MICROCRYSTALLINE SILICON FOR SOLAR CELLS, DEPOSITED AT HIGH RATE BY VHF-GD AT HIGH PRESSURE

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ABSTRACT

Microcrystalline silicon (μc-Si:H) is an attractive indirect low-band gap absorber material for thin-film solar cells. However, due to the thick absorber layers needed, high deposition rates are required to achieve cost reduction for industrial production. Therefore a comparison of state-of-the-art, high-rate techniques is needed. In this study, the impact of high deposition pressures on the growth of μc-Si:H has been investigated, applied to the VHF-GD PECVD deposition process. Hereby, μc-Si:H layers deposited at rates up to 25 Å/s [1] were obtained. These films show device-grade quality, e.g. the defect absorption (as measured by CPM) is low enough ($\alpha(0.8eV) \approx 2\ cm^{-1}$) and "midgap" character: from dark current measurements (σ_d) is obtained. The present contribution deals with a loss of quantum efficiency for longer wavelengths encountered while incorporating such high-rate layers into full pin-type μc-Si:H solar cells.

Introduction

Reduction of manufacturing costs is a key point for thin-film silicon solar cells, focusing on the so-called "micromorph" (amorphous/ microcrystalline) tandem cell [2]. For this, high-rate deposition processes for microcrystalline silicon (μc-Si:H) have to be achieved.

The optical indirect band gap characteristic of μc-Si:H, demands, for microcrystalline cells, an absorber layer with a thickness of at least 1 – 2 μm to ensure sufficient absorption of sunlight.

Right now within PECVD (plasma-enhanced chemical vapour deposition), three techniques have been established to achieve high-rate μc-Si:H: a) RF-PECVD at high pressures [3,4], b) VHF-PECVD combined with high pressure depletion, using a Triode Reactor Configuration [3] and c) VHF-GD at high pressures in a simple, parallel-plate capacitively-coupled reactor [1]. One has to investigate now which of these techniques can play a key role with respect to industrial production: This is the main motivation for the present study of high rate deposition VHF-GD PECVD at high pressures.

Recently a convincing increase in deposition rate upto 15 Å/s (fluxes of 30 sccm SiH_4 and 570 sccm H_2 at 200 W [3]) was reported, applying high pressures in RF-PECVD [3,5]. To achieve higher deposition rates (>10 Å/sec) in the high pressure regime of RF-plasmas, very high gas flows are involved even for laboratory size electrodes, and this especially for hydrogen. This means, in the case of industrial production, an increase in cost.

It is known that changing the excitation frequency from the standard 13.56 MHz to the VHF (Very High Frequency) range leads to changes in the plasma impedance [6]. We believe that going to high pressure conditions introduces similar changes, and that this could lead to even further increase in growth rate when combined with VHF.

Indeed, recent studies have reported promisingly high deposition rates (~ 60 Å/s) of device-grade μc-Si:H material obtained by VHF-PECVD combined with HPD (high pressure depletion regime) , using a Triode Reactor Configuration [3]. The Triode Reactor Configuration is based on a conventional diode-type parallel-plate VHF-PECVD electrode configuration with an additional grounded mesh that is only very few mm away from the sample [7]. Using this novel Triode technique, a solar cell efficiency of 3.4% was obtained at a deposition rate of ~60Å/s [8].

However, in this case, as well, high gas flows (hundreds sccm of hydrogen and 30 to 50 sccm of silane for laboratory-size electrodes) are needed to achieve the high depostion rates [3,5,9,10]. Due to the small dimensions of the electrode configuration, a construction of such a Triode Reactor system would be very complex and therefore very expensive for industrialisation.

Focussing on low production costs of solar cells based on microcrystalline silicon, an intrinsic μc-Si:H absorber layer with a "reasonable" gas utilisation is needed. In order to overcome the high rate - high gas utilisation problem, and also avoid potential up-scaling problems for systems in the square meter size, we suggest that VHF-GD at high working pressures is the key technique to achieve high deposition rates. Using VHF and HPD, a solar cell of 8.1% efficiency for 12 Å/s was obtained [8]. However, a general tendency of deterioration of crystallinity and defect density was observed when increasing growth rate, by increasing VHF-Power [8,11].

