X-ray photoelectron spectroscopy of CuInSe₂

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In x-ray photoemission, we have observed negative shifts of the valence-band maximum with conduction-type conversion from p to n type, induced by a decrease in the [Cu]/[In] ratio of the Cu₁₋ₓInₓSe₂ thin films, deposited by a molecular-beam method. We found no evidence of Cu 2p poorly screened peaks, representing Cu d⁹ electron configuration in the p-type films. Holes in the p-type films are located at the d-p antibonding orbital, dominated by the Se p state in the crystal. The binding energy of the Cu d state, dominating the d-p bonding orbital, is larger than that of the Se p state.

I. INTRODUCTION

Cu₁₋ₓInₓSe₂ (CIS) is of interest for thin-film solar cell applications since it possesses a relatively high absorption coefficient (10⁴-10⁵ cm⁻¹). But its direct band-gap energy (approximately 1 eV) is not appropriate for the optimum efficiency of photovoltaic conversion.

The electric properties of CIS are highly dependent on the stoichiometry. It is believed that an excess of Cu is responsible for p-type conductivity and a deficiency of Cu corresponds to n-type conductivity. The molecular-beam deposition method is particularly suitable for the precise control of the composition and the structure. Stoichiometric or nonstoichiometric CIS thin films can be obtained by molecular-beam deposition in situ. Both the conduction type and the conductivity vary with the change of the [Cu]/[In] ratio, even in the molecular-beam-deposited CIS films. This electrical-property change was probably brought about by the change of electronic structure in the valence and the conduction bands.

Self-consistent band-structure calculations of CIS were performed and could predict the valence-band spectra obtained by Al Kα x-ray and synchrotron radiations. But there is still a discussion of the relative position of the Cu 3d and Se 4p states in x-ray emission spectroscopy. The x-ray emission process is rather complicated and obeys certain selection rules.

An advantage of x-ray photoelectron spectroscopy (XPS) for the investigation of the electronic structure is that it gives the density of states of the materials directly. In this experiment, we obtained the results while being in situ. The Cu 3d and Se 4p states in the x-ray emission spectroscopy. The x-ray emission process is rather complicated and obeys certain selection rules.

A. Sample preparation

CIS films with 1.5-μm thickness were used in this experiment. The conditions of the CIS molecular-beam deposition are described elsewhere in detail. At various substrate temperatures ranging from 670 to 770 K, the films were deposited onto quartz substrates while controlling the temperatures with three elemental effusion cells. Those cells are water cooled and provided with liquid-nitrogen shrouds. The temperatures of the sources were 1400–1450 K for Cu, 1100–1150 K for In, and 400–450 K for Se. The constancy of the beam fluxes was better than 5%. The order of the base pressure in the deposition chamber was 1×10⁻⁹ Torr.

The composition of the films was determined by both inductively coupled plasma-optical-emission spectroscopy and electron-probe microanalysis (EPMA). Based on the EPMA, the components (Cu, In, and Se) were found to be distributed homogeneously throughout the plane of the films. The composition, the conduction type, and the conductivity of the films are listed in Table I. The [Cu]/[In] ratio is clearly the key parameter for controlling the electrical properties of the films.

Secondary electron microscopy demonstrated that the grain size was strongly affected by the [Cu]/[In] ratio of the film. The grains are larger in a Cu-rich film than in an In-rich film. X-ray diffraction essentially indicated the polycrystalline structure of the films. The tetragonal chalcopyrite structure was confirmed by the (101) reflection. Higher preferred (112) orientation was observed for the films with larger [Cu]/[In] ratio. In Raman spectroscopy of the films, an intense peak around 185 cm⁻¹, assigned to the A₁ mode of CIS, was observed for all the films. No apparent shift of the A₁ peak due to the change in the [Cu]/[In] ratio was observed. For the other modes of CIS, the lattice vibrations could not be detected. Any lattice vibrations due to second phases could not be observed in this experiment. By electron diffraction and the lattice images of transmission-electron microscopy, it became clear that films consisted of the crystals of tetragonal chalcopyrite structure with...
TABLE I. Composition and electrical properties of molecular-beam-deposited CIS films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (at.%)</th>
<th>In (at.%)</th>
<th>Se (at.%)</th>
<th>Conduction type</th>
<th>Conductivity ($\Omega^{-1}\text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>29.1</td>
<td>22.4</td>
<td>48.5</td>
<td>$p$</td>
<td>$1.2 \times 10^1$</td>
</tr>
<tr>
<td>b</td>
<td>25.6</td>
<td>24.4</td>
<td>50.0</td>
<td>$p$</td>
<td>$1.9 \times 10^1$</td>
</tr>
<tr>
<td>c</td>
<td>24.3</td>
<td>25.8</td>
<td>49.9</td>
<td>$n$</td>
<td>$5.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>d</td>
<td>23.4</td>
<td>26.5</td>
<td>50.1</td>
<td>$n$</td>
<td>$4.0 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

lattice defects such as twin boundaries, stacking faults, and dislocations. Near the grain boundaries of the films, there was no second phase in either the Cu-rich or In-rich films.

