



Silicon thin-film solar cells at high growth rate under constant power-to-flow ratio plasma conditions



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ABSTRACT

This work approaches the problem of increasing the growth rate of device quality a-Si:H by using the simplest case, a standard RF-PECVD system and pure silane as feedstock gas. Starting from plasma conditions which provided a high-quality material at very low deposition rates, the silane flow and the applied power (*RFP*) were proportionally increased. As a result, the growth rate showed an almost linear increase with the *RFP*. An exhaustive analysis of the material obtained revealed the existence of a wide window in which the structural/optoelectronic properties remain unchanged. Within this window, a-Si:H p-i-n solar cells were fabricated in order to verify the applicability of the procedure proposed to the development of device structures. The initial results showed an excellent behaviour of the solar cells at higher growth rates, without any relevant detriment in the collection capability and fill factor. Thus, the constant power-to-flow ratio is presented as an easy and reliable method to reduce the deposition time which, additionally, could be applied to any variant of plasma CVD system.

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1. Introduction

One of the most important issues for the photovoltaic technology based on silicon thin films is to find deposition conditions that lead to a high-quality material at high growth rates. For hydrogenated amorphous silicon (a-Si:H), radiofrequency (13.56 MHz) plasma-enhanced chemical-vapour deposition (RF-PECVD) is the most commonly used technique, since films present good optoelectronic properties and a high degree of homogeneity over large areas [1,2].

The deposition rate in an RF-PECVD system can be easily improved by simply applying a higher RF power, which means that more electrons in the plasma have enough energy to decompose the silane molecules (SiH₄). However, electrons with too high energies cause the formation of short-lifetime radicals (SiH₂, SiH, Si), whose low diffusion length on the growing surface leads to more defects in the a-Si:H [3,4]. Moreover, a higher concentration of SiH₂ radicals can also originate the formation of higher-order silane radicals (Si_xH_y where $x \geq 2$, $y \leq 2x + 2$) in the plasma [5,6]. These complex molecules have been related to the increase of the concentration of dihydride bonds (Si—H₂) in the material structure [7,8], and hence, to a lower stability against photodegradation.

It is a fact that the deposition of a device-quality a-Si:H can only be assured if the plasma is dominated by SiH₃ radicals [9,10,11]. This growth precursor shows a higher diffusion capability and does not

react with other silane species, thus avoiding the two mentioned problems. Unfortunately, since the energy required to create the SiH₃ radical is the minimum necessary to break the SiH₄ molecule, the thermal speed of the electrons in the plasma has to be reduced. Thus, an a-Si:H for optoelectronic applications at high growth rate cannot simply be obtained by increasing the RF power [12].

A priori, the increase of process pressure would seem the best way to address this problem. A denser plasma, with a higher electron density, would favour a higher precursor-production rate without boosting the average electron energy. Furthermore, since the residence time of growth precursors is increased at greater pressure, it would also help improve the deposition rate. However, silane plasmas show an anomalous behaviour at high densities due to polymerization [13,14]. In that sense, pressure does not offer much leeway to improve the deposition conditions. On the contrary, hydrogen dilution has been used as a feasible method to decrease electron temperature and simultaneously contribute to the neutralization of the SiH₂ radicals by means of the chemical reaction $\text{SiH}_2 + \text{H}_2 \rightarrow \text{SiH}_4$. Nevertheless, the higher concentration of atomic hydrogen in the plasma intensifies the etching process on the growing surface and, as a consequence, a reduction of the deposition rate is also observed [3,13].

Actually, the most reliable strategies to improve the deposition rate without affecting the a-Si:H quality mean changes in the configuration of the standard RF-PECVD. An example of that is the triode RF-PECVD, in which a mesh is inserted between electrode and anode to reduce the contribution to the film growth of the higher order silanes [15,16]. On the other hand, the use of very high frequency VHF-PECVD has shown a high effectiveness to decrease the electron temperature at

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high deposition rate [17,18], although in this case, the film homogeneity can be affected for large areas [19].

The present work approaches the problem of increasing the growth rate of high-quality a-Si:H by using the simplest case, a standard RF-PECVD system and pure silane as feedstock gas. We propose that, for given deposition conditions corresponding to device-quality material, there is a wide range in which the deposition rate can be improved by proportionally increasing the feedstock gas flow and the applied power. The idea behind this method is that, while the mean energy dissipated per silane molecule is constant, the properties of the resulting a-Si:H should remain unchanged. On the other hand, since a higher number of growth precursors are produced per unit time, a higher deposition rate should be obtained. Thus, a priori our procedure could be extrapolated to any kind of PECVD reactor and plasma conditions.

In the following sections, the influence of the deposition rate on the properties of intrinsic a-Si:H films obtained by this procedure will be presented. The limitations of the constant power-to-flow-ratio method will be later discussed. In the second part, the evolution of the performance of p-i-n solar cells obtained from these intrinsic a-Si:H films will be studied. Finally, we will discuss the influence of the deposition conditions on the absorber properties and on the device electrical behaviour.

2. Experimental

For this work we used a conventional RF-PECVD (13.56 MHz) reactor manufactured by MVSsystems Inc. The PECVD system consists of two deposition chambers for the preparation of intrinsic and doped material respectively. Every chamber contains a capacitively-coupled square electrode having an area (A) of $10 \times 10 \text{ cm}^2$. The inter-electrode distance (d) for the i-chamber was fixed to 15 mm. The silane gas is fed into the plasma in such a way that it experiences a laminar flow parallel to the electrodes and is extracted by means of a turbomolecular pump Varian TV301-Navigator in series with a rotary pump Oerlikon Trivac-D25. This meant that the maximum gas flow value was limited to 100 sccm by the maximum load supported by the turbo pump.

