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Chemical interaction of Na with cleaved (011) surfaces of CuInSe₂

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To study the beneficial effect of sodium-containing substrate material on the photovoltaic properties of thin-film CuInSe₂ solar cells the chemical interaction of Na with CuInSe₂ has been investigated by synchrotron excited photoelectron spectroscopy. A clean CuInSe₂ (011) surface was prepared by cleaving an oriented single crystal in UHV. The cleaved surface exhibits an electron affinity of $\chi \approx 4.6$ eV. The Se 3*d* level shows a surface core level shift of -0.4 eV. Na was sequentially deposited in UHV in small steps from a commercial dispenser source. Initially ionized Na adsorbs on the surface leading to a shift of the surface Fermi level by 0.3 eV closer to the conduction band. Removal of Cu from the surface is observed. For higher Na deposition a chemical reaction of Na with the CuInSe₂ surface occurs leading to the formation of metallic indium and Na₂Se. © 1996 American Institute of Physics. [S0021-8979(96)06221-4]

INTRODUCTION

The chalcopyrite semiconductors have received much attention in recent years. They are ternary analogs of the more common 3-5 or 2-6 compound semiconductors. Their physical properties, however, are more complex than those of their binary counterparts because of the metal *d*-state contribution to the valence-band density of states.¹ Research on ternary compounds is stimulated by their potential use in advanced optoelectronic devices. CuInSe₂ has been extensively explored as a thin-film solar cell absorber material. Within the last decade solar cells on the basis of thin-film CuInSe₂ could be optimized such that efficiencies are now at almost 17% in laboratory cells.² The physical and chemical properties of the interfaces appearing in the solar cells, however, are not yet completely understood. Since the interfaces may dominate charge carrier transport and lifetime properties a detailed analysis appears worthwhile.

A considerable efficiency leap in the CdS/CuInSe₂ solar cell system was achieved by the use of soda lime glass as substrate material for thin-film deposition.³ Outdiffusion of sodium from the substrate and dispersion into the CuInSe₂ layer was evidenced by x-ray photoelectron spectroscopy (XPS) (see, e.g., Ref. 4). Because of the high surface sensitivity of XPS, the observation with this technique implies the presence of Na on top of the absorber film prior to the preparation of the CdS buffer layer. In addition to its effects on the growth and properties of the absorber layer Na may, therefore, also influence the CdS interface formation. The valence-band discontinuity for CdS/CuInSe₂ prepared by UHV evaporation of CdS on single-crystal CuInSe₂ has been determined by photoelectron spectroscopy to be 0.8 eV.⁵ This corresponds to a conduction-band offset of 0.65 eV, a value that is obviously not operative in the real solar cell.⁶ For the achieved performance a conduction-band offset close to zero is necessary.

To study the influence of Na on the CdS/CuInSe₂ interface we investigated in a first step the interaction of sodium with CuInSe₂ surfaces. Adsorbate free surfaces which are

representative of the bulk crystal structure are best suited for this kind of investigation. This is most easily done by cleaving, since sputtering and annealing may lead to deviations of the surface stoichiometry from bulk composition values.⁷ With photoelectron spectroscopy the chemical changes of the surface can be monitored in the course of increasingly deposited amounts of Na.

EXPERIMENT

The experiments were performed in a commercial UHV chamber (base pressure 3×10^{-11} mbar) equipped with an angle resolving hemispherical photoelectron spectrometer (VG ADES 500). The chamber was connected to the TGM 7 beam line of the electron storage ring BESSY in Berlin. Photon energies between 20 and 120 eV were available. The combined resolution of the monochromator and the analyzer, as determined from the Gaussian broadening of the Fermi edge emission of the sputter cleaned metallic sample holder, ranges from 150 to 450 meV for excitation energies $h\nu = 20$ –80 eV, respectively.

The CuInSe₂ crystals were grown by chemical-vapor transport (CVT). As-grown crystals were oriented in (011) direction by x-ray diffraction and cut into pieces. The crystals were fixed to the rapid transfer Cu-sample holders. Notches were put on the crystals for cleavage in the UHV preparation chamber (base pressure 1×10^{-10} mbar) with blade/anvil cleaving pincers.

Na was deposited from a SAES alkali dispenser cell in the preparation chamber. Deposition rates were tuned by the dispenser current. Deposition and characterization was performed at room temperature. All spectra were taken in normal emission. Binding energies are given with respect to the Fermi level.

