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Plasma deposition of thin film silicon: kinetics monitored by optical emission spectroscopy

Luc Feitknecht[a,]*, Johannes Meier[a], Pedro Torres[b], Jerôme Zürcher[b], Arvind Shah[b]

[a] *Institute of Microtechnology (IMT), rue A.-L. Breguet 2, CH-2000 Neuchâtel, Switzerland*
[b] *VHF-Technologies SA, Hôtel de Ville 7, CH-2400 Le Locle, Switzerland*

Abstract

The optical emission spectroscopy technique is used to characterise the temporal behaviour of a pure silane plasma in the first 90 s after ignition of a static closed-chamber very high frequency glow discharge. Special interest is drawn to the formation of microcrystalline silicon (μc-Si:H) in absence of any hydrogen feedstock gas dilution. The kinetics of the emission lines of SiH* and H_α is reported. The deposited films are characterised by photothermal deflection spectroscopy, Fourier transform infra red (FT-IR) absorption and show typical microcrystalline fingerprints; for the first time, such material is used as absorber layer in n–i–p type solar cell devices.

Keywords: Optical emission spectroscopy OES; μc-Si:H; VHFGD; Closed-chamber plasma; Thin-film silicon; Incubation layers; Solar cells

1. Introduction

Plasma enhanced chemical vapour deposition (PECVD) is commonly used to produce amorphous (a-Si:H) and microcrystalline (μc-Si:H) silicon thin-film solar cells [1]. Parameters like hydrogen dilution, plasma power, deposition pressure, etc. strongly influence the chemistry in the plasma reaction and, thus, the characteristics and quality of the deposited film. The necessity of having a reliable tool for plasma-process control is evident. A good candidate is optical emission spectroscopy [2]. The optical emission lines of excited molecules of SiH* and H_α of the closed-chamber

*Corresponding author. Tel.: +41-32-718-33-62; fax: +41-32-718-32-01.
E-mail address: luc.feitknecht@unine.ch (L. Feitknecht).
URL: http://www-micromorph.unine.ch.

growth regime are identified and compared with the respective emission lines of our standard PECVD process. In fact, it has been shown with OES measurements [3,4] that a high ratio for the $[SiH^*]/[H_\alpha]$ emission lines characterises the formation of an amorphous silicon layer, whereas a low ratio is typical for microcrystalline silicon deposition thus a fingerprint of the growth process is established. This can be understood by the competing mechanisms during the very high frequency glow discharge (VHFGD) deposition process of both growth and etching [5,6]. In this paper, we report on the transient behaviour of the Static closed chamber very high frequency glow discharge (SCC VHFGD) plasma used for the deposition of μc-Si:H films, as monitored in situ by OES.

2. Experimental

For the growth of microcrystalline silicon films we used AF45 Schott glass substrates at a temperature $T_S = 270°C$, no hydrogen gas flow at all, silane gas flow of 1 sccm at 0.1 mbar, no use of a gas purifier, an injected plasma power of up to 30 W, and a VHF plasma excitation frequency of 130 MHz. These are similar parameters as proposed by Matsuda et al. [5] and we call it a SCC VHFGD process, in contrast to the cyclic process proposed by Koynov et al. [7]. There is no cycling between two deposition regimes like in the layer-by-layer method, but a steady and constant and, thus, a *static* process. The deposition chamber is therein not fully isolated but a small quantity of used gas is pumped out. The doped films for solar cells were deposited by conventional VHFGD (no closed chamber condition) on TCO coated AF45 glass and stainless steel substrates. The intrinsic μc-Si:H absorber layer is deposited in the static closed-chamber VHFGD condition, as mentioned above. The OES characterisation technique consists, in our case, of decomposing the light emitted from the plasma with a monochromator and spectrally detecting the intensity with a photodiode at the exit slit (see Fig. 1).

