Photoluminescence of epitaxial $CuGaS_2$ on Si(111): Model for intrinsic Defect Levels

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Using three-elemental-source molecular beam epitaxy (MBE), the epitaxial $CuGaS_2$ (CGS) films were grown on commercial Si(111) substrates of 100 mm diameter [1-5]. The native oxygen layer of the substrates was removed by means of a heat treatment under exposure to the Ga molecular beam, followed by a sulphur termination of the clean silicon surface. The CGS films were grown at a substrate temperature of 800 K. Rutherford backscattering spectroscopy (RBS) was used to determine the composition of the epitaxial CGS films. Photoluminescence (PL) was excited by the 457.5-nm line of a continuous-wave Ar^+ laser. The emission was dispersed by a 0.75 m focal-length-double grating monochromator and analysed with liquid-nitrogen cooled charged coupled device camera.

Fig. 1 shows typical PL spectra at 5 K of epitaxial CGS samples, grown on Si(111) by means of MBE. The Ga-rich sample shows a broad defect related luminescence at approximately 2.4 eV only, while the PL of the Cu-rich sample reveals an intense excitonic emission and a well-structured defect related emission again at approximately 2.4 eV. So we shall confine the following discussion to the Cu-rich case.

Fig. 2 shows PL spectra of the Cu-rich sample measured at 5 K under different intensities of the incident light. For a least-square fit of the data (solid line), we assumed four lines of Gaussian shape, i. e. the acceptor-bound exciton (A^0X) at 2.489(2) eV, a free-to-bound transition (FB-1) at 2.433(2) eV, a donor-acceptor transition (DA-1) at

2.411(2) eV, and a second donor-acceptor line (DA-2) at 2.391(2) eV. The given energies refer to the case of minimum intensity (1mW).

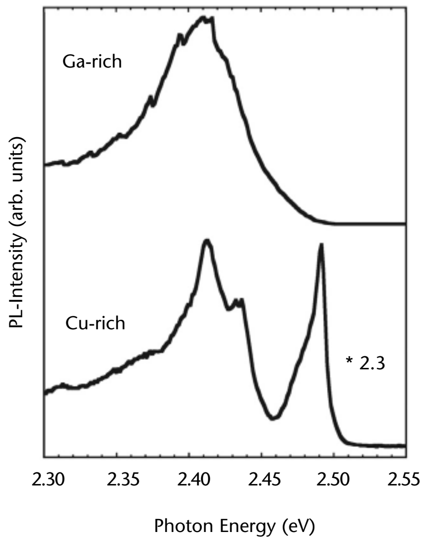

Figure 1:
PL spectra at 5 K of two epitaxial CGS layers with Cu-rich and Ga-rich composition

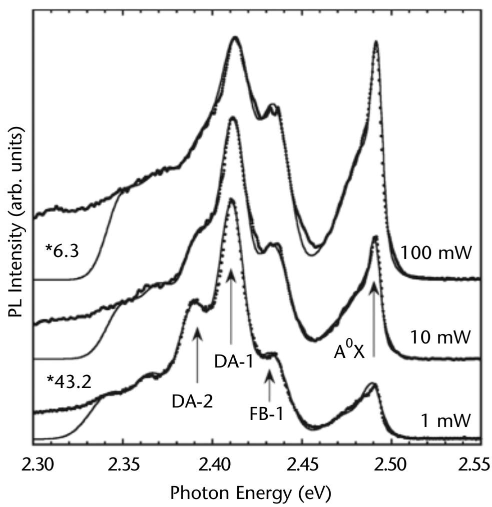

Figure 2:
PL spectra at 5K of a Cu-rich CGS sample measured with different intensities of the incident light. The solid lines represent least-squares fits to the data assuming an acceptor-bound exciton A^0X and three defect-related transitions FB-1, DA-1, and DA-2.

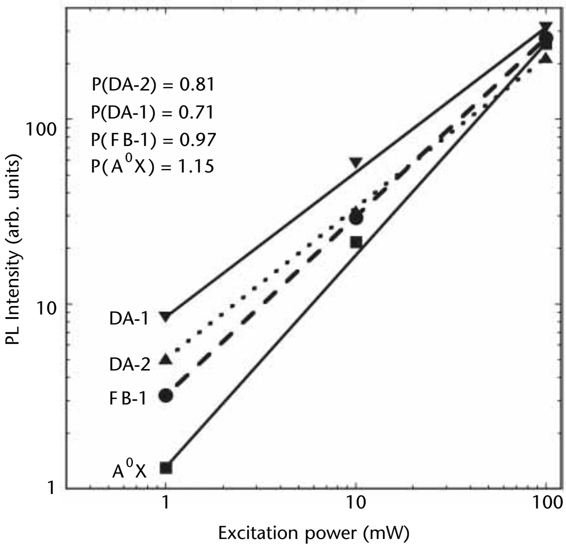

Figure 3:

Double logarithmic plot of the PL line intensities as a function of excitation power. DA-1 and DA-2 exhibit sublinear, FB-1 linear, and A^0X superlinear power dependences.

