Application Note AN R520

Contactless Characterization of Amorphous and Microcrystalline Silicon using Raman Micro Spectroscopy

Thin film silicon layers are widely applied in solar panels, photovoltaic devices, and thin film transistors e.g. as used for TFT displays.

Over the past few years, silicon based solar cells, as they belong to the renewable energy sector, gained new interest since they provide a chance to overcome the threat of global warming caused by fossil fuel consumption.

In particular thin film solar cells with the stacking of microcrystalline (µc Si:H) and amorphous (a-Si:H) layers are increasingly being used for the photovoltaic generation of electricity. Production costs for thin film modules are basically lower than those of wafer-based crystalline silicon modules. The better cost reduction potential is due to savings of raw material and energy consumption.

Amorphous and microcrystalline silicon

Raman spectroscopy and in particular Raman microscopy is a non-destructive method which is ideally suited for contactless analysis with high spatial resolution. Therefore Raman spectroscopy is considered as a powerful technique for the characterization of thin film silicon layers.

The Raman spectra of the different forms of silicon are described in detail in the literature. The Raman spectra of single crystal Si (wafer), microcrystalline Si and amorphous Si both on a glass substrate are displayed in Figure 1.

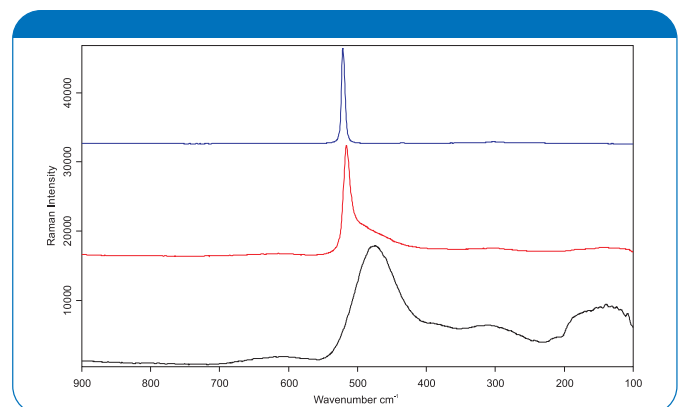| Keywords	Instruments and software
Crystallinity	SENTERRA II
Amorphous silicon	SureCAL™
Solar cells	OPUS spectroscopic software
Silicon thin films	

Figure 1: Blue: Raman spectrum of a silicon wafer, red: Raman spectrum of microcrystalline silicon on glass, black: Raman spectrum of amorphous silicon on glass.

Wafer grade crystalline Si (c-Si) has a sharp and symmetrical phonon band at about 520 cm^{-1}. For microcrystalline silicon the typical phonon band is seen at around 515 cm^{-1}. The Raman spectrum of amorphous silicon is typically characterized by four bands with the most intense peak located at 480 cm^{-1} (TO mode). The other modes are found at 380 cm^{-1} (LO mode), 301 cm^{-1} (LA mode) and 150 cm^{-1} (TA mode).

Various properties of thin film silicon layers such as stress, amorphous/crystalline volume fraction and moreover crystal size can be evaluated by Raman spectroscopy. Raman lines are shifting and broadening from the crystalline to amorphous state, allowing to discriminate and quantify poly, single, micro (also called nano) crystalline and the amorphous phase.

