

Deposition of Thin-Film Silicon for Photovoltaics: Use of VHF-GD and OES

P. Torres, U.Kroll, H. Keppner, J. Meier, E. Sauvain and A.Shah
Institut de Microtechnique, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland
Tel.: +41 32 718 33 54, Fax.: +41 32 718 32 01, e-mail: peter.torres@imt.unine.ch

Keywords: OES, $\mu\text{c-Si:H}$, VHF-GD, Thin-Film Silicon, Photovoltaics

Abstract

Deposition rates over 10 \AA/s can be obtained for device-grade microcrystalline silicon with the VHF-GD (Very High Frequency - Glow Discharge) method, as applied to hydrogen-diluted silane plasmas. The morphological phase transition from amorphous to microcrystalline silicon can be controlled by varying e.g. the applied VHF-power or the dilution level. The glow of the plasma associated with this morphological phase transition is monitored by optical emission spectroscopy (OES). Thereby, we find that the decisive criteria for $\mu\text{c-Si:H}$ growth is the OES-ratio between the $\text{H}\alpha$ - line (atomic hydrogen line at 656 nm) and the SiH^* - line (at 414 nm); in our case, as soon as this ratio becomes lower than 1.7 one obtains microcrystalline growth.

Introduction: a-Si:H and $\mu\text{c-Si:H}$ for solar cells

The search for new device concepts, for suitable photosensitive materials and for economically attractive, low-temperature processes has become a priority in the field of photovoltaic solar cells. However, of all the possible materials, only silicon holds at present the promise of providing solar cells that can be used on a large scale. In fact, silicon is the only non-toxic and widely available photovoltaic material, that has already proved its effectiveness in commercial solar cells. Silicon solar cells based, however, on the use of wafers clearly necessitate the investment of too large quantities of raw material (ultra pure silicon), as well as of tremendous amounts of production energy. They therefore do not constitute a viable solution for the future large-scale application of photovoltaics. One has therefore to concentrate efforts on thin-film silicon. Here, amorphous silicon thin films (a-Si:H) have been the first option. A new option, as pioneered by our institute, is the use of plasma-deposited microcrystalline silicon thin films ($\mu\text{c-Si:H}$).

The viability of using hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) deposited within a silane-hydrogen plasma as an active photovoltaic material has been demonstrated by

fabricating a 8.5 % efficient single-junction thin-film silicon solar cell [1]. This result became possible mainly thanks to three factors: First, an efficient passivation of grain boundaries and other defects by atomic hydrogen due to the plasma. Secondly, the use of a "soft" plasma deposition technique, such as the VHF-GD that avoids high energy bombardment, as discussed elsewhere [2]. Thirdly, the use of p-i-n and n-i-p diodes with the intrinsic (i) layer as photovoltaically active layer; thereby care is taken to keep the Fermi-level of this (i) layer at midgap, by careful exclusion (or alternatively compensation) of impurities with a dopant character, such as oxygen [3].

$\mu\text{c-Si:H}$ has the same gap as crystalline silicon (1.1 eV) but shows an enhanced apparent optical absorption. Recent studies suggest that this effect is due to scattering on the surface and in the bulk [4]. It is therefore the ideal partner for a-Si:H with its gap of 1.7 eV in a double-junction tandem cell. We have called such a $\mu\text{c-Si:H/a-Si:H}$ tandem cell the micromorph cell and have reached so far a stable cell efficiency of 12 % [5].

For the fabrication of a micromorph tandem cell we need an a-Si:H absorber for the top cell and a $\mu\text{c-Si:H}$ layer for the bottom cell. Hydrogen-diluted silane plasmas lead both to the deposition of high quality $\mu\text{c-Si:H}$ as well as to the deposition of more stable a-Si:H. Several process parameters can influence the morphological transition from a-Si:H to $\mu\text{c-Si:H}$, as the applied dilution, the VHF-power, the temperature, the excitation frequency and the process pressure. In order to get more insight in hydrogen-diluted silane plasmas we used OES as a process monitor. OES is a quite simple and efficient in-situ characterisation technique which does not disturb the plasma.

OES for hydrogen-diluted silane plasmas

OES 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). Comparisons to other systems can be only done on a relative basis, since no absolute calibration of the spectra is done.

