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STRUCTURE, SURFACE MORPHOLOGY AND OPTICAL PROPERTIES OF THIN FILMS OF ZnS AND CdS GROWN BY ATOMIC LAYER EPITAXY

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In this communication we report successful growth of monocrystalline cubic ZnS and monocrystalline and polycrystalline cubic and wurtzite films of CdS by atomic layer epitaxy. Structural and optical properties of these films are analysed. ZnS (and CdS/ZnS) films grown on GaAs substrate are cubic. Atomic layer epitaxy grown films provide several advantages over ZnS and CdS materials grown by other techniques, especially compared to bulk material, which is grown at higher temperatures. First results for ZnS/CdS/ZnS quantum well structures are also discussed.

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A fundamental benefit of the atomic layer epitaxy (ALE) method is that chemical reactions proceed only in the adsorbed film. This allows to avoid the common problem of conventional chemical vapour deposition (CVD) processes, where gas precursors also react in the vapour phase above the substrate. Until now wurtzite films of ZnS, used in thin film electroluminescence displays [1], were deposited by the ALE method on either Al_2O_3-covered or uncovered soda glass substrates. These films were polycrystalline. Thus, the technique was often called ALE-CVD or atomic layer deposition and correctness of epitaxy-related name was argued. We report here the first successful growth of monocrystalline cubic ZnS and monocrystalline and polycrystalline films of CdS, and their quantum well (QW) structures, by ALE using the exchange reaction of hydrogen sulphide with chlorides of zinc (for ZnS growth) and cadmium (for CdS growth). Gas-flow version of the ALE, as used by us[†], offers good possibilities to engage chemical exchange reactions, which, for example, is difficult in the case of ALE processing by molecular beam epitaxy.

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The ZnS films were deposited on either (111) or (001) GaAs substrates at 510°C temperature [2, 3]. Crystal structure of these films and the morphology of their surfaces were studied with X-ray diffraction, reflection high-energy electron diffraction (RHEED) and scanning electron (SEM) and atomic force (AFM) microscopies. The X-ray data of our ZnS films deposited on (001) and (111) GaAs substrates, supplemented by RHEED analysis, show that ZnS films are monocrystalline and cubic. While ZnS films on (001) GaAs are expected to be cubic (for example by analogy to cubic films of GaN grown on (001) GaAs [4]), pure cubic growth of ZnS on (111)-oriented GaAs is a new interesting property of the ALE-grown films. Moreover, RHEED investigations indicate that microtwins (inclined planar defects) are absent, even though the ALE-grown films show granular microstructure, as follows from the roughness examination by AFM. The ALE films have relatively flat surfaces, showing only small granular substructure in sub-μm range.

CdS deposition on uncoated and ZnS-coated (001) GaAs was led using H_2S and $CdCl_2$ (at the temperature of 460°C) precursors. The substrate temperature was 510°C, the same as for ZnS [2, 3], and the parameters of ZnS deposition in the multilayer processing were the same, as used previously. The cubic CdS films deposited on (001) GaAs substrate coated with ALE-grown ZnS maintain (001) orientation (Fig. 1a). The cubic structure is, however, slightly tetragonally

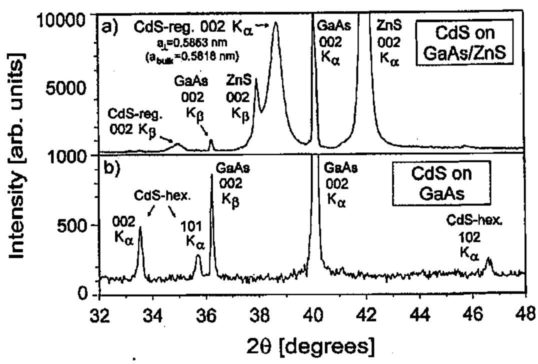

Fig. 1. X-ray diffraction patterns obtained in the "polycrystalline" mode by $\Theta-2\Theta$ scan with Co K_α radiation, wide slits and sample rotated around normal to the surface of two CdS films grown by ALE on (001) GaAs: covered with 900 nm ZnS layer (a) or uncovered (b).

distorted by strain built into the epilayer. Till now, CdS films grown directly on GaAs substrate (both for (001) and (111) orientations) have been wurtzite and polycrystalline (Fig. 1b). We have also grown first single quantum well (QW) GaAs/ZnS/CdS/ZnS structures on either (001) or (111) GaAs substrates.

