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Fourier transform infrared photocurrent spectroscopy in microcrystalline silicon

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Abstract

A fast and sensitive method for measurement of spectral dependence of the optical absorption coefficient $\alpha(E)$ in thin films of photosensitive materials is introduced. A Fourier transform infrared (FTIR) spectrometer is used with a photoconductive sample as an external detector. Experimental conditions and procedures to obtain $\alpha(E)$ from normalized FTIR signal are described and results are compared to the standard measurements of transmittance and reflectance, and the constant photocurrent method. The FTIR method is applied to thin microcrystalline silicon layers and the resulting optical data are discussed in terms of optical absorption connected with defects and disorder. The measurement of $\alpha(E)$ is extended down to very low photon energy and reveals the threshold energy for the dangling bond optical absorption in microcrystalline silicon. Photoionization cross section of the silicon dangling bonds is measured over several orders of magnitude and full dynamical range of $\alpha(E)$ exceeds nine orders of magnitude.

1. Introduction

The study of hydrogenated microcrystalline silicon thin films and solar cells has shifted from basic research to successful large area applications [1]. Frequently, all measurements have to be performed over a large area to verify the homogeneity of the thin film properties. One of the most important material parameters for solar cell performance is the defect concentration, which determines the carrier lifetime. 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 state due to the photon absorption [2].

The spectral dependence of the optical absorption coefficient $\alpha(E)$ in thin films of hydrogenated microcrystalline silicon is routinely measured by constant photocurrent method (CPM) or photothermal deflection spectroscopy (PDS). Both these techniques have some limitations and, moreover, both are quite time consuming (hours). In this paper we suggest a method which is more sensitive; therefore, it extends the measurement range to low photon energy (typical range 0.4–1.9 eV) and the whole measurement takes few minutes only. We call this method Fourier transform infrared

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photocurrent spectroscopy (FTPS). In the experiment we utilize FTIR spectrometer as a light source and interferometer, and our microcrystalline silicon sample as the external detector. The signal from the sample is compared with the signal from spectrally independent detector [3]. Details of our new approach, how to extract the optical absorption coefficient spectrum $\alpha(E)$ from the normalized signal, are explained here.

Finally, the numerical fit of photoionization cross section of silicon dangling bonds in microcrystalline silicon and model of density of states (DOS) of singly occupied silicon dangling bonds in the gap of microcrystalline silicon is presented.

2. Experimental

Samples of microcrystalline hydrogenated silicon (μc-Si:H) thin films and solar cells were prepared by very high frequency glow discharge of silane diluted with hydrogen, under a large variety of deposition conditions [4]. Samples are typically 2 μm thin, deposited on low alkaline glass.

Fig. 1 shows the experimental scheme. FTIR spectrometer (Nicolet, model Nexus) is equipped by CaF_2 beamsplitter and white light and IR light source (globar) for near infrared region measurement. Spectrometer has option of an external beam output and an external detector. A thin film sample is connected as the external detector (photoresistor, or in the case of solar cell as photodiode) into electric circuit with an ultra low noise voltage source and current preamplifier. Solar cell samples are usually used without external voltage, with a load resistor and voltage preamplifier. The output of the preamplifier is digitized by A/D converter and finally the signal is Fourier transformed from the time domain into frequency domain using a computer. To get the normalized photocurrent spectrum for the constant number of impinging photons, the FTIR photocurrent signal from the sample is compared with the signal from an auxiliary thermal (pyroelectric) or photon (Si photodiode) detector. (In the case of thermal detector, to get the number of impinging photons, the signal has to be divided by the photon energy E).

