

Investigation of Sputtering Damage around pn Interfaces of Cu(In,Ga)Se₂ Solar Cells by Impedance Spectroscopy

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ABSTRACT

The application of impedance spectroscopy (IS) analytical theory to the characterization of the *pn*-interface of Cu(In,Ga)Se₂ (CIGS)-based solar cells was investigated with a focus on directly observing the sputtering damage during deposition of an *n*-layer. We develop an equivalent circuit of the CIGS solar cell involving series and parallel resistances and a “capacitance-like element,” called a constant phase element (CPE), around the *n*-layer/*p*-CIGS interface. The CPE index of the impedance is shown to reflect the quality of the *n*-layer/*p*-CIGS interface in terms of the sputtering damage and defects of the heterojunction. These results demonstrate the possibility of applying IS practically as a simple method for characterizing the sputtering damage around *pn*-interfaces in semiconductor devices.

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1. Introduction

Chalcopyrite semiconductors such as Cu(In,Ga)Se₂ (CIGS) are ideal for fabricating thin-film solar cells because of their stability, high conversion efficiency, and relatively low cost [1]. In fact, several companies have started commercial manufacturing of such cells. Despite these advantages, however, the electrical properties of CIGS solar cells are yet to be comprehensively clarified because these solar cells exhibit a complex composite structure that consists of stacked layers of several materials: a transparency conductive oxide (TCO)/*n*-type semiconductor/*p*-type CIGS/Mo back contact/soda-lime glass (SLG) substrate [1].

Currently, most researchers and companies tend to use CdS as an *n*-type layer [2,3]. However, CdS has several disadvantages including the Cd toxicity classification, the need for a non-vacuum chemical bath deposition (CBD) process, and absorption of blue light due to the small bandgap energy. Therefore, several groups have proposed alternative *n*-type layers that can be fabricated using simple and conventional dry physical processes such as RF sputtering [4]. We have noted in some earlier reports that amorphous Zn-Sn-O (ZTO) [5–9] deposited by RF sputtering is a suitable candidate for the *n*-type layer because the material is inexpensive and less hazardous [10,11]. Moreover, using an amorphous film may also improve the solar cell properties [12] because there are fewer

grain boundaries, which are carrier recombination sites, than in polycrystalline films.

One serious problem with sputtering techniques is the sputtering damage at the surface of the *p*-type CIGS layer during deposition of the *n*-type layer. Sputtering is a simple and convenient technique for depositing thin films, but the substrate tends to be bombarded by the sputtering plasma; sputtering damage induces defects as a result of collisions between the high-energy ions and the substrate. In particular, since a large electric field is employed and a depletion layer is formed in the *pn*-junction, the solar cell performance is more sensitive to sputtering damage around the *pn*-interface than at other interfaces. However, sputtering damage at a *pn*-interface is difficult to investigate without destroying the cell.

Impedance spectroscopy (IS) analytic theory is increasingly being applied as an analytical tool in chemical material research [13–15] and has been shown to be invaluable for studies of polycrystalline semiconductor materials and devices such as CIGS- [16–20], CdTe- [21,22] and Cu₂ZnSnS₄- [23] related solar cells. We have previously investigated the defects at the CdS/CIGS *pn*-interface by examining the constant phase element (CPE) index through IS. The CPE reflects the depletion layer thickness and the uniformity and quality of the *pn*-interface [24]. In particular, the CPE-*p* value, which is an index of the impedance of the CPE, expresses the quality around the CdS/CIGS interface in terms of defect existence and inhomogeneity of the heterojunction. Our previous result showed that IS is a simple method for characterizing the heterogeneity around a *pn*-interface, and therefore, IS may be a promising tool for directly observing and examining the sputtering damage. In this paper, the sputtering damage around

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the *pn*-interface in a CIGS solar cell is investigated by IS. We first investigate the relationship between the impedance properties and equivalent circuit of the CIGS solar cells through observation of impedance variations under dark conditions. We then critically discuss the application of IS as a simple method for characterizing the heterogeneity around the *pn*-interface in CIGS solar cells with different materials and deposition techniques of the *n*-type layer.

