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Fourier transform photocurrent spectroscopy applied to a broad variety of electronically active thin films (silicon, carbon, organics)

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Abstract

Steady state and low frequency photocurrent spectroscopies have proved as a valuable tool for investigation of many different semiconductors, used for example as an absorber in photovoltaic solar cells or in the large area sensors. Fourier transform photocurrent spectroscopy (FTPS), described here, exhibits advantages as a high sensitivity (we demonstrate dynamical range up to 9 orders of magnitude of the optical absorption coefficient, connected with the absorption process leading to free carriers; or sensitivity for dopant detection better than 1 part-per-billion), fast acquisition of data (it can be of the order of seconds) or high resolution (under more lengthy acquisition of data). Results on amorphous silicon, microcrystalline silicon, diamond layers, nanocrystalline diamond and very thin organic films, as poly(2-methoxy-5-(3′,7′-dimethyl-octyloxy))-p-phenylene-vinylene (MDMO-PPV), regioregular poly(3-hexylthiophene (P3HT) and their blends with (6,6)-phenyl-C61-butyric-acid (PCBM) are reported, together with the results measured on various thin film silicon or polymer solar cells.

Keywords: Optical spectroscopy; Photoconductivity; Semiconductors; Solar cells

1. Introduction

Electronic defects in semiconducting thin films can hinder successful application of these materials in active electronic devices. A fast and sensitive detection method and straightforward interpretation is desirable for investigation of thin layers and devices. We present a quantitative interpretation of photocurrent spectra in the subgap spectral region, measured with the help of Fourier transform infrared spectrometer. We point to the advantage of these measurements, which we call Fourier transform photocurrent spectroscopy, FTPS [1,2] and compare them with older "standard" photocurrent spectra measurements with a dispersive monochromator, as "Dual beam photocurrent spectroscopy" [3], "Constant photocurrent method", CPM, [4,5] or "Photothermal ionization spectroscopy", PTIS, [6,7]. We present also a quantitative interpretation of measured spectra in terms of defect concentration, what was not the case in a previous usage of Fourier transform spectrometers for photocurrent spectra measurements [8,9].

All semiconducting or semiinsulating films or devices incorporating these active layers can be used for the investigation. We report experimental data on amorphous silicon, microcrystalline silicon, diamond layers, nanocrystalline diamond and very thin organic films, as poly(2-methoxy-5-(3′,7′-dimethyl-octyloxy))-p-phenylene-vinylene, MDMO-PPV, regioregular poly(3-hexylthiophene, P3HT, and their blends with (6,6)-phenyl-C61-butyric-acid, PCBM. We also report measurements on devices incorporating these layers, as the solar cells or large area solar panels (homogeneity studies).

2. Experimental method (Fourier transform photocurrent spectroscopy)

The basic principle of Fourier transform photocurrent spectroscopy, FTPS, is shown in Fig. 1. Fourier transform spectrometer equipped for the near infrared region, NIR, (CaF_2 beamsplitter, globar or white light source) or for visible-NIR (quartz beamsplitter) has an external light beam output and can operate with an external detector. For example, we use our microcrystalline (nanocrystalline) silicon thin film with coplanar contacts as the external detector. The silicon layer with two ohmic contacts serves as a photoresistor, we put typically10–

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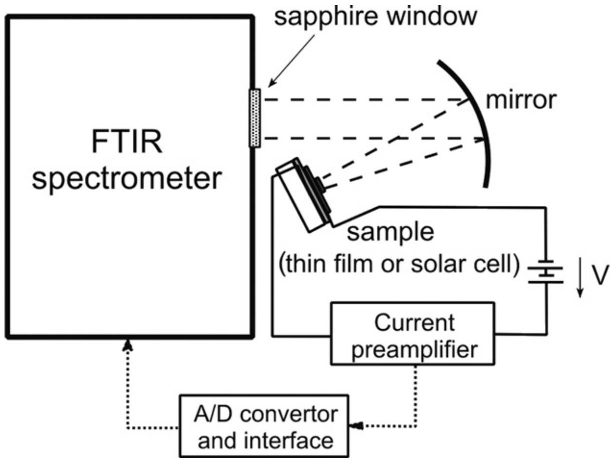

Fig. 1. Schematic picture of the Fourier transform photocurrent spectroscopy, FTPS, setup.

100 V across a 2 mm gap. Alternatively, microcrystalline silicon solar cell without applied bias is used for the measurements; in this case a correction has to be made for infrared absorption in transparent conductive oxide.

The photocurrent, which is carried by electrons, is amplified by a current preamplifier, its voltage output is finally digitized by an A/D converter of the external interface of the FTIR spectrometer (the “external detector option” of FTIR spectrometer). We normalize the FTIR signal from the sample to the signal from a spectrally independent (or calibrated) detector, for example a pyrodetector of deuterated triglycine sulfate (DTGS), or a Si photodiode. Signal from the thermal detector (pyrodetector) is corrected by a factor $1/E$, E being the photon energy, in order to be proportional to the number of photons impinging the detector, as it is for the quantum detector (Si photodiode).

