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Photovoltaic properties of Cu_2O-based heterojunction solar cells using n-type oxide semiconductor nano thin films prepared by low damage magnetron sputtering method

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Abstract: We improved the photovoltaic properties of Cu_2O-based heterojunction solar cells using n-type oxide semiconductor thin films prepared by a sputtering apparatus with our newly developed multi-chamber system. We also obtained the highest efficiency (3.21%) in an AZO/p-Cu_2O heterojunction solar cell prepared with optimized pre-sputtering conditions using our newly developed multi-chamber sputtering system. This value achieves the same or higher characteristics than AZO/Cu_2O solar cells with a similar structure prepared by the pulse laser deposition method.

Key words: Cu_2O; AZO; solar cell; oxide thin film; magnetron sputtering

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1. Introduction

Since p-type cuprous oxide (p-Cu_2O) has a high theoretical conversion efficiency of about 20%, it has long attracted research attention as a solar cell material[1–9]. In addition, solar cells based on p-Cu_2O have attracted significant interest owing to the material's nontoxicity, its suitability for sustainable semiconductor material usage, and its potential for cost-effective manufacturing[10–17]. We previously achieved significantly enhanced efficiencies in n-type Al-doped ZnO (AZO)/p-Cu_2O heterojunction solar cells fabricated by depositing an AZO thin film on a thermally oxidized p-Cu_2O sheet using low-damage and -temperature deposition techniques[18–20]. Using pulsed-laser deposition (PLD) at room temperature (RT), AZO thin films have been fabricated not only as n-type semiconductor window layers but also as transparent electrodes in heterojunction solar cells, which exhibited efficiencies exceeding 3%[21]. However, PLD methods suffer from technical disadvantages for the practical fabrication technology of solar cells, such as a low deposition rate and complicated large area deposition. On the other hand, the magnetron sputtering (MSD) method easily prepared the large area deposition and obtained a high deposition rate. But the photovoltaic properties of the Cu_2O-based heterojunction solar cells fabricated by it were poorer than those of PLD.

In this paper, we describe the improvement of the photovoltaic properties of Cu_2O-based heterojunction solar cells using AZO thin films prepared by the sputtering apparatus with our newly developed multi-chamber system.

2. Experimental

Cu_2O sheets were prepared by oxidizing copper sheets (0.2-mm thick with 99.96% purity) using heat treatment in a furnace with a controlled ambient atmosphere, described in detail elsewhere[18 – 20].

To incorporate Na into the oxidized Cu_2O sheets, the sheets impregnated with NaCl powder (purity: 99.9%, KANTO KAGAKU Co. Ltd.) were heat-treated at 700 °C in an Ar gas atmosphere for 1 h[22]. After cooling to 500 °C, the Cu_2O sheets were exposed to air at RT. The resulting sodium-doped Cu_2O (Cu_2O:Na) sheets were polycrystalline p-type semiconductors with a hole concentration of the order of 10^{15} cm^{-3} and a Hall mobility as high as 100 $cm^2V^{-1}s^{-1}$. Since the carrier concentration of the Cu_2O sheet can be controlled by Na doping[15], we carried out Na doping to optimize the carrier concentration of the Cu_2O sheet. We prepared transparent conducting AZO thin films on p-Cu_2O sheets using a multi-chamber MSD apparatus. The AZO thin film is not only an n-type semiconductor layer but also a transparent electrode. The multi-chamber MSD apparatus, which has loading and deposition chambers, used a direct current (DC) and a radio frequency (RF, 13.56 MHz) power supply that was applied either separately or together. The deposition was performed at RT using a target-substrate distance of 10–40 mm; the targets were a sintered AZO (Al_2O_3 content 2 wt %, Tosoh Speciality Materials Corp.) in a pure Ar gas atmosphere at pressures of 0.2 and 0–8 Pa. The 200-nm-thick AZO thin films, which functioned not only as an n-type layer but also as transparent electrodes, exhibited resistivity of the order of 10^{-3} Ωcm and a carrier concentration of the order of 10^{20} cm^{-3}. To evaluate the electrical and optical properties of the resulting AZO thin films, simultaneous and/or additional depositions were also conducted on glass substrates. Solar cells were fabricated by forming an AZO/p-Cu_2O:Na structure on the front surface of the Cu_2O:Na sheets and an Au ohmic electrode on the back surface (Fig. 1). The solar cell with the AZO/Cu_2O structure (Fig. 1) had a type II heterojunction structure based on the measurement results of the work functions of AZO and Cu_2O by X-Ray Photoelectron Sepctroscopy (XPS, ULVAC-PHI, model 1600). The photovoltaic properties of the