Basically, we performed OES for two selected series deposited under VHF-GD conditions in the range 110-130 MHz where the morphological transition (a-Si:H/ $\mu\text{c-Si:H}$) has been controlled by varying one parameter alone. In the first series, the morphology has been controlled by the applied dilution of silane alone; the dilutions ($\text{SiH}_4/(\text{SiH}_4+\text{H}_2)$) were set to 1.25 / 2.5 / 5 and 7.5 %. All deposited layers are $\mu\text{c-Si:H}$ except the one deposited at 7.5 % which showed to be amorphous [6, 7]. Here the VHF-power was set to 6 W. In the second series we fixed the dilution at 7.5 % and systematically increased the applied VHF-power from 20 to 70 W. All layers are $\mu\text{c-Si:H}$ except the one deposited at 20 W is amorphous [8, 9].

Fig. 1 shows a typical OES as obtained with our set-up, for a deposition condition leading to $\mu\text{-Si:H}$ growth (2.5 % dilution, 6 W VHF-power). The spectral lines of main interest which will be considered hereafter are situated at 414 and 656 nm. The former line is associated to the SiH^* radical and the latter to atomic hydrogen $\text{H}\alpha$. These lines of our interest are marked in Fig. 1 and we will further analyse how they evolve by changing the process parameters.

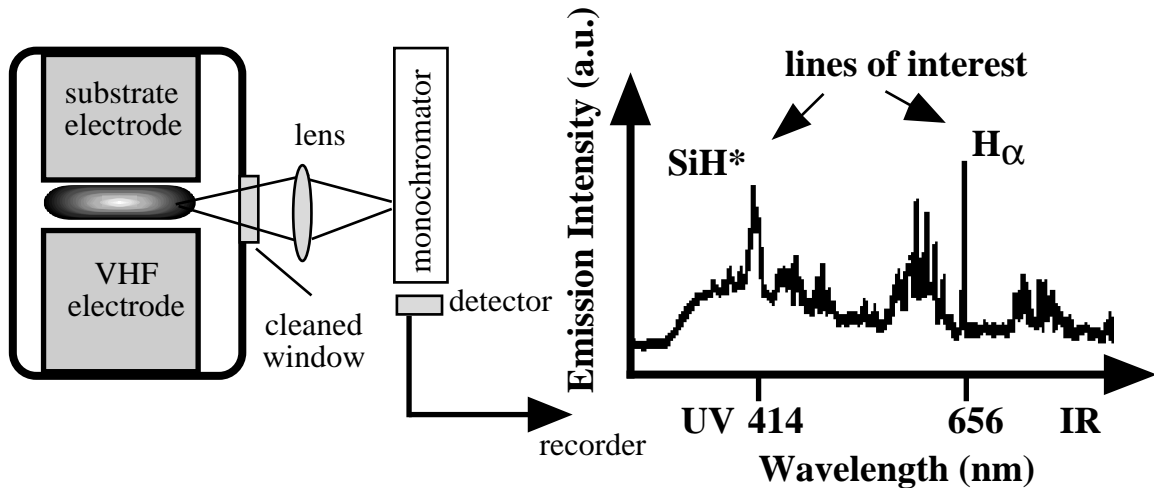


Fig. 1. Experimental set-up for measuring the optical emission spectroscopy (OES) with a typical spectrum. The lines of interest are at 414 nm which is associated to the SiH^* radical and at 656 nm which corresponds to atomic hydrogen ($\text{H}\alpha$).

Fig. 2 shows the intensity of the OES of the SiH^* and $\text{H}\alpha$ lines versus the dilution employed for their deposition. Note that the morphology changes from $\mu\text{-Si:H}$ to a-Si:H when the dilution level is changed from 5 to 7.5 %, as shown elsewhere by X-ray measurements and optical absorption [6, 7]. In agreement with observations previously reported in the literature, $\mu\text{-Si:H}$ growth is observed as soon as enough atomic hydrogen is available [10, 11]. This can be seen in Fig. 2 where samples with the lowest silane flow ratio of 1.25 to 5 % exhibit the lowest $\text{SiH}^*/\text{H}\alpha$ ratio. On the other hand, if the $\text{SiH}^*/\text{H}\alpha$ ratio is high, the obtained layer is a-Si:H (as it is the case for the samples deposited at a silane gas phase ratio of 7.5 and 10 %).

