Cu_2O-based solar cells using oxide semiconductors

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Abstract: We describe significant improvements of the photovoltaic properties that were achieved in Al-doped ZnO (AZO)/n-type oxide semiconductor/p-type Cu_2O heterojunction solar cells fabricated using p-type Cu_2O sheets prepared by thermally oxidizing Cu sheets. The multicomponent oxide thin film used as the n-type semiconductor layer was prepared with various chemical compositions on non-intentionally heated Cu_2O sheets under various deposition conditions using a pulsed laser deposition method. In Cu_2O-based heterojunction solar cells fabricated using various ternary compounds as the n-type oxide thin-film layer, the best photovoltaic performance was obtained with an n-$ZnGa_2O_4$ thin-film layer. In most of the Cu_2O-based heterojunction solar cells using multicomponent oxides composed of combinations of various binary compounds, the obtained photovoltaic properties changed gradually as the chemical composition was varied. However, with the ZnO–MgO and Ga_2O_3–Al_2O_3 systems, higher conversion efficiencies (η) as well as a high open circuit voltage (V_{oc}) were obtained by using a relatively small amount of MgO or Al_2O_3, e.g., $(ZnO)_{0.91}$–$(MgO)_{0.09}$ and $(Ga_2O_3)_{0.975}$–$(Al_2O_3)_{0.025}$, respectively. When Cu_2O-based heterojunction solar cells were fabricated using Al_2O_3–Ga_2O_3–MgO–ZnO (AGMZO) multicomponent oxide thin films deposited with metal atomic ratios of 10, 60, 10 and 20 at.% for the Al, Ga, Mg and Zn, respectively, a high V_{oc} of 0.98 V and an η of 4.82% were obtained. In addition, an enhanced η and an improved fill factor could be achieved in AZO/n-type multicomponent oxide/p-type Cu_2O heterojunction solar cells fabricated using Na-doped Cu_2O (Cu_2O:Na) sheets that featured a resistivity controlled by optimizing the post-annealing temperature and duration. Consequently, an η of 6.25% and a V_{oc} of 0.84 V were obtained in a MgF_2/AZO/n-(Ga_2O_3–Al_2O_3)/p-Cu_2O:Na heterojunction solar cell fabricated using a Cu_2O:Na sheet with a resistivity of approximately 10 Ω·cm and a $(Ga_{0.975}Al_{0.025})_2O_3$ thin film with a thickness of approximately 60 nm. In addition, a V_{oc} of 0.96 V and an η of 5.4% were obtained in a MgF_2/AZO/n-AGMZO/p-Cu_2O:Na heterojunction solar cell.

Key words: Cu_2O; n-type oxide semiconductor; heterojunction solar cells; high efficiency
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1. Introduction

Cuprous oxide (Cu_2O)-based solar cells have attracted a great deal of interest due to the material's nontoxicity, suitability for sustainable semiconductor material usage and potential for cost-effective manufacturing[1−7]. We have recently reported that significantly enhanced efficiencies could be achieved in Al-doped ZnO (AZO)/n-type semiconductor/p-type Cu_2O heterojunction solar cells fabricated by preparing an oxide semiconductor thin film on a thermally oxidized p-Cu_2O sheet using low-damage and low-temperature deposition techniques[7−11]. In Cu_2O-based heterojunction solar cells prepared with p-Cu_2O sheets, conversion efficiencies higher than 4 or 5% were achieved in solar cells fabricated with a ZnO or Ga_2O_3 thin film, respectively, as the n-type semiconductor layer, using a pulsed laser deposition (PLD) method. More recently, we reported that an efficiency of 6.1% could be achieved by optimizing the chemical composition of a multicomponent oxide composed of two binary compounds: MgF_2/AZO/n-type semiconductor/p-type Cu_2O heterojunction solar cells fabricated by preparing a multicomponent oxide thin film at a low temperature on Na-doped Cu_2O sheets using PLD[12, 13]. The efficiency obtained in heterojunction solar cells fabricated by depositing a multicomponent oxide thin film with an appropriate composition was higher than that obtained in heterojunction solar cells fabricated using either of the two binary compounds. In addition to solar cells fabricated with a sheet form of p-Cu_2O, it has been reported recently that a conversion efficiency over 2% was obtained in MgF_2/AZO/n-type semiconductor/p-type Cu_2O heterojunction solar cells fabricated using an atomic layer deposition (ALD) to deposit n-type multicomponent oxide or binary compound thin films at low temperature on p-Cu_2O thin films prepared with high-temperature treatments[14−18]. In solar cells fabricated with a thin film form of p-Cu_2O, a conversion efficiency of 3.97% has been reportedly obtained in MgF_2/AZO/n-Ga_2O_3/p-Cu_2O solar cells fabricated using ALD to deposit a Ga_2O_3 thin film at low temperatures[16]. In addition to the application as the n-type oxide semiconductor thin-film layer of Cu_2O-based heterojunction solar cells described above, transparent and conductive multicomponent oxide thin films have recently attracted a great deal of interest for transparent electrode[19−22] and thin-film transistor applications[23−25].

In this paper, we describe the photovoltaic properties

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of AZO/n-type multicomponent oxide semiconductor/p-type Cu_2O heterojunction solar cells fabricated using thermally oxidized Cu_2O in a sheet form. The influence of the inserted n-type oxide semiconductor thin film on the obtainable photovoltaic properties in the Cu_2O-based heterojunction solar cells was investigated by inserting various multicomponent oxide thin films prepared by varying their chemical compositions and the deposition conditions.

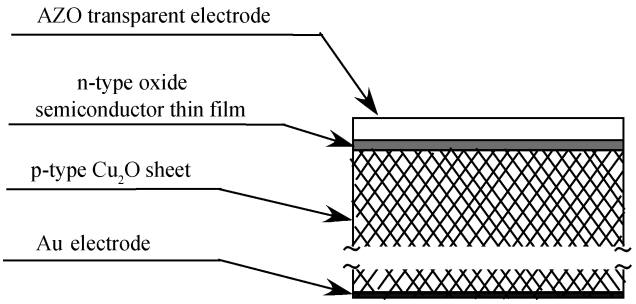


Figure 1. Schematic structure of a heterojunction solar cell.