Intrinsic amorphous silicon films were prepared at a substrate temperature (T_S) of 240 °C. The gas pressure was kept constant at 400 mTorr. In order to improve the material deposition rate (ν), the RF power (RFP) was increased in the range between 1 and 5 W, while the SiH_4 gas flow (Φ) was proportionally varied in the range between 20 and 100 sccm. Thus, the power-to-flow ratio or specific power (P_S) applied to the plasma was fixed to $5 \times 10^{-2} \text{ W/sccm}$ (see Eq. (1)).

$$RFP(W) = P_S \cdot \Phi(\text{sccm}) = 5 \times 10^{-2} \cdot \Phi(\text{sccm}) \quad (1)$$

The a-Si:H films were deposited onto Corning 7059 glass for UV-vis transmittance-reflectance measurements. From these data, film thickness (around 500 nm for all the samples), refraction index (n), and absorption coefficient (α) were obtained by using an in-house developed software. By means of the Tauc plot of the absorption coefficient, the energy gap (E_{GAP}) was extracted. Coplanar aluminium contacts were subsequently evaporated on each sample in order to determine their dark conductivity (σ_{dark}) at 25 °C, and photoconductivity (σ_{ph}) under 25 °C, 100 mW/cm², AM1.5G conditions. From these parameters, the material photosensitivity ($\sigma_{\text{ph}}/\sigma_{\text{dark}}$) was determined. A thermostatic bath was used to control the sample temperature. Illumination was provided with a Steuernagel Lichttechnik SC-575 model Class A solar simulator. Combined with optical parameters, electrical measurements were additionally used for the calculation of the mobility-lifetime product for the carriers ($\mu\tau$). The analysis of the $\mu\tau$ changes after light-soaking allowed the study of the a-Si:H stability (Staebler–Wronski effect). Light-induced degradation of these thin films was carried out under 40 °C and white light 100 mW/cm², during around 100 h (after this time, a degradation stabilization was observed). a-Si:H layers were

simultaneously co-deposited onto $\langle 100 \rangle$ highly resistive c-Si wafers for Fourier-transform infrared (FTIR) measurements. The total hydrogen content (C_H) and the microstructure parameter (R^*) were determined in order to analyse the evolution of the concentration and type of silicon-hydrogen bonds in each sample.

Based on the plasma conditions previously described for intrinsic a-Si:H, p-i-n solar cells were subsequently prepared onto $10 \times 10 \text{ cm}^2$ glass/SnO₂:F Asahi-U substrates. The a-Si:H structure consisted of a 7.5-nm-thick p-type a-SiC:H layer, a 5-nm-thick carbon-graded buffer layer, a 400-nm-thick absorber and a 30-nm-thick n-type a-Si:H layer. Different i-layer growth rates were used in order to analyse their effect on the device performance. Specifically, the absorber was deposited at power values $RFP = 1, 3, 4$, and 5 W. The deposition time was fitted in each case to obtain the mentioned i-layer thickness. Solar cells with an area of 1 cm² were later obtained by evaporating aluminium back contacts. A total of 12 homogeneously distributed devices were defined on each $10 \times 10 \text{ cm}^2$ a-Si:H p-i-n deposit. Thus, it was possible to simultaneously study how the absorber growth rate influenced the efficiency and the uniformity of the solar cells.

The current-density vs. voltage (J - V) characteristic of the resulting devices was measured under standard test conditions (STC) of 100 mW/cm² AM1.5G at 25 °C [20]. The external quantum efficiency (EQE) in short-circuit-conditions was obtained in the wavelength (λ) range 300–800 nm. This standard characterisation was complemented with the variable-illumination measurement (VIM) method [21,22] extended to the case of monochromatic light. For this purpose, a home-made J - V measurement setup based on LED light was used [23]. J - V curves were obtained at fixed illumination wavelengths of 453 nm and 627 nm, while the level of irradiance was varied between $\sim 1 \mu\text{W/cm}^2$ and $\sim 10 \text{ mW/cm}^2$. Thus, the device electrical behaviour could be analysed in detail, identifying the effect of the i-layer growth rate on the bulk and interface properties of the a-Si:H p-i-n structure.

3. Results and discussion

3.1. Characteristics of a-Si:H thin films at high growth rate under constant power-to-flow ratio plasma conditions

The simultaneous increase of RFP and Φ led to a progressive improvement of the deposition rate. For $RFP \geq 2 \text{ W}$, the ν dependence on the power applied to plasma showed a clear linear trend (see Fig. 1). This phenomenon was a consequence of the higher generation rate of growth precursors as the rates of supply of both silane molecules and energy were increased in equal proportions. Specifically, for our starting

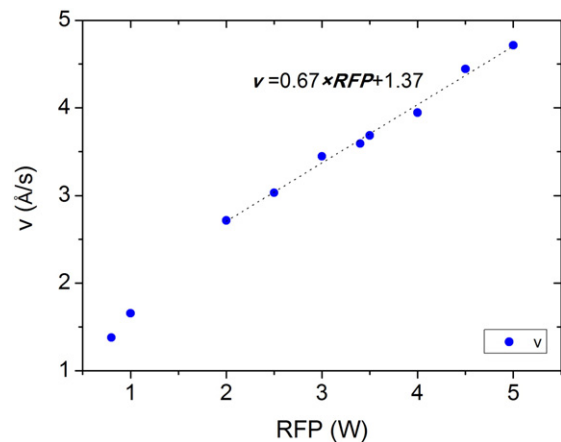


Fig. 1. Evolution of the a-Si:H growth rate (ν) as the power applied to the plasma (RFP) is increased. For $RFP \geq 2 \text{ W}$, the deposition rate showed a linear dependence.

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