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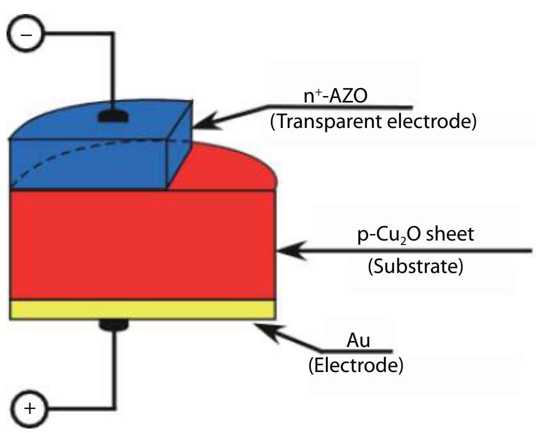

Fig. 1. (Color online) Cross-sectional structure of AZO/p-Cu_2O solar cell.

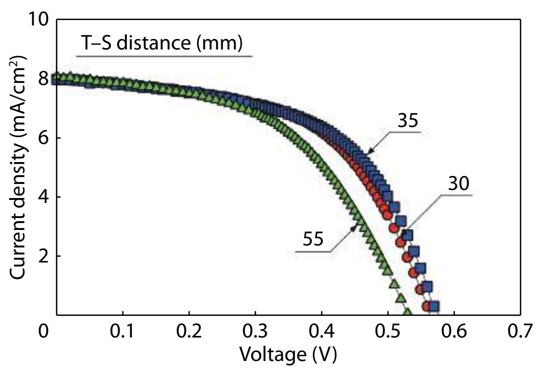

Fig. 2. (Color online) Typical *J*–*V* characteristics for AZO/p-Cu_2O heterojunction solar cells prepared with different target-Cu_2O sheet distances.

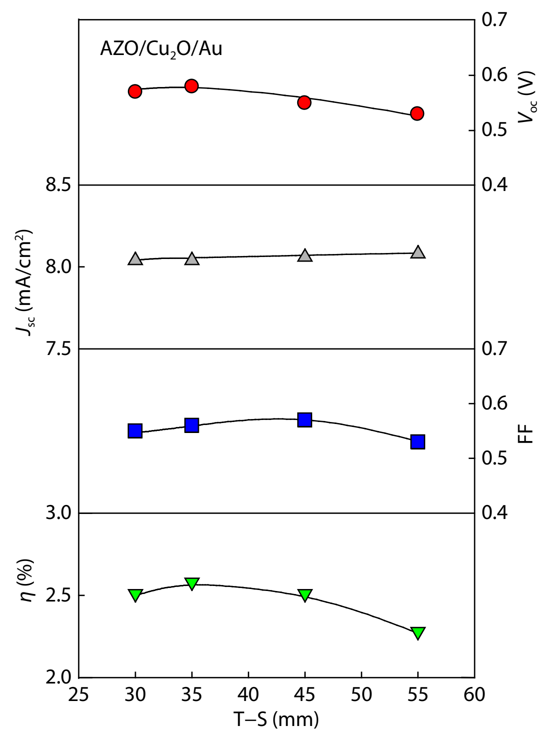

Fig. 3. (Color online) Conversion efficiency (η), fill factor (FF), V_{OC}, and J_{SC} as functions of target-Cu_2O sheet distance for AZO/p-Cu_2O heterojunction solar cells.

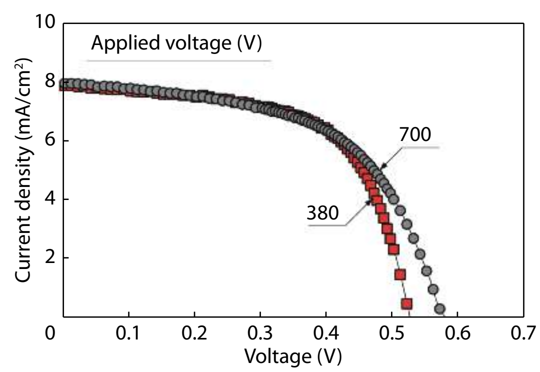

Fig. 4. (Color online) Typical *J*–*V* characteristics for AZO/p-Cu_2O heterojunction solar cells prepared with different sputtering voltages: 380 and 700 V.