2. Experimental

Polycrystalline *p*-type CIGS films approximately 2.0 μm thick were prepared by a conventional three-stage process on a Mo-coated soda-lime glass substrate. Several different *n*-type layers such as ZnO/CdS or ZTO were deposited on CIGS films. Conventional *n*-type CdS films (~ 50 nm) were formed by CBD using aqueous solutions of 0.001-M cadmium iodide (CdI_2) and 0.5-M thiourea ($\text{CH}_4\text{N}_2\text{S}$) as precursors with 0.013-M ammonia (NH_4) as the complexing agents at a bath temperature of 80 $^\circ\text{C}$. Subsequently, *n*-type ZnO layers (~ 50 nm) were deposited by RF sputtering. Instead of ZnO/CdS layers, the *n*-type ZTO thin films (~ 100 nm) were deposited by RF sputtering using a ZTO ($\text{ZnO}:\text{SnO}_2 = 6.5:3.5$ at%) target. Finally, a window layer was deposited (~ 600 nm) on the *pn*-junction by RF sputtering using indium tin oxide (ITO). Typical efficiencies of the solar cells are about 6% (with a CdS layer) or less than 3% (with a ZTO layer) under AM 1.5 and 100 mW/cm^2 illumination.

These various *pn*-interfaces were investigated using IS performed with an NF FRA5087 frequency response analyzer with frequencies ranging from 10 Hz to 1 MHz. For all the measurements, a 10-mV AC signal was applied to the device without DC bias under dark conditions at room temperature. The obtained data were fitted using the Z-plot software.

3. Results and Discussion

An equivalent circuit of a simple heterojunction generally consists of three elements: a series resistance (R_s), a parallel circuit with a parallel resistance (R_p), and a constant capacitance (C) or “capacitance-like element,” i.e., the CPE. The CPE is an impedance that displays non-ideal, frequency-dependent properties and a constant phase over the entire frequency range. The non-ideal behavior generally originates from the current density distribution due to the material inhomogeneity. The impedance of the CPE (Z_{CPE}) is defined by the CPE index p and constant T as follows;

$$Z_{\text{CPE}} = \frac{1}{(j\omega)^p T}, \quad (1)$$

where j is the imaginary unit, and ω is the frequency. A typical band diagram and the proposed equivalent circuit model of the CIGS solar cell for the impedance analysis are shown in Fig. 1. Since the surface of the CIGS layer has a large number of defects and grains, the *n*-layer/CIGS interface represents a “non-ideal capacitance-like element” and resistance. The TCO/*n*-layer interface, however, is flat and uniform, with a smaller number of grains compared with the *n*-layer/CIGS interface. Therefore, this interface represents an “ideal capacitance” and resistance. In general, the equivalent circuit of a layered-structure CIGS solar cell has a resistance component of several thin-film layers and an R_p -C or R_p -CPE parallel component of around several interfaces. However, the C or CPE values around the TCO/*n*-layer and *n*-layer/*p*-CIGS interfaces tend to be larger than those of the other layers and interfaces because the valence and conduction bands around these interfaces are bent by the existence of a space charge region, as shown in Fig. 1(a). Therefore, the C or CPE elements at the other interfaces can be neglected. As a result, the *n*-layer/*p*-CIGS interface (CdS/CIGS or ZTO/CIGS) is described by R_j -CPE $_j$ parallel components; there are many defects and grain

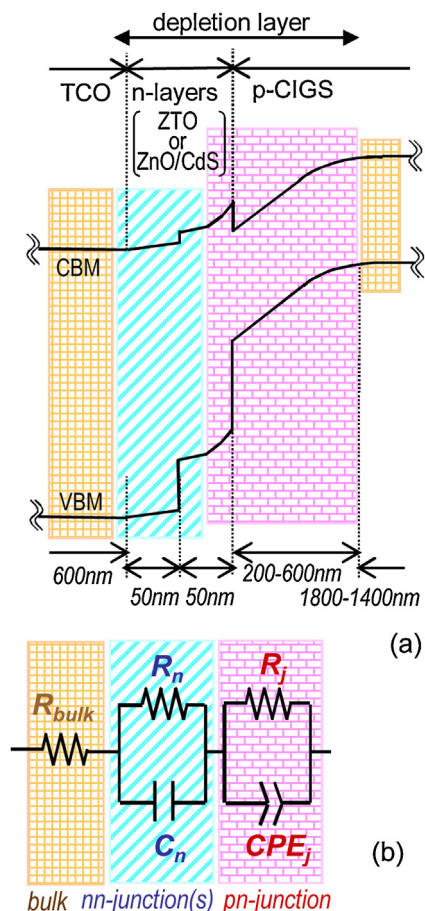


Fig. 1. (a) Representative band alignment of the CIGS solar cells and (b) proposed equivalent circuit models of the CIGS solar cells for IS.