The Raman spectrum of a microcrystalline silicon layer as included in a micromorph tandem cell and shown in Figure 2 can be deconvoluted into three contributions: A relatively sharp line centered around 515 cm^{-1} which corresponds to the microcrystalline phase, a peak centered around 510 cm^{-1} which is attributed to the defective crystalline phase and a broad band located at 480 cm^{-1} for the amorphous phase. The ratio of the crystalline to the amorphous fraction of the Raman signals can be used as a measure for the crystalline fraction of thin film solar cells. The crystalline/amorphous ratio provides insight into the electrical properties. The ratio and shape of the microcrystalline and amorphous bands are useful for the optimization of production parameters such as deposition temperature or hydrogen dilution and moreover for controlling the homogeneity of solar modules.
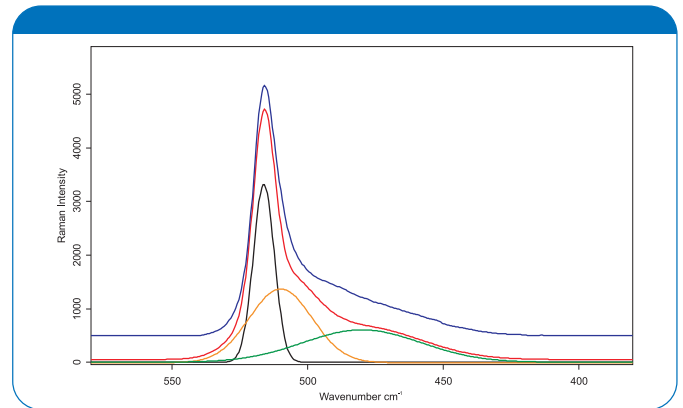

Figure 2: Deconvolution of a Raman spectrum of a microcrystalline layer in a micromorph tandem cell with band fit analysis.
Blue: Raman spectrum, (spectrum was offset for clarity)
Red: Fit spectrum
Black: Peak centered at around 515 cm^{-1} corresponding to the microcrystalline phase
Yellow: Peak centered at around 510 cm^{-1} corresponding to the defective crystalline phase
Green: Broad band at about 480 cm^{-1} corresponds to the amorphous phase.

Crystalline silicon

Not only crystallinity but also residual stress of the silicon surface structure is measured by the Raman peak shift. For example compressive stress results in an upshift and tensile stress in a downshift of the phonon line.
In Figure 3 the result of a Raman mapping (210 μm x 160 μm) which was created across the forced contact of a diamond on crystalline silicon is shown. The dark area corresponds to the region on which the silicon surface was contacted by the diamond. A significant peak shift to lower wavenumbers of the phonon line was observed (Figure 4).
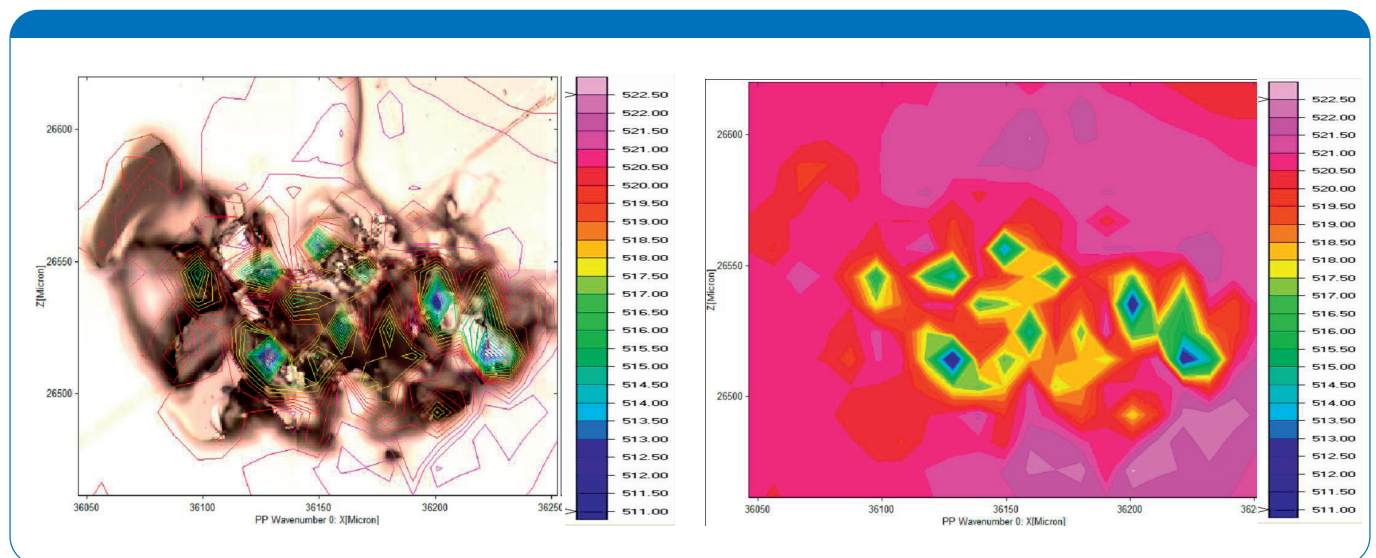

