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ELECTROREFLECTANCE OF THIN ZINC SULFIDE FILMS GROWN BY ATOMIC LAYER EPITAXY AND ELECTRON BEAM EVAPORATION TECHNIQUES

J.A. Lahtinen and T. Tuomi

Laboratory of Physics, Helsinki University of Technology, SF-02150 Espoo 15, Finland

Résumé - Nous avons mesuré les spectres d'électroréflectance de couches minces polycristallines de ZnS:Mn obtenues par "atomic layer epitaxy" et par évaporation. De l'énergie E_0 de la transition électronique directe observée à 3,74 et 3,705 eV respectivement, on déduit que les couches minces de ZnS formées par épitaxie en couche atomique sont essentiellement de structure hexagonale, alors que la structure des couches déposées par évaporation à l'aide d'un canon à électrons est proche de celle des polytypes 4H ou 6H.

Abstract - We have measured electroreflectance spectra of polycrystalline ZnS:Mn thin films grown using atomic layer epitaxy and electron beam evaporation techniques for electroluminescent devices. From the E_0 direct electron transition observed at 3.74 eV and 3.705 eV it is concluded that the ZnS thin films grown by atomic layer epitaxy are predominantly hexagonal whereas the crystal structure of the films grown by electron beam evaporation is close to polytype 4H or 6H.

Because of their derivative nature, the modulation techniques have become an important tool in studying optical structure of solids /1-4/. In this investigation we have exploited electric field modulation (electroreflectance, ER) to obtain information about the absorption edge of zinc sulfide.

Theoretical analysis of the ER spectra starting from the coupling of the field to the electrons is very complicated (e.g. because of the insufficient knowledge of the effective field /2/), and therefore it has become customary to determine the critical point parameters (energy gap E_g , lifetime broadening Γ etc.) by fitting the measured spectrum to the resonance lineshapes of the form /5-6/:

$$\frac{\Delta R}{R} = \text{Re}\{C e^{i\theta} (E - E_g + i\Gamma)^{-n}\}. \quad (1)$$

Zinc sulfide crystallizes in cubic, hexagonal and several polytype structures, each of them having the first electron transition E_0 at different photon energies. By determining E_0 from the ER spectrum it is possible to assess the crystal structure of the zinc sulfide sample.

I Experimental

The ZnS samples were grown using two different methods. The ZnS:Mn film in the layer structure of the EL device of Fig. 1 (a) was grown by atomic layer epitaxy (ALE) at about 500°C /7/. The ZnS:Mn thin film shown in the EL device of Fig. 1 (b) was deposited by electron beam evaporation (EBE) on a substrate at a temperature of about 180°C /8/. The Mn concentration of the samples was about 0.5% by weight.

Fig. 1. Samples used in the ER measurements: (a) grown using ALE (b) grown using EBE.

ER spectra were measured with a standard equipment /1/ at room temperature. The light source consisted of a xenon lamp and a Jobin-Yvon HRD1 double monochromator with a 2.6 nm bandwidth. The signal from the photomultiplier was analyzed by a PAR 124A lock-in amplifier and the spectra were registered with an Apple II microcomputer. The output signal level of the photomultiplier was held constant (1V) by automatic adjustment of the bias voltage. The modulating voltage was 5V and its frequency was 289 Hz. The average field strength in the ZnS:Mn layer was about $4 \times 10^6 \text{ Vm}^{-1}$ in the ALE films and $1.5 \times 10^6 \text{ Vm}^{-1}$ to $2.0 \times 10^6 \text{ Vm}^{-1}$ in the EBE films. The modulating voltage was well below the threshold voltage (about 130V) of electroluminescence.

II Results and discussion

The low field electroreflectance spectra of polycrystalline ZnS:Mn films in the energy range from 3.5 eV to 4.0 eV are shown in Fig. 2. The energy E_0 and the broadening parameter Γ were determined from the spectra by the three-point method /5/, in which the baseline and two dominant peaks are used to fit the spectrum to eq. (1). The values of E_0 and Γ are 3.74 eV and 58 meV in the spectrum a of Fig. 2 and 3.705 eV and 60 meV in the spectrum b. The E_0 values measured from several samples do not differ from these (average) values by more than $\pm 10 \text{ meV}$ in the ALE films and $\pm 5 \text{ meV}$ in the EBE films.

The calculated change of the first direct gap ΔE_0 caused by the different thermal expansion coefficients of the dielectric layer and the ZnS layer is $\sim 2 \text{ meV}$ in ALE samples (grown at 500°C). This value is so

Fig. 2. Electroreflectance spectrum of polycrystalline ZnS:Mn thin films grown using (a) atomic layer epitaxy and (b) electron beam evaporation.

small that no correction need be made to the measured E_0 due to macrostrain.

From earlier reflectivity measurements /9-12/, it has been suggested that wurtzite type ZnS crystals can be distinguished from zinc blende type crystals with the aid of the location of the E_0 transition peak. Variation of the gap E_0 measured with light polarized perpendicularly to the hexagonal c-axis (ELc) with structure of ZnS is presented in Fig. 3. The E_0 values of the two types of thin film studied in the present work are marked by arrows. On the ground of x-ray diffraction studies /14/ we had in the ER measurements on the ALE samples the electric field of light nearly perpendicular to the c-axis of the hexagonal ZnS (ELc).

From Fig. 3 it can be concluded, that the crystal structure of the polycrystalline ZnS thin films grown by the ALE method at about 500°C is mainly hexagonal, whereas the structure of the zinc sulfide films deposited by EBE is close to polytype 4 H or 6 H. The results of the present work are in good qualitative agreement with the electroluminescence, photoluminescence and x-ray diffraction measurements /14-17/.

Fig. 3. Variation of the first direct energy gap E_0 measured with light polarized perpendicularly to the hexagonal c -axis with structure of ZnS. $k/(k+h)$ is the proportion of cubic packing. $\square$, $\circ$, Δ , $\times$ and ∇ are taken from the room temperature reflectivity /9-12/ and wavelength modulated reflectivity /13/ spectra of ZnS single crystals, respectively. The results of the present work are marked by arrows.

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