

Co-incorporation effects of O and Na with CuInS_2 thin films

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By using x-ray photoelectron spectroscopy we have examined changes in the electronic structure of CuInS_2 thin films with co-incorporation of O and Na that raised up the photovoltaic performance of CdS/CuInS_2 solar cells. The electron binding energies of both the core levels and valence band for the film with the co-incorporation were smaller by 0.9 eV than those for the film without the co-incorporation. For the co-incorporated film an increase in the spectral intensity of the valence band was observed below 1–6 eV from the $\text{Cu } 3d^{10}$ nonbonding states, and it was due to both the $\text{Na } s$, p - S p hybridization and the $\text{In } s$ - O p hybridization. The surface of the co-incorporated film can be expressed as $(\text{Cu, Na})\text{In}(\text{S, O})_2$. The $(\text{Cu, Na})\text{In}(\text{S, O})_2$ phase is related to the enlarged open-circuit voltage (0.75 eV) of n - CdS/p - CuInS_2 solar cells. © 2000 American Institute of Physics. [S0003-6951(00)02143-4]

For fabrication of high-efficiency thin film solar cells, CuInS_2 with chalcopyrite structure is appropriate since the optical band gap (E_g) of approximately 1.5 eV well matches with the solar spectrum. Cu-deficient CuInS_2 thin films are naturally p -type semiconductor because of a deviation from stoichiometry due to the presence of intrinsic defects such as Cu vacancies (V_{Cu}): electronic-band-structure calculations show that the antibonding states between $\text{Cu } 3d$ and $\text{S } 3p$ orbitals are located near the top of the valence band, resulting in weak Cu–S bonds.¹ As the number of V_{Cu} increases, the resistivity of p -type CuInS_2 increases due to bad crystallinity. Thus, the control of V_{Cu} as the dominant intrinsic defects is a key technology for the fabrication of good conductive p -type CuInS_2 thin films. We have demonstrated that the energy-conversion efficiency (η) of 6.6% for n - CdS/p - CuInS_2 cell with the Na incorporation is due to the $(\text{Na, Cu})\text{InS}_2$ phase formation at the CuInS_2 surface.² For CdS/CuInSe_2 cells it has been reported that postdeposition annealing in air or O_2 optimizes the photovoltaic performance.³ The η of the CdS/CuInS_2 cell was raised up to 9.4% by the co-incorporation of O and Na with the CuInS_2 .⁴ It is still of great interest to understand the way in which the O_2 annealing affects the n - p heterojunction and raises up the η . In this letter we report that the co-incorporation of O and Na with the CuInS_2 ($[\text{Cu}]/[\text{In}]=0.75$) results in the new $(\text{Cu, Na})\text{In}(\text{S, O})_2$ phase at the CuInS_2 surface which is responsible for the elevated open-circuit voltage (V_{oc}) to 0.75 eV and η to 9.4%.

The stoichiometric and Cu deficient CuInS_2 films were

used for the reference and for the O and Na co-incorporation, respectively. The films without the co-incorporation (the reference) and with the O and Na co-incorporation were prepared by annealing the precursor films at 550 °C for 2 h in the atmospheres of 5% $\text{H}_2\text{S}/\text{Ar}$ and of 5% $(\text{H}_2\text{S}+\text{O}_2)/\text{Ar}$ ($[\text{O}_2]/[\text{H}_2\text{S}]=0.1$), respectively.^{2,4} The Cu–In–S precursor for the film without the co-incorporation was deposited by reactive sputtering in H_2S gas on the Mo layer fabricated on soda lime glass substrate. The layer stacked In–S/Cu/Na–O/In precursor for the O and Na co-incorporated film was deposited on the Mo/Ti layer on the soda lime glass substrate. Using a hybrid sputtering system, the stacked layers were continuously deposited on the Mo/Ti layer. The In–S layer was formed by reactive sputtering with $\text{H}_2\text{S}/\text{Ar}$ gas. The Na–O layer was evaporated by effusion from an alumina-covered filament. The $[\text{Cu}]/[\text{In}]$ value of 0.75 for the co-incorporated film was determined by atomic absorption spectroscopy. The annealing successfully sulfurized the stoichiometric and Cu deficient films, and crystallized them to chalcopyrite structure.

