MICROWAVE PECVD OF MICRO-CRYSTALLINE SILICON

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ABSTRACT

The deposition of micro-crystalline silicon with a new linear microwave plasma source is investigated. Advantages of this plasma source are the high deposition rates and the large area on which a homogeneous deposition can be achieved. Since this source has not yet been applied for deposition of micro-crystalline silicon before, we explored a large parameter space in order to find optimum growth conditions. It is observed that with this microwave source it is possible to grow micro-crystalline layers at higher silane/hydrogen ratios and deposition rates than for conventional RF PECVD. In this paper, structural properties of silicon layers deposited by microwave assisted PECVD are discussed.

INTRODUCTION

Micro-crystalline silicon (μc-Si) has received much interest from the PV community recently because this material can be fabricated as thin layers at low temperatures. In solar cells, the material does not suffer from degradation like amorphous silicon. In the past few years, solar cells and modules based on micro-crystalline silicon layers, have been made both on laboratory scale [1,2,3] and on pilot production scale [4]. A severe handicap for a large scale production of solar cells based on μc-Si is that with conventional deposition techniques such as, e.g., RF-PECVD the growth rate of the intrinsic Si layer is unacceptably low. Alternative techniques which enable a larger growth rates like VHF-PECVD have the disadvantage that it is more difficult to obtain homogeneous deposition on large areas.

In this paper we present a new deposition technique – microwave PECVD – which enables both large deposition rates of intrinsic μc-Si and homogeneous deposition on large areas. We will report on the structural properties of these layers obtained under various plasma conditions.

EXPERIMENTAL SETUP

The depositions were performed in a single chamber reactor, in which a substrate holder with a width of 75 cm moves underneath a linear microwave plasma source. This plasma source, which is depicted in Figure 1 has been developed by Roth&Rau (Germany) and has successfully been introduced in the PV industry for deposition of anti-reflecting and passivating SiN:H layers on mc-Si wafer based solar cells [5].

The MW source consists of a 2 cm diameter quartz tube, with a length of about 1 m , with a copper antenna in its center. Microwaves are coupled in to the antenna from both sides from two 1 kV generators via rectangular waveguides. The inner side of the quartz tube is cooled with air, on the outside of the tube the microwaves will generate a plasma. The plasma then acts as a co-axial waveguide for the microwaves [6]. Downstream, a few centimeters above the substrates, there are two linear arrays of permanent magnets. If the pressure is sufficiently low (typically below 0.1 mbar), these magnets provide an enhanced confinement of the electrons, leading to an increased efficiency of the dissociation of the process gasses. At higher pressures the effect of the magnets is negligible since the plasma does not extend far enough from the quartz tube into the magnetic field.

We have investigated the growth of μc-Si injecting H_2, eventually mixed with Ar, near to the microwave source and adding SiH_4 downstream in the plasma just above the moving substrate.

Information on plasma chemistry was obtained by means of Residual Gas Analysis (RGA) and by Optical Emission Spectroscopy (OES). We deposited μc-Si layers simultaneously on alkali-free glass substrates and on double-polished CZ wafers. After deposition the layers were analyzed by Raman spectroscopy, SEM, XRD and FTIR. Bonded hydrogen contents were obtained by FTIR by numerical integration of the SiH-rocking-wagging mode at 640 cm^{-1}. We used a proportionality constant equal to 2.1E19 cm^{-2} for this mode [7].
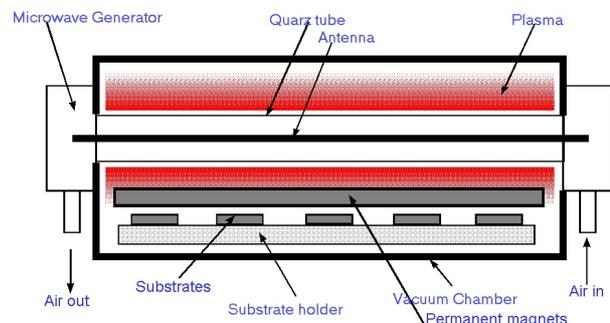

Figure 1: Schematic view of the plasma source.

