Characterization and monitoring technologies for CIGS

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ABSTRACT

Among the various thin-film solar module options available, $Cu(In,Ga)(Se,S)_2$ (CIGS) is especially interesting as it exhibits the highest efficiency potential. These chalcopyrite-based solar cells are manufactured on glass or flexible substrates using various thin-film coating methods for each layer. The central CIGS absorber layer is deposited by co-evaporation, selenization of elemental layers, and other methods. In order to achieve highest quality and reproducibility, the absorber properties must be properly monitored and characterized. In this contribution we shed some light on the most important analysis methods used for CIGS solar cell research, development, and production such as x-ray fluorescence, surface analysis, and Raman spectroscopy.

Introduction

Thin-film solar modules are expected to rapidly increase their market share by about 4% per annum in the coming years [1]. Key issues for their success are low materials cost, module integration, scalability of the manufacturing processes and visual design. Successful thin-film technologies like thin-film silicon, CdTe, and the chalcopyrite-based solar modules such as CIGS are already available on the market. Thin-film silicon has the longest market experience, but suffers from relatively low efficiencies for single junctions, although the a-Si/μc-Si tandems are best equipped to pass the 10% hurdle. CdTe is currently very successful, profiting from low-cost manufacturing and reasonably high efficiencies. Amongst the three thin-film technologies, however, CIGS exhibits the highest efficiency potential by far for lab cells – with the current world record at 19.9% [2] – and also for modules produced in large-scale manufacturing [3]. The current module record is 13.5% for a $3459cm^2$ aperture area [4]. The typical thin-film layers of these solar cells are shown in the coloured scanning electron micrograph cross-section in Fig. 1. The CIGS layer is also known as the 'absorber' because the photons absorbed in this layer generate the charge carriers which are then used to generate useful electricity. The other layers form the contacts and the heterojunction diode.