X-ray photoelectron spectra were measured with a Surface Science Laboratories SSX-100 spectrometer using monochromatized $\text{AlK}\alpha$ radiation in vacuum pressure less than 6×10^{-11} Torr at room temperature. The spectrometer was calibrated by the $\text{Au } 4f_{7/2}$ (83.79 eV) electrons. Charging was referenced to the $\text{C } 1s$ (284.6 eV) electrons. The estimated electron energy uncertainty was ± 0.15 eV in this experiment. The $\text{Cu } 2p$, $\text{In } 3d$ and $\text{S } 2p$ spectra of the CuInS_2 films with and without the co-incorporation of O and Na are shown in the lower, middle, and upper panels of Fig. 1, respectively. The $\text{Cu } 2p$, $\text{In } 3d$ and $\text{S } 2p$ peaks shifted by -0.9 eV with the co-incorporation. With the co-

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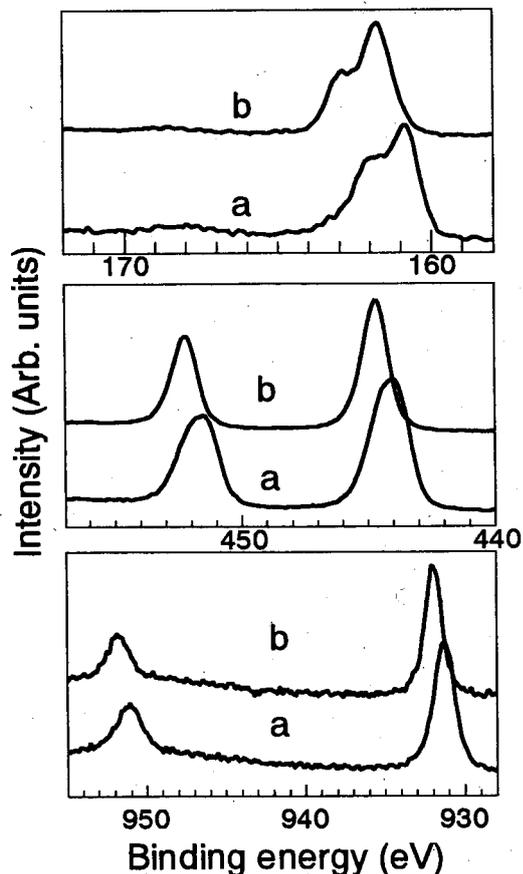


FIG. 1. X-ray photoelectron spectra of the Cu 2*p* (lower panel), In 3*d* (middle panel), and S 2*p* (upper panel) of the CuInS₂ films with (a) and without (b) the co-incorporation of O and Na.

incorporation the full width at half maximum of the Cu 2*p*_{3/2} and In 3*d*_{5/2} peaks broadened from 1.2 to 1.5 eV and from 1.2 to 1.8 eV, respectively, although that of the S 2*p* peak remained the same.

It is reported that electrons were delivered from the Na at the Cu site, Na_{Cu}, into the valence band (VB) when the (Cu, Na)InS₂ phase was formed by the Na incorporation. The Na incorporation resulted in the electron energy shift of both the core levels and VB to the lower energy side by 0.5 eV in spite of the invariance of the linewidths of core levels.² It is readily understood that charge transfer from the 2*s* orbital of Na atom to the 3*p* orbitals of S atoms neighboring to the Na_{Cu} gave rise to a considerable energy shift towards the lower energy region of the VB consisting of primarily the S 3*p* states, and it brought about stabilization of ionic charge distribution in the (Cu, Na)InS₂ phase. Therefore, the incorporation of Na to the vacant Cu site decreased the concentration of donor states *V*_S (vacancy at the sulfur site), and enhanced the *p*-type characteristics of the Cu deficient CuInS₂.