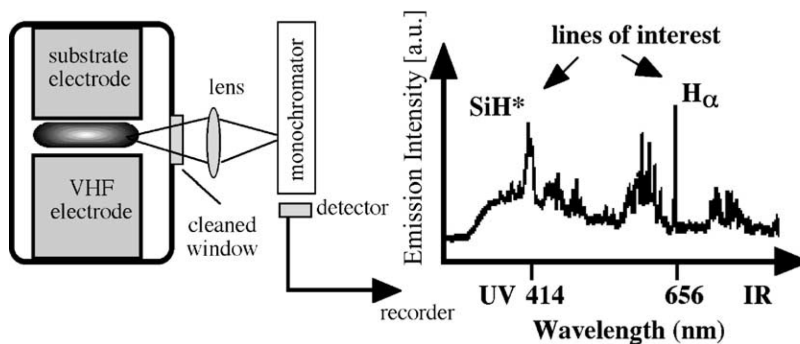

Fig. 1. Experimental set-up for measuring the optical emission spectroscopy (OES) with a typical spectrum. The emission lines of interest are at a wavelength $\lambda = 414$ nm and at $\lambda = 656$ nm which are associated to the SiH^* radical and the atomic hydrogen (H_α) emission line, respectively.

The parallel-plate electrode configuration permits a lateral sampling of the light emission through a quartz glass window. Comparisons with other systems can only be done on a relative basis, since no absolute calibration for the OES spectra has been carried out. The temporal evolution of the closed-chamber plasma OES was observed at two fixed monochromator positions, in two separate runs, for the two emission lines, i.e. for the SiH*-line of silane at a wavelength of $\lambda = 414$ nm and the H_α-line of hydrogen at $\lambda = 656$ nm. These emission lines have been identified in reference OES measurements under conventional VHF plasma deposition conditions with silane diluted in hydrogen, by varying the wavelength of the monochromator; this experiment allowed us to determine the typical values for the ratio of the emission lines, for μc-Si:H growth in a known gas phase mixture. A Perking Elmer FT-IR 1720X spectrometer was used to measure the absorption spectra between 4000 and 400 cm^{-1} of the thin films deposited on double-side-polished $\langle 100 \rangle$ silicon wafers. The hydrogen content C_H was obtained by numerical integration of the Si–H rocking-wagging mode at 640 cm^{-1}. The complete procedure is well described by Kroll et al. [8]. As the authors point out, this evaluation method is valid for the estimation of the hydrogen content of thin-silicon films of both amorphous and microcrystalline morphology; we consider it also suitable to characterise our novel SCC GD silicon films.

3. Results and discussion

3.1. Kinetics in the static closed-chamber VHFGD

In the first 30 s after ignition, a high intensity of the SiH*-line and a low intensity of the H_α-line is observed (see Fig. 2). This is identified with a pure silane plasma

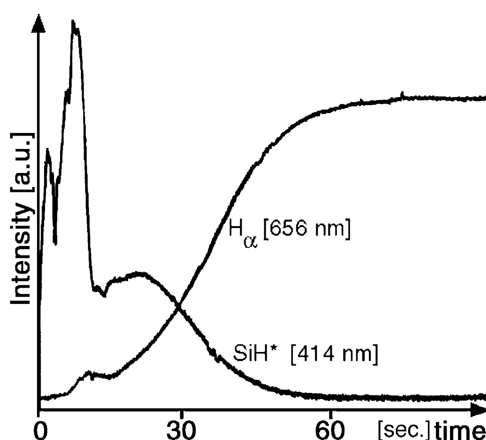

Fig. 2. Temporal evolution of the emission intensities (measured with OES) of the hydrogen and silane lines, respectively. More and more hydrogen is dissociated in the pure silane gas phase during the first 90 s just after the plasma ignition.

without any noticeable hydrogen precursors, as one should expect from the deposition conditions (no hydrogen dilution).

Then in the next 30 s, the emission intensity of the H_α-line gradually becomes more pronounced. This is explained by a dissociation of the SiH_4 gas molecules: The growth of the film consumes Si-atoms, the low silane flow permits only a reduced gas phase regeneration and, therefore, dissociated H-species start populating the plasma reaction. An increasing amount of H-species is generated by the dissociation of the depleted plasma and a much lower ratio of the $[SiH^*]/[H_\alpha]$ emission is observed.

