

# Cu<sub>2</sub>O-based heterojunction solar cells with an Al-doped ZnO/oxide semiconductor/thermally oxidized Cu<sub>2</sub>O sheet structure

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## Abstract

This paper introduces the present status and prospects for further development of Al-doped ZnO (AZO)/n-type metal oxide semiconductor/p-type Cu<sub>2</sub>O hybrid heterojunction (HbH) solar cells that feature a structure that is fabricated by inserting an n-oxide semiconductor thin film between an AZO transparent electrode and a Cu<sub>2</sub>O sheet. An improvement of photovoltaic properties was achieved by both stabilizing the surface of polycrystalline p-Cu<sub>2</sub>O sheets that had been prepared by thermal oxidization of Cu sheets and also developing low-temperature and low-damage deposition technology for applying thin films as an n-oxide semiconductor layer. It should be noted that the obtainable photovoltaic properties in AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells were found to be considerably more affected by the surface condition of the p-Cu<sub>2</sub>O layer, *i.e.*, the interface at the heterojunction, than the diffusion potential resulting from the difference of work functions between the p-Cu<sub>2</sub>O and n-oxide semiconductor layers. To achieve a higher efficiency in AZO/n-oxide semiconductor/p-Cu<sub>2</sub>O HbH solar cells, it was necessary to improve the interface at the heterojunction as well as reduce the series resistance and increase the parallel resistance of the HbH solar cells. The effect of the inserted n-oxide semiconductor thin film on the obtainable photovoltaic properties was investigated in the Cu<sub>2</sub>O-based HbH solar cells by inserting various kinds of n-oxide semiconductor thin films prepared under various deposition conditions using a pulsed laser deposition (PLD) method. Although either a non-doped ZnO or Ga<sub>2</sub>O<sub>3</sub> thin film deposited at room temperature by PLD is suitable as the n-oxide semiconductor layer, an amorphous Ga<sub>2</sub>O<sub>3</sub> thin film with a high resistivity was found to be the most suitable oxide. The improvement of the p–n junction, as seen in the Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O heterojunction, could be achieved by decreasing the defect levels at the interface, which decreases not only the recombination associated with defects at the interface between the Ga<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O, but also the conduction band discontinuity. We have achieved a maximum conversion efficiency of 5.38% in an AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O heterojunction solar cell fabricated by depositing a Ga<sub>2</sub>O<sub>3</sub> thin film on a Cu<sub>2</sub>O sheet with a resistivity on the order of 10<sup>2</sup> Ω cm.

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## 1. Cu<sub>2</sub>O-based hybrid heterojunction solar cells

Recently, oxide semiconductor heterojunction solar cells have been extensively studied using polycrystalline p-type

cuprous oxide (Cu<sub>2</sub>O) prepared by various deposition methods on thermally oxidized copper sheets (Minami et al., 2004; Mittiga et al., 2006; Minami et al., 2013a). Although low cost and nontoxic Cu<sub>2</sub>O, a semiconductor with a direct energy gap of 2.1 eV, has long attracted much interest for solar cell applications, it has been very difficult to achieve a high-energy conversion efficiency in solar cells

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fabricated using this material as the active layer, because  $\text{Cu}_2\text{O}$  is intrinsically a p-type semiconductor and the surface of  $\text{Cu}_2\text{O}$  is chemically unstable since cupric oxide ( $\text{CuO}$ ) is more stable than  $\text{Cu}_2\text{O}$  at temperatures below about 400 °C (Olsen et al., 1982; Rakhshani, 1986; Fujinaka and Berezin, 1983; Sears et al., 1983). Recently, the preparation of n-type  $\text{Cu}_2\text{O}$  films by electrodeposition from an aqueous solution as well as the fabrication of thin-film p–n junction  $\text{Cu}_2\text{O}$  solar cells also using this deposition method have been reported (McShane et al., 2010; Shiu et al., 2011; Kramm et al., 2012; McShane and Choi, 2012). For example, McShane and Choi (2012) obtained a conversion efficiency of 1.06% in a p–n junction  $\text{Cu}_2\text{O}$  thin-film solar cell, which is low in comparison to the theoretical energy conversion efficiency of a  $\text{Cu}_2\text{O}$  solar cell that is as high as 20% (Rakhshani, 1986). Since fabricating  $\text{Cu}_2\text{O}$  p–n homojunction solar cells has proven to be a problem due to the difficulty of preparing n-type  $\text{Cu}_2\text{O}$ , there have been many reports on various p–n heterojunction solar cells fabricated using p-type  $\text{Cu}_2\text{O}$  as the active layer (Olsen et al., 1979; Herion et al., 1980; Papadimitriou et al., 1981; Iwanowski and Trivich, 1986; Rai, 1988; Briskman, 1992; Suehiro et al., 2001). Minami et al. (2004) reported that conversion efficiencies over 1% were obtained in n-type oxide semiconductor/p- $\text{Cu}_2\text{O}$  hybrid heterojunction (HbH) solar cells fabricated by depositing transparent conducting oxide (TCO) thin films on thermally oxidized polycrystalline p- $\text{Cu}_2\text{O}$  sheets. The TCO thin films such as Al- or Ga-doped ZnO (AZO or GZO), which also act as a transparent electrode, and the oxide semiconductor thin films such as ZnO and multi-component oxides were prepared using various physical deposition techniques such as a pulsed laser deposition (PLD), radio frequency magnetron sputtering deposition and vacuum arc plasma evaporation methods (Minami et al., 2004; Minami, 2005; Tanaka et al., 2004; Tanaka et al., 2005; Minami et al., 2006). In addition to TCO/ $\text{Cu}_2\text{O}$  HbH solar cells, TCO/n-type oxide semiconductor/p- $\text{Cu}_2\text{O}$  HbH solar cells were fabricated by inserting an n-type oxide semiconductor thin film as a buffer layer between the TCO electrode and the  $\text{Cu}_2\text{O}$  sheet (Miyata et al., 2006). It also has been reported that the obtained photovoltaic properties in n-oxide semiconductor/p- $\text{Cu}_2\text{O}$  HbH solar cells were considerably dependent on the kind of deposition method used for preparing the oxide semiconductor thin films (Tanaka et al., 2005; Minami et al., 2006, 2013a; Nishi et al., 2012a). Mittiga et al. (2006) reported a conversion efficiency of 2.01% obtained in a  $\text{Cu}_2\text{O}$ -based HbH solar cell with an  $\text{MgF}_2$ /indium-tin-oxide (ITO)/ZnO/ $\text{Cu}_2\text{O}$ /Cu structure that was fabricated by depositing a ZnO thin film on thermally oxidized polycrystalline p- $\text{Cu}_2\text{O}$  sheets using an ion beam sputtering method. In addition to  $\text{Cu}_2\text{O}$ -based HbH solar cells, Izaki et al. (2007) reported that a conversion efficiency of 1.28% was obtained in an n-oxide semiconductor/p- $\text{Cu}_2\text{O}$  thin-film heterojunction (TFH) solar cell with an F-doped

$\text{SnO}_2$  (FTO)/ZnO/ $\text{Cu}_2\text{O}$ /Au structure fabricated by depositing first a ZnO thin film followed by a  $\text{Cu}_2\text{O}$  film onto FTO-coated glass substrates using electrodeposition from an aqueous solution. Recently, Fujimoto et al. (2013) also reported that a conversion efficiency of 1.43% was obtained in an n-oxide semiconductor/p- $\text{Cu}_2\text{O}$  TFH solar cell fabricated with the same structure as described above using electrodeposition from a pH-adjusted electrolyte consisting of LiOH.

Minami et al. (2011) reported that a TCO/n-oxide semiconductor/p-type  $\text{Cu}_2\text{O}$  HbH solar cell with a conversion efficiency of 3.83% could be fabricated by inserting a thin nondoped ZnO film between a transparent AZO electrode and the front surface of polycrystalline  $\text{Cu}_2\text{O}$  sheets that had been prepared by a thermal oxidization of copper sheets. This drastic improvement of conversion efficiency was made possible by the formation of an n-type ZnO thin-film layer (prepared with an appropriate thickness) using a low damage and low temperature deposition technique on high quality polycrystalline  $\text{Cu}_2\text{O}$  sheets (Nishi et al., 2011, 2012b, 2013; Minami et al., 2013b). In addition, Minami et al. (2013c) reported recently that a gallium oxide ( $\text{Ga}_2\text{O}_3$ ) thin film and various  $\text{Ga}_2\text{O}_3$ -based multi-component oxides are suitable for the n-oxide semiconductor layer of AZO/n-oxide semiconductor/p- $\text{Cu}_2\text{O}$  HbH solar cells. A conversion efficiency and an open circuit voltage over 5% and 0.8 V, respectively, were obtained in an AZO/n-oxide semiconductor/ $\text{Cu}_2\text{O}$  HbH solar cell fabricated with either an amorphous  $\text{Ga}_2\text{O}_3$  or a  $\text{Ga}_2\text{O}_3$ -based multi-component oxide thin film as the n-oxide semiconductor layer (Minami et al., 2013d). The above described improvements of photovoltaic properties are attributed mainly to a decrease of the height of the conduction band discontinuity resulting from the difference in electron affinity between the oxide semiconductor thin film and the  $\text{Cu}_2\text{O}$  sheet used in the heterojunction (Minami et al., 2013a,c,d). In a similar manner, Lee et al. (2013) recently reported that a conversion efficiency of 2.65% was obtained in a  $\text{Cu}_2\text{O}$ -based TFH solar cell with an AZO/amorphous ZnO– $\text{SnO}_2$  (a-ZTO) multi-component oxide/ $\text{Cu}_2\text{O}$ /Au structure fabricated by using an atomic layer deposition to place an ultrathin a-ZTO thin film onto a  $\text{Cu}_2\text{O}$  film that had been deposited previously on a Au-coated silica substrate using electrodeposition from an aqueous solution. It should be noted that the above reported improvements of obtainable photovoltaic properties in  $\text{Cu}_2\text{O}$ -based TFH solar cells have yet to produce results comparable to those found in  $\text{Cu}_2\text{O}$ -based HbH solar cells, which may be attributable to the difference of crystallinity between the  $\text{Cu}_2\text{O}$  thin films and  $\text{Cu}_2\text{O}$  sheets.

