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High-Efficiency Oxide Solar Cells with ZnO/Cu_2O Heterojunction Fabricated on Thermally Oxidized Cu_2O Sheets

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High conversion efficiencies were achieved in low cost n–p heterojunction oxide solar cells with an Al-doped ZnO (AZO)/non-doped ZnO (ZO)/Cu_2O structure. This achievement was made possible by the formation of an n-ZO thin-film layer, prepared with an appropriate thickness by low damage deposition, on high quality Cu_2O sheets produced by the thermal oxidization of copper sheets: n-ZO thin film optimal thickness ranges from 30 to 50 nm. Photovoltaic characteristics such as an open circuit voltage of 0.69 V, a fill factor of 0.55 and a conversion efficiency of 3.83% were attained under simulated AM1.5G solar illumination.

Cuprous oxide (Cu_2O), a semiconductor with a direct energy gap of 2.1 eV, is a low cost and nontoxic oxide material that has long attracted much interest for application as an active layer in solar cells. The theoretical limit of the energy conversion efficiency of a Cu_2O solar cell is as high as 20% under air mass (AM) 1 solar illumination.[1)] In particular, Cu_2O solar cells exhibit high efficiencies for solar light in the range from about 550 nm to near ultraviolet, a region where the efficiency of crystalline silicon solar cells begins to decrease significantly. However, it is very difficult to achieve a high efficiency because of the difficulty in obtaining an n-type semiconductor since Cu_2O is spontaneously a p-type semiconductor. There are many reports on metal–semiconductor solar cells such as Cu/Cu_2O and various n–p heterojunction solar cells fabricated using Cu_2O as the active layer.[1–8)] However, an efficiency over 1% has been difficult to achieve in Cu_2O-based solar cells fabricated with these structures, with the exception of Cu–Cu_2O solar cells (maximum reported efficiency (η) of 1.76%).[5,9)] It is known that the deposition method and conditions are important when depositing oxide thin films on Cu_2O sheets because a Cu metal or an insulating CuO thin film can easily be created at the interface by reducing or oxidizing the Cu_2O surface, respectively.[6,10)]

Recently, a conversion efficiency of 1.52% has been obtained in a heterojunction solar cell with a Ga-doped ZnO (GZO)/Cu_2O structure by improving the preparation method of the Cu_2O sheets and decreasing the damage in the GZO thin-film deposition.[11,12)] However, the n^+-GZO/p-Cu_2O heterojunction solar cells, consisting of a degenerated semiconductor and p-Cu_2O, functioned as a Schottky barrier (SB) contact in regard to diode characteristics. To improve the obtainable efficiency in Cu_2O-based solar cells, it may be necessary to form a n–p heterojunction by inserting an appropriate n-type semiconductor layer.[13)] A high efficiency of 2.01% has recently been obtained in an n–p heterojunction solar cell, MgF_2/indium–tin-oxide (ITO)/ZnO/Cu_2O/Cu structure, that was fabricated by depositing thin films on thermally oxidized Cu_2O sheets at room temperature using an ion beam sputtering method.[14)] This result suggests that the deposition of a thin film on Cu_2O sheets is necessary to decrease the resulting damage in the film deposition. In this paper, we describe Al-doped ZnO (AZO)/ZO/Cu_2O n–p heterojunction solar cells fabricated by optimizing not only the thermal oxidization process involved in Cu_2O sheet formation but also the deposition technology used for the AZO and ZO thin-film layers, resulting in conversion efficiencies above 3%.

Polycrystalline Cu_2O sheets were prepared by oxidizing Cu sheets using a heat treatment process that consisted of three steps in an ambient gas controlling furnace. The first step was annealing in an Ar or N_2 gas atmosphere; Cu sheets ($30 \times 30\,mm^2$) with a purity of 99.9% were heated up to 1010 °C at a rate of 17 °C/min and kept at a temperature of 1010 °C for 1 h. The second step was oxidization in air; air was introduced into the furnace, and the temperature was kept at 1010 °C for 2 h. The third step resulted in the formation of superior Cu_2O; after the air was purged, an Ar or N_2 gas atmosphere was introduced into the furnace, and then the sheets were annealed at 1010 °C for 2 h. Subsequently, the temperature was lowered to 500 °C at a rate of 8.0 °C/min, and, finally, the Cu_2O sheets were brought out to the air environment at room temperature. The resulting Cu_2O sheets were polycrystalline p-type semiconductors composed of grains whose size, in the range from approximately 1 to 100 mm^2, could be controlled by varying the heat treatment conditions described above. However, the obtained electrical properties, such as resistivity, on the order of $10^3\,\Omega cm$, hole concentration, on the order of $10^{13}\,cm^{-3}$, and Hall mobility, as high as $110\,cm^2/Vs$, were relatively independent of the observed grain size.