2. Experimental

Ternary compounds, such as $ZnGa_2O_4$, $MgIn_2O_4$, $ZnSnO_3$, Zn_2SnO_4, $GaInO_3$, Zn_2SiO_4, Zn_2GeO_4, Zn_2FeO_4, $CuInO_2$, $CuGaO_2$ and $AgInO_2$, and multicomponent oxides composed of a combination of two or more than binary compounds, such as ZnO, MgO, Ga_2O_3, Al_2O_3, In_2O_3 and SnO_2, were used as the n-oxide semiconductor thin-film layer. AZO and 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^2) under the following deposition conditions: target-substrate distance, 40 mm; deposition temperature, room temperature (RT); target, sintered AZO (Al_2O_3 content of 2 wt.%) and sintered oxide pellets; and atmosphere and pressure, vacuum below 4.0 $\times$ 10^{-4} Pa or O_2 gas at 0.1–2.7 Pa[7–11]. The AZO thin films used as the transparent electrode with a thickness of approximately 200 nm were always prepared at an oxygen pressure of 0.2 Pa. In order to evaluate the chemical composition as well as the electrical and optical properties of the resulting AZO and oxide semiconductor films, simultaneous and/or additional depositions were also conducted on OA-10 glass (Nippon Electric Glass Co., Ltd.) substrates. The Cu_2O sheets were prepared by oxidizing 99.96% purity Cu sheets (thickness of 0.2 mm) using a heat-treatment process at a temperature of 1015 ℃ in a furnace with a controlled ambient atmosphere, described elsewhere in detail[7–11]. The thermally oxidized Cu_2O sheets were polycrystalline p-type semiconductors which exhibited electrical properties such as resistivity on the order of 10^2–10^3 Ω·cm, hole concentration on the order of 10^{13}–10^{14} cm^{-3} and Hall mobility above approximately 100 cm^2/(V·s). The incorporation of Na into the thermally oxidized Cu_2O sheets was carried out by postannealing Cu_2O sheets that were placed together with NaCl powder: treatment at 700 ℃ for 1 h in an Ar gas atmosphere[12, 13]. After cooling down to 500 ℃, the Cu_2O sheets were always brought out to an air environment at RT. The resistivity of the heat-treated Cu_2O sheets could be controlled in the range of 10^3 to 10^{-2} Ω·cm by doping Na with the range of annealing temperatures and durations noted above. The solar cells were fabricated by forming an AZO/n-oxide semiconductor/p-Cu_2O structure on the front surface of the Cu_2O sheets and an Au ohmic electrode on the back surface of the Cu_2O sheets; the Cu_2O sheets function as the active layer as well as the substrate, as shown in Figure 1. The photovoltaic properties of the Cu_2O-based solar cells (electrode area of 3.14 mm^2) were evaluated by exposing only the AZO transparent electrode area to AM 1.5 G solar illumination (100 mW/cm^2) at 25 ℃.

3. Multicomponent oxide thin films as the n-type semiconductor layer

3.1. Ternary compounds

We have reported the obtainable photovoltaic properties in various AZO/n-type semiconductor/p-type Cu_2O heterojunction solar cells fabricated by depositing many kinds of binary compound thin films as the n-type oxide semiconductor layer on thermally oxidized Cu_2O sheets using PLD[11]. Conversion efficiencies above 2% could be achieved only in Cu_2O-based heterojunction solar cells that used an n-type TiO_2, Ga_2O_3, CdO or impurity- or non-doped ZnO thin-film layer prepared on the Cu_2O sheets at RT. It should be noted that most binary compound thin films, except for CdO and ZnO thin films, deposited on glass substrates at RT by PLD were amorphous, as evidenced by X-ray diffraction (XRD) analyses. In this work, the material composition (the chemical symbol for a molecular) of the deposited oxide thin films identified as amorphous have been indicated with those of sintered oxide pellets using PLD, corresponding to start materials, as evidenced by XRD analyses. It should also be noted that the obtainable efficiency was significantly affected by the deposition conditions such as the oxygen pressure introduced into the deposition chamber. The obtained conversion efficiency (η) as a function of the oxygen pressure is shown in Figure 2 for AZO/n-type binary compound/p-type Cu_2O heterojunction solar cells fabricated by preparing a 50-nm-thick TiO_2, CdO or ZnO thin-film layer using PLD. The oxygen pressure dependence of obtainable η was mainly related to the interface layer formed between the deposited oxide thin films and the surface of Cu_2O sheets rather than the resulting electrical properties as well as crystallographical properties in deposited oxide thin films[7–11]. This was also supported by the fact that the oxygen pressure dependence of obtained η in the heterojunction solar cells was correlated to that of the obtained current density–voltage (J–V) characteristics measured under dark conditions on the solar cells; that is, the leak current measured under a reverse bias increased as the obtained η was decreased[10]. As can be seen in Figure 2, when the binary compound thin films used as the n-type semiconductor layer were prepared by PLD, the optimal oxygen pressure needed to achieve the highest η depended significantly on the kind of binary compound material used.

In the same way as the heterojunction solar cells were fabricated with a binary compound thin-film layer, solar cells were fabricated using ternary compounds composed of two binary compounds as the n-type oxide semiconductor thin-film

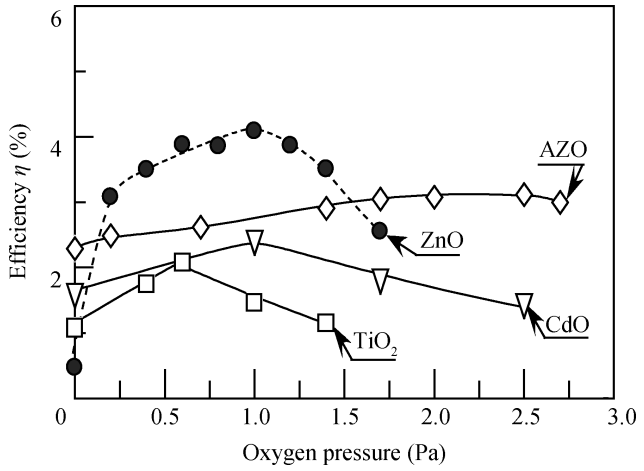


Figure 2. Oxygen pressure dependence of obtained efficiency (η) in AZO/n-oxide semiconductor/p-Cu_2O heterojunction solar cells fabricated by depositing various binary compound thin films in an O_2 gas atmosphere.