The observed broadening for the core levels of Cu and In atoms with the invariance for that of S atom suggests that O atoms occupied at the S sites in the film during the incorporation process. Since both the O and S are the same VI family elements and the electronegativity of O (3.5) is larger than that of S (2.5), the O at the S site, O_S, would cause a substantial energy shift to the lower energy side for the VB, and would enhance the *p*-type characteristics of the CuInS₂. Coexistence of M–S and M–O bonds in the co-incorporated

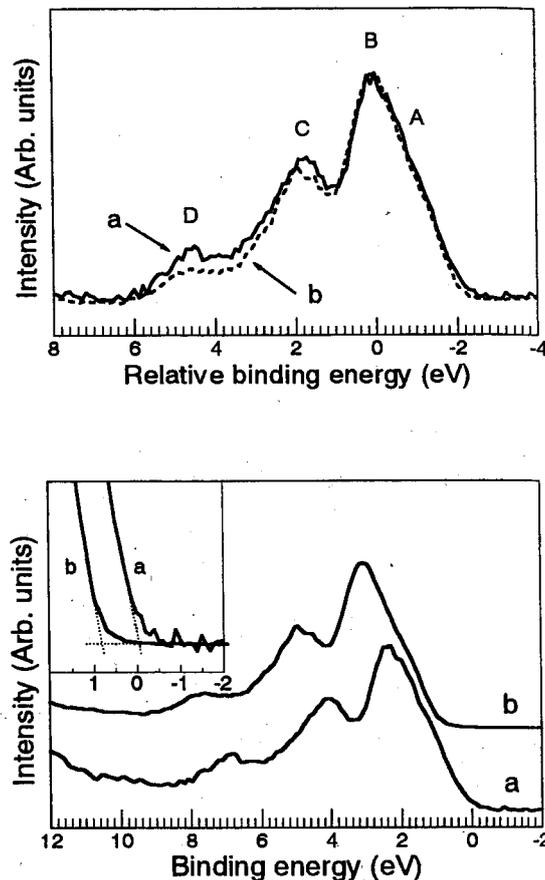


FIG. 2. X-ray photoelectron VB spectra of the CuInS₂ films with (a) and without (b) the co-incorporation of O and Na. Inset: the VBM of the films with (a) and without (b) the co-incorporation. VB spectra (lower panel) aligned at the Cu *d*¹⁰ peak top of the CuInS₂ films with (a) and without (b) the co-incorporation of O and Na (upper panel).

film would broaden the observed linewidths of core levels of M atoms. Therefore, the chemical state of the co-incorporated film can be expressed as (Cu, Na)In(S, O)₂ which is responsible for the observed decreasing potential energy by 0.9 eV.

Both the O and Na atoms locating at S and Cu sites, respectively, should result in an increase of the density of states (DOS) in the VB region. The lower panel of Fig. 2 shows the VB spectra of the films with and without the co-incorporation. The positions of nonbonding Cu *d*¹⁰ peak and the valence band maximum (VBM) shown in the lower panel of Fig. 2 shifted by -0.9 eV with the co-incorporation similarly observed for the core electrons. The VB spectra aligned at the Cu *d*¹⁰ peak top are shown in the upper panel of Fig. 2. Increments in the spectral intensity of the VB with the co-incorporation of O and Na appeared at below 1–6 eV from the Cu 3*d*¹⁰ nonbonding states. They are due to both the Na 3*s*, 3*p*–S 3*p* hybridization and the In 5*s*–O 2*p* hybridization.

In order to clarify the co-incorporation effects of O and Na with CuInS₂, we have carried out a first-principle band structure calculation using the augmented spherical wave method with the local density treatment of electronic exchange and correlation. The calculation is described elsewhere in detail.^{5,6} We employed 3*d*–4*p* orbitals for Cu atoms, outermost *s* and *p* orbitals for Na, In, O, and S atoms as the valence electrons. Under periodic boundary conditions of