Silicon powder is formed when increasing the working pressure to higher pressures (>1 mbar). Comparing the three technologies, powder is formed in every process. Applying the Triode Reactor Configuration with the mesh leads to the advantage of a fairly suppressed powder formation [12].

Fortunately, powder seems not to harm deposition processes and device performance –as long as the powder does not deposit on the layers-, even in large-area systems. In order to avoid deposition of powder on the substrate, a process regulation is adapted [13]. Good performances for solar cells up to 8.1 % conversion efficiency deposited at high pressures, at 12 Å/s [4,8] confirm this as well.

This paper focuses on a comprehensive study of μc-Si:H films deposited under high working pressures and VHF-conditions. Films were characterised by different methods, with respect to sub band gap absorption and crystallinity.

Finally, a series with increasing deposition pressures of intrinsic layers was incorporated in pin solar cells in order to study the influence of deposition pressures on device performance.

2. Experimental

A laboratory-size VHF-GD reactor (~8x8 cm^2) was used for all depositions, whilst varying the working pressure up to 3 mbar. In order to avoid oxygen contamination of the feedgas, the gas purifier technique developed by our laboratory [14], was applied.

In contrast to the other studies mentioned in the introduction, we were using a relatively low total gas flux (Φ_{tot}= flux of H_2 and SiH_4) of ~100 sccm containing up to 11.5 % silane. Hereby, the VHF-GD reactor was supplied with up to 120 W at an excitation frequency of 70.0 MHz.

Bare Schott glass AF45 as well as such glass clad with LP-CVD ZnO layers [15] were used as substrates. Deposition rate/thickness of deposited films were determined by an alpha-step thickness profiler. All films reported here show a homogeneous thickness (± 5 %) over the total substrate area (8×8cm^2).

The characterisation of the films was done by Raman spectroscopy (Renishaw Raman 2000) with a Ne/He- (λ_{excit}= 633 nm) and an Ar (λ_{excit}= 514 nm) laser. Dark conductivity (σ_{dark}) at room temperature, and activation energy (E_{act}) and optical absorption measurements by CPM (Constant Photocurrent Measurement) for the determination of sub bandgap defect-related absorption (α(0.8eV)) were carried out on certain films deposited on the bare glass substrates.

Pin-type single-junction solar cells were deposited on the glass substrates clad with LP-CVD ZnO. A series of cells with various i-layers, not yet optimised with respect to the a-Si/ μc-Si transition and with respect to the pi-interface, were deposited at increasing pressures of 0.5 to 3.0 mbar. In order to get a good microcrystalline growth for high pressure deposited solar cells from the beginning, an initial μc-Si:H nucleation layer was introduced. For this seeding layer, soft conditions were chosen, e.g. low SiH_4 concentration and low VHF power (20W) under standard pressure (0.5 mbar).

3. Results and Discussion

In order to have an overall view of the influence of using higher pressures, the deposition pressure was examined with respect to the deposition rate of microcrystalline silicon. Hereby, an increase is observed (Fig. 1) when passing from the conventional pressure range to pressures above 1.2 mbar. The depostion rate does not vary much more with increasing pressure above 1.5 mbar, and this may be due to an excessive silane depletion condition. Therefore, we subsequently increased the total flux of hydrogen/silane mixture in order to reduce the resident time of the radicals. To retain the same amount of power per molecule we also increased the VHF-power to the same extent.

When applying higher gas flows (Φ_{tot}= 30-80 sccm) the VHF-power (40-100 W) was increased as well to enhance the creation of radicals. Thus, at 3 mbar working pressure a maximal increase in deposition rate up to 17 Å/s was obtained.