Photoluminescence (PL), time-resolved PL and monochromatic, spatially-resolved cathodoluminescence spectroscopy was used to determine optical properties of ZnS and CdS films and their QW structures. The relationship between surface morphology and the optical properties of the films was also studied. Both ZnS and

CdS films show rather weak self-activated PL emissions. These emissions are weak even though our films are likely Cl-doped, since zinc and cadmium chlorides are used in the growth process. We infer that self-compensation of the ZnS and CdS can thus be avoided in the ALE process. This result means that the use of the low growth temperature ALE technique leads to the reduced formation of both planar and intrinsic point defects. This appears to be a very important advantage of the ALE-grown films. For example, very effective self-compensation process leads to a high resistivity material and prohibits wider use of ZnS material in light emitting devices, for ZnS grown in a conventional way.

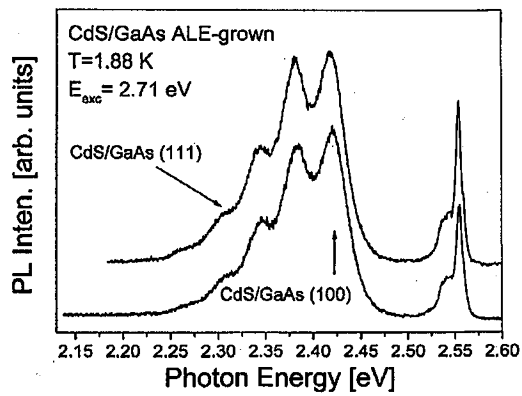

Fig. 2. 2 K photoluminescence spectrum of two wurtzite CdS epilayers grown on either (001) or (111) GaAs.

In CdS the "edge" PL emission, shown in Fig. 2 for two layers grown directly on GaAs, is dominated by two overlapping transitions of free electron-to-shallow acceptor and shallow donor-to-shallow acceptor pair (DAP) nature, with well-resolved longitudinal optical (LO) phonon replica at each 38 meV, which agrees with 38.07 meV value of LO-phonon of bulk CdS crystals of wurtzite structure. The relative intensity of these two emissions depends on excitation conditions and on sample temperature. At low temperature the DAP transition dominates, as confirmed in our time-resolved experiments. We have observed a typical energy-dependent and nonexponential decay of the PL, which is related to the distance distribution of recombining D–A pairs. Unexpectedly, the shallow DAP PL is more intense and is better resolved in polycrystalline wurtzite films than in monocrystalline cubic affected, however, by the lattice parameter mismatch. A double line PL is also observed (see Fig. 2), with the maximum at about 2.555 eV. By analogy to bulk CdS, this emission may be due to either A-exciton (observed at 2.552 eV) or I_2-exciton (donor bound exciton).

Shallow DAP PL is also observed in our first ZnS/CdS/ZnS single QW structures grown on either (001) or (111) GaAs. A weaker double line excitonic PL is also observed, with the maxima at about 2.564 eV and 2.547 eV for QW 8.5 nm wide. Confinement energy remains, however, unknown since QW is likely of cubic structure and the band gap energy of cubic CdS remains unknown. It is close to that of wurtzite CdS, but exact value is missing [5]. It is difficult to determine this value, at present. We do not know the magnitude of strain effects. For example, the DAP PL has zero-phonon line at about 2.42 eV, which is higher by about 25 meV with respect to the relevant position of the shallow DAP recombination in bulk CdS of wurtzite structure. For bulk CdS samples, the shallow DAP transition is related to the 18.7 meV deep donor of unknown chemical origin. In the case of our Cl-rich growth conditions chlorine may be introduced into CdS. Chlorine is likely to introduce shallow donor states in CdS lattice and thus may be active in DAP transitions. We are unable to determine, however, if the shallow donor active in the DAP transition in our samples is of the same origin as for bulk CdS crystals.

In conclusion, we report here successful growth of monocrystalline ZnS and monocrystalline and polycrystalline CdS films by the ALE method. The ZnS films show good structural quality and are of pure cubic phase. No microtwins are observed and self-compensation mechanism is less efficient. CdS films grown on GaAs coated with ZnS are cubic and monocrystalline. The films grown directly on GaAs are polycrystalline but show intense PL in the band edge region.

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