

Impact of incorporating sodium into polycrystalline p-type Cu₂O for heterojunction solar cell applications

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The resistivity was controlled in the range of 10^3 to 10^{-2} Ω cm in polycrystalline p-type Cu₂O sheets (incorporating sodium (Na)), which are suitable for Cu₂O-based heterojunction solar cell applications. The Na-doped Cu₂O sheets exhibited a hole concentration that ranged from 10^{13} to 10^{19} cm⁻³. In particular, a hole concentration of 10^{13} – 10^{16} cm⁻³ was obtained while maintaining a high Hall mobility above 100 cm²/V s, and, in addition, a degenerated semiconductor exhibiting metallic conduction was realized with a hole concentration above about 1×10^{19} cm⁻³. The mechanism associated with the Na doping can be explained by a copper vacancy produced due to charge compensation effects that result when a Na atom is incorporated at an interstitial site in the Cu₂O lattice. For solar cell applications, the use of the Cu₂O:Na sheet in a heterojunction solar cell successfully improved the obtained efficiency over that found in heterojunction solar cells fabricated using an undoped Cu₂O sheet. © 2014 AIP Publishing LLC.

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Being abundant, low cost and nontoxic, cuprous oxide (Cu₂O) with a direct energy gap of 2.1 eV is a promising semiconductor for photovoltaic applications. Although the theoretical limit of the energy conversion efficiency of a Cu₂O solar cell is as high as 20% under AM1 solar illumination,¹ it is very difficult to achieve a high efficiency because of the difficulty of obtaining an n-type semiconductor as well as the chemical instability of the Cu₂O surface.^{1–5} However, a significant improvement of this situation was recently achieved by the development of n-type oxide semiconductor/p-type Cu₂O heterojunctions fabricated by preparing n-oxide semiconductor thin films using low damage deposition techniques such as a pulsed laser deposition (PLD),^{6,7} ion beam sputtering,⁸ and atomic layer deposition.⁹ A conversion efficiency of 5.38% has been obtained in an Al-doped ZnO (AZO)/Ga₂O₃/Cu₂O heterojunction solar cell fabricated by depositing an n-type amorphous Ga₂O₃ thin film at room temperature (RT) on a polycrystalline Cu₂O sheet prepared with a high Hall mobility of 100–110 cm²/V s using PLD.¹⁰ In these heterojunction solar cells, it is necessary to reduce the resistivity while maintaining the high mobility in Cu₂O sheets prepared by thermally oxidizing a copper sheet; the Cu₂O sheets act as the active layer as well as the substrate.

A decreased resistivity, in the range from 10^3 to 10^1 Ω cm, due to an increase of hole concentration while maintaining Hall mobility, was reported obtained by doping chlorine into Cu₂O sheets with a high temperature process above 1000 °C.^{11,12} The increase of hole concentration with chlorine doping is attributable to an acceptor which could originate from either chlorine incorporated at an interstitial site in the lattice or a copper vacancy produced due to charge compensation effects that result when chlorine substitutes for an oxygen site and acts as a donor;¹¹ the doping mechanism is

not yet clear. In regard to Cu₂O thin films prepared by various deposition methods, there are many reports that the resistivity of Cu₂O thin films could be significantly decreased by doping various impurities.^{13–16} However, the obtained Hall mobility not only was lower than that of Cu₂O sheets but also decreased as the hole concentration was increased with impurity doping. Thus, a further improvement of Cu₂O-based heterojunction solar cell performance requires controlling the resistivity of Cu₂O sheets or thin films while maintaining high mobility as well as reducing the contact resistance on the metal electrode. This paper describes the impact of incorporating sodium (Na) into polycrystalline p-type Cu₂O sheets prepared by thermally oxidizing copper sheets. As a result, the resistivity could be controlled in the range from 10^3 to 10^{-2} Ω cm, while the hole concentration was increased by the incorporation of the Na into the Cu₂O sheets.