This paper presents the current state and prospects of achieving higher conversion efficiency  $\text{Cu}_2\text{O}$ -based HbH solar cells fabricated using  $\text{Cu}_2\text{O}$  sheets prepared by thermally oxidizing copper sheets. The effect of inserting an n-type metal oxide semiconductor thin-film layer on the obtainable photovoltaic properties in  $\text{Cu}_2\text{O}$ -based HbH

solar cells with a transparent conductive AZO thin film/n-oxide semiconductor thin film/p-Cu<sub>2</sub>O sheet thin film structure is described.

## 2. Experimental details

Cu<sub>2</sub>O sheets were prepared by oxidizing Cu sheets (overall dimensions of 30 mm × 30 mm with a thickness of 0.2 mm and a purity of 99.96%) using a heat treatment process that consisted of three steps in a furnace with a controlled ambient atmosphere, described elsewhere in detail (Minami et al., 2011; Nishi et al., 2011, 2012a; Minami et al., 2013a). The resulting Cu<sub>2</sub>O sheets were polycrystalline p-type semiconductors: resistivity on the order of 10<sup>2</sup>–10<sup>3</sup> Ω cm, hole concentration on the order of 10<sup>13</sup>–10<sup>14</sup> cm<sup>-3</sup> and Hall mobility in the range of 100–110 cm<sup>2</sup>/vs. In the device fabrication, the CuO surface layer of the oxidized Cu<sub>2</sub>O sheets was removed by chemical wet etching (Miyata et al., 2006). AZO and metal oxide semiconductor thin films were deposited with a PLD using an ArF excimer laser (wavelength, 193 nm; repetition rate, 20 Hz; pulse width, 20 ns; and fluence, 350 mJ/cm<sup>2</sup>) under the following deposition conditions: target-substrate distance, 40 mm; deposition temperature, room temperature (RT)–300 °C; target, sintered AZO (Al<sub>2</sub>O<sub>3</sub> content of 2 wt.%) and sintered oxide pellet; and atmosphere and pressure, vacuum below 4.0 × 10<sup>-4</sup> Pa or O<sub>2</sub> gas at 0.1–2.2 Pa. In the final step, the solar cells were fabricated by forming an AZO/n-metal oxide semiconductor/p-Cu<sub>2</sub>O structure on the front surface of the Cu<sub>2</sub>O sheets and an Au ohmic electrode on the back surface of the Cu<sub>2</sub>O sheets; the Cu<sub>2</sub>O sheets function as the active layer as well as the substrate (Minami et al., 2004, 2011; Miyata et al., 2006), as shown in Fig. 1. The AZO thin films, functioning as the transparent electrode and prepared at RT at an O<sub>2</sub> gas pressure of 0.2 Pa with a thickness of 200–490 nm, exhibited a resistivity on the order of 10<sup>-4</sup> Ω cm and a carrier concentration of 10<sup>20</sup>–10<sup>21</sup> cm<sup>-3</sup>. In order to evaluate the electrical and optical properties of the resulting AZO and metal oxide semiconductor films, simultaneous and/or additional depositions were also conducted on OA-10 glass

(Nippon Electric Glass Co., Ltd.) substrates. The photovoltaic properties of the Cu<sub>2</sub>O-based solar cells (electrode area of 3.14 mm<sup>2</sup>) were evaluated by exposing only the AZO transparent electrode area to AM1.5G solar illumination (100 mW/cm<sup>2</sup>) at 25 °C.

## 3. Influence of inserting an oxide thin-film layer on photovoltaic properties

### 3.1. Influence of materials used as the oxide thin-film layer

We have reported that the obtainable photovoltaic properties in AZO/n-oxide semiconductor/p-Cu<sub>2</sub>O HbH solar cells are affected by the material parameters and crystallographical characteristics of both the Cu<sub>2</sub>O and the oxide semiconductor layers as well as the surface condition of the Cu<sub>2</sub>O layer (Minami et al., 2011, 2013a,d; Nishi et al., 2012b, 2013; Minami et al., 2013a,d; Nishi et al., 2013). In particular, the influence of the kind of metal oxide semiconductors inserted (as the n-oxide semiconductor thin-film layer) on the obtainable photovoltaic properties were investigated in AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells fabricated by depositing various n-metal oxide semiconductor thin films on thermally oxidized Cu<sub>2</sub>O sheets at RT using the PLD method; Table 1 summarizes the obtained photovoltaic properties in AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells fabricated with various n-metal oxide semiconductor thin films. Fig. 2 shows typical current density–voltage (J–V) characteristics for AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells fabricated with various n-metal oxide semiconductor thin films and measured under AM1.5G solar illumination. The metal oxide semiconductor thin films were prepared without intentional impurity doping on Cu<sub>2</sub>O substrates at RT under the oxygen gas pressure (*P*<sub>O</sub>) introduced during the film depositions and with the thickness (*d*) indicated in Table 1. Here, the deposited metal oxide thin films are indicated with the same name as the oxide powder material (binary compounds) used for preparing the sintered oxide pellets provided for PLD. It should be noted that, except for the ZnO thin films, all the deposited metal oxide thin films were amorphous, irrespective of the *P*<sub>O</sub>, as evidenced from X-ray diffraction (XRD) analyses. It should also be noted that, other than for the ZnO, Ga<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> thin films, the optimization of the deposition conditions has not been sufficiently conducted to obtain higher conversion efficiency. In addition, most of the metal oxide thin films deposited in a vacuum (without introducing O<sub>2</sub> gas during the film deposition) using the PLD method produced metal rich oxide films. For comparison, the J–V characteristics of an AZO/Cu<sub>2</sub>O HbH solar cell fabricated without the insertion of an n-oxide semiconductor thin-film layer is also shown in Fig. 2. The obtained photovoltaic properties in AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O and AZO/ZnO/Cu<sub>2</sub>O HbH solar cells benefited significantly from the insertion of the non-doped Ga<sub>2</sub>O<sub>3</sub> and nondoped ZnO thin-film layer, respectively, as evidenced by comparison with the AZO/Cu<sub>2</sub>O heterojunc-

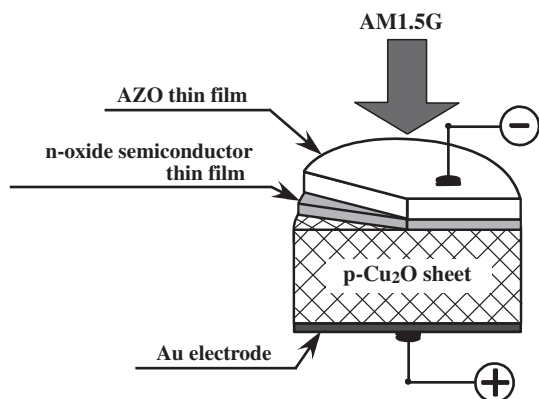


Fig. 1. Schematic structure of an AZO/n-oxide semiconductor/p-Cu<sub>2</sub>O HbH solar cell.

Table 1

Obtained  $\eta_{\max}$ ,  $V_{OC}$ ,  $J_{SC}$  and FF in AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells fabricated using various oxide semiconductor thin films prepared at  $P_o$  with  $d$  and  $\rho$ .

Oxide	$P_o$ (Pa)	$\rho$ ( $\Omega$ cm)	$d$ (nm)	$V_{OC}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	$n$ (%)
ZnO	1.0	$3.5 \times 10^3$	50	0.71	9.69	0.60	4.13
Ga <sub>2</sub> O <sub>3</sub>	1.7	$10^5$ – $10^6$	75	0.80	9.99	0.67	5.38
TiO <sub>2</sub>	0.6		50	0.47	7.98	0.55	2.07
	(vacuum)	$(2.4 \times 10^{-1})$	(50)	(0.41)	(6.64)	(0.41)	(1.09)
In <sub>2</sub> O <sub>3</sub>	0.5	$5.3 \times 10^{-4}$	50	0.37	8.33	0.35	1.08
Ta <sub>2</sub> O <sub>5</sub>	1.0		50	0.03	0.06	0.27	0.00
	(vacuum)	$(4.7 \times 10^{-1})$	(50)	(0.36)	(5.83)	(0.49)	(1.03)
V <sub>2</sub> O <sub>5</sub>	1.0		50	0.00	0.02	0.25	0.00
	(vacuum)	(2.7)	(50)	(0.29)	(5.58)	(0.52)	(0.84)
Nb <sub>2</sub> O <sub>5</sub>	1.0		50	0.38	6.14	0.50	1.16
	(vacuum)	$(1.1 \times 10^{-1})$	(50)	(0.36)	(3.42)	(0.55)	(0.68)
Gd <sub>2</sub> O <sub>3</sub>	1.0		50	0.02	0.00	0.35	0.00
	(vacuum)	–	(50)	(0.43)	(5.34)	(0.28)	(0.64)
SnO <sub>2</sub>	0.5		50	0.48	8.14	0.34	1.32
	(vacuum)	–	(50)	(0.40)	(0.53)	(0.31)	(0.07)
WO <sub>3</sub>	1.0	$1.0 \times 10^{-2}$	50	0.32	6.16	0.47	0.91
	(vacuum)	$(8.8 \times 10^{-2})$	(50)	(0.51)	(6.21)	(0.51)	(1.10)
MoO <sub>3</sub>	1.7	$1.0 \times 10^{-1}$	50	0.04	1.92	0.25	0.02
	(vacuum)	$(2.4 \times 10^{-3})$	(50)	(0.37)	(4.63)	(0.47)	(0.81)