boundaries in the nonuniform CIGS layer near this interface. In contrast, the lack of a depletion layer around the TCO/*n*-layer interface (TCO/ZnO/CdS or TCO/ZTO) means the interface can be described by R_n - C_n parallel components. In fact, these layers have a uniform surface and are less affected by the space charge region or depletion layer. Finally, the resistance values of several layers, especially TCO, Mo, and the CIGS bulk layers, are summarized as R_{bulk} .

Nyquist plots of the impedance of the ZTO-CIGS solar cells as a function of the oxygen partial pressure, $\text{O}_2/(\text{O}_2 + \text{Ar})$, during RF sputtering of the ZTO layer are shown in Fig. 2(a). The horizontal (real) axis represents the resistance of the solar cell, and the vertical (imaginary) axis represents the capacitance. All of the Nyquist plots draw double semicircles with their centers located below the imaginary axis. A simulated plot for an oxygen partial pressure of 5.0% is shown by the dotted line. The radii of the semicircles tend to decrease with increasing oxygen partial pressure. To distinguish the two components, Bode plots of the impedance are shown in Fig. 2(b). There are two critical frequencies of the order of 10^3 Hz (due to the TCO/*n*-layer interface) and 10^5 Hz (due to the *n*-layer/CIGS interface). These results reflect the inhomogeneity around the ZTO/CIGS interface (e.g., defects, grain boundaries, Zn or Sn diffusion into the CIGS layer) and indicate that there are probably fewer defects and inhomogeneities around the TCO/ZTO interface.

The sputtering-related damage around the ZTO/CIGS interface was investigated using the CPE- p values with other *n*-layer materials. The obtained values of CPE- p as a function of the oxygen partial pressure during ZTO sputtering are shown in Fig. 3. In the case of the impedance model of a dye-sensitized solar cell,

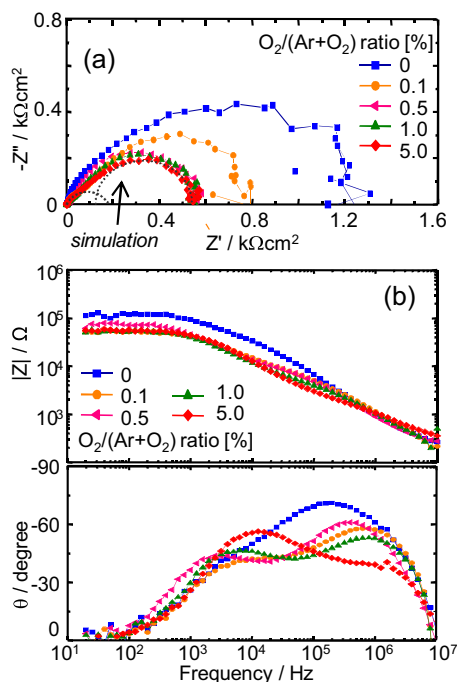


Fig. 2. (a) Nyquist plots and (b) Bode plots (amplitude $|Z|$ and phase θ) of the impedance of the ZTO-CIGS solar cells as a function of the oxygen partial pressure during RF sputtering of the ZTO layer.