RESULTS

Since no calibration of deposition rate for Na was available, we determined the actual Na coverages from the evolution of relative intensities of adsorbate to substrate levels. The thickness curve matches closely the applied deposition times and dispenser currents. The maximum Na coverage

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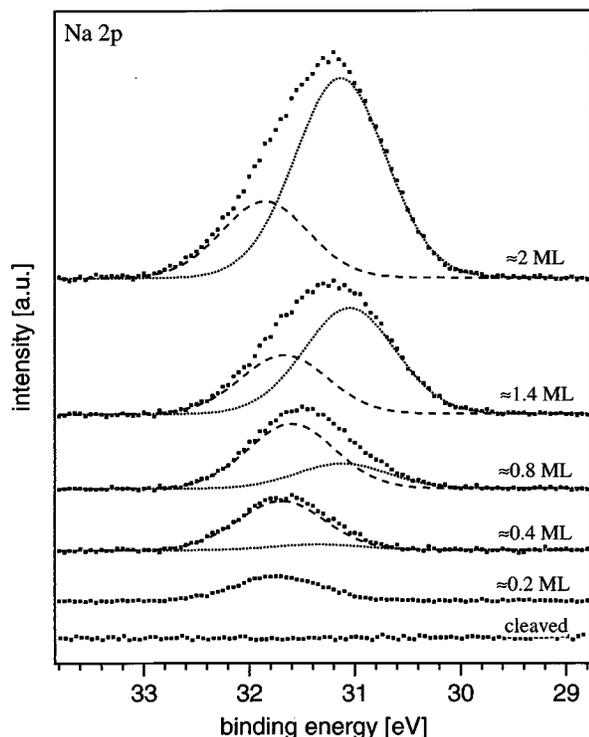


FIG. 1. Na $2p$ core level spectra of the Na/CuInSe₂ interface for increasing amounts of deposited Na. An excitation energy of $h\nu=80$ eV has been applied.

was estimated from the relative intensities after the last deposition step using tabulated photoionization cross sections⁸ and analyzer transmission as a function of kinetic energy. From this procedure we estimated the maximum amount of deposited Na to be about 2 monolayers (ML).

In Fig. 1 we show a selection of adsorbate Na $2p$ core levels in the course of increasing Na deposition. The spectra were excited with photon energy $h\nu=80$ eV. For low Na coverage the Na $2p$ line shows a single emission feature at binding energy (BE) of 31.8 eV (the spin-orbit splitting of the Na $2p$ level cannot be resolved). With further deposition the Na $2p$ level becomes asymmetrically broadened. The spectra can be deconvoluted into two components as indicated in Fig. 1 by the dotted and dashed curves, respectively. The high-BE component becomes saturated in intensity at a coverage of 0.4–0.5 ML, while the low-BE component at BE \approx 31.1 eV increases with increasing Na deposition. Both components show only small variations in BE and linewidth with coverage.

Figure 2 shows the evolution of the In $4d$ substrate emission in the course of deposition of Na. The spectra are taken with an excitation energy of $h\nu=80$ eV. After deposition of \approx 0.2 ML the In $4d$ emissions are shifted to higher BE (Fermi level moves closer to conduction band) by \sim 300 meV and are slightly broadened. Since the broadening is again reduced with further Na deposition we attribute it to Fermi-level inhomogeneities due to incomplete surface coverage (see, e.g., Refs. 9 and 10), rather than to a chemical reaction. For deposition of \approx 0.4 ML a new chemical species is clearly observed at BE=16.7 eV, characteristic for metal-