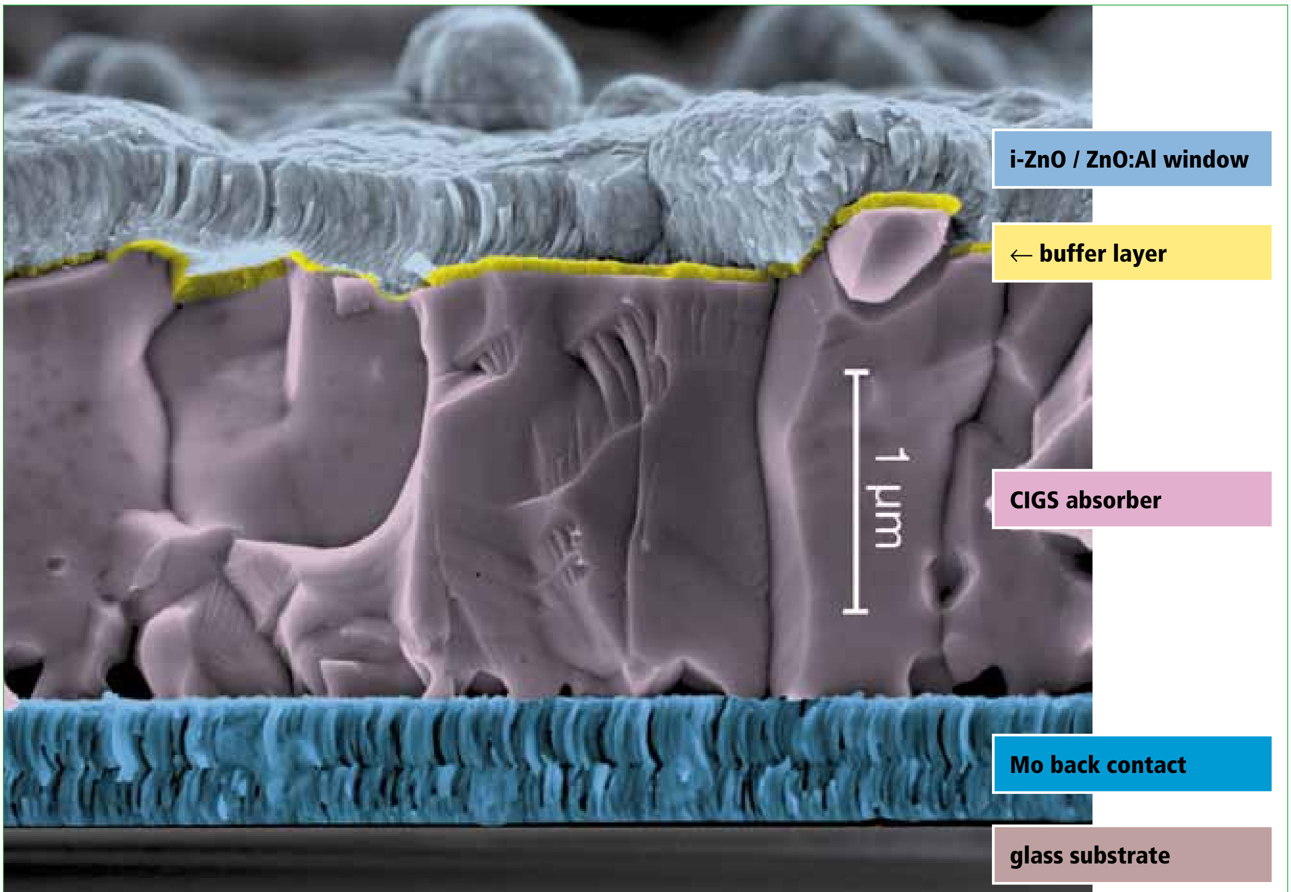

Figure 1. SEM cross-section image of the layer structure of a CIGS solar cell.

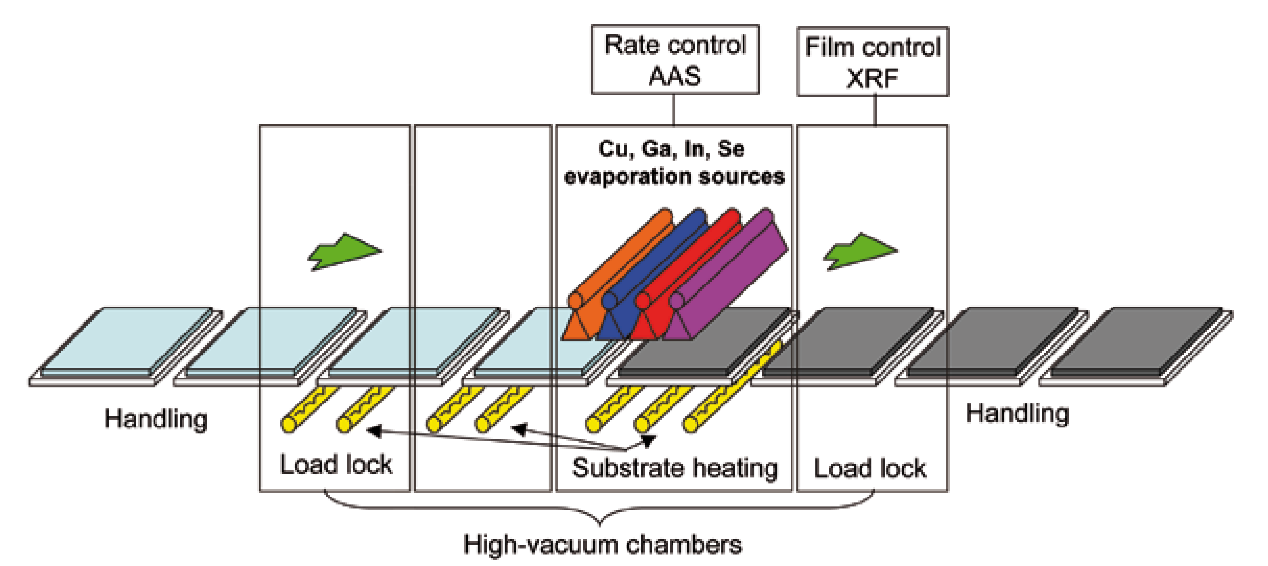

Figure 2. Schematic diagram of a CIGS coating plant indicating processing chambers and control systems.

The key to high-efficiency CIGS solar cells is the quality of the CIGS absorber layer itself, as it is the most complicated layer. CIGS is a quaternary compound semiconductor whose growth and composition must be carefully controlled in order to achieve highest efficiencies. The focus of this contribution is therefore on the characterization and process control of the CIGS absorber layer as used in the production, development, and research of thin-film chalcopyrite-based solar modules. The discussion will start by describing CIGS processing and the methods used in process control during production, and will then continue with special methods used in research and development to better understand and improve CIGS-based solar cells and modules.