During device fabrication, the CuO surface layer of the oxidized Cu_2O sheets was removed by etching.[13)] Oxide heterojunction solar cells were fabricated by forming an AZO/ZO/Cu_2O structure on the front surface of the prepared high quality Cu_2O sheets, which function as the active layer as well as the substrate, and a Au or Cu_2S ohmic electrode on the back surface of Cu_2O sheets.[13)] The AZO and ZO thin films were prepared by pulsed laser deposition (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; target, sintered AZO and ZO pellets; and atmosphere and pressure, vacuum below 4.0×10^{-4} Pa and O_2 gas at 0–1.5 Pa. The electrical and optical properties of the AZO and ZO films were evaluated using thin films that were deposited on glass substrates simultaneously with the AZO/ZO/Cu_2O depositions.

It was found that the obtainable photovoltaic characteristics in the fabricated AZO/ZO/Cu_2O heterojunction solar cells were considerably affected by the deposition conditions

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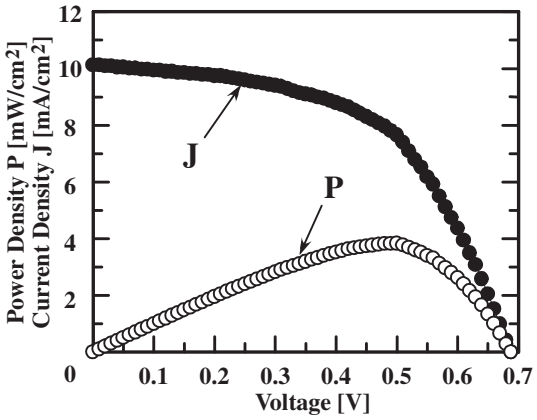

Fig. 1. J–V and P–V characteristics of an AZO/ZO/Cu_2O solar cell fabricated with a 50-nm-thick ZO thin-film layer prepared at an O_2 gas pressure of 1.2 Pa.

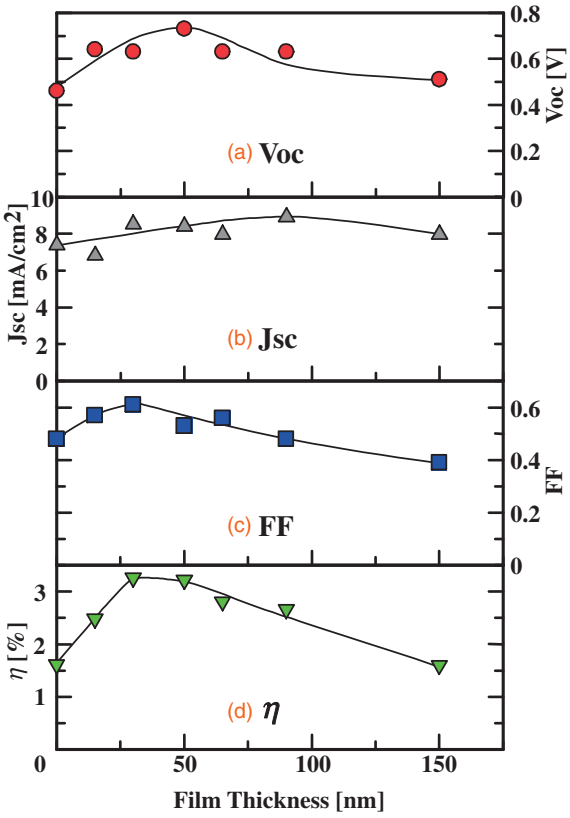

Fig. 2. V_{OC}, J_{SC}, FF, and η as functions of the ZO thin-film layer thickness in AZO/ZO/Cu_2O solar cells.