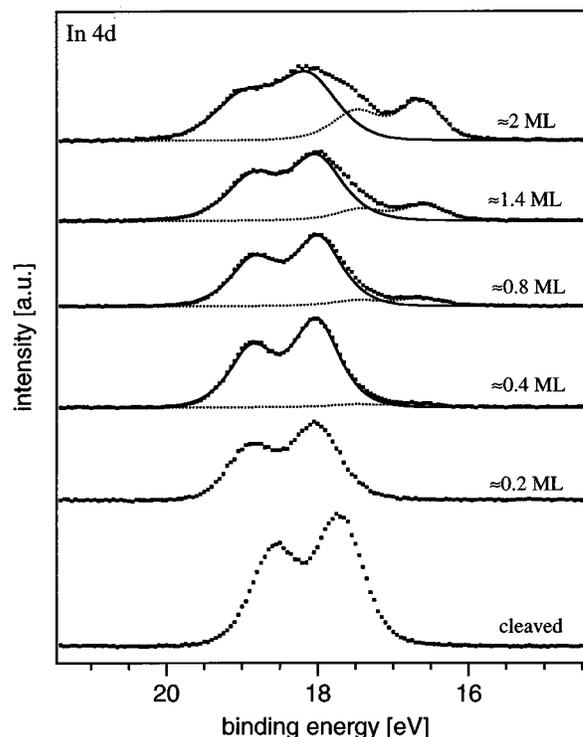


FIG. 2. In $4d$ core level spectra of the Na/CuInSe₂ interface for increasing amounts of deposited Na. An excitation energy of $h\nu=80$ eV has been applied. With increasing Na deposition, a metallic In component grows in (dotted line). The high-BE component (solid line) broadens for higher Na coverages and is assumed to contain more than one chemical species.

lic indium. The intensity of the metallic In $4d$ component increases almost parallel to the intensity of the low-BE Na $2p$ component. The results of a deconvolution of the In $4d$ levels into two components is indicated in Fig. 2 by the solid and dotted lines. Significant broadening of the high-BE component (solid line) is observed for the highest coverages. In addition a BE shift of Δ BE \approx +120 meV with respect to the spectra obtained after deposition of \approx 0.2 and \approx 0.4 ML sodium is observed. After the final deposition step, the intensity ratio of the metallic to the nonmetallic In $4d$ emissions is given by \sim 0.5.

Figure 3 shows the evolution of the Se $3d$ core level with increasing Na deposition. As excitation energy again $h\nu=80$ eV has been used. The spectra taken from the freshly cleaved surface clearly exhibits a shoulder on the low-BE side, as also indicated by deconvolution results. We attribute this shoulder to emissions from surface atoms. The surface core level shift (SCLS) is given by Δ BE_{surf}= -0.4 (\pm 0.05) eV. The intensity ratio of surface to bulk component amounts to 0.46. The amplitude and the negative sign of Δ BE_{surf} is comparable to the SCLS commonly observed for the anion levels of the binary 3-5 compounds.¹¹ From analogy to the binary semiconductors we would expect the In $4d$ level to show a SCLS of opposite sign and comparable magnitude. Although there is some asymmetry on the high-BE side of the In $4d$ level taken from the cleaved surface (see bottom spectrum in Fig. 2), the intensity of this “surface component” is much smaller than that of the respective

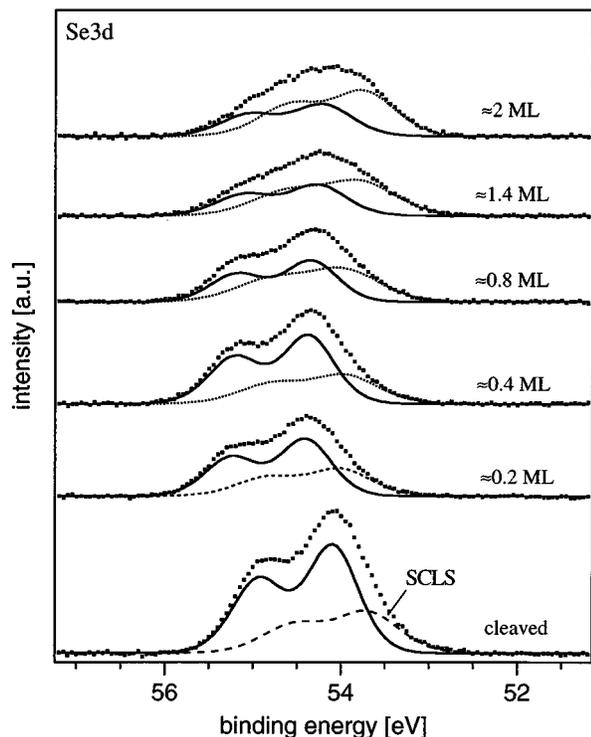


FIG. 3. Se 3d core level spectra of the Na/CuInSe₂ interface for increasing amounts of deposited Na. An excitation energy of $h\nu=80$ eV has been applied. The spectrum of the cleaved surface exhibits a surface core level shift of $-0.4 (\pm 0.05)$ eV (dashed line). With increasing Na deposition a chemically shifted component is observed (dotted line) which is assumed to contain more than one chemical species.