CIGS production processes

There are several different pathways to manufacture CIGS absorber films. The main routes leading to the highest efficiencies so far are co-evaporation of the single elements or the selenization of stacked or intermixed precursor layers – mostly metal layers, which may be grown by standard coating processes like sputtering. Low-cost approaches generally avoid all vacuum processes using e.g. printing of nanoscale materials or electrodeposition. Usually, at least one thermal processing step is necessary for the film formation and to achieve sufficient quality. The ZSW has focused its expertise on the dynamic thermal co-evaporation process and runs a complete in-house processing line for the laboratory-scale production of 30cm × 30cm CIGS photovoltaic modules. Up to 19.6% cell efficiency could be achieved at the ZSW, the current European record, using the lab's in-line system [5]. Some of the process control methods applied in this system – which can be upscaled for mass production – will be described in the following sections.

Process control methods

Highest-quality CIGS deposition requires various growth phases for optimal film quality and phase composition. Laboratory research supports the development of growth schemes. In order to successfully implement the results in a production line, both the sources themselves and their integration into the system must be carefully designed. Finite element simulations helped in the profile optimization of line sources for these homogeneous films.

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Fig. 2 schematically illustrates a ZSW in-line CIGS vacuum coating system. The Mo-coated glass substrates are transported using carriers that are moved out of a preheating magazine along a heating passage into the process chamber. In the CIGS deposition chamber, the elemental metals copper, indium and gallium are thermally evaporated from separate linear effusion sources downwards onto the heated substrate. The homogeneity of the film in the transport direction is maintained by the constant substrate speed and constant evaporation rates. The metal evaporation rates are controlled using atomic absorption spectrometry (AAS), coupled into the chamber with optical fibers. With this method, the metal rates can be measured independently and very constant rates can be achieved. Sufficient selenium incorporation and film quality is only guaranteed when the selenium flux is several times higher than the metal rates. The final growth stage is carefully controlled, since the electronic quality of the photovoltaic device is particularly sensitive to the CIGS surface, where the metallurgical p-n junction is formed during later processing.

In addition, ZSW employs x-ray fluorescence (XRF) for the process control subsequent to the absorber deposition. This system is specifically programmed to be able to quickly determine both the integral film composition and the absorber film thickness. The results of this measurement are used as feedback parameters for a loop-back control of the evaporation rates. The XRF results also serve as a quality control measure to remove off-parameter films from the processing line and to provide parameters for correlating with the final module performance parameters.

Additional methods commonly used for process control are for example endpoint detection (laser scattering or thermal), in-situ Raman spectroscopy, and photoluminescence.

Analysis of CIGS absorber layers

A wide spectrum of additional methods is applied to study CIGS films for process development and scientific understanding. The following is a description of chemical, structural and morphological methods for the detailed analysis of CIGS thin films.

Chemical analysis

For the chemical characterization of CIGS films, scientists are generally interested in the film composition, either integral or in profile. As outlined earlier, the

XRF method can be integrated into a production line for process control. The energy-dispersive x-ray (EDX) method provides similar information with higher spatial resolution but requires an electron beam source. Raman spectroscopy is useful to gain information about phases and binding states. Furthermore, a wide array of profiling methods is available to investigate the distribution of elements through the depth of a film. Only the profiling methods are intrinsically destructive, since they involve sputtering through the film to acquire the depth profile. The other methods are limited by the size of the measuring chamber. The defining characteristics of these methods are outlined in the following sections.

XRF

In the XRF method, the sample is exposed to x-ray radiation, which knocks electrons out of the inner atomic shells. Upon relaxing, an x-ray is emitted whose energy is characteristic of the atomic element. The elements with atomic numbers from sodium up to uranium can be detected using this method. After calibration with suitable standards, XRF spectra can be quantified. XRF is a common method for determining the final CIGS composition either integrated into a production line for process control or externally for specific analysis. XRF systems can also be integrated into the deposition section of the coating plant, allowing the film composition to be determined after every step of a multistage process. Since the x-rays penetrate the entire film stack, the composition and thickness of each layer of a complete solar cell can be determined from a single measurement. Furthermore, XRF mapping techniques can be applied to investigate the lateral homogeneity.

