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Optical simulation of external quantum efficiency spectra of $CuIn_{1-x}Ga_xSe_2$ solar cells from spectroscopic ellipsometry inputs

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ABSTRACT

Applications of in-situ and ex-situ spectroscopic ellipsometry (SE) are presented for the development of parametric expressions that define the real and imaginary parts (ε_1, ε_2) of the complex dielectric function spectra of thin film solar cell components. These spectra can then be utilized to analyze the structure of complete thin film solar cells. Optical and structural/compositional models of complete solar cells developed through least squares regression analysis of the SE data acquired for the complete cells enable simulations of external quantum efficiency (EQE) without the need for variable parameters. Such simulations can be compared directly with EQE measurements. From these comparisons, it becomes possible to understand in detail the origins of optical and electronic gains and losses in thin film photovoltaics (PV) technologies and, as a result, the underlying performance limitations. In fact, optical losses that occur when above-bandgap photons are not absorbed in the active layers can be distinguished from electronic losses when electron-hole pairs generated in the active layers are not collected. This overall methodology has been applied to copper indium-gallium diselenide ($CuIn_{1-x}Ga_xSe_2$; CIGS) solar cells, a key commercialized thin film PV technology. CIGS solar cells with both standard thickness (>2 μm) and thin (<1 μm) absorber layers are studied by applying SE to obtain inputs for EQE simulations and enabling comparisons of simulated and measured EQE spectra. SE data analysis is challenging for CIGS material components and solar cells because of the need to develop an appropriate (ε_1, ε_2) database for the CIGS alloys and to extract absorber layer Ga profiles for accurate structural/compositional models. For cells with standard thickness absorbers, excellent agreement is found between the simulated and measured EQE, the latter under the assumption of 100% collection from the active layers, which include the CIGS bulk and CIGS/CdS heterojunction interface layers. For cells with thin absorbers, however, an observed difference between the simulated and measured EQE can be attributed to losses via carrier recombination within a ~0.15 μm thickness of CIGS adjacent to the Mo back contact. By introducing a carrier collection probability profile into the simulation, much closer agreement is obtained between the simulated and measured EQE. In addition to the single spot capability demonstrated in this study, ex-situ SE can be applied as well to generate high resolution maps of thin film multilayer structure, component layer properties and their profiles, as well as short-circuit current density predictions. Such mapping is possible due to the high measurement speed of <1 s per (ψ, Δ) spectra achievable by the multichannel ellipsometer.

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1. Introduction

Spectroscopic ellipsometry (SE) is an optical analysis technique with broad applications in the study of thin films [1,2]. SE is based on the measurement of the polarization change that occurs upon oblique specular reflection of a polarized light beam from the interface(s) and surface of a substrate/thin-film structure. Thus, the technique has been utilized extensively in multilayer thin film photovoltaics (PV) technology for determination of the component layer thicknesses and optical properties of layers in devices [3]. In fact, the physical structure of the thin film PV device and the complex dielectric function spectra $\varepsilon(E)$ of the device materials, including semiconductors, transparent conducting oxides (TCOs), and metals, control the spectroscopic optical behavior of the device, e.g., the overall reflectance and transmittance spectra as well as the component layer absorbance spectra [4,5]. For all types of materials, the spectra in $\varepsilon(E)$ with real and imaginary parts {$\varepsilon_1(E)$,

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$\varepsilon_2(E)$}, respectively, can be understood in terms of one or more bound electron oscillators; for TCOs and metals one or more free charge carrier contributions are also added [2,6]. When applied in conjunction with least squares regression analysis methods, SE is a powerful tool, in principle, for extracting the photon energy independent parameters that characterize the PV device structure, including the layer thicknesses, as well as the bound and free carrier parameters that define the (ε_1, ε_2) spectra of the component materials [7]. In practice, however, least squares regression analysis of complicated multilayered PV stacks can present a considerable challenge if one seeks information simultaneously on both layer thicknesses and material optical characteristics. Considerable effort has focused on overcoming such a challenge in SE data analysis through independent determination of device-relevant (ε_1, ε_2) spectra given as parametric expressions.