The Cu₂O sheets were prepared by oxidizing 200 μm thick 99.96% purity copper sheets using a heat-treatment process at a temperature of 1015 °C, as reported elsewhere.^{6,7,17} Subsequently, the CuO surface layer of the oxidized Cu₂O sheets was removed by etching.¹⁸ The resulting Cu₂O sheets were polycrystalline p-type semiconductors which exhibited electrical properties (at RT) such as resistivity on the order of 10^3 Ω cm, hole concentration on the order of 10^{13} – 10^{14} cm⁻³, and Hall mobility above 100 cm²/V s. The incorporation of Na into the oxidized Cu₂O sheets, thickness of approximately 200 μm, was carried out by post-annealing Cu₂O sheets covered with an appropriate Na compound powder at 400–800 °C for 1–30 h in an Ar or N₂ gas atmosphere. Subsequently, the Na-incorporated Cu₂O sheets were always brought out to the air environment at room temperature. Hall effect measurements were carried out using the van der Pauw configuration in the temperature range from 100 K to RT. Ohmic gold contacts were formed on the Cu₂O sheets by vacuum evaporation.

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We found that resistivity could be decreased from 10^3 to $10^{-2} \Omega \text{ cm}$ by the incorporation of Na into the oxidized Cu_2O sheets with a heat treatment, in an Ar or N_2 gas atmosphere, of the Cu_2O sheets covered with various sodium compounds. Figure 1 shows resistivity (ρ) measured at RT as a function of the annealing temperature (T_a) for postannealed Cu_2O sheets that were covered with Na_2CO_3 or NaCl powder and heat treated for 1 h in an Ar gas atmosphere. The obtained ρ in the postannealed Na-incorporated Cu_2O sheets decreased as the T_a was increased above approximately 400°C , whereas that in postannealed non-doped Cu_2O sheets was relatively independent of the T_a (Ar gas atmosphere). In addition, it was found that a decrease of ρ could also be obtained by postannealing Cu_2O sheets that were covered with other sodium compounds such as NaI and NaF . However, the level of ρ and the T_a dependence of ρ obtained in Na-incorporated Cu_2O sheets were dependent on the kind of sodium compound used. Analyses of the postannealed Cu_2O sheets using secondary ion mass spectrometry (SIMS) measurements showed that the Na in the sheets was distributed uniformly from the surface inwards and the incorporated Na content increased as the T_a was increased with the use of Na_2CO_3 or NaCl . On the other hand, Cl and C were relatively undetectable in all postannealed Cu_2O sheets, except for near the surface. It should be noted that the SIMS measurements showed a segregation of Cl at the grain boundaries (grain size ranged from about 0.5–3 mm) of Cu_2O sheets treated with NaCl .

The decrease of ρ with increasing T_a can be attributed mainly to the increase of hole concentration (p). Although the resulting p increased in postannealed Na_2CO_3 or NaCl treated Cu_2O sheets as the T_a was increased to about 800°C , the Hall mobility (μ) was unchanged when the postannealing occurred below about 600°C ; μ started to decrease when the T_a was increased to a level over approximately 650°C . It was also found that the resulting p increased gradually as the annealing time (t_a) was increased under a constant T_a . It was found that the obtained μ in Na-doped Cu_2O ($\text{Cu}_2\text{O}: \text{Na}$)