Table 1 summarises, for some samples with high deposition rate, the results of these characterisations. First, “Raman crystallinity factor” Φ_c [16] reveals clearly a high crystallinity for all films.

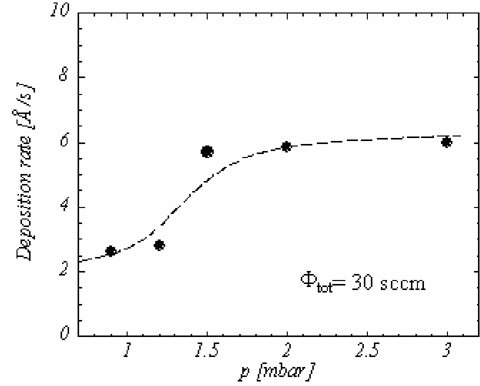

Fig. 1. Deposition rate vs. deposition pressure (dashed line is a guide for the eyes).

Second, the low sub band gap absorption values at 0.8 eV as observed by CPM proves that these films have a rather low defect concentration; this bening a necessary condition for obtaining device-grade μc-Si:H material. From the dark conductivity measurements we obtained activation energies of around 0.5 eV with dark conductivities at room temperature around 10^{-7} S cm^{-1}. Such conductivity characteristics indicate clearly the “midgap character” (E_F is in the middle of the gap) of these high-rate microcrystalline films:

Table I. “Raman crystallinity factor” (Φ_c), optical absorption α(CPM) and electrical conductivity (σ_{dark}, E_{act}) of high-rate deposited μc-Si:H layers on glass substrates.

Deposition rate [Å/sec]	Φ_c $\frac{I_{520}+I_{510}}{I_{tot}}$	α (0.8 eV) [cm^{-1}]	σ_{dark} @RT [S cm^{-1}]	E_{act} [meV]
13.7	0.656	~3.2	$5.3\cdot10^{-7}$	530
15.6	0.733	~2.0	$1.20\cdot10^{-7}$	497
16.8	0.639	~2.1	$2.03\cdot10^{-7}$	520

In order to search for a further increase of the deposition rate, we investigated the influence of even higher VHF-powers, higher total gas flows and higher silane concentrations (in hydrogen), on the growth of μc-Si:H. In Fig. 2 a series of high-rate microcrystalline films could be obtained when applying a VHF-power of 120 W and a total gas flow of 100 sccm at a working pressure of 3 mbar. As can be seen, the rate continuously increases with higher silane concentrations leading to deposition rates of up to 25 Å/sec.

Raman spectra prove, as quick indication, that these high-rate films all clearly show a basically crystalline behaviour. Only the last two ones with the highest level of silane concentration show a significant level of amorphous volume fraction in the material. The experiments reported in Fig. 2 demonstrate that using VHF excitation frequencies combined with the high pressure regime allows us to achieve high deposition rates (~25 Å/sec) and still keep the gas flow reasonably low. These particular intrinsic high rate layers were sofar even achieved without any initial nucleation layers. Hence, crystalline layers at even higher deposition rates might be achieved by using suitable initial μc-Si:H nucleation layers.

However, the initial growth phase of such µc material as obtained under these high rate conditions first has to be examined and proven to be reasonable. To this end,

