

High rate growth of microcrystalline silicon by VHF-GD at high pressure

U. Graf*, J. Meier, U. Kroll, J. Bailat, C. Droz, E. Vallat-Sauvain, A. Shah

Institut de Microtechnique, Université de Neuchâtel, Rue A.-L. Breguet 2, CH-2000 Neuchâtel, Switzerland

Abstract

Microcrystalline silicon growth using very high frequency-glow discharge PECVD has been studied under conditions of high pressure and high VHF-power conditions. Hereby, the influence of the total gas flow and the silane concentration on the deposition rate has been investigated. Deposition rates of over 25 Å/s have been achieved at relatively low total gas flows of 100 sccm. These high-rate films show device-grade quality with respect to subband gap absorption and microcrystalline structure. Dark conductivity measurements reveal midgap character and transmission electron microscopy investigations confirm a highly crystalline microstructure from the bottom to the top of the $\mu\text{c-Si:H}$ films. These high-rate $\mu\text{c-Si:H}$ layers are very interesting candidates for solar cell and other devices.

Keywords: Thin-film microcrystalline silicon layers; High rate deposition; VHF-GD

1. Introduction

Microcrystalline silicon ($\mu\text{c-Si:H}$) is an attractive low band gap absorber material for integration in thin-film solar cells, especially in the so-called 'micromorph' (amorphous/microcrystalline) tandem cell concept [1]. As the optical band gap of $\mu\text{c-Si:H}$ is indirect, the absorber thickness of microcrystalline cells has to be in the order of at least of 1–2 μm to ensure a sufficient absorption of sunlight. To reduce production costs high deposition rates of intrinsic $\mu\text{c-Si:H}$ have to be achieved. The development of a high rate deposition process for microcrystalline silicon is of fundamental importance in order to reduce manufacturing costs for microcrystalline and 'micromorph' silicon solar cells. This fact motivates the investigation of high rate deposition methods for high quality microcrystalline silicon absorbers.

Recent works with high pressures in r.f.-plasmas [2,3] report about a convincing increase in deposition rate to 15 Å/s (fluxes of 30 sccm SiH_4 and 570 sccm H_2 at 200 W [3]). We believe that these special conditions lead to similar changes in the plasma impedance as an increase in excitation frequency from the standard 13.56

MHz to frequencies in the very high frequency (VHF) range. Therefore, VHF combined with high pressure could provoke even further beneficial effects.

To achieve higher deposition rates (>10 Å/s) in the high pressure regime of r.f.-plasmas very high gas flows are involved. In case of modified¹ very high frequency-glow discharge (VHF-GD) deposition of microcrystalline silicon in the high pressure regime, high rates towards 60 Å/s have been reported [4]. However, in this case as well high gas flows (around several hundreds standard cubic centimetre per minute of hydrogen and 30–50 sccm of silane for laboratory size electrodes) are needed for the deposition [2–6]. High gas flows on the other side also contribute to increasing the fabrication costs of solar cells based on microcrystalline silicon based solar cells as well. Therefore, a high deposition rate process for intrinsic $\mu\text{c-Si:H}$ with a 'reasonable' gas utilisation is needed. To overcome the high rate–high gas utilisation problem we suggest that VHF-GD is the key technique. In this paper a comprehensive study of $\mu\text{c-Si:H}$ films deposited under high working pressures and VHF-conditions is given. Films were characterised by different methods, with respect to subband gap absorption and crystallinity.

*Corresponding author. Tel.: +41-32-718-3337; fax: +41-32-718-3201.

E-mail address: urs.graf@unine.ch (U. Graf).

¹ The term 'modified' applies to the utilisation of a mesh between the parallel plate electrodes.

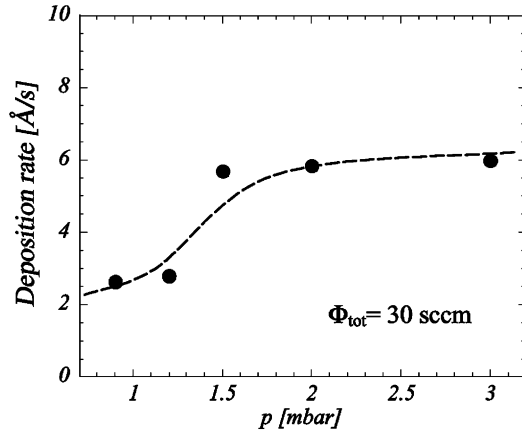


Fig. 1. Deposition rate vs. working pressure, starting in the conventional pressure regime and increasing to 3.0 mbar (dashed line is just a guideline).

