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Photoluminescence and photoconductivity of $CuInSe_2$

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In this paper we report for the first time the results of photoluminescence (PL) and photoconductivity (PC) measurements on stoichiometric and well-defined off-stoichiometric copper indium diselenide. The energy gap at 10 K is 1.050 ± 0.005 eV and free-exciton emission at 1.030 ± 0.005 eV is the dominant feature in the PL spectra of stoichiometric nominally undoped $CuInSe_2$. For Cu:In and metal:selenium ratios > 1 recombination between Se-vacancy donors (-70 meV) versus the conduction-band edge, Cu_{In} antisite acceptors [40 meV versus the valence-band edge (VBE)], and In-vacancy acceptors (80 meV versus the VBE), respectively, dominates the PL spectra. Excitation from the above two acceptor states contributes to the PC spectra with complimentary temperature dependence as compared with the deep emission.

I. INTRODUCTION

The excellent reliability and high power-conversion efficiency of polycrystalline thin-film $CuInSe_2$ solar cells has stimulated research on the fundamental properties of this ternary chalcopyrite structure semiconductor. Both the electrical transport properties[1-5] and optical properties[6-11] of $CuInSe_2$ are dominated by native defects. Attempts at identifying the most prevalent point defects have remained inconclusive thus far primarily for a lack of well-defined stoichiometric single crystals. Based on a detailed study of the solidus-liquidus tie lines in the system Cu, In, Se we have recently reported on the preparation of stoichiometric single crystals of $CuInSe_2$ that is an incongruently melting material requiring growth from a unique off-stoichiometric liquidus composition.[12] In this paper we report on a combination of photoconductivity (PC) and photoluminescence (PL) measurements that, for the first time, allow the characterization of donor-acceptor transitions and of the free-exciton emission in $CuInSe_2$ under well controlled conditions.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the PL spectra obtained from a natural (112) facet on a $CuInSe_2$ single crystal. The insert in Fig. 1 represents the PL spectra from a cleaved (110) face of the same crystal. The luminescence of the cleaved face is dominated by a sharp peak of 9 meV full width at half maximum (FWHM) at 1.030 ± 0.005 eV. For the free-surface facet deep emission centered at 0.94 and 0.90 eV, respectively, is observed. In addition two small peaks at 1.01 and 1.05 eV are detected.

Electron microprobe scans of the cleaved face show a uniform bulk composition at atom ratio $Cu:In = 1.00 \pm 0.005$ and metal-to-selenium ratio $(Cu+In):Se = 0.99 \pm 0.005$. Electron microprobe analysis of the (112) facet reveals an off-stoichiometric composition at atom ratio $Cu:In = 1.01 \pm 0.005$ and $(Cu+In):Se = 1.04 \pm 0.005$. The change in the composition near to the free surface is attributed to exchange with the In_2Se (gas phase) and selenium (gas phase) containing vapor atmosphere during cooling of the crystal from the melting temperature to room temperature. Although for off-stoichiometric bulk $CuInSe_2$ this exchange may result in *p*- to *n*-type conversion near to the free surface, the particular stoichiometric crystal under study is *p* type through its entire volume.

Figure 2 shows the PC spectra for the same crystal. At 10 K a featureless edge is observed while at higher-temperature excitation of carriers from deep states contributes to the PC. The inserts in Fig. 2 represent difference spectra in reference to the spectra at 10 K revealing two excitations centered at 0.94 and 0.90 eV with the onset of the 0.94-eV excitation at lower temperature. As shown in Fig. 3(a), the temperature dependence of the deep emission in the PL spectra (Fig. 1) is complementary to the above contributions of deep states to the PC. Therefore, we conclude that these