of the ZO thin films, particularly atmosphere and pressure. Transparent ZO films were obtained when the films were deposited in an introduced O_2 gas atmosphere at a pressure above approximately 0.08 Pa; in contrast, with depositions in a vacuum, the resulting film transmittance decreased markedly and the film was colored. The obtainable electrical and optical properties of ZO thin films deposited in an O_2 gas atmosphere were relatively independent of the introduced O_2 gas pressure in the range from approximately 0.1 to 1.2 Pa. The ZO thin films were n-type semiconductors with a carrier concentration on the order of 10^{19} cm^{-3}. In addition, since the obtained carrier concentration and Hall mobility increased with film thickness, the obtained resistivity in n-ZO thin films tended to decrease as the thickness increased. The obtained current density–voltage (J–V) and output power density–voltage (P–V) characteristics are shown in Fig. 1 for an AZO/ZO/Cu_2O heterojunction solar cell fabricated by inserting a ZO thin-film layer prepared with a thickness of 50 nm at an O_2 gas pressure of 1.2 Pa. The photovoltaic properties of the solar cell (electrode area of 3.14 mm^2) were evaluated under AM1.5G solar illumination (100 mW/cm^2): notably, an open-circuit voltage (V_{OC}) of 0.69 V and a short-circuit current density (J_{SC}) of 10.1 mA/cm^2 were obtained.

Figure 2 shows the conversion efficiency (η), fill factor (FF), V_{OC}, and J_{SC} as functions of the ZO film thickness for AZO/ZO/Cu_2O heterojunction solar cells fabricated by inserting a ZO thin film prepared with various thicknesses at an O_2 gas pressure of 0.1 Pa. For comparison, the obtained photovoltaic characteristics in an AZO/Cu_2O SB solar cell, i.e., fabricated with a ZO thickness of 0, also are shown in Fig. 2. The obtainable photovoltaic characteristics were improved markedly by inserting an n-ZO thin-film layer; η, FF, V_{OC}, and J_{SC} all increased as the thickness of the ZO thin-film layer inserted between the AZO and Cu_2O layers increased up to approximately 50 nm. It should be noted that high conversion efficiencies above 3% were attained in AZO/ZO/Cu_2O solar cells fabricated by inserting an n-ZO thin-film layer having a thickness in the range from approximately 30 to 50 nm. It was also found that AZO/ZO/Cu_2O heterojunction solar cells, in comparison with AZO/Cu_2O SB solar cells, exhibited an enhanced photocurrent at shorter wavelengths (around 400 nm) in the measured spectral response[13,14] as well as an improved J–V characteristic measured under dark conditions resulting from a decreased leak current (data not shown). Therefore, the improvement of η that could be achieved by inserting the n-ZO thin-film layer is mainly attributable to increases in both FF and V_{OC}, resulting from the formation of a n–p heterojunction. As can be seen in Fig. 2, however, η, FF and V_{OC} each reached a peak at a ZO film thickness around 30–50 nm, and then decreased with any further increase of the thickness, whereas J_{SC} increased with increasing ZO film thickness up to about 100 nm. The obtained increases exhibited by η, FF, and V_{OC} as the ZO film thickness was increased up to approximately 50 nm may be attributable to an improvement of film quality, because the increase in thickness of the ZO film was accompanied by a marked decrease in resistivity and improvement in crystallinity, as previously reported.[15,16] On the other hand, the decrease found in η and FF as the ZO film thickness was increased above approximately 50 nm may be attributable to the short lifetime of minority carriers in the n-ZO thin film, because a photo-generated positive hole in the ZO film could recombine through defects in the near interface before that it reaches the depletion layer, as shown in Fig. 3.

Figure 4 shows the obtained η as a function of O_2 gas pressure for AZO/ZO/Cu_2O heterojunction solar cells fabricated with a 50-nm-thick-ZO thin film prepared under various O_2 gas pressures. As can be seen in Fig. 4, η increased considerably as the introduced O_2 gas pressure increased; η, approximately 3% with the deposition of ZO

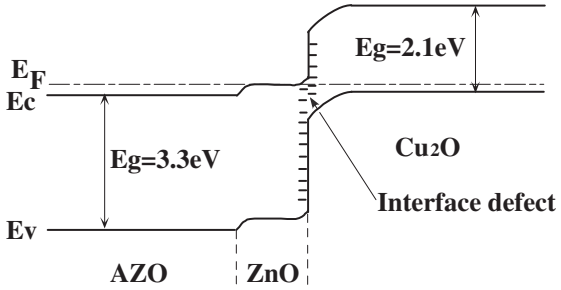

Fig. 3. Energy band diagram of the AZO/ZO/Cu_2O structure.

