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$Cu(In,Ga)Se_2$ thin film solar cells with solution processed silver nanowire composite window layers: Buffer/window junctions and their effects

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ABSTRACT

We quantitatively and analytically investigate the properties of buffer/window junctions and their effects on the energy band alignment and the current-voltage characteristics of $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells with solution processed silver nanowire (AgNW) composite window layers. AgNWs are generally embedded in a moderately conductive matrix layer to ensure lateral collection efficiency of charge carriers photogenerated in the lateral gaps present between AgNWs. Studies on the junctions between a buffer and AgNW-composite window layers and their effects on the performances of CIGS thin film solar cells have seldom been addressed. Here, we show that solution processed AgNW-composite window layers could induce defect states at the buffer/window interface, resulting in poor energy band alignment impeding carrier transport in the solar cells. On the basis of our analysis, we suggest an analytical expression of $\frac{n_{matrix}}{D_i^2} \geq \frac{3.46 \times 10^{-5}}{\varepsilon}$ cm to avoid losses in the power conversion efficiency of the solar cells. n_{matrix} is the carrier concentration in a matrix layer embedding AgNWs, D_i is the negative defect density at the buffer/window interface, and ε is the relative dielectric constant of the matrix layer embedding AgNWs.

1. Introduction

Most research efforts for the realization of low cost $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells have been dedicated to the development of non-vacuum processing methods for the preparation of CIGS absorber layers [1–8]. However, recently, research interest on low-cost solution processed silver nanowire (AgNW) based window layers to replace a vacuum processed i-ZnO/ZnO:Al window layer has been also increased to further reduce the cost of producing CIGS photovoltaic modules [9–17]. Lee et al. first demonstrated AgNW mesh transparent electrodes applicable to thin film solar cells [18]. Chung et al. suggested the necessity of a moderately conductive metal oxide matrix layer filling the lateral gaps present between AgNW networks for the AgNW-based window layer to be properly incorporated into CIGS thin film solar cells [9]. Since the aforementioned reports, additional studies have followed on alternative materials, processing methods and stacking structures for matrix layers embedding AgNWs in CIGS solar cells [10–16].

Some CIGS devices presented in the aforementioned reports showed a crossover between dark and light current [10] or kinks causing a significant loss in fill factor (*FF*) [11,12,17] for certain materials or processing methods for matrix layers embedding AgNWs. Therefore, for these solution processed AgNW-composites, which are composed of a matrix layer embedding AgNWs, to perfectly replace and/or achieve superior performance to a sputter deposited i-ZnO/ZnO:Al window layer, a deep understanding of the effects of the junction properties between a buffer layer and AgNW-composite window layers on the performance of CIGS solar cells is necessary. Here, we investigate the effects of the junction properties, including interfacial defects at the CdS/AgNW-composite and electrical properties of the AgNW-composite on the energy band alignment and current density-voltage (*J-V*) characteristics of CIGS solar cells.

2. Device fabrication and characterization

For the study of the effects of the buffer/AgNW-composite junction on the performance of CIGS thin film solar cells, two type of window layers have been applied the onto the structure of CdS(~50 nm)/CIGS (~2 μm)Mo(~1 μm)/soda-lime glass(~1.1 mm). One is a sputtered i-

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ZnO/ZnO:Al window layer, the other is an AgNW–ITO-np window layer. The Mo bottom electrodes were prepared by direct-current sputtering, the CIGS absorber layers by hydrazine solution processing, and the CdS buffer by chemical bath deposition. AgNW-composite window layers, composed of indium tin oxide-nanoparticles (ITO-nps) embedding AgNWs, were prepared by successive spin coating of ethanol-based 0.5% AgNW dispersion solutions (Sigma Aldrich) at a spin speed of 1000 rpm for 30 s, and 30 wt% ITO-np dispersion solutions (Sigma Aldrich) at a spin speed of 2000 rpm for 30 s. Thermal annealing was followed to dry solvent out at 100 °C a few minutes on a hot plate. The diameter and length of AgNWs were approximately 115 nm and 20–50 µm. More detailed procedures can be found elsewhere [7,19]. The composite will be denoted as AgNW-composite or AgNW–ITO-np in this manuscript. Top metal contact grids (Ni/Al) were evaporated onto the window layers. To test reproducibility of J-Vs of devices with two types of window layers, we have repeated the fabrication of samples without any intentional change in the processing steps. After completing CdS, samples were randomly assigned for two different window layers.

A cross-sectional image of a fabricated CIGS device was obtained using a scanning electron microscope. The *J-V* characteristics of CIGS solar cells were measured under a red-light illumination condition and a white-light illumination condition (100 mW/cm^2, AM1.5G). The red-light condition was created by placing a 700 nm long-pass filter onto the devices under the white-light illumination as shown in Fig. 1. External quantum efficiencies (*EQEs*) were measured with a light intensity of approximately 1 mW/cm^2. Various forward bias values ranging from 0 V to 0.35 V were also used during the measurement of *EQEs*.

