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Electrodeposition of $CuIn_{1-x}Ga_xSe_2$ solar cells with a periodically-textured surface for efficient light collection

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ABSTRACT

The photoresponse of $CuIn_{1-x}Ga_xSe_2$ (CIGS) solar cells is improved using a periodically-textured structure as an antireflection layer. The CIGS absorber layers were prepared by one-step electrodeposition from an aqueous solution containing 12 mM $CuSO_4$, 25 mM $In_2(SO_4)_3$, 28 mM $Ga_2(SO_4)_3$, and 25 mM SeO_2. The electrodeposited CIGS films exhibit the (112)-preferred orientation of the chalcopyrite structures and feature improved film stoichiometry after the selenization process. In addition, the lower bandgap value of 0.97 eV is caused by the discrepancy of the reduction potentials for each constituent, resulting in insufficient Ga content in the deposited films. Using self-assembled silica nanoparticles as the etching mask, periodically-textured structures can be easily formed on an indium tin oxide (ITO)-coated soda lime glass to achieve a low average reflection ($<10.5\%$) in a wide wavelength and incident angle range. With the periodic textured structures suppressing light reflections from the front surface, the photogenerated current in the semi-transparent CIGS solar cells made with transparent conducting electrodes is 1.82 times higher than they otherwise would be.

1. Introduction

In the past decade, $CuIn_{1-x}Ga_xSe_2$ (CIGS) thin-film technology has emerged as a promising candidate for the realization of cost-effective photovoltaic systems due to their unique properties including a large optical absorption coefficient, long-term reliability and low manufacturing costs [1]. A typical CIGS solar cell with surface absorption geometry is composed of a transparent window bilayer (undoped ZnO/Al doped ZnO, *i*:ZnO/ZnO:Al), a CdS buffer layer, a CIGS absorber layer and a Mo back contact. In these devices, the opaque properties of Mo electrodes will impede light hitting the back side of such cells. To overcome this issue, another modified structure of CIGS solar cells was fabricated with a transparent conducting oxide (TCO) back contact, known as a semi-transparent CIGS solar cell [2]. In addition, these devices could also be used in a multi-junction solar cell as a top cell to improve short wavelength absorption.

For solar cells fabricated without a light-trapping scheme (e.g., a $\lambda/4$-thick antireflection coating), the normal incidence of light will partially suffer from the Fresnel reflection at the air/semiconductor interface without contributing to the photogenerated current. In experiments, the performance of such single-layer antireflection coatings was affected by the refractive index and the thickness of the coating material. In addition, the corresponding minimum reflectance is localized within a narrow wavelength range [3]. In contrast, broadband antireflection coatings based upon periodic surface-relief structures provide an alternative to effectively suppress the amount of reflected light in a wide range of incident angles [4].

This study reports the fabrication and characterization of CIGS solar cells with a TCO back contact. The CIGS absorber layer was formed by electrodeposition, a simple, low cost,

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non-vacuum process which provides large deposition areas [5]. In experiments, different values of the reduction potentials for each constituent (Cu^{2+}, In^{3+}, Ga^{3+}, and SeO_3^{2-}) in the one-step electrodeopsition process caused only a small amount of Ga atoms to appear in the CIGS. Otherwise, a well-ordered self-assembled monolayer of silica nanoparticles was used as an etching mask to transfer a periodic nanostructure onto the front surface of the CIGS solar cells. As a result, the fabricated solar cells with a periodic textured surface exhibit improved photoresponse in short-circuit current density (J_{sc}).

2. Experimental

Fig. 1(a) shows the schematic diagram of a semi-transparent CIGS solar cell. The experimental setup for the one-step electrodeposition of CIGS consisted of a conventional three-electrode potentiostatic system with a saturated Ag/AgCl electrode as the reference electrode, while the Pt mesh was used as the counter electrode.

