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Temperature dependence of the optical absorption coefficient of microcrystalline silicon

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Abstract

The optical absorption coefficient of amorphous and microcrystalline silicon was determined in a spectral range 400–3100 nm and a temperature range 77–350 K. Transmittance measurement and Fourier transform photocurrent spectroscopy were used. The measured data served as an input for our optical model of amorphous/microcrystalline tandem solar cell. Differences in the current generated in the amorphous and microcrystalline parts were computed, for an operating temperature between −20 °C and +80 °C. Optical spectra of microcrystalline silicon were compared to the spectrum of silicon on sapphire (without hydrogen and hydrogenated) and the observed difference was interpreted in terms of a different density of defects and higher disorder of microcrystalline Si.

1. Introduction

Microcrystalline silicon is gaining an increasing importance for thin film solar cells. Monitoring the changes of material parameters such as an optical absorption coefficient with temperature is important from a practical point of view, because the operating temperature of solar cells can vary from −20 to +80 °C. The knowledge of the temperature dependence can help to predict the current density generated by solar cells at different temperatures [1]. That is important for current matching in micromorph (tandem amorphous–microcrystalline silicon) cells.

Moreover, a study of the temperature dependence of the optical absorption coefficient can provide an additional information about the electronic structure, disorder and defects, if the measurement is extended down to the sub-bandgap absorption region [2,3]. Recently, Fourier transform photocurrent spectroscopy (FTPS) was introduced as a method suitable for fast and very sensitive evaluation of spectral dependence of the optical absorption coefficient, e.g. in microcrystalline silicon thin films and solar cells [4,5], in a broad spectral region.

2. Experimental details

Microcrystalline hydrogenated silicon (μc-Si:H) thin films were deposited by standard plasma enhanced chemical vapor deposition PE-CVD and very high frequency (VHF) PE-CVD from silane diluted with hydrogen, under a large variety of deposition conditions [5,6]. Samples of amorphous hydrogenated silicon (a-Si:H) thin films were prepared by standard PE CVD and hot wire (HW) technique [7]. Samples are typically 1–2 μm thick, deposited on a low alkaline glass. To exclude the influence of light scattering effects at naturally rough silicon surface on all optical measurements (mainly of microcrystalline silicon), we chose either samples with smooth surface or surface was smoothed by chemomechanical polishing.

Transmission spectra in the wavelength region 400–920 nm were obtained by the M40 spectrophotometer. They were complemented in the red and infrared region

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(645–3100 nm) by the Fourier transform photocurrent spectroscopy (FTPS) measurements. Samples were placed into a liquid nitrogen cryostat with a temperature regulation. Absorption coefficient of microcrystalline silicon thin films was measured in the temperature range from 77 to 350 K, in the visible and infrared spectral regions, down to the photon energy $E = 0.4$ eV. FTPS spectra were collected by FTIR spectrometer (Nicolet, model Nexus, with an external beam output and an external detector option) equipped by CaF_2 beamsplitter and white light source (halogen lamp). Appropriate filters (red glass, infrared glass and thick crystalline silicon wafer) were used to ensure the signal linearity over the entire energy range. Signal linearity was also checked by the neutral density (mesh) filters. To monitor the temperature changes of the Fermi level position, the FTPS data are supplemented with the dark and photo conductivity measurements as a function of temperature.

Commercial crystalline silicon on sapphire (SOS) 1 μm thin layer was used as the reference sample. This SOS thin film was also annealed in PE CVD hydrogen plasma at 360 °C for 1 h to deactivate the defects (Si dangling bonds) by hydrogenation.

3. Results

The optical absorption coefficient spectra $\alpha(E)$, as a function of temperature, are presented below. They served as input data for modeling the current matching of amorphous silicon–microcrystalline silicon tandem solar cell, presented in Section 3.2. Finally, the optical data for microcrystalline Si are compared to the data for silicon on sapphire.

