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## LUMINESCENCE OF $Zn_xMg_{1-x}Se$ LAYERS OBTAINED BY THERMAL DIFFUSION OF Mg INTO ZnSe AND $Zn_xMg_{1-x}Se$ EPILAYERS GROWN BY MOLECULAR BEAM EPITAXY\*

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This work deals with the study of photoluminescence properties of  $Zn_xMg_{1-x}Se$  epilayers grown by molecular beam epitaxy on (001) GaAs and (111) ZnTe substrates and  $Zn_xMg_{1-x}Se$  layers obtained by thermal diffusion of Mg into ZnSe single crystals. Luminescence spectra of  $Zn_xMg_{1-x}Se$  layers are dominated by blue and violet emission bands with maxima positioned in the range of photon energies: 3.05–3.28 eV, 2.88–3.04 eV, 2.81 eV and 2.705 eV, depending on preparation conditions. In some samples the blue luminescence is observed up to room temperature.

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Wide-band gap  $A_2B_6$  compounds are attractive for optoelectronic applications, especially for light-emitting devices that operate in the blue-green region of the spectrum. Very large differences in lattice constants between binary compounds require the development of mixed alloys. Mixed ternary and quaternary compounds of Mg halcogenides with wide-gap  $A_2B_6$  semiconductors have been recently proposed to produce a variety of new materials for optoelectronics. The usefulness of these materials arises from the possibility of tuning of band-gap energies and lattice constants by adjusting the content of particular elements. Since major defect-related problems associated with superlattices arise from interfacial lattice mismatch, the use of lattice-matched combinations is essential for constructing light emitting devices. It is crucial to know the limiting conditions that lead to pseudomorphic growth by the accommodation of the strain due to lattice mismatch. The ZnSe and  $Zn_xMg_{1-x}Se$  epilayers with large concentration of Mg have a close lattice match to GaAs and ZnTe, respectively.

In this work photoluminescence properties of  $Zn_xMg_{1-x}Se$  layers prepared by different methods were studied.  $Zn_xMg_{1-x}Se$  mixed crystal layers were obtained by: (a) thermal diffusion of Mg metal into ZnSe single crystal grown by Bridgman

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method, and (b) epitaxial growth on (001) GaAs and (111) ZnTe substrates by molecular beam epitaxy (MBE).

Wafers of *n*-type ZnSe crystals ( $\rho = 0.12 \Omega \text{ cm}$ ) were subjected to diffusion of magnesium. The diffusion source for Mg was metallic magnesium placed in an evacuated quartz ampoule together with ZnSe plates and zinc metal. The diffusion process was performed for 40–160 hours in the temperature range from 1120 K to 1200 K [1].

The growth of  $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$  layers was performed using elemental Zn (6N), Se (6N), and Mg (3N) sources in independent carbon effusion cells. The substrate temperature during the growth was kept in the range of 550–580 K. Growth rates of ZnSe and  $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$  layers were in the range between 0.07 nm/s and 0.2 nm/s provided thicknesses of obtained epilayers up to 3  $\mu\text{m}$ .

Photoluminescence (PL) and reflectivity spectra were measured in the temperature range from 7 K to 330 K using a closed cycle cryogenic system DE-202 (APD – Cryogenics Inc.), an SPM-2 monochromator and a photomultiplier R-375 (Hamamatsu). PL was excited with 325 nm radiation from He–Cd laser. Low-temperature reflectance measurements were performed in backscattering geometry using a 100 W tungsten–halogen lamp as a light source.

PL spectra of  $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$  epilayers grown on (111) ZnTe and (001) GaAs substrates are presented in Figs. 1a and 1b, respectively.

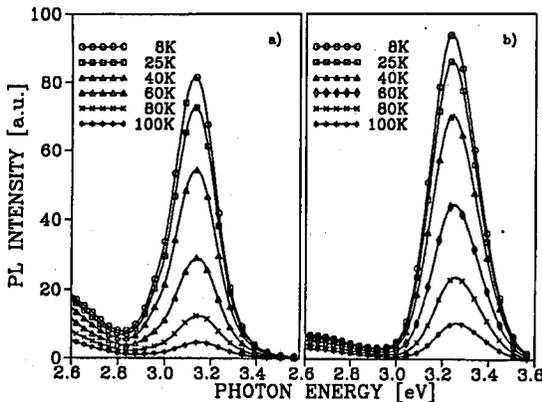


Fig. 1. Photoluminescence spectra of  $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$  epilayers grown on (111) ZnTe (a), and (001) GaAs (b) at different temperatures.

