Investigation of compositional inhomogeneities in complex polycrystalline Cu(In,Ga)Se₂ layers for solar cells

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In-depth resolved composition inhomogeneities of polycrystalline Cu(In,Ga)Se₂ (CIGS) complex layers for high efficiency solar cells were investigated with Raman scattering measurements. In-depth resolved analysis of the frequency of the main CIGS Raman mode in the spectra measured after sputtering of the layers at different depths lead to identification of different compositions across the layer thickness. These data are in good agreement at both qualitative and quantitative levels with the in-depth resolved composition analysis of the samples by sputtered neutral mass spectroscopy. In addition, Raman measurements also allow detection of additional phases as ordered vacancy compounds. © 2009 American Institute of Physics. [doi:10.1063/1.3280049]

Cu(In,Ga)Se₂ (CIGS) based alloys have shown promising potential for the development of high efficiency thin film solar cells as a record efficiency of 19.9% has been reported at laboratory scale.¹ It is well known that chemical composition, especially the Ga/(Ga+In), Cu/(In+Ga) ratios in CIGS play a critical role in achieving high photovoltaic conversion efficiency since they influence the microstructure, optical and electronic properties of the quaternary semiconductor compound. Incorporation of Ga in the CuInSe₂ chalcopyrite lattice allows to change the direct band gap in the semiconductor between the values corresponding to the parent compounds (CuInSe₂: 1.04 eV, CuGaSe₂: 1.68 eV) while ordered vacancy compound (OVC) group-III rich phases, e.g., Cu(In,Ga)₃Se₅ yield to quite different optical and electrical properties but still relevant for solar cells. Depth profile composition measurements—performed with sputtered neutral mass spectroscopy (SNMS)—of the high efficiency solar cells have revealed that CIGS absorber layers have a complex graded composition across the layer thickness. Control of the in-depth distribution of Ga is a key feature in order to achieve layers with double graded band-gap profiles for the development of higher efficiency devices.^{2,3} Development of such a complex layer with inhomogeneous composition profiles implies also the need for characterization techniques able to give relevant information related to the Ga incorporation at different regions in the layers using simple experimental procedures. Here we report that in-depth resolved Raman scattering measurements of the vibration modes of the layer lead to identification of different compositions and phases across the layer thickness. These data agree with the in-depth resolved compositional analysis of the samples by SNMS.

Raman scattering is an optical non destructive technique specially suited for the characterization of complex semiconductors and alloys. The use of Micro-Raman measurements has been recently reported for the investigation, at qualitative level, of composition inhomogeneities in CuIn(S,Se)₂ layers.⁴ In the case of CIGS alloys, the frequency of the main A₁ Raman mode increases linearly with the Ga content^{5,6} from the position corresponding to stoichiometric CuInSe₂ (reported at 173 cm⁻¹ at 300 K)⁷ to that of stoichiometric CuGaSe₂ (reported at 184 cm⁻¹ at 300 K).⁸ This linear dependence has been employed to make a quantitative estimation of the Ga/(Ga+In) content ratio at different regions of the layer.

Investigations were performed on evaporated CIGS layers grown on Mo coated soda-lime glass substrates that contain Si₃N₄ as intermediate diffusion barrier layer. CIGS layers of about 2 μm thickness were grown with a three stage co-evaporation process,⁹⁻¹¹ substrate temperature during deposition was kept below 450 °C and a controlled amount of Na was added in CIGS with a postdeposition treatment method.¹² Such a low temperature growth process—relevant for flexible solar cell development on polymer film—yields high photovoltaic conversion efficiencies in the range of 14% to 14.5%, while deposition at higher temperature (above 550 °C) yields >18% efficiency cells on glass substrates.

Figure 1 shows a typical cross-section image of a solar cell developed with a low temperature grown CIGS layer with inhomogeneous grain size distribution across the layer thickness. This image was obtained using a Zeiss LEO 1530 scanning electron microscope (SEM). A comprehensive characterization was performed with in-depth resolved Raman spectroscopy and SNMS. Raman scattering measurements were performed in backscattering configuration by focusing the 514.5 nm line of an Ar⁺ laser on the samples. In-depth resolved measurements were made by acquiring sequentially

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FIG. 1. SEM image of the cross-section of a solar cell developed with the low temperature grown CIGS layer.

a series of Raman spectra after sputtering the sample with the Ar^+ beam from a Phi 670 scanning Auger nanoprobe.¹³ Estimated penetration depth of scattered light is about 100 nm. To minimize damage in the sputtered region, the energy of the Ar^+ beam during ion sputtering was kept below 5 keV. The estimated sputter rate is about 47 nm/min. To avoid effects related to lateral inhomogeneities as well as potential heating effects that might appear when using a microscopic objective, measurements were performed with a macroscopic excitation spot (about 100 μm), with an excitation power of 20 mW. In-depth chemical composition profiles in the layer were investigated by means of SNMS using a LHS10 system with SSM 200 (electron-beam SNMS). For sputter erosion the samples were etched by a focused 5 keV Ar^+ ion beam incident at 60° to the surface normal, scanned over an area of $3 \times 2 \text{ mm}^2$. The elemental concentrations were obtained by normalizing the spectra to the overall layer concentration as measured by x-ray fluorescence.