EXPERIMENTAL RESULTS

Residual gas analysis shows that the MW source is very efficient in dissociation of SiH_4. In Figure 2 a typical mass analysis spectrum during a deposition is shown. From these data we can extract a depletion rate (defined as the ratio of mass concentrations with MW power off and on) for silane that is between 85 and 90%. We expect that SiH_4 is mainly dissociated into SiH_3, but more sophisticated techniques like Threshold Ionization Mass Spectroscopy or Cavity Ringdown Spectroscopy are required to confirm this assumption.
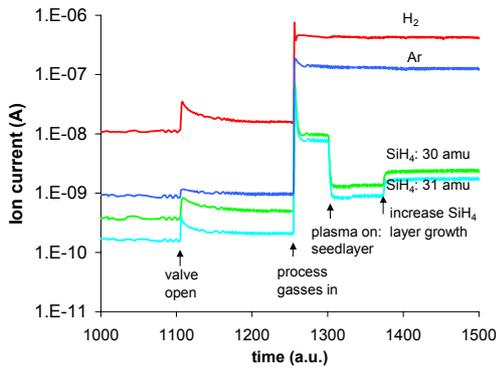

Figure 2: RGA spectra showing the large dissociation of SiH_4.

The dissociation of H_2 is not well observed by RGA because the large majority of atomic hydrogen species recombines on the walls before it can reach the mass spectrometer. Optical emission measurements however show that a significant amount of atomic hydrogen is produced in the plasma. In
Figure 3 an OES spectrum of a pure hydrogen plasma is shown. The typical Balmer lines of atomic hydrogen: H_α at 656 nm, and H_β at 486 nm are clearly visible.
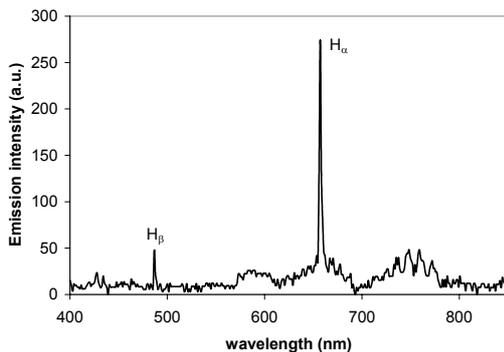

Figure 3: OES spectrum of a pure hydrogen plasma

Growth of intrinsic Si layers was investigated for a wide range of deposition parameters. Details of the deposition conditions can be found in Table I. The uniformity of the

layer thickness over the width of the deposition area can made better than ± 10 % and is optimized by fine tuning of the power of both microwave generators.

Table I: Process conditions for MW-PECVD depositions. Tsubstrate = 250 ^{o}C.

H2 (sccm)	SiH4 (sccm)	Ar (sccm)	Pressure (mbar)	Power (W)
100-200	2-20	0-50	0.04-0.70	600-1800

Silicon layers with various crystalline fractions have been grown by varying the SiH_4/H_2 flow ratio . In Figure 4 Raman spectra of layers grown at a pressure of 0.1 mbar are shown. At this pressure, micro-crystalline layers are grown for SiH_4/H_2 ratios smaller than 10 %. The growth rate for these micro-crystalline films is between 0.5 and 1 nm/s.
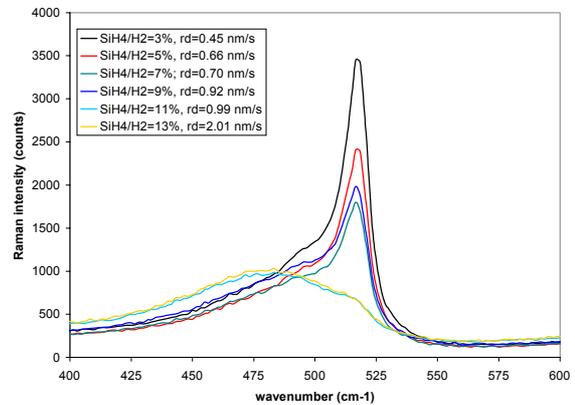

Figure 4: Raman spectra of layers (μc-Si on glass) obtained by depositions at 0.1 mbar.

