



In situ manipulation of the sub gap states in hydrogenated amorphous silicon monitored by advanced application of Fourier transform photocurrent spectroscopy

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ABSTRACT

A profound comprehension of the nanostructure of hydrogenated amorphous silicon (a-Si:H) and the defect states in this material is currently still lacking despite several decades of research on this topic. Investigating the nature of defects in a-Si:H devices is especially important in view of the poorly understood Staebler–Wronski effect (SWE). Therefore we present the latest insights into the gap states in the a-Si:H bandgap by manipulating these sub gap states in three different ways: via the application of a voltage bias, via *in situ* light soaking, and via *in situ* annealing. To monitor the changes in the sub gap absorption we employ an advanced application of Fourier Transform Photocurrent Spectroscopy (FTPS). A recently published optical model that removes interference fringes from the photocurrent spectrum is presented to obtain the absorption coefficient. For FTPS measurements on solar cells the photocurrent spectrum is scaled to the external quantum efficiency (EQE) of the solar cell. Further, a mathematical data fitting routine is employed to accurately quantify the sub gap absorption and the changes therein during light soaking and annealing. The high sensitivity of FTPS is particularly helpful in identifying the sub gap states that play a role in the SWE in a-Si:H devices.

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1. Introduction

Due to the complex nature of hydrogenated amorphous silicon (a-Si:H) there is still no consensus on its nanostructure and the defects with respect to the local network environment despite several decades of research. The lack of fundamental understanding of the native and metastable defects and recombination in a-Si:H has proven to be a major obstacle in finding the origin of the Staebler–Wronski effect (SWE) [1]. To gain more insight into the defects in a-Si:H, photoconductivity measurements have been commonly used to obtain the sub gap absorption, which is linked to defect states located in the forbidden bandgap [2–11]. Previously used photoconductivity based techniques include the Constant Photocurrent Method (CPM) [12], Dual Beam Photoconductivity (DBP) [13], and more recently Fourier Transform Photocurrent Spectroscopy (FTPS) [14,15]. Among these

techniques FTPS has two important advantages, which makes it the preferred technique to quantify the sub gap photocurrent. First, FTPS has the highest demonstrated sensitivity among the three photoconductivity methods. Secondly, FTPS can be used to characterise both films on glass and solar cell absorber layers.

Precisely quantifying the sub gap absorption, especially in solar cell absorber layers, is of critical importance when trying to understand the origin of the SWE and how it affects the performance of an a-Si:H solar cell. Furthermore, the differences between light-induced photoconductivity changes in films on glass and light-induced performance changes in solar cells with corresponding absorber layers are not well understood. However, understanding the different light soaking behaviour of films on glass and solar cells is hampered by four fundamental differences between such samples. First, the photoconductivity in films on glass is typically measured between two metal contacts deposited on top of the film, which means that the laterally flowing current is affected by states associated with defects located near the surface. In a solar cell, the current passes transversely through the absorber layer and the doped layers, so surface states do not

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significantly contribute to the photocurrent. Secondly, the electric field between the contacts deposited on top of a film is constant, whereas the electric field in a solar cell absorber layer varies throughout its thickness. This affects the carrier collection efficiency in films and solar cells. Thirdly, films are typically deposited on flat glass, whereas the absorber layer is deposited on a textured substrate, which means that the light scattering and interference effects are substantially different in these samples. Finally, an a-Si:H solar cell typically contains partially absorbing doped layers and a transparent conductive oxide (TCO). This means that the spectrum of the light that can be potentially absorbed in an absorber layer is not the same as it is in a film on glass.

It is imperative to account for the mentioned differences between films and solar cells when analysing sub gap FTPS data and aiming to link the sub gap absorption to gap states in a-Si:H. In this view we present the latest progress on the study of the relation between the energy dependent sub gap photocurrent and the gap states, obtained by an advanced application of FTPS. This novel approach is based on combining FTPS monitoring with the external manipulation of sub gap states using voltage biasing, *in situ* light soaking, and *in situ* thermal annealing. It is shown that such external manipulations can provide detailed insights in the energy positions and occupation of various gap states. By using an advanced and custom-designed sample stage that includes a temperature controller and light biasing with light emitting diodes of various colours, we can carefully monitor any SWE-related changes in the photocurrent spectrum of an a-Si:H solar cell.

In addition to the advanced hardware, we employ a recently published optical model that removes interference fringes from FTPS data obtained from measurements on films on glass [16]. However, this model is inadequate in quantifying the interference-free sub gap absorption of absorber layers in solar cells deposited on a textured substrate like Asahi VU, because it fails to describe the wavelength-dependent light scattering induced by the substrate roughness. Nonetheless, the interference fringes in sub gap FTPS data obtained from measurements on single-junction a-Si:H solar cells with thin absorber layers (< 300 nm) are not pronounced and can therefore be neglected. We suggest to interpret the FTPS data obtained from solar cells as an external quantum efficiency (EQE) measurement with spectral values extending to energies below the bandgap E_g .

