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Non-intrusive plasma diagnostics for the deposition of large area thin film silicon

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ABSTRACT

Plasma diagnostics for large area, industrial RF parallel-plate reactors can be useful for process optimization and monitoring, provided that their implementation is practical and non-intrusive. For instance, Fourier transform infrared (FTIR) absorption spectroscopy and/or time-resolved optical emission spectroscopy (OES) can easily be retro-fitted into the pumping line of a reactor. Both techniques were used to measure the fractional depletion of silane in silane/hydrogen plasmas. By means of a simple analytical plasma chemistry model, it is shown that the silane depletion is related to the silicon thin film properties such as microcrystallinity. Uses of the diagnostics are demonstrated by two examples: (i) the optimal plasma parameters for high deposition rate of microcrystalline silicon, along with efficient gas utilization, are shown to be high input concentration and strong depletion of silane; and (ii) the optimal reactor design, in terms of fast equilibration of the plasma chemistry, is shown to be a closed, directly-pumped showerhead reactor containing a uniform plasma.

1. Introduction

Capacitively-coupled, parallel plate radio-frequency (RF) reactors are commonly used for plasma-enhanced chemical vapor deposition (PECVD) of thin films such as amorphous and microcrystalline silicon. Large area (>1 m^2) reactors are used, for example, for the production of photovoltaic solar cells, and thin film transistors for flat displays.

Microcrystalline hydrogenated silicon (μc-Si:H) is a material of choice for photovoltaic (PV) solar cell contacts and also as a PV active layer [1]. The deposition rate by hydrogen-diluted PECVD, however, is usually limited to a few $ÅS^{-1}$. The difficulty is to achieve high deposition rate whilst maintaining optimal material quality for photovoltaic solar cells, i.e. at the transition between a-Si:H and μc-Si:H, as proposed by Kroll *et al* [2].

The transition zone from a-Si:H to μc-Si:H cannot be simply defined as a function of the deposition process parameters (pressure, RF power, frequency, flow rates, hydrogen dilution, discharge gap, etc) because of their inter-dependence on the plasma properties [3]. For example, high silane dilution with hydrogen is a well-known technique for reaching the transition zone. However, depending on the different deposition process parameters and reactor configuration, the transition can occur between silane input concentration as low as 3% [4] and as high as 10% [5] and covers the whole intermediate range [6–9]. Good μc-Si:H at reasonable deposition rate (4 $Ås^{-1}$) can even be deposited from pure silane input flow [10–14]. Most of the μc-Si:H PECVD optimization has been done by experimental empirical parametric studies, due to the difficulty of applying relevant and simple plasma diagnostics in real deposition conditions.

There is therefore a need to develop a simple methodological approach based on simple plasma measurements in order to better understand the behavior of the transition zone from a-Si:H to μc-Si:H as a function of the deposition parameters. The first aim of this paper is to show that the measurement of the silane concentration in the plasma can be used for such a purpose. In Section 2, the steady-state silane concentration is measured using infrared absorption spectroscopy [15]. In Section 3, the transient approach to steady-state of the silane concentration after plasma ignition is monitored by optical emission spectroscopy [16]. The second aim is to show that the optimal design, for fast equilibration of the plasma chemistry after ignition, is a closed, directly-pumped showerhead reactor with a uniform plasma which fills the whole reactor volume.

2. Silane concentration in the plasma as a determining factor for the silicon microstructure

2.1. Empirical description

The percentage of silane in the silane/hydrogen flow ratio is a commonly-used parameter to define experimental conditions for deposition of thin film silicon. For example, it is frequently assumed that a high dilution (i.e. a low concentration, typically <5%) of silane in hydrogen is necessary to obtain microcrystalline silicon. This seems to be intuitively true because film growth models show that a high flux of atomic hydrogen is favorable for promoting the re-arrangement of silicon atoms. Consequently, it appears logical that much more hydrogen than silane must be added to the reactor to ensure a dominance of hydrogen atom production from dissociation of hydrogen molecules. Experimentally, this viewpoint is apparently justified because microcrystalline silicon is almost always obtained from highly-diluted silane/hydrogen mixtures, virtually independent of which plasma conditions are used.

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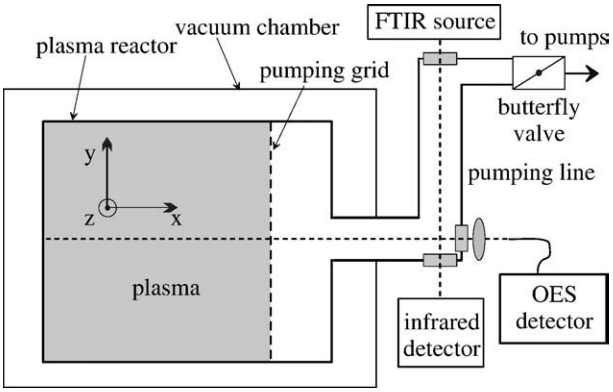

Fig. 1. Schematic plan view of the plasma reactor inside the vacuum chamber. FTIR absorption spectroscopy was performed in the pumping line of the plasma reactor (before the butterfly valve), by a single pass through ZnSe windows to an external infrared detector. Optical emission spectroscopy (OES), via a glass window and collimation lens, optical fibre and detector, was also combined into the pumping line. The plasma reactor box is 47 cm wide and 57 cm long [15,16].

Nevertheless, it is known that the plasma conditions also have an influence, although this is much more difficult to quantify because of the unknown inter-dependence of several parameters such as pressure, total flow rate, electrode gap, RF power and frequency, etc. There are many studies in the literature which investigate the dependence on one parameter, all else being fixed, but it is then difficult to generalize these results to other reactors and plasma conditions if those fixed parameters are not there the same.

