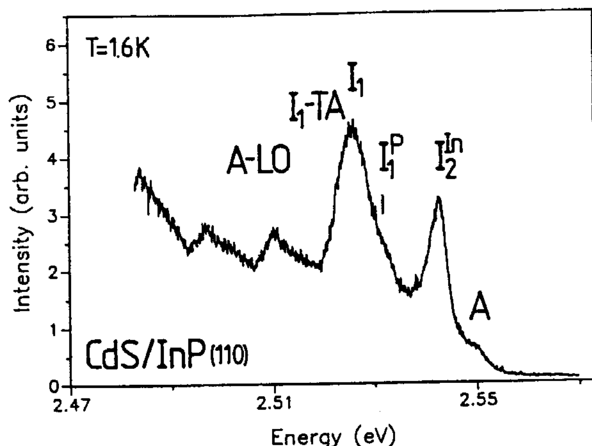

Fig. 4. An enlarged part of spectrum (b) of Fig. 3 in the excitonic energy range

low-energy series (LES), in agreement with results from bulk CdS.[7] Furthermore, the LO replica most clearly observable in the spectrum of sample (a) reproduces with an energy of 38 meV, in excellent agreement with Ref. 8.

The excitonic region of the spectrum of sample (b) is enlarged in Fig. 4. Here a weak feature from the free exciton A can be seen at the same energy position as previously evaluated from the reflection measurement. The spectrum is dominated, however, by donor-bound (I_2) and acceptor-bound (I_1) excitons. I_2 is assigned to indium, while the high-energy shoulder of the I_1 feature is attributed to phosphorus. Both elements may occur in the grown CdS layer as a result of out-diffusion from the InP substrate. The I_1 feature, on the other hand, is most likely induced by contaminants present in the CdS source material.

CONCLUSIONS

From the experimental results described above, it can be concluded that for the given growth parameters a phase transition takes place at approximately 200 nm from the substrate-stabilized cubic modification to the naturally preferred hexagonal wurtzite structure. The thickness of its appearance is much larger than the critical thickness of about 21 nm for the CdS/InP system. However, dislocations formed at or beyond the critical thickness can probably lead to a roughening of the surface for subsequent growth. This roughening will then finally lift the condition of substrate-stabilized growth and this obviously happens at a thickness approximately 10 times larger.

Considering that the binding energies of free excitons are equal for the cubic and hexagonal modifications, an estimation of the energy difference of the band gaps for the two modifications can be made as approximately 100 meV. The value for the direct band gap of cubic CdS at liquid helium temperature is thus close to 2.48 eV.

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REFERENCES

1. D. R. T. Zahn, Ch. Maierhofer, A. Winter, M. Reckzügel, R. Srama, A. Thomas, K. Horn and W. Richter, *J. Vac. Sci. Technol. B*, 1991, **9**, 2206.
2. D. R. T. Zahn, Ch. Maierhofer, A. Winter, M. Reckzügel, R. Srama, U. Rossow, A. Thomas, K. Horn and W. Richter; *Appl. Surf. Sci.*, 1992, **56–58**, 684.
3. C. Nowak, D. R. T. Zahn, U. Rossow and W. Richter, *J. Vac. Sci. Technol. B*, 1992, **10**, 2066.
4. M. Cardona, M. Weinstein and G. A. Wolf, *Phys. Rev.*, 1965, **140**, A633.
5. V. V. Sobolev, V. I. Donetskikh and E. F. Zagainov, *Phys. Semicond.*, 1978, **12**, 646.
6. D. W. Langer, R. N. Eumema, E. Koh and K. Takeo, *Phys. Rev. B*, 1970, **2**, 4005.
7. D. G. Thomas, R. Dingle and J. D. Cuthbert, *Proc. 7th Int. Conf. on Semiconducting Compounds*, Providence, R.I., USA, W. A. Benjamin Inc., New York, 1967, p. 863.
8. D. C. Reynolds, C. W. Litton, T. C. Collins and E. N. Frank, *Proc. 10th Int. Conf. on Semiconductors*, Cambridge, MA, United States Atomic Energy Commission, Division of Technical Information, Oak Ridge, Tennessee, 1970, p. 519.