Steady conditions for the plasma can finally be observed after 60 s. A balance of SiH^* and H_α species is then achieved, conditions for microcrystalline growth are established and the typical OES-fingerprint for a microcrystalline growth (ratio of the $[SiH^*]/[H_\alpha]$ below unity) may be observed. In agreement with observations previously reported in the literature, μc-Si:H growth is indeed observed as soon as enough atomic hydrogen is available [10,11] . The bulk of the film deposition is made in this plasma condition.

3.2. Film quality and solar cells

The shape of the absorption spectra (see Fig. 3) of the μc-Si:H layer deposited by SCC VHFGD follows the parabolic shape of c-Si [12] over a wide range of energy,

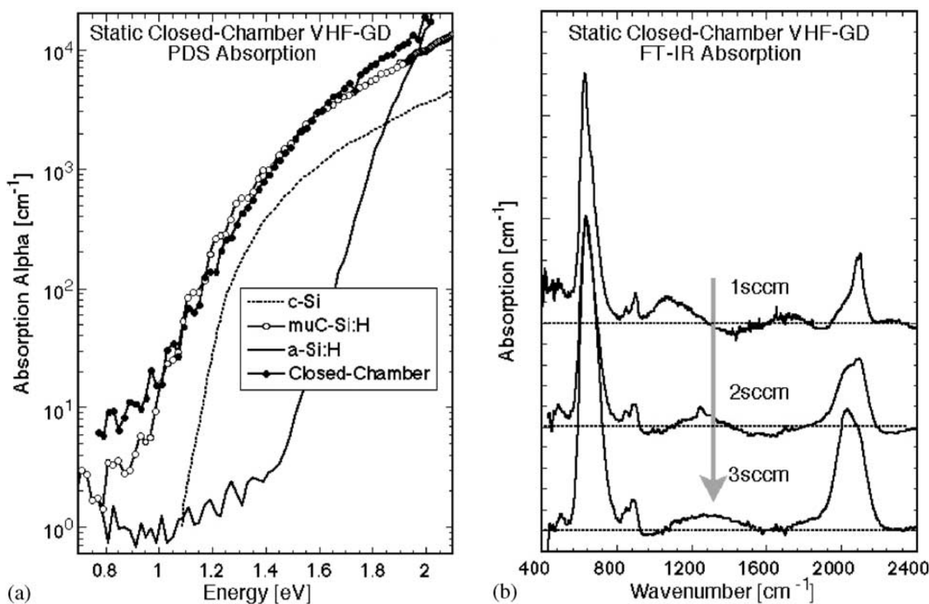

Fig. 3. (a) Absorption spectra of the film deposited by closed-chamber VHF-GD (full dots) compared to c-Si (dashed line), a-Si:H (solid line) and μc-Si:H (empty dots) material. (b) Infrared absorption of μc-Si:H films deposited by the static closed-chamber method. The more fresh silane gas is introduced into the chamber the more the film shows amorphous absorption characteristics.

but is shifted to lower energies and higher absorption values. Both, the enhancement and the shift of the absorption edge are typical characteristics of device-grade μc-Si:H material, apparently independent of the two observed deposition methods so far in our lab i.e. standard VHFGD or here SCC VHFGD. This encouraging result motivated us to investigate further in this novel deposition method.

