# ENLARGED PARAMETER SPACE BY USE OF VHF-GD FOR DEPOSITION OF THIN <p> TYPE μc-Si:H FILMS

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## ABSTRACT

In this paper new results on thin p - type μc-Si:H films deposited at low temperatures of 170 ˚C by the Very High Frequency - Glow Discharge technique (VHF-GD) are presented. The "tolerated" amount of diborane added in the gas phase ratio as well as the influence of three different plasma excitation frequencies (70, 100 and 130 MHz) in obtaining high electrical conductivity are investigated. The goal is to optimise very thin ($< 400$ Å) and hence optically transparent films by maintaining high conductivities for the application as window layers of solar cells.

## INTRODUCTION

Hydrogenated microcrystalline silicon deposited at low temperatures by plasma methods is in general an interesting photovoltaic material [1, 2], and it is indeed also a promising material for optoelectronic applications. Doped μc-Si:H films in particular, result in excellent contact layers for photovoltaic applications due to their higher conductivity compared to amorphous silicon [3].

However, the major drawback to grow very thin boron doped μc-Si:H layers is that it is technologically quite a delicate task to find appropriate parameters. One has to ensure that the layer is indeed microcrystalline and thus avoid a phase transition to amorphous silicon. This morphological requirement is mainly achieved by highly diluting silane in hydrogen. Standard 13.56 MHz PE-CVD requires, in general, dilution ratios higher than 1% $SiH_4$/total gas flow; on the other hand, the VHF-GD technique allows for lower dilution ratios, i.e. of gas flows up to 5 % $SiH_4$/total for μc-Si:H growth [4]. As our earlier studies on p - type μc-Si:H have shown [5] doping has to be carefully adjusted: The optimal diborane doping ratio ($B_2H_6/SiH_4$) for highly conductive films has to be determined empirically: On one hand, enough doping is needed to push the Fermi level close to the valence band, on the other hand, a too high doping will result in the amorphisation of the layers.

Earlier studies [4, 6] have shown that VHF - conditions are favourable for microcrystalline growth. The better growth of μc-Si:H at higher plasma excitation frequencies motivated us to further increase the excitation frequency in order to try to obtain even higher conductivities. So far, comparative excitation frequency studies for μc-Si:H film growth have been carried out only on n-type μc-Si:H [6]; however, growth of excellent p-type μc-Si:H has recently been demonstrated at the single high excitation frequency of 170 MHz [7].

## EXPERIMENTAL

All films in this study were deposited on AF45 glass from Schott (alkali free) in a single-chamber parallel-plate reactor by the VHF-GD technique at plasma excitation frequencies of 70, 100 and 130 MHz. To avoid cross-contamination from outgasing, the chamber walls were heated overnight, thus leading to a base pressure of $5 \times 10^{-8}$ mbar at room temperature. To achieve good reproducibility, all layers were deposited with the same chamber history. The electrodes have a surface of 139 cm$^2$ and are separated by a gap of 15 mm. The substrate is positioned upside down on the upper electrode, where the effective substrate temperature is kept at 170 °C for all the films. The radio frequency is capacitively coupled to the lower electrode providing impedance matching for the entire frequency range of 55 to 200 MHz.

The employed gases were silane ($SiH_4$), hydrogen ($H_2$), and diborane ($B_2H_6$) diluted at 500 ppm in $H_2$. The gas pressure was kept at 0.4 mbar and the dilution level of silane was 1.5 % over a total gas flow of 100 sccm.

The effective power, determined by the subtractive method [8, 9] was kept approximately at 3,5 W. This corresponds to setpoint values of 4, 5 and 9 W for 70, 100 and 130 MHz respectively. One can observe from this measurements that the power coupling into the reactor becomes worse at higher frequencies. Therefore it is important for a comparative study like this one, where the frequency is changed, to actually check the effective power in the plasma.

We selected as a <u>monitor</u> to determine the optimal doping, the value of the room temperature dark conductivity $\sigma_d$ of μc-Si:H layers as measured on a coplanar electrode configuration under an $N_2$ atmosphere at 10 mbar after a standard temperature annealing step up to 150 °C.

