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Wurtzite $CuGaO_2$: A New Direct and Narrow Band Gap Oxide Semiconductor Applicable as a Solar Cell Absorber

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Supporting Information

ABSTRACT: An oxide semiconductor β-$CuGaO_2$ with a wurtzite-derived β-$NaFeO_2$ structure has been synthesized. Structural characterization has been carried out by Rietveld analysis using XRD and SAED, and it was shown that the lattice size is very close to that of zinc oxide. The optical absorption spectrum indicated that the band gap is 1.47 eV, which matches the band gap required to achieve the theoretical maximum conversion efficiency for a single-junction solar cell. The thermoelectromotive force indicated p-type conduction in its intrinsic state. Density functional theory calculations were performed to understand the electronic structure and optical properties of the semiconductor. These calculations indicated that β-$CuGaO_2$ is a direct semiconductor and intense absorption of light occurs near the band edge. These properties render this new material promising as an absorber in solar cells.

Oxide semiconductors that consist of cations of main group elements with an $nd^{10}(n+1)s^0$ electronic configuration have attracted much attention in recent decades because of their emerging applications, for example, as active layers in thin film transistors, light-emitting diodes in the ultraviolet region, and as transparent electrodes.[1−3] Wide band gap plays a key role in the performance of oxide semiconductors. Little attention has been paid to narrow band gap oxide semiconductors ($Eg < 2$ eV) because there is a variety of III−V pnictides and II−VI chalcogenides with narrow band gaps.[4] However, great abundance and nontoxicity of oxygen and excellent stability of the oxide in air and water at ambient conditions are very attractive features of oxide semiconductors. The exploration of oxide semiconductors with narrow band gaps is expected to greatly extend the application areas of these materials. For example, oxide semiconductors with band gaps of 1−1.5 eV are attractive as solar cell absorbers.[5]

The direct band gap is one of the most important features of semiconductor materials applied in photoelectric devices. Materials with diamond-related wurtzite or zincblende structures are good candidates as direct semiconductors; however, such oxides comprise wurtzite-type ZnO and BeO with an energy band gap of >3 eV.[6] Cation mixing in the wurtzite structure and superstructure formation introduce wurtzite-derived β-$NaFeO_2$-type ternary oxides,[7] such as β-$LiGaO_2$, β-$LiAlO_2$, β-$AgGaO_2$, and β-$AgAlO_2$,[8−13] which are oxide analogues to ternary I−III−VI_2 chalcogenide semiconductors such as $CuInSe_2$. Among these oxide semiconductors, β-$AgGaO_2$ has the narrowest band gap of 2.2 eV.[11,14] Comparison of the delafossite-type α-$AgGaO_2$ and α-$CuGaO_2$, and chalcopyrite-type $AgInS_2$ and $CuInS_2$ semiconductors indicates that the band gaps of the copper-containing compounds are smaller than those of the silver-containing compounds. This is because the copper 3d orbitals, which contribute significantly to the valence band maximum (VBM), are shallower energy than the silver 4d orbitals.[15] It is therefore assumed that the band gap of wurtzite-derived β-$CuGaO_2$ would be narrower than that of β-$AgGaO_2$, although the existence of β-$CuGaO_2$ has yet to be reported.

In this work, we synthesized β-$CuGaO_2$ for the first time. We found that it has a narrow band gap of 1.47 eV, which matches the band gap required to achieve the theoretical maximum conversion efficiency in a single-junction solar cell.[5] Density functional theory calculations indicated that this is a direct semiconductor and that the copper 3d orbitals contribute significantly to the VBM, indicating intense absorption of light near the band edge similar to that for $Cu(In,Ga)Se_2$. The p-type conduction of β-$CuGaO_2$ and its small lattice mismatch with ZnO are promising for developing p/n-heterojunctions with n-type ZnO.

β-$CuGaO_2$ was synthesized via ion-exchange of Na^+ ions in the β-$NaGaO_2$ precursor with Cu^+ ions in CuCl, similar to the synthesis of β-$AgGaO_2$. The β-$NaGaO_2$ precursor was prepared by the solid-state reaction of Na_2CO_3 and Ga_2O_3. Na_2CO_3 and Ga_2O_3 were weighed and mixed, and then pressed into 17.2-mm-diameter disks at 256 MPa. The disks were fired at 900 °C for 20 h and then crushed and mixed with CuCl to achieve a β-$NaGaO_2$:CuCl molar ratio of 1:1. The mixed powder was then heated at 250 °C for 48 h under vacuum and the product was washed with ultrapure water to eliminate the soluble byproduct, NaCl. Finally, the obtained powder was dried at room temperature in a vacuum desiccator. The sample changed from white (β-$NaGaO_2$ precursor) to black after ion-exchange. Inductively coupled plasma atomic emission spectrometry