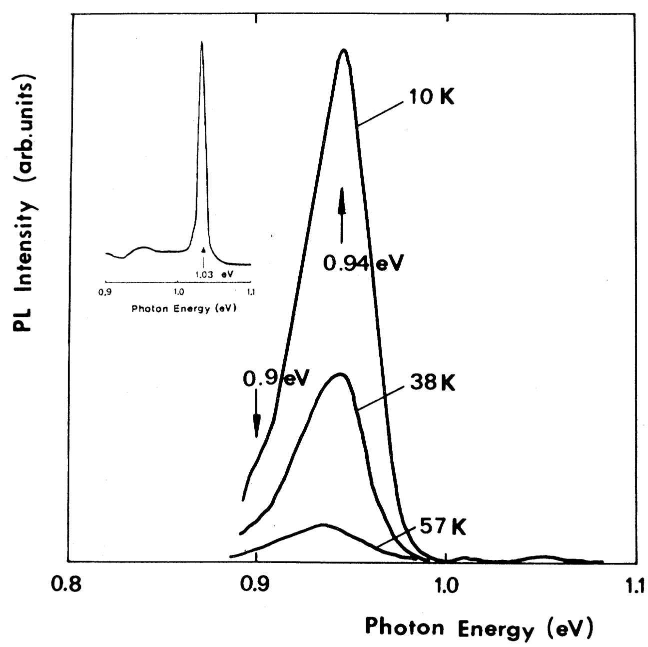

FIG. 1. Photoluminescence spectra of the free (112) surface of a $CuInSe_2$ single crystal for different temperatures showing broad-band emission. The insert reveals free exciton emission at 1.03 eV for the cleaved (110) face of the same crystal at 10 K. Excitation wavelength 514.5 nm at 150 mW.

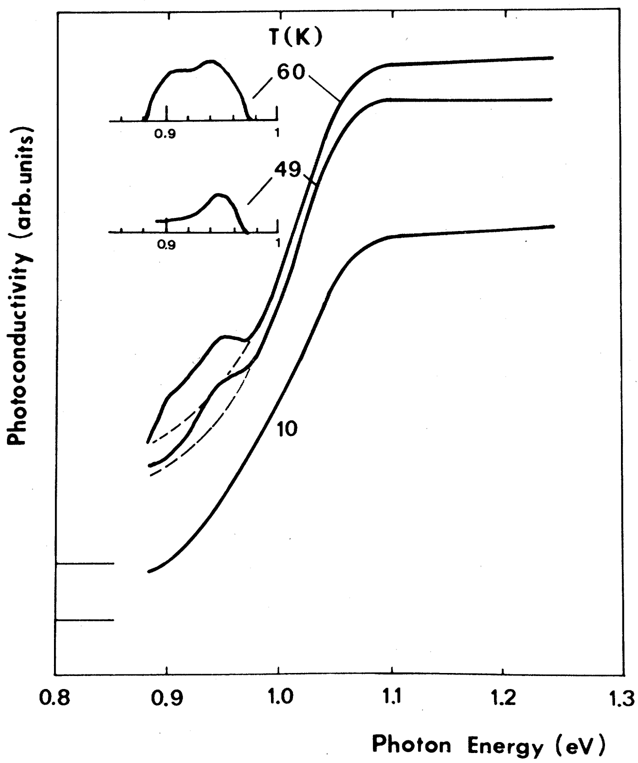

FIG. 2. Photoconductivity as a function of the photon energy for different temperatures. Same $CuInSe_2$ crystal irradiated on the free (112) surface. Difference spectra are shown in the inserts.