sheets remained approximately the same as that in undoped Cu_2O sheets as well as independent of p at levels of p up to approximately $1 \times 10^{16} \text{ cm}^{-3}$; however, a further increase of p resulted in a significant decrease of μ . Figure 2 shows the obtained μ - p relationship in undoped Cu_2O and $\text{Cu}_2\text{O}: \text{Na}$ sheets postannealed with Na_2CO_3 or NaCl under varying T_a or t_a . A p of $1.85 \times 10^{19} \text{ cm}^{-3}$ was obtained in a Cu_2O sheet postannealed with Na_2CO_3 at a T_a of 800°C for 30 h, i.e., the lowest obtained Cu_2O sheet resistivity of $3.95 \times 10^{-2} \Omega \text{ cm}$. It was also found that the content of Na incorporated into a Cu_2O sheet with a p of $1.85 \times 10^{19} \text{ cm}^{-3}$ was the same level as that of the p , as evidenced from X-ray photoelectron spectroscopy. It should be noted that because the increase of p with increasing T_a was more significant than the decrease of μ with increasing T_a , the resistivity could be controlled in the range from 10^3 to $10^{-2} \Omega \text{ cm}$. To investigate the decrease of μ at levels of p above $1 \times 10^{16} \text{ cm}^{-3}$, the crystallographic properties of $\text{Cu}_2\text{O}: \text{Na}$ sheets (postannealed with NaCl) were evaluated using x-ray diffraction (XRD) analyses. All Cu_2O sheets, i.e., with or without incorporated Na, exhibited (110) out-of-plane preferred orientation. However, the position and full-width at half maximum (FWHM) at the (110) XRD peak observed from the $\text{Cu}_2\text{O}: \text{Na}$ sheets postannealed with NaCl were strongly dependent on the T_a . The position and crystallite size estimated by Scherrer's equation from the FWHM at the (110) XRD peak as functions of the T_a are shown in Fig. 3 for the $\text{Cu}_2\text{O}: \text{Na}$ sheets postannealed with NaCl . The crystallinity of the $\text{Cu}_2\text{O}: \text{Na}$ sheets, estimated by the distance between the (110) planes as well as the crystallite size in the (110) direction, degraded as the T_a was increased, corresponding to the increase of p . It should be noted that, although the degradation of crystallinity had already started at a T_a of 400°C , the decrease of μ only starts when T_a is greater than about 650°C . Thus, the result showing a decrease of μ in the $\text{Cu}_2\text{O}: \text{Na}$ sheets as p was increased to levels greater than about $1 \times 10^{16} \text{ cm}^{-3}$ is difficult to attribute solely to a degradation of crystallinity. This suggests the importance of investigating the origin of the

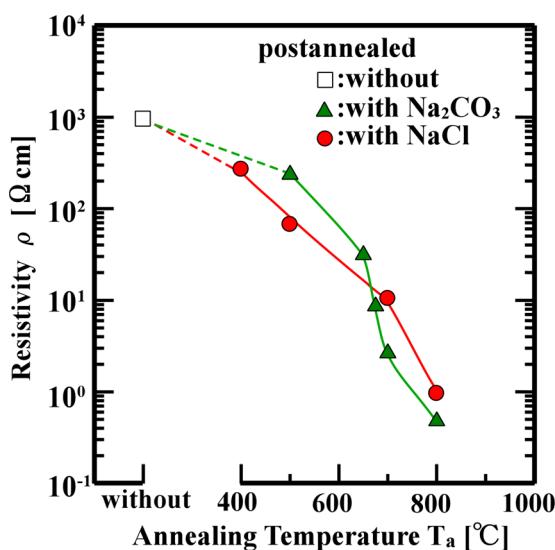


FIG. 1. Annealing temperature (T_a) dependence of obtained resistivity (ρ) in undoped Cu_2O (open symbols) and $\text{Cu}_2\text{O}: \text{Na}$ sheets: Na incorporated by postannealing with NaCl (red circle) or Na_2CO_3 (green triangle).

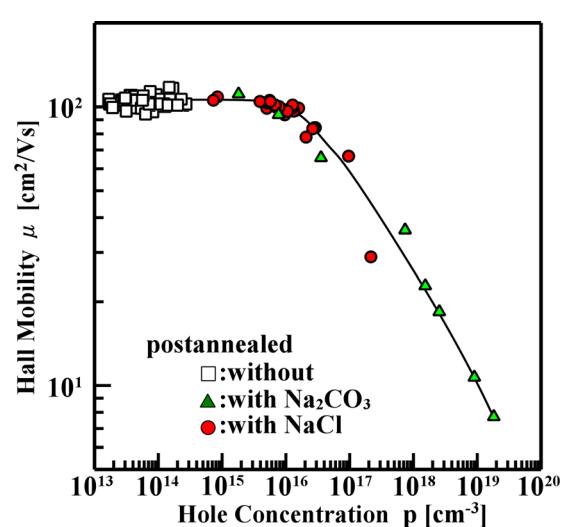


FIG. 2. Relationship between obtained hole concentration (p) and Hall mobility (μ) for undoped Cu_2O (open symbols) and $\text{Cu}_2\text{O}: \text{Na}$ sheets: postannealed with NaCl (red circle) or Na_2CO_3 (green triangle).

