Microwave PECVD of Micro-Crystalline Silicon

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ABSTRACT

The deposition of micro-crystalline silicon by means of PECVD with a new linear microwave plasma source is investigated. This plasma source has successfully been introduced in the large scale production of multi-crystalline Si solar cells for the deposition of passivating silicon nitride layers. Advantages of this linear plasma source are the high deposition rates and the large area (up to 80 cm width, no length limitations) on which a homogeneous deposition can be achieved. Since this source has not been applied for deposition of micro-crystalline silicon before, we explored a large parameter space (substrate temperature, pressure, MW-power, gas flow rates), in order to find optimum growth conditions. It is observed that with this microwave source it is possible to grow micro-crystalline layers at significantly higher silane/hydrogen ratios and higher deposition rates than for conventional RF PECVD. In this paper, structural properties of the silicon layers, as investigated by Raman and FTIR spectroscopy, XRD and SEM measurements are discussed.

INTRODUCTION

Electricity generated by photovoltaic devices can acquire a significant share of the total energy production only if it's costs are reduced drastically with respect to present price levels. One important factor for the high costs of PV devices today is the usage of relatively large amounts of ultra-pure semiconductor material (mainly silicon). Several options are investigated world wide to tackle this problem and one very promising option is the usage of thin film silicon layers, grown at low temperatures on cheap substrates. These layers are typically 1 µm thick, whereas the silicon wafers, which are commonly used in the PV industry have a thickness of about 300 µm.

A well known example of thin film silicon grown at low temperatures is amorphous silicon. This material is applied in the PV industry for several decades but it suffers from some serious disadvantages, blocking its application for PV devices with moderate to high conversion efficiencies, namely light-induced degradation and low absorption at longer wavelengths. Recently, however, it has been discovered that it is possible to grow a crystalline form of silicon too at low temperatures, in the range of 150 – 300 °C. This material, commonly called micro-crystalline (µc) silicon [1], does not suffer from light induced degradation. Micro-crystalline silicon has been applied in single junction solar cells, for which efficiencies of 10 % have been achieved [2]. Another very interesting application of µc-Si is its usage as a low band gap material in a multi-junction cell. Such multi-junction cells in which µc and amorphous silicon layers are combined have a perspective of conversion efficiencies of more than 20 % [3], where the thickness of the total cell is still only a few microns.

A real large scale production of such PV devices, however, is still hindered by the fact that the growth rate of μc-Si by conventional deposition techniques is small. Typical growth rates nowadays are about 0.1 nm/s, which implies that the deposition of a layer with a thickness of 1 micron requires several hours. Such long deposition processes do not match with an inline production of complete devices in which the other processing steps typically require minutes of time. For a successful introduction of μc-Si into the PV industry, the deposition rates therefore have to be increased drastically.

The usual method of depositing amorphous or μc-Si is by plasma decomposition of silane gas SiH_4 and hydrogen H_2, with other gasses added for doping [4]. Most common are radio-frequency (RF) plasma reactors in which the plasma is confined between two parallel electrodes. Deposition usually takes place at a gas pressure of 0.1- 1 mbar, which is the optimum pressure to sustain the plasma. Typical growth rates for μc-Si are 0.1 nm/s. Higher pressures can give rise to higher deposition rates [5], but also introduce the risk of powder formation. The rather low deposition rates of μc-Si by means of RF-PECVD has stimulated the search for alternative, faster deposition techniques. An important development was the usage of higher frequencies, up to 100 MHz, in a parallel electrode system. It is assumed that at these frequencies, which are well above the plasma frequency, layer growth is more effective than at lower frequencies because of the absence of ion bombardment in the growth zone. Indeed it has been shown that these very high frequency depositions (VHF-PECVD) allow for growth rates well above 1 nm/s [6]. A major disadvantage of VHF-PECVD, however, is that it is quite difficult to obtain uniform deposition on large areas.

Even higher frequencies, namely micro-wave frequencies (2.45 GHz) are applied in Electron-Cyclotron-Resonance (ECR) CVD. With this technique however, only low deposition rates (0.1 nm/s) have been obtained for μc-Si [7].