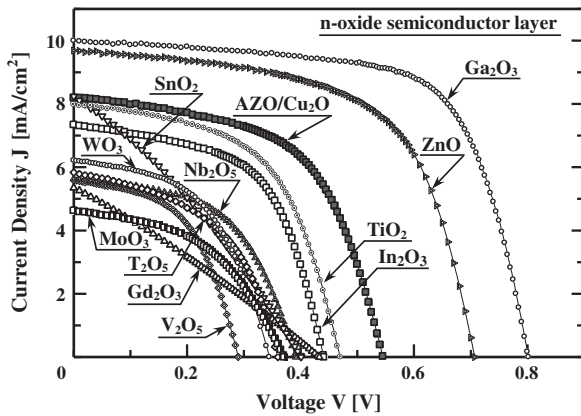


Fig. 2. J–V characteristics of AZO/n-oxide semiconductor/p-Cu<sub>2</sub>O HbH solar cells fabricated by inserting various oxide semiconductor thin films and measured under AM1.5G solar illumination.

tion solar cell. However, it was difficult to measure the electrical properties in most of the deposited oxide thin films, because of the high resistivity of oxide thin films deposited at RT as well as the difficulty of forming an ohmic contact on the films. For example, the nondoped Ga<sub>2</sub>O<sub>3</sub> and ZnO thin films prepared on glass substrates at the same time as on the Cu<sub>2</sub>O sheets at a  $P_o$  of 1.7 and 1.0 Pa, respectively, exhibited resistivities on the order of  $10^5$ – $10^6$  and  $10^{-2}$ – $10^{-3}$   $\Omega$  cm. Thus, it seems that the nondoped Ga<sub>2</sub>O<sub>3</sub> thin film used in the AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cell and the nondoped ZnO thin film used in the AZO/ZnO/Cu<sub>2</sub>O HbH solar cell act as an n-type semiconductor layer. As noted above, the obtained photovoltaic properties in most AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells fabricated by inserting a metal oxide semiconductor thin film other than Ga<sub>2</sub>O<sub>3</sub> or ZnO were not improved significantly.

As described above, Cu<sub>2</sub>O-based HbH solar cells with a high-conversion efficiency could be achieved by depositing

the AZO thin films as well as the metal oxide semiconductor thin films on low-temperature Cu<sub>2</sub>O sheets using a low-damage deposition technique. As can be seen in Table 1, the obtained maximum energy conversion efficiency ( $\eta_{\max}$ ), open-circuit voltage ( $V_{OC}$ ), short-circuit current density ( $J_{SC}$ ) and fill factor (FF) exhibited in the AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O and AZO/ZnO/Cu<sub>2</sub>O HbH solar cells were all higher than those in the other solar cells. We have also reported that the wavelength dependence of the external quantum efficiency (EQE) obtained in Cu<sub>2</sub>O-based HbH solar cells fabricated with or without the insertion of an n-oxide semiconductor thin-film layer was considerably affected by the kind of oxide semiconductor inserted (Minami et al., 2013a). Typical normalized EQE data are shown in Fig. 3 for the AZO/ZnO/Cu<sub>2</sub>O and AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cells fabricated under the deposition conditions shown in Table 1. For comparison, the normalized EQE of an AZO/Cu<sub>2</sub>O HbH solar cell (fabricated without an inserted oxide semiconductor thin-film layer) is also shown

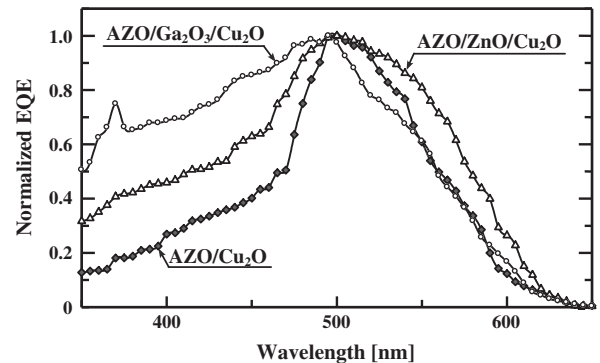


Fig. 3. Normalized EQE spectra observed from AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O (open circle), AZO/ZnO/Cu<sub>2</sub>O (open triangle) and AZO/Cu<sub>2</sub>O (solid diamond) HbH solar cells.



in Fig. 3. A comparison of the wavelength dependence of the EQE obtained in the AZO/Cu<sub>2</sub>O HbH solar cells with those obtained in AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O and AZO/ZnO/Cu<sub>2</sub>O HbH solar cells shows that the effect on EQE is enhanced in both the AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O and AZO/ZnO/Cu<sub>2</sub>O heterojunction solar cells at wavelengths below approximately 500 nm; *i.e.*, EQE is significantly decreased in AZO/Cu<sub>2</sub>O at wavelengths below about 500 nm. This may be a result of decreased degradation of the surface condition of the Cu<sub>2</sub>O sheets, *i.e.*, the interface, occurring during the low temperature depositions of the Ga<sub>2</sub>O<sub>3</sub> and ZnO films relative to that of the AZO film, possibly attributable to the different O<sub>2</sub> gas pressure introduced for each type of film (Minami et al., 2011, 2013c). However, it is known that the photovoltaic properties are affected by the height of the conduction band discontinuity, resulting from the difference in electron affinity between the oxide semiconductor thin film and the Cu<sub>2</sub>O sheet used in the heterojunction (Minami et al., 2013a,c,d). It was also found that AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells with higher efficiency exhibited a tendency to exhibit a decrease in current density under a reversed bias. A comparison of the J–V characteristics measured under dark conditions obtained in various AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells is shown in Fig. 4. The heterojunction solar cells used in the measurements are the same as those shown in Fig. 1. The leakage current of the AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cell measured under a reversed bias was significantly lower, on the order of one magnitude, than that measured on the AZO/ZnO/Cu<sub>2</sub>O HbH solar cell. This also suggests that the obtained photovoltaic properties in AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells may be affected considerably by the pre-deposition surface condition of the Cu<sub>2</sub>O sheet and/or the surface condition at the initial stage in the thin-film depositions as well as the height of the conduction band discontinuity.

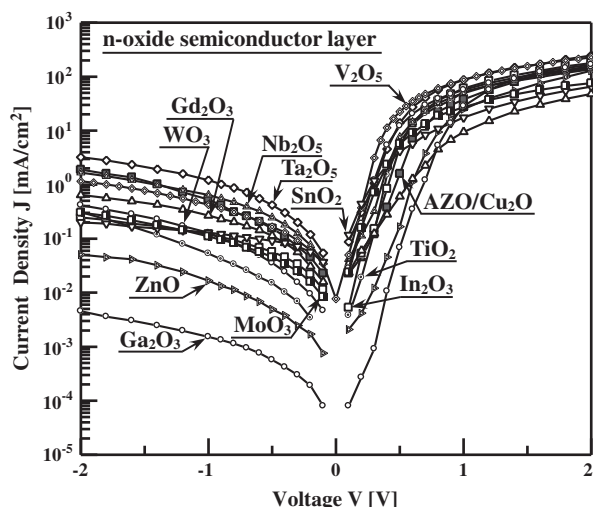


Fig. 4. J–V characteristics of AZO/n-oxide semiconductor/p-Cu<sub>2</sub>O HbH solar cells measured under dark conditions.

As can be seen in Fig. 2 and Table 1, the obtained  $V_{OC}$  in AZO/n-oxide semiconductor/p-Cu<sub>2</sub>O HbH solar cells varied considerably, depending on the kind of oxide semiconductor thin films used: *i.e.*, from  $V_{OC} = 0.29$  V in V<sub>2</sub>O<sub>5</sub> thin film to 0.8 in Ga<sub>2</sub>O<sub>3</sub>. It is known that the obtained  $V_{OC}$  in n-oxide semiconductor/p-Cu<sub>2</sub>O HbH solar cells is related to the diffusion potential in the p–n heterojunctions, which is based on the work functions of the n-oxide semiconductor thin films and the Cu<sub>2</sub>O sheet used. We have also found that the  $V_{OC}$  obtained in all the AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells shown in Table 1 is approximately equal to that of the diffusion potential estimated by measuring the capacitance ( $C$ )–voltage ( $V$ ) characteristics of the p–n heterojunctions, *i.e.*, the  $1/C^2 - V$  relationship. However, the diffusion potentials observed from the fabricated AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells are not consistent with those expected from theoretical estimations based on the work functions of the oxide semiconductor thin films and the p-Cu<sub>2</sub>O sheet used. It should be noted that the available information regarding the work functions of metal oxide semiconductor thin films, necessary to estimate the diffusion potentials resulting in the heterojunctions, is insufficient because most of the deposited oxide semiconductor thin films are amorphous; *i.e.*, only the work functions concerning crystalline oxides identified as special binary compounds have been reported in previously published literature. However, explanations concerning the values of obtained  $V_{OC}$  and diffusion potential as well as the difference among them found in the fabricated heterojunctions of various n-metal oxide semiconductor thin films deposited on the p-Cu<sub>2</sub>O sheets require knowing the work functions of the oxide semiconductor thin films and the Cu<sub>2</sub>O sheets used.

