

FAST AND SENSITIVE DEFECT CHARACTERIZATION AND SPECTRAL RESPONSE MEASUREMENT OF THIN FILM SILICON SOLAR STRUCTURES

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ABSTRACT

Fourier Transform Photocurrent Spectroscopy (FTPS) has been used for a fast and sensitive quality assessment of photovoltaic thin films, such as the microcrystalline silicon. Because the properties of this material strongly depend on the substrate used, we demonstrate here how to utilize the FTPS for measurement of films grown on conductive TCO covered glass substrate, as it is the case of solar cells. Further, we have studied homogeneity of the optoelectronic properties of layers over large areas (30x30 cm²) and for one case correlated the results with the cell efficiency over the area. Moreover, we show a possibility to interpret the FTPS data on cells as the quantum efficiency (spectral response) measurement and to extend the measuring range from near IR over the whole visible region.

1. INTRODUCTION

Hydrogenated microcrystalline silicon is a low bandgap material for tandem "micromorph" solar cell structures (combined with amorphous hydrogenated silicon). The potential for stabilized efficiency around 15% is the main reason for a large research and industrial interest in this area.

Higher deposition rates for device quality intrinsic microcrystalline silicon are now important for the widespread expansion of this technology into industry. Different approaches have been suggested to increase the deposition rate, such as transfer to a higher deposition pressure or discharge frequency [1,2]. Another challenge is the enlargement of the deposited area and good enough homogeneity over the whole area. Hence, a sensitive, efficient and fast tool for characterization of layers, part of cells or whole cells is necessary.

Our samples, both layers and solar cells have been deposited in up-scaled deposition systems for cell deposition with the active area 30 x 30 cm². In this study we have concentrated on the measurement of homogeneity over the whole area. One of the most important material parameter influencing a solar cell performance is the defect concentration, which determines the carrier recombination. Defect density can be correlated with the value of the optical absorption coefficient $\alpha(E)$ at energy (E), corresponding to the electronic transitions from/to the defect states due to the absorption of photons [3]. Fourier Transform Photocurrent Spectroscopy (FTPS) is a fast and

sensitive method for the measurement of spectral dependence of the optical absorption coefficient $\alpha(E)$ [4]. Because the properties of microcrystalline silicon strongly depend on the substrate used [5,6], we have demonstrated here how to use FTPS for measurement of films grown on conductive, TCO covered glass substrate, as it is in the solar cell structure. Detection of $\alpha(E)$ curves from photocurrent measurement in sandwich configuration is not easy because of problems with contact behavior (band bending effects) and dependence of measured results on applied voltage. We again utilize an advantage of FTPS that whole spectrum is found within one minute and therefore the correct measurement conditions corresponding to the secondary photocurrent measurement can be quickly verified.

Moreover, in case of solar cells, where 36 cells with dimension of 1 cm² are measured over 30 x 30 cm², we have compared our results of FTPS in both near IR and visible region with the measurement of quantum efficiency (QE) determined by standard QE set-up. FTPS defect concentration map is then also correlated with the results of cell performances measured under AM 1.5 / 1000 Wm⁻² sun simulator.

2. EXPERIMENTAL DETAILS

Recently, the Fourier Transform Photocurrent Spectroscopy has been introduced for the defect characterization of thin film silicon layers [4,7]. A scheme of the utilization of the Fourier transform infrared (FTIR) spectrometer in the FTPS set-up is shown in Fig.1. FTIR spectrometer equipped for the near infrared and visible region (quartz beamsplitter and white light source) has possibility of an external beam output and an interface for the external detector. Our microcrystalline silicon sample (layer on TCO with the second contact from pasted colloidal graphite or a complete solar cell) connected into an electrical circuit with an ultra low noise voltage source and current preamplifier serves as the external detector.

We normalize the FTIR signal from the sample with the signal from spectrally independent detector (pyroelectric detector from deuterated triglycine sulfate, DTGS, or Si photodiode). Of course, a different frequency dependency of measured samples and detectors have to be found (e.g., from the measurements at different scan velocity) and taken into account.

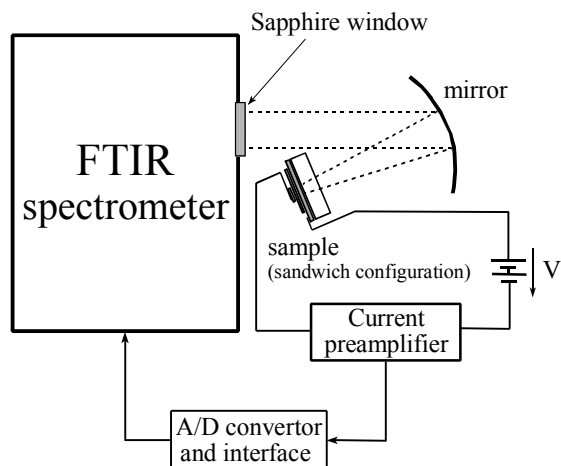


Fig.1. Scheme of the Fourier Transform Photocurrent Spectroscopy (FTPS) set-up.