There were reports suggesting the presence of second phases of Cu$_2$Se in the grain and Cu$_{2.5}$Se at the grain boundary of the excess Cu CIS film, but we could not observe a second phase in the grain and at the grain boundaries even in the Cu-rich film. Many lattice defects (twin boundaries, stacking faults, and dislocations) and grain boundaries, which can act as carrier recombination centers and reduce the carrier lifetime greatly, were found in the as-grown CIS films deposited by the molecular-beam method. Therefore, it becomes feasible to observe the change of electronic structure due to the [Cu]/[In] ratio change because the carrier concentration must be high enough to change the conductivity of the films.

B. XPS measurement

XPS and x-ray-induced Auger electron spectra were measured by a hemispherical electron spectrometer with Al $K\alpha$ radiation in vacuum pressure less than $3 \times 10^{-8}$ Pa at 300 K. The spectrometer was calibrated, utilizing the Au 4f$_{7/2}$ (84.0 eV), Pd 3d$_{5/2}$ (335.4 eV), and Ag 3d$_{5/2}$ (368.3 eV) electrons. The satellite x-ray ($K\alpha_3$) contributions to the spectra have been subtracted numerically but no attempt has been made to remove the instrumental broadening. The resolution of the XPS measurement, defined as the full width at half maximum of the Ag 3d$_{5/2}$ line, was 1.15 eV in this experiment. The estimated electron-energy uncertainty was 0.1 eV. The sample temperature was controlled by cooling with air through the cooling pipe leading to the suction pump. The measurement of the electron spectra was carried out after in situ scraping of the film surface with a diamond file until no further change in the XPS spectra was observed.

The partial photoionization cross sections of the Cu 3d, Se 4p, and In 5s orbitals for 1486.6-eV photons were $0.12 \times 10^{-1}$, $0.26 \times 10^{-2}$, and $0.10 \times 10^{-2}$ Mb ($= 10^6$ b), respectively. Therefore, we can expect to observe the change of the valence-band structure due to the [Cu]/[In] ratio change by XPS measurement.

III. RESULTS AND DISCUSSION

A. Valence-band spectra

A self-consistent band calculation revealed that the Cu 3d$^{10}$ orbital, not its 4s orbital, made up most of the charge in the upper valence band. The Cu 4s orbital is repelled upwards from the valence band to the conduction band because the binding energy of the Cu 4s orbital is smaller than that of the Se 4s orbital and the occupied bonding combination is made predominantly from the Se 4p orbitals. The Se 4p orbitals form a threefold-
degenerate state in a cubic crystal field. The fivefold-degenerate Cu 3d orbitals in a cubic crystal field transform into a threefold-degenerate combination with orbital lobes pointing and overlapping with the nearest-neighbor Se ions, and into a twofold-degenerate combination with lobes pointing between the nearest-neighbor Se ions toward the next-nearest shell. The states of the same (threefold) symmetry representation can interact with each other, forming a lower bonding and upper antibonding state. These states are separated from each other by an amount inversely proportional to the Se 4p–Cu 3d energy difference and directly proportional to the Se 4p–Cu 3d coupling matrix element. The band structure is constructed by the delocalization of those states through the whole crystal. Similar arguments hold in the presence of tetragonal chalcopyrite crystal field. In CIS, the valence band has a calculated width of 4.8 eV and the antibonding combination forms the valence-band maximum (VBM). The bonding-antibonding energy separation amounts to 3–4 eV. The twofold-degenerate states do not form any sigma bonds with the nearest-neighbor atoms and correspond to the nonbonding Cu 3d state in the valence band.

