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Correlative microscopy analyses of thin-film solar cells at multiple scales

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ABSTRACT

In the present work, a brief overview is given on how to apply transmission (TEM) as well as scanning electron microscopy (SEM) and their related techniques (electron diffraction, energy-dispersive X-ray spectrometry, electron energy-loss spectroscopy, electron holography; electron backscatter diffraction, electron-beam-induced current, cathodoluminescence) for the analysis of interfaces between individual layers or extended structural defects in a thin-film stack. All examples given in the present work were recorded on Cu(In, Ga)Se_2 thin film solar cells, however, the shown experimental approaches may be used on any similar thin-film semiconductor device. A particular aspect is the application of various techniques on the same identical specimen area, in order to enhance the insight into structural, compositional, and electrical properties. For (aberration-corrected) TEM, the spatial resolutions of such measurements can be as low as on the subnanometer scale. However, when dealing with semiconductor devices, it is often necessary to characterize electrical and optoelectronic properties at larger scales, of few 10 nm up to even mm, for which SEM is more appropriate. At the same time, these larger scales provide also enhanced statistics of the analysis. In the present review, it is also outlined how to apply SEM techniques in combination with scanning-probe and optical microscopy, on the same identical positions. Altogether, a multiscale toolbox is provided for the thorough analysis of structure-property relationships in thin-film solar cells using correlative microscopy approaches.

1. Introduction

The research and development of thin-film solar cells aims at providing a low-cost alternative to the Si wafer-based solar modules, which currently dominates the photovoltaic market [1]. The term "thin-film solar cells" should be conceived as a stack of functional thin films, which can be deposited on any substrate (glass, metal or plastic foils, etc.). Thus, the growth of these thin films does not require epitaxial deposition on monocrystalline substrates. As a consequence, all layers of the thin-film stack are polycrystalline.

The best conversion efficiencies for thin-film solar cells of more than 22% have been achieved by devices based on Cu(In,Ga)$(S,Se)_2$ [2–4] or CdTe absorber layers [5]. Novel device concepts based on methylammonium lead halide (perovskite) thin films have (apparently) equally surpassed the 22% level [6], but still suffer from a poor stability. For a further improvement of the thin-film photovoltaic technologies towards the 25% level and beyond (i.e., the current performance limit of monocrystalline, wafer-based Si solar cells), electron microscopy and its related techniques provide a valuable tool box for the in-depth analysis of individual layers as well as their interfaces in the thin-film stack.

When discussing the analysis of thin-film solar cells by electron-microscopy techniques, it is important to point out the issue of the corresponding scale. The structural and compositional properties of interfaces between layers and of line or planar defects can be studied at the atomic scale (orders of magnitude of 0.1–1 nm) by various techniques in (scanning) transmission electron microscopy ((*S*)TEM), including imaging, electron diffraction, electron energy-loss spectroscopy (EELS), and energy-dispersive X-ray spectroscopy (EDX). Also, electron holography can be employed to acquire electromagnetic potential distributions in materials. However, while the crystal structure or the composition may vary at very small scales of about few nm, electrical or magnetic fields often extend over larger ranges of 0.01–1 μm. Also, due to the limited field of view, statistics of (*S*)TEM studies are often poor.

In order to overcome these limitations, various techniques are available in scanning electron microscopy (SEM), which provide access to structural, compositional, electrical, and optoelectronic properties at larger scales (0.01–100 μm, at times also up to 1 cm): imaging, electron backscatter diffraction (EBSD), EDX, electron-beam-induced current (EBIC) measurements, and

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cathodoluminescence (CL). In (S)TEM or SEM, the quality of the obtained results is enhanced substantially when applying various of the given techniques on the identical specimen areas. Particularly, microscopic structure-property relationships can be extracted directly. Furthermore, such relationships can be revealed not only by combining the techniques on one specific instrument, but also by correlation of methods in electron, scanning-probe (SPM), and optical microscopy (OM) at the identical specimen areas.

The present work will give an overview of this correlative, multiscale approach in order to study individual layers and their interfaces in thin-film solar cells by applying multiple (S)TEM, SEM, SPM, and OM techniques. Various examples for these studies will be presented.

2. Results and discussion

2.1. Analyses by (scanning) transmission electron microscopy

2.1.1. Imaging, electron diffraction, and compositional analysis at medium resolution

When analyzing structural and compositional properties of individual layers and their interfaces in thin-film solar cells, (S)TEM provides a valuable and versatile toolbox, which may be applied at various magnification levels. A general introduction into (S)TEM and its corresponding analysis techniques can be found in Refs. [7,8].