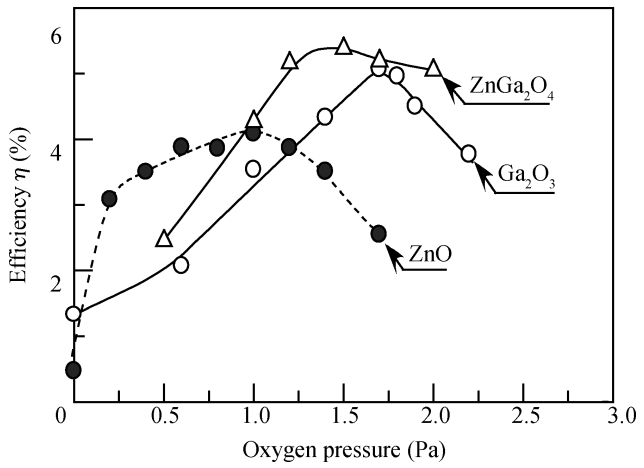
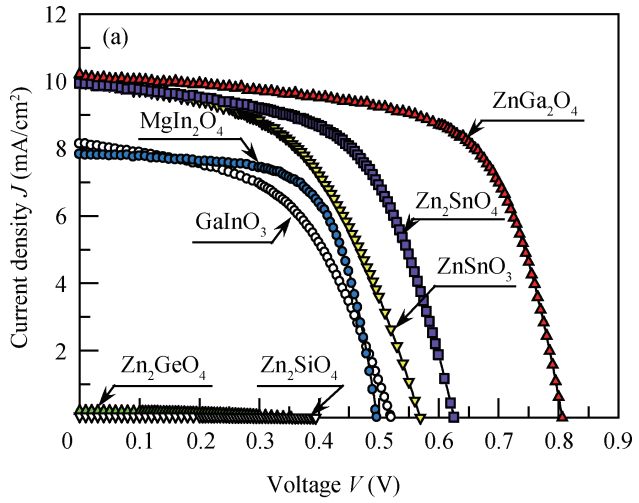


Figure 3. Oxygen pressure dependence of obtained η in AZO/n-oxide semiconductor/p-Cu_2O heterojunction solar cells fabricated by depositing a ZnO, Ga_2O_3 or $ZnGa_2O_4$ thin film in an O_2 gas atmosphere.



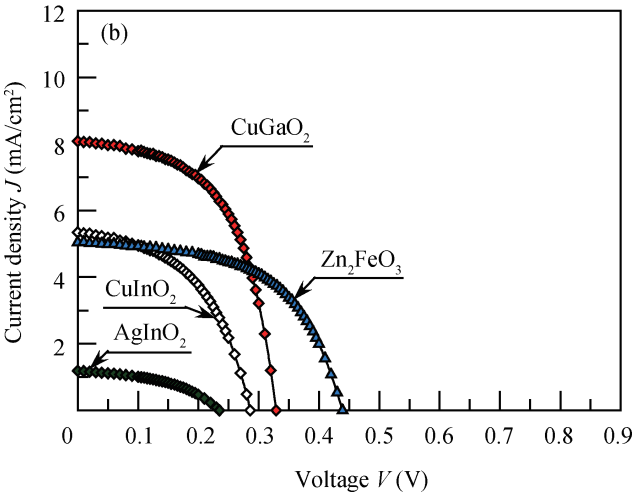


Figure 4. (Color online) Typical obtained J–V characteristics for heterojunction solar cells fabricated using various ternary compound thin films as (a) the n-semiconductor layer or (b) either the n- or p-oxide semiconductor layer: measured under AM 1.5 G solar illumination.

layer. In comparison with AZO/n-type binary compound/p-type Cu_2O heterojunction solar cells fabricated with a 50-nm-thick ZnO or Ga_2O_3 thin-film layer, Figure 3 shows the oxygen pressure dependence of obtained η in AZO/n-$ZnGa_2O_4$/p-Cu_2O heterojunction solar cells fabricated with an n-type oxide thin-film layer that was deposited at various oxygen pressures on the Cu_2O sheets at RT by PLD using a sintered $ZnGa_2O_4$ pellet. The highest η was obtained in a heterojunction solar cell fabricated by depositing a $ZnGa_2O_4$ thin film at an oxygen pressure of approximately 1.5 Pa, a level that is between the optimized 1 Pa in the ZnO thin-film depositions and 1.7 Pa in the Ga_2O_3 thin-film depositions. However, the $ZnGa_2O_4$ thin films deposited with a thickness of 50 nm were always amorphous with a Zn content (Zn/(Zn + Ga) atomic ratio) of 33.3 at.%, which corresponds to the chemical composition of $ZnGa_2O_4$, irrespective of the oxygen pressure. It was also found that the oxygen pressure dependence of obtained η in AZO/n-$ZnGa_2O_4$/p-Cu_2O heterojunction solar cells was correlated to that of the J–V characteristics of the solar cells measured under dark conditions.

Using the same approach as described above, AZO/n-ternary compound/p-Cu_2O heterojunction solar cells were fabricated using various ternary compounds as the inserted thin-film layer that was deposited at RT by PLD. Typical obtained J–V characteristics are shown in Figure 4 for Cu_2O-based heterojunction solar cells fabricated by depositing various 50-nm-thick oxide thin films at a roughly optimized oxygen pressure (that depended on the ternary compounds used) and measured under AM 1.5 G solar illumination. As can be seen in Figure 4(a), the photovoltaic performance observed from Cu_2O-based heterojunction solar cells fabricated using a transparent conducting $ZnGa_2O_4$, Zn_2SnO_4, $ZnSnO_3$, $MgIn_2O_4$ or $GaInO_3$[20–22] as the n-type semiconductor layer is significantly better than that from solar cells fabricated using an insulating Zn_2SiO_4 or Zn_2GeO_4[26, 27]. In addition, the photovoltaic performance observed from solar cells fabricated using $CuGaO_2$, Zn_2FeO_4, $ZnSnO_3$, $CuInO_2$ or $AgInO_2$, known as n-type and/or p-type conducting ternary compound semiconductors, is shown in Figure 4(b). Table 1 presents a sum-

Table 1. Obtained V_{OC}, J_{SC}, FF and η in maximum efficiency AZO/n-type semiconductor/p-type Cu_2O heterojunction solar cells fabricated using various ternary compounds.