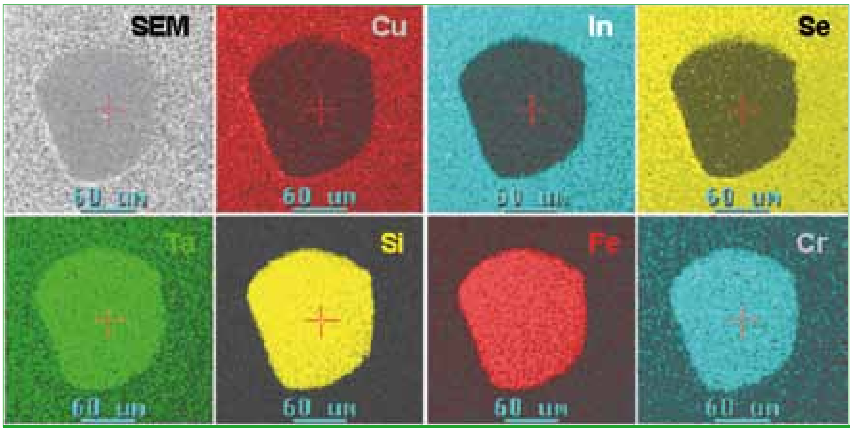

Figure 3. EDX mapping of a defect in CIGS deposited on chrome steel.

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EDX

The EDX method is very similar to XRF in that it also analyses the characteristic x-ray energy spectra. The major difference is that an electron beam supplies the energy to remove electrons from the inner atomic shells. The penetration depth is lower than for x-rays, so the EDX method has a reduced information depth of about 0.5 to 2µm, which is also dependent on the element being analyzed and the acceleration energy of the bombarding electrons. Elements down to boron can be detected. EDX also has a higher lateral resolution down to 300nm, which makes it useful for the analysis of specific features and defects.

Fig. 3 provides an example of defect analysis on a CIGS film coated on chrome steel. A mapping procedure was applied in which a fast EDX spectrum was measured for each pixel. The grey image to the upper left illustrates the standard secondary electron image from the scanning electron microscope (SEM). The round defect in the centre of the image showed stronger signals from the underlying steel components due to the reduced CIGS film thickness at this location. The defect likely resulted from a loose particle that fell onto the substrate during the CIGS deposition process.

Raman spectroscopy

Raman spectroscopy provides information about the vibrational modes of the sample and can be used to identify

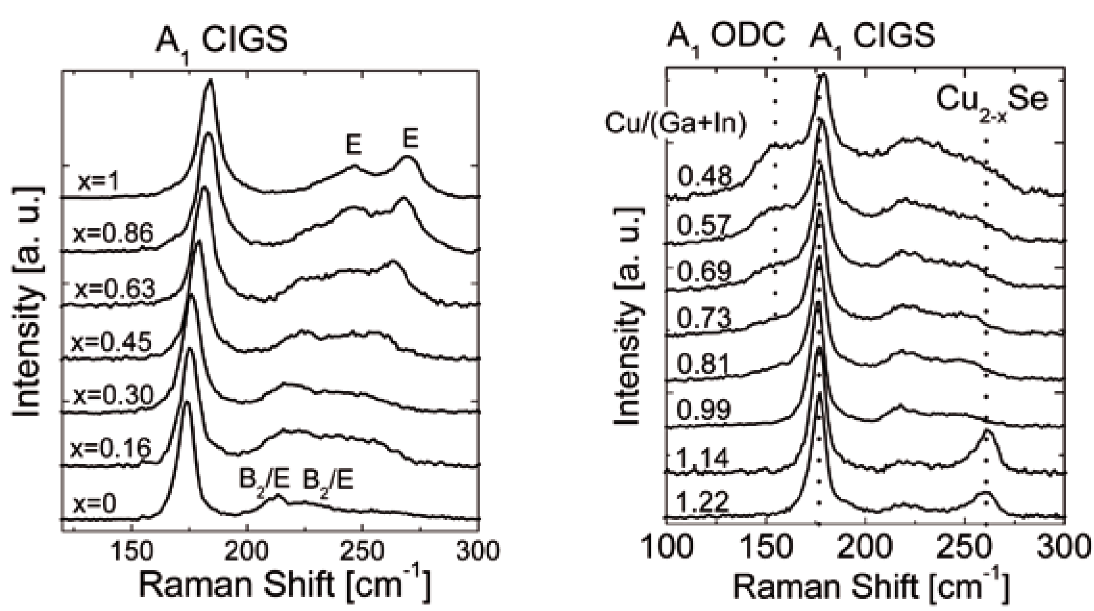

Figure 4. Raman spectra of $CuIn_{1-x}Ga_xSe_2$ layers with different Ga content x (left) and varying Cu content at a fixed Ga content x = 0.3 (right).