Se 3d component. This may be due to the fact that the In–Se bond is weak in CuInSe₂ as described by Jaffe and Zunger.¹²

The Se 3d emissions originating from CuInSe₂ bulk atoms show a BE shift of $\Delta BE \approx +0.3$ eV for initial Na deposition. For the first two deposition steps, the intensity ratio and BE difference between the two Se 3d components remains almost constant. With further deposition of Na the low-BE component increases in intensity. The BE difference between the two components increases from 0.4 to 0.46 eV after the last deposition step. The linewidth of the low-BE component remains constant for all deposition steps. After the final deposition step the low-BE component is shifted by $\Delta BE \approx -100$ meV with respect to the spectra obtained after deposition of ≈ 0.2 ML. The intensity ratio of the low- to the high-BE component after the final deposition step is given by ~ 1.5 .

In Fig. 4 we show the valence-band spectra of CuInSe₂ excited with 80 eV photons in the course of Na deposition. From the extrapolation of the onset of photoelectron emission, the energy difference between the valence-band maximum and the Fermi level is $E_F - E_V \approx 0.4$ eV for the cleaved surface. Again the shift to higher BE for initial Na deposition is observed. For increasing deposition the typical valence-band features of CuInSe₂ are completely lost, however, significant changes of the valence-band structure are already observed after deposition of ≈ 0.2 ML. This is evident from the difference spectra that are shown at the bottom of Fig. 4. To obtain the difference spectra we multiplied the spectrum

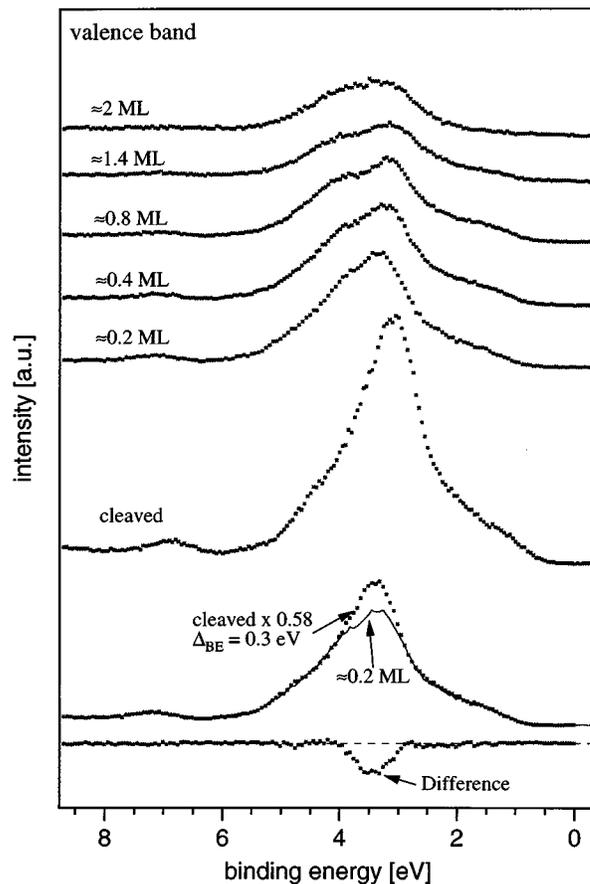


FIG. 4. Valence-band spectra of the Na/CuInSe₂ interface for increasing amounts of deposited Na and difference spectra of valence bands taken from cleaved surface and after deposition of ≈ 0.2 ML Na. For difference formation the spectrum from the cleaved surface has been shifted by $\Delta BE = +0.3$ eV and multiplied by 0.58. All spectra were recorded with an excitation energy of $h\nu=80$ eV.

of the cleaved surface by a factor of 0.58 and shifted its BE by $\Delta BE = +0.30$ eV. These values are adopted without any further modification from BE and intensity changes of the corresponding In 4d spectra. Finally, the modified spectrum is subtracted from the one obtained after deposition of ≈ 0.2 ML Na. The difference is zero for most BE, justifying the applied procedure; however, at BE around $BE=2.8$ eV there is a considerable intensity loss induced by Na deposition.