In *fig. 3* we have plotted the respective line intensities as a function of excitation power in a double logarithmic scale. The slopes *P* of the resulting straight lines agree well with the theoretically expected ones and we get $P \approx 0.8$ for the donor-acceptor transitions, $P \approx 1.0$ for the free-to-bound transitions, and a superlinear behavior for the excitonic emission. Additionally, DA-1 and DA-2 exhibit blue shifts of 1.5 and 3.5 meV per intensity decade, while FB-1 and A^0X do not show a shift in energy. This behavior is in good agreement with the theory for recombination in semiconductors and give us the possibility to identify the observed transitions.

Fig. 4 depicts the temperature dependence of the PL spectrum up to 90 K measured with 100 mW laser intensity. The spectra were fitted by the same set of transitions. However, the apparent blue shift of line DA-1 with rising temperature was accounted for by the assumption of a second free-to-bound (FB-2)transition located at 2.415(2) eV.

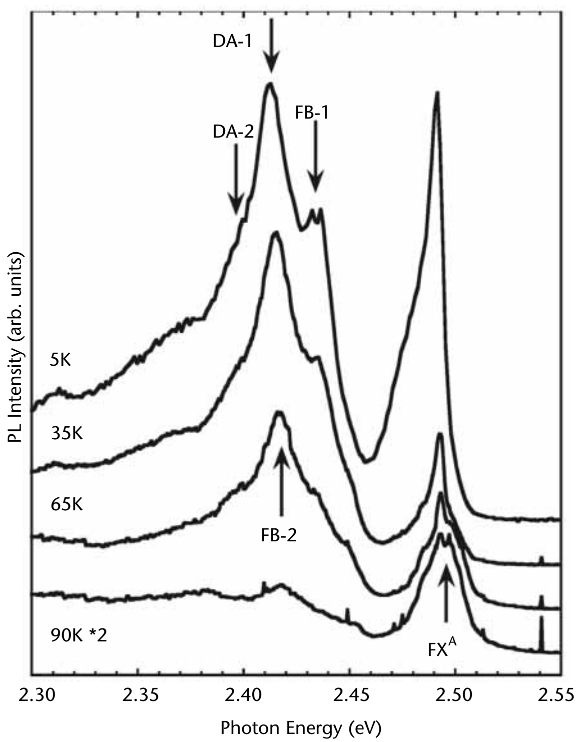

Figure 4:
PL spectra of Cu-rich epitaxial CGS for different measuring temperatures (100 mW excitation power). The apparent blue shift of DA-1 with rising temperature is accounted for by the assumption of an additional free-to-bound transition FB-2.

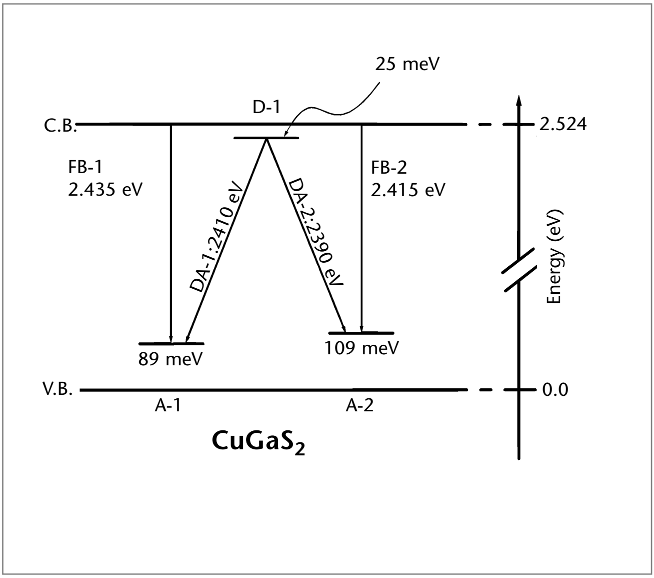

Figure 5:
Defect level scheme for CGS based on the presented PL data. The model involves one shallow donor (D-1) and two acceptor states (A-1 and A-2), which are tentatively assigned to the S vacancy and the two metal vacancies, respectively.

In *fig. 5*, the described PL results are summarized in a level scheme with a self-consistent set of data [6]. The band gap of the CGS layers was calculated as the sum of the energy of the free A-exciton (2.503 eV as determined in photoreflectance measurements [5]) and its binding energy of 21 meV. The model includes one shallow donor D-1 (tentatively assigned to the sulphur vacancy) and two acceptor states A-1 and A-2 which are tentatively attributed to the metal vacancies. *Fig. 5* is consistent with the generally observed p-type conductivity of CGS (without extrinsic doping) and with existing literature data.

Literature

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