

Priority communication

Shift of the excitonic resonances by thermal strain and lattice mismatch in CdS thin epitaxial layers

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CdS was grown on BaF₂ and SrF₂ by hot wall epitaxy and on BaF₂ by pulsed laser evaporation. Reflection measurements on the epitaxial layers showed energy shifts of A- and B-excitons. The shift on the surface of the film is different from that on the interface side. Calculations of the shift using known data of the deformation potentials confirmed the experimental results. We give here an explanation of these results taking into account thermal strain on the surface side and additional mismatch strain on the interface side.

II–VI wide-gap semiconductors are of new interest, since a breakthrough concerning II–VI semiconductor lasers happened in 1991 [1]. Presently, the successful activities concerning blue-green laser diodes are based on ZnSe. The II–VI semiconductors offer, however, several other wide gap materials, namely ZnS, ZnO and CdS, which are capable of laser emission in the blue-green to UV spectral region. We concentrate here on the latter, since we have a lot of experience with this material. The lasing transitions result from optical transitions near the band gap. Therefore the influence of strain on optical and electrical properties of semiconductors is presently one of the main points of interest during the growth process of epitaxial thin films and of quantum wells. Critical thickness and dislocation formation are among the most important parameters in strained layers. In the results presented here, we found evidence of different strain

contributions in linear optical spectroscopy, associated with thermal and mismatch strain. The samples are thin epitaxial CdS layers grown by hot wall epitaxy (HWE) on the (111) surfaces of freshly cleaved BaF₂ and SrF₂ crystals and deposited on polished BaF₂ (111) by pulsed laser evaporation epitaxy (PLEE). The HWE growth started at an initial growth temperature, which was varied from 340 to 410°C for the films grown on BaF₂. During the growth the substrate temperature was raised to the source temperature and kept on this temperature for several minutes, before growth continued at the initial temperature or 100°C below the source temperature. This procedure avoided growth of pyramids on the surface which appear on CdS surfaces and lead to an improved luminescence due to bound excitons and higher energy transitions [2]. The latter could not be identified for sure. The substrate temperatures for SrF₂ ranged from 460 to 550°C and were kept constant during growth. The source temperatures were 600°C for BaF₂ substrates and 630°C for SrF₂ substrates. The thickness of the films ranged from 0.5 to 2.8 μm. PLEE growth was performed on freshly cleaved BaF₂ at 400°C and on polished BaF₂ (111) at 300°C, which was

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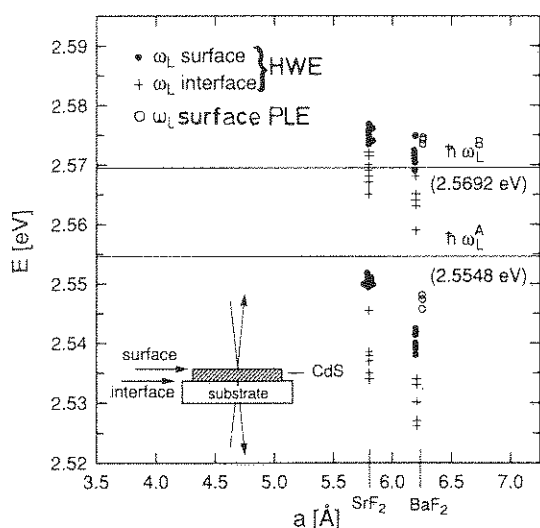


Fig. 1. The position of the longitudinal $A\Gamma_5^-$ and $B\Gamma_5^-$ exciton resonance of CdS deduced from reflection spectra for layers grown on the designated substrates. The lattice constants on the abscissa refer to the hexagonal unit mesh at room temperature. Horizontal lines: bulk values.

cleaned with acetone, deionized H_2O , ethanol and deionized H_2O again, respectively. The substrates were preheated to 400°C in vacuum for 30 min before growth started.

Measurements were made of the reflection and of the absorption near band edge at 4 K. Reflection spectra were taken from the surface and from the interface sides, respectively. The films showed clear excitonic features in lumines-

cence, absorption or/and in reflection spectra [2]. The latter were used to determine the exciton energies. The longitudinal resonance energies were evaluated from the reflectivity minimum of the signal [3]. Fig. 1 shows the longitudinal energies of A- and B-excitons measured in the films. All excitonic resonances are shifted compared to the values of bulk CdS [4,5]. On the fluorides the exciton energy split is larger on the surface side than at the interface side. Furthermore the low energy shift of the A-exciton in the films grown on BaF_2 is larger than that for CdS on SrF_2 . The values for PLE grown films (open circles) show no significant difference from the values of the HWE grown films. Interface values of these samples are not available. Because of the poor interface quality no clear excitonic reflection structures could be detected.

One can discuss these observations taking into account the lattice constants of the materials and strain in semiconductors due to the misfit of substrate and layer and due to the thermal strain in analogy to refs. [6,7]. The misfit of the hexagonal cell of CdS to the (111) surface of SrF_2 during growth ranges from -0.035% to -0.2% [8,9], depending on the substrate temperature, if misfit is defined as $\epsilon = (a_{\text{sub}} - a_{\text{CdS}})/a_{\text{CdS}}$. For the films grown on BaF_2 the misfit ranges from 6.53% to 6.65% [9,10] at the initial growth temperatures. At 4 K, the misfits alter their values to $\epsilon = -1.2\%$ for CdS/ SrF_2 and to $\epsilon = 5.6\%$ for CdS/ BaF_2 by thermal contraction.