We have recently reported that the actual work functions of the polycrystalline ZnO and amorphous Ga<sub>2</sub>O<sub>3</sub> thin films and the polycrystalline Cu<sub>2</sub>O sheet used in AZO/ZnO/Cu<sub>2</sub>O and AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O heterojunction solar cells are 4.5, 5.06 and 5.08 eV, respectively, as evaluated from the wavelength dependence of the photoemission of electrons using ultraviolet photoelectron spectroscopy (Minami et al., 1998, 2013c). The work functions measured on the polycrystalline ZnO and amorphous Ga<sub>2</sub>O<sub>3</sub> thin films are larger than or equal to those of ZnO and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> reported in previously published literature as 4.45 (Sanghyun et al., 2008) and 4.11 eV (Mohamed et al., 2012), respectively. This difference in the work function of Ga<sub>2</sub>O<sub>3</sub> may be related to the fact that the Ga<sub>2</sub>O<sub>3</sub> thin films prepared at RT and used in this work were amorphous, rather than to differences in the measurement method used. In addition, the work function measured on single crystal Cu<sub>2</sub>O is higher than the 4.7 eV reported in previously published literature (Assimos and Trivich, 1974), 4.66 eV being approximately equal to that of Cu<sub>2</sub>O thin films reported in previously published literature (Jeong et al., 2008). The difference between the work function measured for Cu<sub>2</sub>O in this work and that of the single crystal Cu<sub>2</sub>O may be attributable to the influence of CuO

(work function, reported as 5.0–5.2 eV (Liao et al., 2009; Yun et al., 2009)) formed on the surface of  $\text{Cu}_2\text{O}$ , because the measurement used in this work was carried out in air. The diffusion potentials calculated theoretically in  $\text{ZnO}/\text{Cu}_2\text{O}$  and  $\text{Ga}_2\text{O}_3/\text{Cu}_2\text{O}$  heterojunctions are 0.2 V (using the work function measured by us) or 0.25 V (using the work function reported in previously published literature) and 0.36 V or 0.59 V, respectively, when using 4.7 eV as the work function of  $\text{Cu}_2\text{O}$  (reported by Assimos and Trivich, 1974). As shown in Fig. 2 and Table 1, however, the obtained  $V_{\text{OC}}$  in the  $\text{ZnO}/\text{Cu}_2\text{O}$  and  $\text{Ga}_2\text{O}_3/\text{Cu}_2\text{O}$  heterojunctions are 0.71 and 0.80 V, respectively. Thus, it is difficult to explain the high  $V_{\text{OC}}$  obtained in the heterojunction using only the difference in work functions between the  $\text{Ga}_2\text{O}_3$  or  $\text{ZnO}$  thin film and the  $\text{Cu}_2\text{O}$  sheet. This suggests that the obtained  $V_{\text{OC}}$  and diffusion potentials in AZO/oxide semiconductor/ $\text{Cu}_2\text{O}$  heterojunction solar cells may be affected considerably by the characteristics of the oxide semiconductor/ $\text{Cu}_2\text{O}$  interface, which can be greatly affected by the  $\text{Cu}_2\text{O}$  surface condition at the initial stage in the thin-film deposition.

### 3.2. Influence of film deposition temperature

As described above, the following description concerning the influence of inserting an n-oxide semiconductor thin-film layer on the obtainable photovoltaic properties is focused on the AZO/n- $\text{Ga}_2\text{O}_3/\text{p-Cu}_2\text{O}$  and AZO/n- $\text{ZnO}/\text{p-Cu}_2\text{O}$  HbH solar cells, because a sufficient improvement of photovoltaic properties could be achieved only in these HbH solar cells. In addition, we have found that depositing the AZO and/or oxide semiconductor thin films on  $\text{Cu}_2\text{O}$  sheets at RT by using a low damage deposition method is exceptionally important to obtain higher conversion efficiency in AZO/oxide semiconductor/ $\text{Cu}_2\text{O}$  HbH solar cells. That is, the obtained photovoltaic characteristics were considerably dependent on the deposition temperature ( $T_d$ ) of both the AZO and oxide semiconductor thin films. The obtained  $V_{\text{OC}}$ ,  $J_{\text{SC}}$ ,  $\eta$  and FF as functions of the  $T_d$  are shown in Fig. 5 for AZO/ $\text{ZnO}/\text{Cu}_2\text{O}$  (open triangle data points) and AZO/ $\text{Ga}_2\text{O}_3/\text{Cu}_2\text{O}$  (open circle data points) HbH solar cells fabricated by depositing the AZO and  $\text{ZnO}$  or  $\text{Ga}_2\text{O}_3$  thin films at the same  $T_d$  under optimized deposition conditions, as shown in Table 1 (Nishi et al., 2013; Minami et al., 2013a). All the obtained photovoltaic properties ( $V_{\text{OC}}$ ,  $J_{\text{SC}}$ ,  $\eta$  and FF) in both the AZO/ $\text{ZnO}/\text{Cu}_2\text{O}$  and AZO/ $\text{Ga}_2\text{O}_3/\text{Cu}_2\text{O}$  HbH solar cells degraded markedly as the  $T_d$  was increased. It was also found that the obtainable photovoltaic properties in various AZO/oxide semiconductor/ $\text{Cu}_2\text{O}$  HbH solar cells (fabricated both with or without the insertion of a metal oxide semiconductor thin-film layer) always degraded as the  $T_d$  was increased above RT. For comparison, the  $V_{\text{OC}}$ ,  $J_{\text{SC}}$ ,  $\eta$  and FF as functions of the  $T_d$  are shown in Fig. 5 for the AZO/ $\text{Cu}_2\text{O}$  (solid diamond data points) HbH solar cells (fabricated without the insertion of an oxide semiconductor thin-film layer) (Nishi et al., 2012a).

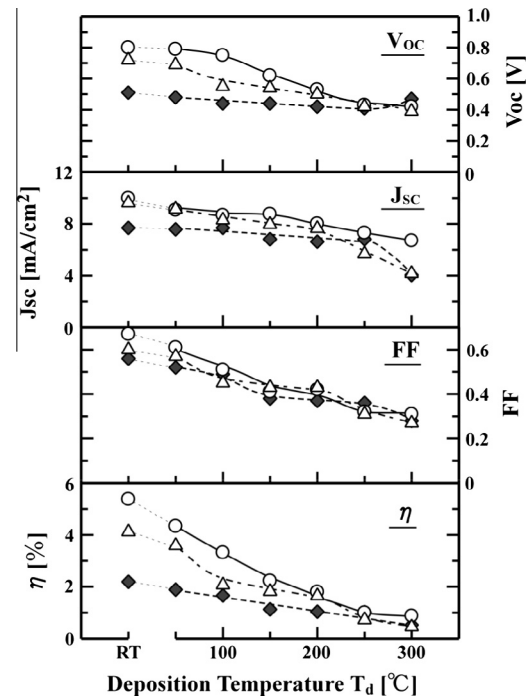


Fig. 5. Obtained  $V_{\text{OC}}$ ,  $J_{\text{SC}}$ , FF and  $\eta$  as functions of  $T_d$  in AZO/ $\text{Ga}_2\text{O}_3/\text{Cu}_2\text{O}$  (open circle), AZO/ $\text{ZnO}/\text{Cu}_2\text{O}$  (open triangle) and AZO/ $\text{Cu}_2\text{O}$  (solid diamond) HbH solar cells.

It should be noted in Fig. 5 that the obtained  $V_{\text{OC}}$ ,  $\eta$  and FF in the three HbH solar cells shown generally tend toward equality as the  $T_d$  rises above about 250 °C, irrespective of the kind of oxide thin films deposited on the  $\text{Cu}_2\text{O}$  sheets. It should be noted that the  $\text{Ga}_2\text{O}_3$  thin films deposited in the  $T_d$  range from RT to 300 °C were amorphous, whereas the crystallinity of polycrystalline  $\text{ZnO}$  and AZO thin films improved as the  $T_d$  was increased up to 300 °C. In addition, the resistivity of  $\text{ZnO}$  thin films increased gradually as the  $T_d$  was increased up to approximately 200 °C, and then increased markedly as the  $T_d$  was increased above 250 °C, as shown in Fig. 6. The increase in resistivity is related to a decrease of both carrier concentration and Hall mobility. In contrast, the resistivity of AZO

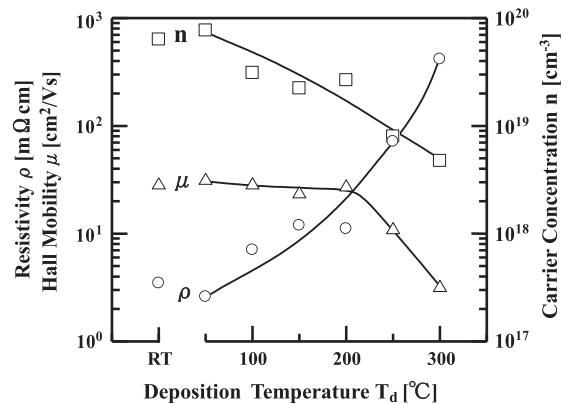


Fig. 6. Obtained  $\rho$ ,  $n$  and  $\mu$  as functions of  $T_d$  in  $\text{ZnO}$  thin films prepared at a  $P_o$  of 1.0 Pa by PLD.

thin films decreased gradually as the  $T_d$  was increased; *i.e.*, Hall mobility increased gradually, whereas carrier concentration remained relatively constant (not shown here). As described above, the resistivity of  $\text{Ga}_2\text{O}_3$  thin films deposited at a  $T_d$  in the range from RT to 300 °C was difficult to measure accurately. In the AZO/ZnO/ $\text{Cu}_2\text{O}$  and AZO/ $\text{Cu}_2\text{O}$  HbH solar cells shown in Fig. 5, the decrease of obtained  $V_{\text{OC}}$  with increasing  $T_d$  was difficult to relate to the work function of these thin films, because the carrier concentration of the AZO thin films remained relatively constant with increasing  $T_d$ , whereas that of the ZnO thin films decreased markedly. The above results may also support the supposition that the obtained  $V_{\text{OC}}$  or diffusion potentials in AZO/oxide semiconductor/ $\text{Cu}_2\text{O}$  HbH may be affected considerably by the oxide semiconductor/ $\text{Cu}_2\text{O}$  interface, which can be greatly affected by the  $\text{Cu}_2\text{O}$  surface condition at the initial stage in the thin-film deposition.

