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Effect of the thin Ga_2O_3 layer in n^+-ZnO/n-Ga_2O_3/p-Cu_2O heterojunction solar cells

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ABSTRACT

The influence of inserting a Ga_2O_3 thin film as an n-type semiconductor layer on the obtainable photovoltaic properties in Cu_2O-based heterojunction solar cells was investigated with a transparent conductive Al-doped ZnO (AZO) thin film/n-Ga_2O_3 thin film/p-Cu_2O sheet structure. It was found that this Ga_2O_3 thin film can greatly improve the performance of Cu_2O-based heterojunction solar cells fabricated using polycrystalline Cu_2O sheets that had been prepared by a thermal oxidization of copper sheets. The obtained photovoltaic properties in the AZO/Ga_2O_3/Cu_2O heterojunction solar cells were strongly dependent on the deposition conditions of the Ga_2O_3 films. The external quantum efficiency obtained in AZO/Ga_2O_3/Cu_2O heterojunction solar cells was found to be greater at wavelengths below approximately 500 nm than that obtained in AZO/Cu_2O heterojunction solar cells (i.e., prepared without a Ga_2O_3 layer) at equivalent wavelengths. This improvement of photovoltaic properties is mainly attributed to a decrease in the level of defects at the interface between the Ga_2O_3 thin film and the Cu_2O sheet. Conversion efficiencies over 5% were obtained in AZO/Ga_2O_3/Cu_2O heterojunction solar cells fabricated using an n-Ga_2O_3 thin-film layer prepared with a thickness of 40–80 nm at an O_2 gas pressure of approximately 1.7 Pa by a pulsed laser deposition.

1. Introduction

Recently, we reported that n-type semiconductor/p-type Cu_2O heterojunction solar cells with a conversion efficiency of 3.83% could be fabricated by forming an Al-doped ZnO (AZO)/non-doped ZnO/Cu_2O structure on the front surface of polycrystalline Cu_2O sheets that had been prepared by a thermal oxidization of copper sheets [1]. 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 deposition technique on high quality polycrystalline Cu_2O sheets [2–4]. It is known that the obtainable open-circuit voltage is strongly dependent on the kind of n-type semiconductor layer used for forming the p–n heterojunction, such as the Cu_2O-based heterojunction [1–10]. In this regard, we have recently reported that the obtained conversion efficiency and the open-circuit voltage in n^+-AZO/n-$Zn_{1-x}Mg_xO$/p-Cu_2O heterojunction solar cells (non-doped $Zn_{1-x}Mg_xO$ thin films used as an n-type semiconductor layer) increased as the Mg content (Mg/(Zn + Mg) atomic ratio: x) was increased in the range from 0 to 0.09 [11]. In addition, it has been reported that the obtainable photovoltaic properties in n-semiconductor/p-Cu_2O heterojunction solar cells also are affected by the surface condition of the p-Cu_2O layer, that is, the interface at the heterojunction, rather than the diffusion potential resulting from the difference of work functions between the p-Cu_2O and n-semiconductor layers [12–15]. We have reported more recently that a non-doped gallium oxide (Ga_2O_3) thin film is suitable as an n-semiconductor layer in n-semiconductor/p-Cu_2O heterojunction solar cells [16]. A high efficiency over 5% was obtained in an n^+-AZO/n-Ga_2O_3/p-Cu_2O heterojunction solar cell fabricated with a non-doped Ga_2O_3 thin film as the n-semiconductor layer.

For this paper, the influence of inserting a non-doped Ga_2O_3 thin-film layer on the obtainable photovoltaic properties in Cu_2O-based heterojunction solar cells was investigated with a transparent conductive AZO thin film/n-Ga_2O_3 thin film/p-Cu_2O sheet structure. To improve the photovoltaic properties, the preparation conditions of the inserted non-doped Ga_2O_3 thin-film layer were optimized for use in n^+-AZO/n-Ga_2O_3/p-Cu_2O heterojunction solar cells that were fabricated by forming this Ga_2O_3 thin film on the front surface of thermally oxidized Cu_2O sheets using a pulsed laser deposition (PLD) method.