Ternary compound	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
$ZnGa_2O_4$	0.81	10.22	0.65	5.36
$MgIn_2O_4$	0.50	7.82	0.66	2.58
Zn_2SnO_4	0.63	9.93	0.59	3.64
$ZnSnO_3$	0.57	9.99	0.51	2.92
$GaInO_3$	0.52	8.13	0.52	2.22
Zn_2GeO_4	0.35	0.21	0.40	0.03
Zn_2SiO_4	0.39	0.04	0.48	0.01
$CuInO_2$	0.29	5.35	0.49	0.75
$AgInO_2$	0.24	1.19	0.45	0.12
$CuGaO_2$	0.33	8.09	0.56	1.49
Zn_2FeO_4	0.44	5.04	0.56	1.24

mary of the obtained η, V_{OC}, short circuit current density (J_{sc}) and fill factor (FF) of the heterojunction solar cells that exhibit maximum efficiency in regard to the various ternary compounds inserted as an oxide thin film between the AZO thin film and the Cu_2O sheet. The best photovoltaic performance in a heterojunction solar cell using a ternary compound as the n-oxide semiconductor layer was obtained with $ZnGa_2O_4$. It should be noted that the photovoltaic properties exhibited in the AZO/n-$ZnGa_2O_4$/p-Cu_2O solar cells are approximately at the same level as those exhibited in the AZO/n-Ga_2O_3/p-Cu_2O heterojunction solar cells. An η of 5.36% was achieved in an AZO/n-$ZnGa_2O_4$/p-Cu_2O heterojunction solar cell fabricated by depositing a $ZnGa_2O_4$ thin film at the optimized oxygen pressure.

3.2. Multicomponent oxides composed of two binary compounds

We have reported that a significantly enhanced conversion efficiency could be achieved by using a binary compound such as Ga_2O_3 or ZnO as the n-oxide semiconductor thin-film layer of AZO/n-type oxide semiconductor/p-type Cu_2O heterojunction solar cells[7–11]. In addition, we found that a ternary compound composed of Ga_2O_3 and ZnO, i.e., $ZnGa_2O_4$, also was suitable for use as the n-type oxide semiconductor thin-film layer of Cu_2O-based heterojunction solar cells, as described above. To evaluate the suitability of multicomponent oxides such as the Ga_2O_3–$ZnGa_2O_4$–ZnO system, the obtainable photovoltaic properties were investigated for AZO/n-type multicomponent oxide semiconductor/p-type Cu_2O heterojunction solar cells fabricated by depositing multicomponent oxide thin films with various chemical compositions and deposition conditions onto Cu_2O sheets using PLD. Typical obtained J–V characteristics as a function of the Zn content are shown in Figure 5 for AZO/n-type oxide semiconductor/p-type Cu_2O heterojunction solar cells fabricated with a 50-nm-thick-(Ga_2O_3–ZnO) multicomponent oxide thin-film layer prepared with various chemical compositions at a constant oxygen pressure of 1.7 Pa by PLD using sintered (Ga_2O_3–ZnO) pellets: results measured under AM 1.5 G solar illumination. The Zn content in the deposited oxide thin films was evaluated by X-ray photoelectron spectroscopy (XPS). Although the obtained J–V characteristics remained relatively unchanged as the Zn content was increased to about 33.3 at.%, i.e., the chemical composition between Ga_2O_3 and $ZnGa_2O_4$, they degraded significantly as the Zn content was increased from 33.3 to 50 at.%. Typical obtained V_{oc}, J_{sc}, FF and η as functions of the Zn content are shown in Figure 6 for the heterojunction solar cells shown in Figure 5. The obtainable photovoltaic properties remained approximately constant as the Zn content was increased to about 33.3 at.%, degraded abruptly as the Zn content was increased from about 33.3 to 50 at.% and then degraded more gradually with a further increase of the Zn content. The gradual degradation of photovoltaic properties associated with increasing the Zn content above about 50 at.% may be a consequence of conducting all of the film depositions at an oxygen pressure of 1.7 Pa, a level found to optimize η in Ga_2O_3 thin-film depositions, as shown in Figure 2. However, the actual optimal oxygen pressure in the multicomponent oxide thin-film depositions decreased gradually as the Zn content was increased. It was also found that the Zn content dependence of the obtained photovoltaic properties in AZO/n-(ZnO–Ga_2O_3)/p-Cu_2O heterojunction solar cells, shown in Figure 6, was correlated to that of the J–V characteristics measured under dark conditions on the solar cells, shown in Figure 7. As can be seen in Figure 7, the leak current measured on the AZO/n-(ZnO-Ga_2O_3)/p-Cu_2O heterojunction solar cells under a reverse bias

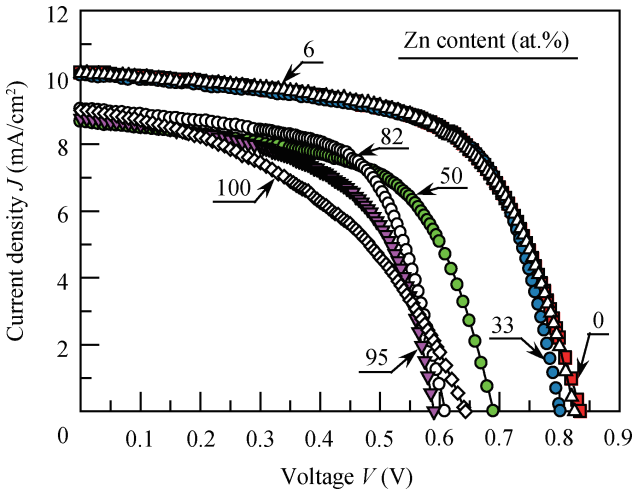


Figure 5. (Color online) Obtained J–V characteristics as a function of Zn content for heterojunction solar cells fabricated using multicomponent oxides composed of Ga_2O_3 and ZnO and measured under AM 1.5 G solar illumination.