In Fig. 3 the same measurement is shown for the VHF-power controlled transition (at a fixed gas phase ratio of 7.5 % silane). Increasing the VHF-power leads to a continuous decrease of the $\text{SiH}^*/\text{H}\alpha$ ratio and also here we can find $\mu\text{-Si:H}$ growth when this ratio is low enough. Furthermore, owing to much higher plasma densities all the measured OES intensities are shifted to much higher values (the arbitrary units on the y-axis of measured

intensity are the same in both figures); the overall emitted intensities are increased by about a factor of five and we assume thus a higher dissociation rate in the plasma. This increased dissociation rate might explain the approximately 5 times higher deposition rates observed for all the samples (whether a-Si:H or μ c-Si:H) of this VHF-power series compared with the dilution series. Further, as can be seen in Figs. 3 and 4, the deposition rate scales with the intensity of the SiH* line for both, the dilution and the VHF-power series. This has been also observed for the growth of a-Si:H [12].

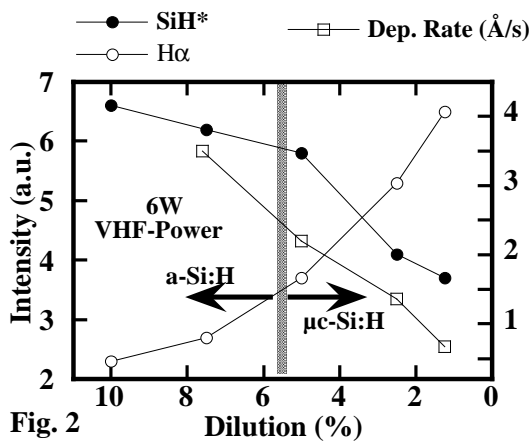


Fig. 2

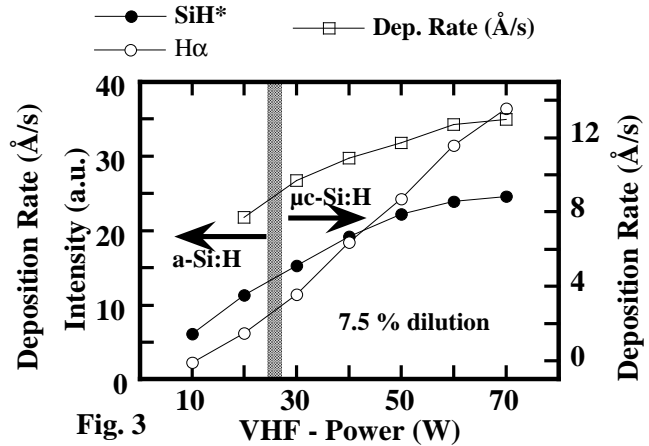


Fig. 3

Fig. 2 and 3. OES for the SiH* and the H α lines of a morphological transition controlled by one process parameter alone: For both, the dilution as well as for the VHF-power controlled series, the morphology becomes μ c-Si:H as soon as the ratio SiH*/H α is low enough. Further, an increase of the deposition rate is accompanied by an increase of the SiH* line.

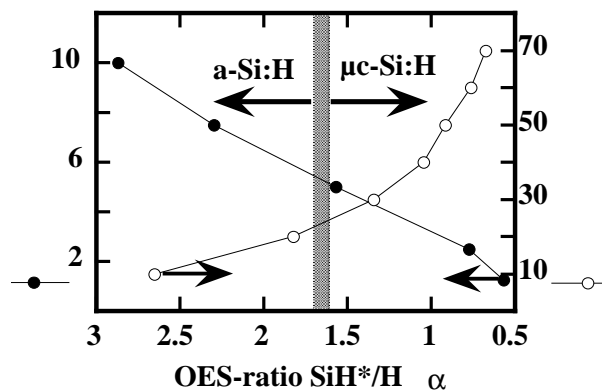


Fig. 4. OES-ratio of the SiH*/H α lines both for the dilution and VHF-power series. As soon as the OES - ratio falls below 1.7 we observe μ c-Si:H growth.