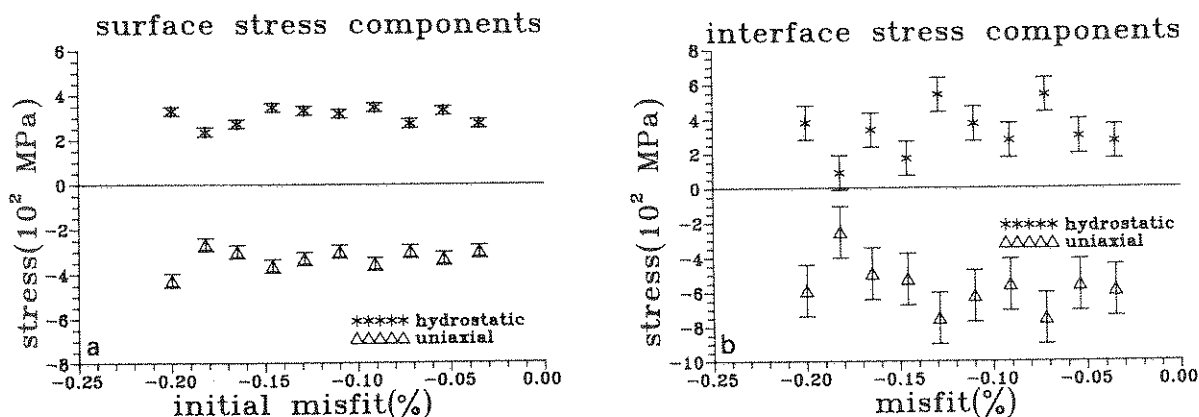


Fig. 2. Evaluated stress values for CdS on SrF_2 (111): (a) surface side, (b) interface side.

In the following we concentrate on the system CdS on SrF_2 . Since the misfit is almost negligible at the growth temperature we perform a quantitative analysis. The parameter during growth was the substrate temperature and therefore the lattice misfit during growth. As is known, the resulting biaxial strain can be decomposed into a hydrostatic and a uniaxial component [7,11]. The hydrostatic strain shifts essentially the A- and B-band gaps to higher energies and the uniaxial component changes the splitting of the A- and B-exciton resonances [12,13]. Fig. 2 shows the results of the stress calculation versus the mismatch at growth temperature on the surface and interface side respectively. The calculations are based on results in the work of [12,13], where the pressure dependencies have been measured and the resulting deformation potentials determined. Values have been found of $\delta E_g/\delta p = 4.5$ meV/kbar for the band gap under hydrostatic pressure, $\delta E_A/\delta p = 5.1$ meV/kbar and $\delta E_B/\delta p = 2.0$ meV/kbar for the A- and B-excitons under uniaxial pressure. Since the misfit during growth is close to zero, the stress appearing in the films originates from pure thermal strain. Due to the linear thermal expansion coefficient, which is 4 to 5 times larger for the fluorides than that for CdS [8–10], the CdS film is under biaxial stress after growth is finished and the sample is cooled to room temperature. This induces a strain in the direction perpendicular to the surface. X-ray diffraction on the (004) lattice plane of selected samples confirms an increased distance of the lattice planes parallel to the substrate surface by an amount of $\Delta d/d$ of 0.6%. In the calculation this effect appears as positive hydrostatic stress which shifts the band gap of CdS [5] and a negative uniaxial stress which increases the splitting between the A- and B-excitons [12,13]. No systematic misfit dependency is seen at all in fig. 2. Notice that the thicknesses of the films are different but the strain on the surface shows also no thickness dependency. This is a strong indication that residual strain is responsible for the shifts of the surface side. The biaxial stress induced by thermal strain is relaxed to a constant value in a thin layer due to the formation of a dislocation network and is then constant up to the surface of

the CdS film. A pure thermal strain of -1% should result already in energy shifts of -588 meV for ΔE_A and 2.3 eV for ΔE_B in contrast to the much smaller experimental values.

For the interface side no further conclusion can be drawn. The signals of the interface values are associated with larger errors due to broadening of the optical resonances and cannot be taken for quantitative discussion. Only the tendencies can be shown and they agree with the previously given explanations. The optical signal is an integration over the penetration depth of light in the exciton resonance (approximately 100nm) and therefore a response from a region in which the lattice relaxation takes place and broadens the signal. Referring to fig. 1, the experimental data in the films grown on BaF_2 show an increased shift and split of the A- and B-excitons, in comparison with the result of the films on SrF_2 . This is a clear indication for an additional misfit strain in the films on the BaF_2 substrates. The larger shift of the resonances in the CdS films grown on BaF_2 can be explained by the means of larger mismatch at the growth temperature compared to that on SrF_2 , since the thermal expansion of both fluorides has almost the same value. But due to the growth temperature variation during growth [2], the evaluation needs more work to see whether the calculation must be modified. The lower substrate temperature of the PLEE grown films is responsible for the slightly smaller shift of the A-excitons than in HWE grown films. In this case the contribution of the change of the band gap and of the excitonic A–B split might be altered due to a partial cancellation of the contributions from lattice mismatch and thermal strain.

In summary we observed a stress induced shift of the excitonic resonances in CdS on BaF_2 and on SrF_2 , which are grown by HWE and PLEE. Both growth procedures show the same order of magnitude of the shifts. Comparisons with stress measurements on bulk CdS and calculations based on these results were applied to CdS on SrF_2 which exhibits almost pure thermal strain. The surface signals reveal a hydrostatic stress, which is around 0.3GPa and a uniaxial component of around 0.33GPa. Physically there is a strain in the direction perpendicular to the surface. No misfit

dependency is observed. In CdS on BaF₂ there is an indication of an additional influence of the misfit.

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