Microwave Plasma Assisted VHF-PECVD of Micro-Crystalline Silicon

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ABSTRACT

Growth of intrinsic micro-crystalline silicon layers by means of VHF-PECVD, assisted by remote microwave (MW) plasma has been investigated. The aim of the microwave plasma is to enhance the deposition rate by introducing additional excited hydrogen and Ar atoms in the VHF deposition zone. For this purpose a remote microwave plasma source was constructed in which a H_2/Ar plasma is generated in a 20 mm diameter quartz tube. A gas-shower has been constructed for homogeneous distribution of the flow of excited gas species from the microwave source into the deposition zone of the VHF-PECVD reactor where the dissociation of silane takes place. At high microwave power (> 500 W) and undiluted hydrogen in the MW source, an increase of the deposition rate of silicon by 20 % with respect to pure VHF deposition was observed. The silicon layers grown with MW assistance had a high oxygen content as a result of a strong reduction of the quartz tube by the hydrogen plasma. In a second series of experiments Ar dilution and reduced MW power were used to eliminate the effect of etching of the tube by the microwave hydrogen plasma. In this series of experiments an increase of the growth rate of micro-crystalline silicon by about 15 % due to assistance of the microwave plasma was found. Optical emission spectroscopy indicates that – in these experiments – the main mechanism for the increased dissociation of silane is through molecular quenching reaction of Ar^* metastables.

INTRODUCTION

Micro-crystalline silicon is a promising material for application in film silicon solar cells. A very attractive application is the so-called micromorph cell, as developed at IMT [1], consisting of an a-Si:H top cell and a μc-Si:H bottom cell. Stable efficiencies of more than 11 % have been obtained by IMT, by research groups of Jülich [2], Canon Corp. [3] and Kaneka Corp. [4] for such tandem cells. These efficiencies already approach the values of wafer based mc-Si solar cells, but still have large potential for improvement if the best individual values for V_{oc}, J_{sc} and fill factors could be combined [5].

A bottleneck for large scale production of film silicon solar cells based on μc-Si:H is the rather low deposition rate by which this material – with an appropriate, 'solar grade' quality – can be grown so far. Commonly, μc-Si:H is grown by a silane-based glow discharge technique with parallel-plate reactors in which the silane is diluted by hydrogen (and sometimes Ar). In the early days the standard industrial frequency of 13.56 MHz was used and this allowed for deposition rates up to approximately 0.1 nm/s. Later, the Very High Frequency Glow Discharge (VHF-GD) process was introduced by IMT, using plasma excitation frequencies in the VHF bands above 50 MHz, which enabled an increase of the deposition rate by roughly a factor 5 [6]. Despite some successful efforts to increase the deposition rate of the VHF technique [7], there is still an urgent need for higher growth rates of 'solar grade' μc-Si:H. One basic idea to achieve

this goal is to supply more atomic hydrogen to the plasma. This idea is based on a growth model for μc-Si:H in which the growth of the crystalline phase is a balance of sticking of SiH_n (preferably SiH_3) species at the surface and a removal by atomic H of those Si atoms at the surface which are not at a well ordered lattice position. Secondly, the presence of atomic hydrogen in the VHF-GD plasma can help the dissociation of SiH_4 and hence will increase the flux of SiH_3 to the substrate.

In the default glow discharge deposition the required atomic hydrogen is supplied by a strong dilution of the silane gas with H_2, resulting in SiH_4/H_2 ratios typically of about 5 % and less. A more efficient way, though, could be to supply the atomic hydrogen to the growth interface through an external source such that all the power in the VHF glow discharge can be used for the dissociation of silane.

To investigate this option, we have constructed a micro-wave source for generation of atomic hydrogen. The atomic hydrogen then is guided via a quartz tube to the substrate which is positioned in a VHF reactor. In this paper we will report on the results of experiments on deposition of intrinsic μc-Si:H with this setup.

EXPERIMENTAL

The equipment used for the experiments on microwave plasma assisted VHF-PECVD of μc-Si:H is shown in Figure 1. At the left side the VHF reactor is shown. The substrate holder for 10×10 cm^2 substrates is mounted on the upper electrode. Prior to depositions the chamber is evacuated to approximately 5 – 10 E-7 mbar by means of a turbo-molecular pump. During depositions the pressure (typically in the range 0.1 – 1.5 mbar) is controlled by a roots pump in combination with a butterfly valve. The substrate temperature was kept at 200 ºC for all depositions reported here. The plasma excitation frequency of the VHF glow discharge is 70 MHz.