Normalized photocurrent signal is proportional to the absorbance A or in a low absorption region directly to the optical absorption coefficient $\alpha(E)$. To obtain the correct value of the optical absorption coefficient (mainly in the IR region), the front TCO transparency has to be taken into account.

We have used FTPS method to characterize two large area microcrystalline silicon samples. The first one was undoped $\mu\text{c-Si:H}$ layer deposited on TCO (rough CVD ZnO [8]) covered glass substrate. The second sample had the complete p-i-n cell structure grown on sputtered ZnO [9] (front side contact) with small cell areas defined by a silver back reflector (back contact). For the measurement purposes (easier handling), each $30 \times 30 \text{ cm}^2$ sample has been cut into 9 pieces with dimension $10 \times 10 \text{ cm}^2$.

All experimental details concerning the utilization of FTIR spectrometer in FTPS set-up as well as the conditions and corrections necessary to interpret the measured data as the absorbance or directly absorption coefficient can be found in [4,7,10].

3. EXPERIMENTAL RESULTS

Fig.2 shows the FTPS results measured for the center point of the large area sample ($30 \times 30 \text{ cm}^2$) in sandwich configuration glass – TCO – undoped $\mu\text{c-Si:H}$ – graphite electrode with the parameter: applied voltage. Low forward bias below 0.5 V as well as reverse voltage (not shown) lead to the primary photocurrent conditions (defect connected absorption invisible or underestimated). Forward bias above 2 V leads to an overestimated defect concentration due to the current injection and SCLC (Space Charge Limited Currents) regime. For the $1.3 \mu\text{m}$ thick undoped microcrystalline silicon layer we have found that the reproducible results can be measured in the forward bias range $0.5 - 2.0 \text{ V}$, as expected. In this region we have also observed linear part of volt-ampere characteristics (ohmic region of secondary photocurrent). Similar behavior (voltage dependence) has been detected for all other measured points of this sample (sample area defined by the back colloidal graphite electrode).

Defect concentration in thin microcrystalline silicon film used to be usually connected with value of the optical absorption coefficient α at energy 0.8 eV [3]. Fig.3 shows

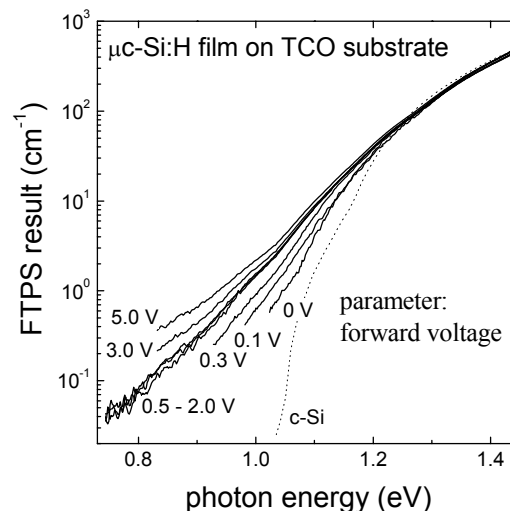


Fig.2. FTPS results of thin film on TCO substrate measured in sandwich configuration with a different forward voltage

values of $\alpha(0.8\text{eV})$ measured over the whole area (defect map) of this $30 \times 30 \text{ cm}^2$ sample except the part close to the end of y-axis. Homogeneity of the defect properties seems to be very good (20 % deviation of $\alpha(0.8\text{eV})$) for data plotted in fig.3.

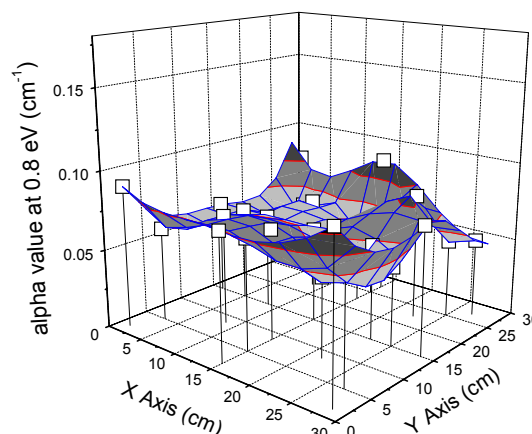


Fig.3. "Defect map" of the $\mu\text{c-Si:H}$ sample deposited on the $30 \times 30 \text{ cm}^2$ TCO substrate.