Figure 3: Raman mapping showing crystallinity changes induced by the forced contact of a diamond into mono crystalline silicon. 2D image (left image with underlay of the video picture) shows the position of the phonon band over the analyzed area. Excitation laser 532 nm, 0.5 mw, area: 210 μm x 160 μm, microscope objective: 50x, integration time: 1 sec per spectrum.
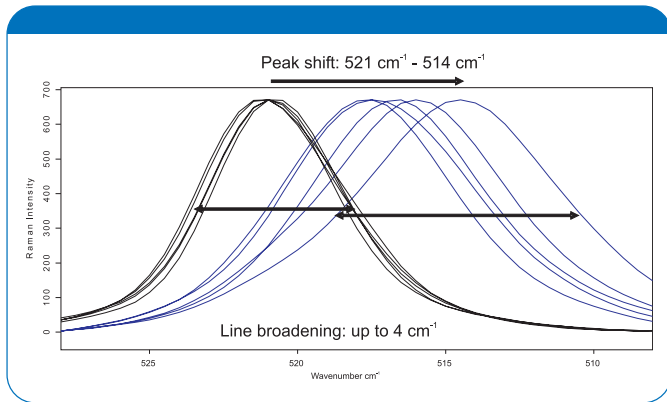
Figure 4: Raman spectra showing line shift and peak broadening due to crystallinity changes induced by the forced contact of a diamond into mono crystalline silicon; laser 532 nm.
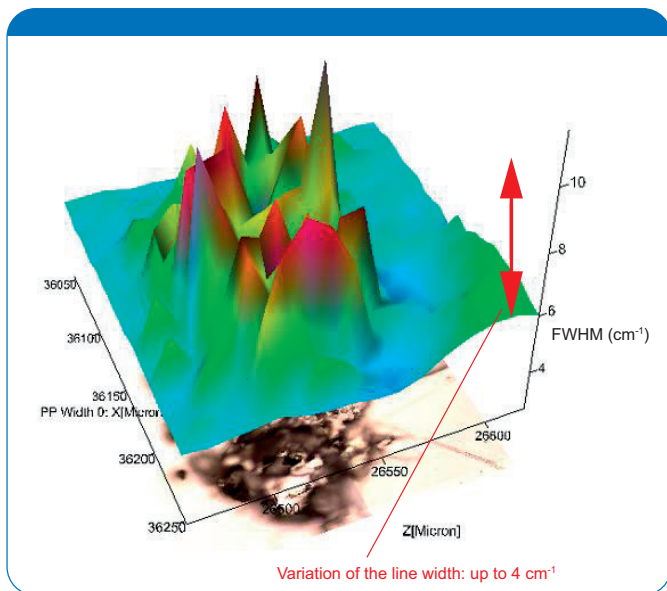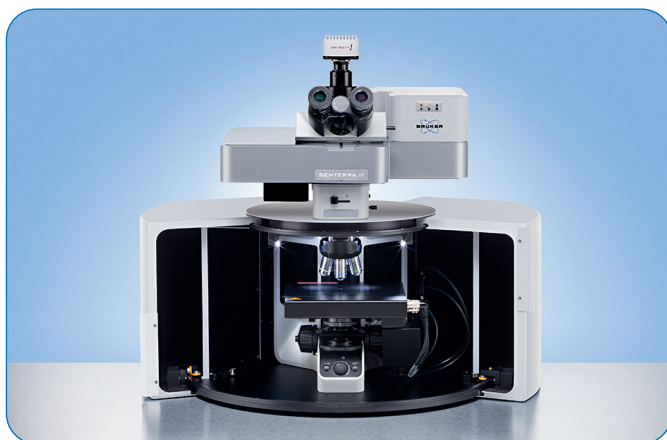