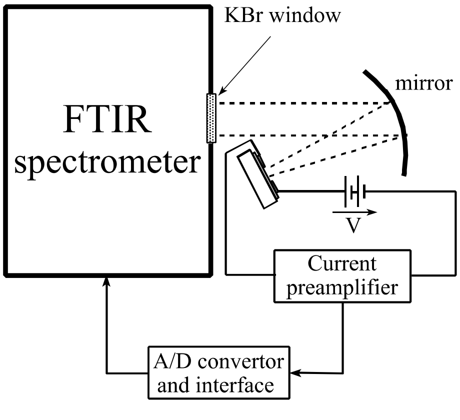

Fig. 1. Experimental set-up. Light from the external port of FTIR spectrometer is focused on microcrystalline silicon film between the coplanar electrodes.

The sample, Si photodiode and pyroelectric detector have a different frequency response of an electrical signal. Because in FTIR spectrometer the spectra are scanned at constant scan velocity, we have to convert the scan velocity to the modulation frequency for each wavenumber and use this correction [5]. Frequency dependence of detectors or samples can be simply monitored by changing the scan velocities.

Signal linearity was checked using mesh filters. The dynamic range of the FTIR spectrometer is limited by the A/D converter. To extend this range, a low-bandpass filter is used. In our case this is a polished 2 mm thick silicon wafer. When measuring the solar cells, correction has to be made for reduced transparency of conductive oxide window in the IR region.

3. Results

Result of the FTPS for the microcrystalline silicon (μc-Si:H) sample (2.3 μm thin film on glass) is shown in Fig. 2 for the IR light source irradiation. All spectra are scanned with 0.158 cm/s scan velocity. It is seen that the dynamic range can be extended by using 2 mm double polished crystalline silicon wafer, which reduces the signal level by removing high energy photons from the incident spectrum. Typical signals from deuterated

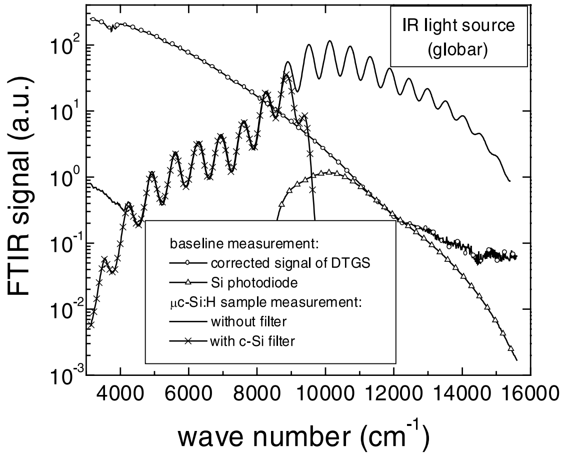

Fig. 2. FTIR spectrometer signal from the spectrally flat detectors (baseline signals) and from 2.3 μm thin film of microcrystalline silicon. Signal from thermal detector is corrected to be proportional to the number of photons impinging the detector. Microcrystalline silicon sample is measured with and without the crystalline silicon filter in the light beam.

triglycine sulfate (DTGS) pyroelectric detector and crystalline silicon photodiode detector are also shown in Fig. 2. Output of the pyroelectric detector is recalculated to be proportional to the number of photons. Pyrodetector, measuring the baseline with a globar light source, gives a noisy signal in a high wavenumber region, therefore, silicon photodiode is preferred here.

Photocurrent, in general, is not linearly dependent on light intensity. We have verified that in our measurements on microcrystalline silicon, under FTIR spectrometer typical illumination conditions, in samples with the dark current comparable or higher than the photocurrent, the linearity is fulfilled. Fig. 3 compares the normalized FTPS signal with standard CPM data [6]. Both standard (S)-CPM and normalized FTPS signal are proportional to the absorptance A, ($A = 1 - R - T$), where R is the reflectance and T the transmittance. It means, both curves should have identical shape. We can see a very good agreement between (S)-CPM and FTPS results, the FTPS curve being extended more into infrared due to a higher sensitivity of FTPS. Difference in the modulation depth of interference fringes is a result of different spectral resolution of each apparatus.

