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Effect of annealing treatment on CdS/CIGS thin film solar cells depending on different CdS deposition temperatures

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ABSTRACT

$Cu(In,Ga)Se_2$ (CIGS) is one of the most promising light-absorbing materials. The high-efficiency CIGS solar cells normally have included a CdS buffer layer deposited by a chemical bath deposition (CBD) technique. To measure the thickness of the CBD–CdS, the quartz crystal microbalance (QCM) system was introduced in this study. Using this system, the effect of the CdS thickness (reaction temperature versus reaction time), the impact of the reaction rate with constant thickness (reaction temperature versus thickness), and the characteristics of the CdS annealing effect were investigated. When the reaction time was fixed, the efficiency was affected by the thickness of CdS. Nevertheless, when the thickness of CdS was fixed in the thickness of the best efficiency, the reaction temperature did not affect it. By annealing the CdS film, the cell performance was improved. In the case of the sample with a low reaction temperature (60 °C), the efficiency improvement was better than with different reaction temperatures because impurity of CdS was reduced more after the heat treatment. On the other hand, according to the XPS spectra, CdS with high temperatures had less impurity, so the annealing process had less impact on the efficiency.

1. Introduction

In recent decades, solar cells have been the subject of various enquiries in the interest of high efficiency and low cost [1]. Especially, $Cu(InGa)Se_2$ (CIGS) is highlighted as being one of the most promising semiconductors owing to low price, high absorption coefficient, tunable band gap, low radiation damage, and long-term stability [1,2]. Until now, the CIGS solar cell shows the highest efficiency of 21.7% in ZSW [3] and is considered to be contestable to the crystalline silicon solar cell. As a CIGS has a direct band gap, it can be produced with much thinner layers than those of silicon-based PV technology, resulting in less material use and energy expense [4].

The highest efficiencies for thin film solar cells based on a $Cu(In,Ga)Se_2$ (CIGS) need a buffer layer [5]. The buffer layers on CIGS absorbers are used to enhance the lattice match between the absorber and the window; the layers preserve the CIGS surface from ion loss during ZnO/ZnO:Al sputtering [6]. Usually, CdS, ZnS, ZnSe, and In_2S_3 are used as buffer materials in CIGS solar cells, but the best efficiency has been observed with the CdS buffer layer [7]. These materials can be deposited by the methods such as chemical bath deposition (CBD), evaporation, atomic layer deposition (ALD), metal organic chemical vapor deposition (MOCVD), electro-deposition (ED), sputtering, and ion layer gas reaction (ILGAR) [8,9]. Among these methods, CBD is known to be a very simple technique with low price and low temperature, adjusting to a large area. Additionally, the films can be deposited on diverse substrates with the CBD technique and the thickness of the films can easily be controlled by deposition time variation [10].

The CdS buffer layer deposited by the CBD process is very appealing because of high solar conversion efficiency and high comparative photoconductivity [11,12]. CdS is a direct band gap semiconductor, on account of its intermediate band gap between CIGS and TCO, high absorption coefficient, low resistivity, and easy ohmic contact [13]. CdS has a band gap of approximately 2.4 eV, which is appropriate for accepting a good portion of the incident light by the p-type CIGS. In addition to having high optical transmission, CdS is also apt to be an n-type semiconductor. Therefore, it is presumed that CdS helps in the formation of the hetero-junction along with the transparent conducting oxide layer [14].

The CBD–CdS is based on the cadmium and sulfide ions in the solution. Chemical deposition can be attained generally via two methods: (i) a homogeneous reaction and (ii) a heterogeneous reaction [15]. The first stage in the homogeneous deposition is the adhesion of the hydroxide to the substrate. Next, $Cd(OH)_2$ forms an

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initial deposit of CdS clusters. During the reaction, extra $Cd(OH)_2$, CdS, and partially changed hydroxide diffuse to the substrate. Finally, the CdS is formed with the produced S^{2-} ion and the $Cd(OH)_2$:

$$Cd^{2+}+2OH^- \rightarrow Cd(OH)_2$$

followed by

$$Cd(OH)_2+S^{2-} \rightarrow CdS+2OH^-$$

The synthesized CdS particles through this homogeneous reaction are attached on the substrate during the reaction.

On the other hand, the heterogeneous reaction occurs by sequential ionic reactions. The origin of this mechanism, demonstrated for CdS, is given by

$$Cd^{2+}+S^{2-} \rightarrow CdS$$

CdS should not precipitate in the solution but develop a film on the substrate [16].

Therefore, the homogeneous reaction shows a rough surface because the reaction rate is fast. Moreover, in the heterogeneous reaction, the surface is smooth due to the low rate of reaction [15,17].

In this study, the relationships between the reaction temperature, reaction time, and reaction rate were examined. Furthermore, to improve the efficiency of a CIGS solar cell, the CdS films on the CIGS were annealed in air.