The microwave source is shown on the right side of Figure 1. Microwaves, with a frequency of 2.45 GHz are generated by the 1 kW magnetron at the lower side of this figure. The waves are transmitted through a rectangular copper waveguide to the applicator consisting of a water cooled cavity and a quartz tube with a diameter of 2 cm. Microwave discharge takes place within the quartz tube, through which a mixture of Ar and H_2 is flowing. Impedance matching for the microwaves is achieved by the adjustable short (rough matching) and tuning stubs (fine tuning). Excited hydrogen and argon enters the VHF deposition area at the outlet of the quartz tube. We applied a gas shower mounted on the outlet of the quartz tube, in order to obtain a homogeneous distribution of the excited gas species from the MW source in the VHF deposition zone.

Alkaline free Schott glass was used as substrate, in combination with small pieces of polished Si Cz-wafers for FTIR measurements. The crystallinity of the layers was examined by Raman spectroscopy. The electronic quality of the layers was determined by dark conductivity and by PDS measurements.

Optical Emission Spectroscopy (OES) in the wavelength range of 250-900 nm was applied to investigate relative concentrations of excited species in the VHF plasma .

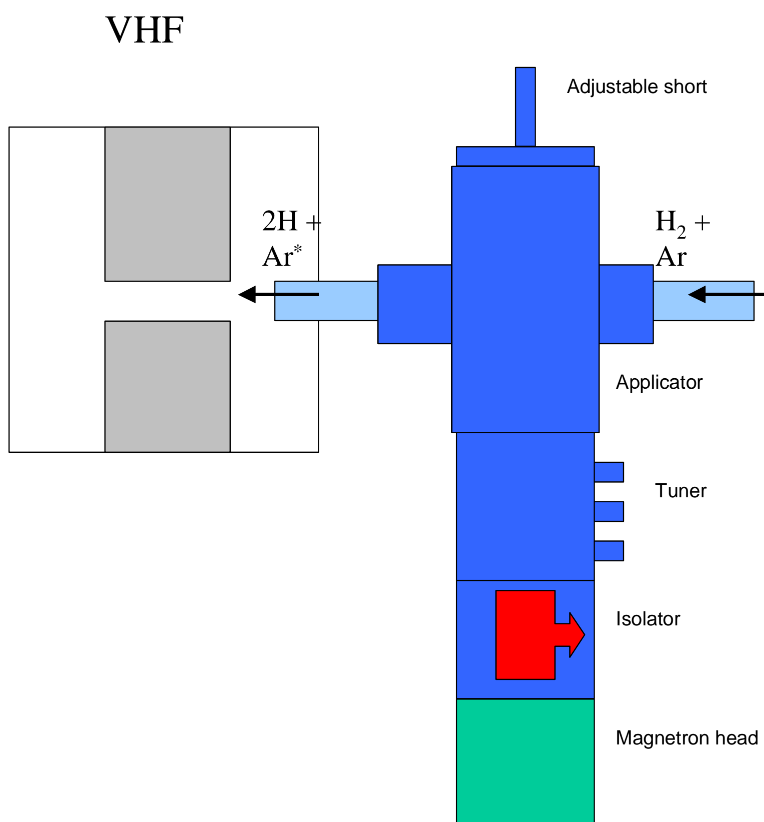

Figure 1: Setup for microwave plasma assisted VHF-PECVD

RESULTS AND DISCUSSION

VHF depositions with assistance of pure hydrogen MW plasma

In order to achieve a sustainable pure H_2 plasma in the MW-source, the pressure has to be larger than a certain threshold value. In our configuration, this threshold pressure is about 0.9 mbar. For lower pressures, a sustainable plasma is only obtained if the hydrogen is mixed with a certain amount of argon. This relatively high threshold pressure for a pure H_2 plasma is probably caused by a high expulsion rate of H_n^+ ions (due to their low weight) from the plasma followed by a quick neutralization of these species on the walls.

The microwave source is a very effective tool for production of hydrogen radicals. With the assistance of the MW plasma, we obtained an increase of the deposition rate of about 20 %. However, all layers grown with MW plasma assistance under these conditions were amorphous. A drawback of the effective production of hydrogen radicals is that if undiluted hydrogen is used as a source gas and high microwave powers are applied (in the range of 500 W), the quartz tube is seriously attacked in the MW plasma zone. We have observed local reduction of SiO_2 into Si under these conditions. The remaining oxygen partly has been incorporated in the grown Si

layers. We therefore reduced the applied MW power and diluted the hydrogen by argon in the second series of experiments.