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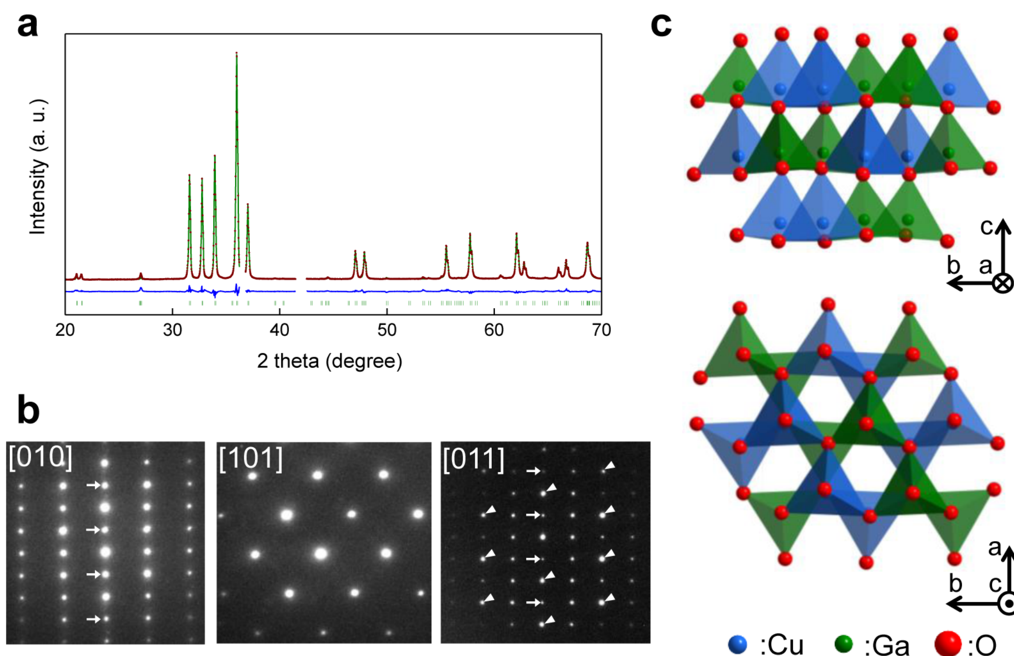

Figure 1. Characterization and schematic illustration of the β-$CuGaO_2$ crystal structure. (a) Powder X-ray diffraction and Rietveld plots. (b) Selected area electron diffraction in the [010], [101], and [011] zone axes. The arrows indicate double diffraction. No superlattice diffraction appears in the [010] and [101] zone axes, and all diffraction spots correspond to the fundamental diffraction of wurtzite. For the [011] zone axis, the diffraction spots, as indicated by the triangles, correspond to the fundamental diffraction spots of wurtzite, and superlattice diffractions are observed. (c) Schematic illustration of the crystal structure based on Rietveld analysis.

(ICP-AES) performed on the sample after ion-exchange indicated that the atomic ratio of Ga:Cu:Na was 1:1.00656:0.0015. Although a very small amount of sodium impurity was detected, the ICP-AES analysis indicated complete exchange of Cu^+ with Na^+ in the β-$NaGaO_2$. No other impurities were detected in the sample after ion-exchange.

The X-ray diffraction (XRD) pattern of the obtained powder (Figure 1a) was distinctly different from that of the β-$NaGaO_2$ precursor.[16] All diffractions observed were assigned to the wurtzite-derived β-$NaFeO_2$ structure except for diffractions from trace Cu_2O impurity observed at 2θ values of ≈36° and ≈42°. In Figure 1b, the selected area electron diffraction images are presented. Distinct superlattice diffractions appear for the [011] zone axis in addition to the fundamental diffractions of the wurtzite structure. These results indicate that β-$CuGaO_2$ with a wurtzite-derived β-$NaFeO_2$ structure was successfully synthesized. Rietveld refinement of the XRD profiles using the code RIETAN-FP[17] was performed by assuming that the obtained material possesses a β-$NaFeO_2$ structure with a space group of $Pna2_1$ (Figure 1a and Table S1 in the Supporting Information). The bond lengths for Ga−O and Cu−O were determined to be 1.79−1.95 and 2.00−2.17 Å, respectively, and the bond angles of O−Ga−O and O−Cu−O were similar to the tetrahedral angle of 109.5° (Figure S1 in the Supporting Information). Because the spatial sizes of the GaO_4 and CuO_4 tetrahedra are comparable, the distortion of the wurtzite-like framework is very small as shown in Figure 1c. The pseudohexagonal wurtzite lattice parameters of β-$CuGaO_2$, a_w = 3.231 Å and c_w = 5.278 Å, are very close to those of ZnO, a = 3.250 Å and c = 5.207 Å;[18] that is, the lattice mismatch between β-$CuGaO_2$ and ZnO is only 0.6% in the ab-plane and 1.4% along the c-axis. Such a small lattice mismatch is an attractive feature as this suggests that β-$CuGaO_2$ grows epitaxially on single crystals and/or on preferentially oriented polycrystalline ZnO substrates.