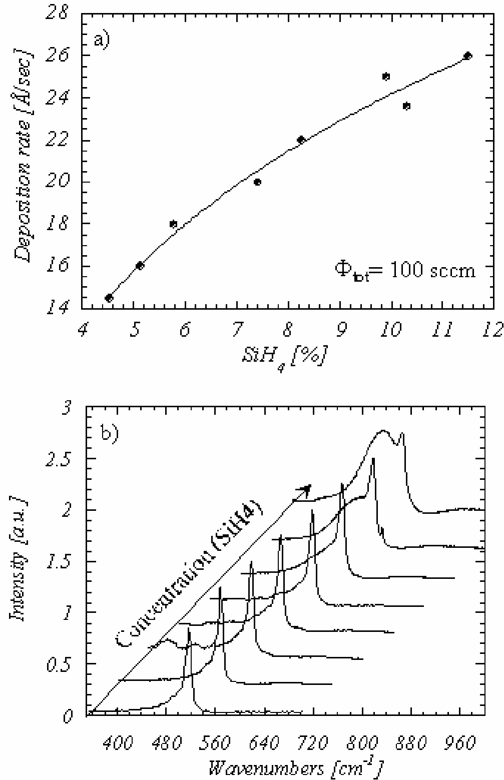

Fig. 2. a) The deposition rate vs. SiH_4 concentration of µc-Si films, with high pressure (3 mbar), b) corresponding series of Raman spectra, for increasing values of the silane concentration, measured on the film side with a He/Ne laser (633 nm).

the crystalline structure of the layers was analysed by Raman spectroscopy from both sides of the film in order to obtain information on the initial growth zone adjacent to the substrate and compare it with the "final" growth zone. Fig. 3 shows the Raman spectra obtained with an Ar laser (514 nm wavelength, i.e. average penetration depth of 100 to 200 nm) of a film deposited at a rate of 14 Å/sec. These measurements indicate a pronounced crystalline structure, even at the initial growth stages of the film, a fact that may be useful for fabrication of entirely microcrystalline silicon devices.

An estimation based on the reactor area covered by the microcrystalline film and its growth per time unit in comparison with the incoming SiH_4 feed gas flow leads to the conclusion that a silane utilisation of at least 50 % is obtained for actual film deposition. This high gas utilisation rate combined with a relatively low hydrogen flow is an important factor in cost reduction for the deposition process. Recently we started incorporating this type of intrinsic µc-Si:H layers deposited under VHF conditions, at high pressures, into pin solar cells. Solar cells deposited under standard (low-pressure) conditions

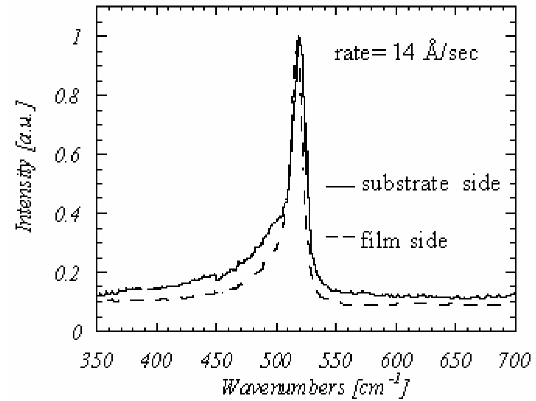

Fig. 3. Raman spectrum of a high rate µc-Si:H film deposited with 4.5% silane concentration measured from the substrate (full line) and from the film side (dashed line) with an Ar laser (514 nm).

(< 1 mbar) in the same "crystallinity range" (i.e. near the µc-Si/ a-Si transition point) show a typical µc-Si:H quantum efficiency (QE) in the red and near-infrared part of the spectrum. In contrast to that, our intrinsic layers deposited under high pressure conditions show a lower response for the red and near-infrared. Observing the variation of the quantum efficiency on a series of solar cells deposited under increasing pressures, we can clearly see a disappearance of the strong absorption "shoulder" in

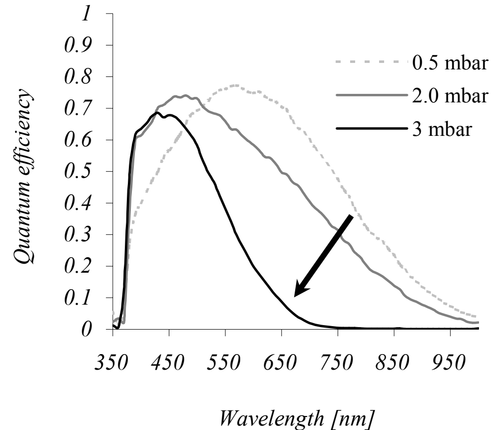

Fig. 4 Quantum efficiency curves of solar cells deposited at pressures varied between 0.5 and 3.0 mbar showing a decrease in response of the red and near-infrared towards 3 mbar.

the spectra above 700 nm, as we increase the pressure. Fig. 4 shows the quantum efficiency curves for cells deposited at 0.5, 2.0 and 3.0 mbar. Even though the Quantum efficiency decreases in the red and near-infrared range, when going from 0.5 to 3 mbar, the Raman spectrum remains microcrystalline.

