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Cu₂O-based heterojunction solar cells with an Al-doped ZnO/oxide semiconductor/thermally oxidized Cu₂O 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 Cu₂O 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 Cu₂O sheet. An improvement of photovoltaic properties was achieved by both stabilizing the surface of polycrystalline p-Cu₂O 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/Cu₂O HbH solar cells were found to be considerably more affected by the surface condition of the p-Cu₂O layer, *i.e.*, the interface at the heterojunction, than the diffusion potential resulting from the difference of work functions between the p-Cu₂O and n-oxide semiconductor layers. To achieve a higher efficiency in AZO/n-oxide semiconductor/p-Cu₂O 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 Cu₂O-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 nondoped ZnO or Ga₂O₃ thin film deposited at room temperature by PLD is suitable as the n-oxide semiconductor layer, an amorphous Ga₂O₃ 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 Ga₂O₃/Cu₂O 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 Ga₂O₃ and Cu₂O, but also the conduction band discontinuity. We have achieved a maximum conversion efficiency of 5.38% in an AZO/Ga₂O₃/Cu₂O heterojunction solar cell fabricated by depositing a Ga₂O₃ thin film on a Cu₂O sheet with a resistivity on the order of 10² Ω cm.

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1. Cu₂O-based hybrid heterojunction solar cells

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

cuprous oxide (Cu₂O) 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 Cu₂O, 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 Cu₂O is intrinsically a p-type semiconductor and the surface of Cu₂O is chemically unstable since cupric oxide (CuO) is more stable than Cu₂O 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 Cu₂O films by electrodeposition from an aqueous solution as well as the fabrication of thin-film p-n junction Cu₂O 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% was in a p-n junction Cu₂O thin-film solar cell, which is low in comparison to the theoretical energy conversion efficiency of a Cu₂O solar cell that is as high as 20% (Rakhshani, 1986). Since fabricating Cu₂O p-n homojunction solar cells has proven to be a problem due to the difficulty of preparing n-type Cu₂O, there have been many reports on various p-n heterojunction solar cells fabricated using p-type Cu₂O 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-Cu₂O hybrid heterojunction (HbH) solar cells fabricated by depositing transparent conducting oxide (TCO) thin films on thermally oxidized polycrystalline p-Cu₂O 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/Cu₂O HbH solar cells, TCO/n-type oxide semiconductor/p-Cu₂O HbH solar cells were fabricated by inserting an n-type oxide semiconductor thin film as a buffer layer between the TCO electrode and the Cu₂O sheet (Miyata et al., 2006). It also has been reported that the obtained photovoltaic properties in n-oxide semiconductor/p-Cu₂O 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 Cu₂O-based HbH solar cell with an MgF₂/indium-tin-oxide (ITO)/ZnO/Cu₂O/Cu structure that was fabricated by depositing a ZnO thin film on thermally oxidized polycrystalline p-Cu₂O sheets using an ion beam sputtering method. In addition to Cu₂O-based HbH solar cells, Izaki et al. (2007) reported that a conversion efficiency of 1.28% was obtained in an n-oxide semiconductor/p-Cu₂O thin-film heterojunction (TFH) solar cell with an F-doped

SnO₂ (FTO)/ZnO/Cu₂O/Au structure fabricated by depositing first a ZnO thin film followed by a Cu₂O 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-Cu₂O 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 Cu₂O 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 Cu₂O 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 Cu₂O sheets (Nishi et al., 2011, 2012b, 2013; Minami et al., 2013b). In addition, Minami et al. (2013c) reported recently that a gallium oxide (Ga₂O₃) thin film and various Ga₂O₃-based multicomponent oxides are suitable for the n-oxide semiconductor layer of AZO/n-oxide semiconductor/p-Cu₂O 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/Cu₂O HbH solar cell fabricated with either an amorphous Ga₂O₃ or a Ga₂O₃-based multicomponent 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 Cu₂O 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 Cu₂O-based TFH solar cell with an AZO/amorphous ZnO-SnO₂ (a-ZTO) multi-component oxide/Cu₂O/Au structure fabricated by using an atomic layer deposition to place an ultrathin a-ZTO thin film onto a Cu₂O 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 Cu₂O-based TFH solar cells have yet to produce results comparable to those found in Cu₂O-based HbH solar cells, which may be attributable to the difference of crystallinity between the Cu₂O thin films and Cu₂O sheets.

This paper presents the current state and prospects of achieving higher conversion efficiency Cu₂O-based HbH solar cells fabricated using Cu₂O 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 Cu₂O-based HbH

solar cells with a transparent conductive AZO thin film/n-oxide semiconductor thin film/p-Cu₂O sheet thin film structure is described.

