Available online at www.sciencedirect.com

ScienceDirect

Solar Energy 105 (2014) 206–217

SOLAR ENERGY

www.elsevier.com/locate/solener

Cu_2O-based heterojunction solar cells with an Al-doped ZnO/oxide semiconductor/thermally oxidized Cu_2O sheet structure

Tadatsugu Minami *, Toshihiro Miyata, Yuki Nishi

Optoelectronic Device System R&D Center, Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

Received 7 February 2014; accepted 27 March 2014
Available online 4 May 2014

Communicated by: Associate Editor Frank Nuesch

Abstract

This paper introduces the present status and prospects for further development of Al-doped ZnO (AZO)/n-type metal oxide semiconductor/p-type Cu_2O hybrid heterojunction (HbH) solar cells that feature a structure that is fabricated by inserting an n-oxide semiconductor thin film between an AZO transparent electrode and a Cu_2O sheet. An improvement of photovoltaic properties was achieved by both stabilizing the surface of polycrystalline p-Cu_2O sheets that had been prepared by thermal oxidization of Cu sheets and also developing low-temperature and low-damage deposition technology for applying thin films as an n-oxide semiconductor layer. It should be noted that the obtainable photovoltaic properties in AZO/oxide semiconductor/Cu_2O HbH solar cells were found to be considerably more affected by the surface condition of the p-Cu_2O layer, *i.e.*, the interface at the heterojunction, than the diffusion potential resulting from the difference of work functions between the p-Cu_2O and n-oxide semiconductor layers. To achieve a higher efficiency in AZO/n-oxide semiconductor/p-Cu_2O HbH solar cells, it was necessary to improve the interface at the heterojunction as well as reduce the series resistance and increase the parallel resistance of the HbH solar cells. The effect of the inserted n-oxide semiconductor thin film on the obtainable photovoltaic properties was investigated in the Cu_2O-based HbH solar cells by inserting various kinds of n-oxide semiconductor thin films prepared under various deposition conditions using a pulsed laser deposition (PLD) method. Although either a nondoped ZnO or Ga_2O_3 thin film deposited at room temperature by PLD is suitable as the n-oxide semiconductor layer, an amorphous Ga_2O_3 thin film with a high resistivity was found to be the most suitable oxide. The improvement of the p–n junction, as seen in the Ga_2O_3/Cu_2O heterojunction, could be achieved by decreasing the defect levels at the interface, which decreases not only the recombination associated with defects at the interface between the Ga_2O_3 and Cu_2O, but also the conduction band discontinuity. We have achieved a maximum conversion efficiency of 5.38% in an AZO/Ga_2O_3/Cu_2O heterojunction solar cell fabricated by depositing a Ga_2O_3 thin film on a Cu_2O sheet with a resistivity on the order of $10^2\ \Omega$ cm.

Keywords: Cu_2O; Hybrid heterojunction solar cell; Thin film; Oxide semiconductor; AZO

1. Cu_2O-based hybrid heterojunction solar cells

Recently, oxide semiconductor heterojunction solar cells have been extensively studied using polycrystalline p-type cuprous oxide (Cu_2O) prepared by various deposition methods on thermally oxidized cupper sheets (Minami et al., 2004; Mittiga et al., 2006; Minami et al., 2013a). Although low cost and nontoxic Cu_2O, a semiconductor with a direct energy gap of 2.1 eV, has long attracted much interest for solar cell applications, it has been very difficult to achieve a high-energy conversion efficiency in solar cells

* Corresponding author.
E-mail address: minami@neptune.kanazawa-it.ac.jp (T. Minami).