An alternative and more promising application of microwaves for plasma generation is the remote microwave plasma source as developed by the German company Roth&Rau. With this linear source deposition takes place over a width of 60 cm or more so that deposition on large areas is guaranteed. The Roth&Rau source has successfully been introduced in the PV industry for deposition of silicon nitride as passivation and anti-reflection layer on multi-crystalline silicon solar cells [8] and is currently investigated at ECN for deposition of film silicon. In this paper we report on results of depositions of intrinsic Si layers with this source.

EXPERIMENTAL

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 is depicted in Figure 1. We have investigated the growth of μc-Si by 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. For pressures above 0.15 mbar a sustainable plasma of pure H_2 can be obtained, for lower pressures a certain amount of Ar has to be added. Information on plasma chemistry was obtained by means of 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.

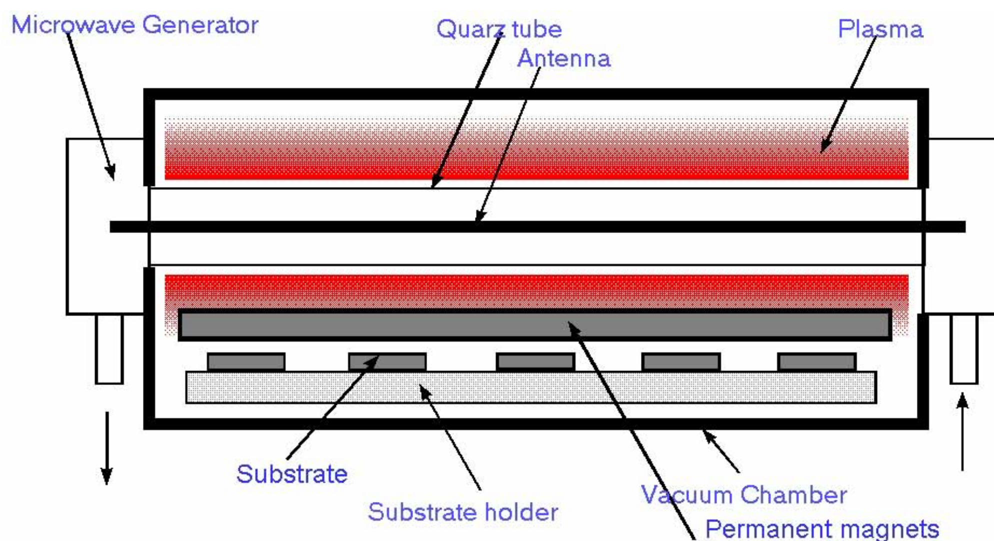

Figure 1: Schematic view of the micro-wave plasma source

RESULTS AND DISCUSSION

Growth of intrinsic Si layers was investigated for a wide range of deposition parameters. Details of the deposition conditions can be found in Table 1. 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

H_2 (sccm)	SiH_4 (sccm)	Ar (sccm)	Pressure (mbar)	Power (W)	$T_{substrate}$ (C)
100-200	2-20	0-50	0.04-0.70	600-1800	250

We observe a general tendency that for lower pressures larger SiH4/(SiH4+H2+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. 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 SiH4/(SiH4+H2+Ar) ratios. For pressures larger than 0.5 mbar, the plasma enters the γ' regime, which is accompanied by dust formation. In Figure 2, a cross-sectional SEM picture of a typical µc-Si layer on glass is shown. The structure is columnar, with an apparent column width of about 0.3 µm. XRD measurements (Figure 3) show that the preferential orientation of the grown layers is (111). The grain size, as determined by Scherrers formula decreases with increasing silane fraction and with increasing growth rate (see Figure 4). A maximum grain size of about 20 nm indicates that the columns observed by SEM contain several grains in the lateral direction.

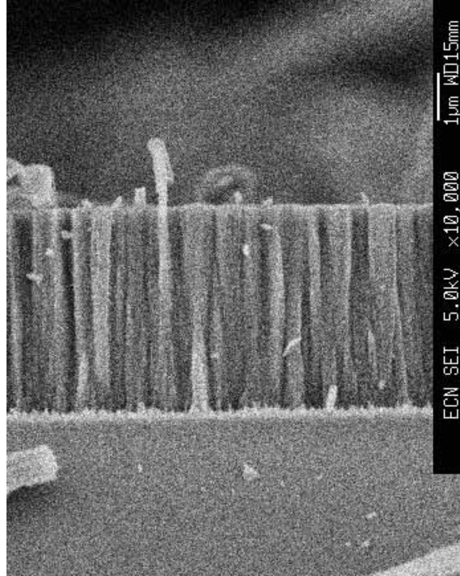

Figure 2: Cross-sectional SEM picture of μc-Si layer on glass, as grown by MW-PECVD at a pressure of 0.04 mbar with a deposition rate of 1.2 nm/s.

