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Relationship between the electrical properties of the n-oxide and p-Cu_2O layers and the photovoltaic properties of Cu_2O-based heterojunction solar cells

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ABSTRACT

We investigated the relationship between the electrical properties (of the n-oxide semiconductor layer and the p-Cu_2O sheet) and the obtainable photovoltaic properties of Al-doped ZnO (AZO)/n-oxide/p-Cu_2O heterojunction solar cells that were fabricated using either p-type non-doped Cu_2O or Na-doped Cu_2O (Cu_2O:Na) sheets (prepared by thermally oxidizing a Cu sheet) functioning as the active layer as well as the substrate. We fabricated some heterojunction solar cells using p-Cu_2O (non-doped) sheets and n-ZnO thin films with various electron concentrations (N) in the range of 10^{17}–10^{20} cm^{-3}; non-doped and Al- or Cu-doped ZnO thin films were deposited under various O_2 or O_3 gas atmosphere pressures using a pulsed laser deposition (PLD) method. The obtained photovoltaic properties exhibited a tendency to increase as N was increased from 10^{17} to about 3×10^{19} cm^{-3}; the values remained at these maximum levels as N was increased to about 8×10^{19} cm^{-3}, and then they decreased as N was increased further. With an N on the order of 10^{20} cm^{-3}, the reduction of photovoltaic properties was attributed to an increase in the discontinuity of the conduction band at the interface between the n-ZnO and p-Cu_2O layers. In addition, we found that the hole concentration (P) in Cu_2O:Na sheets (i.e., Cu_2O sheets post-annealed with various Na compounds) could be controlled in the range of 10^{14}–10^{19} cm^{-3} by varying the annealing temperature and duration. As another example, the obtained photovoltaic properties in heterojunction solar cells that were fabricated by depositing n-$(Ga_{0.975}Al_{0.025})_2O_3$ thin films on p-Cu_2O:Na sheets by PLD remained constant as P was increased to approximately 1×10^{16} cm^{-3}, and then they decreased significantly as P was increased further. The reduction of the obtained photovoltaic properties in heterojunction solar cells fabricated using Cu_2O:Na sheets with a P above about 1.4×10^{16} cm^{-3} was attributed mainly to decreases of both the depletion layer width and the diffusion length.

1. Introduction

Cuprous oxide (Cu_2O) with a direct band gap of 2.1 eV is a promising semiconductor for solar cell applications. Although the theoretical limit of the energy conversion efficiency of a Cu_2O solar cell is as high as 20% under AM1 solar illumination, it is very difficult to achieve a high efficiency because of the difficulty of obtaining an n-type semiconductor as well as the chemical instability of the Cu_2O surface [1–6]. Recently, Cu_2O-based p–n heterojunction solar cells with significantly improved efficiency have attracted much interest due to the material's nontoxicity, suitability for sustainable semiconductor material usage and potential for cost-effective manufacturing. Enhanced efficiency could be achieved in n-type semiconductor/p-type Cu_2O heterojunction solar cells fabricated by preparing a n-semiconductor thin film on a p-Cu_2O sheet or thin film using low-damage and low-temperature deposition techniques such as a pulsed laser deposition (PLD) and atomic layer deposition (ALD) [7–12]. In addition, the effect of introducing various kinds of n-semiconductor thin films on the obtainable photovoltaic properties in Cu_2O-based solar cells was investigated by using thin films such as binary compounds and multi-component oxides, prepared under various deposition conditions [12–22]. We reported that Al-doped ZnO (AZO)/n-ZnO/p-Cu_2O heterojunction solar cells with an energy conversion efficiency over 4% could be fabricated by using the PLD method to deposit n-ZnO thin films on unheated (room temperature; RT) p-Cu_2O sheets prepared by thermally oxidizing a Cu sheet; the 0.2-mm-thick Cu_2O sheets act as the active layer as well as the substrate [10]. In addition, we have recently reported that conversion efficiencies over 5% were obtained in Cu_2O-based p–n heterojunction solar cells fabricated by depositing an n-Ga_2O_3 thin film at RT on thermally oxidized Cu_2O sheets using the PLD