phases and estimate the film composition. Fig. 4 illustrates shifts of Raman modes related to film composition and additional modes related to secondary phases. The left diagram depicts Raman spectra of $CuIn_{1-x}Ga_xSe_2$ absorber films with various Ga contents x at room temperature. The frequency values of the dominant CIGS A_1 mode of the spectra increase linearly with the Ga content x. The B_2 and E CIGS modes are also labelled. Small frequency shifts of the A_1 mode are also observed in the Raman spectra of CIGS layers with various Cu contents from very Cu-poor to Cu-rich compositions at a fixed Ga content. They are illustrated in the diagram on the right of Fig. 4 [6]. A mode originating from a Cu-poor compound known as ordered defect compound (ODC) is apparent as a broad shoulder. $Cu_{2-x}Se$ appears in the Raman spectra of Cu-rich CIGS films. Furthermore, Raman spectroscopy can be used to determine the Se/S ratio when sulphur is incorporated into the absorber layer [7].

Raman spectroscopy is therefore useful for estimating composition and identifying secondary phases. It is a promising method for process control after CIGS deposition or even as an in-situ characterization method during the CIGS deposition process. When combined with a microscope, inhomogeneities can be investigated on the micrometre scale.

Depth profiling

The depth profiling methods are all surface-sensitive techniques coupled with sputter etching to measure through the depth of the sample. Entire photovoltaic devices can be investigated, whereby the sample is destroyed in the process. However, very useful information can be gained, for example about the gallium gradient in the CIGS absorber film.

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The ZSW employs SIMS (secondary ion mass spectroscopy) and SNMS (secondary neutral mass spectroscopy). The difference between the two is that with SIMS ionized atoms are detected by a mass spectrometer, while for SNMS the neutral atoms must be first ionized by a filament to enable their detection. SIMS enables extremely high detection limits in the ppb range, but can only be quantified for specifically calibrated cases due to matrix effects. SNMS, on the other hand, can be quantified, but is less sensitive with a detection limit of 0.01 at.%. The ZSW system can achieve a lateral resolution of 125μm for both methods as determined by the size of the sputter crater, and a depth resolution as sensitive as 1 to 3 monolayers. Typical SNMS depth profiles of CIGS with various Ga contents on Mo are shown in Fig. 5. This series indicates the effect of Ga content on the CIGS/Mo interface. Evidently, additional selenium is incorporated at the interface for low Ga contents.

GDOES (glow discharge optical emission spectroscopy) is a related technique used by other groups. Similarly to SIMS and SNMS, an ion beam sputters off atoms from the layer surface. These atoms are transported to a plasma where they are excited and emit light, the spectrum of which is analyzed. Furthermore, these atoms are ionized in the plasma and can be detected by a mass spectrometer. This is the principle of GDMS (glow-discharge mass spectroscopy). GDMS allows quantification comparable to SNMS at a detection limit from sub-ppb to ppt. ERDA, RBS and XPS, as described later, are normally used for surface analysis. By combining these techniques with argon ion beam sputtering, a depth profile can be recorded.