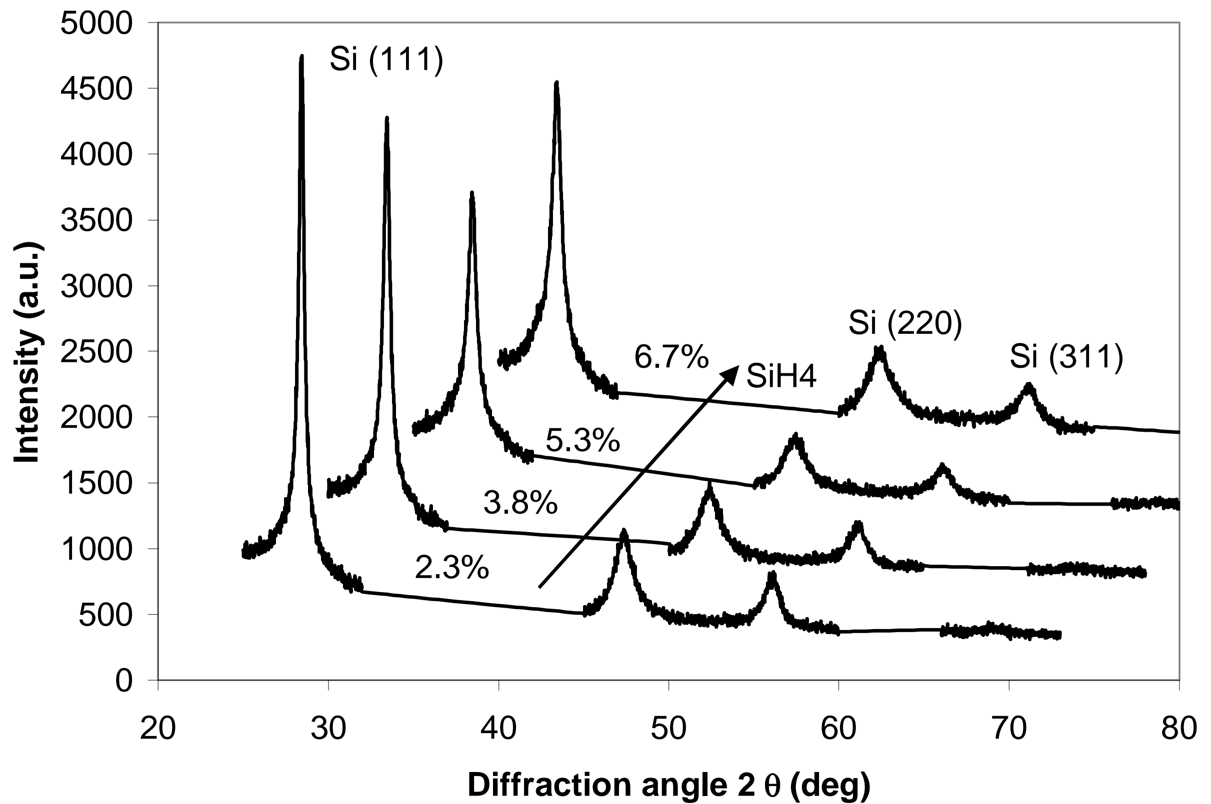

Figure 3: XRD patterns for Si layers grown with various SiH_4 concentrations at a pressure of 0.1 mbar.