VHF depositions with assistance of MW plasma of Ar and H_2

We have performed a series of depositions of intrinsic Si to investigate the effect of a supply of excited Ar and H species to the VHF growth zone. Three variants of MW plasma assistance have been used: I: no MW power, II: MW plasma of pure Ar, III: MW plasma of Ar + H_2. The process conditions of the experiments are displayed in Table I. Note that in the cases where the MW power was set to zero, nonetheless 50 sccm of argon and 0 or 5 sccm of hydrogen entered the VHF deposition area through this inlet.

Visual inspection showed that the inner surface of the quarz tube was not deteriorated after the experiments.

Table I: process conditions for experiments with Ar diluted hydrogen MW plasma in quartz tube.

H_2 VHF (sccm)	H_2 MW (sccm)	SiH_4 VHF (sccm)	Ar MW (sccm)	Pressure (torr)	Power MW (W)	Power VHF (W)
50-75	0/5	5-10	50	0.8	0/100	10

In Figure 2 the deposition rate versus the silane concentration (expressed as the fraction $SiH_4/[Ar+H_2+SiH_4]$), is shown. Raman measurements showed that up to a silane concentration of about 8 % the structure of the layers is micro-crystalline. Structural differences between samples which were grown with and without assistance of a MW plasma were not observed.

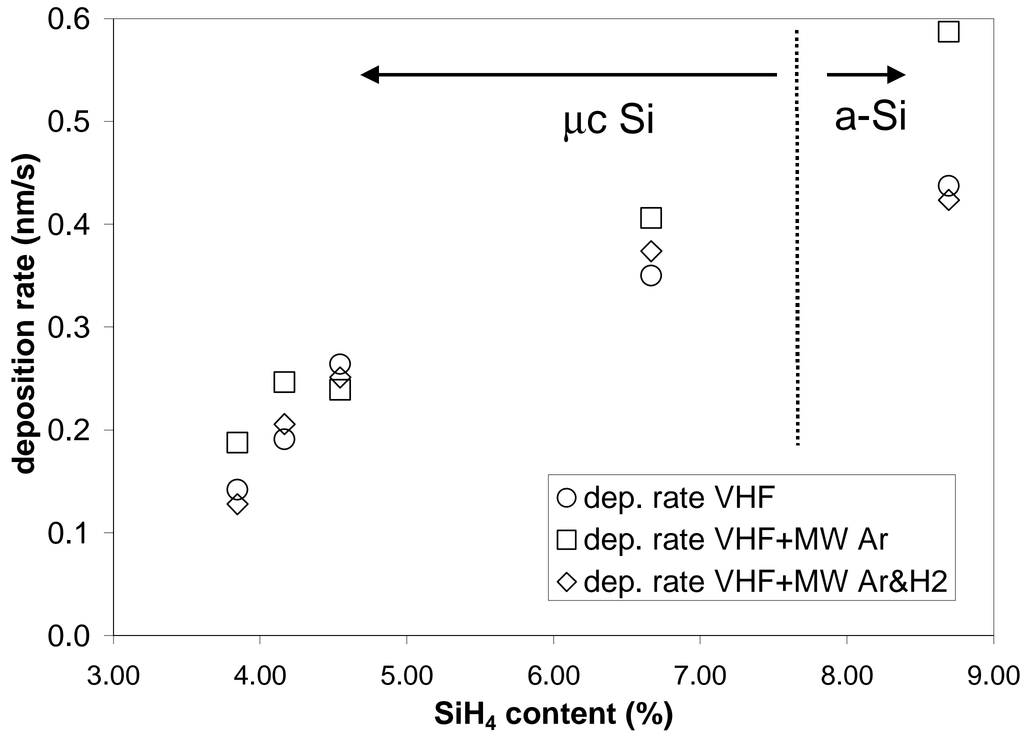

Figure 2: Deposition rates for depositions with pure Ar and H_2 diluted by Ar.

The growth rate too, is not strongly effected by the additional MW plasma. For the depositions in which a MW-plasma of argon plus hydrogen was applied we do not observe a significant difference in growth rate in comparison to pure VHF depositions. Highest growth rates are obtained for depositions with assistance of a MW plasma of pure Ar. For this variant the mean deposition rate is on the average 15 % larger than for the pure VHF depositions.

Our OES measurements show that in these experiments the growth rates can not straightforwardly be associated with the intensity of the SiH^* (412 nm) lines, nor that the transition μc-Si to a-Si can be associated with the $H\alpha/SiH^*$ ratios, as reported in the literature[8,9]. For all three deposition variants applied, the intensity of the $H\alpha$ and the SiH^* emission is constant with respect to the silane flow (also for the case where a-Si is grown). The mean values of the emission intensity ratios $H\alpha/SiH^*$ for variants I, II and III are respectively 1.00, 1.03 and 1.24.