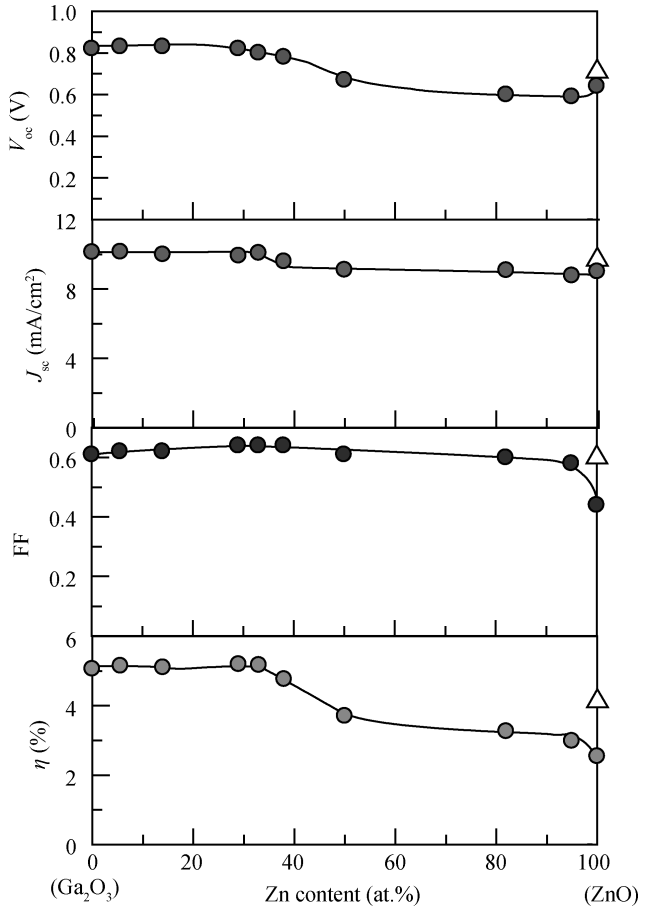


Figure 6. Obtained V_{oc}, J_{SC}, FF and η as functions of Zn content for heterojunction solar cells fabricated using multicomponent oxides composed of Ga_2O_3 and ZnO.

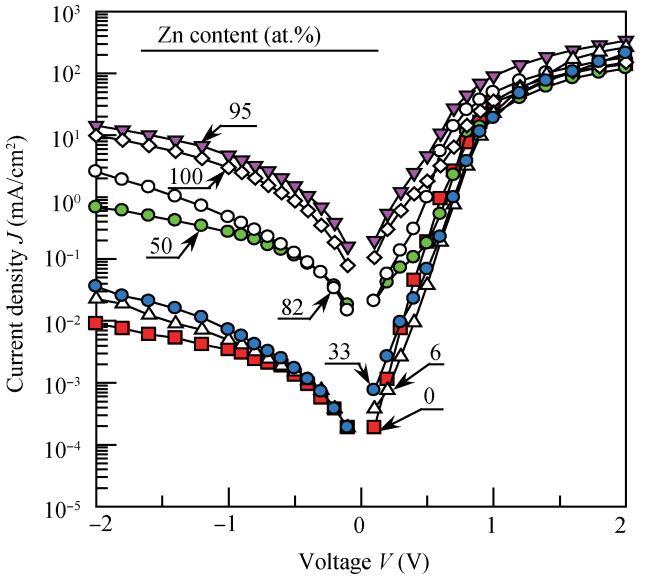


Figure 7. (Color online) Obtained J–V characteristics as a function of Zn content for heterojunction solar cells fabricated using multicomponent oxides composed of Ga_2O_3 and ZnO and measured under dark conditions.

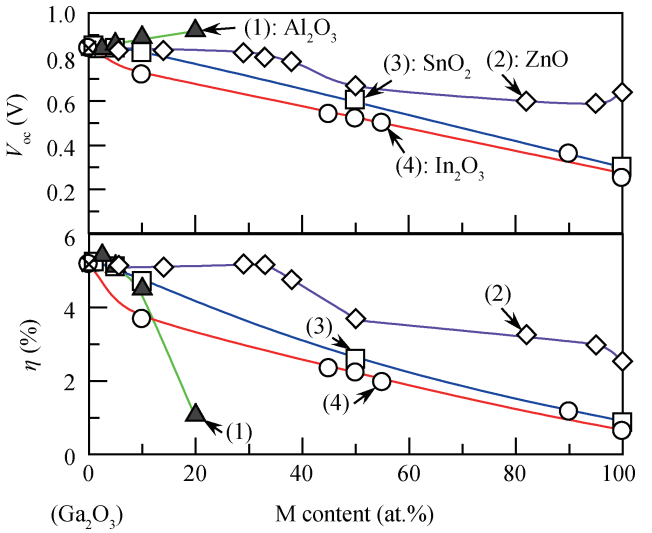


Figure 8. (Color online) Obtained η and V_{oc} as functions of M content (metal atomic ratio) for heterojunction solar cells fabricated using various multicomponent oxides composed of Ga_2O_3 and various kinds of metal oxide (MO): (1) Ga_2O_3–Al_2O_3, (2) –ZnO, (3) –SnO_2, (4) –In_2O_3.

increased significantly when the Zn content was increased from approximately 33.3 to 50 at.%. Note that the photovoltaic properties (indicated with open triangle data points at the Zn content of 100 at.% on the horizontal axis in Figure 6) obtained in an AZO/n-ZnO/p-Cu_2O heterojunction solar cell fabricated by depositing a ZnO thin film at the optimal oxygen pressure of 1.0 Pa show significant improvement over those (circle data points) measured in a solar cell fabricated with a ZnO thin film deposition at an oxygen pressure of 1.7 Pa, as seen in Figures 2 and 3. In addition, we have reported that the obtainable photovoltaic properties in heterojunction solar cells fabricated with an n-Ga_2O_3 thin-film layer were always better than those fabricated with an n-ZnO thin-film layer, being attributable to not only a lower level of defects at the interface (which would decrease the recombination associated with defects at the interface between the Ga_2O_3 and Cu_2O), but also a smaller conduction band discontinuity[9, 11]. As described above, in Cu_2O-based heterojunction solar cells fabricated using Ga_2O_3–ZnO multicomponent oxide thin films deposited with various chemical compositions, the chemical composition dependence of the resulting photovoltaic properties was related to the existence of a ternary compound in this system, but the deposited oxide thin films were amorphous nevertheless.