In the present section, characterization at medium resolution shall be highlighted. Diffraction-contrast imaging in bright-field or dark-field mode allows for the determination of layer thicknesses and grain-size distributions in individual layers. In these modes, an objective aperture is positioned around the reflection of the undiffracted beam (bright field) or a diffracted beam (dark field) in the back focal plane. An example for a bright-field image providing diffraction contrast is given in Fig. 1a, showing an In_2S_3/Cu(In,Ga)Se_2 interface, which is applied as *p-n* junction in corresponding thin-film solar cells. From this bright-field image, grain sizes in the In_2S_3 layer of few ten nanometers can be estimated. Over the same identical interface, the electron diffraction pattern given in Fig. 1b was acquired using a selected-area aperture in the image plane, in order to determine the crystal structures of the layers. The diffraction pattern contains reflections from both, the In_2S_3 and the Cu(In,Ga)Se_2 layers (oriented along the [331] and the [110] zone axes). This electron diffraction pattern gives rise to an orientation relationship between the atomic lattices of In_2S_3 and Cu(In,Ga)Se_2, since the reflections of the Cu(In,Ga)Se_2 thin film superimpose those of the In_2S_3 layer (both layers exhibit a tetragonal lattice, and the interplanar distances in the In_2S_3 lattice are about twice of those in the Cu(In,Ga)Se_2 lattice). Also, additional (weaker) reflections are visible in the diffraction pattern in Fig. 1b, which can be attributed to twinning in the Cu(In,Ga)Se_2 layer.

In contrast to diffraction-contrast imaging (bright-field or dark-field mode), for which the image formation is mainly influenced by changes in the amplitude $A(x,y)$ of the electron wave function $\psi(x,y)=A(x,y)\exp(i\varphi(x,y))$ at the exit plane of the TEM lamella, in high-resolution TEM, the image contrast is dominated mainly by local changes in the phase $\varphi(x,y)$, while the amplitude $A(x,y)$ can be assumed (ideally) to be constant. In order to image the projection of the atomic lattice of a crystalline specimen, it has to be oriented to a (low-indexed) zone axis, i.e., with the atomic columns (nearly) parallel to the incident electron beam. By such a high-resolution TEM image of the In_2S_3/Cu(In,Ga)Se_2 interface in Fig. 1a, given in Fig. 1c, the orientation relationship indicated by the electron diffraction pattern in Fig. 1b can indeed by visualized. Such an interface formation is favorable for optoelectronic devices, since it features low degrees of misfit and thus of extended structural defects, which may be the origin of electronic defect states, possibly affecting the device performance.

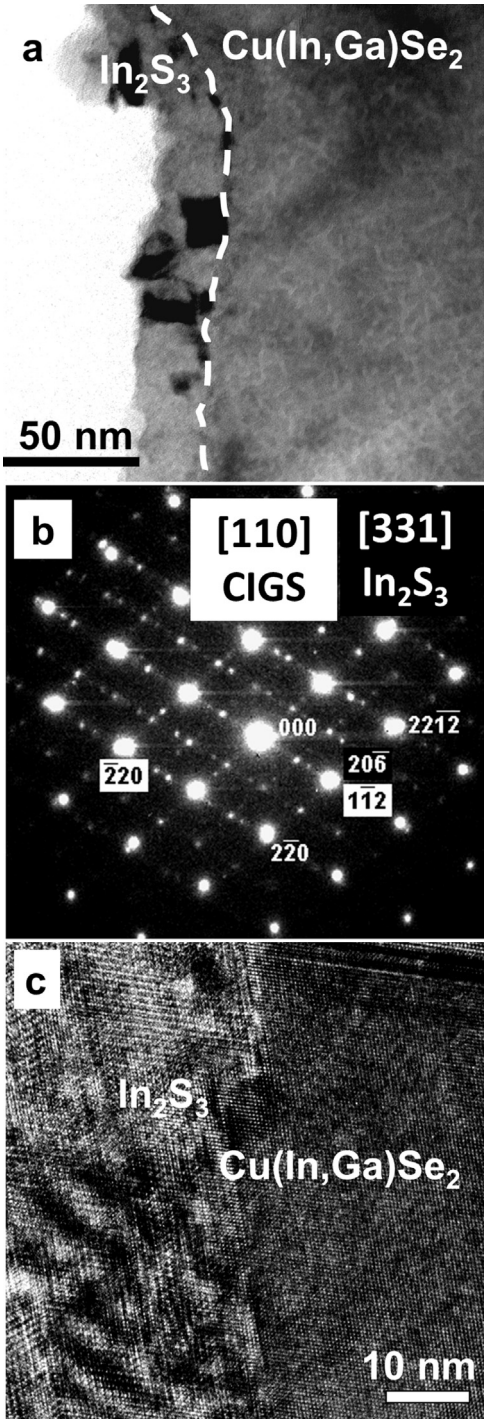

Fig. 1. (a) Bright-field TEM image, (b) electron diffraction pattern, and (c) high-resolution image obtained on the same In_2S_3/Cu(In,Ga)Se_2 interface in a thin-film solar cell. In the bright-field image (a), individual grains in the In_2S_3 layer are visible by diffraction contrast. The electron diffraction pattern (b) indicates an orientation relationship between the Cu(In,Ga)Se_2 and In_2S_3 thin films, which both exhibit tetragonal crystal lattices (oriented to the [110] and [331] zone axes). This orientation relationship is visualized by the high-resolution TEM image (c). Adapted from Ref. [9].

Apart from structural properties, EDX elemental distribution analysis in STEM provides information on the interdiffusion of elements and the presence of additional phases. Examples for such elemental distributions are given in Fig. 2, acquired at the same

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