To investigate further the influence of  $T_d$  on the obtainable photovoltaic properties, the  $T_d$  dependence of parallel ( $R_{\text{sh}}$ ) and series ( $R_s$ ) resistances as well as EQE was measured on the three kinds of HbH solar cells shown in Fig. 5. We have reported that the wavelength dependence of the EQE obtained in AZO/ $\text{Cu}_2\text{O}$  and AZO/ZnO/ $\text{Cu}_2\text{O}$  HbH solar cells changed in a similar manner as the  $T_d$  of the AZO and/or ZnO thin films was increased (Nishi et al., 2013). Fig. 7 shows typical normalized EQE as a function of  $T_d$  for AZO/ $\text{Ga}_2\text{O}_3$ / $\text{Cu}_2\text{O}$  HbH solar cells fabricated by depositing the AZO and  $\text{Ga}_2\text{O}_3$  thin films at the same  $T_d$  under the deposition conditions shown in Table 1. It should be noted that the EQE of both the AZO/ $\text{Ga}_2\text{O}_3$ / $\text{Cu}_2\text{O}$  and AZO/ZnO/ $\text{Cu}_2\text{O}$  HbH solar cells began to approach the EQE of AZO/ $\text{Cu}_2\text{O}$  HbH solar cells as the fabrication, *i.e.*, film deposition, temperature was increased (data not shown). This suggests that the influence of the inserted  $\text{Ga}_2\text{O}_3$  or ZnO thin-film layer degraded as the  $T_d$  was increased over RT, following the degradation of the photovoltaic properties with increasing film deposition temperature. As can be seen in Fig. 7, and as also reported for the three kinds of HbH solar cells described above, increasing the  $T_d$  above approximately 200 °C results in an enhanced EQE at wavelengths above approximately

500 nm; *i.e.*, the EQE peak is blue-shifted (Nishi et al., 2013). This result may also be attributable to degradation of the surface of the  $\text{Cu}_2\text{O}$  sheets as well as an interdiffusion of metals at the interface between AZO, ZnO or  $\text{Ga}_2\text{O}_3$  and the  $\text{Cu}_2\text{O}$  surface.

The  $R_s$  and  $R_{\text{sh}}$  estimated from the AZO/ZnO/ $\text{Cu}_2\text{O}$  (open triangle data points), AZO/ $\text{Ga}_2\text{O}_3$ / $\text{Cu}_2\text{O}$  (open circle data points) and AZO/ $\text{Cu}_2\text{O}$  (solid diamond data points) HbH solar cells are shown in Fig. 8(a and b), respectively. It should be noted that the  $R_s$  obtained in the three kinds of HbH solar cells similarly increased gradually as the  $T_d$  was increased from RT up to about 200 °C, and then increased markedly as the  $T_d$  was increased over about 250 °C. The  $T_d$  dependence of  $R_s$  may be closely related to that of  $J_{\text{SC}}$ , as shown in Fig. 5. In AZO/ZnO/ $\text{Cu}_2\text{O}$  HbH solar cells (fabricated by depositing nondoped ZnO thin films on the surface of  $\text{Cu}_2\text{O}$  sheets), the increase of  $R_s$  with increasing  $T_d$  may be related to the increase of the resistivity of the ZnO thin films shown in Fig. 6, whereas the resistivity of AZO thin films decreased gradually as the  $T_d$  was increased up to 300 °C. In contrast, the values of  $R_{\text{sh}}$  obtained in the three kinds of HbH solar cells were considerably dependent on the kind of oxide thin films deposited on the surface of  $\text{Cu}_2\text{O}$  sheets. However, the obtained  $R_{\text{sh}}$  in all the HbH solar cells decreased markedly as the  $T_d$  was increased. In reference to Fig. 5, the decrease in  $R_{\text{sh}}$  with increasing  $T_d$  is equivalent to a decrease in  $\eta$  that is mainly related to that of FF. These observed decreases may be attributable to an increase of leakage current that results from degradation of the surface of  $\text{Cu}_2\text{O}$  sheets as well as an interdiffusion of metals at interface between the AZO, ZnO or  $\text{Ga}_2\text{O}_3$  and the  $\text{Cu}_2\text{O}$  surface, which could promote an increase of defects created at this interface. The degradation of the surface of  $\text{Cu}_2\text{O}$  sheets may also be evidenced from the transmission electron microscopy (TEM) images at the interface between nondoped ZnO and  $\text{Cu}_2\text{O}$  in AZO/ZnO/ $\text{Cu}_2\text{O}$  HbH solar cells fabricated by depositing the ZnO thin films at a  $T_d$  of (a) RT or (b) 200 °C, as shown in Fig. 9; at RT, the interface is demarcated sharply, whereas, at 200 °C, it is obscure, indicating interdiffusion. Thus, to further improve the photovoltaic properties in  $\text{Cu}_2\text{O}$ -based HbH solar cells, it is desirable to use an appropriate n-semiconductor thin film and/or buffer layer that minimizes the lattice mismatch to the lattice constant of the  $\text{Cu}_2\text{O}$ .

### 3.3. Influence of $\text{O}_2$ gas introduction pressure and film thickness

As described above, we have reported that the obtainable photovoltaic properties in AZO/oxide semiconductor/ $\text{Cu}_2\text{O}$  HbH solar cells are considerably affected by the deposition conditions of the oxide thin films used as the n-oxide semiconductor layer. In addition to the influence of the kind of material used and the deposition temperature, we investigated optimizing the deposition pressure with or without the introduction of  $\text{O}_2$  gas in the film depo-

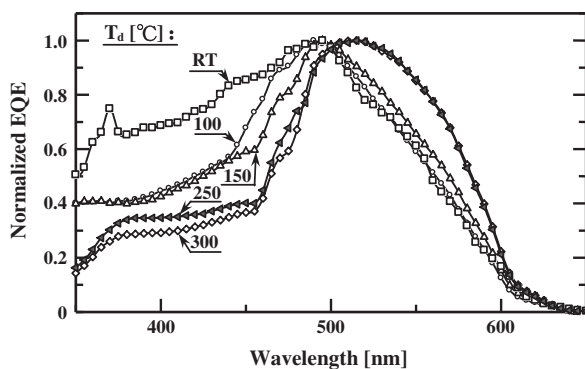


Fig. 7. Normalized EQE spectra as a function of  $T_d$  in AZO/ $\text{Ga}_2\text{O}_3$ / $\text{Cu}_2\text{O}$  HbH solar cells.

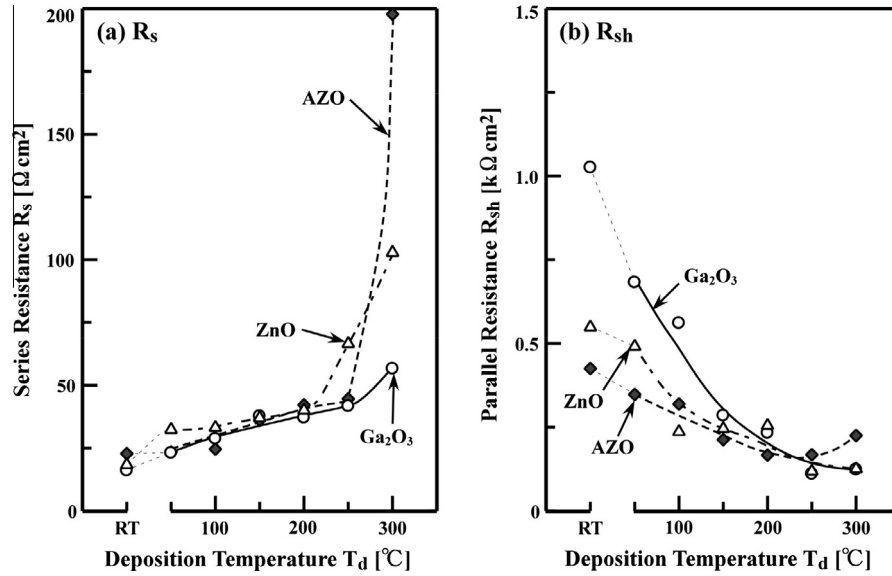


Fig. 8. (a)  $R_s$  and (b)  $R_{sh}$  as functions of  $T_d$  in AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O (open circle), AZO/ZnO/Cu<sub>2</sub>O (open triangle) and AZO/Cu<sub>2</sub>O (solid diamond) HbH solar cells.

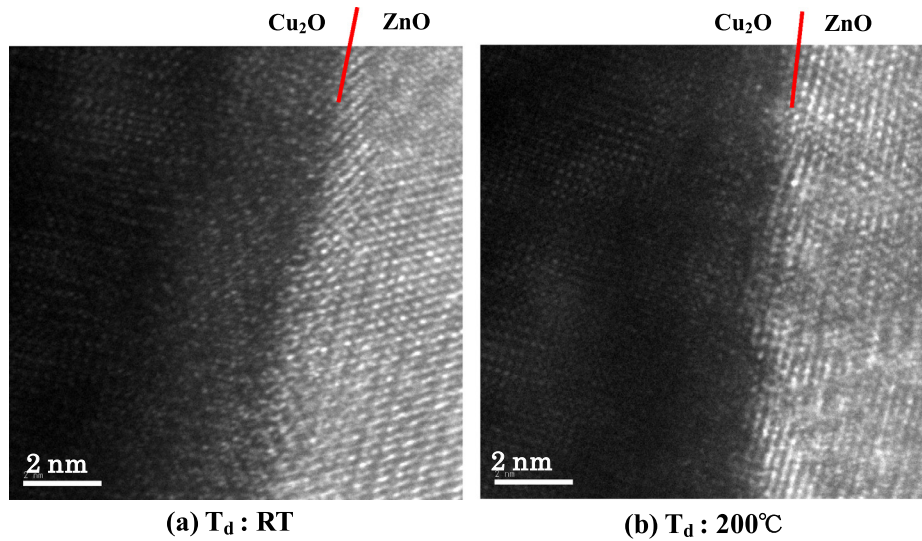


Fig. 9. Cross TEM images of the interface of AZO/ZnO/Cu<sub>2</sub>O solar cells fabricated with a  $T_d$  of (a) RT and (b) 200 °C.