3. Barrier of photocurrent in CIGS solar cells

S-shaped kinked *J-V* curves are due to a substantial decrease of photocurrent (J_{ph}) in a certain forward bias region which causes a loss in mainly FF. Extremely strong kink can also cause a loss in short-circuit current density (J_{SC}) and open circuit voltage (V_{OC}). This kink originates from the spike-type energy band alignment of CIGS solar cells in which the electron affinity (χ_{CIGS}) of the CIGS layer is greater than that (χ_{buffer}) of an adjacent buffer layer as shown in Fig. 2 [20–22]. Notably, the spike-type energy band alignment is beneficial for achieving high efficiency CIGS solar cells.

In spike-type CIGS solar cells, for photogenerated electrons in a CIGS layer to convert to J_{ph}, the electrons must surmount the barrier ($\Delta E_C = \chi_{CIGS} - \chi_{buffer}$) mainly by means of thermionic emission. As long as the thermionic emission current density (J_{TE}) is larger than the photogenerated current density (J_{gen}), a decrease in the value of J_{ph} will not be observed. Otherwise, a substantial fraction of photogenerated electrons cannot jump over and, thus, does not contribute to the J_{ph} value, inducing the kinked *J-V* curves [22].

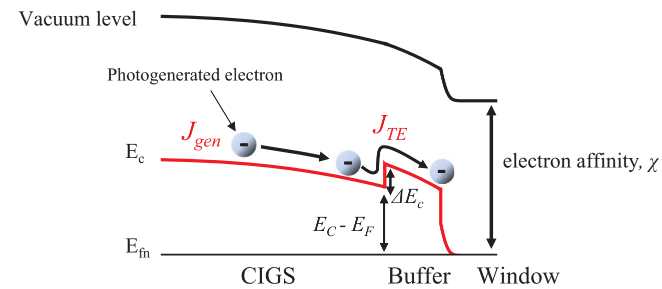

Fig. 2. The transport of photogenerated electrons under the spike-type energy band alignment of CIGS thin film solar cells. Once thermionic emission current density (J_{TE}) is lower than photogenerated current density (J_{gen}), a kink, decrease in photocurrent in at certain bias region, will be observed.

Thermionic emission current density (J_{TE}) is described as follows:

$$J_{TE} \propto n_o \exp\left(-\frac{\Delta E_C}{kT}\right) = N_C \exp\left(-\frac{E_C - E_F}{kT}\right)\exp\left(-\frac{\Delta E_C}{kT}\right) \tag{1}$$

where n_o is the conduction electron concentration in the CIGS layer near the CIGS/buffer interface, exp(-ΔE_C/kT) is the probability of jumping over the barrier (ΔE_C) by means of thermionic emission, k is the Boltzmann constant, T is absolute temperature, N_C is the effective density of states in the conduction band of the CIGS layer, and E_C - E_F is the difference between the conduction band minimum (E_C) and the Fermi level (E_F) in the CIGS layer at the CIGS/buffer interface. E_C - E_F is the only variable in Eq. (1) that is dependent on the applied bias and the defect states present in CIGS solar cells. These defects and applied forward bias can cause less energy band bending in the CIGS layer, which in turn increase the value of E_C - E_F. Therefore, highly defective CIGS solar cells under forward bias have a sufficiently large E_C - E_F to limit the J_{TE} value and consequently make it less than the J_{gen} value, resulting in a loss of efficiency (*Eff*) of CIGS solar cells.

4. Results and discussion

4.1. Characteristics of the fabricated CIGS solar cells

AgNW-composite window layers were composed of a network of AgNWs embedded in an ITO-np matrix with a thickness of ~700 nm as shown in Fig. 3. In this AgNW-composite, the AgNW network provides long-range lateral electrical current paths, and the matrix layer is responsible for providing electrical current paths in the spaces present between AgNWs. The sheet resistance of the matrix layer, ITO-np in our case, is required to be less than 1M Ω/sq to 1G Ω/sq, depending on the

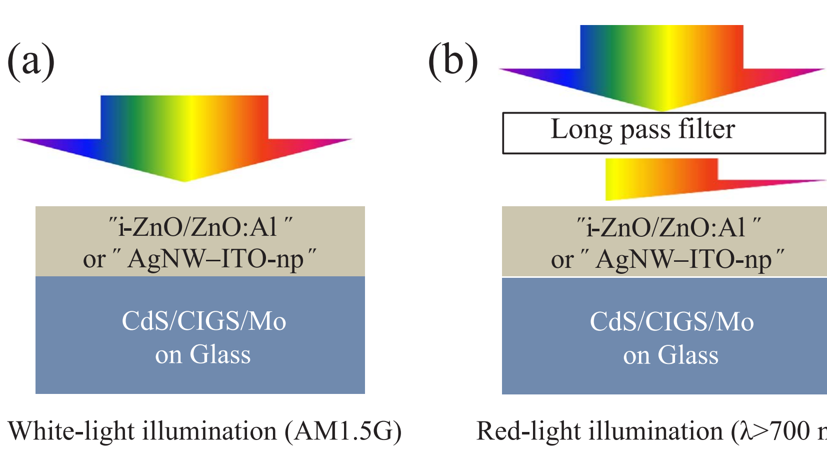

Fig. 1. (a) White-light illumination condition (b) A red-light illumination condition was created by placing a 700 nm long-pass filter onto the devices under white-light.