Figure 5: Raman mapping showing crystallinity changes caused by the forced contact of a diamond into a silicon wafer. 3D image shows the variation of the line width (FWHM) of the phonon line at 520 cm^{-1}. Excitation laser 532 nm, 0.5 mw, area: 210 μm x 160 μm, microscope objective: 50x, integration time: 1 sec per spectrum.

This is in contradiction to the general finding that compressive stress would lead to a shift to higher wavenumbers. Obviously, the comparatively large Raman shift of 4 cm^{-1} can be related to a change in crystallinity rather than compressive stress.

Moreover, the phonon lines which were located close to the areas where the diamond fractured the silicon surface were significantly broadened up to 4 cm^{-1} (Figure 4 and 5). The strong broadening of the phonon lines clearly indicated that instead of compression the change of the crystallinity was the prevailing influence introduced by the forced contact.

Polycrystalline silicon

Band shifts on silicon surfaces can be relatively low. For example in Figure 6 the Raman mapping of the peak shift on two differently crystallized zones on polycrystalline silicon are displayed. The peak shift is in the range of a few tenths of a wavenumber (Figure 7). Therefore wavenumber stability is a crucial issue for both research applications for highly accurate determination of band shifts and routine identification in QA/QC laboratories. The Bruker dispersive Raman spectrometers including the SENTERRA II provide automated and continuous calibration of the wavenumber axis. Thanks to the patented SureCAL™ technology Bruker Raman spectrometers are automatically calibrated to better than 0.1 cm^{-1} accuracy without the need for manual intervention.

Besides silicon crystallinity analysis by means of Raman spectroscopy, Bruker also provides FT-IR solutions for the impurity analysis of poly and single crystal silicon based on the respective international ASTM SEMI standards. From routine Carbon and Oxygen analysis at room temperature to the automated low temperature silicon analysis by the unique CryoSAS system, various solutions are available.

Experimental

Measurements in this paper have been carried out with the Raman microscope SENTERRA II using a 50x and 100x MPLN Olympus objective with 532 nm excitation. It is important to mention that the use of the excitation laser influences the penetration depth. E.g. for 532 nm laser excitation the penetration depth is around 100 nm for a-Si:H, 300 nm for μc-Si:H and 1 μm for c-Si [1]. Furthermore silicon samples are sensitive to sample heating. To prevent sample heating and subsequent recrystallization the power density of the incident Raman laser has to be kept low enough. The laser power of all samples was kept at 0.5 mW.
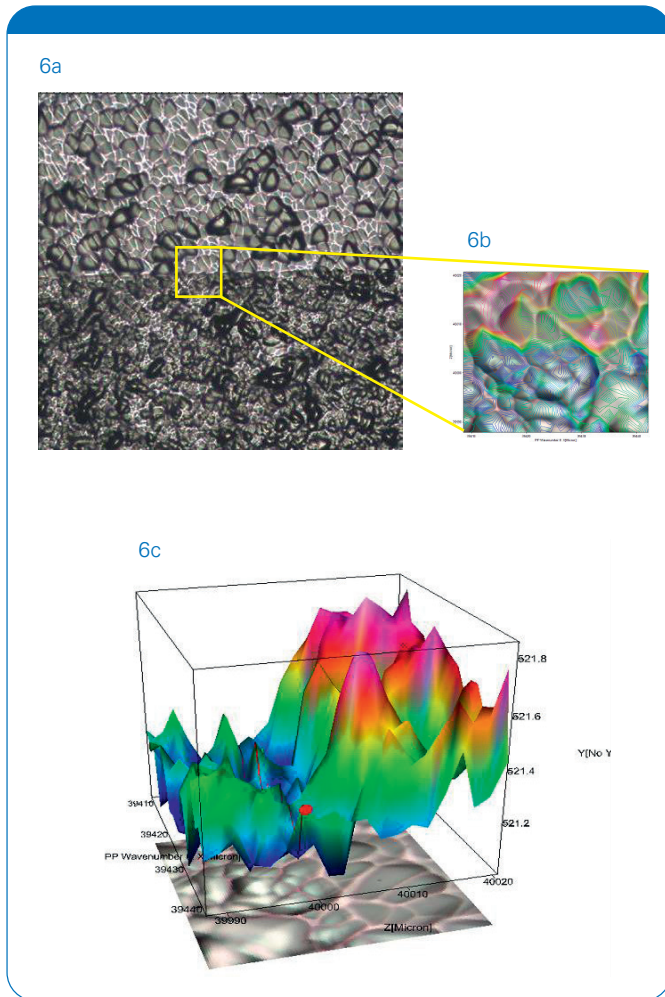
6a