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method [11]. In addition, Lee et al. have recently reported that efficiencies over 3% were obtained in thin-film heterojunction solar cells that were fabricated using the ALD method to deposit an n-Ga_2O_3 or n-Zn–Sn–O multi-component oxide thin film at a low temperature on p-Cu_2O thin films [17,18]. It should be noted that the obtained photovoltaic properties in n-oxide semiconductor/p-Cu_2O heterojunction solar cells were significantly affected by not only the kind and preparation technique of the oxide thin films used as the n-semiconductor layer, but also the form (thin film or sheet) and preparation technique of the p-Cu_2O layer.

In this paper, we describe improvement of conversion efficiencies in Cu_2O-based p–n heterojunction solar cells with an AZO/n-oxide semiconductor/p-Cu_2O structure fabricated using non-doped or Na-doped Cu_2O sheets prepared by thermally oxidizing Cu sheets. The relationship between the electrical properties in the n-oxide semiconductor layer as well as the p-Cu_2O sheets and the obtainable photovoltaic properties in heterojunction solar cells was investigated, resulting in improvements of the photovoltaic properties that were achieved by optimizing the electrical properties in the n-type oxide thin films as well as the p-Cu_2O sheets.

2. Experimental

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 °C in a furnace with a controlled ambient atmosphere, described elsewhere in detail [7,10,16]. Subsequently, the CuO surface layer of the oxidized Cu_2O sheets was removed by etching [14]. 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/Vs. The incorporation of Na into Cu_2O sheets was carried out by postannealing Cu_2O sheets that were placed together with an appropriate sodium compound powder, such as NaCl, NaI, NaF and Na_2CO_3, at 400–800 °C for 1–30 h in an Ar gas atmosphere [23]. After cooling down to 500 °C (or 400 °C), 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 10^3–10^{-2} Ω cm by doping Na with the range of annealing temperatures and durations noted above. All non-doped ZnO (ZO), Al-doped ZnO (AZO or ZnO:Al), Cu-doped ZnO (ZnO:Cu) and $(Ga_{0.975}Al_{0.025})_2O_3$ thin films were deposited with a PLD using an ArF excimer laser (wavelength, 193 nm; repetition rate, 20 Hz; pulse width, 20 ns; fluence, 350 mJ/cm^2) under the following deposition conditions: target-substrate distance, 40 mm; deposition temperature, RT; target, sintered AZO (2 wt% Al_2O_3), ZO, ZnO:Cu or $(Ga_{0.975}Al_{0.025})_2O_3$; and atmosphere and pressure, vacuum below 4.0×10^{-4} Pa or O_2 (or O_3) gas at 0–2.8 Pa. The solar cells were fabricated by forming an AZO/n-oxide semiconductor/p-Cu_2O structure on the front surface of Cu_2O sheets and an Au ohmic electrode on the back surface (the sheets function as the active layer as well as the substrate). The AZO thin films, functioning as the transparent electrode and prepared at a pressure of 0.2 Pa in an O_2 gas atmosphere with a thickness of 200 nm, exhibited a resistivity on the order of 10^{-4} Ω cm and a carrier concentration on the order of 10^{20} cm^{-3}. The ZO and ZnO:Al thin films, functioning as the n-semiconductor layer with a thickness of 50 nm, were prepared under various O_2 or O_3 and O_2 gas atmosphere pressures, respectively. The Al content (Al/(Al+Zn) atomic ratio) in the AZO and ZnO:Al thin films was 2.5 at%. In order to evaluate the electrical properties of the resulting AZO and oxide semiconductor thin films, simultaneous and/or additional depositions were also conducted on OA-10 glass (Nippon Electric Glass Co., Ltd.) substrates. Measurements of the electrical properties in the prepared Cu_2O sheets in the temperature range from −173 °C (100 K) to RT and in the deposited oxide semiconductor thin films at RT were carried out using the van der Pauw method (HL-5500PC by Accent). The photovoltaic properties such as open-circuit voltage, short-circuit current density, fill factor and efficiency in the Cu_2O-based solar cells (electrode area of 3.14 mm^2) were evaluated using a measurement system (HAL-320 by Asahi Spectra Co., Ltd.) with only the AZO transparent electrode area exposed to the AM 1.5 G solar illumination (100 mW/cm^2) at 25 °C.