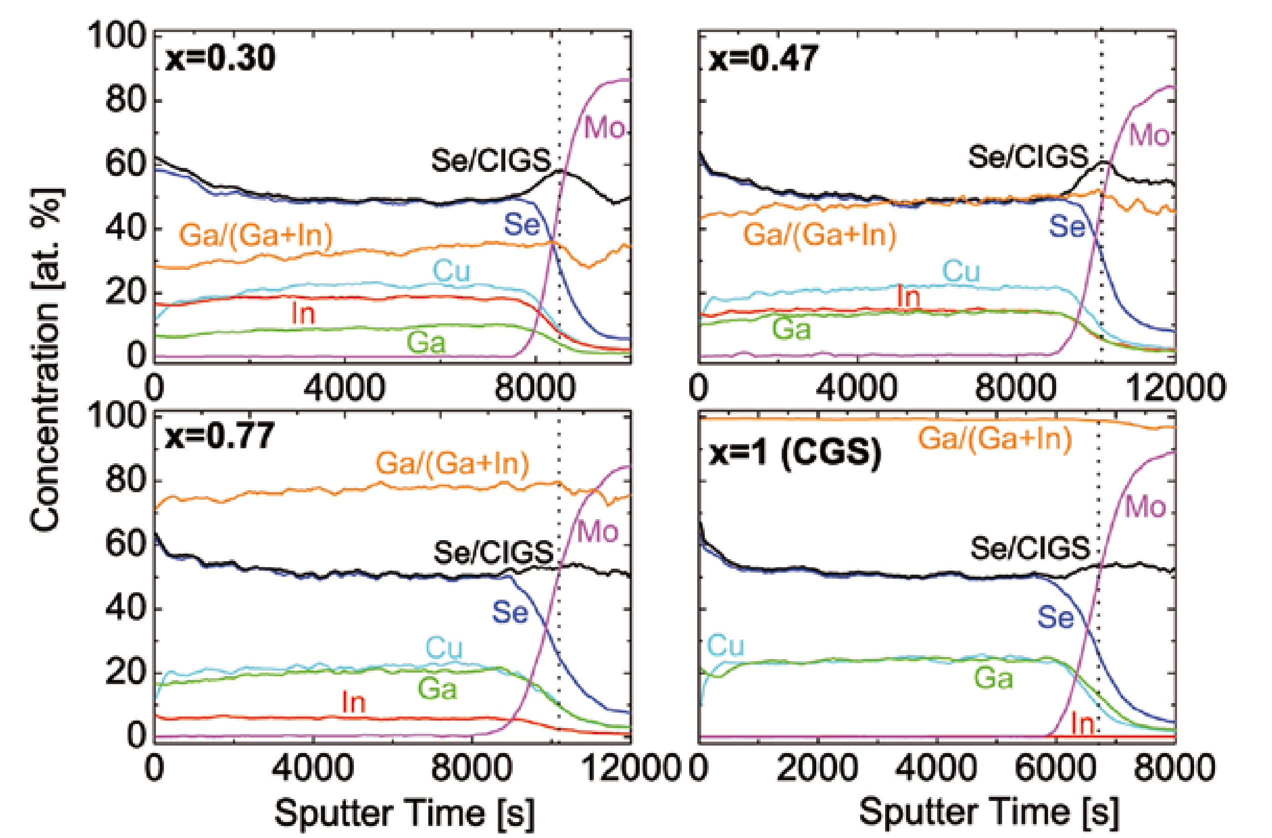

Figure 5. SNMS depth profiles for CIGS films with different Ga contents x as indicated. An increased Se/CIGS ratio is found at the Mo/CIGS interface for the lower Ga contents.

Surface analysis

The CIGS/buffer interface plays an important role in high-efficiency solar cells. The band structure at the interfaces affects charge transport. The so-called ODC surface composition of Cu-poor CIGS appears to provide a type-inverted surface, moving the region where similar concentrations of electrons and holes are present away from the defect-rich metallurgical heterointerface. Surface analysis methods are required to study only the CIGS surface layer. These techniques have a small depth resolution and include XPS, AES, UPS, RBS and ERDA. XPS is available at the ZSW. The principles behind them are described briefly in the following section.

For XPS (x-ray photoelectron spectroscopy), an aluminium or magnesium x-ray source is used to eject electrons out of the surface atoms. Measuring the kinetic energy of these electrons supplies information on the surface elements and their chemical binding states in the compound matrix. The depth resolution is about 1 to 10 atomic layers.

AES (Auger electron spectroscopy) is a related method in which an electron is ejected out of an inner atomic shell and is replaced by an electron from an outer shell. The energy released by this relaxation process ejects a secondary electron out of the atom, which is then analyzed. Unfortunately, Auger lines do not exist for all elements. AES is useful for further interpretation of XPS data, particularly when the energetic lines from different elements superimpose. XPS and AES measurements can also give spatial information through mapping.

UPS (ultraviolet photoelectron spectroscopy) applies ultraviolet light as the excitation source. Its main application is to detect the position of the valence band. Band structures of heterojunctions can be studied in this way.

RBS (Rutherford backscattering spectroscopy) and ERDA (elastic recoil detection analysis) require an ion beam as the source. In RBS the backscattered ions are analyzed. It is sensitive to heavy elements in a matrix of light elements. ERDA analyzes recoiled ions and is sensitive to light elements in a heavy-element matrix. H- or He-ion beams are required for these techniques.