Data close to the end of y-axis are not plotted here, because the microcrystalline material starts to change into the amorphous one (as it can be seen from Fig.4). Therefore the measured $\alpha(0.8\text{eV})$ does not reflect the correct value of defect concentration. For amorphous silicon we usually take value of $\alpha(1.2\text{eV})$ for the defect density evaluation (with a different proportionality factor compared to microcrystalline silicon). Fig.4. shows that good microcrystalline silicon material is presented over more than 90% of the whole area and a very sharp transition to amorphous phase is located close to the one edge of the substrate. This was exactly confirmed by the Raman spectroscopy and transmission measurements.

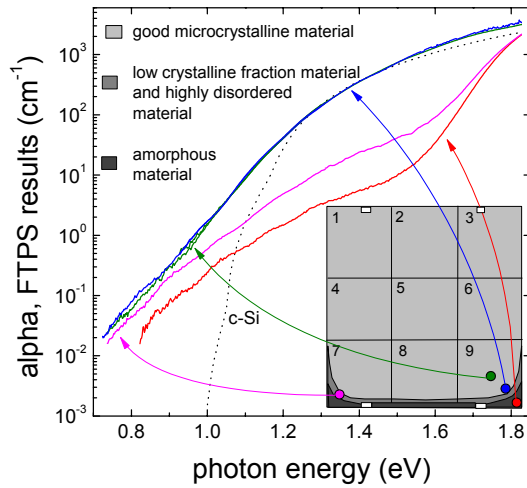


Fig.4. FTPS results measured at different places of the 30 x 30 cm² undoped μ c-Si:H sample on TCO substrate, absorption coefficient of the crystalline silicon is shown for the comparison

The second set of FTPS results was measured for complete p-i-n structures with dimension (0.5 or 1 cm²) defined by the silver back contact, located again over the area 30 x 30 cm². Fig.5 shows FTPS spectra measured at cells in the central area 15 x 15 cm², while Fig.6 shows all FTPS results measured for this sample (36 cells).

We can observe a perfect homogeneity of the optical and “defect” properties within the center area. Again, cells from one part (namely one corner) of the large area sample contain material with slightly higher defect concentration (as can be seen from the defect map shown in Fig.7) and also with slightly higher amorphous fraction (detected from change in the quantum efficiency and transmittance spectra). Nevertheless, the defect absorption in the whole measured region is extremely low which guarantees the complete collection of photogenerated carriers in the cell.

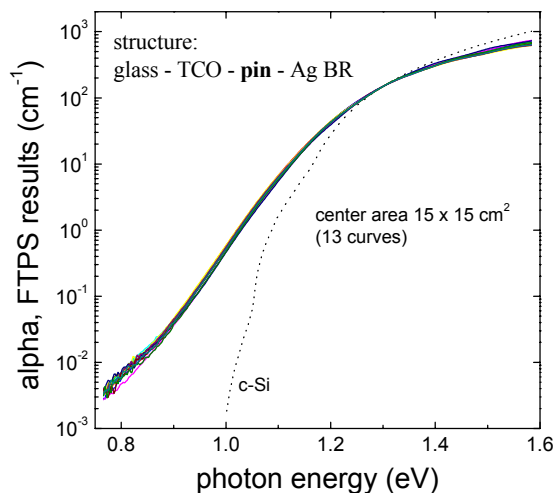


Fig.5. FTPS results from the central area (15 x 15 cm²) of the p-i-n microcrystalline silicon cell on rough TCO substrate

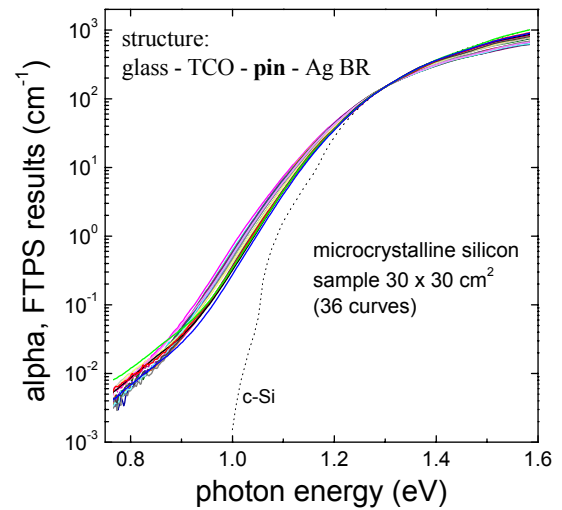


Fig.6. FTPS results from whole sample area (30 x 30 cm²) of the p-i-n microcrystalline silicon sample on rough TCO substrate

Moreover, we compared this “defect map” with the 3-dimensional graph of the short circuit current I_{sc} of the corresponding cells and we found an excellent agreement. Typical short circuit current density was 17 - 18 mA/cm².