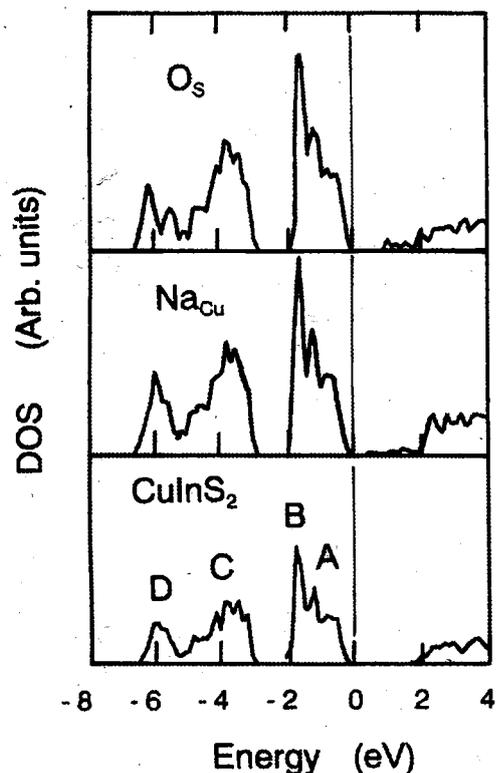


FIG. 3. Calculated total DOS of intrinsic CuInS_2 (lower panel), $(\text{Cu}_{0.9375}\text{Na}_{0.0625})\text{InS}_2$ (middle panel), and $\text{CuIn}(\text{S}_{0.875}\text{O}_{0.125})_2$ (upper panel). In the lower panel, letters A, B, C, and D refer to the Cu $3d$ - $3p$ antibonding states, Cu $3d^{10}$ nonbonding states, Cu $3d$ - $3p$ bonding states, and In $5s$ - $3p$ bonding states, respectively.

the chalcopyrite structure, we generated the super cells having 128 atoms with 64 empty spheres and replaced one of 16 sites of Cu atoms by Na to simulate the Na incorporation effect at the vacant Cu sites. The composition amounts to $(\text{Cu}_{0.9375}\text{Na}_{0.0625})\text{InS}_2$. For the simulation of the O incorporation effect at the vacant S sites, we also constructed a unit cell with monoclinic symmetry of 32 atoms with 16 empty spheres, and we replaced one of eight sites of S atoms with O. The composition amounts to $\text{CuIn}(\text{S}_{0.875}\text{O}_{0.125})_2$.

The total DOS of intrinsic CuInS_2 , $(\text{Cu}_{0.9375}\text{Na}_{0.0625})\text{InS}_2$, and $\text{CuIn}(\text{S}_{0.875}\text{O}_{0.125})_2$ are shown in the lower, middle and upper panels of Fig. 3, respectively. Letters A, B, C, and D in the lower panel of Fig. 3 refer to the Cu $3d$ - $3p$ antibonding states with a higher Cu $3d$ contribution, Cu $3d^{10}$ nonbonding states, Cu $3d$ - $3p$ bonding states with a higher S $3p$ contribution, and In $5s$ - $3p$ bond-

ing states, respectively. Lower and middle panels show a little difference in the shape of the DOS. Although the difference is based on the formation of Na-S chemical bonds; strong interactions occur between the Na $3p$ and S $3p$ states located at -3 eV in the region C and between the Na $3s$ - $3p$ states at -5 eV.⁵ As shown by the Fig. 3, it is obvious that with the substitution of Cu by Na the DOS from the Na $3p$ and $3s$ - $3p$ bonding states appear at below 1-4 eV from the nonbonding Cu $3d^{10}$ states. Calculated Madelung energy of $\text{CuInS}_2:\text{Na}_{\text{Cu}}$ is smaller by 7 eV than that of intrinsic CuInS_2 .⁵ As seen in the upper panel of Fig. 3, the substitution of S by O widens the bandwidth slightly at around the energy region D below 5 eV from the nonbonding Cu $3d^{10}$ states by forming the In $5s$ - $\text{O}2p$ bond.⁶ As mentioned above, the electronegativity of O is larger than that of S; the effect of O_S atom on the VB electronic structure would be more apparent for the region D corresponding to the In $5s$ - $3p$ bonding states because there exists an excess electron in the case of octet electron configuration for the In $5s^25p^1$ - $3s^23p^4$ bond. The O_S atom stabilizes the ionic charge distribution of p - CuInS_2 more effectively. The band calculation revealed that the co-incorporation of O and Na with CuInS_2 tends to increase the intensity and to extend slightly the width of VB below 1-5 eV from the nonbonding Cu $3d^{10}$ state. The experimental result of the O and Na co-incorporation increasing the VB spectral intensity at below 1-6 eV from the nonbonding Cu $3d^{10}$ states agrees with the theoretical one mentioned above.

We showed that the decrements of electron binding energy for both the core levels and VB by 0.9 eV by the co-incorporation of O and Na with CuInS_2 is ascribed to the In-O and Na-S bonds of the $(\text{Cu, Na})\text{In}(\text{S, O})_2$ phase. The change of the potential energy due to $(\text{Cu, Na})\text{In}(\text{S, O})_2$ is primarily responsible for the enhanced cell performance such as V_{oc} of 0.75 eV and η of 9.4% with the co-incorporation.

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