

Reconciliation of luminescence and Hall measurements on the ternary semiconductor CuGaSe₂

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Previous Hall and photoluminescence investigations on CuGaSe₂ yielded conflicting results: defect depths determined by luminescence are lower than the ionization energy found in electrical measurements. In this contribution, we present time and spatially resolved cathodoluminescence measurements that necessitate a new interpretation of the luminescence data, leading to a consistent model for luminescence and Hall data with three acceptors with ionization energies of 60, 100, and 150 meV. Luminescence decay times are long, in the range of 100 ns, indicating strong capture. Luminescence is spatially inhomogeneous, indicating inhomogeneous distribution of defects. © 2005 American Institute of Physics. [DOI: 10.1063/1.1872215]

The chalcopyrite CuGaSe₂ and its alloys with CuInSe₂ are used as absorbers in thin-film solar cells, with efficiencies in the lab approaching 20%.¹ Despite the enormous technical progress, the basic understanding of these materials has not yet reached the same level,² although these materials show unique properties due to their low-defect formation energies.³ One of the most important consequences is the doping by native defects. As-grown CuGaSe₂ is always *p*-type by native defects.⁴ For an understanding of the doping behavior, a better knowledge of these native defects is needed.

In a previous photoluminescence (PL) investigation, it was shown that besides the excitonic emission,⁵ the luminescence spectrum is dominated by two donor-acceptor pair (DAP) transitions.⁶ A third defect-related transition was identified as a phonon replica, based on its energy position and intensity and on their compositional dependence.⁶ The defects giving rise to the DAP transitions are a donor with ionization energy of 12 meV and two acceptors with ionization energies of 60 and 100 meV. On the other hand, a detailed Hall study revealed only one acceptor with an ionization energy of 150 meV in the infinite dilution limit.⁷ A comparison with literature does not help to resolve this discrepancy, since in general, luminescence measurements yield lower ionization energies of the defects than Hall measurements.⁸

In this contribution, we investigate the time evolution and the lateral distribution of the three defect-related luminescence transitions by cathodoluminescence (CL). The CuGaSe₂ epitaxial films are grown under Cu excess on (001) GaAs substrates by metalorganic vapor phase epitaxy.^{6,9} Epitaxial quality of the films is ascertained by x-ray diffraction, electron microscopy, and electron channeling. The CL system¹⁰ is based on a JEOL JSM6400 scanning electron microscope. During one single scan, it acquires and stores a complete spatially and spectrally resolved data set

$I_{CL}(x, y, \lambda)$.¹¹ Resolution up to 100 nm and 30 ps is obtained.

Figure 1 shows the CL spectrum obtained under steady state conditions at 6 K. The same transitions are observed as in PL spectra. The interpretation of the transitions is based on a previous detailed temperature- and intensity-dependent PL analysis.⁶ The emission labeled “D” was previously attributed to a phonon replica of DAP2.

The temporal evolution of this spectrum after blanking the electron beam is shown in Fig. 2. The excitonic emission decays very fast, while the defect-related transitions are still clearly visible after 80 ns. The two DAP transitions show a clear redshift with time, as expected for DAP transitions with independent distribution of donors and acceptors due to the higher recombination probability of close pairs (with higher Coulomb term and thus higher emission energy).¹² In contrast, much less shift or no shift is observed for the third defect-related transition D. From the current measurements,

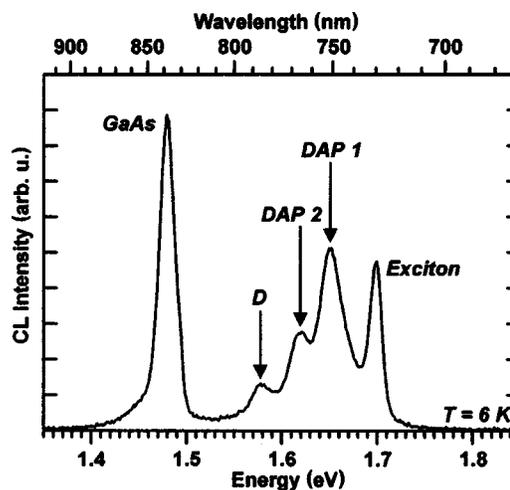


FIG. 1. CL spectrum obtained at steady state conditions, “GaAs” denotes the luminescence from the substrate, “exciton” the excitonic luminescence, “DA1” and “DA2” DAP transitions, and “D” a third defect-related transition.