Structural analysis and morphology

Structure, crystallinity, morphology, and thickness of the films can be determined using several specific methods. Only the film thickness as calculated from the XRF measurement can be integrated into a production line for process control. The other methods are mostly employed for research and development purposes. Besides the XRF measurement, film thickness can be measured over a step structure with a contact or optical profilometer or analyzed in cross-section in a scanning electron microscope (SEM). The latter also provides information about the crystallite growth, compactness, and other morphology aspects. Surface roughness can be determined e.g. with an atomic force microscope (AFM) or a confocal 3D microscope. X-ray diffraction (XRD) provides information about the phases and crystalline quality of the films as well as the orientation of the crystallites (texture) and strain. With the exception of the 3D microscope, all of these methods are available at the ZSW.

"By cleaving the sample and investigating the cross-section, the growth of the crystallites as well as their compactness and contact with the substrate can be investigated."

SEM

The scanning electron microscope has a high resolution for imaging the surface and microscopic defects. An EDX system combined with the SEM allows further chemical analysis of specific features. By cleaving the sample and investigating the cross-section, the growth of the crystallites as well as their compactness and contact with the substrate can be

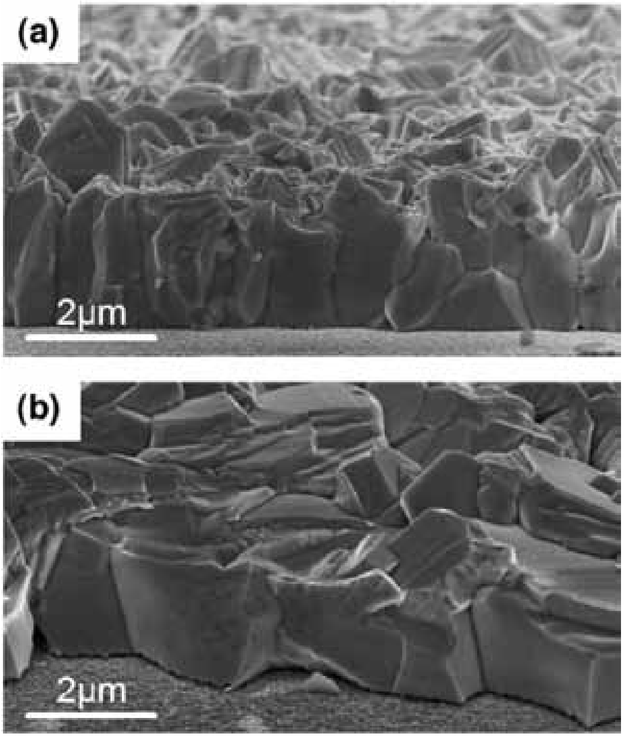

Figure 6. Scanning electron micrograph (SEM) cross-sections of Cu(In,Ga)Se_2 absorbers deposited in a standard (a) and a multistage (b) in-line process.

investigated. The thickness and growth of each layer can be studied for the entire solar cell. Furthermore, the conformality and degree of coverage of the extremely thin (20-80nm) buffer layer can be best imaged with SEM. Fig. 6 illustrates an example of the difference between the grain size and shape of 'standard' and 'multistage' CIGS films on Mo-coated glass. The multistage CIGS crystallites are more than twice as wide as the standard CIGS crystallites. Their surface also has a flatter morphology.

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Profilometry/microscopy

A contact profilometer drives a sharp needle at a constant, low force over the sample surface. Masking or other pattering methods can create a sharp vertical step for measuring film thicknesses. A soft sample may be difficult to measure with this method due to indentation or movement of the sample material. The measurement also occurs only along one line, which is suitable for a step height measurement. An AFM uses a cantilever tip to scan across a two-dimensional surface area for extremely high-resolution 3D images and data on surface roughness. Variations of the AFM method also allow non-contact imaging. An optical profilometer or 3D microscope based on the confocal technique can not only measure step heights without mechanical contact, but also image surfaces with high-resolution height information. This data is useful for analyzing surface roughness. None of these methods are suitable for production line process control because they are slow and only image a very small area.