Finally, we introduce a method to resolve possible defect states from the sub gap photocurrent by using a mathematical fitting routine involving error functions or Gaussian functions. It appears that a minimum of four functions is required to fit the sub gap data accurately. This suggests the presence of four defect states with energies in between 0.6 eV and 1.5 eV below the conduction band of the a-Si:H.

2. Experimental details

2.1. Deposition of a-Si:H films and solar cells

A thickness series has been deposited to verify the correctness of the optical model that we use to obtain an interference-free absorption coefficient spectrum from an FTPS measurement. A series of a-Si:H films with various thicknesses was deposited on Corning Eagle XG glass substrates using radio frequency plasma-enhanced chemical vapour deposition (rf-PECVD). All films in this thickness series were deposited from pure silane gas using the same plasma conditions ($P_{\text{rf}}=0.024 \text{ W/cm}^2$, $p=0.7 \text{ mbar}$, $T_{\text{substrate}}=180 \text{ }^\circ\text{C}$) but with different deposition times: 24, 48, and 72 min. As determined by FTIR spectroscopy, the resulting films have the same material properties: a total hydrogen content of $c_{\text{H}}=8.3 \text{ at}\%$, a nanostructure parameter $R^*=0.03$ and a mass density of $\rho_{\text{a-Si:H}}=2.24 \text{ g/cm}^3$. By means of Raman spectroscopy it was verified that all films are fully amorphous. However, due to the varying thickness (246 nm, 537 nm and 797 nm) different interference patterns arise in a photoconductivity measurement such as FTPS.

A series of three single-junction *pin* solar cells was deposited on Asahi VU-type substrates using a similar thickness variation as for the a-Si:H absorber layer described above. The structure of the solar cells is as follows: Asahi VU-type/*p*-type a-SiC:H (10 nm)/*i*-type a-Si:H (300/600/900 nm)/*n*-type a-Si:H (20 nm)/Ag–Cr–Al back contact (100–30–300 nm). The surface area of this solar cell structure is 0.16 cm^2 . The plasma deposition conditions used for the absorber layer were the same as described for the films above. A solar cell deposited on an Asahi U-type substrate with an absorber layer thickness of $d_i=300 \text{ nm}$ grown from undiluted silane and a 5 nm SiC:H buffer layer sandwiched between the *p*-layer and *i*-layer was used for the voltage bias experiment described in section 3.4. The solar cell used in the *in situ* light soaking and thermal annealing experiments of sections 3.5 and 3.6 has the same structure as the solar cells described in the absorber layer thickness series above, but has no SiC:H buffer layer and an a-Si:H absorber layer of 250 nm that is deposited at a hydrogen-to-silane gas flow rate ratio of 10.

2.2. Fourier transform photocurrent spectroscopy

The sub gap absorption in a-Si:H is assumed to arise from photo-excitation of trapped charge carriers that are located at defect states below the conduction band. These defect states contribute to the photocurrent measured with FTPS. The FTIR spectrometer used to modulate the white light is a Thermo Electron Nicolet 8700 equipped with a quartz beamsplitter. The photocurrent collected from the sample is amplified using a Keithley 428-PROG current preamplifier. Other characteristics of the measurement system and data processing routine can be found elsewhere [11]. Measuring FTPS at a low velocity of the moving mirror in the FTIR spectrometer generally results in more accurately resolved photocurrent data. However, at very low mirror velocities the photocurrent is not resolved significantly more accurately while the measurement time gets unnecessarily long. Based on these considerations the typical mirror velocity used in an FTPS measurement is 0.1581 cm/s . In order to accurately correct for the frequency response of each measured sample, measurements at mirror velocities of 0.3165 cm/s and 0.4747 cm/s are conducted as well. Since the lowest photon energy for which an FTPS signal on a-Si:H samples can be typically resolved is $0.6\text{--}0.4 \text{ eV}$, it is not possible to detect charge carriers with a lifetime exceeding $780\text{--}980 \mu\text{s}$, respectively, when conducting FTPS measurements at a mirror velocity of 0.1581 cm/s .

2.3. FTPS characterisation of films on glass

Two aluminium contact electrodes with a spacing of 0.5 mm were evaporated on top of the a-Si:H films to conduct FTPS measurements on films on glass. During the measurements, a DC voltage of 1 kV was applied to the contacts using a Keithley 2410 external voltage source to efficiently extract the photogenerated carriers from the a-Si:H film. In addition, the absorption coefficient spectrum of band-to-band transitions obtained from a reflectance/transmittance (RT) measurement was used to translate the relative FTPS photocurrent spectrum obtained from FTPS to an absolute reference. Interference in the FTPS data was removed using the optical model described in section 3.1. Details of the RT measurement system are described elsewhere [10]. For both FTPS and RT measurements the samples were illuminated through the glass substrate. Depending on the nanostructural quality of the material, particularly the defect density, the typical measurement time for an a-Si:H film on glass was about 30–60 min.

2.4. FTPS characterisation of solar cells

Since the doped layers induce an electric field in the absorber layer of the solar cells, it is not necessary to apply an external voltage to the solar cell terminals for extracting the photogenerated

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