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Fabrication and Characterization of CdS/GaAs Films and CdS/ZnS Strained-Layer Superlattice Grown by Low-Pressure MOCVD Method

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Heteroepitaxial CdS films with good optical quality have been grown on (100) and (111)A GaAs substrates around 300 °C by low-pressure metalorganic chemical-vapour-deposition (MOCVD) using $(CH_3)_2Cd$ and H_2S gases. The (100) oriented film exhibits a cubic modification, but involves dislocations and stacking faults. On the other hand, the film grown on (111)A substrate shows a hexagonal structure and its 4.2 K photoluminescence (PL) is dominated by strong I_2 (neutral-donor bound exciton) line at 2.547 eV and I_1 (neutral-acceptor bound exciton) line at 2.534 eV, and a donor-acceptor pair band at 2.447 eV. CdS/ZnS strained-layer superlattice has for the first time been fabricated on GaAs substrate by MOCVD. 2MeV plan-view TEM was adopted to characterize the structural properties.

1. Introduction

CdS holds much promise for use in efficient photovoltaic solar cell consisting of CdS/CdTe[1)] and CdS/ZnTe[2)] heterojunction because of the energy band gap of CdS (~2.3 eV at room temperature) suitable for a window material. However, it has in fact been known that it is very difficult to grow thin film of a cubic modification with excellent optical quality below 400 °C. It has been reported so far that CdS layers grown by a metalorganic chemical-vapour-deposition (MOCVD) method, have the hexagonal wurtzite structure in the temperature range 350 to 450 °C.[3,4)] In spite of large lattice mismatch between CdS film and GaAs substrate, the good surface morphology can be obtained. However, the electrical and optical properties of the MOCVD-grown CdS films have not been reported until now in detail in comparison with other II-VI compound films such as ZnSe, ZnS and CdTe.

If CdS with a cubic modification is possible to fabricate by MOCVD, the CdS-ZnS strained-layer superlattice (SLS)[5)] which indicates a type I structure can provide a large quantum confinement effect for electrons in CdS well compared with ZnSe-ZnS SLS.

The purpose of this paper is to characterise single heteroepitaxial CdS/GaAs films and CdS-ZnS SLSs grown by low-pressure MOCVD using X-ray diffraction, 2 MeV transmission electron microscope (TEM) and 4.2 K photoluminescence (PL). Particularly, it concerns with a preliminary survey as to whether or not excitonic luminescence observed in the present SLS occurs in the type I superlattice structure.

2. Experimental procedures

2.1 Growth of CdS film and CdS/ZnS SLS

Dimethylcadmium $[(CH_3)Cd$, DMCd] in He gas mixture was used as metalorganic alkyl source material. A DMCd concentration of 0.1 % was used together with 10 % H_2S in H_2 gas for the epitaxial growth. Cr-doped semiinsulating GaAs substrates with (100), and (111) A and B faces were used. A low-pressure MOCVD reactor and growth system were described in ref. 6). The growth condition is shown in Table 1.

CdS-ZnS SLSs were fabricated using same computer-controlled MOCVD system. Dimethylzinc $[(CH_3)_2Zn$, DMZn, 1 %] diluted in He gas and DMCd as the MO sources, and 10 % H_2S in H_2 gas were used for the growth of superlattices. The growth rate is estimated to be 0.42 and 0.32 μm/h for CdS and ZnS films. The growth condition is also listed in Table 1.

Table 1 Growth Conditions

	CdS Film	CdS-ZnS Superlattice
Substrate	GaAs(100),(111)	GaAs(100),(111)
Substrate Temp.	250°C - 350°C	300°C - 350°C
Flow Rate of DMCd	5.80×10^{-6} mol/min	5.80×10^{-6} mol/min
Flow Rate of DMZ		6.70×10^{-6} mol/min
Flow Rate of H_2S	1.34×10^{-3} mol/min	1.34×10^{-3} mol/min
VI/II Ratio	23	23 (CdS), 20 (ZnS)
Pressure	0.8 Torr	0.4-0.8 Torr

2.2 Characterization

The films and SLSs were assessed by both observation and analysis of X-ray diffraction peaks (satellite peaks for SLS) and electron diffraction patterns. PL measurements were performed at 4.2 K using a conventional lock-in detection technique and a He-Cd (325 nm, 1.8 mW) laser as an excitation source in conjunction with a 1 m Jobin-Yvon single grating monochromator. A 2 MeV high voltage transmission electron microscope (HVTEM) was used to evaluate the microstructure of the epitaxial films and SLSs. All samples, after the removal of the substrate by chemical etching, were observed in a plan-view bright-field image with a resolution of 4.6 Å.