The valence-band spectra of the samples, shown in Fig. 1(a), indicated the negative shifts of the VBM, determined from the linear extrapolation of the leading edge. This VBM determination is somewhat arbitrary and can account for the errors in the determination. But the VBM shifted, with the decrease of the [Cu]/[In] ratio, from 0.3 to −0.4 eV. This VBM negative shift corresponds to the conduction-type conversion from p to n type. The Fermi level of the CIS film surface should be pinned at the center of the band gap. The Phillip’s-bond ionicity of CIS was estimated to be 0.5. Essentially, CIS is a covalently (Cu-Se) -bonded semiconductor. It is well known that the Fermi level is pinned at the center of the band gap in covalent semiconductor surfaces. It is further more, the as-deposited CIS films used in this experiment contain a lot of crystal imperfections, such as grain boundaries, dislocations, stacking faults, and twins. These crystal imperfections act as the electron donor and acceptor levels, as well as the electron and hole trap levels. The trap levels, positioned below the conduction band and above the valence band, compensate each other and do not alter the Fermi level.

The substantial width of the observed upper valence-band spectra agrees with that of the calculated result.8 The binding energies of the peak maximum of the Cu-Se d–p-hybridized upper valence band, In-Se s–p bond, Se 4s level, and In 4d level were 3.0, 6.5, 12.6, and 17.9 eV, respectively. These values are in agreement with the results (upper valence band, 3.3 eV; In-Se bond, 6.3 eV; Se 4s level, 13.0 eV; and In 4d level, 17.6 eV), reported by Rife et al.9 We could observe the reported main peak around 3 eV and the shoulder peak below 1 eV in the upper valence band.

The electron binding energies (BE’s) of the In 4d and In 3ds/2 (Table II) levels lie constantly within the experimental uncertainty, although the conduction-type conversion from p to n type occurred with the composition change from Cu rich to In rich. This can be well understood and is consistent with the self-consistent band calculation.8 In the CIS electronic charge-density distribution of the upper valence band, the Cu-Se contact appeared covalently bonded with a significant ionic component, whereas the In-Se contact appeared to be nonbonding. The In atom merely filled up the space without forming a strong bond with the Se atom.8

The upper valence-band spectra of the samples and their difference spectra are shown in Fig. 1(b) with the reproduced histogram of the calculated density of states of CIS.8 On the basis of molecular-orbital predictions, the valence band from 0 to 5 eV consisted of the Cu-Se antibonding, Cu 3d nonbonding, and Cu-Se 3d-4p bonding orbitals. The peak intensity around 3 eV decreased and the shoulder peak around 1.2 eV (A) increased prominently, as seen in the difference spectra, with the decrease of the [Cu]/[In] ratio of the samples. Here the peaks around 1.2 eV and 3 eV correspond to the d–p antibonding and 3d nonbonding orbitals, respectively. The emission intensity from 1.2 eV (A) to −1.2 eV (B) across the Fermi level also increased gradually with the decrease of the [Cu]/[In] ratio of the samples. The emission-intensity increase around the Fermi level reflects the increase of trapped electron density in the band gap, resulting in Fermi-level pinning at the surface. It is well known that the lowest conduction band with the width of 1 eV, which is the unoccupied Cu 4s level, is located at 1 eV lower in the binding-energy scale relative to the top of the valence band.19 The observed increase of photoelectron emission above VBM originates in both the occupied states in the band gap and at the lowest conduction band. Stoichiometric CIS exhibits semiconductor characteristics with a filled valence band. In the p-type Cu-rich CIS films, the holes are located at the d–p antibonding orbitals. In the n-type In-rich CIS films, the electrons are located at the lowest conduction band whose symmetry is s. It is the unoccupied state in the

| TABLE II. Photoelectron BE’s and Auger electron KE’s of the CIS thin films (eV). |
|-----------------|----|----|----|----|
| Samples | a | b | c | d |
| Cu 2p3/2 | 932.6 | 932.3 | 932.1 | 932.1 |
| In 3d3/2 | 444.8 | 444.8 | 444.6 | 444.6 |
| Se 3d | 54.5 | 54.5 | 54.4 | 54.3 |
| Cu L2,3MM | 917.7 | 917.5 | 917.4 | 917.4 |
| In M4,5NN | 408.0 | 408.1 | 408.4 | 408.3 |
| Se L2,3MM | 1307.3 | 1307.3 | 1307.3 | 1307.3 |
stoichiometric semiconductor. In this experiment, we observed the process of electron injection into the top of the valence band and the lowest conduction band by decreasing the [Cu]/[In] ratio to convert the conduction type from p to n type.

