Verification of CuInSe\textsubscript{2} Density of States Features by Reflection Electron Energy Loss Spectroscopy

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Abstract. Reflection electron energy loss measurements of CuInSe\textsubscript{2} single crystals are reported and when possible, the losses are compared with former results by Kazmerski and Jamjoum et al. Their identification of the transitions is confirmed and refined by spectrum simulations with total and partial densities of states from band structure calculations of Jaffe, Bendt, Zunger, and Bullett.

New conduction-band maxima at energies not covered by the available calculations, are proposed and their consistency with the experimental loss energies is shown by another simulation with Lorentzian density peaks.

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During the past one and a half decades the Cu-derived \textit{I-III-VI\textsubscript{2}} ternary compounds have attracted considerable interest because of their potential for terrestrial and space photovoltaic applications [1]. With solar cells based on CuInSe\textsubscript{2} conversion efficiencies above 10\% have been obtained together with a superior long-term stability, and photovoltaic detectors match very well the damping minimum of fibre glass [2, 3]. A direct band gap of 1.02 eV and extraordinary high absorption coefficients [2] are in favour of such applications [1]. While optical properties of single crystals and thin films [4] were studied fairly extensively, the CuInSe\textsubscript{2} band structure and density of states (DOS) need detailed confirmation by appropriate spectroscopies. The chalcopyrite structure of CuInSe\textsubscript{2} [5-8] makes band-structure calculations difficult to accomplish, and, in addition, the inclusion of the \textit{d}-electron contribution poses considerable problems. This is the reason why such data have become available only recently. In contrast to the valence-band DOS usually deduced from ultraviolet photoemission, the determination of the conduction-band features is more difficult. Reflection electron energy loss spectroscopy (REELS or ELS for short) is one of the most established methods [9, 10] to study final states. By use of the so-called density-of-states model [10] loss spectra of CuInSe\textsubscript{2} crystals obtained under uhv conditions, will be compared with band structure and DOS calculations at hand, and also with reflectivity measurements. Further some conduction-band DOS maxima are proposed from the spectra.

1. Experimental

CuInSe\textsubscript{2} single crystals were fabricated by the vertical Bridgman technique [11] employing a powdered, polycrystalline charge, pre-reacted from a stoichiometric melt [12]. The crystals were cut perpendicular to the direction of growth and had an orientation close to the (112). In the chalcopyrite structure the (112) plane contains the highest atomic packing density.

In this work p-type crystals were used with a resistivity of 0.2 $\Omega \cdot \text{cm}$ and with dimensions $5 \times 5 \times 1 \text{mm}^3$. The surface was polished and after
degreasing subsequently treated for some minutes with the following etchants: 25% H₂SO₄, 25% H₂O₂, 50% H₂O, and 17% HNO₃, 17% HCl, 66% H₂O. After rinsing in a neutralizing liquid, aqua dest. and methanol, the crystals were clamped to a molybdenum sheet and put into a stainless-steel ultra-high-vacuum system. They were cleaned by low-energy argon ion bombardment (300 eV, 10 μA/cm², 5 h) followed by a 4 min bombardment with 1000 eV electrons (20 μA/cm²) and annealing at 300–400 °C. The working pressure in the baked ion getter and titanium sublimation pumped system was about 4 × 10⁻⁸ Pa. The surface contamination was monitored by Auger spectra. AES and ELS spectra were taken with a LEED retarding-field analyser of own construction by modulation and lock-in techniques. The first derivative of the energy distribution of the scattered electrons was accumulated in a multichannel analyzer (NTA 1024, EMG Hungary). The spectra were transferred to a desk computer, and, after smoothing, the second derivative and the loss maxima were determined.

2. Results

After the bake-out cycles the CuInSe₂ surface shows carbon and oxygen contamination, as usually observed. Some additional Auger peaks are connected with the vacuum history of the system but only the In transition at about 400 eV is indicative of the bulk composition. While xenon bombardment was not found very effective, apart from the reduction of carbon contamination, argon ions produced an almost clean surface, which was further processed by electron bombardment and annealing. The cleaned surface showed after a residual gas exposure of five days the Auger spectrum of Fig. 1a, its small P, S, and Cd peaks being obviously produced by gas-wall interaction. An argon ion and subsequent electron bombardment restored the clean surface as demonstrated by the spectrum b and the Cu and Se peaks of the inset d. (Here only primary energies between 1000 and 1250 eV could be used for technical reasons).

Figure 2 shows (part of) a loss spectrum taken at 200 eV primary energy as the first derivative of the energy distribution. Subsequent smoothing by folding with sin(k₀E)/E (k₀ = 1.5) and numerical differentiation −N²(E). The second derivative is rich in structure and reveals numerous peaks. While the non dispersive retarding field analyzer has some well known drawbacks as compared with the other analyzers, it has the advantage of a large acceptance solid angle. Therefore well resolved RFA spectra generally display the highest possible number of maxima which indicate electronic transitions [10, 13].

It is obvious from Figs. 2 and 3 that the spectra change considerably with the primary energy E₀ as expected but that certain features arise at the same