The proposition of this paper is that the silane/hydrogen ratio is indeed the determining factor for the silicon microstructure, but that it is the silane/hydrogen ratio in the plasma which is determinant, and not uniquely the input flow ratio. The plasma composition can be very different from the input flow ratio because the silane is depleted by plasma dissociation and radical deposition, whereas molecular hydrogen dissociated by the plasma is re-formed due to surface recombination of atomic hydrogen. The concentration of silane is therefore always lower in the plasma than in the input gas flow mixture. The influence of the silane/hydrogen ratio on the silicon microstructure is further considered in Section 2.4.

In RF parallel-plate reactors, the molecular densities dominate the radical densities because the latter undergo surface and volume reactions. Therefore, the total pressure in the plasma is essentially given by the sum of the silane and molecular hydrogen partial pressures. Consequently, if plasma conditions are such that the silane is almost totally depleted, then the gas pressure in the plasma consists almost entirely of molecular hydrogen, irrespective of the input flow rates [12]. Microcrystalline silicon can therefore be deposited even using a flow of pure silane and no hydrogen flow [10–14] provided that the silane is almost completely depleted, leaving a plasma of almost-pure hydrogen. This is explained further in the following sections.

2.2. Depletion: the plasma dimension

The depletion of silane by the plasma represents the single, combined effect of all the plasma parameters such as pressure, total flow rate, electrode gap, RF power and frequency, etc. The fractional depletion of silane, D, can be defined in terms of the silane partial pressure without plasma, $p^0_{\mathrm{SiH_4}}$, and the silane partial pressure with plasma, $p_{\mathrm{SiH_4}}$, as follows [15]:

$$\text{depletion}: D = \frac{p^0_{\mathrm{SiH_4}} - p_{\mathrm{SiH_4}}}{p^0_{\mathrm{SiH_4}}}. \tag{1}$$

The depletion is the fractional drop in silane pressure due to plasma dissociation.

The silane input concentration depends on the silane input flow fraction $\Phi_{\mathrm{SiH_4}}/\Phi_{\mathrm{tot}}$. Defining the silane input concentration in terms of pressure without plasma, we have

$$\text{input concentration}: c = \frac{p^0_{\mathrm{SiH_4}}}{p}, \tag{2}$$

where p is the process pressure which we assume to be maintained constant by feedback from a pressure gauge to a pumping speed regulator such as a butterfly valve. The silane concentration in the plasma, $c_{\mathrm{p}} = p_{\mathrm{SiH_4}}/p$, is therefore directly given by:

$$\text{plasma concentration}: c_{\mathrm{p}} = c(1-D). \tag{3}$$

The respective hydrogen pressures are given by the chosen condition of fixed process pressure, so that $p = p^0_{\mathrm{SiH_4}} + p^0_{\mathrm{H_2}} = p_{\mathrm{SiH_4}} + p_{\mathrm{H_2}}$. The hydrogen pressure without plasma, $p^0_{\mathrm{H_2}} = p(1-c)$, increases to $p_{\mathrm{H_2}} = p(1-c_{\mathrm{p}})$ with plasma.

The gas composition of the plasma, using Eq. (3), is therefore determined by two parameters: the silane input concentration, c, and the silane fractional depletion, D. The two-dimensional parameter space for the plasma composition is bounded by the input concentration $0<c\leq 1$ along one axis, and the plasma dimension is represented by $0\leq D<1$ along the other axis. A contour for constant plasma composition is given by $c_{\mathrm{p}} = c(1-D) = \text{constant}$. According to this approach, it is the silane concentration in the plasma which determines the microstructure of the deposited silicon film. This is demonstrated by an intuitive model in Section 2.4.

2.3. A non-intrusive FTIR diagnostic to measure depletion

The process pressure p is essentially the same in the pumping line as in the plasma reactor. Since the radical densities are negligibly small in the reactor, the silane and hydrogen partial pressures are also unchanged between the reactor and the pumping line. FTIR absorption spectroscopy was used to determine the partial pressure of silane in the pumping line flow and hence the silane partial pressure in the discharge [15]. Alternatively, a multi-pass gas cell and/or a laser diode infrared source could be used instead of FTIR.

FTIR absorption spectroscopy was performed by a single pass measurement in the pumping line of the reactor, as shown in Fig. 1. Everywhere in this paper, 'pumping line' refers to the outlet of the plasma reactor before the pumping speed controller (i.e. the butterfly valve), as shown in Fig. 1. Fig. 2 shows a measured absorption spectrum

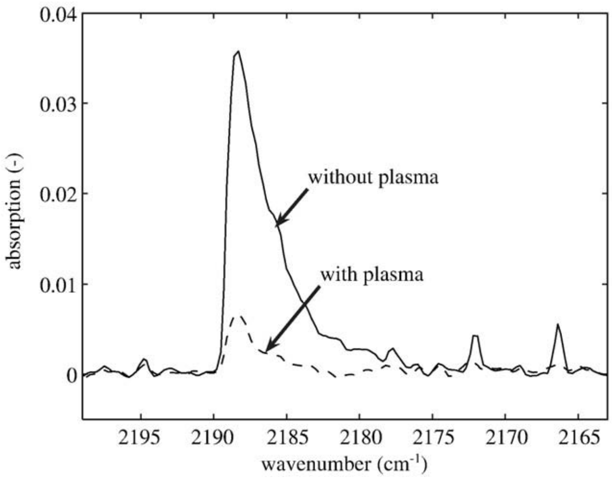

Fig. 2. Infrared absorption spectrum of a 2% $\mathrm{SiH_4}$ in $\mathrm{H_2}$ mixture at 4 mbar with (dashed line) and without (solid line) plasma in the reactor. The abscissa limits correspond to the integration limits (2199–2163 cm^{-1}) used for integrating the absorption curve.