6b

6c

Figure 6: Raman mapping (6c) of polycrystalline silicon showing peak shifts in the range of 0.5 cm^{-1} caused by local variations in crystallinity.
6a: Overview picture
6b: Analyzed area showing the phonon band position over the sample
6c: 3D Raman image
Excitation laser 532 nm, 0.5 mw, area: 36 µm x 36 µm, spatial resolution: 2 µm, microscope objective: 100x, integration time: 1 sec per spectrum.
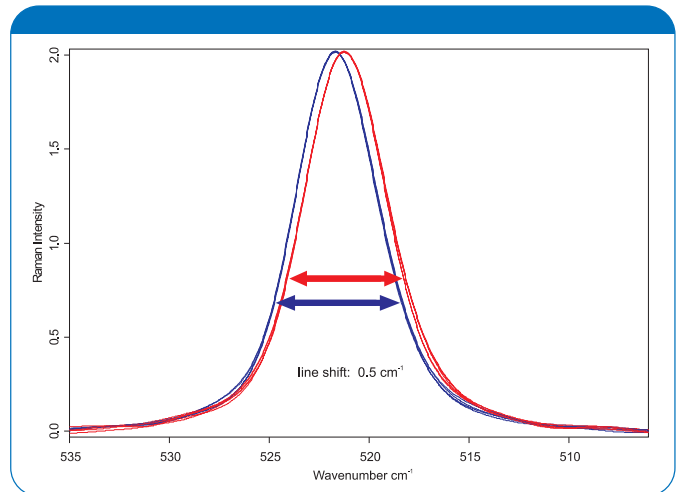

Figure 7: Raman spectra of polycrystalline silicon (see Figure 6) showing spectral peak shifts of the phonon line at 521 cm^{-1} of up to 0.5 cm^{-1} induced by local variations in crystallinity; laser 532 nm.

Conclusions

Raman spectroscopy is an ideal method for the characterisation of the crystalline/amorphous fraction of thin film solar cells. The ratio of the microcrystalline phase is a direct measure for the electrical properties and moreover the quality of the solar cell. It was shown that Raman microscopy is an efficient and sensitive tool for the determination of small changes in crystallinity.

As Raman spectroscopy provides results on crystallinity in a fast and non contact manner it is predestinated for the integration in process lines.

References

[1] A.V. Shah, H. Schade, M. Vanecek, J. Meier, E. Vallat-Sauvain, N. Wyrsch, U. Kroll, C.Droz and J.Bailat, Prog. Photovolt: Res Appl. 12, 113 (2004)