sition of oxide semiconductors using the PLD method to improve the obtainable photovoltaic properties in the HbH solar cells. A higher efficiency in HbH solar cells fabricated using oxide semiconductors such as ZnO and Ga<sub>2</sub>O<sub>3</sub> was achieved by optimizing the pressure of O<sub>2</sub> gas introduced during the oxide thin-film depositions, whereas when using oxide semiconductors such as Ta<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub>, a higher efficiency was achieved using depositions without introducing O<sub>2</sub> gas (in vacuum, less than 10<sup>−4</sup> Pa), as shown in Table 1. The  $P_o$  dependences of the obtained photovoltaic properties are shown in Fig. 10 for AZO/ZnO/Cu<sub>2</sub>O (open triangle data points) and AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O (open circle data points) HbH solar cells fabricated by depositing a ZnO or Ga<sub>2</sub>O<sub>3</sub> thin film

on Cu<sub>2</sub>O sheets at a  $T_d$  of RT using the PLD method (Nishi et al., 2012b; Minami et al., 2013d). The obtained  $J_{SC}$ ,  $\eta$ , FF and  $V_{OC}$  in both the AZO/ZnO/Cu<sub>2</sub>O and AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cells increased as the  $P_o$  was increased up to approximately 1.0 and 1.7 Pa, respectively, and then they decreased as the  $P_o$  was increased further, with the exception of the  $V_{OC}$  in the AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cells, which increased as the  $P_o$  was increased up to approximately 2.2 Pa. It should be noted that the  $P_o$  dependence of  $V_{OC}$  obtained in the AZO/ZnO/Cu<sub>2</sub>O HbH solar cells was not related to the work function, because the carrier concentration of the deposited ZnO thin films remained relatively constant in the  $P_o$  range from vacuum to 1.7 Pa; i.e., with increasing  $P_o$ , the



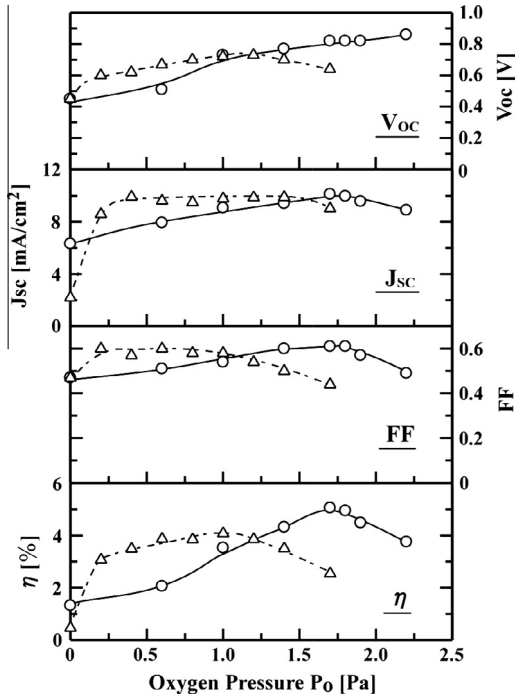


Fig. 10. Obtained  $V_{OC}$ ,  $J_{SC}$ , FF and  $\eta$  as functions of  $P_o$  in AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O (circle) and AZO/ZnO/Cu<sub>2</sub>O (triangle) HbH solar cells.

resistivity of the ZnO thin films exhibited a slight decrease, related to a slight increase of Hall mobility (data not shown).

It was also found that the  $P_o$  dependences of the photovoltaic properties obtained in both the AZO/ZnO/Cu<sub>2</sub>O and AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cells, as shown in Fig. 10, were related to those of the  $R_{sh}$  rather than  $R_s$  estimated from these HbH solar cells.  $R_{sh}$  and  $R_s$  as functions of the  $P_o$  are shown in Fig. 11 for the AZO/ZnO/Cu<sub>2</sub>O

(open triangle data points) and AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O (open circle data points) HbH solar cells fabricated at a  $T_d$  of RT shown in Fig. 10. The decrease in  $R_{sh}$  with increasing  $P_o$  is equivalent to a decrease in  $\eta$  that is mainly related to that of FF, as shown in Fig. 10. These decreases may be attributable to an increase of leakage current that results from degradation of the surface of Cu<sub>2</sub>O sheets, which could promote an increase of defects created at the interface between the metal oxides and the surface of the Cu<sub>2</sub>O. The above results suggest that the  $P_o$  dependence of the photovoltaic properties obtained in AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells may be affected considerably more by the pre-deposition surface condition of the Cu<sub>2</sub>O sheet and/or the surface condition at the initial stage in the thin-film depositions than the electrical and crystallographical properties of the deposited metal oxide thin films.

In addition, achieving an improvement of photovoltaic properties in AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells requires optimizing the thickness of the oxide semiconductor thin-film layer inserted between the AZO transparent electrode and the Cu<sub>2</sub>O sheet. Although, other than ZnO, Ga<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, the optimal film thickness of the oxide semiconductor thin-film layers indicated in Table 1 has not yet been investigated, it seems that the optimal thickness may be around 50 nm for oxide thin films deposited at a  $T_d$  of RT by the PLD method. The film thickness ( $d$ ) dependences of the obtained photovoltaic properties are shown in Fig. 12 for AZO/ZnO/Cu<sub>2</sub>O (open triangle data points) and AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O (open circle data points) HbH solar cells fabricated by depositing a ZnO thin film at a  $P_o$  of 1.0 Pa or Ga<sub>2</sub>O<sub>3</sub> thin film at a  $P_o$  of 1.7 Pa on Cu<sub>2</sub>O sheets at RT (Nishi et al., 2012b; Minami et al., 2013d). The  $J_{SC}$ ,  $\eta$ , FF and  $V_{OC}$  plotted at a  $d$  of 0 nm indicate the data obtained in a AZO/Cu<sub>2</sub>O HbH solar cell fab-

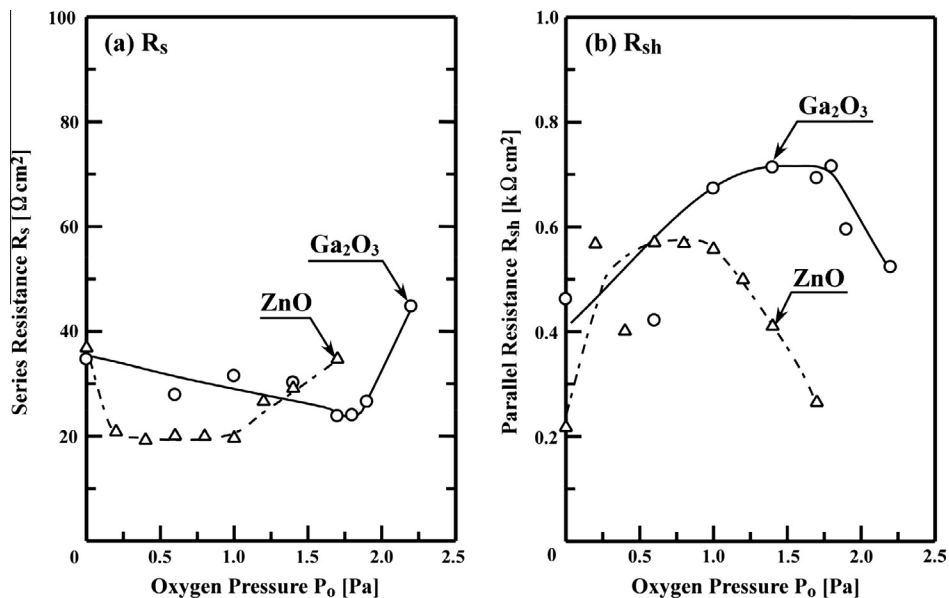


Fig. 11. (a)  $R_s$  and (b)  $R_{sh}$  as functions of  $P_o$  in AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O (circle) and AZO/ZnO/Cu<sub>2</sub>O (triangle) HbH solar cells.

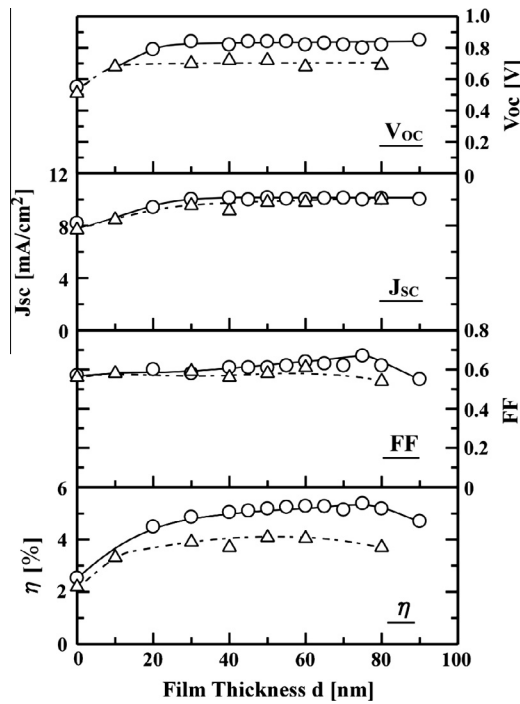


Fig. 12. Obtained  $V_{OC}$ ,  $J_{SC}$ , FF and  $\eta$  as functions of  $d$  in AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O (circle) and AZO/ZnO/Cu<sub>2</sub>O (triangle) HbH solar cells.

ricated by depositing an AZO thin film at a  $P_o$  of 0.2 Pa on a Cu<sub>2</sub>O sheet at RT. The obtained  $J_{SC}$ ,  $\eta$ , FF and  $V_{OC}$  in both the AZO/ZnO/Cu<sub>2</sub>O and AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cells increased as  $d$  was increased up to approximately 50 and 75 nm, respectively, and then  $J_{SC}$ ,  $\eta$  and FF decreased gradually with increasing film thickness, whereas  $V_{OC}$  remained relatively constant. In the AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cells, the decrease of  $\eta$  at a  $d$  greater than approximately 80 nm (related to that of FF, as seen in Fig. 12) was found to correlate to the increase of the  $R_s$  estimated from the HbH solar cells; this may be attributable to an increase of resistance of Ga<sub>2</sub>O<sub>3</sub> thin films due to the thickness increase. Thus, a thickness of approximately 75 nm was suitable for the n-oxide semiconductor thin-film layer of AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cells fabricated using Cu<sub>2</sub>O with a thickness of about 0.2 mm and a resistivity on the order of  $10^2$ – $10^3$   $\Omega$  cm. However, if it is possible to reduce the thickness and/or resistivity in the high quality Cu<sub>2</sub>O sheets, higher conversion efficiencies will become achievable by optimizing the thickness of the n-oxide semiconductor thin film.