## RESULTS AND DISCUSSION

The layer thickness was kept constant at around 400 Å for optimisation of the boron doping experiment. This was done in order to avoid errors due to the strong thickness effect on $\sigma_d$, as observed for very thin layers [7]. In order to optimise $\sigma_d$, a doping-study was carried out for the different plasma excitation frequencies: 70, 100 and 130 MHz. From Fig. 1 it is obvious that the doping range for highly conductive p - type μc-Si:H films is broadened when the plasma excitation frequency is increased. Thus, we can deduce, that higher excitation frequencies will favour the growth of p - type μc-Si:H layers. This effect is also interesting from the point of view of plasma physics, since it provides further experimental evidence that the VHF-GD technique at high plasma excitation frequencies is indeed an appropriate tool for the growth of μc-Si:H. Here, we observe that even higher "doses" of diborane in the gas phase ratio do not hinder crystalline nucleation if one moves to higher plasma excitation frequencies.
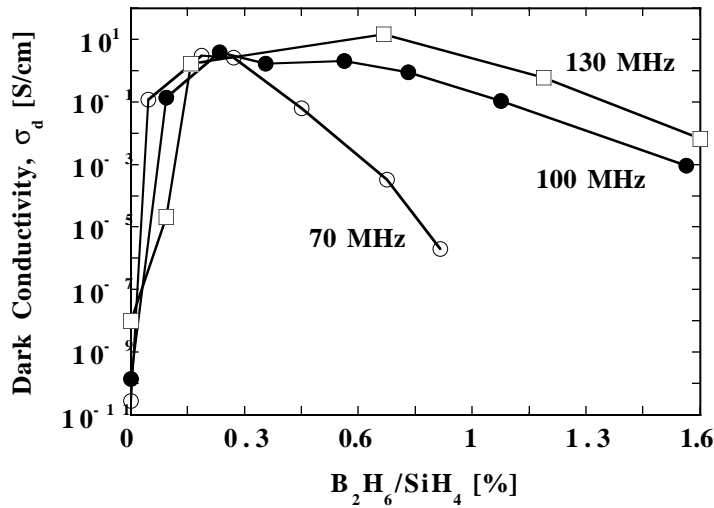
Fig. 1: Room temperature dark conductivity as a function of diborane doping for three different rf-plasma excitation frequencies. Film thickness is nominally 400 Å.

From Fig. 1 we deduce that the optimal diborane doping ratio ($B_2H_6/SiH_4$) for the 70 MHz series is about 0.2 % and that this optimum is shifted to a higher value of about 0.7 % for the 130 MHz series. To compare this 130 MHz p - type films with an earlier study done at 70 MHz [5], we deposited a thickness series at 0.7 % $B_2H_6$ doping as assumed to be optimal for 130 MHz (fig. 1). It is well known that for thicknesses under a critical value, the dark conductivity $\sigma_d$ will drop substantially.
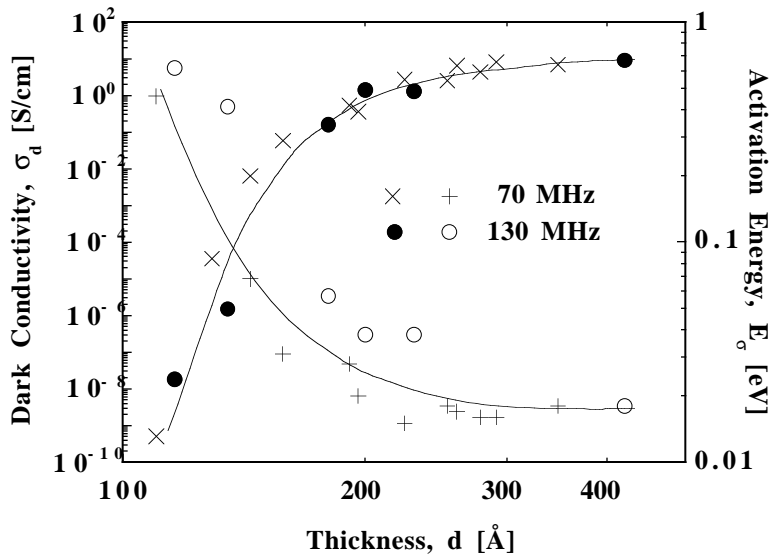


Fig. 2: Room temperature dark conductivity and dark conductivity activation energy, as a function of film thickness. Note that the 70 MHz series are taken from a previous work [5] and are deposited in an equivalent reactor under similar conditions as the present series.

**Film thickness (Å)**
**115**
**135**
**180**
**200**
**230**
**420**

Transmission (y-axis): 1, 0.8, 0.6, 0.4, 0.2, 0
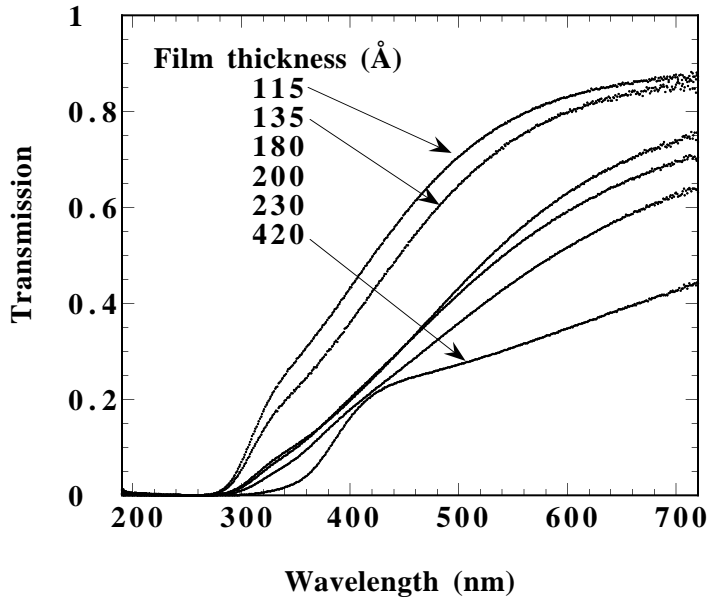
Wavelength (nm) (x-axis): 200, 300, 400, 500, 600, 700