The evolution of the sample work function as function of Na deposition is shown in Fig. 5. With photoelectron spectroscopy the work function is determined from the cutoff of secondary electron emission. For the cleaved surface we obtained a work function of $\phi=5.25$ eV. Together with $E_F - E_V \approx 0.4$ eV (see above), this corresponds to an ionization energy of $I_p \approx 5.65$ eV and with $E_g = 1.04$ eV,¹ to an electron affinity of $\chi=4.6 (\pm 0.15)$ eV. With increasing Na deposition the work function decreases monotonically and seems to saturate at a value of $\phi=3.6$ eV.

DISCUSSION

Obviously UHV-cleaved (011) surfaces of CuInSe₂ and sodium form a chemically reactive interface. This is most evident from the appearance of the metallic In 4d compo-

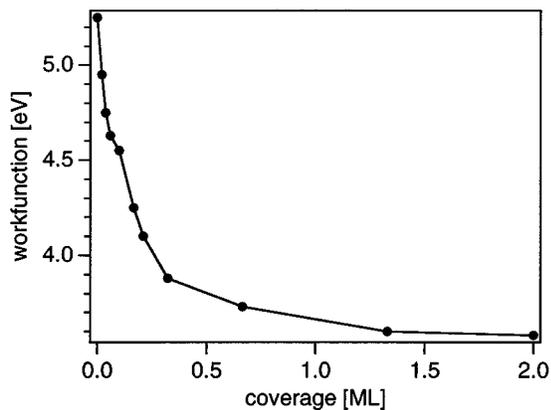


FIG. 5. Evolution of work function for CuInSe₂ in the course of Na deposition. The work function has been derived from the extrapolation of the secondary electron cutoff of valence-band spectra taken with $h\nu=21$ eV.

ment, which indicates the decomposition of the substrate, at least for higher Na coverage. For smaller coverages no change of substrate core level emissions is observed. Therefore, a division between a high- and low-coverage regime can be drawn which is also corroborated from the evolution of the Na 2*p* core level.

For low coverages a Na 2*p* component with a higher BE than for the reacted state is observed. Identical behavior of the Na 2*p* level has been observed by Prietsch *et al.* for Na deposited on cleaved GaAs substrates.¹³ The higher BE of the Na 2*p* level at low coverages has been attributed to Na⁺ ions adsorbed on the surface. The transfer of electrons to the substrate is reflected in the band bending induced by Na deposition. The intensity of Na⁺ should therefore saturate in parallel with the band bending as indeed observed for Na on GaAs.¹³ For nonreactive interfaces this saturation generally occurs already at very low coverages, i.e., considerably less than 0.1 ML.¹¹ However, as evident from Fig. 1, the intensity of the high-BE component saturates after 0.4–0.5 ML coverage for the Na/CuInSe₂ interface, while the band bending is already fully developed after 0.2 ML (or even less).

Although there is no evidence from core levels for an interface reaction at low Na coverage, the valence-band difference spectra in Fig. 4 show a significant loss of substrate emissions at BE ≈ 2.8 eV. This BE regime corresponds to the most intense valence-band emissions at an excitation energy of $h\nu=80$ eV. Because of the energy dependence of photoionization cross sections⁸ the valence bands taken at higher photon energies only reflect the contribution of Cu to the density of states.^{14,15} The intensity loss for low coverages is thus most likely explained by a stoichiometric reduction of Cu within the sampling depth (~10 Å). As pointed out by Jaffe and Zunger, and optical band-gap transition in CuInSe₂ stabilizes the Cu—Se bonds, because an electron is removed from the antibonding Cu 3*d*–Se 4*p* orbital combinations.¹² The donation of electrons into the Cu 4*s* conduction states by electropositive adsorbates may in turn lead to breaking of Cu—Se bonds. Diffusion of Cu⁺ ions into the substrate is then favored by the electric field at the surface which is induced by band bending.