The Raman spectra between 400 and 600 cm^{-1} do not only show the characteristic scattering peaks at 480 cm^{-1} (a-Si TO phonon scattering mode) and at 520 cm^{-1} (c-Si TO phonon mode) but also a peak at approximately 505 cm^{-1}. This last peak is often observed for micro-crystalline silicon and is usually assigned to Raman scattering by localized phonons in small crystallites [8]. We have fitted the spectra with three Lorenzian peaks in order to obtain an estimate of the fraction of crystalline material V_f. V_f is defined as $I_{520}/(I_{520}+0.1+m \times I_{480})$ where *m=exp(-d/45)* [9]. Here *d* is the grain size, which we estimated to be 20 nm (see the XRD results later in this paper). Since we do not take the contribution of the 505 cm^{-1} peak into account, the values obtained with this method can be considered as underbound estimates.
In the figure below, the crystal fractions for the series of depositions performed at an operating pressure of 0.1 mbar are shown. The fraction of crystalline silicon varies between 70 and 45% and decreases with increasing SiH_4 concentration. For a silane concentration larger than approximately 8% the layers are completely

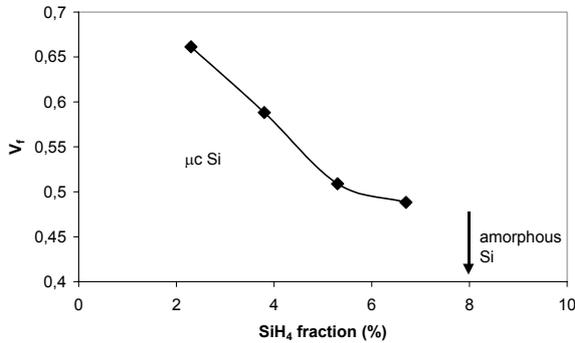amorphous (for p=0.1 mbar and $T_{substrate}$=250 C) and V_f drops to zero.

Figure 5: Fractions of crystalline material in the Si layers grown at 0.1 mbar, as obtained by Raman spectroscopy

We observe a general tendency that for lower pressures larger $SiH_4/(SiH_4+H_2+Ar)$ ratios can be applied for growth of μc-Si. As a result, larger growth rates of μc-Si layers are obtained at low pressures. This is probably a result of the enhanced electron confinement by the permanent magnets, at lower pressures.

At a pressure of 0.04 mbar we obtained a growth rate of 1.2 nm/s for a 4 μm layer μc-Si on glass. The effect of addition of Ar is a slight decrease of the deposition rate, so we added minimum amounts of Ar just for maintaining a stable plasma. For pressures larger than 0.3 mbar we obtained only amorphous layers, even for very small $SiH_4/(SiH_4+H_2+Ar)$ ratios. For pressures larger than 0.5 mbar, the plasma enters a powder-formation regime in which dusty layers are deposited.

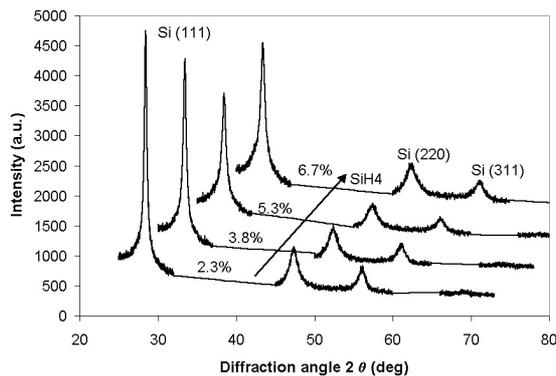XRD measurements (Figure 3) show that the preferential orientation of the grown layers is (111).