3.1. Optical measurements

Fig. 1 shows the results of transmission spectroscopy of amorphous hydrogenated silicon sample prepared by hot wire technique [8] measured at different temperatures in the range from liquid nitrogen temperature up to 350 K. We can observe clear shift of the absorption edge with the temperature. A negligible shift of the positions of the interference fringes as well as modulation depth of fringes is due to not perfectly homogeneous film thickness and possible change of the measured spot (5×4 mm) rather than by temperature change of the index of refraction. The same temperature dependencies of the transmission spectra were measured for two samples of amorphous and two samples of microcrystalline silicon. Moreover, for each of these four samples we measured the transmission and reflection spectrum at room temperature in the same sample spot (1 mm spot diameter) to calculate the absorption coefficient from the $(1 - R - T)/T$ ratio, spectral dependence of the index of refraction and verify the negligible

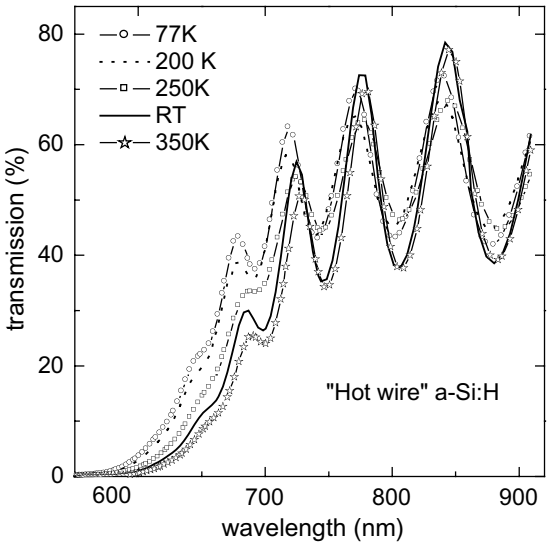

Fig. 1. Transmission spectra of amorphous hydrogenated silicon prepared by hot wire technique measured at various temperatures.

surface roughness [3]. Knowing the spectral dependence of the refractive index and supposing its negligible temperature change, the absorption coefficient is then calculated from the smoothed transmission spectrum. Smoothing was done by standard spline method but in the logarithmic scale of transmission. Fig. 2 shows the results of such procedure for temperatures 250, 300 and 350 K corresponding to the presumable outdoor working temperature range of solar cells both for one amorphous and one microcrystalline silicon sample.

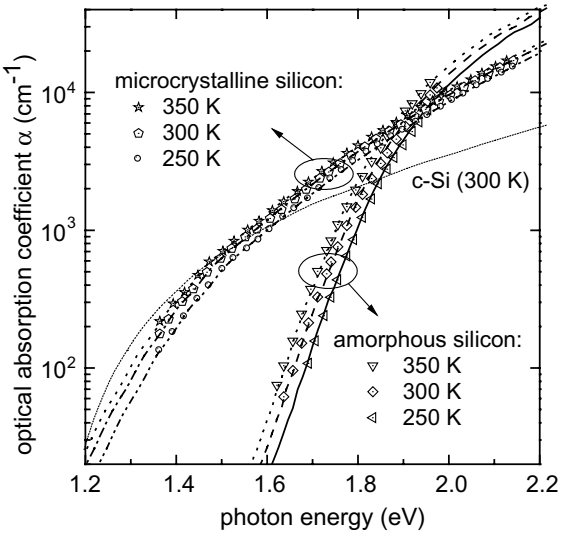

Fig. 2. Optical absorption coefficient of amorphous and microcrystalline silicon samples at the temperatures 250, 300 and 350 K calculated from transmission spectra (symbols). Low absorption data are taken from CPM (a-Si:H) or FTPS (μc-Si:H) measurements, data in the high energy range were extrapolated from the transmission measurement of very thin samples (lines).

Symbols show the data calculated from transmission measurements while lines are taken in the low absorption range from CPM (a-Si:H) or FTPS (μc-Si:H) and in the high energy region extrapolated according to the results measured for very thin samples.

3.2. Tandem cell modeling in a broad temperature range

The scheme of the model structure of micromorph (amorphous–microcrystalline silicon tandem) cell is shown in Fig. 3.

In our optical model for the silicon thin film solar cells [9,10], the coherent contribution of the multilayer structure is calculated using the wave theory taking into account scattering losses at each surface/interface. Then ray tracing of scattered photons is calculated up to the final absorption in any layer of the solar cell or the photon loss due to the reflection into air. We use experimentally determined optical constants of all materials and experimentally deduced absorption losses in rough ZnO/Ag back reflector [11].

We consider that only photons absorbed in the intrinsic layer of p–i–n cell contribute to the photogeneration of free electrons and holes. Assuming a 100% carrier collection, absorptance in the intrinsic silicon layer equals to the external quantum efficiency (QE). Finally, the short circuit current is obtained by multiplying QE with the AM 1.5 spectrum, 100 mW/cm^2 and elementary charge.