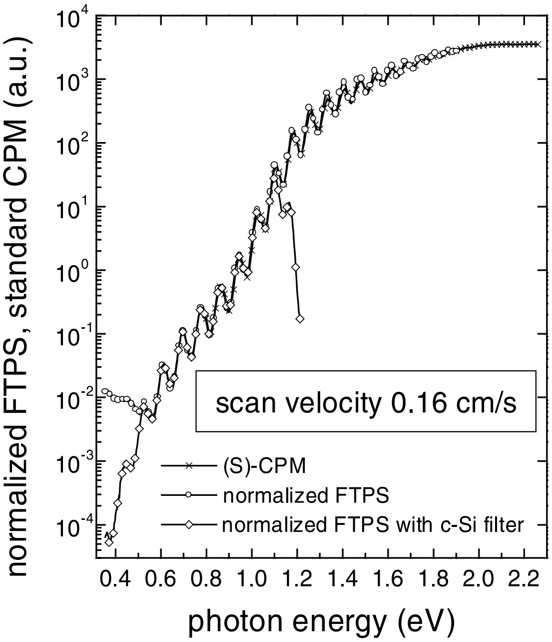

Fig. 3. Normalized FTPS signal (with and without the crystalline silicon filter) and standard CPM signal, as a function of photon energy.

Light scattering at a rough surface of microcrystalline silicon thin films makes average optical path longer than the film thickness and an apparent optical absorption coefficient is measured if this effect of light scattering is not taken into account [6]. We use our procedure to correct for this effect and to get the true value of the optical absorption coefficient [7]. Thick line in Fig. 4 shows the result of such procedure. For a comparison, spectral dependence of the apparent optical absorption coefficient obtained by FTPS and T/R measurement is also shown.

In Fig. 5 the true optical absorption coefficient $\alpha(E)$ data are presented for a representative set of samples, deposited under very different deposition conditions in order to get a widely ranging silicon dangling bond density [2].

4. Discussion

Spectrum $\alpha(E)$ of microcrystalline silicon sample in Fig. 4 spans over nine orders of magnitude.

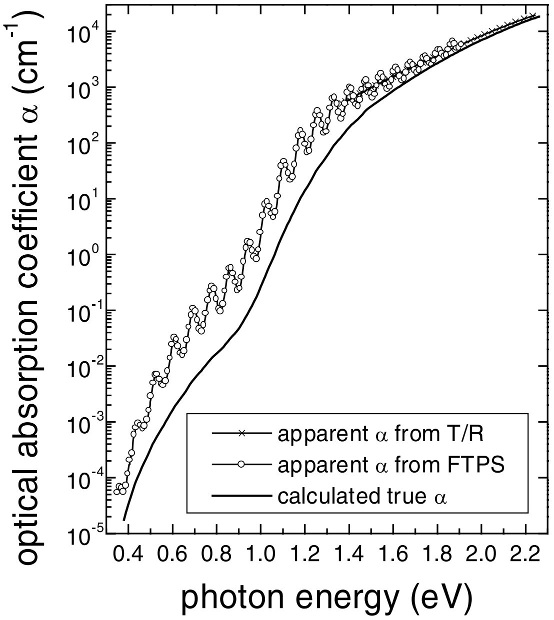

Fig. 4. Optical absorption coefficient α as a function of photon energy. We obtain an apparent value of the optical absorption coefficient α from the conventional transmittance/reflectance (T/R) measurement or from FTPS if we do not consider an increased optical path due to the light scattering. If the correction for this effect is done [7], we obtain the true value of α, connected with the optical excitation of electrons into the conduction band.

This is the highest dynamic range ever obtained from measurement on just approximately 2 μm thin microcrystalline silicon samples. Origin of this high dynamic range is clear from Fig. 2. Light intensity from globar source decreases several orders of magnitude towards the high wavenumber region while sensitivity of the sample increases in this direction. This, together with use of low-pass filter and the effect of light trapping in this rough film, strongly increases the dynamic range.