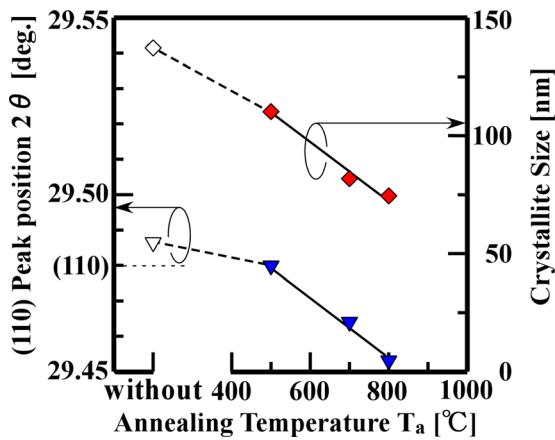


FIG. 3. Position at (110) XRD peak (red diamond) and crystallite size (blue triangle-down) as functions of annealing temperature for undoped Cu₂O (open symbols) and Cu₂O:Na.

increase in p as well as the conduction mechanism of the Cu₂O:Na sheets.

The temperature (T) dependencies of p and μ are shown in Figs. 4(a) and 4(b), respectively, for undoped Cu₂O and Cu₂O:Na sheets with various p (μ): 6.72×10^{13} (103), 4.23×10^{15} (102), 1.04×10^{17} (62.2), 4.01×10^{17} (40.3), 9.3×10^{18} (10.2), and $1.85 \times 10^{19} \text{ cm}^{-3}$ ($8.54 \text{ cm}^2/\text{V s}$) at RT. It should be noted that Cu₂O:Na sheets with p above approximately $1 \times 10^{19} \text{ cm}^{-3}$ are degenerated p-type semiconductors, as evidenced from the fact that the p is independent of the temperature. This indicates a suitability for solar cell applications, because p⁺-Cu₂O:Na sheets could facilitate the forming of ohmic contacts as well as a reduction of contact resistance and series resistance when used as the substrate. As can be seen in Fig. 4(a), the p of undoped Cu₂O and Cu₂O:Na increased exponentially as the temperature was increased, with the exception of p⁺-Cu₂O:Na. These temperature dependencies of p are consistent with those of p-type semiconductors containing acceptors (N_A) that are partially ionized and compensated by donors (N_D). The activation energy (E_A) of acceptor levels and the compensation ratio (N_D/N_A) were estimated by fitting the experimental results involving the temperature dependencies of p to results (indicated with solid lines in Fig. 4(a)) calculated using the

theoretical formula¹⁹ concerning the temperature dependence of p as well as using the same values for the physical parameters of Cu₂O as those used in previously reported literature.^{14,19,20} The estimated E_A in the test samples significantly decreased, while the estimated N_D/N_A slightly decreased, as the p of the samples was increased, as indicated in Fig. 4. The decrease of E_A may be explained as a result of an increase in Fermi energy associated with the increasing p on the basis of the formation of an impurity band resulting from the increase of N_A. This suggests that the increase of p resulting from an increase of the content of Na incorporated into the Cu₂O sheets was achieved by the increase of N_A.

It is well known that, in undoped Cu₂O, a copper vacancy (V_{Cu}) which acts as an acceptor is self-compensated by an oxygen vacancy (V_O) which acts as a donor. Although the ion radius (0.096 nm) of Cu⁺ is close to that of Na⁺ (0.093), it is impossible for a Na atom incorporated at any substitutional site in the Cu₂O lattice to act effectively as an acceptor. Regarding the mechanism of increasing N_A, we have deduced that a V_{Cu} is produced due to charge compensation effects that result when a Na atom is incorporated at an interstitial site in the Cu₂O lattice and acts as a donor. This formation model of a V_{Cu} occurring due to the incorporation of Na at an interstitial site in the Cu₂O lattice is also supported by the fact that the distance between adjacent (110) planes was expanded by the incorporation of Na, as shown in Fig. 3. As a result, the increase of p obtained as the content of incorporated Na was increased is attributed to a V_{Cu} produced due to charge compensation effects that result when a Na atom is incorporated at an interstitial site in the Cu₂O lattice and acts as a donor.

