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Wavelength modulated optical reflectivity spectra of $CuAl_{1-X}Ga_XSe_2$ crystals

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Abstract
Exciton spectra of $CuAl_{1-X}Ga_XSe_2$ solid solutions are investigated by wavelength modulated optical reflectivity at low temperatures (10 K). The energy position of $n = 1$ and 2 lines of the $\Gamma_4(A)$, $\Gamma_5(B)$ and $\Gamma_5(C)$ exciton series, as well as the $\Gamma_7(V_1)$–$\Gamma_6(C_1)$, $\Gamma_6(V_2)$–$\Gamma_6(C_1)$, $\Gamma_7(V_3)$–$\Gamma_6(C_1)$ energy intervals, and the crystal field and spin–orbit splitting of the valence band are determined. The effective electron mass (m^*_{C1}) and hole masses (m^*_{V1}, m^*_{V2}, m^*_{V3}) are estimated for $CuAl_{1-X}Ga_XSe_2$ solid solutions as a function of the X value.

Keywords: reflection spectra in semiconductors, optical constants, excitons and polaritons

1. Introduction

$CuGaSe_2$ and $CuAlSe_2$ compounds, as well as their solid solutions belonging to the I–III–VI_2 materials crystallize in the chalcopyrite structure with the $I42d$–D^{12}_{2d} space group. Stimulated emission and second harmonic generation at 10.6 μm as well as generation of infrared (IR) radiation in the region of 4.6 and 12 μm was realized in these compounds [1–4]. Biexcitons [5], interference of additional waves [6], resonance Raman scattering [7–9] and intense emission due to exciton polaritons and bound excitons [10–12] have been observed in these crystals. Optoelectronic devices and solar cells are developed on the basis of these materials [13–19]. The photoluminescence properties of $CuAlSe_2$ crystals doped with Er^{3+} ions [15] as well as the photoelectrical properties of surface barrier structures on the basis of $CuAlSe_2$ have been studied [17, 18]. These materials possess a strong anisotropy of optical properties in the visible and infrared spectral ranges which is very important for the development of polarized optoelectronic devices.

The goal of this paper is to investigate the main exciton parameters as well as the energy gaps at the center of the Brillouin zone as a function of composition of $CuAl_{1-X}Ga_XSe_2$ solid solutions. The energy position of $n = 1$ and 2 lines of the $\Gamma_4(A)$, $\Gamma_5(B)$ and $\Gamma_5(C)$ exciton series, as well as the $\Gamma_7(V_1)$–$\Gamma_6(C_1)$, $\Gamma_6(V_2)$–$\Gamma_6(C_1)$, $\Gamma_7(V_3)$–$\Gamma_6(C_1)$ energy intervals, are determined from wavelength modulated optical reflectivity spectra. The effective electron mass (m^*_{C1}), and hole masses (m^*_{V1}, m^*_{V2}, m^*_{V3}), are estimated from the analysis of exciton reflectivity spectra according to a single-oscillator model of dispersion relations. The asymmetry parameters of reflectivity spectra are determined.

2. Experimental details

$CuAl_{1-X}Ga_XSe_2$ crystals in the form of platelets with 2.5 × 1.0 cm^2 mirror-like surfaces and thicknesses of 300–400 μm were grown by chemical vapor transport [16]. The surface plane of the platelets contains the C-axis. The optical reflectivity and wavelength modulated spectra were measured using a MDR-2 (LOMO, Russia) spectrometer. For low-temperature measurements, the samples were mounted on the cold station of a LTS-22 C 330 optical cryogenic system.

3. Results and discussions

According to theoretical calculation of the band structure of $CuAl_{1-X}Ga_XSe_2$ crystals with $I42d$–D^{12}_{2d} space group [20, 21], the minimum energy gap is formed by direct electron transitions at the center of the Brillouin zone. The lower conduction band has a Γ_6 symmetry, while the upper V_1, V_2, and V_3 valence bands are of Γ_7, Γ_6, and Γ_7 symmetry, respectively.

The interaction of electrons from the conduction band Γ_6 and holes from the valence band Γ_7 is determined by the product of irreducible representations $\Gamma_1 \times \Gamma_6 \times \Gamma_7 = \Gamma_3 + \Gamma_4 + \Gamma_5$ [21, 22]. The $\Gamma_4(A)$ exciton allowed in $E \parallel c$ polarization, Γ_5 exciton allowed in $E \perp c$ polarization