2. Experimental details

Cu₂O 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 Cu₂O sheets were polycrystalline p-type semiconductors: resistivity on the order of 10²–10³ Ω cm, hole concentration on the order of 10¹³–10¹⁴ cm⁻³ and Hall mobility in the range of 100–110 cm²/Vs. In the device fabrication, the CuO surface layer of the oxidized Cu₂O 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/cm²) under the following deposition conditions: target-substrate distance, 40 mm; deposition temperature, room temperature (RT)-300 °C; target, sintered AZO (Al₂O₃ content of 2 wt.%) and sintered oxide pellet; and atmosphere and pressure, vacuum below 4.0 × 10⁻⁴ Pa or O₂ 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-Cu₂O structure on the front surface of the Cu₂O sheets and an Au ohmic electrode on the back surface of the Cu₂O sheets; the Cu₂O 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 O₂ gas pressure of 0.2 Pa with a thickness of 200–490 nm, exhibited a resistivity on the order of 10⁻⁴ Ω cm and a carrier concentration of 10²⁰–10²¹ cm⁻³. 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 Cu₂O-based solar cells (electrode area of 3.14 mm²) were evaluated by exposing only the AZO transparent electrode area to AM1.5G solar illumination (100 mW/cm²) 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-Cu₂O HbH solar cells are affected by the material parameters and crystallographical characteristics of both the Cu₂O and the oxide semiconductor layers as well as the surface condition of the Cu₂O 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/Cu₂O HbH solar cells fabricated by depositing various n-metal oxide semiconductor thin films on thermally oxidized Cu₂O sheets at RT using the PLD method; Table 1 summarizes the obtained photovoltaic properties in AZO/oxide semiconductor/Cu₂O 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/Cu₂O 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 Cu₂O substrates at RT under the oxygen gas pressure (P_o) 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_o , as evidenced from X-ray diffraction (XRD) analyses. It should also be noted that, other than for the ZnO, Ga₂O₃ and TiO₂ 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 O₂ gas during the film deposition) using the PLD method produced metal rich oxide films. For comparison, the J–V characteristics of an AZO/Cu₂O 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/Ga₂O₃/Cu₂O and AZO/ZnO/Cu₂O HbH solar cells benefited significantly from the insertion of the non-doped Ga₂O₃ and nondoped ZnO thin-film layer, respectively, as evidenced by comparison with the AZO/Cu₂O heterojunc-

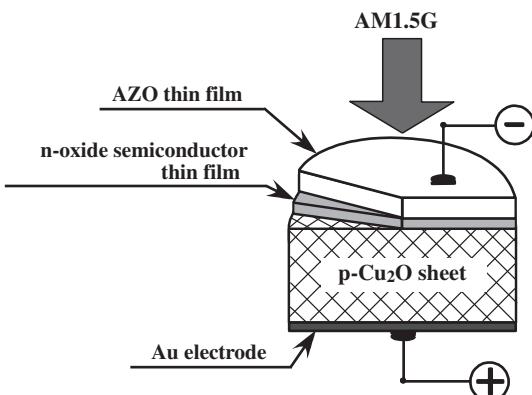


Fig. 1. Schematic structure of an AZO/n-oxide semiconductor/p-Cu₂O HbH solar cell.

Table 1

Obtained η_{\max} , V_{OC} , J_{SC} and FF in AZO/oxide semiconductor/Cu₂O HbH solar cells fabricated using various oxide semiconductor thin films prepared at P_o with d and ρ .

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

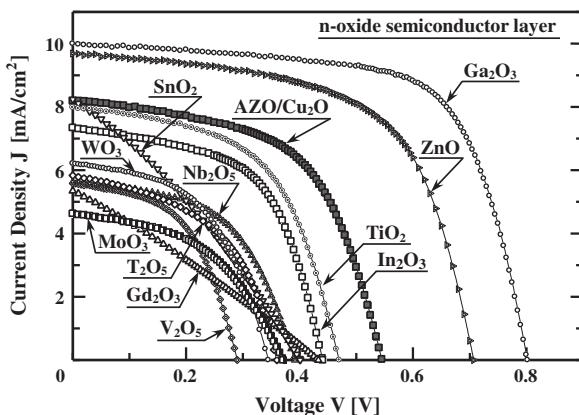


Fig. 2. J-V characteristics of AZO/n-oxide semiconductor/p-Cu₂O HbH solar cells fabricated by inserting various oxide semiconductor thin films and measured under AM1.5G solar illumination.

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 Ga₂O₃ and ZnO thin films prepared on glass substrates at the same time as on the Cu₂O 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} Ω cm. Thus, it seems that the nondoped Ga₂O₃ thin film used in the AZO/Ga₂O₃/Cu₂O HbH solar cell and the nondoped ZnO thin film used in the AZO/ZnO/Cu₂O HbH solar cell act as an n-type semiconductor layer. As noted above, the obtained photovoltaic properties in most AZO/oxide semiconductor/Cu₂O HbH solar cells fabricated by inserting a metal oxide semiconductor thin film other than Ga₂O₃ or ZnO were not improved significantly.