In addition to the Ga_2O_3–ZnO system, the chemical composition dependence of the obtained photovoltaic properties in AZO/n-type oxide semiconductor/p-type Cu_2O heterojunction solar cells fabricated with an n-type multicomponent oxide thin-film layer was investigated using various multicomponent oxides composed of the combination of other binary compounds. It was found that the obtained photovoltaic properties were significantly affected by the multicomponent oxide material system used as well as the chemical composition. Typical obtained V_{oc} and η as functions of the metal element (M) content are shown in Figure 8 for AZO/n-type oxide semiconductor/p-type Cu_2O heterojunction solar cells fabricated using multicomponent oxide thin films composed of various Ga_2O_3–MO systems, with various chemical compositions, as the n-type oxide semiconductor layer. As an ex-

Table 2. Obtained η, V_{oc}, J_{sc} and FF in maximum efficiency AZO/n-type semiconductor/p-type Cu_2O heterojunction solar cells fabricated using multicomponent oxides composed of two binary compounds.

Multicomponent oxide	η (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF
AZO/$(Ga_{0.975}Al_{0.025})_2O_3$/$Cu_2O$	5.42	0.84	10.11	0.64
AZO/$(Zn_{0.91}Mg_{0.09})_2O_3$/$Cu_2O$	4.29	0.80	9.11	0.59

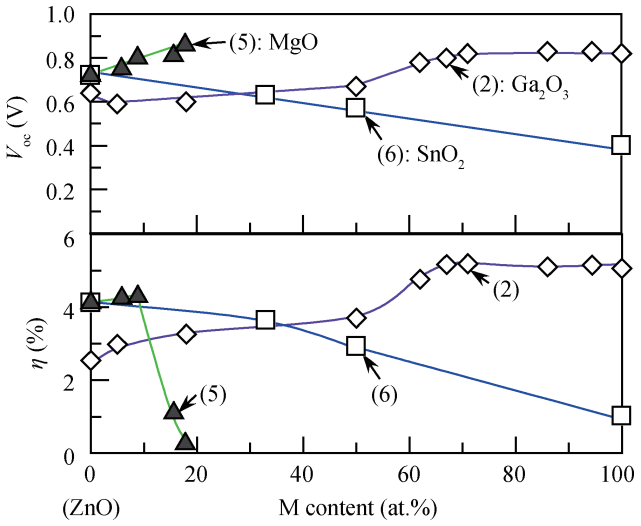


Figure 9. (Color online) Obtained η and V_{oc} as functions of M content (metal atomic ratio) for heterojunction solar cells fabricated using various multicomponent oxides composed of ZnO and various kinds of metal oxide (MO): (2) ZnO–Ga_2O_3, (5) –MgO, (6) –SnO_2.

ample, in heterojunction solar cells with Ga_2O_3–Al_2O_3 multicomponent oxide thin films, the highest efficiency as well as a high V_{oc} of 0.85 V was obtained with an Al content of 2.5 at.%, a content that is relatively small in relation to that of Ga, i.e., $(Ga_{0.975}Al_{0.025})_2O_3$. The obtained V_{oc} increased to 0.92 V as the Al content was increased up to approximately 20 at.%; however, evaluations of photovoltaic properties were difficult to conduct at Al contents higher than 20 at.% because the deposited ZnO–Al_2O_3 multicomponent oxide thin films exhibited very high resistivity or acted as an insulating material. In contrast, the obtained photovoltaic properties in AZO/n-(Ga_2O_3–In_2O_3)/Cu_2O heterojunction solar cells degraded gradually as the In content in the Ga_2O_3–In_2O_3 multicomponent oxide thin films was increased from 0 at.% (i.e., Ga_2O_3) to 100 at.% (i.e., In_2O_3), as seen in Figure 8. Figure 9 shows typical obtained V_{oc} and η as functions of the M content for AZO/n-type oxide semiconductor/p-type Cu_2O heterojunction solar cells fabricated using multicomponent oxide thin films deposited with various ZnO–MO systems and chemical compositions as the n-type oxide semiconductor layer. In Figures 8 and 9, the M content is indicated with an M / (M + Ga) or M / (M + Zn) atomic ratio, respectively, in the deposited thin films, as measured by XPS. As can be seen in Figure 9, the highest efficiency using MgO as well as a high V_{oc} on the order of 0.8 V were obtained in an AZO/n-(ZnO–MgO)/p-Cu_2O heterojunction solar cell fabricated with a Mg content of 9 at.%, an amount relatively small in relation to that of Zn, i.e., $Zn_{0.91}Mg_{0.09}O$. The obtained V_{oc} increased to 0.85 V as the Mg content was increased up to approximately 18 at.%; however, the photovoltaic properties were difficult to evaluate at higher Mg contents because the deposited ZnO–MgO multicomponent oxide thin-film layers exhibited a very high resistivity or insulating properties. In contrast, the obtained photovoltaic properties in AZO/n-(ZnO–SnO_2)/p-Cu_2O heterojunction solar cells degraded gradually as the Sn content in the ZnO–SnO_2 multicomponent oxide thin films was increased from 0 at.% (ZnO) to 100 at.% (SnO_2). As is well-known, transparent conducting $ZnSnO_3$ (corresponding to a Sn content of 50 at.%) and Zn_2SnO_4 (corresponding to a Sn content of 33.3 at.%) have been reported in the ZnO–SnO_2 system[18–21]. However, singular photovoltaic properties have not been obtained in solar cells fabricated using ZnO–SnO_2 multicomponent oxide thin films with either a Sn content of 33.3 or 50 at.% as the n-type semiconductor layer. Table 2 summarizes the obtained η (maximized), V_{oc}, J_{sc} and FF in AZO/n-type multicomponent oxide/p-type Cu_2O heterojunction solar cells fabricated using multicomponent oxide thin films prepared using multicomponent oxides composed of a combination of different binary compounds with a chemical composition (M content) optimized for efficiency: Ga_2O_3–Al_2O_3 and ZnO–MgO systems. The best photovoltaic performance using a multicomponent oxide as the n-oxide semiconductor layer was obtained in a heterojunction solar cell fabricated with $(Ga_{0.975}Al_{0.025})_2O_3$: an η of 5.42% and a V_{oc} of 0.84 V in an AZO/$(Ga_{0.975}Al_{0.025})_2O_3$/$Cu_2O$ heterojunction solar cell.