2. Experimental

The depositions were carried out in a laboratory size VHF-GD reactor ($\sim 8 \times 8 \text{ cm}^2$) by varying the working pressure up to 3 mbar. For all depositions our gas purifier technique was applied [7] to clean to the feed gas from oxygen contaminants. All films reported here show a thickness homogeneity ($\pm 5\%$) over the total substrate size. In contrast to other studies our total gas flux ($\Phi_{\text{tot}} = \text{flux of H}_2 \text{ and SiH}_4 \text{ together}$) was varied between 30 and maximum 100 sccm containing silane concentrations of 4.5–11.5%. Hereby, the process of VHF-GD was supplied with upto 120 W at an excitation frequency of 70 MHz. As substrates bare Schott glass AF45 as well as such clad with LP-CVD ZnO layers [8] were used.

The thickness of deposited films was determined by an alpha-step thickness profiler. The characterisations of the films were done by Raman spectroscopy (Renishaw) with a Ne/He- ($\lambda_{\text{excit}} = 633 \text{ nm}$) and an Ar ($\lambda_{\text{excit}} = 514 \text{ nm}$) laser. On some of the films on bare glass substrates dark conductivity (σ_{dark} at room temperature and activation energy E_{act}) and optical absorption measurements by constant photocurrent measurement (CPM) for the determination of subgap related defect absorption (α (0.8eV)) were carried out as well. A further check of the crystalline growth structure of such deposited $\mu\text{c-Si:H}$ films was investigated by transmission electron microscopy (TEM) [9].

3. Results and discussion

First, the influence of the deposition pressure was examined with respect to the deposition rate of microcrystalline silicon. Hereby, we observe an increase when passing from the conventional pressure range to pressures above 1.2 mbar. Fig. 1 shows the deposition rate

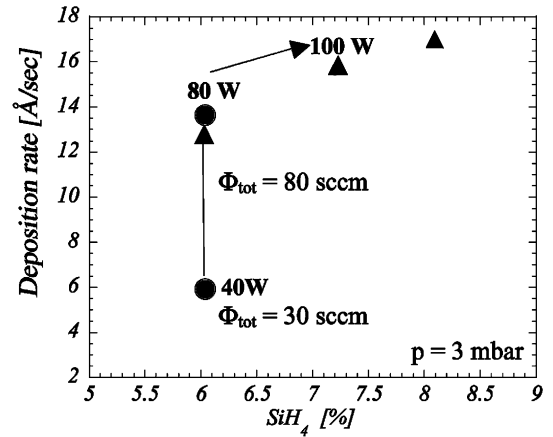


Fig. 2. Deposition rate of $\mu\text{c-SiH}$ vs. silane concentration ($[\text{SiH}_4]/([\text{SiH}_4] + [\text{H}_2])$) at high pressure.

of films deposited at a power of 40 W and a silane concentration of 6% in function of the pressure. Hereby, all films showed microcrystalline behaviour.

The deposition rate above 1.5 mbar does not vary much more with increasing pressure which may be due to an excessive silane depletion condition. Therefore, we increased the total flux of the hydrogen/silane mixture in order to reduce the resident time of the gas radicals. Unfortunately, keeping the power constant this leads, however, to amorphous films. By applying higher gas flows the VHF-power was increased as well to enhance the creation of radicals. Fig. 2 shows that a remarkable increase in the rate can be observed when the total flux is increased from 30 to 80 sccm (keeping the dilution constant) and the power is doubled to 80 W. The rate for the microcrystalline films can be increased to 14 \AA/s . A further increase of the applied power and an additional enhancement of the silane concentration allows even higher deposition rates approaching 17 \AA/s .