As described above, Cu₂O-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 Cu₂O sheets using a low-damage deposition technique. As can be seen in Table 1, the obtained maximum energy conversion efficiency (η_{\max}), open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}) and fill factor (FF) exhibited in the AZO/Ga₂O₃/Cu₂O and AZO/ZnO/Cu₂O 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 Cu₂O-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/Cu₂O and AZO/Ga₂O₃/Cu₂O HbH solar cells fabricated under the deposition conditions shown in Table 1. For comparison, the normalized EQE of an AZO/Cu₂O HbH solar cell (fabricated without an inserted oxide semiconductor thin-film layer) is also shown

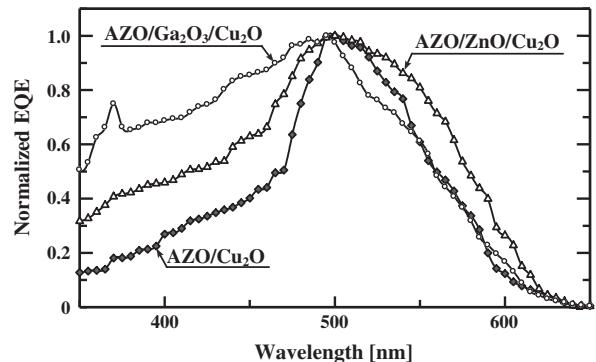


Fig. 3. Normalized EQE spectra observed from AZO/Ga₂O₃/Cu₂O (open circle), AZO/ZnO/Cu₂O (open triangle) and AZO/Cu₂O (solid diamond) HbH solar cells.

in Fig. 3. A comparison of the wavelength dependence of the EQE obtained in the AZO/Cu₂O HbH solar cells with those obtained in AZO/Ga₂O₃/Cu₂O and AZO/ZnO/Cu₂O HbH solar cells shows that the effect on EQE is enhanced in both the AZO/Ga₂O₃/Cu₂O and AZO/ZnO/Cu₂O heterojunction solar cells at wavelengths below approximately 500 nm; *i.e.*, EQE is significantly decreased in AZO/Cu₂O at wavelengths below about 500 nm. This may be a result of decreased degradation of the surface condition of the Cu₂O sheets, *i.e.*, the interface, occurring during the low temperature depositions of the Ga₂O₃ and ZnO films relative to that of the AZO film, possibly attributable to the different O₂ 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 Cu₂O sheet used in the heterojunction (Minami et al., 2013a,c,d). It was also found that AZO/oxide semiconductor/Cu₂O 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/Cu₂O 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/Ga₂O₃/Cu₂O HbH solar cell measured under a reversed bias was significantly lower, on the order of one magnitude, than that measured on the AZO/ZnO/Cu₂O HbH solar cell. This also suggests that the obtained photovoltaic properties in AZO/oxide semiconductor/Cu₂O HbH solar cells may be affected considerably by the pre-deposition surface condition of the Cu₂O 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.

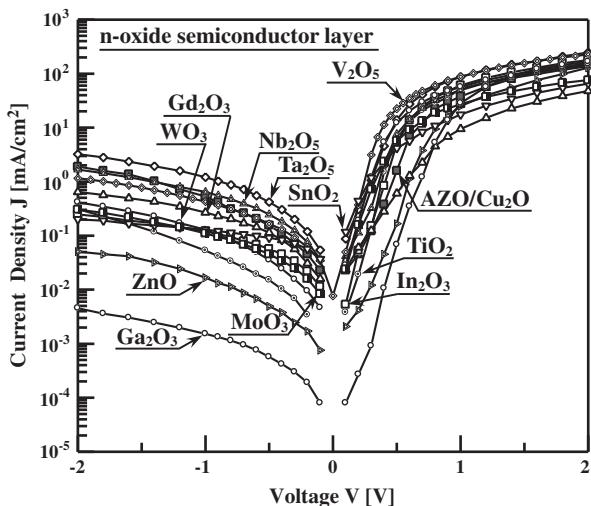


Fig. 4. J–V characteristics of AZO/n-oxide semiconductor/p-Cu₂O HbH solar cells measured under dark conditions.

As can be seen in Fig. 2 and Table 1, the obtained V_{OC} in AZO/n-oxide semiconductor/p-Cu₂O HbH solar cells varied considerably, depending on the kind of oxide semiconductor thin films used: *i.e.*, from $V_{OC} = 0.29$ V in V₂O₅ thin film to 0.8 in Ga₂O₃. It is known that the obtained V_{OC} in n-oxide semiconductor/p-Cu₂O 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 Cu₂O sheet used. We have also found that the V_{OC} obtained in all the AZO/oxide semiconductor/Cu₂O 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/Cu₂O 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-Cu₂O 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-Cu₂O sheets require knowing the work functions of the oxide semiconductor thin films and the Cu₂O sheets used.