As seen in Fig. 4(b), the μ in both the undoped Cu₂O and Cu₂O:Na sheets, except for the p⁺-Cu₂O:Na sheet, decreased as the temperature was increased above approximately 200 K. The above result suggests that Cu₂O sheets, except for the p⁺-Cu₂O:Na sheets, are dominated by acoustic and optical phonon scattering in the measured temperature range.^{20,21} However, fitting the amount of μ experimentally measured with that theoretically calculated, when limited by acoustic and longitudinal-optical phonon scattering, was difficult because the experimental μ was too small.²⁰ In addition, it should also be noted that at temperatures lower than

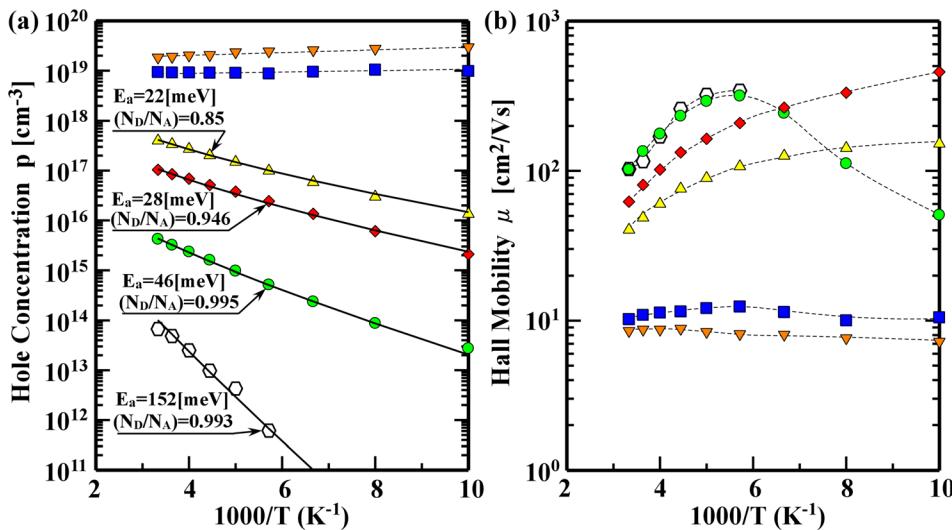


FIG. 4. Temperature dependencies of (a) hole concentration (p) and (b) Hall mobility (μ) for undoped Cu₂O and Cu₂O:Na sheets with hole concentrations of 6.72×10^{13} (open symbols), 4.23×10^{15} (green circle), 1.04×10^{17} (red diamond), 4.01×10^{17} (yellow triangle-up), 9.3×10^{18} (blue square), and $1.85 \times 10^{19} \text{ cm}^{-3}$ (orange triangle-down). Solid lines present the best-fit results calculated theoretically.

approximately 200 K, an increase of μ associated with increasing temperature was only observed from undoped Cu₂O and Cu₂O:Na sheets with a p below approximately $1 \times 10^{16} \text{ cm}^{-3}$. Accordingly, we attempted fitting the temperature dependence of the μ experimentally obtained in undoped Cu₂O and Cu₂O:Na sheets with that theoretically calculated according to the Brooks and Herring formula²² when limited by ionized impurity scattering, taking into account the compensation of acceptor due to donor as the concentration of ionized impurity. The theoretically calculated temperature dependence of μ fit the experimental results obtained in undoped Cu₂O and Cu₂O:Na sheets with p below approximately $1 \times 10^{16} \text{ cm}^{-3}$, whereas there was a large discrepancy in the results obtained in Cu₂O:Na sheets with p on the order of $10^{16}\text{--}10^{17} \text{ cm}^{-3}$ because the theoretical μ , limited by ionized impurity scattering, increased as the temperature was increased. On the other hand, the μ remained at a high level above $100 \text{ cm}^2/\text{V s}$ at RT, even when p was increased to approximately $1 \times 10^{16} \text{ cm}^{-3}$. As mentioned above, the estimated crystallinity for the Cu₂O:Na sheets showed degradation as the T_a was increased with following an increase of p. That is, a drastic decrease of μ and a significant degradation of crystallinity in Cu₂O:Na sheets both resulted when the level of p was increased to greater than approximately $1 \times 10^{16} \text{ cm}^{-3}$, following an increase of Na content doped. Thus, we conclude that the μ obtained in undoped Cu₂O and Cu₂O:Na sheets at RT is limited by phonon scattering and ionized impurity scattering as well as grain boundary scattering.²³