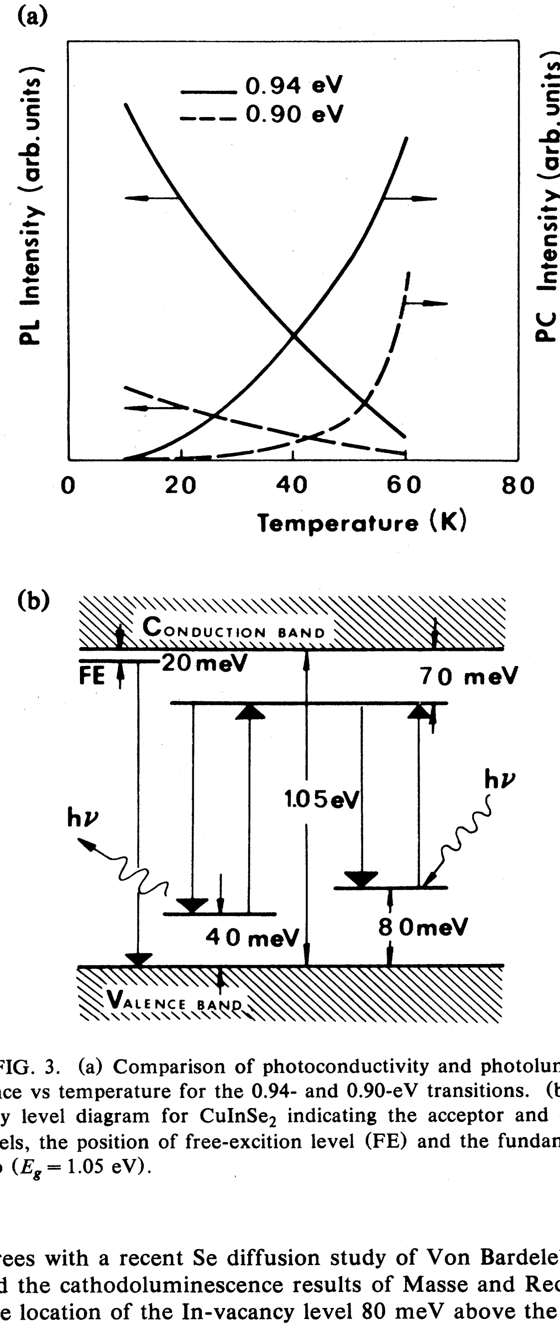

FIG. 3. (a) Comparison of photoconductivity and photoluminescence vs temperature for the 0.94- and 0.90-eV transitions. (b) Energy level diagram for $CuInSe_2$ indicating the acceptor and donor levels, the position of free-exciton level (FE) and the fundamental gap ($E_g = 1.05$ eV).

phenomena involve the same defect states.

Figure 3(b) shows an energy level diagram that illustrates the transitions observed by us. In agreement with Ref. 11 we obtain an energy gap of 1.050 ± 0.005 eV that exhibits little variation in the temperature range $10 \leq T \leq 60$ K. The sharp emission feature in the PL at 1.030 eV we assign to the free exciton that is located 20 meV below the conduction-band edge (CBE). The deep emissions at 0.94 and 0.90 eV are identified as donor-acceptor transitions between selenium vacancy donors and copper on indium antisite acceptors and indium vacancy acceptors, respectively. This identification of the predominant native donor and acceptor states is consistent with our microprobe data that show the deep emission is associated with a deficiency of selenium and indium. The simultaneous presence of Cu_{In} and $In_{\square}$ follows from the pertinent point defect equilibria. The high compensation level of nearly stoichiometric $CuInSe_2$ is well documented in the literature.[1-4]

The location of the Se-vacancy donor state 70 meV below the CBE is in agreement with previous results by Shay and co-workers,[6] but is 10 meV deeper than assumed by Masse[11] and is at variance with the interpretation of Rincon and Wasim[5] and of Abou-Eltofouh *et al.* who place the Se-vacancy state 130 meV above the valence-band edge (VBE).[10] The Cu_{In} antisite level 40 meV above the VBE agrees with a recent Se diffusion study of Von Bardeleben[13] and the cathodoluminescence results of Masse and Redjai.[11] The location of the In-vacancy level 80 meV above the VBE agrees within the error limits with the previous assignments of Refs. 10 and 13. Since the shallower Cu_{In} level becomes thermally ionized before the In-vacancy level we assign the contributions to the PC at 0.94 and 0.90 eV to excitations originating at filled Cu_{In} antisite and In-vacancy acceptors, respectively.

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