The OES is an efficient monitor to identify either amorphous or $\mu\text{c-Si:H}$ growth, both for the dilution series and the VHF-power series. This is illustrated in Fig. 4, where on the x-axis the OES ratio of the SiH^* and $\text{H}\alpha$ lines are shown for both series: On the left y-axis we can read the values for the dilution series and on the right y-axis the applied VHF-power for the power series. For the particular measurement set-up used here, we see that when the $\text{SiH}^*/\text{H}\alpha$ ratio is well below 1.7 we obtain $\mu\text{c-Si:H}$ growth. Such a behaviour which determines the morphology is consistent with other studies in the literature [10, 13, 14] and is a further proof how helpful OES measurements can be to gather new deposition conditions.

Conclusions

In conclusion, OES is a powerful tool for monitoring the influence of plasma parameters. Even though the two OES series investigated here come from quite different deposition conditions, it is shown that the $\text{SiH}^*/\text{H}\alpha$ ratio is a powerful parameter to determine the microstructure of the deposited film. It is observed that the emission of the SiH^* line scales with the deposition rate independently of the obtained morphology of the layers.

The higher deposition rates using VHF-GD (when compared to standard 13.56 MHz plasma) for both a-Si:H and $\mu\text{c-Si:H}$ can significantly reduce the process time and thus the production cost. Herein OES is an efficient and easy to handle in-situ tool that will certainly contribute to monitor the deposition process.

References

1. MEIER J. et al., "Microcrystalline Single-Junction And Micromorph Tandem Thin-Film Silicon Solar Cells", to be publ. in Proc. of Mat. Res. Soc., San Francisco, (1998).
2. HEINTZE M. and ZEDLITZ R., "VHF Plasma Deposition For Thin-Film Solar Cells", Pr. in PV: R. and Appl. **1**, (1993), 213-224.
3. TORRES P. et al., "Device Grade Microcrystalline Silicon Owing to Reduced Oxygen Contamination", Appl. Phys. Lett. **69**, (1996), 1373-1375.
4. VANECEK M. et al., "Optical Properties of Microcrystalline Materials", to be published in Journal of Non-Crystalline Solids (ICAMS 17), (1998).
5. MEIER J. et al., "Recent Progress in Micromorph Solar Cells", to be published in Journal of Non-Crystalline Solids (ICAMS 17), (1998).

6. BECK N. et al., "Optical and Electrical Properties of Undoped Microcrystalline Silicon Deposited by the VHF-GD with Different Dilutions of Silane in Hydrogen", *Mat. Res. Soc. Symp. Proc.* **452**, (1997), 761-766.
7. GOERLITZER M. et al., "Electronic Transport and Structure of Microcrystalline Silicon Deposited by the VHF-GD Technique", to be publ. in *Proc. of Mat. Res. Soc.*, San Francisco, (1997).
8. TORRES P. et al., "Fast Deposition of $\mu\text{-Si:H}$ by Restrictive Dilution and Enhanced HF-Power", *Phys. Status Sol. (a)*; 163, (1997), R9-R10.
9. TORRES P. et al., "Fast Deposited Microcrystalline Silicon Solar Cells", *Proc. of the 26th IEEE PVSC*, (1997), 711-714.
10. MISHIMA Y. et al., "Characterisation of Plasma-Deposited Microcrystalline Silicon", *Phil. Mag. B* **46**, (1982), 1-12.
11. OTOBE M. and S. Oda, "The Role of Hydrogen Radicals in the Nanocrystallization of Silicon", *Proc. Jpn. Plasma Chem.* **5**, (1992), 123-128.
12. HOWLING A. A. et al., "Frequency Effects in Silane Plasmas for Plasma Enhanced Chemical Vapour Deposition", *J. Vac. Sci. Technol. A* **10**, (1992), 1080.
13. MATSUDA A. "Formation Kinetics and Control of Microcrystallite in $\mu\text{-Si:H}$ from Glow Discharge Plasma", *J. of Non-Cryst. Solids* **59&60**, (1983), 767-774 .
14. ODA S. et al., "Diagnostic Study of VHF Plasma and Deposition of Hydrogenated Amorphous Silicon Films", *Jpn. J. Appl. Phys.* **29**, (1990), 1889-1895 .