3. Results and discussion

3.1 CdS/GaAs films

Characteristics of CdS epitaxial films were studied as a function of growth temperature (T_S) and substrate orientation at a constant VI/II ratio (23).

Figs. 1 (A) and (B) show the surface morphologies observed by SEM of CdS films grown on (100) substrates at T_S=250 and about 300 °C (thickness ~0.4 μm). Above 300 °C, specular surface morphology can be obtained and the X-ray diffraction spectrum shows only (200) peak at 2θ=30.6 ° which is representative of pure cubic CdS. Consequently, the lattice constant is calculated to be 5.848 Å. On the other hand, at T_S=350 °C, the X-ray spectrum includes (006) peak at 2θ=87.1 °, indicating a hexagonal structure.

In order to confirm the cubic structure, we have measured the electron diffraction patterns and plan-view bright-field image using 2 MeV TEM. Figs. 2 (A) and (B) show the bright field TEM images of CdS films grown on (100) (Ts=300 °C), (111)A (Ts=350 °C), respectively. The diffraction pattern of Fig. (A) indicates clearly regular diffraction spots and suggests that the film obtained has a perfect cubic modification. However, there exist several dislocations and stacking fault fringes arising from lattice mismatch. Similarly, Fig. (B) shows the clear diffraction spots, but is different from that of (A). In this case, the hexagonal structure is certainly approved and large densities of stacking faults are seen.

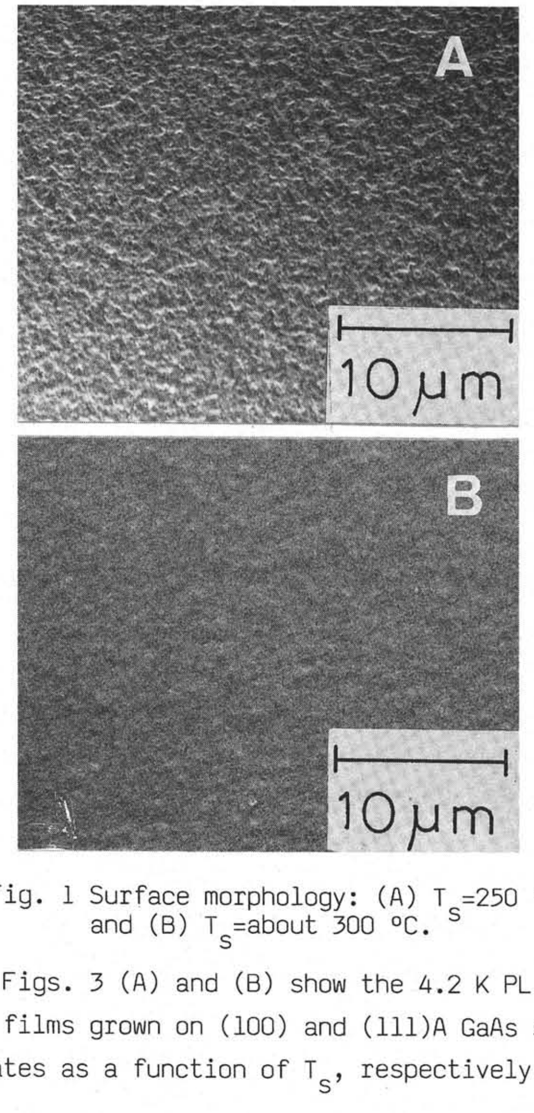

Fig. 1 Surface morphology: (A) T_S=250 °C and (B) T_S=about 300 °C.

Figs. 3 (A) and (B) show the 4.2 K PL of CdS films grown on (100) and (111)A GaAs substrates as a function of T_S, respectively.