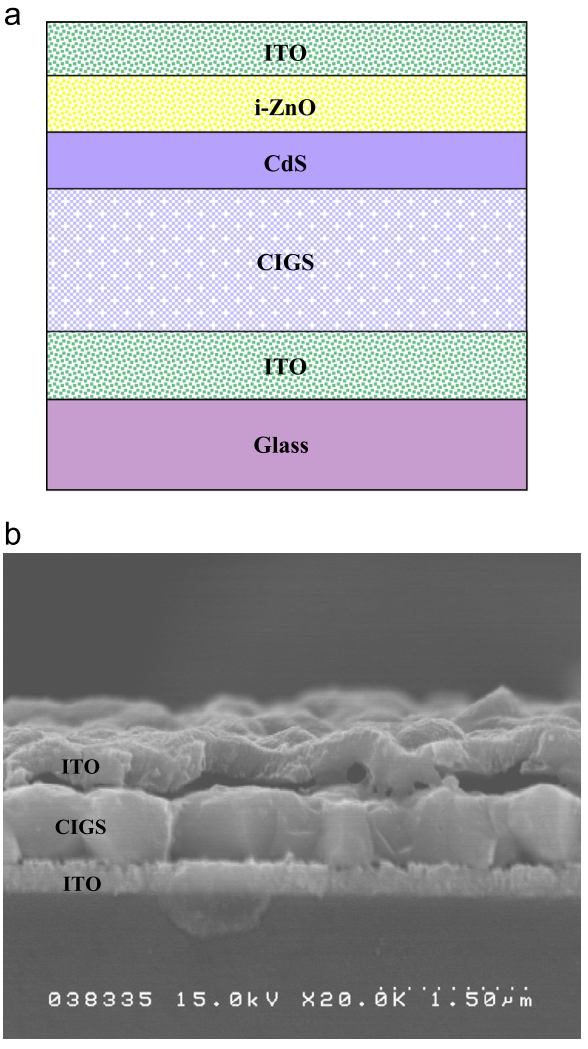

Fig. 1. (a) Schematic diagram of a semi-transparent CIGS solar cell. (b) Cross-sectional FE-SEM image of the completed CIGS solar cells.

A high transparency ($T > 95\%$ at 550 nm) indium tin oxide (ITO) with a sheet resistivity of 8 sq^{-1} was coated onto the soda lime glass (SLG) substrate by RF magnetron sputtering to act as the working electrode. The dimensions of the ITO coated substrates are 1 cm × 2 cm. These substrates were subsequently immersed in an aqueous electrolyte solution containing 12 mM $CuSO_4$, 25 mM $In_2(SO_4)_3$, 28 mM $Ga_2(SO_4)_3$ and 25 mM SeO_2. The pH value of the electrolyte was adjusted to 1.3 with sulfuric acid, and the deposition temperature was kept at 25 °C. Ten millimolar sodium dodecyl sulfate (SDS) was added to the growth solution to suppress the formation of hydrogen bubbles during the deposition, thus improving the film quality [6]. In experiments, a voltage of −0.6 V was applied to electrodeposit the CIGS films with a Se/(Cu+In+Ga) atomic ratio close to 1. To further optimize film stoichiometry, the electrodeposited films were thermally treated at 500 °C for 40 mins in a vacuum-sealed quartz tube containing the selenium powder. Afterward, the CdS buffer layer was coated onto the top of the CIGS by chemical bath deposition (CBD), and layered films of *i*:ZnO and ITO were subsequently deposited to terminate the device process flow. Fig. 1(b) presents a field-emission scanning electron microscopy (FE-SEM) (Hitachi S5000) image of the cross-section of the completed cells. These cells have an active area of 0.25 cm^2 for light absorption, and the thickness of the CIGS absorber layer is about 0.85 μm. A periodic surface-relief structure was used as the antireflection layer and was formed by nanolithography techniques with self-assembled nanoparticles used as the etching mask. It is known that periodic close-packaged structures can be spontaneously obtained from a monodisperse particle suspension due to the presence of a variety of dynamic interactions between these particles [7]. In experiments, the ITO layer was spin-coated with a monodisperse colloidal suspension of silica particles with a diameter of 500 nm (purchased from Thermo Fisher Scientific Inc.). Given good control of the surfactant (Triton X-100) mixed with methanol in the monodisperse suspensions and spin coating parameters, we can obtain a uniform distribution of highly-ordered monolayer silica nanoparticles, as shown in Fig. 2. The wafer was then etched by reactive ion etching (RIE) using Ar with the silica nanoparticle masks to form a periodic surface texturing structure. Fig. 2(b) shows the surface morphology of the ITO observed by atomic force microscopy (AFM) (DI Dimension-3100) with a scan area of 100 μm^2 following the removal of the silica nanoparticles. The respective root-mean-square roughness of the ITO films with and without a periodic textured surface is about 34.8 nm and 5.9 nm. This result indicates that the probability of light becoming trapped within the solar cells could be increased through the use of an adequately textured structure [8].

The structural and optical properties of the CIGS films were characterized by X-ray diffraction (XRD) (Bruker AXS D5005, CuKα) and cathodoluminescence (CL) (JEOL JSM-7001F). Energy dispersive X-ray spectroscopy (EDS) (Hitachi S-3000/Oxford EX-200) was used to analyze the film's compositions. Furthermore, the photovoltaic properties of the fabricated solar cells were evaluated using illuminated current–voltage (*I*–*V*) measurements with an AM 1.5 G