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Combined Raman scattering/photoluminescence analysis of Cu(In,Ga)Se_2 electrodeposited layers

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Abstract

This work reports the optical non-destructive assessment of the relative Ga content in Cu(In,Ga)Se_2 absorbers synthesized from electrodeposited precursors using combined photoluminescence (PL) and Raman scattering. Comparison of the PL measurements with the Auger Spectroscopy characterization of the layers has allowed performing a calibration of the dependence of the PL peak energy on the absorber composition. This opens the possibility for the nondestructive chemical assessment of the absorbers synthesized with these low cost processes. Extension of these measurements using a confocal microscope demonstrates their viability for the nondestructive quantitative chemical profiling of the layers. Correlation of these data with Raman spectra measured with the same experimental setup allows deepening in the interpretation of the spectra, giving additional information related to the microcrystalline quality of the layers and the presence of secondary phases.

Keywords: Cu(In,Ga)Se_2; Thin film cells; Photoluminescence; Confocal microscopy; Raman scattering; Process monitoring

1. Introduction

Cu(In,Ga)Se_2 (CIGS) based alloys generate strong interest for the development of high efficiency solar cells, with a record efficiency recently achieved at laboratory scale of 20.8% (on glass substrates) (ZSW press release, 2013) and 20.4% (on flexible polymeric substrates) (EMPA press release, 2013). Chalcogenide based photovoltaic (PV) technologies have already entered the industrial productions stage, with stable commercial module efficiencies in the range 12–13%. Achievement of higher efficiency values at the module level is challenging due to the difficulty of controlling the different process steps on large area substrates. In particular, the overall performance of PV modules is highly sensitive to local changes in the absorber composition which result in fluctuations of the optoelectronic properties of the absorber layer. This is especially relevant in the case of cells based in the Cu(In,Ga)Se_2 alloy. Incorporation of Ga in the $CuInSe_2$ lattice allows changing

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the direct bandgap in the semiconductor between the values corresponding to the parent compounds ($CuInSe_2$: 1.04 eV, $CuGaSe_2$: 1.68 eV). High efficiency CIGS cells require for a precise control of the Ga content profile through the depth of the layer (Dhingra and Rothwarf, 1996; Song et al., 2004). Development of devices and modules with higher efficiency is strongly conditioned to the ability to improve the level of control of the synthesis of quaternary absorbers with this complex gradual depth profile. This requires the availability of characterization tools suitable for the non-destructive analysis of the chemical composition of the layers and compatible with their implementation at in-line level for quality control and process monitoring.

This gives a strong interest to the study of optical non-destructive techniques such as photoluminescence (PL) and Raman scattering, due to their ability to provide information directly related to the optoelectronic properties of the layers as the energy band-gap, chemical composition and microstructure at different processes stages (Izquierdo-Roca et al., 2011a, 2011b; Unold and Gütay, 2011). Local inhomogeneities in the Ga overall content can be detected by X-ray fluorescence (XRF) based techniques that can be implemented at in-line level for process monitoring. However, compositional depth resolved inhomogeneities usually require for the use of destructive techniques as Secondary Ion Mass Spectroscopy (SIMS), depth resolved Auger Electron Spectroscopy (AES) or glow discharge optical emission spectroscopy (GDOES). Raman scattering measurements in combination with controlled etching processes have also been reported for the depth resolved analysis of the Ga relative content (Fontané et al., 2009a). Micro Raman measurements performed on cross-section of the samples can also provide relevant information on the presence of compositional depth resolved inhomogeneities in the layers (Fontané et al., 2009b). Higher depth resolution can be achieved by combined Atomic Force Microscopy (AFM)/Raman microprobe mapping of cross sections of samples prepared in the form of standard Transmission Electron Microscopy (TEM) specimens (Schmid et al., 2009). However, none of these techniques is suitable for implementation at in-line level for quality control and process monitoring. In addition, quantification of the relative Ga/(In + Ga) content from the Raman data is also compromised by the potential presence of additional effects affecting the position of the main CIGS Raman line, as stress or structural defects.

In this framework, this work describes the optical characterization by combined PL and Raman scattering measurements of $Cu(In,Ga)Se_2$ absorbers synthesized by electrodeposition-based processes with different kinds of Ga depth profiles. These are processes that are of strong interest because of their potential for cost reduction at mass production stages. Spectra measured at room temperature are characterized by a broad PL band, in addition to the Raman peaks. Analysis of the dependence of this band with the excitation power has allowed identifying this PL band with band to band transitions. The position of this band is sensitive to the Ga content in the alloy. The existence of a direct correlation between the energy of the peak of this band and the relative Ga content as measured by AES has allowed performing a quantitative calibration of the dependence of the PL peak energy with the relative Ga content in the layer. Even if the dependence of PL on the chemical composition has already been reported in the literature (Unold and Gütay, 2011; Rega et al., 2005), to our knowledge this is the first time that the viability of these measurements is demonstrated for the quantitative chemical analysis of the electrodeposited CIGS layers in the whole range of compositions of the CIGS alloy. This opens promising perspectives for the nondestructive chemical composition assessment of CIGS absorbers by purely optical techniques. In addition, the use of the same experimental setup for the measurement of both Raman and PL spectra allows identifying the presence of additional features affecting the spectral characteristics of the Raman lines as stress or defect and or composition induced effects, providing additional relevant information related to the microcrystalline quality of the layers and presence of secondary phases. In this sense, correlation of the Raman measurements with the alloy composition estimated from the PL data has allowed to detect a blue shift (towards higher wavenumbers) of the main Raman peak from the chalcopyrite phase that is caused by the Cu poor composition of the layers. The Raman spectra also corroborate the high crystalline quality of the layers, and allow detecting the presence of a Cu poor Ordered Vacancy Compound (OVC) secondary phase at the surface region of the absorbers, in agreement with their Cu poor composition. Extension of the PL measurements with the use of a confocal microscope also demonstrates the possibility to obtain information on the Ga composition depth profile in the absorbers using simple nondestructive optical PL measurements. In this case, selection of the excitation wavelength is determining the analyzed depth region.

2. Experimental details

CIGS absorbers used in this work were prepared with the technology developed at NEXCIS company. This technology is based on the electroplating of Cu/In/Ga multistacks onto Mo/soda-lime glass substrates, followed by a rapid thermal process (RTP) under Se atmosphere. This allows fabrication of cell devices on large area (60×120 cm^2) substrates with small cells efficiency up to 15.4%. Layers were synthesized with different Ga depth profiles, with a relative Ga content at the surface region between 0% and 20% and an overall relative Cu/(In + Ga) content of 0.87. An increase of the Ga content at the surface region of the layer has a direct impact on the optoelectronic properties of the cells, with an improvement experimentally observed up to 630 mV for the open circuit voltage.

PL and Raman scattering measurements were made using a LabRam HR800-UV Horiba–Jobin Yvon