3.3. Multicomponent oxides composed of multiple binary compounds

In addition to multicomponent oxides composed of two binary compounds, transparent conducting multicomponent oxides composed of three or more binary compounds are a promising material for optoelectronic device applications, because the electrical and optical properties are made more controllable with variations in the material system as well as the chemical composition[21, 22]. As an example, AZO/n-type multicomponent oxide/p-type Cu_2O heterojunction solar cells have been fabricated using In_2O_3–Ga_2O_3–ZnO multicomponent oxides, i.e., composed of three binary compounds, as the n-type semiconductor thin-film layer. It well known that In_2O_3–Ga_2O_3–ZnO (or IGZO), an amorphous material with high mobility, has practical uses as thin-film transistors[23–25]. As another example, AZO/n-type multicomponent oxide/p-type Cu_2O heterojunction solar cells have been fabricated using ZnO–MgO–Ga_2O_3–Al_2O ZnO multicomponent oxides, composed of four binary compounds, as the n-type semiconductor thin-film layer. As can be seen in Figures 8 and 9, AZO/n-(ZnO–MgO) or -(Ga_2O_3–Al_2O)/p-Cu_2O heterojunction solar cells exhibited an obtained V_{oc} on the order of 0.8–0.9 V as the Mg or Al content in these multicomponent oxides was increased. However, the other obtained photovoltaic properties such as η, J_{SC} and FF degraded drastically as the con-

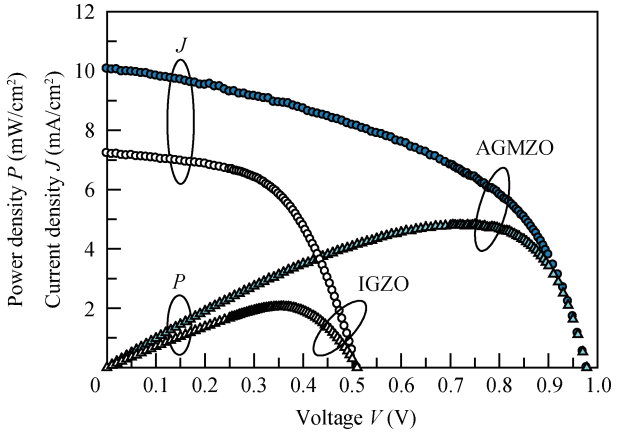


Figure 10. Typical obtained J–V and P–V characteristics in an AZO/n-IGZO or -AGMZO/p-Cu_2O heterojunction solar cell fabricated using multicomponent oxides composed of three binary compounds or four binary compounds, respectively.

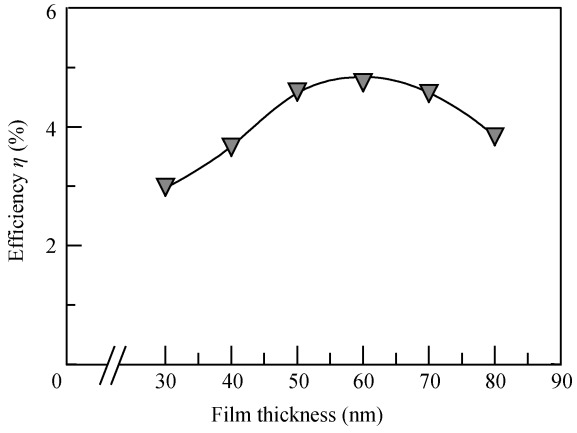


Figure 11. Obtained η as a function of the thickness of AGMZO thin films for AZO/n-AGMZO/p-Cu_2O heterojunction solar cells.

tent was increased above a critical value, as described above. To suppress the degradation of photovoltaic properties resulting from an increase in resistivity of the multicomponent oxides used as the n-type semiconductor thin-film layer, AZO/n-type multicomponent oxide/p-type Cu_2O heterojunction solar cells were fabricated using Al–Ga–Mg–Zn–O (AGMZO) multicomponent oxides, composed of Al_2O_3, Ga_2O_3, MgO and ZnO, as the n-type semiconductor thin-film layer. Typical obtained J–V and power density–voltage (P–V) characteristics are shown in Figure 10 for an AZO/n-IGZO or -AGMZO/p-Cu_2O heterojunction solar cell fabricated by preparing a 50-nm-thick-multicomponent oxide thin-film layer under optimal deposition conditions by PLD and measured under AM 1.5 G solar illumination. The amorphous IGZO thin film was prepared with equal metal atomic ratios of In, Ga and Zn (i.e., 33.3, 33.3 and 33.3 at.%) at an oxygen pressure of 1.7 Pa. The amorphous AGMZO thin film was prepared with the metal atomic ratios of Al, Ga, Mg and Zn being 10, 60, 10 and 20 at.%, respectively, and an oxygen pressure of 1.7 Pa. As can be seen in Figure 10, AGMZO thin films may be a promising material as the n-type semiconductor layer of Cu_2O-based heterojunction solar cells, whereas IGZO thin films are unsuitable for this use. Figure 11 shows obtained η as a function of the thickness of the AGMZO thin films used in AZO/n-AGMZO/p-Cu_2O heterojunction solar cells fabricated with the same chemical composition as the solar cell shown in Figure 10. Note that a high V_{oc} over 0.9 V was achieved in Cu_2O-based heterojunction solar cells fabricated using AGMZO thin films as the n-type semiconductor layer. A V_{oc} of 0.98 V and an η of 4.82% were obtained in an AZO/n-AGMZO/p-Cu_2O heterojunction solar cell using an AGMZO thin-film layer with a thickness of 50 nm. It should be noted that the chemical composition, or metal atomic ratio, in AGMZO thin films has not yet been optimized sufficiently to achieve a higher V_{oc} and η.