The PL spectra of  $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$  layers grown on GaAs and ZnTe substrates are dominated by blue and violet emission bands with maxima positioned, at about 3.05–3.28 eV, 2.88–3.04 eV and 2.81 eV (depending on growth conditions). Energetical positions of particular PL bands in blue and violet emission region, and their relative intensities depend on Mg contents in  $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$  epilayers. The shift of maxima of PL bands toward higher photon energies with increasing Mg concentration is observed. The band-gap energies of all  $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$  epilayers were estimated from measurements of reflection spectra near to the fundamental

absorption edge at different temperatures. The strong interference fringes occur in the reflectivity spectrum for  $h\nu < E_g$  where epilayer is transparent and disappears abruptly for  $h\nu > E_g$ . From these measurements the temperature dependence of band-gap energy for  $Zn_xMg_{1-x}Se$  epilayers on GaAs and ZnTe substrates were estimated.

PL spectrum measured at  $T = 8$  K of *pure* ZnSe crystal annealed in liquid zinc consists of exciton emission line at 2.802 eV, strong shallow donor-acceptor pair emission at 2.705 eV (*R*-band) with LO-phonon replicas and deep levels emission at 1.95 eV. After Mg diffusion a shift of the main blue emission toward higher photon energies, well above the band gap of *pure* ZnSe, is observed which indicates that a mixed  $Zn_xMg_{1-x}Se$  crystal is formed during Mg diffusion process. The PL spectrum of as-diffused samples is dominated by rather wide blue-violet emission bands and deep levels emission is very weak [1, 2]. After partial etching of heavily doped surface layer, blue-violet emission bands become narrower and shift toward lower photon energies due to decrease in the band-gap energy caused by a decrease in Mg concentration with the depth from the surface.

The PL spectrum (near band-edge emission region) at  $T = 8$  K of  $Zn_xMg_{1-x}Se$  layer obtained by diffusion of Mg into ZnSe at 1120 K for 80 h (sample A) is presented in Fig. 2a. This spectrum consists of emission bands with

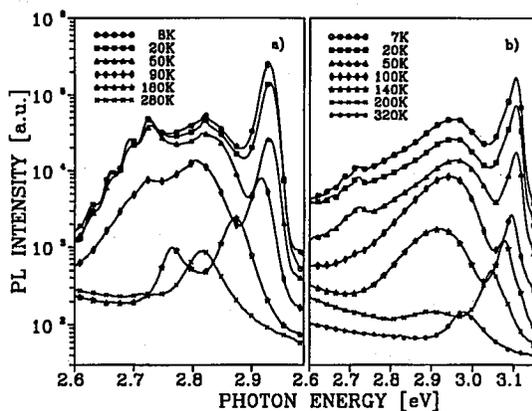


Fig. 2. Near-band edge PL spectra at several temperatures for  $Zn_xMg_{1-x}Se$  layers obtained by thermal diffusion of Mg into ZnSe crystal at 1120 K for 80 h (a), and at 1200 K for 160 h (b).

maxima at 2.91 eV, 2.796 eV and 2.705 eV. Comparing results of measurements of PL spectra of nominally undoped zinc selenide and zinc-magnesium selenide one can conclude that the line at 2.91 eV observed in  $Zn_xMg_{1-x}Se$  mixed crystals at low temperatures is associated with radiative recombination of free excitons. PL bands with maxima at 2.796 eV and 2.705 eV were interpreted as due to the radiative recombination of shallow *D-A* pairs in  $Zn_xMg_{1-x}Se$  and ZnSe, respectively.

In the most heavily doped  $Zn_xMg_{1-x}Se$  layer (sample B) which was obtained by diffusion of Mg at  $T = 1200$  K for 160 h the exciton and *D-A* emission

bands appear at 3.098 eV and 2.94 eV, respectively (Fig. 2b). Only a trace of  $D-A$  emission at 2.7 eV from *pure* ZnSe is observed in this case. The edge luminescence is completely thermally quenched at temperatures higher than 200 K. The line of highest photon energy remains unquenched up to room temperature in all Mg-diffused samples. The half-width of this line at  $T = 10$  K is equal to 20–35 meV for samples with different Mg concentrations and is considerably larger than that in *pure* ZnSe (7 meV), but one must take into account that the observed spectra are influenced by the broadening from the alloy disorder and from the inhomogeneity in Mg concentration across the excited region of the sample.

Using the value 3.6 eV for the energy gap of MgSe and taking into account the variation of energy gap of  $Zn_xMg_{1-x}Se$  with composition presented in [3–5] the concentration of Mg ( $1-x$ ) in our Mg-thermal diffused samples was estimated to be 0.13 and 0.36 for samples *A* and *B*, respectively. It is more difficult to perform such estimations of Mg concentration in  $Zn_xMg_{1-x}Se$  epilayers grown on GaAs and ZnTe substrates because compressive and tensile stresses modify optical properties of strained layers.

The study of the  $Zn_xMg_{1-x}Se$  ( $0.5 \leq x \leq 1$ ) system allowed us to identify the growth conditions that yield layers of high optical quality. Along with tuning of the band-gap energy with concentration of Mg, these alloys are expected to provide tuning of the band offsets to ZnSe [1–4].

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