2. Experimental section

Cadmium sulfate hydrate ($CdSO_4 \cdot xH_2O$, 99.999%, Aldrich), thiourea (NH_2CSNH_2, 99.0%, Aldrich), and ammonia solution (NH_3OH, 28.0–30.0%, Junsei) were purchased for the analytical reagents. All chemical substances were used as received, without additional refinement. Mo-covered soda lime glass was manufactured using a DC magnetron sputtering system that furnished a film thickness of approximately 1.1–1.2 μm. The CIGS absorber layers were grown by a three-stage process using the co-evaporation of In, Ga, Cu and Se. The substrate temperature during the growth was gauged by using a thermocouple in contact with the backside of the substrate. In the first stage, an $(In_{0.7},Ga_{0.3})_2Se_3$ layer (~1 μm) was grown by coevaporating the requisite for In, Ga, and Se on the Mo/glass substrates at 400 °C. In the second stage, Cu and Se were co-evaporated at 550 °C to grow a $(In,Ga)_2Se_3$ layer at 550 °C. The end of the second stage was established by gauging the substrate temperature decrease. At the point where substrate temperature dropped, the CIGS has somewhat Cu-poor organization, namely, $Cu/(In+Ga)<1$. After this alteration, further Cu was increased and the $Cu/(In+Ga)$ ratio was adapted as 1.3 after the second stage. Because only Cu and Se are furnished during the second stage, the surface area included a small quantity $Cu_{2-x}Se$. In the third stage, In, Ga, and Se elements were evaporated on the CIGS layer to transform Cu-rich film into Cu-poor. Finally, the sample was made cool in a Se air to prevent the re-evaporation of Se from the CIGS Layer [18].

To manufacture CIGS thin film solar cells, a CdS buffer layer was deposited onto CIGS films by chemical bath deposition (CBD) using $CdSO_4 \cdot xH_2O$(0.0015 M), NH_3(1.5 M) and a CH_4N_2S(0.05 M) aqueous solution. CBD–CdS buffer layers with a thickness of 60 nm were deposited at 60 °C, 80 °C, and 90 °C. The thickness of CdS was measured by the quartz crystal microbalance (QCM) system. The QCM used the resonant frequency of the quartz crystal resonator and was suitable for measuring the changes in mass. Also, simultaneous measurement of the resonant frequency made it possible to analyze the contribution of the changes in mass on the quartz crystal surface. The measured mass-change was converted to the thickness after the deposition, according to the following equation, where Δm is mass change, A_r is the surface area of an electrode ($=0.2\ cm^2$), μ is the elastic constant of crystal ($=2.947\times10^{11}$ g/cm·s^2), ρ is the density of the crystal ($=2.648$ g/cm^3), ΔF is the calculated frequency change, f_0 is the standard frequency ($=9$ MHz), Δt is the thickness of the thin film, and ρ_c is the density of the buffer material.

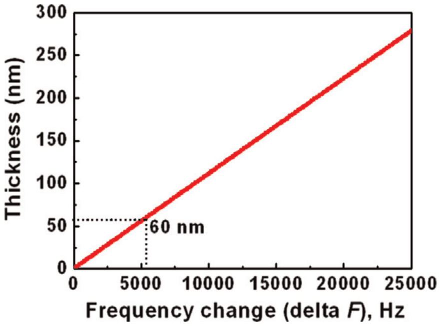

Fig. 1. Theoretically calculated frequency change(ΔF) versus thickness of the CdS.

$$\Delta m = \frac{A_r\sqrt{\mu\rho}}{2f_0^2}\Delta F \rightarrow \Delta t = \frac{\Delta m}{\rho_c \cdot A_r}$$

Additionally, the relations between ΔF and Δt are shown in Fig. 1.

Traditionally, in case of a CIGS solar cell with a CdS buffer, approximately 50 nm of CdS thickness showed the highest efficiency. Also, CBD–CdS were deposited by applying the same reaction time at 60 °C, 90 °C, which is on the basis of the response time in the deposited CdS (approximately 60 nm) at 80 °C.

After depositing the buffer layer, intrinsic and Al-doped ZnO (i-ZnO and ZnO:Al) window layers were deposited by radio-frequency (rf) magnetron sputtering. Finally, Al electrodes were deposited by thermal evaporation. The solar cells had no antireflection coating and the active area of the device was 0.44 cm^2.

The morphology, crystal structure and composition of the CdS layer were examined using the high-resolution scanning electron microscope (HRSEM, XL30SFEG Phillips Co., Holland at 10 kV), field emission scanning transmission electron microscope (FE-STEM; 200 kV; HD-2300 A), energy dispersive X-ray spectroscope (EDS, EDAX Genesis apex, accelerating voltage: 30 kV, collection time: 100 s with a standard-less method), and X-ray diffraction (XRD, Rigaku, D/MAX-2500) using a CuKα radiation source ($\lambda=1.5406$ Å). To obtain more information about the nanoparticles, high-resolution transmission electron microscopy (HRTEM; 200 kV; Philips F20 Tecnai) was also performed. The optical character of the obtained layer was studied using a UV spectrophotometer (UV–vis–NIR3101) in the wavelength range from 300 nm to 1300 nm.

To investigate the chemical information of the CdS films, X-ray photoemission spectroscopy (XPS, K-alpha) was measured. The doping concentration of the CIGS films was investigated by External Quantum Efficiency (EQE) analysis for the completed solar cells. The current–voltage (I–V) measurements were carried out using a solar simulator at AM-1.5 G illumination with a total irradiance of 100 mW cm^{-2}.

3. Results and discussion

As mentioned above in the Introduction, CdS can be attained through two methods: (i) a homogeneous reaction and (ii) a heterogeneous reaction. The homogeneous reaction is that the CdS