This change of electronic structure due to the [Cu]/[In] ratio variation can be reconfirmed by the electron-energy-loss experiment. The electron-energy-loss spectra of the samples, measured by the hemispherical analyzer, and their difference spectra are shown in Fig. 2. The spectral intensities at 3.2 eV (A), and 5.6 eV (B) in Fig. 2 became larger for the samples with increasing [Cu]/[In] ratio, as seen in the difference spectra. The d-electron density of the nonbonding (3 eV) and bonding (4.5 eV) orbitals increases for the samples with increasing [Cu]/[In] ratio. The densities of trapped electrons in the band gap and the lowest conduction band increased with the decrease of the [Cu]/[In] ratio. Therefore, A and B in Fig. 2 can be attributed to the electron transitions from nonbonding d orbital to the electron trap levels around the Fermi level, and from bonding d orbital to the lowest conduction band, respectively. This decrease of electron-transition probability from the occupied states to the unoccupied states directly correlates with the electron injection process into the top of the valence and lowest conduction bands, induced by the decrease of the [Cu]/[In] ratio of the samples.

B. Core-level spectra

The Cu 2p spectra of the samples are shown in Fig. 3. We found no evidence for poorly screened (d⁹) peaks in the spectra even for the Cu-rich p-type samples. The holes are not localized on the Cu site in the Cu-rich films. The holes on the d-p antibonding orbitals are located at the Se site in the p-type films. This result can be readily understood by means of self-consistent band calculations, suggesting that the Cu and Se covalently bonded each other with a significant ionic component. This hole localization at the Se site in the p-type films suggests that the binding energy of the Cu d state, dominating d-p bonding orbitals, is larger than that of the Se p state, dominating antibonding orbitals.

The photoelectron BE’s and Auger electron kinetic energies (KE’s) of the samples are listed in Table II. The BE differences and Auger parameters (AP’s) are listed in Table III. The BE difference seems a convenient parameter for considering the chemical shift because the effect of charge shift must be omitted in that parameter. But it is difficult to analyze some changes in chemical bonds using the BE difference, because the process of photoemission is essentially complicated and the many-electron effects should be reflected on the BE. We must consider the process of photoemission in detail to analyze the effects of the [Cu]/[In] ratio change on the chemical bonding of CIS.

The BE of a level j, \( E_B(j) \), is the difference in the total energy of the system in its ground state and in the state with one electron missing in orbital j. For most situations encountered in XPS, the chemical shift, \( \Delta E_B(j) \), can be divided into two terms:

\[
\Delta E_B(j) = -\Delta \epsilon(j) - \Delta E_R,
\]

where \(-\epsilon\) is the orbital energy and \(E_R\) is the relaxation energy resulting from a flow of negative charge toward the hole created in the photoemission process, in order to screen the suddenly appeared positive charge. The screening lowers the energy of the hole state left behind and it lowers the measured binding energy as well. The relaxation energy can be divided into two terms: intra-atomic relaxation energy (\(E_{R,in}\)) and extra-atomic relaxation energy (\(E_{R,ex}\)). The former is constant for the core-level electrons of a given atom. The latter varies with changes in chemical and physical states.

It is generally stated that the actual photon-absorption process occurs nearly instantaneously (\(<10^{-17} s\)) and the
hole switching occurs in a time much less than $10^{-16}$ s. The localized screening response is very fast ($10^{-16}$–$10^{-15}$ s) in contrast to the delocalized screening response ($10^{-13}$–$10^{-12}$ s).

Delocalized screening is accompanied by core-valence-valence Auger transitions. The KE referenced to the Fermi level of an Auger electron emitted from a transition $jkk$, $E_{\text{kin}}(jkk)$, is given by

$$E_{\text{kin}}(jkk) = E_B(j) - 2E_B(k) - F(kk) + E_{\text{pol}}(kk),$$

where $E_B(j)$ and $E_B(k)$ are the BE’s of the atomic core-level electrons $j$ and $k$, respectively. $F(kk)$ is the interaction energy of the two $k$ holes in the final state and is independent of the change of chemical environment. $E_{\text{pol}}(kk)$ is the static relaxation energy, describing the polarization energy as

$$E_{\text{pol}}(kk) = E_R(kk) - 2E_R(k).$$

$E_R(kk)$ denotes the total two-hole relaxation energy which is four times the one-hole relaxation energy $E_R(k)$. The chemical shift of Auger-electron KE can be written as

$$\Delta E_{\text{kin}}(jkk) = \Delta E_B(j) - \Delta E_B(k) + 2 \Delta E_{R,ex}(k).$$

In the simplest approximation, the change in extra-atomic relaxation energy can be derived from the $P_{\text{Auger}}$ defined as

$$P_{\text{Auger}} = E_B(j) + E_{\text{kin}}(jkk).$$

The difference in the $P_{\text{Auger}}$ for a given element in two different chemical environments is equal to twice the difference in extra-atomic relaxation energies, $\Delta P_{\text{Auger}} = 2\Delta E_{R,ex}(k)$. From a practical point of view, the $P_{\text{Auger}}$ is convenient because it is independent of the absolute energy calibration and of the sample charging. In ionic solids, the extra-atomic relaxation energy can be substituted for the polarization energy of Mott and Gurney. The polarization energy $E_{\text{pol}}$ is given by the following equation in atomic units:

$$E_{\text{pol}} = -(1/2r)(1-1/\epsilon).$$

Here $r$ is the effective hole radius and $\epsilon$ is the dielectric constant at optical frequencies.