Spectral dependence of the absorptance A (or the quantum efficiency QE), together with the reflection loss (R) for the micromorph tandem cell (Fig. 3) is presented in Fig. 4. The spectra are given for the amorphous and microcrystalline cells, at temperatures 250, 300 and 350 K, for the rms surface roughness at each interface 70 nm with ideal cosine (or alternatively experimentally determined 'polyC') angular distribution of the scattered light. For modeling different tandems, the thickness of the a-Si:H top cell was chosen either 200 or 300 nm, respectively, then thickness of the bottom microcrystalline silicon cell has been calculated (by iteration procedure) to achieve the current matching at 300 K.

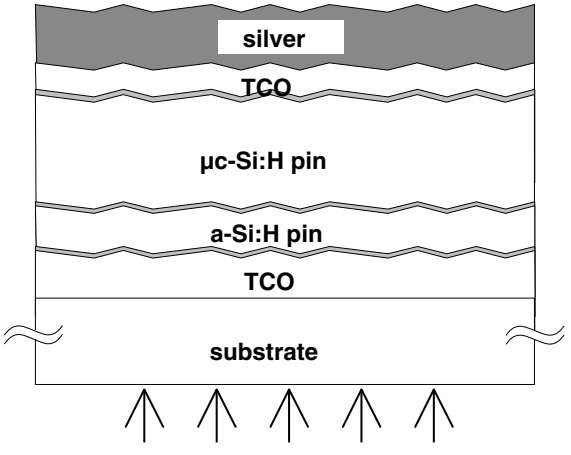

Fig. 3. Structure of micromorph solar cell used for the optical model calculation.

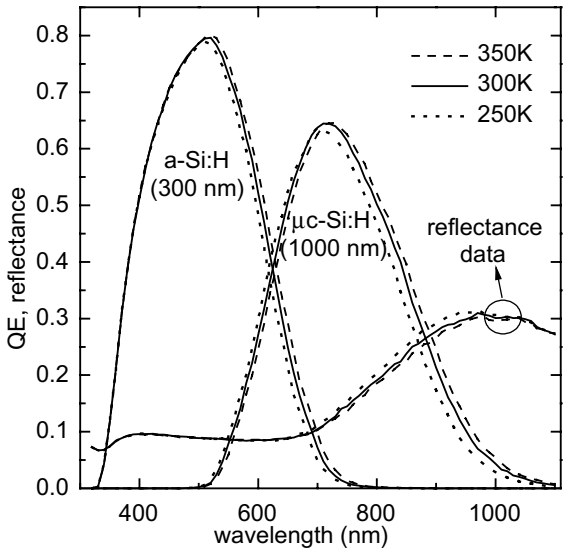

Fig. 4. Calculated quantum efficiency and reflectance spectra of micromorph solar cell (300 nm of a-Si:H and 1000 nm of μc-Si:H with 70 nm of rms roughness of all interfaces and ideal cosine distribution of the scattered light) corresponding to the temperature 250 (dotted line), 300 (solid line) and 350 K (dashed line).

Fig. 5 displays changes in the short circuit current I_{sc} as a function of temperature, for the amorphous silicon top cell and the bottom microcrystalline cell. Typically,

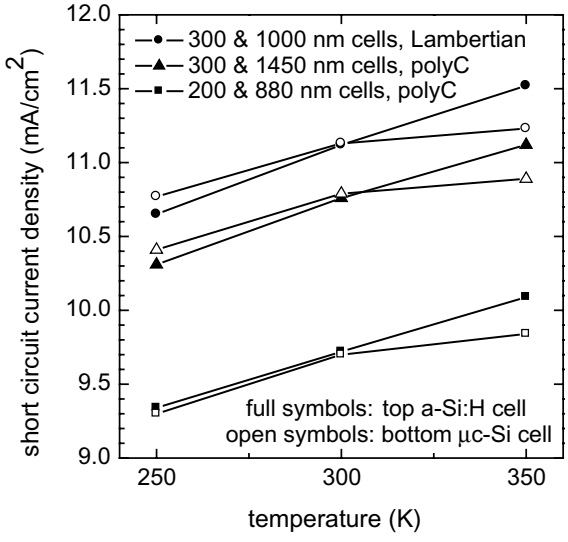

Fig. 5. Calculated short circuit current density of particular amorphous and microcrystalline silicon cells from three types of micromorph cells designed for current matching at room temperature. Angular distribution of scattered light (Lambertian or experimentally determined 'polyC') and thickness of the a-Si:H (300 or 200 nm) were chosen, μc-Si:H thickness was then calculated with respect to the current matching at 300 K.