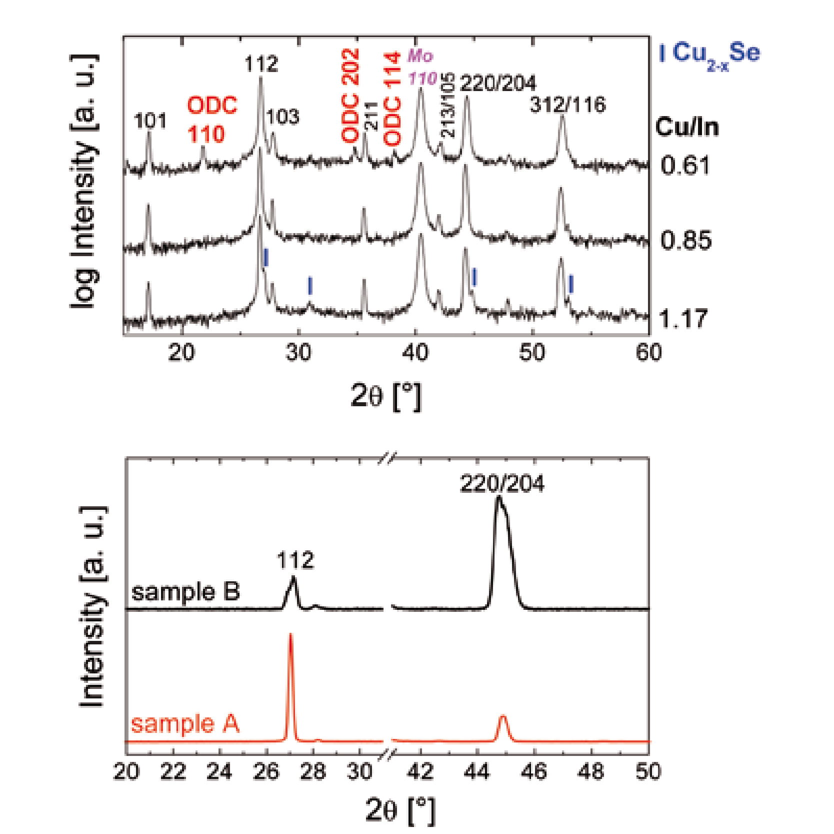

Figure 7. XRD patterns of $CuInSe_2$ thin films with different Cu/In ratios (top) and an example of texture in CIGS samples from different growth processes (bottom).

XRD

X-ray diffraction is a common tool for investigating phase composition. The sample is subjected to collimated x-ray radiation which diffracts on the crystal lattice. The method reveals the phases present in the sample, their crystallographic orientation, lattice constants and strain. The top diagram in Fig. 7 illustrates how additional phases can be identified using XRD. From top to bottom, the curves show measurements from In-rich to Cu-rich $CuInSe_2$, respectively. The In-rich compound known as ODC (ordered defect compound) is apparent in the In-rich film (red labels) and copper selenide is present in the Cu-rich film (blue ticks).

In polycrystalline samples, the crystallites can be randomly oriented, resulting in spectra similar to the powder spectra for the compound. However, polycrystalline thin films often demonstrate a preferred orientation or texture. Whether or not the crystallographic orientation of the crystallites significantly influences the photovoltaic quality of the CIGS solar cell is a current subject of scientific discussion. The bottom diagram in Fig. 7 illustrates how different CIGS deposition processes can lead to different crystallographic orientations of the films. The (112) reflex dominates for randomly oriented grains similar to sample A. In contrast, sample B shows a clear (220/204) preferential orientation.

Summary

This article illustrates the large variety of characterization methods applied for the process control, development and research of thin-film $Cu(In,Ga)Se_2$ layers for photovoltaic modules. Methods that can be integrated into production lines and those that are limited to specific research and development purposes are indicated. Improved understanding of CIGS properties and growth processes has lead to increased performance over the years and is key to achieving best efficiencies.

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Dr.-Ing. Theresa Magorian Friedlmeier began working with CIGS as a student in 1991. She has a B.A. in physics from the University of Colorado and diploma and Ph.D. degrees from the University of Stuttgart (IPE). She joined the ZSW in 2002 and is responsible for the SEM.

Wolfram Witte has a diploma degree in mineralogy from the University of Freiburg and wrote his thesis on CdTe bulk crystals. He joined the ZSW in 2004 and specializes in the deposition and growth of CIGS and its analysis with Raman spectroscopy and XRD.

Dr. Wolfram Hempel studied materials science at the FAU Erlangen and earned his Ph.D. in physics in 2007 at the University of Augsburg through a collaboration with Osram, Munich. He joined the ZSW in 2007 and specializes in the molybdenum back contact and the SNMS, SIMS, XPS, Raman, and AFM methods.

Richard Menner has gained experience as a physicist in the field of CIGS thin-film photovoltaics over the past 25 years, beginning with his time at the University of Stuttgart (IPE). He joined the ZSW in 1993 and is responsible for sputtering as well as photovoltaics measurement and analysis. He supported the ramp-up of the Wuerth Solar pilot line and CISfab.

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