2. Experimental

The solar cells were fabricated by forming an n^+-AZO/n-Ga_2O_3/p-Cu_2O structure on the front surface of Cu_2O sheets (thickness of approximately 0.2 mm) and an Au ohmic electrode on the back surface; the Cu_2O sheets function as the active layer as well as the substrate, as shown in Fig. 1. The Cu_2O sheets were prepared by oxidizing Cu sheets using a heat treatment process that consisted of three steps in a furnace with a controlled ambient atmosphere [3,15]. The first step was annealing in an Ar gas atmosphere: Cu sheets (30 mm × 30 mm)

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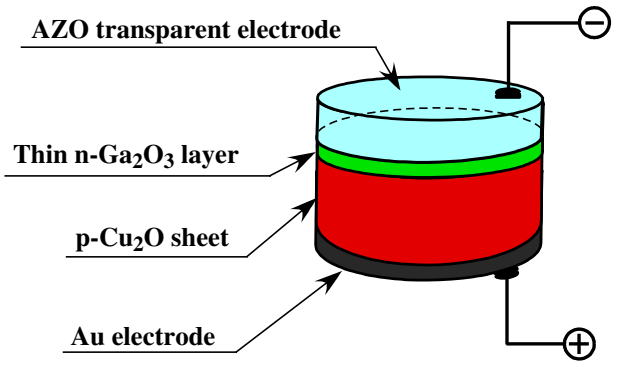

Fig. 1. Schematic structure of an AZO/n-Ga_2O_3/p-Cu_2O solar cell.

with a purity of 99.9 % were heated up to 1025 °C at a rate of 17 °C/min and kept at this temperature for 1 h. The second step was oxidization in air: air was introduced into the furnace, and the temperature was kept at 1025 °C for 2 h. The third step resulted in the formation of superior Cu_2O: after the air was purged, an Ar gas atmosphere was introduced into the furnace, and then the sheets were annealed at 1025 °C for 2 h. Subsequently, the temperature was lowered to 500 °C at a rate of 8 °C/min, and finally, the Cu_2O sheets were brought out to the air environment at room temperature (RT). 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, i.e., resistivity of 10^2–10^3 Ωcm, the hole concentration on the order of 10^{13} cm^{-3} and the Hall mobility above 100 cm^2/Vs, were relatively independent of the observed grain size.

In the first step of device fabrication, the CuO surface layer of the oxidized Cu_2O sheets was removed by chemical wet etching. Subsequently, the AZO and Ga_2O_3 thin films were prepared with a PLD method 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, RT (not intentionally heated); target, sintered AZO or non-doped Ga_2O_3 pellets; and atmosphere and pressure, O_2 gas at 0 (vacuum below 10^{-4} Pa)–2.2 Pa. In order to evaluate the electrical and optical properties of the resulting AZO and Ga_2O_3 films, simultaneous depositions were also conducted on OA-10 glass (Nippon Electric Glass Co., Ltd.) substrates. The AZO thin films, used as the transparent electrode in all the heterojunction solar cells, were always prepared with a thickness of 150–300 nm at an O_2 gas pressure of 0.2 Pa. The AZO thin films exhibited a resistivity of approximately 8×10^{-4} Ωcm and a carrier concentration of approximately 6.5×10^{20} cm^{-3}. The work function of the AZO and Ga_2O_3 thin films and the Cu_2O sheets was evaluated from the wavelength dependence of the photoemission of electrons using ultraviolet photoelectron spectroscopy [17]. The photovoltaic properties of the 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) at 25 °C.