0.2–0.3 mA/cm^2 mismatch in the I_{sc} is observed at 80 °C for the cells matched at the room temperature.

3.3. Comparison of microcrystalline Si and silicon-on-sapphire (SOS)

Fourier transform infrared photocurrent spectra (FTPS) of the device quality microcrystalline silicon sample (prepared by VHF technique) measured at various temperatures are presented in Fig. 6. Neglecting the optical interference effects, these spectra (after correction for different frequency response of the sample and DTGS pyrodetector) can be fixed into the absolute scale from the transmission measurement and then interpreted in the region of homogeneous optical absorption as the spectral dependence of the optical absorption coefficient α (cm^{-1}), as it is shown in Fig. 7. The smoothing here was done with the help simple spline procedure. Similarly, as in the case of transmission spectra we can detect clear temperature shift of the absorption edge. Defect connected absorption exhibits quite interesting behavior when the temperature is changed leading to the effect of crossing the optical absorption spectra. This can be explained by change of the Fermi level and/or dominant transport mechanism. FTPS data at each temperature are supplemented by standard *I–V* curve measurement (dark and photo) from which we really found the change in the activation energy of the dark conductivity from about 0.45 eV at room temperature to about 0.15 eV at the liquid nitrogen temperature.

For comparison, we measured and evaluated the optical absorption coefficient spectra (from FTPS and T/R spectroscopy) for the sample of as grown, high

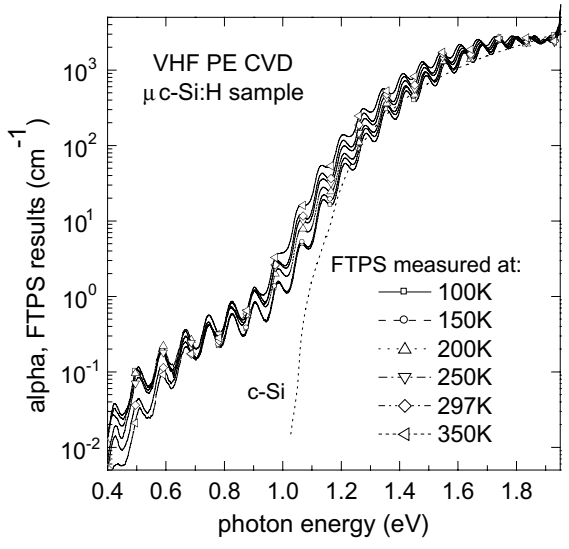

Fig. 6. FTPS spectra of microcrystalline silicon thin film measured for temperature from 100 K up to 350 K, absorption coefficient of crystalline silicon is shown for comparison.

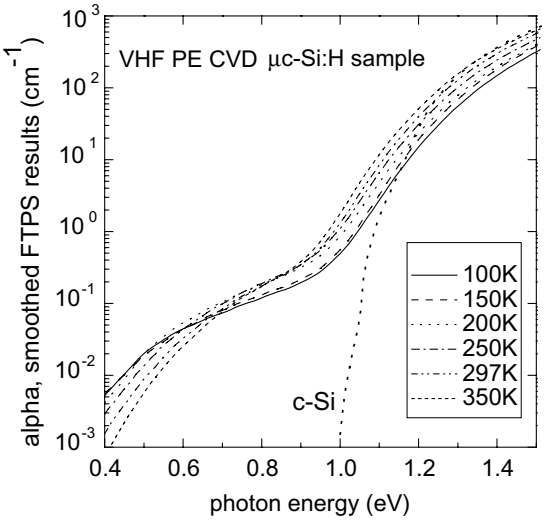

Fig. 7. Smoothed FTPS spectra of microcrystalline silicon sample from Fig. 6 after correction for different frequency responses of the sample and DTGS pyroelectric detector, absorption coefficient of crystalline silicon is shown for comparison.