3. Results and discussion

3.1. Relationship between the electrical properties of n-type ZnO thin films and the resulting photovoltaic properties

We have reported that the obtained photovoltaic properties in AZO/n-oxide semiconductor/p-Cu_2O heterojunction solar cells fabricated using thermally oxidized Cu_2O sheets were significantly affected by the kind and preparation technique of the oxide thin films used as the n-semiconductor layer. In addition to the characteristics of the n-oxide thin-film layer, the photovoltaic properties of the p–n heterojunction solar cells also were dependent on the surface damage of the Cu_2O sheets that occurred during the deposition of the oxide thin films [16,19]. To clarify the effect of the characteristics of the oxide thin films used, the relationship between the electrical properties of the n-oxide semiconductor layer and the obtainable photovoltaic properties in AZO/n-ZnO/p-Cu_2O heterojunction solar cells was investigated by varying both the deposition conditions of the ZnO thin films and the impurity doping into the thin films prepared at RT by PLD. In n-semiconductor/p-Cu_2O heterojunction solar cells fabricated with thermally oxidized Cu_2O sheets, we have reported that high efficiencies over 4% could only be achieved by using ZnO, Ga_2O_3 and multi-component oxides, i.e., or Zn and/or Ga, as the n-oxide thin-film layer [10,11,15,19,22]. However, it was difficult to evaluate resistivity and crystallinity in most oxide thin films prepared with a thickness of 50 nm at RT by PLD. Nevertheless, the evaluation showed that only ZnO thin films prepared by PLD under various deposition conditions and with various amounts of impurity doping into the thin films at RT exhibited a wide range of obtained resistivity and carrier concentration, from 10^2 to 10^{-3} Ω cm and 10^{17} to 10^{20} cm^{-3}, respectively. Typical electron concentration (N) as a function of the pressure of the O_2 or O_3 gas atmosphere introduced during the deposition is shown in Fig. 1 for ZO, ZnO:Al and ZnO:Cu thin films prepared on glass substrates with a thickness of 50 nm at RT by PLD.

The gas pressure dependence of the obtained photovoltaic properties is shown in Fig. 2 for AZO/n-ZnO/p-Cu_2O heterojunction solar cells fabricated with a 50-nm-thick ZO or ZnO:Al thin film, prepared at RT by PLD. The n-ZO and n-ZnO:Al thin-film layers were deposited under a range of introduced O_2 or O_3 gas and O_2 gas pressures, respectively, as shown in Fig. 1. Although previously reported, our results concerning the gas pressure dependence of the obtained photovoltaic properties in AZO/n-ZnO/p-Cu_2O heterojunction solar cells (fabricated with ZO thin films deposited under a range of introduced O_2 gas pressures [19]) are also shown in Fig. 2 for comparison with the results obtained in the heterojunction solar cells fabricated with ZO thin films deposited under a range of introduced O_3 gas pressures. Note that the obtained photovoltaic properties in the heterojunction solar cells fabricated using either a ZO or ZnO:Al thin film as the n-semiconductor layer were dependent on the gas pressure, irrespective of the kind of gas introduced. In addition, the maximum conversion efficiencies, over 4%, were obtained in AZO/n-ZO/p-Cu_2O solar cells fabricated by depositing ZO