3. Results and discussion

3.1. Effect of inserting the Ga_2O_3 thin-film layer

In addition to the photovoltaic properties of solar cells with an n-semiconductor thin film/p-Cu_2O sheet structure being considerably affected by the materials used as the n-type semiconductor layer, it is also known that these properties also are affected by the surface condition of the p-Cu_2O layer in Cu_2O-based heterojunction solar cells, that is, the interface at the heterojunction [12–15,18,19]. Consequently, the obtainable photovoltaic properties such as the open-circuit voltage and the fill factor in Cu_2O-based heterojunction solar cells are considerably dependent on the method as well as the operating conditions that exist when depositing an n-semiconductor thin film. As a result of investigations, we recently have found that a non-doped Ga_2O_3 thin film prepared at RT by a PLD method is a very promising material for the n-semiconductor layer in n-semiconductor/p-Cu_2O heterojunction solar cells [16]. Typical current density–voltage (J–V) characteristics as a function of the Ga_2O_3 thin-film thickness are shown in Fig. 2 for n^+-AZO/n-Ga_2O_3/p-Cu_2O heterojunction solar cells (fabricated with AZO and non-doped Ga_2O_3 thin films) measured under AM1.5G solar illumination. The Ga_2O_3 thin films were prepared at RT with O_2 gas introduced into the deposition chamber at a pressure of 1.7 Pa. As can be seen in Fig. 2, a drastic improvement of the J–V characteristic was obtained by the insertion of a Ga_2O_3 thin-film layer into an AZO/Cu_2O heterojunction solar cell. Both the open-circuit voltage (V_{OC}) and the short circuit current density (J_{SC}) were increased dramatically by inserting an n-Ga_2O_3 thin-film layer, even with a thickness of approximately 20 nm. In addition, the fill factor (FF) gradually improved as the Ga_2O_3 thin-film thickness was increased up to 50–75 nm. The obtained V_{OC}, J_{SC}, FF and conversion efficiency (η) as functions of the Ga_2O_3 thin-film thickness (t) are shown in Fig. 3 for the AZO/Ga_2O_3/Cu_2O heterojunction solar cells shown in Fig. 2. As can be seen in Fig. 3, η reached its peak at a thickness of 50–75 nm and then decreased as the thickness was increased further. The increase of η with increasing Ga_2O_3 thin-film thickness up to approximately 40 nm is related to increases of both V_{OC} and J_{SC}; however, the fluctuation of η at thicknesses above approximately 40 nm is attributed mainly to that of FF. The decrease in FF at thicknesses above approximately 75 nm may be attributed to the increase of series resistance resulting from the thickness increase because the Ga_2O_3 thin films used as the n-semiconductor layer exhibited very high resistivity, as described later. It should be noted that a V_{OC} of 0.80 V and a η of 5.38% were obtained in an AZO/Ga_2O_3/Cu_2O heterojunction solar cell fabricated with a Ga_2O_3 thin-film layer with a thickness of 75 nm.

As can be seen in Fig. 3(a), the obtained J_{SC} was markedly increased by inserting the n-Ga_2O_3 thin-film layer. In addition, the observed external quantum efficiency (EQE) in AZO/Ga_2O_3/Cu_2O heterojunction solar cells improved dramatically as the Ga_2O_3 thin-film layer thickness was increased from 0 to approximately 40 nm and then remained unchanged as the thickness was increased further. The EQE obtained in AZO/Ga_2O_3/Cu_2O heterojunction solar cells was always greater than that obtained in an AZO/Cu_2O heterojunction solar cell, ranging over the full gamut of observable EQE spectra. Typical normalized EQE spectra are shown in Fig. 4 for the AZO/Ga_2O_3/Cu_2O

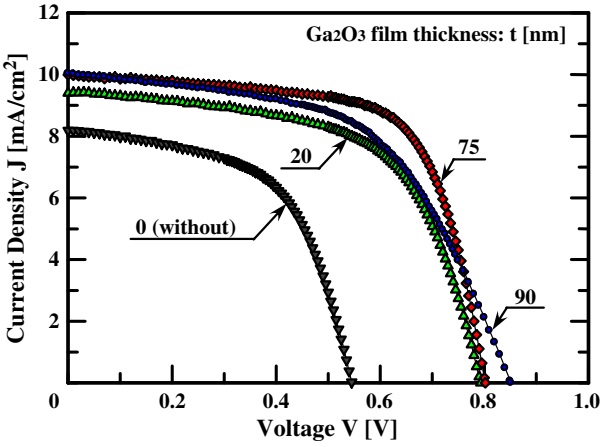

Fig. 2. J–V characteristics of AZO/Ga_2O_3/Cu_2O solar cells fabricated with various Ga_2O_3 film thicknesses (t): 0 (▽), 20(△), 75(◇) and 90 nm (○), measured under AM1.5G solar illumination.