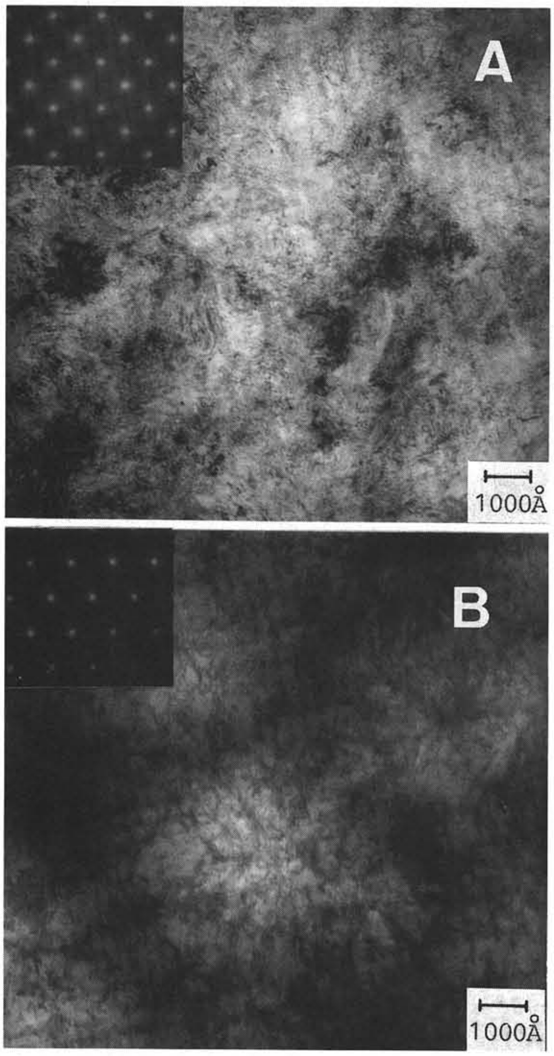

Fig. 2 Plan-view TEM bright-field image and electron diffraction pattern: (A) (100) and (B) (111)A substrate.

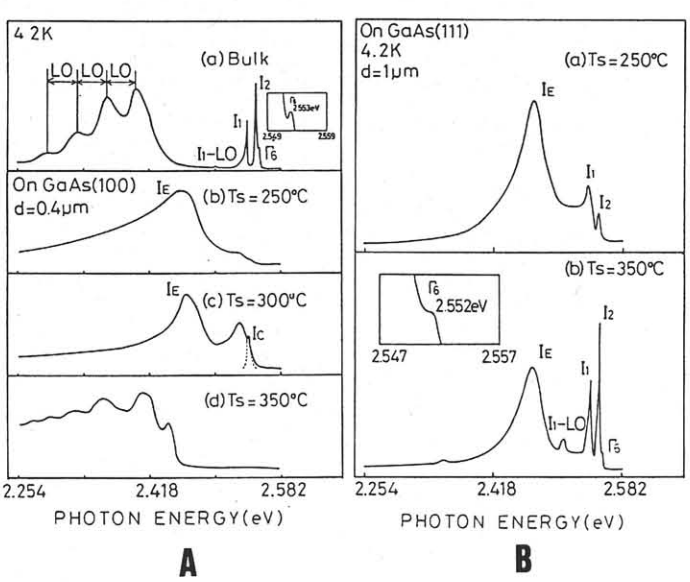

Fig. 3 PL spectra obtained at 4.2 K of CdS bulk and thin films: (A) (100) and (B) (111)A GaAs substrate.

First of all, the PL spectrum of bulk CdS at 4.2 K is shown in (a) of Fig. (A). The I_2 line at 2.545 eV is attributed to a neutral-donor bound exciton (BE) and the I_1 line at 2.532 eV and its LO-phonon side band are due to a neutral-acceptor BE. The Γ_6 is ascribed to free exciton. Usually, the LO-phonon replicated edge-emission band at 2.4 eV is observed at 4.2 K.[6,7]

In MOCVD-grown CdS films on (100) substrate, the observed PL spectra are notably different from that of bulk; with increasing T_s, the deep-level band increases in intensity,but the I_C line at 2.539 eV which appears at T_s= 300 °C may be due to the free-exciton emission. We also consider that other peak just behind the I_C line may be attributed to BE. The most prominent I_E band at 2.459 eV is ascertained to a donor-acceptor pair recombination by excitation-intensity dependence of the emission intensity.