Recently was reported about similar deficiencies in the quantum efficiency when using the Triode Reactor Configuration [7] also for a combination of VHF-PECVD and HPD.

Because of this deficiency in the Quantum efficiency curves, a μc-Si:H nucleation layer, deposited under soft conditions, was introduced. This enables a better crystallisation [17] right from the beginning of the deposition process. When measuring the quantum efficiency of two solar cells deposited under identical conditions, except the initial nucleation layer, a clear difference in the quantum efficiency between 500 and 900 nm is seen (Fig. 5).

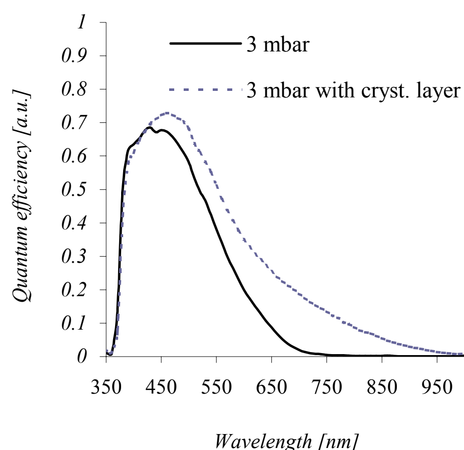

Fig. 5 Quantum efficiency curves of two solar cells deposited at 3 mbar with a deposition rate of ~14Å/s, with and without a nucleation layer.

4. Conclusions

The high pressure regime above 1 mbar has been investigated in combination with the VHF-GD PECVD technique with a view to obtain high deposition rates for microcrystalline silicon, but also keeping industrial aspects in mind. The influence of a change in pressure, on the quality of the films, has been studied with respect to the different deposition parameters. Thereby Raman spectroscopy, sub band gap absorption (by CPM), and dark conductivity measurements were carried out. In doing this work, the main challenge was to evaluate the potential of high-rate μc-Si:H growth at low gas flows, contrary to the high gas flows involved in RF-PECVD at high pressures whenever high deposition rates have been obtained [3]. Low source gas flow at high deposition rates allow one to reduce the gas consumption and therefore the cost of μc-Si based solar cells.

Our results show remarkably high deposition rates of around 25 Å/sec at moderate total gas flows of 100 sccm (SiH_4 + H_2). These films basically possess device quality properties, such as midgap character, low sub band gap absorption and a highly crystalline structure.

First μc-Si:H solar cells were deposited under high pressure conditions. Hereby, we can observe a decrease in the quantum efficiency curve for wavelengths above 700 nm, when increasing the deposition pressure upto 3 mbar. If, then, an intrinsic μc-Si:H initial nucleation layer is introduced for this high-rate deposition (~14 Å/s) at 3 mbar, the response in the red and near-infrared regime is increased again.

The exact reason for the observed decrease in quantum efficiency in the red and near-infrared range has now to be investigated. It will be e.g. necessary to see that this deficiency is not caused by powder formation. It will also be necessary to confirm that this does not harm the solar cell device in any other respect.

If this can be proved and such high-rate μc-Si:H layers lead thus, finally to a satisfactory solar cell performance, VHF-GD in combination with the high pressure regime can be considered to be a key technique to overcome the high gas flow problem associated so far with the high pressure regime.

5. Acknowledgments:

This work was supported by the Swiss Federal Government, Office for Energy (OFEN), under project No. 100.045.

6. References

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