#### 4. Summary and further development to achieve higher efficiency

As described above, a significant improvement in the photovoltaic properties of Cu<sub>2</sub>O-based HbH solar cells using thermally oxidized Cu<sub>2</sub>O sheets was achieved by not only stabilizing the surface of p-Cu<sub>2</sub>O sheets, but also developing low-temperature and low-damage deposition technology for applying oxide thin films as an n-oxide semiconductor layer. In addition, we investigated the effect

of the inserted n-oxide semiconductor thin film on the obtainable photovoltaic properties in AZO/n-oxide semiconductor/p-Cu<sub>2</sub>O HbH solar cells fabricated by inserting various n-oxide semiconductor thin films between the AZO transparent electrode and the p-Cu<sub>2</sub>O sheet, as shown in Table 1. As a result, we have reported that a nondoped ZnO or Ga<sub>2</sub>O<sub>3</sub> thin film deposited at RT by a PLD method is suitable as the inserted n-oxide semiconductor layer; in particular, an amorphous Ga<sub>2</sub>O<sub>3</sub> thin film with a high resistivity is the most suitable oxide. A maximum conversion efficiency of 5.38% was obtained in an AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O heterojunction solar cell fabricated by depositing a Ga<sub>2</sub>O<sub>3</sub> thin film on a Cu<sub>2</sub>O sheet prepared with a resistivity on the order of  $10^2$   $\Omega$  cm. Energy band diagrams constructed for the AZO/ZnO/Cu<sub>2</sub>O and AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cells are shown in Fig. 13: data based on the work functions and electron affinities measured on the oxide materials used in fabrications of the HbH solar cells or reported in previously published literature. For comparison, the energy band diagram of the AZO/Cu<sub>2</sub>O HbH solar cell is also shown in Fig. 13. As described above, the value of diffusion potential estimated by measuring the capacitance–voltage characteristics of the heterojunctions was equal to that of the  $V_{OC}$  obtained in these HbH solar cells. As can be seen in Fig. 13, it is difficult to provide an explanation of the resulting  $V_{OC}$  that is based only on the difference in work functions between the n-oxide semiconductor thin film and the Cu<sub>2</sub>O sheet. The description presented above suggests that the resulting depletion layer in the n-oxide semiconductor/p-Cu<sub>2</sub>O heterojunctions fabricated in this work may have been modified by the formation of another layer at the interface between the oxide semiconductor thin film and the Cu<sub>2</sub>O sheet. That is, the obtained  $V_{OC}$  in AZO/oxide semiconductor/Cu<sub>2</sub>O HbH solar cells may be affected considerably more by the pre-deposition surface condition of the Cu<sub>2</sub>O sheet and/or the surface condition at the initial stage in the thin-film deposition than by the work function of the thin film. Thus, further microscopic investigation of the interface between the oxide semiconductor thin film and the Cu<sub>2</sub>O sheet is necessary to improve the n-semiconductor/p-Cu<sub>2</sub>O heterojunction as well as stabilize the surface of Cu<sub>2</sub>O sheets.

As described above, it is known that photovoltaic properties such as  $V_{OC}$  are also affected by the height of the conduction band discontinuity, resulting from the difference in electron affinity between the n-oxide semiconductor thin film and the Cu<sub>2</sub>O sheet used in the heterojunction. As shown in Fig. 13, the resulting discontinuity of the conduction band in n-Ga<sub>2</sub>O<sub>3</sub>/p-Cu<sub>2</sub>O heterojunctions would be low, because the difference in electron affinity between Ga<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O is not very large (Huang et al., 2006; López et al., 2012; Yang and Rhee, 2007; Jeong et al., 2008; Hsu and Chou, 2012), whereas that in AZO/p-Cu<sub>2</sub>O and n-ZnO/p-Cu<sub>2</sub>O heterojunctions is relatively large. In addition, using a Ga<sub>2</sub>O<sub>3</sub> thin film as the n-semiconductor layer resulted in a dramatic decrease of leakage

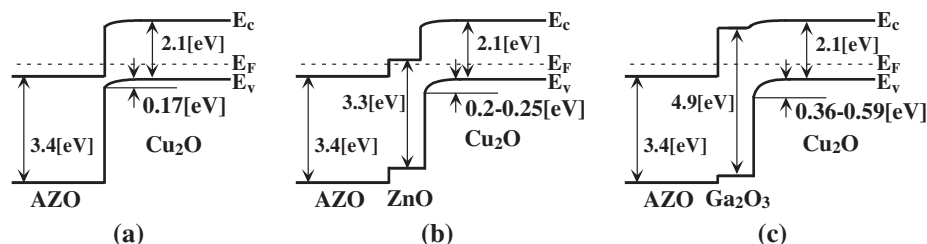


Fig. 13. Energy band diagrams of (a) AZO/Cu<sub>2</sub>O, (b) AZO/ZnO/Cu<sub>2</sub>O and (c) AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cells.

current observed in the J–V characteristic measured under dark conditions as well as an improvement of EQE. The EQE observed from the AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cell was enhanced over those observed from the AZO/ZnO/Cu<sub>2</sub>O heterojunction and AZO/Cu<sub>2</sub>O HbH solar cells at wavelengths below approximately 500 nm, as shown in Fig. 3. It should be noted that the optical transmission spectra of all the AZO, AZO/ZnO and AZO/Ga<sub>2</sub>O<sub>3</sub> thin films prepared on glass substrates at the same time as on the Cu<sub>2</sub>O sheets, under optimal conditions for fabricating the various heterojunctions, exhibited a high transmittance above about 80% at wavelengths longer than 400 nm. The increase of EQE at wavelengths below approximately 500 nm obtained from the AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O HbH solar cell may be attributed to an enhancement in the lifetime of electrons that have been photo-excited in the conduction band near the surface of the Cu<sub>2</sub>O sheet, resulting from the decrease in the defect levels at the interface between the Ga<sub>2</sub>O<sub>3</sub> thin film and the Cu<sub>2</sub>O sheet. These results suggest that an improvement of the p–n junction, as seen in the Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O heterojunction, could be achieved by decreasing the defect levels at the interface, which would decrease not only the recombination associated with defects at the interface between the Ga<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O, but also the conduction band discontinuity. For further improvement of the p–n junction, we have recently proposed various Cu<sub>2</sub>O-based HbH solar cells fabricated by inserting Ga<sub>2</sub>O<sub>3</sub>-based multicomponent oxides as the n-oxide semiconductor thin-film layer.

In addition, it should be noted that in the AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O heterojunction solar cells, only the p-type Cu<sub>2</sub>O acts as the active layer, because the Ga<sub>2</sub>O<sub>3</sub> thin film cannot absorb any of the sunlight. Thus, achieving higher conversion efficiency requires the development of a p–n junction prepared by using an appropriate n-type semiconductor with an energy gap near that of either Cu<sub>2</sub>O or n-type Cu<sub>2</sub>O as the n-type semiconductor layer. In addition, our Cu<sub>2</sub>O-based heterojunction solar cells exhibited relatively high  $R_s$  and low  $R_{sh}$  in comparison with those in conventional Si solar cells, as described above. For the purpose of resolving the remaining problems, we have to carry out further studies on ways of achieving a lower resistivity, resulting from an increase of carrier concentration under keeping mobility greater than 100 cm<sup>2</sup>/V s as well as passivation of the grain boundary and/or the surface of polycrystalline Cu<sub>2</sub>O sheets.