Cu_2O-based solar cells (electrode area of 3.14 mm^2) were evaluated by exposing only the AZO transparent electrode area to AM1.5G solar illumination (100 mW/cm^2, Asahi Spectra, model HAL320) at 25 °C.

3. Results and discussion

3.1. AZO target-Cu_2O sheet distance and sputtering voltage dependence of photovoltaic properties for AZO/p-Cu_2O solar cell

When an AZO layer is formed on a p-Cu_2O sheet by the magnetron sputtering method, the following two causes are considered the cause of the deterioration of the photovoltaic properties: (1) the physical damage on the Cu_2O sheet surface due to bombardment by the sputtered particles; (2) excessive oxidation of the Cu_2O sheet surface by oxygen ions. Fig. 2 shows the typical current–voltage (*J*–*V*) characteristics of the AZO/p-Cu_2O heterojunction solar cells prepared with different target-Cu_2O sheet distances. It should be noted that the *J*–*V* characteristics of the AZO thin film/p-Cu_2O heterojunction solar cells were dependent on the target-Cu_2O sheet distance. Fig. 3 shows the conversion efficiency (η), the fill factor (FF), V_{OC}, and J_{SC} as functions of the target-Cu_2O sheet distance for AZO/p-Cu_2O heterojunction solar cells fabricated with a target-Cu_2O sheet distance from 30 to 55 mm. The photovoltaic properties did not substantially change until the distance between the target Cu_2O sheets became about 35 mm. However, as the distance further increased, the photovoltaic properties gradually decreased. By increasing the distance between the substrate targets, we expect to reduce the physical damage on the surface of the Cu_2O sheet due to the bombardment. Unfortunately, the photovoltaic properties deteriorated. This result suggests that the deterioration of the photovoltaic property accompanying the increase in the distance between the target and the substrate is not primarily caused by the physical damage on the Cu_2O sheet's surface due to the bombardment. In addition, Fig. 4 shows the typical *J*–*V* characteristics for AZO/p-Cu_2O heterojunction solar cells prepared with different sputtering voltages: 380 and 700 V. It should be noted that the *J*–*V* characteristics of the AZO thin film/p-Cu_2O heterojunction solar cells were strongly dependent on the sputtering voltage. As the sputtering voltage increases, the bombardment effect is expected to increase, but the photovoltaic characteristics will slightly improve. Fig. 5 shows the *J*–*V* characteristics measured under dark conditions obtained in an

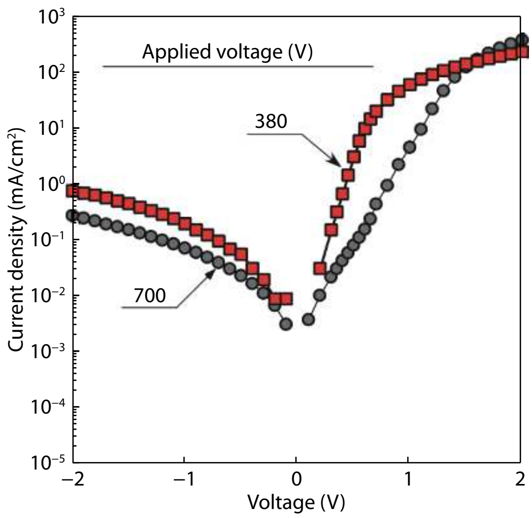

Fig. 5. (Color online) *J–V* characteristics measured under dark conditions obtained in AZO/p-Cu_2O heterojunction solar cell shown in Fig. 4.

AZO/p-Cu_2O heterojunction solar cell (Fig. 4), and when reverse bias voltage was applied, the leakage current decreased in the AZO/p-Cu_2O solar cell fabricated by forming AZO film with higher sputtering voltage. This suggests that an improvement of the p-n junction, as seen in the AZO/Cu_2O heterojunction, was achieved by a higher sputtering voltage. These above results suggest that the cause of the deterioration of the photovoltaic property of the AZO/p-Cu_2O solar cell, fabricated by forming AZO thin film on the Cu_2O sheet by the sputtering method, is not the physical bombardment of the sputtering particles. The cause of the deterioration of the photoelectric conversion characteristics of the AZO/p-Cu_2O solar cell, where AZO thin film is formed on the Cu_2O sheet by the sputtering method, is mainly attributable to excessive oxidation of the Cu_2O sheet's surface by chemically active oxygen ions to the p-n junction interface.