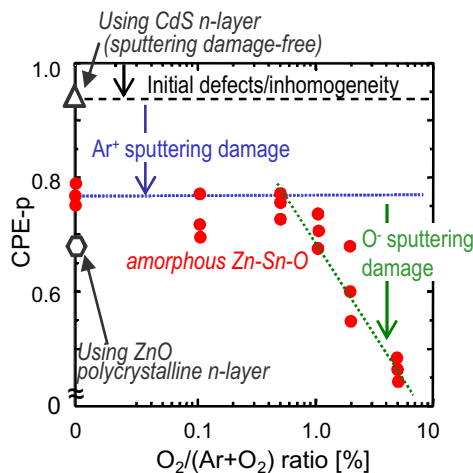


Fig. 3. The CPE- p of the CIGS solar cells as a function of the oxygen partial pressure during RF sputtering of the ZTO layer for several different n -layer solar cells.

the CPE is often used in place of a capacitance-like element to compensate for the inhomogeneity and defects in the TiO_2/dye interface. The CPE- p value, therefore, reflects the ideality of the pn -interface in semiconductor-based solar cells. The CPE- p value is equal to 1 when an ideal capacitor without sputtering damage or defects is obtained and is equal to 0 when a capacitor element cannot be formed because there are too many defects or the pn -interface has a large roughness [24]. In our case, the CPE- p value is about 0.94 (open triangle in Fig. 3) for the n -layer obtained from a conventional CdS buffer grown by the sputtering-damage-free CBD process (a $\text{TOC}/\text{ZnO}/\text{CdS}/\text{CIGS}/\text{Mo}/\text{SLG}$ structure). This value reflects the initial defects around the pn -interface, such as the grain boundaries, vacancies, and point defects [24].

To avoid employing the complex CBD wet process and toxic CdS deposition, polycrystalline ZnO was deposited directly on CIGS layer as an alternative n -type layer by RF sputtering using only Ar

gas to fabricate a $\text{TCO}/\text{ZnO}/\text{CIGS}/\text{Mo}/\text{SLG}$ solar cell structure. Note that TCO/ZnO is described by $R_n\text{--}C_n$ and ZnO/CIGS is described by $R_j\text{--}CPE_j$. The CPE- p value of the ZnO -CIGS solar cell is also shown in Fig. 3 by the open hexagon. Compared to the damage-free CdS-CIGS solar cell, the CPE- p value of the ZnO -CIGS solar cell was smaller (0.67) and reflects the pn -interface properties well, especially in terms of both sputtering damage to the CIGS and the film quality of the polycrystalline ZnO.

To improve the quality of the n -layer, amorphous ZTO was deposited by RF sputtering using only Ar gas to fabricate $\text{TCO}/\text{ZTO}/\text{CIGS}/\text{Mo}/\text{SLG}$ solar cell structures. The CPE- p values (0.75–0.80) of the ZTO-CIGS solar cell (blue squares; Fig. 3) are higher than that of the ZnO -CIGS solar cell (0.67), indicating that the number of grain boundaries and point defects has been reduced by adopting an amorphous n -layer. However, there is still some sputtering damage, and a modified sputtering technique to minimize this damage will be needed if ZTO is used as the n -layer of CIGS solar cells. In addition, oxygen gas is commonly supplied during sputtering to minimize O atom desorption [25] from the ZTO film. In this case, the CPE- p value was relatively constant with increasing oxygen partial pressure from 0 to 1.0% but decreased from 0.75 to 0.45 with increasing oxygen partial pressure from 1.0 to 5%. This implies that a significant number of defects and/or grain boundaries were introduced by not only Ar^+ but also O^- ion bombardment during sputtering for $\text{O}_2/(\text{O}_2 + \text{Ar}) > 1.0\%$.

These results imply that the solar cell quality, especially around the pn -interface, is reflected in the CPE- p value. Further in-depth investigations are necessary to obtain a complete picture of the proper equivalent circuit for CIGS solar cells and perform measurements under illumination and/or applied DC bias conditions. The results of this research indicate that IS is an appropriate method for characterizing the sputtering damage to the heterogeneity around the pn -interfaces in semiconductor devices.

4. Conclusions

An analytical model of IS was applied to investigate CIGS solar cells and the sputtering damage around the pn -interface deposited by RF sputtering. All of the CPE- p values for the CIGS solar cells studied here using several different n -layers deposited by RF sputtering were smaller than that of a CIGS solar cell with a conventional CdS n -layer deposited with a damage-free CBD process. Moreover, the CPE- p value decreased with increasing oxygen partial pressure during ZTO layer deposition due to O^- sputtering damage. The change in the CPE- p value confirms that the solar cell quality, especially around the pn -interface, can be determined using IS. Therefore, we consider IS to be an appropriate technique for conveniently observing the behavior of the depletion layer around the pn -interface under dark conditions without bias.

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