We have recently reported that the actual work functions of the polycrystalline ZnO and amorphous Ga₂O₃ thin films and the polycrystalline Cu₂O sheet used in AZO/ZnO/Cu₂O and AZO/Ga₂O₃/Cu₂O 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 Ga₂O₃ thin films are larger than or equal to those of ZnO and β -Ga₂O₃ 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 Ga₂O₃ may be related to the fact that the Ga₂O₃ 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 Cu₂O 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 Cu₂O thin films reported in previously published literature (Jeong et al., 2008). The difference between the work function measured for Cu₂O in this work and that of the single crystal Cu₂O 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 Cu₂O, because the measurement used in this work was carried out in air. The diffusion potentials calculated theoretically in ZnO/Cu₂O and Ga₂O₃/Cu₂O 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 Cu₂O (reported by Assimos and Trivich, 1974). As shown in Fig. 2 and Table 1, however, the obtained V_{OC} in the ZnO/Cu₂O and Ga₂O₃/Cu₂O heterojunctions are 0.71 and 0.80 V, respectively. Thus, it is difficult to explain the high V_{OC} obtained in the heterojunction using only the difference in work functions between the Ga₂O₃ or ZnO thin film and the Cu₂O sheet. This suggests that the obtained V_{OC} and diffusion potentials in AZO/oxide semiconductor/Cu₂O heterojunction solar cells may be affected considerably by the characteristics of the oxide semiconductor/Cu₂O interface, which can be greatly affected by the Cu₂O 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-Ga₂O₃/p-Cu₂O and AZO/n-ZnO/p-Cu₂O 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 Cu₂O sheets at RT by using a low damage deposition method is exceptionally important to obtain higher conversion efficiency in AZO/oxide semiconductor/Cu₂O 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_{OC} , J_{SC} , η and FF as functions of the T_d are shown in Fig. 5 for AZO/ZnO/Cu₂O (open triangle data points) and AZO/Ga₂O₃/Cu₂O (open circle data points) HbH solar cells fabricated by depositing the AZO and ZnO or Ga₂O₃ 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_{OC} , J_{SC} , η and FF) in both the AZO/ZnO/Cu₂O and AZO/Ga₂O₃/Cu₂O 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/Cu₂O 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_{OC} , J_{SC} , η and FF as functions of the T_d are shown in Fig. 5 for the AZO/Cu₂O (solid diamond data points) HbH solar cells (fabricated without the insertion of an oxide semiconductor thin-film layer) (Nishi et al., 2012a).

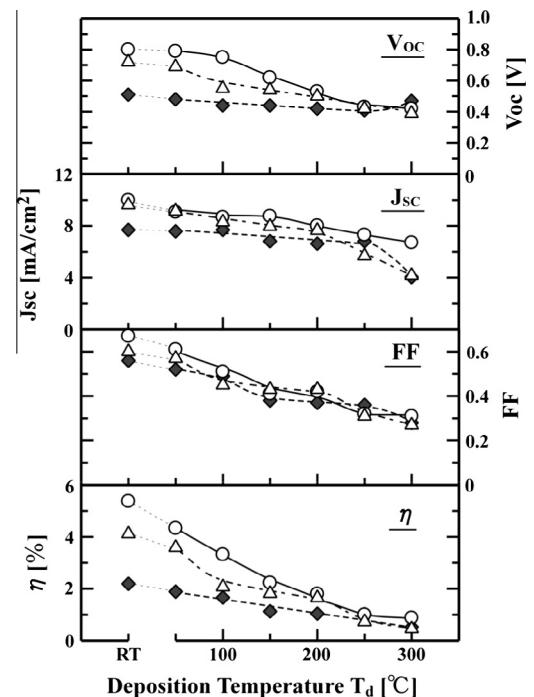


Fig. 5. Obtained V_{OC} , J_{SC} , FF and η as functions of T_d in AZO/Ga₂O₃/Cu₂O (open circle), AZO/ZnO/Cu₂O (open triangle) and AZO/Cu₂O (solid diamond) HbH solar cells.

It should be noted in Fig. 5 that the obtained V_{OC} , η 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 Cu₂O sheets. It should be noted that the Ga₂O₃ thin films deposited in the T_d range from RT to 300 °C were amorphous, whereas the crystallinity of polycrystalline ZnO and AZO thin films improved as the T_d was increased up to 300 °C. In addition, the resistivity of 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

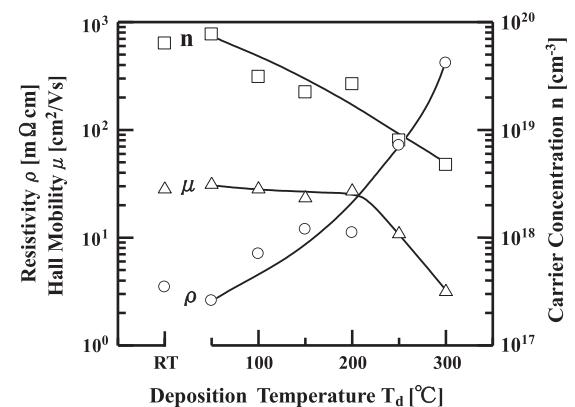


Fig. 6. Obtained ρ , n and μ as functions of T_d in ZnO thin films prepared at a P_0 of 1.0 Pa by PLD.