In order to check the crystallinity and the electronic quality of these high-rate $\mu\text{c-Si:H}$ layers Raman spectroscopy, optical absorption and the dark conductivity measurements were carried out. Table 1 summarises for the samples with the highest deposition rate the results of these characterisations. First, peak ratios (areas) of the Raman peaks reveal clearly a high crystallinity for

Table 1
Crystallinity, optical absorption and electrical quality of high rate deposited $\mu\text{c-Si:H}$ layers on glass substrates

Deposition rate (\AA/s)	Raman ratio $\frac{I_{520} + I_{510}}{I_{\text{tot}}}$	α (0.8 eV) ($1/\text{cm}$)	σ_{dark} at RT (S/cm)	E_{act} (meV)
13.7	0.656	~ 3.2	5.3×10^{-7}	530
15.6	0.733	~ 2.0	1.20×10^{-7}	497
16.8	0.639	~ 2.1	2.03×10^{-7}	520

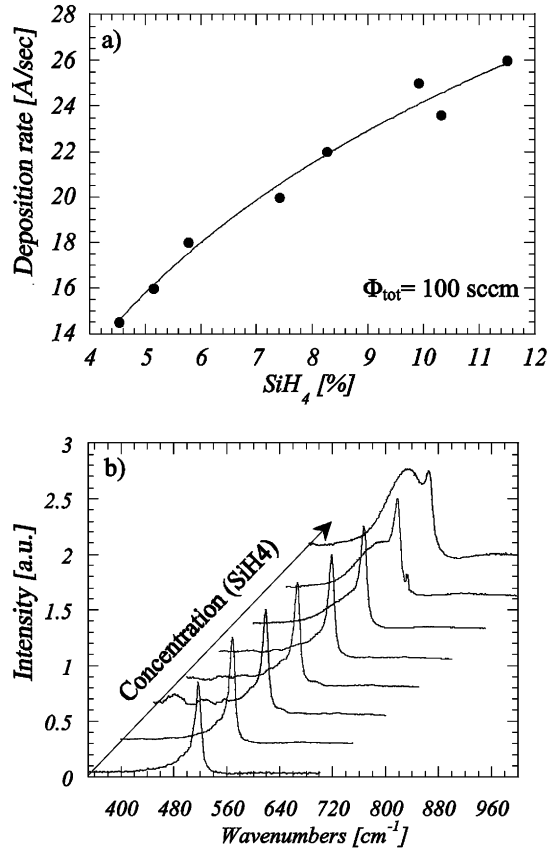


Fig. 3. (a) The deposition rate vs. SiH₄ concentration of $\mu\text{c-Si}$ films, with high pressure (3 mbar); (b) corresponding series of Raman spectra, for increasing values of the silane concentration, measured on the film side with a He/Ne laser (633 nm).

all films. The low subband gap absorption at 0.8 eV by CPM proves that these films have a rather low defect concentration; this contributes a necessary condition for obtaining device-grade $\mu\text{c-Si:H}$ material. From the dark conductivity measurements we obtained activation energies of approximately 0.5 eV with dark conductivities at room temperature approximately 10^{-7} S/cm . These conductivity characteristics indicate clearly the ‘midgap character’ (E_F is in the middle of the gap) of these high-rate microcrystalline films: this constitutes a necessary condition for the application in a p-i-n or n-i-p $\mu\text{c-Si:H}$ solar cell device. Thus, we consider having obtained device quality films at rates up to 17 \AA/s , as given in Table 1.

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 $\mu\text{c-Si:H}$. In Fig. 3 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 remarkable high deposition rates of up to 25 \AA/s .

A quick check with Raman spectroscopy indicates furthermore that these all high-rate films clearly show a crystalline behaviour. Only the films with the two highest levels of silane concentration reveal a significant amorphous volume fraction in the material. The experiments reported in Fig. 3 demonstrate that using VHF excitation frequencies combined with the high pressure regime allows us to achieve high deposition rates ($\sim 25 \text{ \AA/s}$) and keep the gas flow reasonably low.

An estimation based on the reactor area covered by the microcrystalline film and its growth per time unit in comparison with the incoming SiH₄ feed gas flow leads to the result 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. If these films can successfully be applied to produce state of the art solar cells, one will be able to conclude that VHF-GD will play a fundamental role in the future reduction of manufacturing costs for thin-film silicon solar photovoltaic modules.

The ability to produce a full solar cell device with these layers has yet to be demonstrated, in a next step.