Infrared absorption measurements on the deposition layers (see Fig. 3) reveal a close relation between the flow of fresh silane gas introduced into the closed-chamber and the degree of crystallinity. In fact, a transition from microcrystalline to amorphous material is observed, if the silane gas flow is increased from 1 sccm to values above 3 sccm. Films deposited at 1 sccm silane flow are composed of a high crystalline amount whereas films deposited at 3 sccm silane flow tend to incorporate less crystallites and more amorphous material. The increase in deposition rate from 1.5 up to 5.8 Å/s for an increase of the silane flow between 1 and 3 sccm confirms the trend towards an amorphous growth regime. In other words, a morphological transition from μc-Si:H towards a-Si:H is possible in the closed-chamber process without the use of any hydrogen feedstock gas dilution by simply increasing the silane feedstock gas flow. This observation is very similar to these made during investigations on μc-Si:H films deposited by the standard VHF-GD process, when the gas-phase ration of silane to hydrogen is varied. For the determination of the hydrogen content C_H by Fourier transform infra red absorption (FT-IR) spectroscopy the Si–H rocking-wagging mode at 640 cm^{-1} was numerically integrated (see Table 1). The measured C_H values lie between 4 and 8 atomic percentage (at.%) for the SCC VHFGD material. Such values correspond very well to layers deposited in the standard VHFGD process at a silane dilution around $[SiH_4]/[SiH_4 + H_2] \simeq 5\%$.

The best solar cell fabricated so far by the proposed closed-chamber method furnishes an open-circuit voltage $V_{OC} = 419$ mV, a fill-factor FF = 70%, a short-circuit current $J_{SC} = 8.6$ mA cm^2; this results in a conversion efficiency of $\eta = 2.5\%$ for a cell thickness of 2.2 μm under standard AM1.5 test conditions. Some 'device fabrication limitations' specific to the closed-chamber deposition process are observed during the initial phase of the plasma: As we pointed out in the previous paragraph, the OES measurements clearly identify an amorphous growth regime for the first 30 s because of the prevailing (almost) pure silane atmosphere. This time is apparently long enough for the deposition of several hundred Ångstroms of an

Table 1
Hydrogen content C_H as integrated from the 640 cm^{-1} peak of FT-IR absorption spectra of μc-Si:H films fabricated by the two different deposition methods

Static ccGD		Standard VHFGD	
SiH_4-flux (sccm)	C_H (at.%)	Dilution (%) $SiH_4/(SiH_4 + H_2)$	C_H (at.%)
1	3.8	5.5	6.1
2	4.6	6.0	8.5
3	7.8	6.5	11.0

amorphous incubation layer [9], which is detrimental to the μc-Si:H solar cell. The methods presented above for analysing the film quality (i.e. FT-IR and PDS) are only sensible to the bulk and not to the very thin incubation film probably present on the samples, whereas the OES method gives insight into the transient behaviour of the very first seconds of the closed-chamber deposition process. This may explain the mismatch between excellent film quality and a so far poorly performing solar cell. A technological improvement would be the use of a contraption protecting the solar cell from that amorphous incubation layer.

The SCCVHF method reduces considerably the amount of necessary silane feed stock gas: To fabricate a μc-Si:H film by the VHF method a value of 21 000 sccm · s is necessary (thickness 2.2 μm, deposition rate: 7 Å/s) whereas only 10 800 sccm s are needed for a film deposited by the SCCVHF method (deposition rate: 4 Å/s).

4. Conclusions

Basic process viability is demonstrated by the first μc-Si:H solar cell manufactured by the novel static closed-chamber VHFGD (SCC VHFGD) method. A new aspect of the initial phase of the plasma i.e. a transient behaviour is found while monitoring the kinetics by OES. After a first phase of pure silane plasma, hydrogen species start populating the reaction and a typical stable microcrystalline growth regime is established. The deposition conditions favouring deposition of an amorphous incubation layer is demonstrated with this OES method. Other characterisation methods like infrared spectroscopy and PDS absorption measurements failed to give evidence for the presence of this incubation layer, because in these methods the incubation layer is masked by the predominant presence of good quality μc-Si:H bulk material. The OES method has thereby once more proven its utility as a very sensitive tool for process monitoring in plasma deposition. Silane consumption is halved for the deposition of device grade absorber films with the SCC VHF-GD method compared to the standard VHF method. Since there is no need for hydrogen feedstock gas and thus no gas purifier, the closed-chamber method is an ecologically and economically interesting alternative to the conventional plasma deposition process.

Acknowledgements

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