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 Ga_2O_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/Cu₂O and AZO/Cu₂O HbH solar cells shown in Fig. 5, the decrease of obtained V_{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_{OC} or diffusion potentials in AZO/oxide semiconductor/Cu₂O HbH may be affected considerably by the oxide semiconductor/Cu₂O interface, which can be greatly affected by the Cu₂O 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_{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/Cu₂O and AZO/ZnO/Cu₂O 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/Ga₂O₃/Cu₂O HbH solar cells fabricated by depositing the AZO and Ga₂O₃ 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/Ga₂O₃/Cu₂O and AZO/ZnO/Cu₂O HbH solar cells began to approach the EQE of AZO/Cu₂O HbH solar cells as the fabrication, *i.e.*, film deposition, temperature was increased (data not shown). This suggests that the influence of the inserted Ga₂O₃ 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

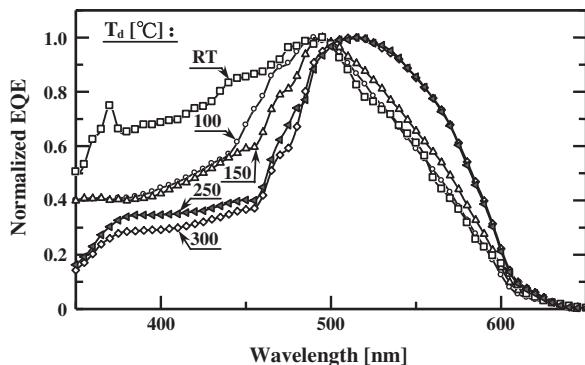


Fig. 7. Normalized EQE spectra as a function of T_d in AZO/Ga₂O₃/Cu₂O HbH solar cells.

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 Cu₂O sheets as well as an interdiffusion of metals at the interface between AZO, ZnO or Ga₂O₃ and the Cu₂O surface.

The R_s and R_{sh} estimated from the AZO/ZnO/Cu₂O (open triangle data points), AZO/Ga₂O₃/Cu₂O (open circle data points) and AZO/Cu₂O (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_{SC} , as shown in Fig. 5. In AZO/ZnO/Cu₂O HbH solar cells (fabricated by depositing nondoped ZnO thin films on the surface of Cu₂O 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_{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 Cu₂O sheets. However, the obtained R_{sh} in all the HbH solar cells decreased markedly as the T_d was increased. In reference to Fig. 5, the decrease in R_{sh} with increasing T_d is equivalent to a decrease in η 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 Cu₂O sheets as well as an interdiffusion of metals at interface between the AZO, ZnO or Ga₂O₃ and the Cu₂O surface, which could promote an increase of defects created at this interface. The degradation of the surface of Cu₂O sheets may also be evidenced from the transmission electron microscopy (TEM) images at the interface between nondoped ZnO and Cu₂O in AZO/ZnO/Cu₂O 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 Cu₂O-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 Cu₂O.

3.3. Influence of O₂ gas introduction pressure and film thickness

As described above, we have reported that the obtainable photovoltaic properties in AZO/oxide semiconductor/Cu₂O 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 O₂ gas in the film depo-

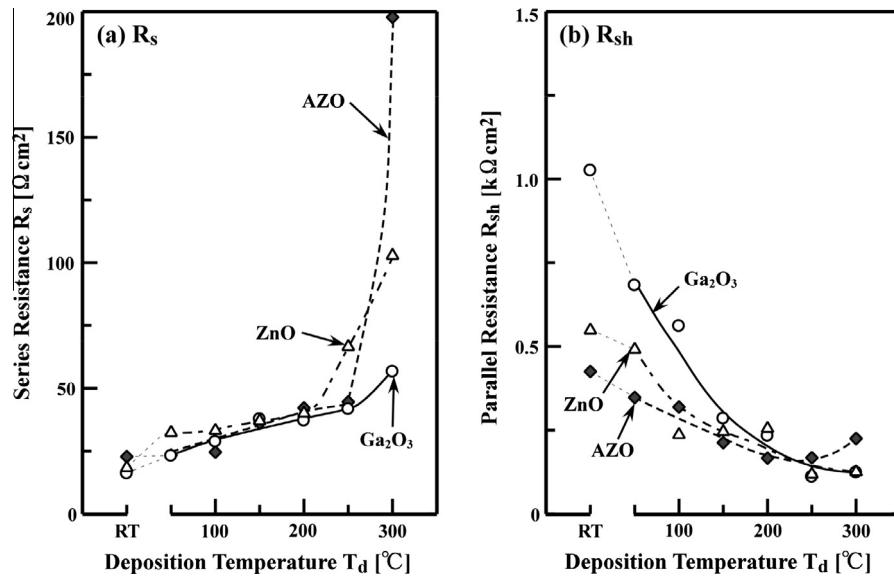


Fig. 8. (a) R_s and (b) R_{sh} as functions of T_d in AZO/Ga₂O₃/Cu₂O (open circle), AZO/ZnO/Cu₂O (open triangle) and AZO/Cu₂O (solid diamond) HbH solar cells.