3.2. Photovoltaic properties for AZO/Cu_2O solar cell prepared using multi-chamber MSD apparatus

As mentioned above, to improve the photovoltaic property of the AZO/p-Cu_2O solar cell fabricated by forming AZO thin film by the sputtering method, the Cu_2O sheet surface's excessive oxidation must be reduced by oxygen ions. However, in the AZO thin film deposition process by the sputtering method, to remove oxygen and moisture from the target surface, we must process the generated plasma using pre-sputtering. In this pre-sputtering process, the Cu_2O sheet's surface is protected by a shutter, but since the sputtering gas pressure is as high as 0.6 Pa, preventing excessive oxidation of the Cu_2O's surface is difficult by a shutter due to plasma wraparound. Our newly developed multi-chamber sputtering apparatus has deposition and loading chambers, and we can prevent excessive oxidation by oxygen ions by retracting the Cu_2O sheet into the loading chamber during the pre-sputtering process.

As one example, as a function of the pre-sputtering time, typical *J–V* characteristics are shown in Fig. 6 for AZO/p-Cu_2O heterojunction solar cells measured under AM1.5G solar illumination. Pre-sputtering was carried out in a deposition chamber before introducing the p-Cu_2O sheet from the loading chamber. Next a p-Cu_2O sheet was introduced into the deposition

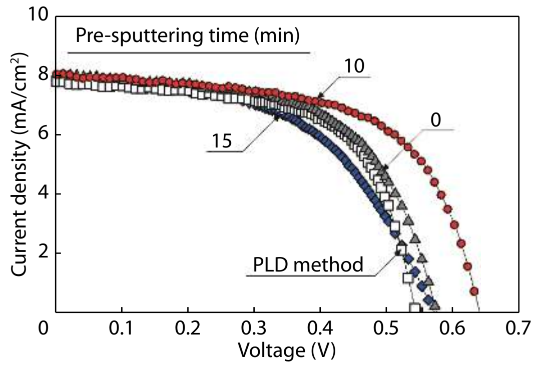

Fig. 6. (Color online) Typical *J–V* characteristics as a function of pre-sputtering time for AZO/p-Cu_2O heterojunction solar cells.

chamber, and then the n^+-AZO thin films were prepared at RT at a pure Ar pressure of 0.6 Pa. As seen in Fig. 6, we drastically improved the *J–V* characteristics by increasing the pre-sputtering time to 10 min. These results suggest that the p-Cu_2O sheet's surface was degraded by exposure to excessive oxygen plasma in the deposition chamber without the pre-sputtering process. On the other hand, when pre-sputtering was performed for more than 15 min, the amount of oxygen, supplied from the moisture adsorbed on the target surface, decreased. As a result, oxygen was deprived on the Cu_2O surface, and the interface state deteriorated. We obtained the highest efficiency of 3.21% in an AZO/p-Cu_2O heterojunction solar cell prepared with a 10 min pre-sputtering time. Fig. 6 also shows typical *J–V* characteristics for AZO/p-Cu_2O heterojunction solar cells prepared using PLD. The *J–V* characteristics of the AZO/p-Cu_2O heterojunction solar cells, prepared using the sputtering method with 10 min pre-sputtering, exhibited better properties than the PLD method (Fig. 6). The solar cell's leakage current prepared by magnetron sputtering with 10 min pre-sputtering, measured under a reversed bias, was as low as the solar cell prepared by PLD. This suggests that greater improvement of the p–n junction, as seen in the AZO/Cu_2O heterojunction, can be achieved by magnetron sputtering methods with 10 min pre-sputtering to decrease the recombination associated with defects at the interface between AZO and Cu_2O.

4. Conclusion

We demonstrated that using a newly developed multi-chamber sputtering apparatus for preparing AZO thin film not only as the n-type semiconductor layer but also as a transparent electrode greatly improves the performance of AZO/p-Cu_2O heterojunction solar cells. We significantly improved the photovoltaic properties by AZO/p-Cu_2O heterojunction solar cells fabricated on p-type Cu_2O sheets that were prepared by the thermal oxidation of Cu sheets. The high efficiency obtained in the heterojunction solar cells may be attributable to a decrease of the defect levels at the interface between the AZO thin film and the Cu_2O sheet. The highest efficiency (3.21%) was obtained in an AZO/p-Cu_2O heterojunction solar cell. This value achieved the same or higher characteristics than the solar cell with a similar structure prepared by the PLD method. Therefore, the newly developed multi-chamber sputtering apparatus is promising as a practical n-type semiconductor thin film that forms technology for Cu_2O-based solar cells.