Fig. 3: Optical transmission of p - type layers deposited at a plasma excitation frequency of 130 MHz for a set of layer thicknesses as shown above in Fig. 2.

In Fig. 2 we compare the 130 MHz series with a 70 MHz series already published [5] which was deposited in an equivalent reactor and under similar conditions. It is surprising that even under such different growth conditions the films have same properties. In Fig. 3 we show the optical transmission of the 130 MHz thickness series. The highly conductive films (d > 180Å) show considerable absorption in the visible range, but the appropriate thickness e.g. for a window layer in a solar cell has to be worked out in the device itself. Just to give an example, the nucleation behaviour on substrates other than glass (as used for this work) can in certain cases result even in epitaxial growth [10] (this is observed on crystalline silicon for identical deposition parameters as those used in this work). For growth on underlying amorphous silicon layers a careful pretreatment is required, otherwise no nucleation occurs and hence the film remains amorphous [11, 12].

The deposition rate of boron-doped films depends strongly on the $B_2H_6$/$SiH_4$ gas phase ratio. To compare the deposition rates of highly conductive films obtained by different plasma excitation frequencies, we kept the gas phase doping ratio at the constant values of 0.2 % $B_2H_6$ / $SiH_4$. Fig. 4 shows the deposition rate in function of the frequency. For comparison, the 130 MHz film with optimal doping of 0.7 % is also shown in the same figure. We see that an increased in excitation frequency results in higher deposition rates, which is even further increased by enhancing the diborane doping ratio. However, this increased deposition rate does not affect the films quality in terms of electrical conductivity as seen in Fig. 1 provided that the excitation frequency is high enough.
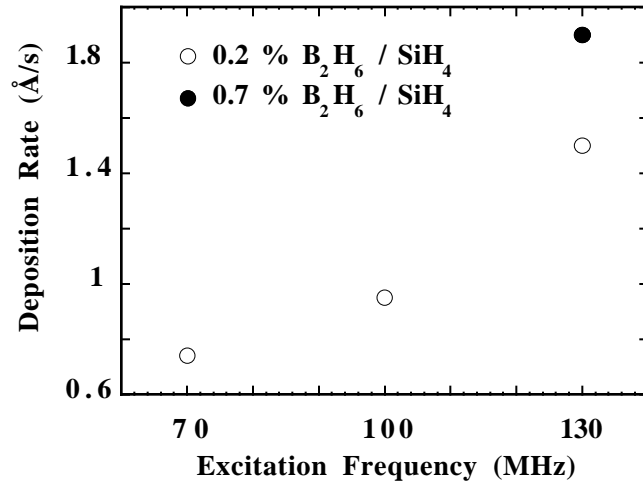
Fig. 4. Deposition rates of diborane doped microcrystalline silicon films deposited at several plasma excitation frequencies on glass. Further doping even more increases the deposition rate.

$P_{eff} = 3.5$ W for all films

## CONCLUSIONS AND OUTLOOK

Starting from previously published results on p - type $\mu$c-Si:H, deposited at an excitation frequency of 70 MHz, where the VHF-GD method had already been shown to give excellent layers , the authors have extended in this paper the plasma excitation frequencies to even higher frequencies of 100 and 130 MHz. Thereby, they found that the parameter range for the diborane gas phase doping ratio is substantially enlarged. This effect supports earlier findings that higher plasma excitation frequencies lead to higher crystallinity and higher deposition rates of the films. The larger parameter space at the higher plasma excitation frequency of 130 MHz should probably also facilitate the growth of boron-doped $\mu$c:Si,C:H layers, i.e. of silicon - carbon alloy. The methane used there in the gas phase is also known to hinder nucleation [13]. Higher plasma excitation frequencies may possibly favour the growth of SiC - crystallites as was found by Hamakawa et al. when using the ECR - process [14]: The enlarged parameter space demonstrated in this work at higher frequencies may possibly constitute a tool to overcome this limitation.

## ACKNOWLEDGEMENTS

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