The release of Cu from crystallographic positions and subsequent diffusion of Cu⁺ into the bulk also explains the large amount of Na⁺ species observed. We expect Cu vacancies in CuInSe₂ to act as electron acceptor states, since the missing Cu 3*d* electrons, which constitute the Cu—Se bonds, will create holes in the conduction band. These will compensate the electron donation from adsorbed Na. Hence, a larger amount of Na⁺ is required to maintain the induced band bending. Thin films of CuInSe₂ grown on sodium-containing substrates show an increased *p*-type conductivity.¹⁶ This corroborates our explanation of acceptor formation induced by Na deposition. Finally the question arises whether Cu vacancies are stable in the presence of Na. Incorporation of Na on Cu vacancies would create Na—Se bonds and is thus expected to be energetically favorable. This energy gain might also be crucial for the removal of Cu from its equilibrium lattice position. However, the substitution of Cu by Na remains to be experimentally verified.

The lower-BE species of Na observed at higher coverages might be assigned to metallic Na; however, metallic Na exhibits a much smaller work function ($\Phi_{\text{Na}}=2.75$ eV)¹⁷ than determined for our reacted overlayer ($\Phi_{\text{Na/CuInSe}_2}=3.6$ eV; see Fig. 5). Moreover, for metallic Na a plasmon loss structure should be observed on the high-BE side of the Na 2*p* line which is not the case in our experiment. Therefore, we attribute the low-BE component of the Na 2*p* line to Na₂Se formed by chemical decomposition of CuInSe₂. This assignment is supported by the appearance of a metallic In component. It is also consistent with a photoemission investigation of the chemically reactive interface of Na with InSe where comparable Na 2*p* and valence-band spectra have been observed.¹⁸ The formation of Na₂Se is further reflected in the low-BE component of the Se 3*d* level which grows with increasing Na deposition as also observed for the Na/InSe interface.¹⁸

The high-BE component of the Se 3*d*- and the In 4*d* levels both directly evolve from the CuInSe₂ species; therefore, they might be attributed to undisrupted CuInSe₂. However, the two components show different behavior of BE for higher Na coverages (see above). In addition the relative intensities of the reacted Se 3*d*- to the high-BE Se 3*d* component is three times that of the metallic In 4*d*- to the high-BE In 4*d* component. Moreover, there is an increase in linewidth of the high-BE In 4*d* component for higher Na coverages. These observations clearly indicate the presence of further chemical species which contribute to the high-BE In 4*d*- and to the low-BE Se 3*d* component, respectively. Therefore, it is only the low-BE species of the Se 3*d* level that still represents undisrupted CuInSe₂. Possible candidates of the spectroscopically unidentified products of the chemical decomposition are InSe, Cu₂Se, or any combinations of these. There is no way for the determination of the relative amount of these additional species from the presented data, especially because of their unknown spatial distribution. It is not expected that curve fitting the In 4*d*- and Se 3*d* spectra with more than two components will give reliable results, because fitting with two components already gives quite good agreement with the data.

As outlined above a depletion of Cu occurs for initial Na deposition. It is thus also possible that for intermediate amounts of Na a vacancy compound like CuIn_3Se_5 is formed. This compound is of technological importance in CuInSe_2 thin-film solar cell structures because of their role in establishing the band discontinuity, especially the small conduction-band offset, at the CdS/CuInSe_2 interface.⁶ Further chemical decomposition may proceed from this intermediate compound.

SUMMARY AND CONCLUSIONS

The chemical interaction of Na with UHV-cleaved CuInSe_2 (011) surfaces has been studied with synchrotron excited photoelectron spectroscopy. The cleaved surfaces exhibit an electron affinity of 4.6 (± 0.1) eV. A surface core level shift of $\Delta\text{BE}_{\text{surf}} = -0.4$ (± 0.05) eV is observed for the Se 3*d* level. Initially Na adsorbs as Na^+ ions on the surface which is a consequence of its electropositive character. The donation of electrons to the substrate induces a band bending and leads to the breaking of Cu—Se bonds. Released Cu^+ diffuses into the substrate driven by the electric field. The amount of Na^+ species observed on the surface is unusually large and exceeds the concentration necessary for band bending several times. This is explained by the formation of electron acceptor states induced by Na deposition, probably accompanied by replacement of Cu by Na. With increasing Na deposition new chemical species are formed by decomposition of CuInSe_2 . Only metallic indium and Na_2Se can be identified unambiguously. However, also InSe and Cu_2Se may form as is evident from a detailed analysis of core levels

as well as from stoichiometric considerations. In the decomposition reaction vacancy compounds like CuIn_3Se_5 may be formed as intermediate reaction steps.

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