Apparently the growth rate in this series of experiments is enhanced by the availability of Ar^* metastables and not by the presence of SiH^* species. This is illustrated by Figure 3 where the ratios of the SiH^* and the Ar(695 nm) lines are shown. If we compare this figure with Figure 2, we see that the deposition rate positively correlates with Ar^* emission intensity. The mechanism behind this is probably the so-called molecular quenching reaction of Ar^* metastables with silane: $SiH_4 + Ar^* \longrightarrow SiH_3 + H + Ar$ [10].

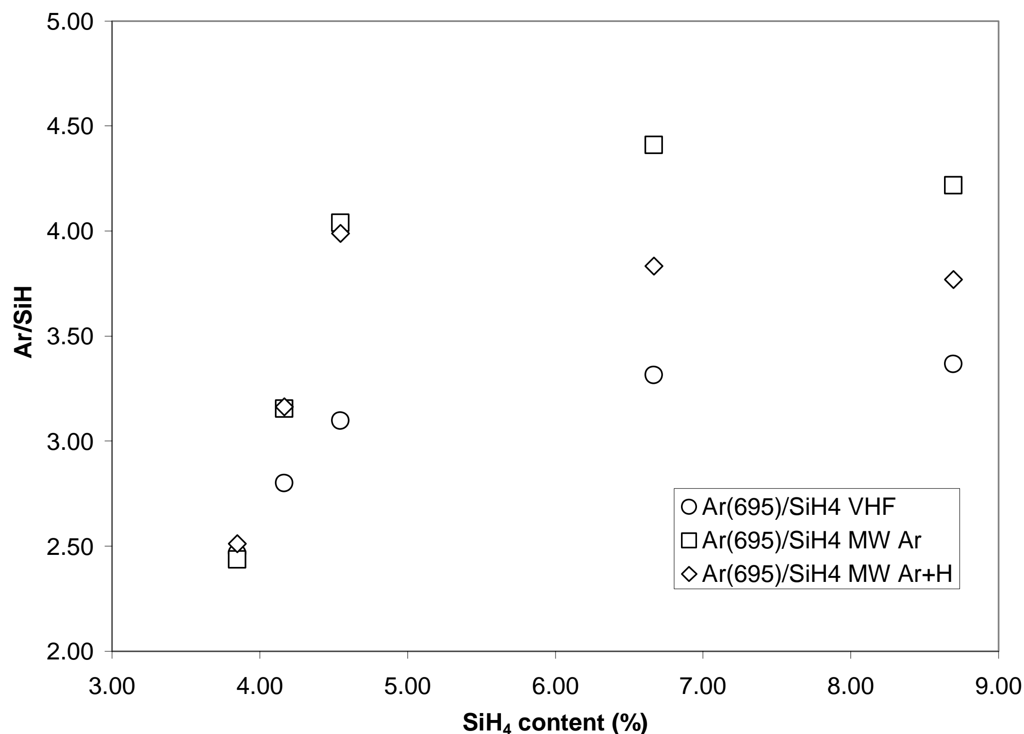

Figure 3: Ratio of emission intensities of Ar(695nm) and SiH_4.

FTIR measurements show that the μc-Si layers are contaminated with a significant amount of oxygen. This could be an effect of post-deposition oxidation of the layers which appear to be

quite rough and poreous (Note that the samples were removed from the vacuum chamber at 200 ˚C). For the highest silane flows, where a-Si layers are grown, no oxygen contamination is observed by FTIR. The amorphous layers are more flat and better closed, preventing post-deposition oxidation. A consequence of large oxygen content is that the electronic quality of the μc-Si layers is not yet satisfactory. PDS measurements indicate that the sub-bandgap absorption (<1 eV) of these layers is in the range 20-50 cm^{-1}.

CONCLUSIONS

Deposition rates of μc-Si layers grown by VHF-PECVD can be increased by assistance of a MW plasma of hydrogen and argon. Care, however, has to be taken to avoid chemical reactions between hydrogen radicals and the quartz tube in which the microwave plasma is generated because this will lead to large incorporation of oxygen in the grown layers. This chemical attack can be avoided by reduction of MW power in combination with dilution by Ar. Under these conditions, the MW plasma enhanced growth rate is mainly caused by enhanced dissociation of SiH_4 by molecular quenching of Ar^* metastables.

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