Here we should note that the FTPS results are proportional to the absorbance in the active i-layer. Thus when we plot these data in the scale of optical absorption coefficient α (cm⁻¹), e.g., together with data for crystalline silicon, then the scale is valid only for $\alpha \cdot d$ product (where d is the film thickness or due to the silver back reflector double of the film thickness) much lower than 1 (region of homogeneous optical absorption). Fitting the spectra into the absolute scale is done with numerical calculation taking into account both TCO transparency and light scattering effects at the front rough TCO - silicon interface and at silver back reflector [11].

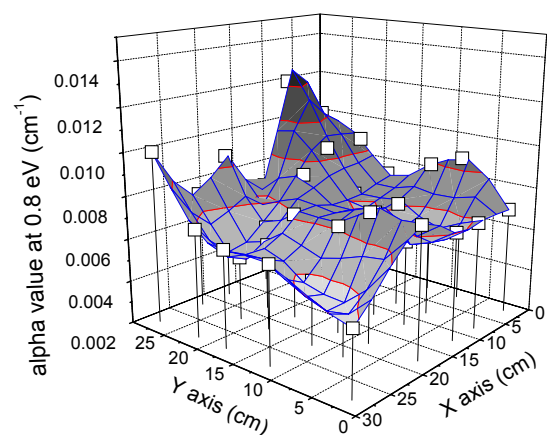


Fig.7. “Defect map” of the p-i-n μ c-Si:H sample deposited on the 30 x 30 cm² rough sputtered TCO substrate.

4. MEASUREMENTS OF QUANTUM EFFICIENCY

All FTPS spectra were measured at the mirror speed velocity (of the FTIR spectrometer) $v = 0.15$ cm/s corresponding to the scanning frequency $f = 2.v.v$, where v denotes the wavenumber. From the principle of the spectrometer, where position of the moving mirror is measured by He-Ne laser, we can detect the spectra at the range with the wavelength higher or lower than 632.8 nm corresponding to the laser wavelength, but not both together. All spectra presented till now were found for the wavelengths above this border with the goal to detect a homogeneity of the defect connected optical absorption. It is clear that the data in this range can be simply interpreted as the quantum efficiency (QE) spectra.

As the second task for this contribution, we decided to verify the possibility of the FTPS measurement in the visible region to be able to find QE data in the whole region of interest. Fig.8. shows such spectra for one p-i-n microcrystalline silicon cell from this large area sample. In this figure we compare our result measured with reverse voltage bias (full and dashed curves) with the QE data obtain by standard QE set-up (squares).

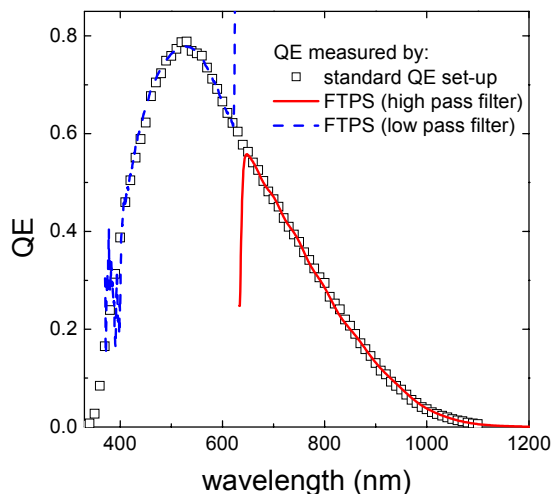


Fig.8. QE results measured by standard QE experimental set-up (squares) and using FTPS method (full and dashed lines) with filters cutting the wavelength part higher or lower than 632.8 nm (HeNe laser)

We can see a very good agreement of results obtained by both method mainly in the near IR range. Discontinuity of FTPS is ensured by using the cut-off filters close to the He-Ne laser wavelength and therefore by measurement in two steps with high and low pass filters, respectively. High noise value below 420 nm is due to the low intensity of the white light source (halogen lamp) in this region.

Moreover, the necessity of measuring both parts of the spectra separately could be avoided by using special FTIR equipment, in which the position of the moveable mirror is calculated not from the wavelength of He-Ne laser but from the half of that. With this arrangement the whole QE curve could be found within few seconds.

5. CONCLUSION

We have demonstrated the possibility of Fourier Transform Photocurrent Spectroscopy method for fast quality assessment and homogeneity study of thin film silicon sandwich structures from the point of defect evaluation. FTPS measured with different voltage bias on photovoltaic structures of microcrystalline silicon gives us also quick information about the collection efficiency. By this way we have pointed out the suitability of the FTPS method both for the defect concentration evaluation and QE measurement.

ACKNOWLEDGMENTS

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