The black color of β-$CuGaO_2$ (Figure 2, inset) suggests that the band gap is smaller than 2 eV. In the optical absorption

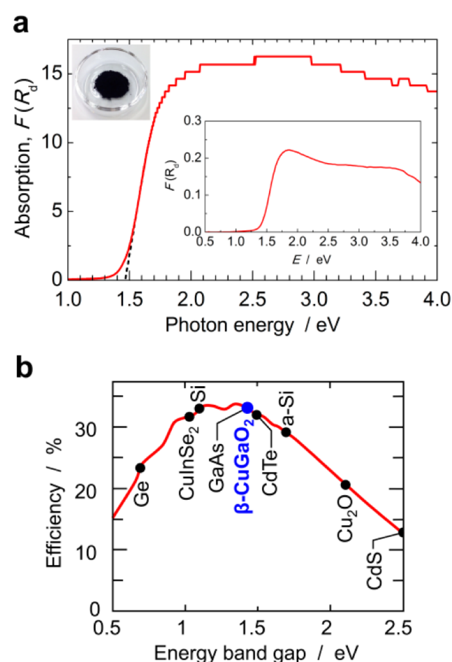

Figure 2. (a) Optical absorption spectrum of β-$CuGaO_2$ obtained using diffuse reflection spectroscopy. The insets are an optical image of the β-$CuGaO_2$ powder and a spectrum of β-$CuGaO_2$ diluted with Ga_2O_3. (b) Conversion efficiency of a solar cell as a function of the band gap energy based on a semiconductor in the Shockley−Queisser limit using an AM1.5G spectrum as the illumination source.

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spectrum, obtained from diffuse reflection (Figure 2a), intense absorption is only observed above 1.47 eV. In the spectrum of the β-$CuGaO_2$ diluted with Ga_2O_3 (Figure 2a, inset), which was recorded to observe the spectral features in the region of intense absorption, no additional absorption to the 1.47 eV absorption appeared above 2 eV. When the absorption starting at 1.47 eV is related to the impurity or defect levels, the absorption intensity is not so high; therefore, the true band edge absorption should be detected above 2 eV. However, as can be seen in Figure 2b, no additional absorption edge above 2 eV is observed. This indicates that the absorption starting at 1.47 eV is not related to impurities or defects but is due to band edge absorption. Thus, we conclude that the band gap of β-$CuGaO_2$ is 1.47 eV. Moreover, the high absorption intensity suggests that the electronic transition is not indirect but direct. The band gap of β-$CuGaO_2$ is very close to that of GaAs and CdTe, and corresponds to the maximum conversion efficiency of a single-junction solar cell according to the Shockley—Queisser theory (Figure 2b).[5]

The electrical conductivity of sintered β-$CuGaO_2$ without intentional doping was 1×10^{-6} Ω^{-1} cm^{-1} at room temperature. It showed a thermoelectromotive force of 400 μV K^{-1}; this indicates that conduction is p-type in β-$CuGaO_2$ without intentional doping (i.e., in its intrinsic state). Consequently, a p/n-heterojunction is expected to form in β-$CuGaO_2$ with n-type ZnO taking the small lattice mismatch into account. This is an excellent feature for the application of β-$CuGaO_2$ in thin-film solar cells even if the β-$CuGaO_2$ p/n-homojunction is difficult to develop.