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## References

- Assimos, J.A., Trivich, D., 1974. *Phys. Status Solidi A* 26, 477.
- Briskman, R.N., 1992. A study of electrodeposited cuprous oxide photovoltaic cells. *Sol. Energy Mater. Sol. Cells* 27, 361–368.
- Fujimoto, K., Oku, T., Akiyama, T., 2013. Fabrication and characterization of ZnO/Cu<sub>2</sub>O solar cells prepared by electrodeposition. *Appl. Phys. Exp.* 6, 086503-1–086503-3.
- Fujinaka, M., Berezin, A.A., 1983. Cuprous oxide-indium-tin oxide thin film photovoltaic cells. *J. Appl. Phys.* 54, 3582–3588.
- Herion, J., Niekisch, E.A., Scharl, G., 1980. Investigation of metal oxide/cuprous oxide heterojunction solar cells. *Solar Energy Mater.* 4, 101–112.
- Hsu, C.W., Chou, L.J., 2012. Bipolar resistive switching of single gold-in-Ga<sub>2</sub>O<sub>3</sub> nanowire. *Nano Lett.* 12, 4247–4253.
- Huang, Y., Yue, S., Wang, Z., Wang, Q., Shi, C., Wu, Z., Bai, X.D., Tang, C., Gu, C., 2006. Preparation and electrical properties of ultrafine Ga<sub>2</sub>O<sub>3</sub> nanowires. *J. Phys. Chem. B* 110, 796–800.
- Iwanowski, R.J., Trivich, D., 1986. Enhancement of the photovoltaic conversion efficiency in Cu/Cu<sub>2</sub>O schottky barrier solar cells by H<sup>+</sup> ion irradiation. *Phys. Status Solidi A* 95, 735–741.
- Izaki, M., Shinagawa, T., Mizuno, K., Ida, Y., Inaba, M., Tasak, A., 2007. Electrochemically constructed p-Cu<sub>2</sub>O/n-ZnO heterojunction diode for photovoltaic device. *J. Phys. D* 40, 3326–3329.
- Jeong, S.S., Mittiga, A., Salza, E., Masci, A., Passerini, S., 2008. Electrodeposited ZnO/Cu<sub>2</sub>O heterojunction solar cells. *Electrochem. Acta* 53, 2226–2231.
- Kramm, B., Laufer, A., Reppin, D., Kronenberger, A., Hering, P., Polity, A., Mayer, B.K., 2012. The band alignment of Cu<sub>2</sub>O/ZnO and Cu<sub>2</sub>O/GaN heterostructures. *Appl. Phys. Lett.* 100, 094102-1–094102-3.
- Lee, Y.S., Heo, J., Siah, S.C., Mailoa, J.P., Brandt, R.E., Kim, S.B., Gordon, R.G., Buonassisi, T., 2013. Ultrathin amorphous zinc-tin-oxide buffer layer for enhancing heterojunction interface quality in metal-oxide solar cells. *Energy Environ. Sci.* 6, 2112–2118.
- Liao, L., Zhang, Z., Yan, B., Zheng, Z., Bao, Q.L., Wu, T., Li, C.M., Shen, Z.X., Zhang, X., Gong, H., Li, J.C., Yu, T., 2009. Multifunctional CuO nanowire devices: p-type field effect transistors and CO gas sensors. *Nanotechnology* 20, 085203-1–085203-6.
- López, I., Nogales, E., Hidalgo, P., Méndez, B., Piqueras, 2012. Field emission properties of gallium oxide micro- and nanostructures in the scanning electron microscope. *Phys. Status Solidi A* 209, 113–117.
- McShane, C.M., Choi, K.S., 2012. Junction studies on electrochemically fabricated p–n Cu<sub>2</sub>O homojunction solar cells for efficiency enhancement. *Phys. Chem. Chem. Phys.* 14, 6112–6118.

- McShane, C.M., Siripala, W.P., Choi, K., 2010. Effect of junction morphology on the performance of polycrystalline  $\text{Cu}_2\text{O}$  homojunction solar cells. *J. Phys. Chem. Lett.* 1, 2666–2670.
- Minami, T., 2005. Transparent conducting oxide semiconductors for transparent electrodes. *Semicond. Sci. Technol.* 20, S35–S44.
- Minami, T., Miyata, T., Yamamoto, T., 1998. Work function of transparent conducting multicomponent oxide thin films prepared by magnetron sputtering. *Surf. Coat. Technol.* 108–109, 583–587.
- Minami, T., Tanaka, H., Shimokawa, T., Miyata, T., Sato, H., 2004. High-efficiency oxide heterojunction solar cells using  $\text{Cu}_2\text{O}$  sheets. *Jpn. J. Appl. Phys.* 43, L917–L919.
- Minami, T., Miyata, T., Ihara, K., Minamino, Y., Tsukada, S., 2006. Effect of ZnO film deposition methods on the photovoltaic properties of ZnO– $\text{Cu}_2\text{O}$  heterojunction devices. *Thin Solid Films* 494, 47–52.
- Minami, T., Nishi, Y., Miyata, T., Nomoto, J., 2011. High-efficiency oxide solar cells with ZnO/ $\text{Cu}_2\text{O}$  heterojunction fabricated on thermally oxidized  $\text{Cu}_2\text{O}$  sheets. *Appl. Phys. Exp.* 4, 062301-1–062301-3.
- Minami, T., Miyata, T., Nishi, Y., 2013a. Efficiency improvement of  $\text{Cu}_2\text{O}$ -based heterojunction solar cells fabricated using thermally oxidized copper sheets. *Thin Solid Films* (Available online 19 November).
- Minami, T., Nishi, Y., Miyata, T., Abe, S., 2013b. Photovoltaic properties in Al-doped ZnO/non-doped  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ / $\text{Cu}_2\text{O}$  heterojunction solar cells. *ECS Transactions* 50, Honolulu, PRiME 2012, Photovoltaics for the 21st century, pp. 59–68.
- Minami, T., Nishi, Y., Miyata, T., 2013c. High-efficiency  $\text{Cu}_2\text{O}$ -based heterojunction solar cells fabricated using a  $\text{Ga}_2\text{O}_3$  thin film as n-type layer. *Appl. Phys. Exp.* 6, 044101-1–044101-3.
- Minami, T., Nishi, Y., Miyata, T., 2013d. Effect of the thin  $\text{Ga}_2\text{O}_3$  layer in  $\text{n}^+\text{-ZnO/n-Ga}_2\text{O}_3/\text{p-Cu}_2\text{O}$  heterojunction solar cells. *Thin Solid Films* 549, 65–69.
- Mittiga, A., Salza, E., Sarto, F., Tucci, M., Vasanthi, R., 2006. Heterojunction solar cell with 2% efficiency based on a  $\text{Cu}_2\text{O}$  substrate. *Appl. Phys. Lett.* 88, 163502-1–163502-3.
- Miyata, T., Minami, T., Tanaka, H., Sato, H., 2006. Effect of a buffer layer on the photovoltaic properties of AZO/ $\text{Cu}_2\text{O}$  solar cells. In: *Proceedings of SPIE, “Device and Process Technologies for Microelectronics, MEMS, and Photonics IV”* 6037, pp. 603712-1–603712-11.
- Mohamed, M., Irmscher, K., Janowitz, C., Galazka, Z., Manzke, R., Fornari, R., 2012. Schottky barrier height of Au on the transparent semiconducting oxide  $\beta\text{-Ga}_2\text{O}_3$ . *Appl. Phys. Lett.* 101, 132106-1–132106-3.
- Nishi, Y., Miyata, T., Nomoto, J., Minami, T., 2011. High-efficiency  $\text{Cu}_2\text{O}$ -based heterojunction solar cells fabricated on thermally oxidized copper sheets. In: *Conference Record of 37th IEEE Photovoltaic Specialists Conference*, pp. 266–270.
- Nishi, Y., Miyata, T., Minami, T., 2012a. Effect of inserting a thin buffer layer on the efficiency in n-ZnO/p- $\text{Cu}_2\text{O}$  heterojunction solar cells. *J. Vac. Sci. Technol. A* 30, 04D103-1–04D103-6.
- Nishi, Y., Miyata, T., Nomoto, J., Minami, T., 2012b. Influence of  $\text{Cu}_2\text{O}$  surface treatment on the photovoltaic properties of Al-doped ZnO/ $\text{Cu}_2\text{O}$  solar cells. *Thin Solid Films* 520, 3819–3822.
- Nishi, Y., Miyata, T., Minami, T., 2013. The impact of heterojunction formation temperature on obtainable conversion efficiency in n-ZnO/p- $\text{Cu}_2\text{O}$  solar cells. *Thin Solid Films* 528, 72–76.
- Olsen, L.C., Bohara, R.C., Urie, M.W., 1979. Explanation for low-efficiency  $\text{Cu}_2\text{O}$  Schottky-barrier solar cells. *Appl. Phys. Lett.* 34, 47–49.
- Olsen, L.C., Addis, F.W., Miller, W., 1982. Experimental and theoretical studies of  $\text{Cu}_2\text{O}$  solar cells. *Solar cells* 7, 247–279.
- Papadimitriou, L., Economou, N.A., Trivich, D., 1981. Heterojunction solar cells on cuprous oxide. *Solar cells* 3, 73–80.
- Rai, B.P., 1988.  $\text{Cu}_2\text{O}$  solar cells: a review. *Solar cells* 25, 265–272.
- Rakhshani, A.E., 1986. Preparation, characteristics and photovoltaic properties of cuprous oxide – a review. *Solid-State Electron.* 29, 7–17.
- Sanghyun, J., Sunkook, K., Saeed, M., David, B.J., Young, G. Ha, Antonio, F., Tobin, J.M., 2008. Interface studies of ZnO nanowire transistors using low-frequency noise and temperature-dependent  $I$ – $V$  measurements. *Appl. Phys. Lett.* 92, 022104-1–022104-3.
- Sears, W.M., Fortin, E., Webb, J.B., 1983. Indium tin oxide/ $\text{Cu}_2\text{O}$  photovoltaic cells. *Thin Solid Films* 103, 303–309.
- Shiu, H., Tsai, C., Chen, S., Yew, T., 2011. Solution-processed all-oxide nanostructures for heterojunction solar cells. *J. Mater. Chem.* 21, 17646–17650.
- Suehiro, T., Sasaki, T., Hiratate, Y., 2001. Electronic properties of thin cuprous oxide sheet prepared by infrared light irradiation. *Thin Solid Films* 383, 318–320.
- Tanaka, H., Shimakawa, T., Miyata, T., Sato, H., Minami, T., 2004. Electrical and optical properties of TCO– $\text{Cu}_2\text{O}$  heterojunction devices. *Thin Solid Films* 469–470, 80–85.
- Tanaka, H., Shimakawa, T., Miyata, T., Sato, H., Minami, T., 2005. Effect of AZO film deposition conditions on the photovoltaic properties of AZO– $\text{Cu}_2\text{O}$  heterojunctions. *Appl. Surf. Sci.* 244, 568–572.
- Yang, W.Y., Rhee, S.W., 2007. Effect of electrode material on the resistance switching of  $\text{Cu}_2\text{O}$  film. *Appl. Phys. Lett.* 91, 232907-1–232907-3.
- Yun, D.J., Lim, S.H., Cho, S.H., Kim, B.S., Rhee, S.W., 2009. Effect of Cu,  $\text{CuO}$ , and Cu– $\text{CuO}$  bilayer source/drain electrodes on the performance of the pentacene thin-film transistor. *J. Electrochem. Soc.* 156, H634.