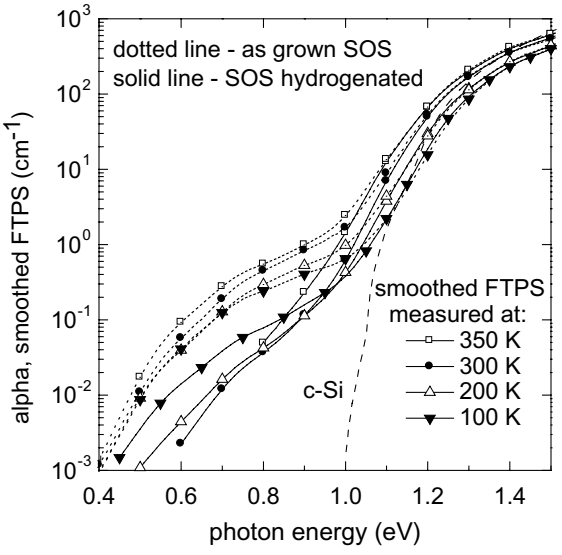

Fig. 8. Smoothed FTPS spectra of as grown (dotted lines) and hydrogenated (full lines) silicon on sapphire sample measured in the temperature range 100–350 K; absorption coefficient of crystalline silicon is shown for comparison.

temperature silicon on sapphire. Results are presented in Fig. 8 by dotted lines. One notices a big difference in these spectra and spectra from Fig. 7, mainly in the region related to defects. There is no cross in absorption spectra measured at different temperatures although the activation energy of the dark conductivity also drops from 0.55 eV at room temperature down to about 0.15 eV at 77 K.

Another experiment with SOS sample was performed to verify the possibility to annihilate deep

defects, mainly at grain boundaries, by plasma hydrogenation. In Fig. 8, the full lines show the optical absorption spectra of the SOS sample measured after exposing it in rf hydrogen plasma at the temperature of 360 °C for 1 h. Defect related absorption decreased in about one order of magnitude and the spectra again exhibit the 'crossing effect'. Dark conductivity increased about a factor of 10, activation energy of the dark conductivity of this hydrogenated SOS sample was about 0.4 eV at 350 K and again about 0.15 eV at 77 K.

4. Discussion

Data of the optical absorption coefficient in a broad spectral range of both amorphous and microcrystalline silicon at the temperature range corresponding to the appropriate solar cell outdoor working temperatures were used as the input data for our optical model of the theoretical estimation of micromorph cell limitations. We have found only about 3% mismatch in the short circuit currents generated by particular cells at different temperatures what is a negligible loss comparing to possible degradation effect of amorphous silicon of 10–20%.

The above-the-gap Si spectra and sub-gap optical spectra were compared for materials with a different defect density, crystalline fraction (50–100%) and hydrogen content (0–10%), in the temperature range 77–350 K. Microcrystalline Si has typically 60–90% of crystalline fraction and 5–10% of hydrogen. On the other hand, SOS is 100% crystalline, without hydrogen and some hydrogen can be introduced into it in hydrogen plasma.

Defects (presumably Si dangling bonds) in the as grown SOS material are supposed to be dominant at the boundaries of relatively large grains keeping the (gaussian) distribution of defects very sharp. Thus a distribution occupation function for defects does not change the shape of defect connected optical absorption with temperature. Defect density (Si dangling bonds) is reduced in one order of magnitude by hydrogenation of SOS, as it can be deduced from a decrease in sub-gap absorption (Fig. 8). By hydrogenation at relatively low temperature (360 °C), we can deactivate only the defects localized close to the path of diffused hydrogen atoms, i.e. just at the grain boundaries. A distribution of defects in the DOS (density of states) model deduced from FTPS spectra of this hydrogenated SOS (as well as all measured microcrystalline silicon samples regardless the defect density) has wider (gaussian) halfwidth and the occupation is strongly influenced by the sharpness of the distribution function (and position of the Fermi level) leading to the 'crossing' effects in the optical absorption spectra.

When comparing the Urbach tail of hydrogenated microcrystalline silicon with that of SOS we see much sharper Urbach tail in SOS. This is also consistent with several times longer ambipolar diffusion length in SOS measured by SSPG as well as with its much higher mobility.

5. Conclusions

Optical absorption coefficient of amorphous and microcrystalline silicon was measured in a spectral range 400–3100 nm and temperature range 77–350 K. The measured data served as an input for optical model of amorphous/microcrystalline solar cell tandem. Differences in the current generated in each sub-cell, for the tandem cells matched at the room temperature, were calculated for operation temperature between −20 °C and +80 °C.

Optical spectra of microcrystalline silicon were compared to the spectra of silicon on sapphire (without hydrogen and hydrogenated) and observed differences were interpreted in terms of different dominant position of defects, defect density and disorder, the main difference being a higher disorder of microcrystalline Si.

Acknowledgements

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