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References

[1] Asima N, Sopiana K, Ahmadib S, et al. A review on the role of materials science in solar cells. Renew Sustain Energy Rev, 2012, 16, 5834

[2] Rakhshani A E. Preparation, characteristics and photovoltaic properties of cuprous oxide – a review. Solid-State Electron, 1986, 29, 7

[3] Pollack G P, Trivichi D. Photoelectric properties of cuprous oxide. J Appl Phys, 1975, 46, 163

[4] Herion J, Niekisch E A, Scharl G. Investigation of metal oxide/cuprous oxide heterojunction solar cells. Sol Energy Mater, 1980, 4, 101

[5] Papadimitriou L, Economou N A, Trivich D. Heterojunction solar cells on cuprous oxide. Sol Cells, 1981, 3, 73

[6] Olsen L C, Addis F W, Miller W. Experimental and theoretical studies of Cu_2O solar cells. Sol Cells, 1982, 7, 247

[7] Sears W M, Fortin E, Webb J B. Indium tin oxide/Cu_2O photovoltaic cells. Thin Solid Films, 1983, 103, 303

[8] Rai B P. Cu_2O solar cells: A review. Sol Cells, 1988, 25, 265

[9] Briskman R N. A study of electrodeposited cuprous oxide photovoltaic cells. Sol Energy Mater Sol Cells, 1992, 27, 361

[10] Minami T, Nishi Y, Miyata T, et al. High-efficiency oxide solar cells with ZnO/Cu_2O heterojunction fabricated on thermally oxidized Cu_2O sheets. Appl Phys Express, 2011, 4, 062301

[11] Lee Y S, Heo J, Siah S C, et al. Ultrathin amorphous zinc-tin-oxide buffer layer for enhancing heterojunction interface quality in metal-oxide solar cells. Energy Environ Sci, 2013, 6, 2112

[12] Minami T, Nishi Y, Miyata T. High-efficiency Cu_2O-based heterojunction solar cells fabricated using a Ga_2O_3 thin film as n-type layer. Appl Phys Express, 2013, 6, 044101

[13] Lee S W, Lee Y S, Heo J, et al. Improved Cu_2O-based solar cells using atomic layer deposition to control the Cu oxidation state at the p–n junction. Adv Energy Mater, 2014, 4, 1301916

[14] Lee Y S, Chua D, Brandt R E, et al. Atomic layer deposited gallium oxide buffer layer enables 1.2 V open-circuit voltage in cuprous oxide solar cells. Adv Mater, 2014, 26, 4704

[15] Minami T, Nishi Y, Miyata T. Heterojunction solar cell with 6% efficiency based on an n-type aluminum–gallium–oxide thin film and p-type sodium-doped Cu_2O sheet. Appl Phys Express, 2015, 8, 022301

[16] Ievskaya Y, Hoye R L Z, Sadhanala A, et al. Fabrication of ZnO/Cu_2O heterojunctions in atmospheric conditions: Improved interface quality and solar cell performanceSol. Energy Mater Sol Cells, 2015, 135, 43

[17] Hoye R L Z, Brandt R E, Ievskaya Y, et al. Perspective: Maintaining surface-phase purity is key to efficient open air fabricated cuprous oxide solar cells. APL Mater, 2015, 3, 020901

[18] Minami T, Miyata T, Nishi Y. Efficiency improvement of Cu_2O-based heterojunction solar cells fabricated using thermally oxidized copper sheets. Thin Solid Films, 2014, 559, 105

[19] Minami T, Miyata T, Nishi Y. Cu_2O-based heterojunction solar cells with an Al-doped ZnO/oxide semiconductor/thermally oxidized Cu_2O sheet structure. Sol Energy, 2014, 105, 206

[20] Minami T, Nishi Y, Miyata T. Cu_2O-based solar cells using oxide semiconductors. J Semicond, 2016, 37, 014002

[21] Nishi Y, Miyata T, Nomoto J, et al. High-efficiency Cu_2O-based heterojunction solar cells fabricated on thermally oxidized copper sheet. Conf Rec 37th IEEE Photovoltaic Specialists Conf, 2011, 266

[22] Minami T, Nishi Y, Miyata T. Impact of incorporating sodium into polycrystalline p-type Cu_2O for heterojunction solar cell applications. Appl Phys Lett, 2014, 105, 212104