Figure 2 shows the sequence of Raman spectra measured after sputtering the layer at different depths. The spectrum from the surface of the layer (curve a) is characterized by the presence of a broad contribution at the 155 cm^{-1} spectral region, in addition to the main A_1 peak from the CIGS phase

FIG. 2. (Color online) Raman spectra measured after sputtering the CIGS layer with different times: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, (f) 25 min, (g) 30 min, (h) 35 min, and (i) 40 min. The spectra are normalized to the intensity of the main A_1 CIGS mode, and spectra obtained after different sputter times are vertically shifted. Inset in the figure shows the plot of the frequency of the A_1 CIGS mode vs sputter time.

FIG. 3. (Color online) Elemental in-depth distribution and relative $\text{Ga}/(\text{In}+\text{Ga})$ concentration as obtained by SNMS measurements.

at about 178 cm^{-1} . The contribution at the 155 cm^{-1} spectral region has been identified as the main vibrational mode characteristic for a Cu-poor OVC phase.¹⁴ The presence of this mode in the spectrum suggests a Cu-poor surface composition in the CIGS layer. On the other hand, the A_1 CIGS mode is shifted toward higher frequencies in relation to that from CuInSe_2 (173 cm^{-1}). This indicates the presence of a significant Ga content at the surface region. Quantification of the exact Ga content in this case is compromised by the possible existence of an additional contribution to the shift of the A_1 mode toward higher frequencies that would be related to the lack of Cu in this region, as reported in Ref. 15.

The spectrum recorded with a sputter time of 5 min shows a similar contribution at the 155 cm^{-1} spectral region, although with a lower relative intensity in relation to that of the main A_1 CIGS mode. For sputter times ≥ 10 min (corresponding to depths larger than about 470 nm), no evidence is obtained on the presence of an OVC phase. The contribution that appears in this spectral region is related to damage induced during the sputter process. Complementary micro-Raman measurements performed with the laser spot directly focused on the sample cross section (not shown) confirm the absence of the OVC contribution inside the layer. On the other hand, the main A_1 CIGS mode in the spectra is not affected by these effects. The inset in Fig. 2 shows the dependence of the frequency of the A_1 mode on the sputter time. These measurements show the existence of an inhomogeneous composition grading: a minimum frequency value of about 173 cm^{-1} —corresponding to a region with very low Ga content—is observed at the intermediate region of the layer. At higher depths, the frequency of the mode increases, and a maximum frequency of about 178.9 cm^{-1} —corresponding to a region with an estimated relative $\text{Ga}/(\text{Ga}+\text{In})$ content of the order of 54%—is observed at the region close to the back interface with the Mo coated substrate.

The observations of double grading, i.e., high Ga content at front surface and back interface with intermediate region of low content are in agreement with the SNMS measurements of elemental depth profile across layer thickness (Fig. 3). SNMS measurements corroborate the existence of a Cu-poor surface region, an intermediate Ga poor region and a Ga rich back region. The relative $\text{Ga}/(\text{In}+\text{Ga})$ content of about

60% at the back region is in good agreement with the value of about 54%, determined by Raman scattering. Differences in these values could be related to additional effects affecting the frequency of the Raman lines, as the presence of stress. In any case, it is interesting to remark the similarity between the quantitative values estimated from both techniques, being their relative difference of the order of 10%.

The present work demonstrates the ability of in-depth resolved Raman scattering measurements for investigation of structural and compositional inhomogeneities in CIGS quaternary layers with complex grading profiles elements and chemical phases. In comparison with other in-depth resolved techniques, such as SNMS, Raman scattering allows also detection of additional phases as those related to OVC compounds. A simpler experimental procedure for detection of in-depth compositional inhomogeneities could be achieved by the use of a Raman microprobe system. In this case, measurements performed with the laser spot directly focused at different positions from the cross-section of the layers could allow detection of regions with different chemical composition without the need for sputtering of the layer surface to different depths.^{4,16} However, these measurements might be conditioned by the relatively high size of the laser spot of the order of 0.7–1 μm , depending on the excitation wavelength. For a compositionally inhomogeneous layer this implies that adjacent regions of different composition in the layer might contribute to the spectrum measured with the laser spot at a given position. In this sense, further advances with higher spatial resolution, e.g., confocal or nano-Raman tools can provide better quantified composition with higher lateral resolution in future.

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