For solar cell applications, n-type oxide semiconductor/p-type Cu₂O heterojunctions were fabricated by forming an AZO/Ga₂O₃ structure on the front surface of Cu₂O:Na sheets (thickness of 200 μm) and a metal (Au) electrode on the back surface: AZO/Ga₂O₃/Cu₂O:Na/Au solar cell, as shown in Fig. 5. The AZO and Ga₂O₃ thin films were prepared with a thickness of 200 and 50 nm, respectively, by a PLD using an ArF excimer laser under optimized deposition conditions, as reported elsewhere.¹⁰ The photovoltaic properties of 16 solar cells (electrode area of 3.14 mm^2) fabricated under the same conditions were evaluated under AM1.5G solar illumination (100 mW/cm^2). In solar cells fabricated using Cu₂O:Na

TABLE I. Obtained maximum efficiency (η_{\max}), V_{OC}, J_{SC}, and fill factor (FF) in an AZO/Ga₂O₃/Cu₂O:Na or /undoped Cu₂O heterojunction solar cell.

Sample (heterojunction)	η_{\max} (%)	V _{OC} (V)	J _{SC} (mA/cm ²)	FF
1 (AZO/Ga ₂ O ₃ /Cu ₂ O:Na)	5.53	0.81	10.18	0.67
2 (AZO/Ga ₂ O ₃ /undoped Cu ₂ O)	5.38	0.80	9.99	0.67

sheets with a p on the order of $10^{13}\text{--}10^{16} \text{ cm}^{-3}$, it was found that the short circuit current density (J_{SC}) increased slightly as the p was increased. The open circuit voltage (V_{OC}) remained relatively unchanged as the p was increased to approximately $1 \times 10^{16} \text{ cm}^{-3}$. As a result, a maximum efficiency of 5.53% was obtained in an AZO/Ga₂O₃/Cu₂O:Na heterojunction solar cell fabricated using a Cu₂O:Na sheet with a p of $5 \times 10^{15} \text{ cm}^{-3}$. As seen in Table I, the obtainable efficiency in a heterojunction solar cell fabricated using the Cu₂O:Na sheet (sample 1) was improved over that in a solar cell fabricated using an undoped Cu₂O sheet (sample 2). To achieve a further improvement of efficiency in heterojunction solar cells, it is necessary to reduce the resistivity of the n-type Ga₂O₃ thin films because the resistance of the Ga₂O₃ thin film layer was at the same level as that of an undoped Cu₂O sheet.

In summary, we have demonstrated the ability to control resistivity in the range from 10^3 to $10^{-2} \Omega \text{ cm}$, associated with a hole concentration in the range of $10^{13}\text{--}10^{19} \text{ cm}^{-3}$, by incorporating Na into Cu₂O sheets. In addition, a high hole concentration of $10^{13}\text{--}10^{16} \text{ cm}^{-3}$ was realized while maintaining a Hall mobility above $100 \text{ cm}^2/\text{V s}$. The Cu₂O:Na sheets prepared with a hole concentration above approximately $1 \times 10^{19} \text{ cm}^{-3}$ were degenerated p-type semiconductors exhibiting metallic conduction. The increase of hole concentration due to Na doping can be attributed to the increase of acceptor concentration resulting from a copper vacancy produced due to charge compensation effects that result when a Na atom is incorporated at an interstitial site in the Cu₂O lattice. A maximum conversion efficiency of 5.53% was obtained in an n-type Ga₂O₃/p-type Cu₂O heterojunction solar cell fabricated using a Cu₂O:Na sheet with a hole concentration of approximately $5 \times 10^{15} \text{ cm}^{-3}$.