SE is a valuable tool in PV research and development because it is non-invasive and contactless, and can be used for thin film analysis in various modes, including ex-situ off-line and on-line analysis, as well as in-situ and real time analysis. SE can be performed either from the film side in the conventional substrate configuration used for solar cells or from the glass side in the superstrate configuration [3,8–10]. It is also possible to perform both film-side and glass-side SE measurements, for example, when opaque back contacts do not cover the entire area of the device structure [10]. In this report, which presents SE analysis results for $CuIn_{1-x}Ga_xSe_2$ (CIGS) thin film solar cells in the substrate configuration, only a conventional film-side measurement is possible, however, due to the lack of transmittance through the opaque Mo back contacts that cover the soda lime glass substrate [3,11]. The goal of SE analysis in PV technology is to determine the component layer thicknesses, including those of interface and surface roughness layers, as well as the (ε_1, ε_2) spectra of the component materials of the solar cell [3]. Once this fundamental structural and optical information is determined by SE, device performance information can be predicted that describes the operational characteristics of the solar cell. First, one can predict the maximum external quantum efficiency (EQE) that is possible for the given solar cell stack specifications, i.e., its layer thicknesses, and the (ε_1, ε_2) spectra of the component layers. This prediction is based on the identification of the active component layers and often on the assumption of specular reflection and transmission conditions at interfaces, as described in previous ex-situ SE studies [12,13]. The SE methodology for solar cell characterization and the EQE predictions can also be expanded to include light scattering at rough interfaces and surfaces if desired [14–16]. By simulating the EQE for variations from the deduced structure or in the optical properties, one can identify approaches for improving the short-circuit current density (J_{SC}) in a solar cell expeditiously, thus avoiding trial-and-error approaches. Second, from the fundamental structural and optical information, the spectra in the reflectance from the solar illumination side can be predicted [10–13]. This prediction is helpful, for example, for determination of the benefits of anti-reflection coatings (ARCs), as well as for optimization of the anti-reflection coating stack design [11,17].

The EQE simulations described here, based on the SE analysis of standard high-performance CIGS solar cells, apply the assumption that all carriers photo-generated within the active layers of the cell are collected without recombination losses. Any differences between the simulated EQE obtained using input parameters from SE analysis and the experimental EQE from the measurement of a completed solar cell can provide information on possible breakdowns of the assumptions applied in the simulations, as has been described in studies of different thin film PV technologies [10,18–20]. Specifically, lower measured EQE values compared with the simulation can be attributed to losses due to recombination of carriers generated by photons absorbed within the active layers. Higher measured EQE values can be attributed to gains by light scattering and breakdown in the assumption used here of specularly reflecting and transmitting interfaces. Light scattering is generated by roughness with structural scales on the order of the probing light wavelength, whereas roughness with scales much less than the wavelength can be treated within a specular analysis as a layer with (ε_1, ε_2) spectra determined by an effective medium of underlying and overlying materials [1–3,7]. The spectral dependences of the CIGS solar cell losses and gains provide insights into these processes [20–22]. Here, SE analysis results of CIGS solar cells without and with ARCs as well as with different CIGS absorber layer thicknesses are described. EQE simulations based on these results are presented and compared to measurements for insights into cell optimization and carrier collection.

As a first step in performing the EQE simulations of this study, the parametric versions of the (ε_1, ε_2) spectra of the CIGS solar cell components are obtained [11]. The components studied here include the sputtered Mo, ZnO, and ZnO:Al back and top contact layers, the thermally evaporated CIGS layers having different Ga contents, the chemical bath deposited CdS, and electron beam evaporated ARC components. SE measurements of these components were performed in idealized sample structures that provide the (ε_1, ε_2) spectra and give insights into the oscillator models required to describe these spectra over the operational range of the solar cell with a minimum number of variable parameters [3,6]. For critical thin film material components, these SE measurements were performed in-situ and in real time to obtain more accurate information on the sample structure, which in turn enables more accurate room temperature (ε_1, ε_2) spectra after cooling the sample (when depositions occur at elevated temperatures). In addition, these in-situ measurements avoid oxidation of the surfaces which, if unrecognized, can lead to distortions of the (ε_1, ε_2) spectra. Using this complex dielectric function database, complete solar cells are measured by ex-situ SE and analyzed by least squares regression to extract thicknesses and key properties of the materials such as absorber Ga content that are included as photon energy independent variables in the analysis [3,20,22]. The SE analyses enable EQE simulations based on the assumptions described in the previous paragraph, and the simulations and measurements are compared in detail. Such comparisons reveal excellent agreement for standard high efficiency devices and enable optimization of single and multilayer ARCs [11,17]. The comparisons also provide insights into the challenges of thinning the CIGS layer motivated by the prospects of higher deposition throughput and reduced materials cost.

2. Experimental

The CIGS absorber layer in the substrate configuration serves as the foundation of one of the thin film PV technologies that has been successfully commercialized. Laboratory scale record cell efficiencies for this technology currently exceed 22% [23]. The CIGS solar cells of the study presented here apply the absorber layer deposition approach that yields the highest laboratory efficiency, namely three-stage co-evaporation of Cu, In, Ga, and Se [24]. In this study, intended 2.2 μm standard thickness and 0.5 μm reduced thickness CIGS absorber layers were deposited on molybdenum (Mo) coated soda lime glass (SLG). A thin CdS window layer deposited on top of the CIGS forms the heterojunction. The complete device structure includes the following component layers (with deduced effective thicknesses defined as the film volume/area) deposited on SLG: two-step dc-sputtered Mo back contact (~0.8–1.0 μm), CIGS absorber layer (~2.2 μm or 0.5 μm), chemical-bath-deposited (CBD) CdS (~50–100 nm), rf-sputtered transparent conducting oxide bilayer of ZnO/ZnO:Al (~50–100 nm/0.2–0.3 μm), and electron beam evaporated Ni/Al/Ni grids. The total cell area

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