Typical measured spectra are presented in Fig. 2. All measurements were done at low scan velocity $v=0.158$ cm/s. Measurement of microcrystalline silicon layer was done at first without using any filter. This curve starts to be noisy at the low energy (wavenumber) region due to the insufficient dynamic range of the external D/A converter. In order to reduce the dynamic range of our measurement we use a 2 mm thick silicon filter removing the high energy photons from the incident light beam. Resulting measurement (crosses) extends down to 3000 cm^{-1}. For the baseline measurement below 11,000 cm^{-1} we can use the DTGS pyroelectrical detector (circles) and above 11000 cm^{-1} the silicon photodiode (triangles). Standard DTGS detector has a high noise level above 11,000 cm^{-1}; this can be reduced by thermoelectrical cooling and the cooled version of DTGS is now being used up to 20,000 cm^{-1}.

All spectra presented in Fig. 2 have been corrected for the different frequency responses of detectors and sample. The necessity to provide such a correction comes from the principle of FTIR detection, where the signal at each wavenumber ν is scanned at different frequency $f=2\cdot\nu\cdot v$, where v is the scan velocity. The frequency dependence can be determined for each sample or detector by measuring the spectrum at several different scan velocities [10].

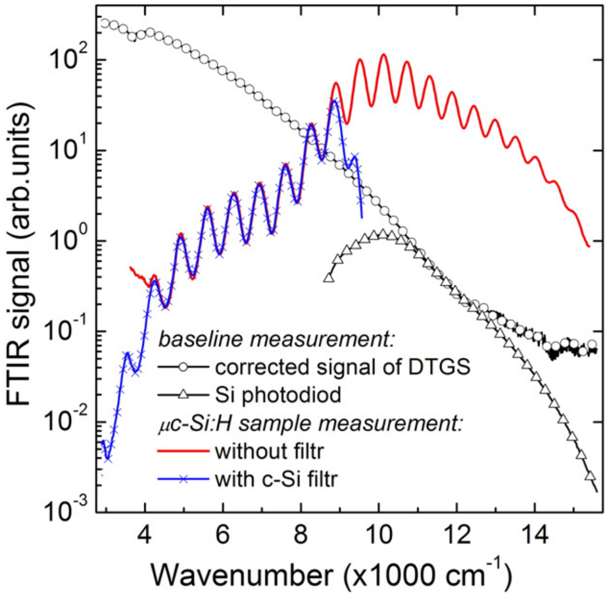

Fig. 2. FTIR spectrometer signal from the microcrystalline silicon film — full line. The same with 2 mm thick crystalline silicon filter in front of the sample — crosses. Baseline signal measurement with silicon photodiode — triangles. Baseline signal measurement with pyrodetector (DTGS) — circles.

The resulting ratio of the sample spectrum and the baseline is presented in Fig. 3. The normalized photocurrent signal is proportional to the absorptance A and in a low absorption region directly to the optical absorption coefficient α, when we average the interferences properly. If we want to interpret the result as the absorptance A, signal linearity is the necessary condition. We have checked the linearity of the photocurrent signal with light intensity with the help of neutral filters (mesh filters) and have found the signal linear over the investigated spectral range. The origin of this behavior is in the relatively

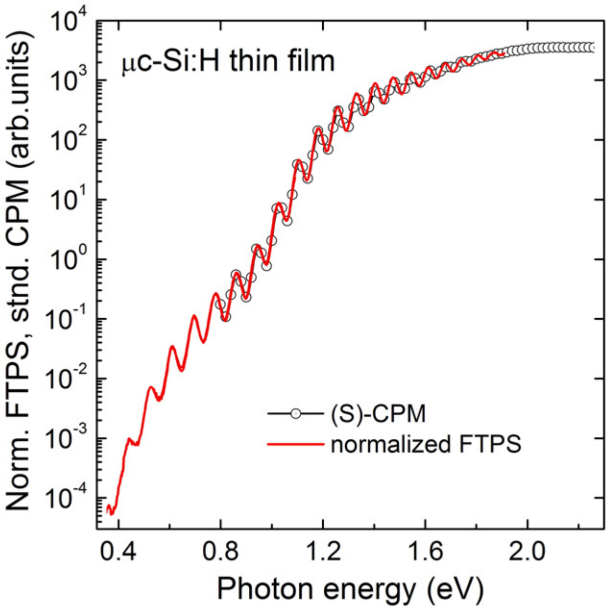

Fig. 3. Normalized FTPS spectrum (full line) compared to the standard CPM spectrum (circles), measured on the same sample.