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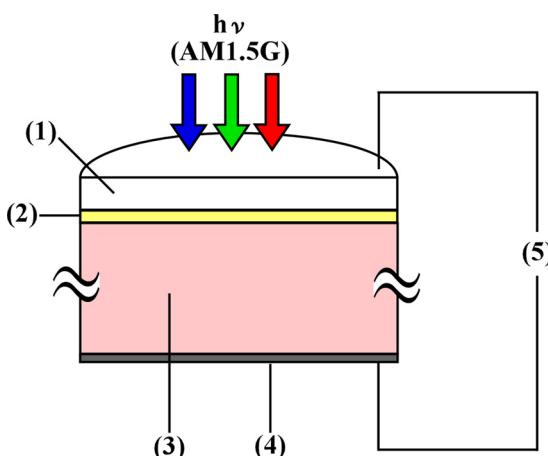


FIG. 5. Schematic structure of heterojunction solar cells: (1) AZO transparent electrode, (2) 50-nm-thick Ga₂O₃ thin film, (3) 200- μm -thick Cu₂O:Na or undoped Cu₂O sheet, (4) Au back contact, and (5) load.

¹L. C. Olsen, R. C. Bohara, and M. W. Uri, *Appl. Phys. Lett.* **34**, 47 (1979).

²W. M. Sears, E. Fortin, and J. B. Webb, *Thin Solid Films* **103**, 303 (1983).

³R. J. Iwanowski and D. Trivich, *Phys. Status Solidi A* **95**, 735 (1986).

⁴B. P. Rai, *Sol. Cells* **25**, 265 (1988).

⁵R. N. Briskman, *Sol. Energy Mater. Sol. Cells* **27**, 361 (1992).

⁶T. Minami, H. Tanaka, T. Shimokawa, T. Miyata, and H. Sato, *Jpn. J. Appl. Phys., Part 2* **43**, L917 (2004).

⁷T. Minami, Y. Nishi, T. Miyata, and J. Nomoto, *Appl. Phys. Express* **4**, 062301 (2011).

⁸A. Mittiga, E. Salza, F. Sarto, M. Tucci, and R. Vasanthi, *Appl. Phys. Lett.* **88**, 163502 (2006).

⁹Y. S. Lee, J. Heo, S. C. Siah, J. P. Mailoa, R. E. Brandt, S. B. Kim, R. G. Gordon, and T. Buonassisi, *Energy Environ. Sci.* **6**, 2112–2118 (2013).

¹⁰T. Minami, Y. Nishi, and T. Miyata, *Appl. Phys. Express* **6**, 044101 (2013).

- ¹¹L. C. Olsen, F. W. Addis, and W. Miller, *Sol. Cells* **7**, 247 (1982–1983).
- ¹²A. O. Musa, T. Akomolafe, and M. J. Carter, *Solar Sol. Energy Mater. Sol. Cells* **51**, 305 (1998).
- ¹³D. Trivich, E. Y. Wang, R. J. Komp, and A. S. Kakar, in *Conference Record of 13th IEEE Photovoltaic Specialists Conference* (IEEE, 1978), pp. 174–179.
- ¹⁴S. Ishizuka, S. Kato, T. Maruyama, and K. Akimoto, *Jpn. J. Appl. Phys., Part 2* **39**, L786 (2000).
- ¹⁵S. Ishizuka, S. Kato, Y. Okamoto, and K. Akimoto, *Appl. Phys. Lett.* **80**, 950 (2002).
- ¹⁶Y. M. Lu, C. Y. Chen, and M. H. Lin, *Thin Solid Films* **480–481**, 482 (2005).
- ¹⁷T. Minami, T. Miyata, and Y. Nishi, *Thin Solid Films* **559**, 105 (2014).
- ¹⁸T. Miyata, T. Minami, H. Tanaka, and H. Sato, Proc. SPIE **6037**, 603712 (2006).
- ¹⁹G. P. Pollack and D. Trivich, *J. Appl. Phys.* **46**, 163 (1975).
- ²⁰Y. S. Lee, M. T. Winkler, S. C. Siah, R. E. Brandt, and T. Buonassisi, *Appl. Phys. Lett.* **98**, 192115 (2011).
- ²¹K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, *Appl. Phys. Lett.* **93**, 202107 (2008).
- ²²K. Seeger, *Semiconductor Physics*, 3rd ed. (Springer-Verlag, Berlin, 1985), p. 160.
- ²³J. Y. W. Seto, *J. Appl. Phys.* **46**, 5247 (1975).