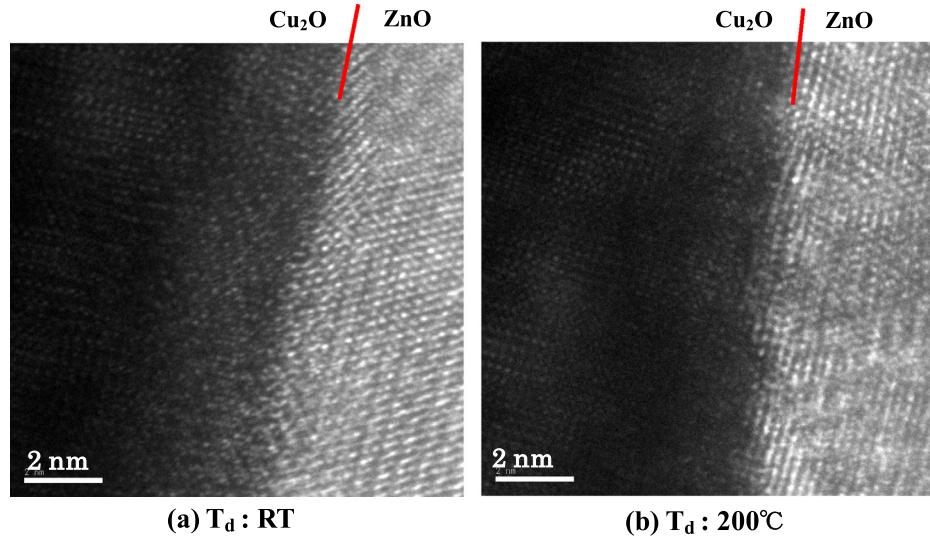


Fig. 9. Cross TEM images of the interface of AZO/ZnO/Cu₂O solar cells fabricated with a T_d of (a) RT and (b) 200 °C.

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 Ga₂O₃ was achieved by optimizing the pressure of O₂ gas introduced during the oxide thin-film depositions, whereas when using oxide semiconductors such as Ta₂O₅ and MoO₃, a higher efficiency was achieved using depositions without introducing O₂ gas (in vacuum, less than 10⁻⁴ Pa), as shown in Table 1. The P_o dependences of the obtained photovoltaic properties are shown in Fig. 10 for AZO/ZnO/Cu₂O (open triangle data points) and AZO/Ga₂O₃/Cu₂O (open circle data points) HbH solar cells fabricated by depositing a ZnO or Ga₂O₃ thin film

on Cu₂O sheets at a T_d of RT using the PLD method (Nishi et al., 2012b; Minami et al., 2013d). The obtained J_{SC} , η , FF and V_{OC} in both the AZO/ZnO/Cu₂O and AZO/Ga₂O₃/Cu₂O 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/Ga₂O₃/Cu₂O 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/Cu₂O 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

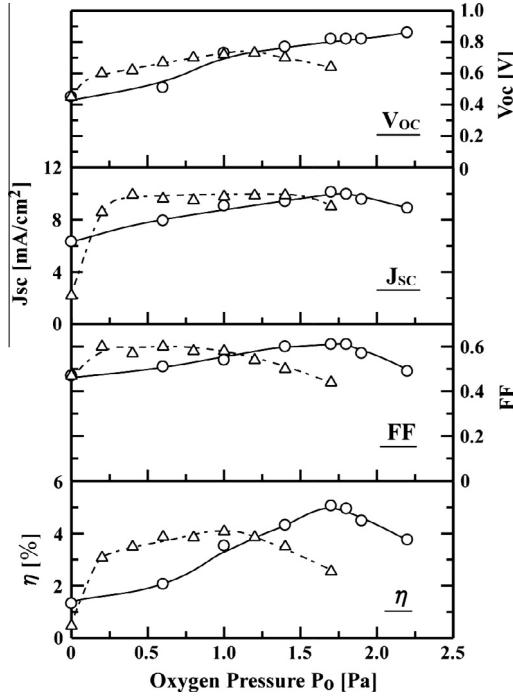


Fig. 10. Obtained V_{oc} , J_{sc} , FF and η as functions of P_o in AZO/Ga₂O₃/Cu₂O (circle) and AZO/ZnO/Cu₂O (triangle) HbH solar cells.