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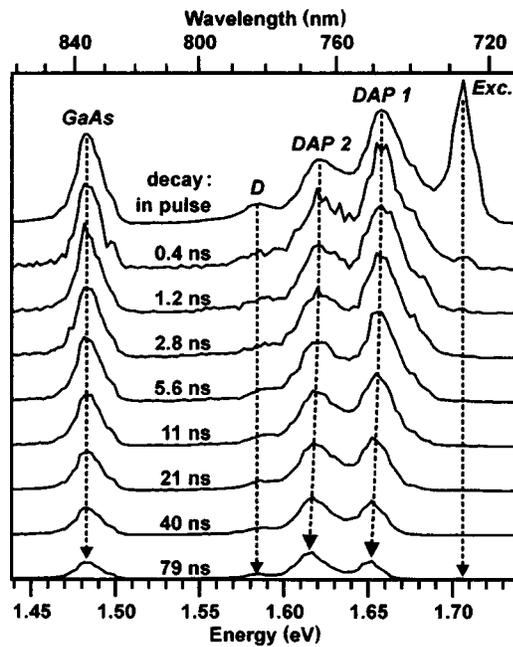


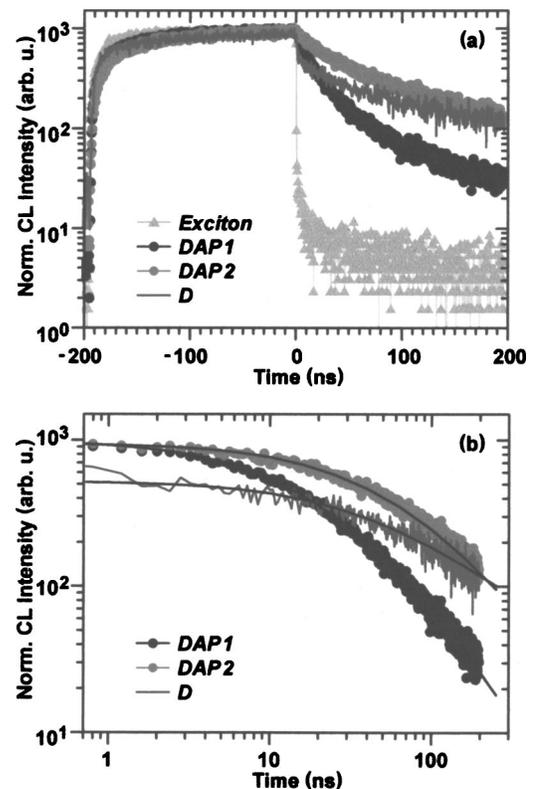
FIG. 2. Temporal development of the CL spectra during decay.

no clear conclusion on the shift of D can be drawn due to the low intensity of this transition and its line overlap with DAP2. Nevertheless, the much smaller shift could indicate that the involved donors and acceptors are not randomly distributed but preferentially paired, which would lead to less variation in the distribution of the Coulomb energies and thus less shift.¹³

The time dependence of the CL intensity of the individual transitions is shown in Fig. 3. The fastest decay is seen from the exciton, which can be best described by a three-exponential decay with time constants of 166 ps, 4 ns, and 203 ns. The multicomponent decay can be attributed to the fact that the excitonic emission is composed of bound and free excitons.⁵ DAP1, DAP2, and transition D show rather long decay times on the order of 100 ns, indicating strongly captured charge carriers. The decay behavior is well described by the model by Thomas *et al.*,¹² using a recombination probability W of the form

$$W(r) = W_{\max} \exp(-2r/r_{\text{Bohr}}), \quad (1)$$

with W_{\max} fit parameter, r the distance between donor and acceptor, and r_{Bohr} the Bohr radius of the donor. r_{Bohr} is determined from the dielectric constant $\epsilon = 11$ (Ref. 14) and an assumption of the electron effective mass $m^* = 0.14$ (Ref. 15): 4.2 nm. The fit is done for the decay curve using the acceptor concentration N_A and the transition probability W_{\max} as fit parameters. Results are given in Table I and Fig. 3(b). DAP1 is the transition with the highest transition probability of the three defect-related transitions; this is reflected in the highest intensity, as well. The acceptors involved in transition DAP2 occur with almost the same concentration as A1, but the transition probability is lower, thus decreasing the intensity and increasing the lifetime as compared to DAP1. This correlation hints at a negligible influence of nonradiative transitions on the lifetime. Transition D is described by the same transition probability as DAP2, but with a lower acceptor concentration. As seen in Fig. 3(b), in the decay of transition D there is a first fast component that cannot be described within the Thomas–Hopfield model. However, after 2 ns the

FIG. 3. Time-resolved intensity of the four CuGaSe₂-related transitions (a) and the fits to the decay behavior of DA1 and DA2 according to Thomas *et al.* (Ref. 12).

decay of this transition is well described by a Thomas–Hopfield-type decay, indicating that in fact this transition is a DAP transition.