Because we have fulfilled all necessary experimental conditions (photocurrent linearity, corrections for frequency dependence of signals and for the light scattering effects), we can interpret our results as the optical absorption coefficient $\alpha(E)$ in microcrystalline silicon, connected with the optical excitation of electrons into the conduction band [7] in this slightly n-type semiconductor. The linearity of the photocurrent (in contrast to a typically sublinear dependence for amorphous silicon) is due to a high dark current (higher or comparable with the photocurrent under typical FTIR spectrometer illumination level) in our microcrystalline silicon. Therefore, the photocurrent in microcrystalline silicon is a relatively small perturbation compared to the total current.

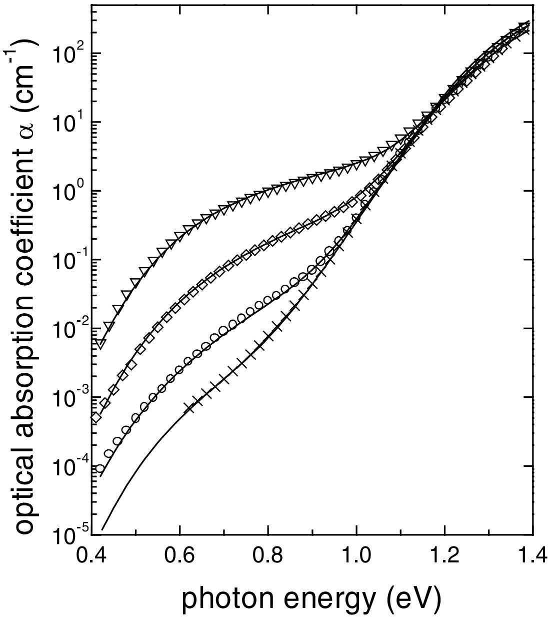

Fig. 5. Spectral dependence of the true optical absorption coefficient α for a set of microcrystalline silicon samples with a different defect density (different spin density due to the silicon dangling bonds). Full curves present the results of numerical fit based on the model of Inkson [9,10].

In the subgap region (below 1.1 eV) our optical absorption is approximately proportional to the spin density, as measured by ESR [2,8], and we can fit our data with a simple model for density of gap states, based on a Gaussian distribution of singly occupied dangling bond states in the gap. The model of Inkson [9,10] is used for the spectral dependence of the photoionization cross section of singly occupied dangling bond and it gives an excellent fit to the measured data (look at full curves in Fig. 5). The fitting yields the position of a Gaussian band of the singly occupied dangling bond states 0.3–0.35 eV above the top of the valence band for a ‘device quality’ material. Full width at half maximum (FWHM) for this band is approximately 0.3 eV. Similar model with nearly the same parameters was suggested by Biegelsen et al. [11] for the silicon dangling bond at the crystalline silicon/amorphous silicon oxide interface.

Investigated samples have 10–20% of amorphous phase, as determined by Raman spectroscopy [2]. Because we get the same position for the dangling bond band in commercial CVD samples of silicon on sapphire (SOS), which have no amorphous phase, we suggest that most of these silicon dangling bonds are at the surface of crystalline nanograins and not in the amorphous part of the microcrystalline silicon.

5. Conclusion

The FTIR photocurrent spectroscopy as introduced here is a fast and very sensitive method for spectral measurement of the optical absorption coefficient $\alpha(E)$, connected with the electron transitions from the defects states or valence band into the conduction band in microcrystalline silicon. Full dynamical range of $\alpha(E)$ can exceed nine orders of magnitude. This enables us to fit the photoionization cross section of the silicon dangling bonds over several orders of magnitude. A model using a Gaussian distribution of silicon dangling bonds in the gap fits our data very well. Position of the singly occupied silicon dangling bond is about 0.3 eV above the top of the valence band, FWHM of this distribution is about 0.3 eV.

Acknowledgements

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