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/Cu₂O and AZO/Ga₂O₃/Cu₂O 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/Cu₂O

(open triangle data points) and AZO/Ga₂O₃/Cu₂O (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 η 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 Cu₂O sheets, which could promote an increase of defects created at the interface between the metal oxides and the surface of the Cu₂O. The above results suggest that the P_o dependence of the photovoltaic properties obtained in AZO/oxide semiconductor/Cu₂O HbH solar cells may be affected considerably more by the pre-deposition surface condition of the Cu₂O 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/Cu₂O HbH solar cells requires optimizing the thickness of the oxide semiconductor thin-film layer inserted between the AZO transparent electrode and the Cu₂O sheet. Although, other than ZnO, Ga₂O₃ and TiO₂, 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/Cu₂O (open triangle data points) and AZO/Ga₂O₃/Cu₂O (open circle data points) HbH solar cells fabricated by depositing a ZnO thin film at a P_o of 1.0 Pa or Ga₂O₃ thin film at a P_o of 1.7 Pa on Cu₂O sheets at RT (Nishi et al., 2012b; Minami et al., 2013d). The J_{sc} , η , FF and V_{oc} plotted at a d of 0 nm indicate the data obtained in a AZO/Cu₂O HbH solar cell fab-

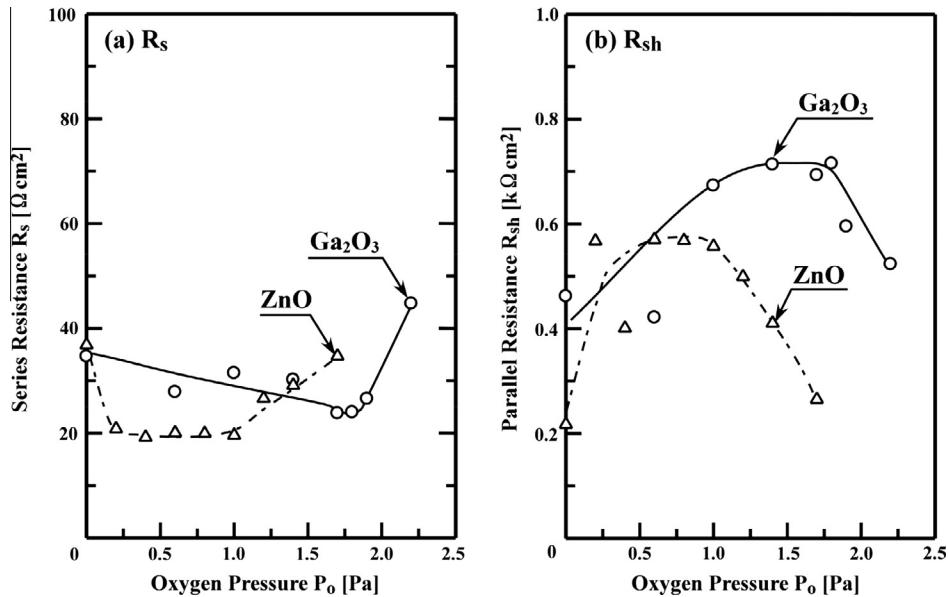


Fig. 11. (a) R_s and (b) R_{sh} as functions of P_o in AZO/Ga₂O₃/Cu₂O (circle) and AZO/ZnO/Cu₂O (triangle) HbH solar cells.

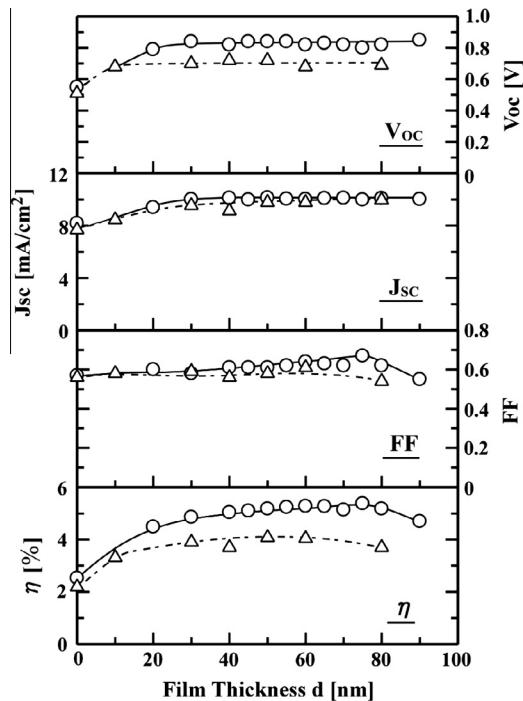


Fig. 12. Obtained V_{OC} , J_{SC} , FF and η as functions of d in AZO/Ga₂O₃/Cu₂O (circle) and AZO/ZnO/Cu₂O (triangle) HbH solar cells.