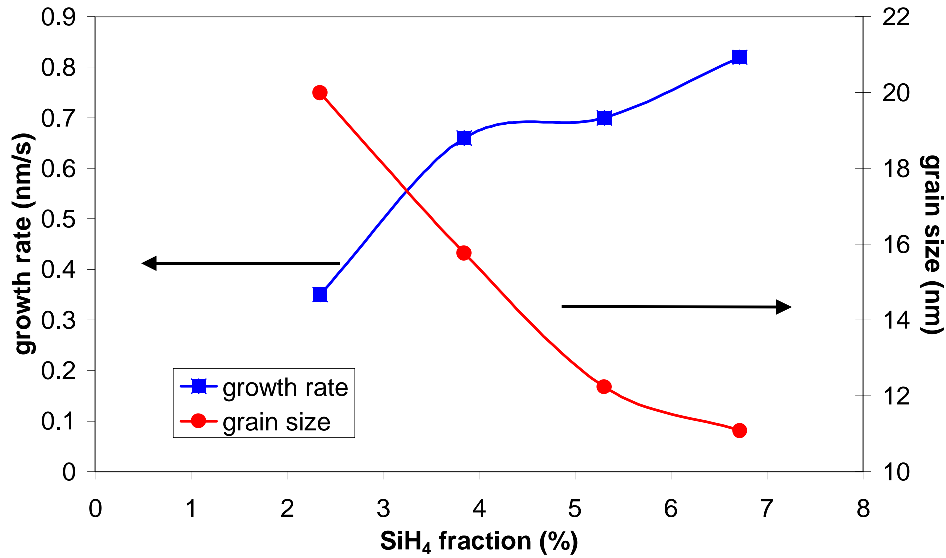

Figure 4: Growth rates and grain sizes for μc-Si layers grown on glass at a pressure of 0.1 mbar.

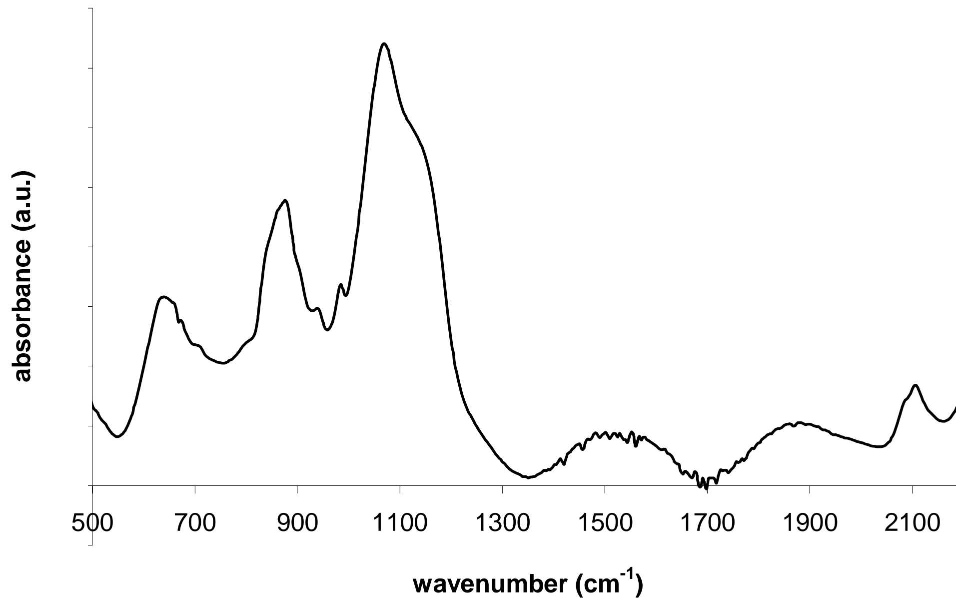

Figure 5: IR absorption spectrum of a μc-Si layer grown at a pressure of 0.1 mbar.

FTIR measurements indicate that the μc-Si layers contain a significant amount of oxygen, giving rise to Si-O and $Si\text{-}O_2$ vibrations at 1060 and 1120 cm^{-1}(Figure 5). A part of this oxygen probably has diffused into the material after the deposition. For the amorphous layers, which are grown under similar conditions and with comparable growth rates no oxygen is detected by FTIR. Nonetheless, the leak rate of the deposition chamber is appreciably large: in the range of

10^{-3} mbar l/s. This is equivalent to a leak (or outgasing) flow of about 0.1 sccm which implies that outgasing is responsible for at least some part of the oxygen contamination too.

CONCLUSIONS

We have shown that with a linear microwave plasma source µc-Si can be deposited with growth rates higher than 1 nm/s. Highest growth rates of crystalline material are obtained at low pressures. The µc-Si layers contain a significant of oxygen. A part of this oxygen probably has diffused in after deposition but outgasing by the deposition chamber is also partly responsible for this contamination.

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