4. Solar cells fabricated using Na-doped Cu_2O sheets

The sheet resistance of a 0.2-mm-thick thermally oxidized Cu_2O sheet used in the heterojunction solar cells, 10^2–10^3 Ω·cm, was higher than that of the deposited 50-nm-thick Ga_2O_3 and $ZnGa_2O_4$ thin films, 10^4–10^5 Ω·cm. Although the resistivity in Ga_2O_3–Al_2O_3 and ZnO–MgO multicomponent oxide thin films might be higher than that in amorphous Ga_2O_3 and $ZnGa_2O_4$ thin films, the resistivity of amorphous AGMZO multicomponent oxide thin films used could be controlled, as described above. In addition, we have recently reported that the resistivity of thermally oxidized Cu_2O sheets could be lowered by incorporating Na into the Cu_2O sheets by post-annealing in an Ar gas atmosphere with various sodium compounds[12,13]. The resistivity in Na-doped Cu_2O (Cu_2O:Na) sheets could be controlled in the range of 10^3–10^{-1} Ω·cm by varying the annealing temperature and duration. It is well known that the resistivity of Si substrates used in single crystal Si solar cells is on the order of 10^{-1}–10^0 Ω·cm. Thus, the use of Cu_2O:Na sheets with a resistivity lower than 10^1 Ω·cm is better for heterojunction solar cell applications: note that the Cu_2O sheets act as the active layer as well as the substrate. However, we have reported that the Hall mobility of Cu_2O:Na sheets decreased as the resistivity was decreased below 10^1 Ω·cm, i.e., as the hole concentration (or Na concentration doped into the sheets) was increased above about 1×10^{16} cm^{-3}. However, this can be resolved by using Cu_2O:Na sheets that are doped with a Na concentration that varies across the thickness direction, from a hole concentration less than about 10^{15} cm^{-3} in the active region (thickness on the order of 10 μm) to a hole concentration higher than about 10^{17} cm^{-3} in the region serving as the substrate[12, 13]. In addition to using Cu_2O:Na sheets, further efficiency enhancement of Cu_2O-based heterojunction solar cells was obtained by reducing the reflection of incident light on the surface of the solar cells. For the non-reflecting film coating, a magnesium fluoride (MgF_2) thin film with a thickness of 75 nm was deposited on the AZO transparent electrode by a vacuum evaporation method[13, 16]. To further enhance efficiency, various AZO/n-multicomponent oxide/p-Cu_2O heterojunction solar cells were fabricated with optimized device preparation techniques as well as using Cu_2O:Na sheets with a resistivity of approximately 10 Ω·cm. The obtained η, V_{oc}, J_{sc}, FF, series resistance (R_s) and shunt resistance (R_{sh}) in heterojunction solar cells exhibiting maximum efficiency that were fabricated by forming multicomponent oxide thin films on

Table 3. Obtained η, V_{oc}, J_{sc}, FF, R_s and R_{sh} in maximum efficiency MgF_2/AZO/n-$(Ga_{0.975}Al_{0.025})_2O_3$ or AGMZO/p-Cu_2O:Na heterojunction solar cells fabricated by forming multicomponent oxide thin films under optimized conditions on Cu_2O:Na sheets.

Heterojunction solar cell	η (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	R_s (Ω/cm^2)	R_{sh} (kΩ/cm^2)
MgF_2/AZO/AGMZO/Cu_2O:Na	5.40	0.96	10.6	0.53	31.8	0.54
MgF_2/AZO/$(Ga_{0.975}Al_{0.025})_2O_3$/$Cu_2O$:Na	6.25	0.84	10.8	0.69	14.8	1.29

Cu_2O:Na sheets under optimized conditions are summarized in Table 3. The highest efficiency of 6.25% and a V_{oc} of 0.84 V were obtained in a MgF_2/AZO/n-$(Ga_{0.975}Al_{0.025})_2O_3$/p-$Cu_2O$:Na heterojunction solar cell fabricated using a Cu_2O:Na sheet with a resistivity of approximately 10 Ω·cm. In addition, the highest V_{oc} of 0.96 V and an η of 5.4% were obtained in a MgF_2/AZO/n-AGMZO/p-Cu_2O:Na heterojunction solar cell.

5. Conclusion

Cu_2O-based heterojunction solar cells were fabricated using multicomponent oxides as the n-type oxide semiconductor thin-film layer and p-type Cu_2O sheets prepared by thermally oxidizing Cu sheets. Multicomponent oxide thin films with various chemical compositions were prepared on non-intentionally heated Cu_2O sheets under various deposition conditions using a pulsed laser deposition method. In Al-doped ZnO (AZO)/n-type oxide semiconductor/p-type Cu_2O heterojunction solar cells fabricated using ternary compounds, the best photovoltaic performance was obtained in a solar cell with an n-$ZnGa_2O_4$ thin-film layer. In Cu_2O-based heterojunction solar cells using multicomponent oxides composed of different binary compounds, the obtained photovoltaic properties in almost all the solar cells changed gradually as the chemical composition was varied. In AZO/n-(ZnO–MgO) or -(Ga_2O_3–Al_2O_3)/p-Cu_2O heterojunction solar cells, the obtained open circuit voltage (V_{oc}) increased as the Mg or Al content (metal atomic ratio) was increased, whereas the other photovoltaic properties degraded as the Mg or Al content was increased above 9 or 2.5 at.%, respectively. To suppress the degradation, Cu_2O-based heterojunction solar cells were fabricated using Al–Ga–Mg–Zn–O (AGMZO) multicomponent oxides, composed of multiple binary compounds, with metal atomic ratios for Al, Ga, Mg and Zn of 10, 60, 10 and 20 at.%, respectively. Improvements of fill factor and conversion efficiency (η) in the heterojunction solar cells could be achieved by optimizing the post-annealing temperature and duration of the Na-doped Cu_2O (Cu_2O:Na) sheets to control the resistivity. Consequently, the highest efficiency of 6.25% was obtained in a MgF_2/AZO/n-$(Ga_{0.975}Al_{0.025})_2O_3$/p-$Cu_2O$:Na heterojunction solar cell fabricated using a Cu_2O:Na sheet with a resistivity of approximately 10 Ω·cm. In addition, a V_{oc} of 0.96 V and an η of 5.4% were obtained in a MgF_2/AZO/n-AGMZO/p-Cu_2O:Na heterojunction solar cell.

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