One of the most important properties of semiconductors employed as thin-film solar cell absorbers is the characteristic of the band gap—direct or indirect—because this determines the absorption intensity of sunlight. We performed first-principle pseudopotential density functional theory (DFT) calculations using the generalized gradient approximation (GGA) with a PBEsol functional. First, we optimized the geometry of the β-$CuGaO_2$ crystal with a space group of $Pna2_1$. The calculated lattice and atomic parameters (Table S2 in the Supporting Information) agreed well with the values obtained from Rietveld analysis of the XRD pattern at room temperature. The calculated electronic band structure (Figure 3a) indicates a direct band gap of 0.001 eV between the VBM and conduction band minimum (CBM) at Γ points. This value is obviously smaller than the experimentally determined value of 1.47 eV at room temperature. Generally, the GGA calculation underestimates the band gap;[19] therefore, the experimentally determined band gap is consistent with the calculated value. We also checked the calculated band gap using the screened-exchange local density approximation (sX-LDA) (Table S3 and Figure S2 in the Supporting Information). The calculation gave a 2.737 eV direct band gap. Because the sX-LDA calculation—unlike the GGA calculation—frequently overestimates the band gap, especially for narrow-band gap semiconductors,[19,20] the experimentally determined band gap of 1.47 eV, which lies between the band gaps determined by GGA and sX-LDA, is quite reasonable. In Figure 3b, the VBM mainly consists of copper 3d orbitals and the CBM is composed of copper and gallium 4s orbitals. The significant contribution of the copper 3d orbitals to the VBM introduces a large density of states around the VBM; this is comparable to the reported electronic structure of $CuInSe_2$.[21] The characteristics of the valence band and the direct band gap suggest the intense absorption of light near the band edge, which is consistent with the observed absorption spectrum. Consequently, β-$CuGaO_2$ is highly suitable as a solar cell absorber in terms of its optical properties.

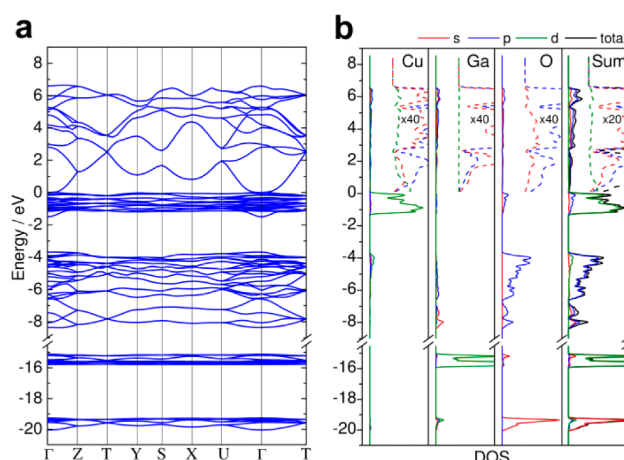

Figure 3. Electronic band structure of wurtzite-derived β-$CuGaO_2$ calculated using the GGA method with a PBEsol functional: (a) the band structure along the symmetry line; (b) corresponding total and partial density of states.

In general, the VBM of most oxides of main group elements is composed predominantly of oxygen 2p orbitals, and the holes introduced in the valence band are highly localized. Thus, realizing p-type conduction in oxides of main group elements is difficult. Among the oxides, Cu_2O, and delafossite-type α-$CuInO_2$, α-$CuGaO_2$, and α-$CuAlO_2$, which include monovalent Cu^+ ions, can achieve p-type conduction.[22−25] In these materials, Cu 3d orbitals contribute significantly to the VBM and modulate the contribution of the O 2p orbital.[26,27] Such an electronic structure is essential for p-type conduction in oxide semiconductors; therefore, the electronic structure around the VBM of β-$CuGaO_2$ that consists of mainly copper 3d orbitals is consistent with the observed p-type conduction in the intrinsic state. On the other hand, the CBM that consists of Cu and Ga 4s orbitals is a common feature of n-type oxide semiconductors. Thus, the electronic band structure and partial density of states of β-$CuGaO_2$ predict that it is essentially a p- and n-type ambipolar conductor, which features a direct and narrow band gap, and strong optical absorption.

In summary, we have synthesized a wurtzite-derived β-$CuGaO_2$ semiconductor with a narrow and direct band gap. Its band gap of 1.47 eV matches the required energy to achieve the theoretical maximum conversion efficiency for a single-junction solar cell. The p-type conduction of the β-$CuGaO_2$ and the small lattice mismatch with ZnO are promising for the development of a p/n heterojunction of β-$CuGaO_2$ with n-type ZnO. These features make this new material suitable as a light absorber in thin-film solar cells. Until now, Cu_2O is the only oxide semiconductor that has been applied in thin-film solar cells; however, conversion efficiencies of Cu_2O-based solar cells still remain at approximately 4%.[28] Our findings are expected to contribute to the fabrication of oxide-based thin-film solar cells that can compete in terms of conversion efficiency with existing chalcogenide-based thin-film solar cells.

■ ASSOCIATED CONTENT

Supporting Information

Additional information including experimental details of the synthesis, characterization, Rietveld refinement, geometry by

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GGA and sX-LDA calculations, and the electronic structure obtained from sX-LDA calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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