It is obvious that the chemical shift with the change of the $[\text{Cu}]/[\text{In}]$ ratio was largest for Cu and that for In was small. From the chemical shifts of BE and $P_{\text{Auger}}$, we can estimate the changes in the orbital energy and extra-atomic relaxation energy. Comparing sample $a$ with sample $b$, the orbital and extra-atomic relaxation energies for Cu decreased by 0.55 and 0.25 eV, respectively, with decreasing Cu content. The decrease of orbital and extra-atomic relaxation energies for Cu from sample $a$ to sample $c$ or $d$ amounted to 0.9 and 0.4 eV, respectively. For Se the decrease of orbital and extra-atomic relaxation energies from sample $a$ to samples $b$, $c$, and $d$ amounted to 0, 0.15, 0.3 eV and 0, 0.05, 0.1 eV, respectively, with decreasing Cu content. The orbital and extra-atomic relaxation energies for both Cu and Se decreased simultaneously but the changes in these energies for Cu were larger than those for Se with changing $[\text{Cu}]/[\text{In}]$ ratio. In CIS, the electrons merging from the Cu site into the nearest-neighbor Se site form a partially covalent bond around both atoms. In the Cu-rich samples, the inclination of this charge distribution from the Cu site to the Se site should be a great deal larger than that in the stoichiometric CIS. The decrease of excess Cu content to the stoichiometry should depress this extreme inclination toward charge distribution by injecting electrons into the top of the valence band that is formed with $d$-$p$ antibonding orbital, and which is partially empty in the Cu excess samples. The charge redistribution induced by the decrease of excess Cu content should largely affect the Cu site rather than the Se site because the electron density on the Cu site is so much smaller than that on the Se site in the Cu excess samples. The enrichment of In, rather than the stoichiometry, enhances the supply of electrons to the Se site through the conduction band. The In enrichment had little influence on the BE’s of In core levels and the polarizability around the In. The change in charge flow from the In site to the Se site is significantly small. The Cu-Se interaction was the bonding interaction but the In-Se bond seems to be the nonbonding interaction. This result can be readily understood from the nature of the chemical bondings expected from the calculated valence-band structure and experimentally observed as described above.

**IV. CONCLUSION**

We have observed directly the process of electron injection into the unoccupied states of nonstoichiometric CIS films deposited by the molecular-beam method. For Cu-rich CIS films, the top of the valence band was filled by the electrons as the $[\text{Cu}]/[\text{In}]$ ratio decreased. For

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 2p$_{3/2}$-Se 3d</td>
<td>878.1</td>
</tr>
<tr>
<td>In 3d$_{5/2}$-Se 3d</td>
<td>390.3</td>
</tr>
<tr>
<td>$P_{\text{Cu}}$</td>
<td>1850.3</td>
</tr>
<tr>
<td>$P_{\text{In}}$</td>
<td>852.8</td>
</tr>
<tr>
<td>$P_{\text{Se}}$</td>
<td>1361.8</td>
</tr>
</tbody>
</table>

**TABLE III.** Photoelectron BE differences and AP’s (eV).
In-rich CIS films, the unoccupied states at the lowest conduction band were filled by electrons as the [Cu]/[In] ratio decreased. The electron-injection process, induced by the decrease of the [Cu]/[In] ratio, brought about negative shifts of VBM and the conduction-type conversion from p to n type, and the change of conductivity. In the p-type Cu-rich CIS films, the holes are located at the d-p antibonding orbitals. The binding energy of the d state is larger than that of the p state.

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9. J. C. Rife, R. N. Dexter, P. M. Bridenbaugh, and B. W. Veal, Phys. Rev. B 16, 4491 (1977). The sharp peak at 2 eV of the upper valence band, reflecting the two branches of the Cu d bands, was observed only in the monochromatized Al Kα radiation XPS measurement. In this unmonochromatized Al Kα XPS experiment, the sharp and less intense peak would become broadened, smeared out, and embedded in the main upper-valence-band peak around 3 eV.
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