ricated by depositing an AZO thin film at a P_o of 0.2 Pa on a Cu₂O sheet at RT. The obtained J_{SC} , η , FF and V_{OC} in both the AZO/ZnO/Cu₂O and AZO/Ga₂O₃/Cu₂O HbH solar cells increased as d was increased up to approximately 50 and 75 nm, respectively, and then J_{SC} , η and FF decreased gradually with increasing film thickness, whereas V_{OC} remained relatively constant. In the AZO/Ga₂O₃/Cu₂O HbH solar cells, the decrease of η 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 Ga₂O₃ 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/Ga₂O₃/Cu₂O HbH solar cells fabricated using Cu₂O with a thickness of about 0.2 mm and a resistivity on the order of 10²–10³ Ω cm. However, if it is possible to reduce the thickness and/or resistivity in the high quality Cu₂O 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 Cu₂O-based HbH solar cells using thermally oxidized Cu₂O sheets was achieved by not only stabilizing the surface of p-Cu₂O 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-Cu₂O HbH solar cells fabricated by inserting various n-oxide semiconductor thin films between the AZO transparent electrode and the p-Cu₂O sheet, as shown in Table 1. As a result, we have reported that a nondoped ZnO or Ga₂O₃ thin film deposited at RT by a PLD method is suitable as the inserted n-oxide semiconductor layer; in particular, an amorphous Ga₂O₃ thin film with a high resistivity is the most suitable oxide. A maximum conversion efficiency of 5.38% was obtained in an AZO/Ga₂O₃/Cu₂O heterojunction solar cell fabricated by depositing a Ga₂O₃ thin film on a Cu₂O sheet prepared with a resistivity on the order of 10² Ω cm. Energy band diagrams constructed for the AZO/ZnO/Cu₂O and AZO/Ga₂O₃/Cu₂O 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/Cu₂O 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 Cu₂O sheet. The description presented above suggests that the resulting depletion layer in the n-oxide semiconductor/p-Cu₂O 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 Cu₂O sheet. That is, the obtained V_{OC} in AZO/oxide semiconductor/Cu₂O HbH solar cells may be affected considerably more by the pre-deposition surface condition of the Cu₂O 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 Cu₂O sheet is necessary to improve the n-semiconductor/p-Cu₂O heterojunction as well as stabilize the surface of Cu₂O 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 Cu₂O sheet used in the heterojunction. As shown in Fig. 13, the resulting discontinuity of the conduction band in n-Ga₂O₃/p-Cu₂O heterojunctions would be low, because the difference in electron affinity between Ga₂O₃ and Cu₂O 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-Cu₂O and n-ZnO/p-Cu₂O heterojunctions is relatively large. In addition, using a Ga₂O₃ thin film as the n-semiconductor layer resulted in a dramatic decrease of leakage

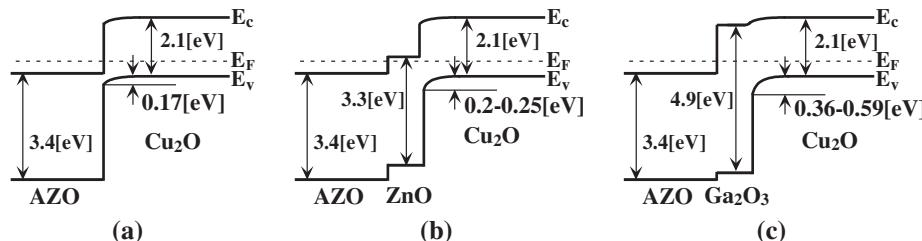


Fig. 13. Energy band diagrams of (a) AZO/Cu₂O, (b) AZO/ZnO/Cu₂O and (c) AZO/Ga₂O₃/Cu₂O HbH solar cells.

current observed in the J–V characteristic measured under dark conditions as well as an improvement of EQE. The EQE observed from the AZO/Ga₂O₃/Cu₂O HbH solar cell was enhanced over those observed from the AZO/ZnO/Cu₂O heterojunction and AZO/Cu₂O 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/Ga₂O₃ thin films prepared on glass substrates at the same time as on the Cu₂O 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/Ga₂O₃/Cu₂O 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 Cu₂O sheet, resulting from the decrease in the defect levels at the interface between the Ga₂O₃ thin film and the Cu₂O sheet. These results suggest that an improvement of the p–n junction, as seen in the Ga₂O₃/Cu₂O 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 Ga₂O₃ and Cu₂O, but also the conduction band discontinuity. For further improvement of the p–n junction, we have recently proposed various Cu₂O-based HbH solar cells fabricated by inserting Ga₂O₃-based multicomponent oxides as the n-oxide semiconductor thin-film layer.

In addition, it should be noted that in the AZO/Ga₂O₃/Cu₂O heterojunction solar cells, only the p-type Cu₂O acts as the active layer, because the Ga₂O₃ 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 Cu₂O or n-type Cu₂O as the n-type semiconductor layer. In addition, our Cu₂O-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 cm²/V s as well as passivation of the grain boundary and/or the surface of polycrystalline Cu₂O sheets.

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