On the other hand, as shown in Fig. (B), we have observed very strong I_2 and I_1 BE lines comparable with those of bulk CdS. Particularly, in (b), the Γ_6 exciton line appears at 2.552 eV. It is noted that there appears a broad non LO-phonon replicated edge emission I_E band at 2.447 eV which has never been detected in bulk CdS. With increasing T_s, the I_2 line becomes strong in intensity than that of the I_1 line. It is therefore suggested that the CdS film grown on (111)A substrate exhibits a typical PL feature associated with hexagonal modification. It is also particular note that the I_E band is commonly observed in both the cubic and hexagonal structured CdS thin films by MOCVD.

3.2 CdS-ZnS SLS

The lattice mismatch between cubic ZnS (a=5.4093 Å) and CdS (a=5.848 Å) is about 7 %, so that a critical thickness for each layer along the <100> growth direction is calculated to be about 30 Å. It is therefore evident that the CdS well receives compressive strain and the ZnS barrier receives tensile strain.

Fig. 4 shows the X-ray diffraction spectrum obtained around the GaAs (222) diffraction peak of CdS(20 Å)-ZnS(42 Å) SLS (200 layers) grown on (111)B substrate. There appear clearly higher-order satellite peaks (n=1~-2) which are a direct identification for an existence of good crystallinity superlattice. The strain -induced spectral changes seem to be same as that of ZnSe-ZnS SLS, but the intensity ratio between n=-1 and n=0 peak is different.

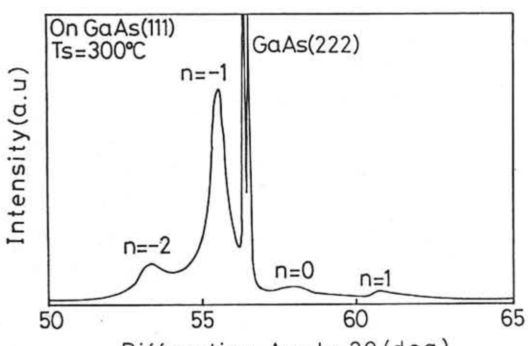

Fig. 4 X-ray diffraction spectrum of CdS (20 Å)-ZnS (42 Å) SLS grown on (111)A substrate.

Figs. 5 (A) and (B) represent the plan-view bright-field TEM images and electron diffraction patterns taken in CdS (23 Å)-ZnS (35 Å) SLS on (100) and in CdS (20 Å)-ZnS (42 Å) SLS on (111)B GaAs substrates after the removal of the substrate by chemical etching, respectively. In Fig. (A), the diffraction spots consist of irregular diffraction spots due to the presence of extra spots. While, in Fig. (B), the diffraction pattern consists of regular spots, indicating that a strained-layer growth is certainly realized.

In CdS (20 Å)-ZnS (42 Å) SLS grown on (111)B substrate, PL spectrum at 4.2 K is dominated by a broad band (the linewidth of 235 meV) locating at about 2.4 eV which is smaller than the band gap (E_g) of CdS. We therefore calculated theoretically the energy peak shifts of the luminescence between the quantized energy levels in CdS-ZnS SLS as a function of CdS well

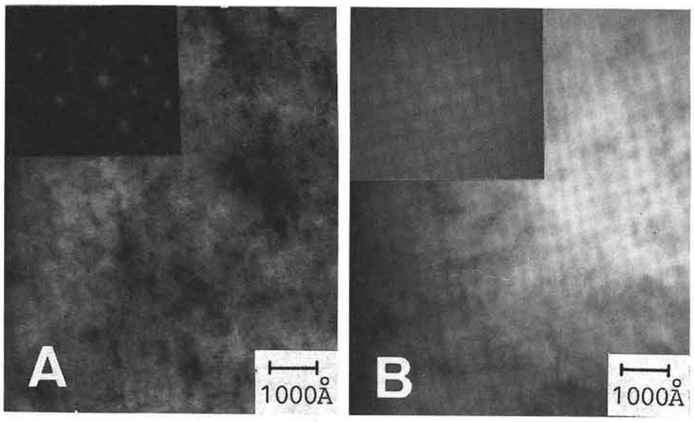

Fig. 5 TEM bright-field image and electron diffraction pattern of SLSs: (A) (100) and (B) (111)B GaAs substrate.

layer thickness by considering the variations of the ΔE_C and ΔE_V, and both the E_g of CdS and ZnS.[8] If the deformation potential constant b is less than about -2 eV, one can expect that the quantized electrons and holes are separeted each other and as a result the type I structure appears when the CdS thickness below about 20 Å. This expectation may result in a weak PL band which locates below the E_g of CdS.

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