Figure 6: XRD spectra for Si layers grown at 0.1 mbar.

The grain size, as determined by Scherrers formula decreases with increasing silane fraction and with increasing growth rate (see Figure 7). A maximum grain

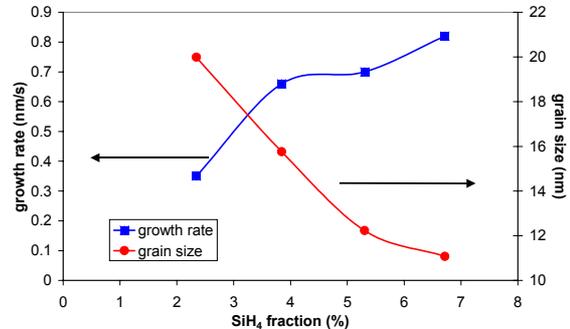size of about 20 nm indicates that the columns observed by SEM contain several grains in the lateral direction.

Figure 7: Growth rates and grain sizes for μc-Si layers grown on glass at a pressure of 0.1 mbar.

The hydrogen concentration, as obtained by FTIR measurements is rather low for the μc-Si samples. In Figure 8 the hydrogen contents are shown for layers grown at 0.1 mbar. We see that the typical concentration for μc-Si is about 3 %, where for the a-Si layer the concentration jumps to about 9%.
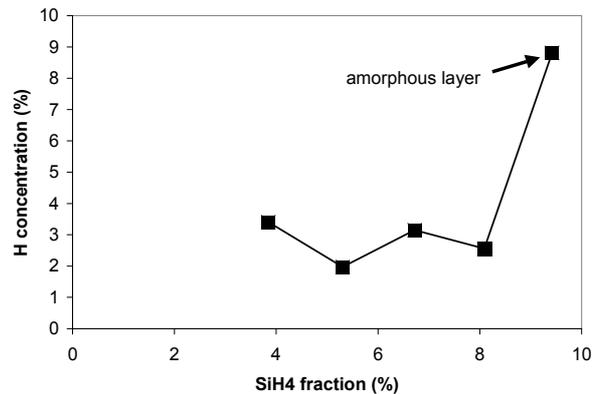

Figure 8: Hydrogen concentrations in layers grown at 0.1 mbar, as obtained from FTIR absorption at 640 cm^{-1}.

From the FTIR measurements we also learned that the μc-Si samples contain a significant amount of oxygen. This is mainly due to the large degassing rate of the single chamber system (without load lock) in which we performed the depositions.

CONCLUSIONS

We have shown that with the linear microwave plasma source at ECN, μc-Si can be deposited with growth rates higher than 1 nm/s. Highest growth rates of crystalline material are obtained at low pressures due to an

enhanced electron confinement by the permanent magnets at lower pressures. An overall view of the depositions obtained with the MW source so far is given in Figure 9.
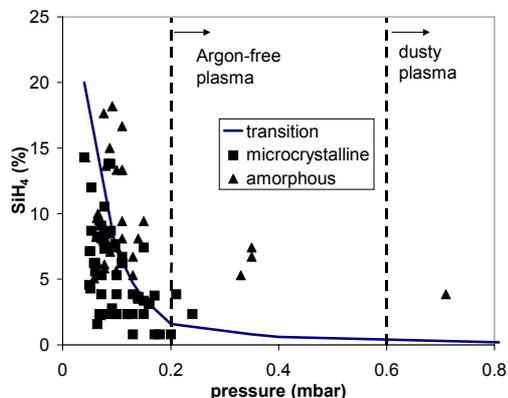

Figure 9: Overview of MW-PECVD conditions for Si layer growth.

The µc-Si layers contain a significant amount of oxygen. RGA measurements have shown that degassing of the deposition chamber is largely responsible for this contamination. In order to be able to grow 'solar grade' silicon with this deposition system, measures have to be taken to reduce this oxygen contamination.

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