However, before it has to be verified if also the initial growth of the microcrystalline material reasonably occurs under these high rate conditions. Therefore, the microcrystalline structure 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. 4 shows the Raman spectra obtained with an Ar laser (514 nm wavelength, i.e. average penetration depth of 100–200 nm) of a film deposited at a rate of 14 \AA/s . These measurements indicate a pronounced crystalline structure even at the initial growth stages of the film, a

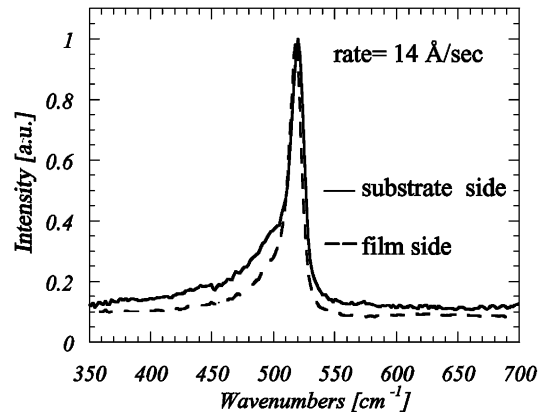


Fig. 4. Raman spectrum of a high rate $\mu\text{c-Si:H}$ film deposited with 4.5% silane concentration measured from the substrate (full line) and from the film side (dashed line) with an Ar laser (514 nm).

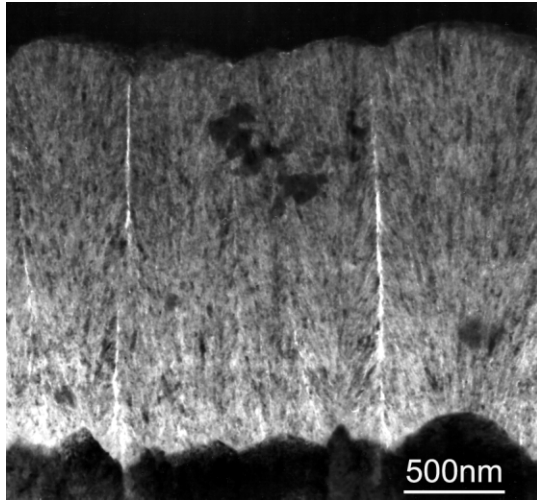


Fig. 5. Profile of an intrinsic $\mu\text{c-Si:H}$ film grown on ZnO (rate = 14 $\text{\AA}/\text{s}$, at high pressure) taken by a transition electron microscopy.

fact that may be useful for the fabrication of entirely microcrystalline silicon devices.

In order to check the microstructure of these new high-rate $\mu\text{c-Si:H}$ films and compare them with that of ‘standard’ layers incorporated into full solar cells we investigated layers deposited on LP-CVD ZnO covered substrates by TEM. Compared to layers deposited by ‘standard’ techniques (i.e. at lower pressures and lower rates), on the same substrates [10] the present film (deposited at 14.5 $\text{\AA}/\text{s}$ in Fig. 5) shows a remarkably high crystallinity. The crystallinity is surprisingly complete and uniform from the bottom to the top of the film. Relatively long cracks appear within the film which consists, however, not of empty voids but of more looser material. Apart from these longer cracks no significant differences can be observed on these high-rate $\mu\text{c-Si:H}$ films compared to previous studies on growth of $\mu\text{c-Si:H}$ films and cells under ‘standard’ condition [10].

4. Conclusions

In order to achieve high deposition rates for microcrystalline silicon the high pressure regime above 1 mbar has been investigated in combination with the VHF-GD PECVD technique. The influence on the quality of the films has been studied with respect to the different deposition parameters by Raman spectroscopy, subband gap absorption (by CPM), and dark conductiv-

ity measurements. Hereby, the main challenge was to evaluate the potential of high-rate $\mu\text{c-Si:H}$ growth at low gas flows, contrary to the high gas flows involved in r.f.-glow discharge plasmas at high pressures and high deposition rate [3]. Low flows at high rates allow reducing the gas consumption and therefore the cost of $\mu\text{c-Si}$ based solar cells.

Our results show remarkably high deposition rates of approximately 25 $\text{\AA}/\text{s}$ at moderate total gas flow of 100 sccm ($\text{SiH}_4 + \text{H}_2$). These films reveal device quality properties, e.g. as midgap character, low subband gap absorption and a highly crystalline structure. In a next step these high quality microcrystalline films have to be incorporated into a full solar cell device, to prove their value as photovoltaic absorber layer. If such high-rate $\mu\text{c-Si:H}$ layers lead to a good solar cell performance, VHF-GD will be a key technique to overcome the high gas flow problem associated so far with the high pressure regime.

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