Figure 4 shows the spatial intensity distributions for different energy regions, corresponding to the excitonic transition, the DAP1 transition, and transition D. The intensities are normalized to the local total CL intensity originating from the CuGaSe₂ film. An electron micrograph is shown for comparison. The excitonic emissions show a considerably decreased intensity along an irregular grid pattern and high intensity in the areas in between. DAP1 [Fig. 4(c)] shows an inverted intensity pattern with a maximum in the normalized intensity along the grid lines where the excitonic emission is negligible. DAP2 (not shown) exhibits the same pattern as DAP1. It can be assumed that the grid lines are due to a net of dislocations, where the excitons recombine nonradiatively. Further investigations by transmission electron microscopy and intensity-dependent CL are under way to clarify the origin of the net structure. There are dark spots in which neither emission of the excitons nor the DAP transitions is observed. These are the locations where the transition D is most intense, indicating that the defects involved in transition D

TABLE I. Fit parameters of the Thomas–Hopfield model for the decay of the three defect-related transitions.

Transition	N_A/cm^{-3}	W_{\max}/s^{-1}
DAP1	$(3.1 \pm 0.1) \times 10^{17}$	$(4.1 \pm 0.2) \times 10^8$
DAP2	$(2.3 \pm 0.3) \times 10^{17}$	$(1.5 \pm 0.1) \times 10^8$
D	$(6.1 \pm 1.3) \times 10^{16}$	$(1.7 \pm 0.1) \times 10^8$

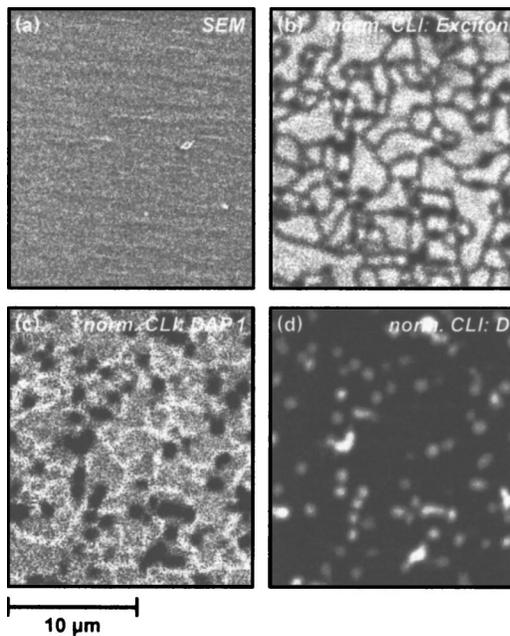


FIG. 4. Electron micrograph (a) and maps of the normalized intensity distribution for the same sample area of the excitonic transition (b), of the DAP1 transition (c), and of the D transition (d).

exhibit a spatial distribution that is inverse to the distribution of the defects involved in DAP1 and DAP2.

From its distinct temporal and spatial behavior, it can be concluded that transition D is not a phonon replica of DAP2. Intensity- and temperature-dependent PL of transition D indicates that it represents a DA transition as well:⁸ Under excitation intensity variation, transition D shows a blueshift of 1.4 meV/decade and a power exponent of the luminescence intensity of 0.87. With increasing temperature the luminescence peak shifts to higher energies, due to the appearance of the corresponding free-to-bound transition, as has been observed for DAP1 and DAP2.⁶ The shift starts at the same temperature (25 K) as in DAP1 and DAP2. Therefore, it can be concluded that the same shallow donor is thermally emptied as in the cases of DAP1 and DAP2. From the energy position of the free-to-bound transition, it is possible to determine the energy of the acceptor. One obtains (135 ± 10) meV, which is, within errors, identical to the energy of the acceptor resulting from Hall measurements.

A previous study of the CL emission around 1.58 eV on a single crystal of CuGaSe₂ (Ref. 16) has found a clear redshift of this emission with decay time, in contrast to our

observation. The difference between the two materials is that the luminescence in this crystal is dominated by transition D, while the emission from our epilayers is dominated by DAP1 and DAP2. This indicates that in the crystal, much more of the defects involved in transition D are present, which could very well break the preferential pairing observed in our case.

Therefore, we conclude that the transition D is not a phonon replica of DAP2 but a DAP transition involving a third acceptor A3, which is the one that is observed in Hall measurements. The two shallower acceptors A1 and A2, observed in PL, are not discerned by the Hall measurements most likely because they are compensated by donors, as the Hall measurements indicate a high degree of compensation.⁷ From this observation together with the fact that the luminescence spectra show no indication of fluctuating potentials, as one would expect in highly compensated semiconductors,¹⁷ it has been proposed that the donors and acceptors are not independently distributed but preferentially paired.⁷ The fact, that the DAP transition D shifts much less than DAP1 and DAP2 during decay, is a hint that such pairs might exist.

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