http://dx.doi.org/10.1016/j.solener.2014.03.036
0038-092X/

fabricated using this material as the active layer, because Cu_2O is intrinsically a p-type semiconductor and the surface of Cu_2O is chemically unstable since cupric oxide (CuO) is more stable than Cu_2O at temperatures below about 400 °C (Olsen et al., 1982; Rakhshani, 1986; Fujinaka and Berezin, 1983; Sears et al., 1983). Recently, the preparation of n-type Cu_2O films by electrodeposition from an aqueous solution as well as the fabrication of thin-film p–n junction Cu_2O solar cells also using this deposition method have been reported (McShane et al., 2010; Shiu et al., 2011; Kramm et al., 2012; McShane and Choi, 2012). For example, McShane and Choi (2012) obtained a conversion efficiency of 1.06% was in a p–n junction Cu_2O thin-film solar cell, which is low in comparison to the theoretical energy conversion efficiency of a Cu_2O solar cell that is as high as 20% (Rakhshani, 1986). Since fabricating Cu_2O p–n homojunction solar cells has proven to be a problem due to the difficulty of preparing n-type Cu_2O, there have been many reports on various p–n heterojunction solar cells fabricated using p-type Cu_2O as the active layer (Olsen et al., 1979; Herion et al., 1980; Papadimitriou et al., 1981; Iwanowski and Trivich, 1986; Rai, 1988; Briskman, 1992; Suehiro et al., 2001). Minami et al. (2004) reported that conversion efficiencies over 1% were obtained in n-type oxide semiconductor/p-Cu_2O hybrid heterojunction (HbH) solar cells fabricated by depositing transparent conducting oxide (TCO) thin films on thermally oxidized polycrystalline p-Cu_2O sheets. The TCO thin films such as Al- or Ga-doped ZnO (AZO or GZO), which also act as a transparent electrode, and the oxide semiconductor thin films such as ZnO and multicomponent oxides were prepared using various physical deposition techniques such as a pulsed laser deposition (PLD), radio frequency magnetron sputtering deposition and vacuum arc plasma evaporation methods (Minami et al., 2004; Minami, 2005; Tanaka et al., 2004; Tanaka et al., 2005; Minami et al., 2006). In addition to TCO/Cu_2O HbH solar cells, TCO/n-type oxide semiconductor/p-Cu_2O HbH solar cells were fabricated by inserting an n-type oxide semiconductor thin film as a buffer layer between the TCO electrode and the Cu_2O sheet (Miyata et al., 2006). It also has been reported that the obtained photovoltaic properties in n-oxide semiconductor/p-Cu_2O HbH solar cells were considerably dependent on the kind of deposition method used for preparing the oxide semiconductor thin films (Tanaka et al., 2005; Minami et al., 2006, 2013a; Nishi et al., 2012a). Mittiga et al. (2006) reported a conversion efficiency of 2.01% obtained in a Cu_2O-based HbH solar cell with an MgF_2/indium-tin-oxide (ITO)/ZnO/Cu_2O/Cu structure that was fabricated by depositing a ZnO thin film on thermally oxidized polycrystalline p-Cu_2O sheets using an ion beam sputtering method. In addition to Cu_2O-based HbH solar cells, Izaki et al. (2007) reported that a conversion efficiency of 1.28% was obtained in an n-oxide semiconductor/p-Cu_2O thin-film heterojunction (TFH) solar cell with an F-doped SnO_2 (FTO)/ZnO/Cu_2O/Au structure fabricated by depositing first a ZnO thin film followed by a Cu_2O film onto FTO-coated glass substrates using electrodeposition from an aqueous solution. Recently, Fujimoto et al. (2013) also reported that a conversion efficiency of 1.43% was obtained in an n-oxide semiconductor/p-Cu_2O TFH solar cell fabricated with the same structure as described above using electrodeposition from a pH-adjusted electrolyte consisting of LiOH.

Minami et al. (2011) reported that a TCO/n-oxide semiconductor/p-type Cu_2O HbH solar cell with a conversion efficiency of 3.83% could be fabricated by inserting a thin nondoped ZnO film between a transparent AZO electrode and the front surface of polycrystalline Cu_2O sheets that had been prepared by a thermal oxidization of copper sheets. 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 and low temperature deposition technique on high quality polycrystalline Cu_2O sheets (Nishi et al., 2011, 2012b, 2013; Minami et al., 2013b). In addition, Minami et al. (2013c) reported recently that a gallium oxide (Ga_2O_3) thin film and various Ga_2O_3-based multicomponent oxides are suitable for the n-oxide semiconductor layer of AZO/n-oxide semiconductor/p-Cu_2O HbH solar cells. A conversion efficiency and an open circuit voltage over 5% and 0.8 V, respectively, were obtained in an AZO/n-oxide semiconductor/Cu_2O HbH solar cell fabricated with either an amorphous Ga_2O_3 or a Ga_2O_3-based multicomponent oxide thin film as the n-oxide semiconductor layer (Minami et al., 2013d). The above described improvements of photovoltaic properties are attributed mainly to a decrease of the height of the conduction band discontinuity resulting from the difference in electron affinity between the oxide semiconductor thin film and the Cu_2O sheet used in the heterojunction (Minami et al., 2013a,c,d). In a similar manner, Lee et al. (2013) recently reported that a conversion efficiency of 2.65% was obtained in a Cu_2O-based TFH solar cell with an AZO/amorphous ZnO–SnO_2 (a-ZTO) multi-component oxide/Cu_2O/Au structure fabricated by using an atomic layer deposition to place an ultrathin a-ZTO thin film onto a Cu_2O film that had been deposited previously on a Au-coated silica substrate using electrodeposition from an aqueous solution. It should be noted that the above reported improvements of obtainable photovoltaic properties in Cu_2O-based TFH solar cells have yet to produce results comparable to those found in Cu_2O-based HbH solar cells, which may be attributable to the difference of crystallinity between the Cu_2O thin films and Cu_2O sheets.

This paper presents the current state and prospects of achieving higher conversion efficiency Cu_2O-based HbH solar cells fabricated using Cu_2O sheets prepared by thermally oxidizing copper sheets. The effect of inserting an n-type metal oxide semiconductor thin-film layer on the obtainable photovoltaic properties in Cu_2O-based HbH