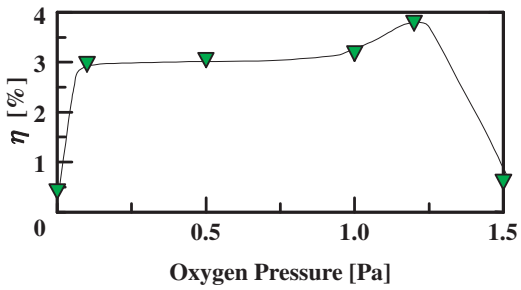

Fig. 4. η as a function of the O_2 gas pressure used for depositing the ZO thin-film layer in AZO/ZO/Cu_2O solar cells.

thin-film layer at an O_2 gas pressure of 0.1 Pa, gradually increased with an increase of the pressure up to approximately 1.2 Pa, and then decreased markedly at a pressure of 1.5 Pa. It was also found that the obtained FF, V_{OC}, and J_{SC} in AZO/ZO/Cu_2O heterojunction solar cells were similarly dependent on the O_2 gas pressure. It should be noted that a high efficiency of 3.83% and a fill factor of 0.55 were obtained in an AZO/ZO/Cu_2O heterojunction solar cell fabricated by inserting a ZO thin-film layer prepared with a thickness of 50 nm at an O_2 gas pressure of 1.2 Pa.

In conclusion, we have demonstrated low cost Al-doped ZnO (AZO)/non-doped ZnO (ZO)/Cu_2O heterojunction solar cells with a high conversion efficiency of 3.83%. The high efficency resulted from the formation of an n-type ZO thin film with a thickness of 30–50 nm by a low damage deposition method on high quality Cu_2O sheets prepared by thermally oxidizing copper sheets. In particular, high-efficiency Cu_2O-based solar cells fabricated with low cost and abundant oxide materials that could make up for the achievable efficiency of crystalline silicon solar cells will motivate further development of Cu_2O-based solar cells.

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1) A. E. Rakhshani: Solid-State Electron. **29** (1986) 7.
2) G. P. Pollack and D. Trivichi: J. Appl. Phys. **46** (1975) 163.
3) J. Herion, E. A. Niekisch, and G. Scharl: Sol. Energy Mater. **4** (1980) 101.
4) L. Papadimitriou, N. A. Economou, and D. Trivich: Sol. Cells **3** (1981) 73.
5) L. C. Olsen, F. W. Addis, and W. Miller: Sol. Cells **7** (1982) 247.
6) W. M. Sears, E. Fortin, and J. B. Webb: Thin Solid Films **103** (1983) 303.
7) B. P. Rai: Sol. Cells **25** (1988) 265.
8) R. N. Briskman: Sol. Energy Mater. Sol. Cells **27** (1992) 361.
9) R. J. Iwanowski and D. Trivich: Phys. Status Solidi A **95** (1986) 735.
10) L. C. Olsen, R. C. Bohara, and M. W. Urie: Appl. Phys. Lett. **34** (1979) 47.
11) T. Minami, T. Miyata, K. Ihara, Y. Minamino, and S. Tsukada: Thin Solid Films **494** (2006) 47.
12) H. Tanaka, T. Shimakawa, T. Miyata, H. Sato, and T. Minami: Appl. Surf. Sci. **244** (2005) 568.
13) T. Miyata, T. Minami, H. Tanaka, and H. Sato: Proc. SPIE **6037** (2006) 603712.
14) A. Mittiga, E. Salza, F. Sarto, M. Tucci, and R. Vasanthi: Appl. Phys. Lett. **88** (2006) 163502.
15) T. Minami and T. Miyata: Thin Solid Films **517** (2008) 1474.
16) J. Nomoto, T. Hirano, T. Miyata, and T. Minami: Proc. 17th Int. Display Workshops, 2010, p. 371.