Introduction

In LPICM, we firstly introduced the $SiF_4/H_2/Ar$ plasma to deposit microcrystalline silicon (µc-Si:H) materials for the special application of thin film transistors (TFT) [1] at the beginning of 2000s. Later on, on this topic, studies focused on the growth mechanism and electrical properties, as well as the role of nanoparticles during the growth process of µc-Si have been carried out by several Ph.D. candidates and researchers. Afterwards, the SiF_4 thematic in our laboratory extended to the photovoltaic application about the investigation of silicon epitaxial growth on different substrates: crystalline silicon (c-Si), gallium arsenide (GaAs) and FeNi42.

More recently, comprehensive work is dedicated to the $SiF_4/H_2/Ar$ plasma and its application on photovoltaic with the fabrication of µc-Si:H single junction solar cells [2]. The general consensus to obtain the PIN microcrystalline silicon solar cells with good performance is to use an absorber layer deposited at the amorphous-microcrystalline transition. Generally, the decrease of the open-circuit voltage (V_{OC}) is encountered when the crystalline fraction of the absorber layer is increased. The short-circuit current density (J_{SC}) increases with the thickness of the layer, whereas the carrier collection will be restrained when the absorber layer is too thick. That is the reason why thicknesses around 2 µm are generally used. In LPICM, we propose a new paradigm for microcrystalline solar cells where negligible fraction of amorphous silicon is present but the material still has a good defects passivation of grain boundaries and of crystallites. By doing so, thicker layers (more than 4 µm) can be used because higher crystalline fraction means better carrier transport and therefore less carrier collection issues for a given thickness.

Standard Radio Frequency Sources

Extensive work has been carried out about the materials and solar cell devices optimization with $SiF_4/H_2/Ar$ plasma by using *standard radio frequency capacitively coupled plasma (RF-CCP)* system [3]. A so-called phenomenological model has been proposed to understand the $SiF_4/H_2/Ar$ plasma. The key phenomenon happening in such plasma is the formation of HF molecules via the spontaneous reaction of atomic F with molecular H_2. The direct consequence is the identification of the H_2-limited regime and the F-limited regime. For given plasma conditions, the knowledge of the type of regime (H_2- or F-limited) can be determined by a simple measurement of the H_2 depletion (Figure 1) by a Residual Gas Analyser (RGA) [4][5]. It allows us to easily tune the amorphous-to-microcrystalline transition as well as to have a practical way to increase deposition rate by simultaneously increasing the RF power and the H_2 flow rate. It turns out that the deposition rate scales with the H_2 consumption which can also be easily measured with the RGA.

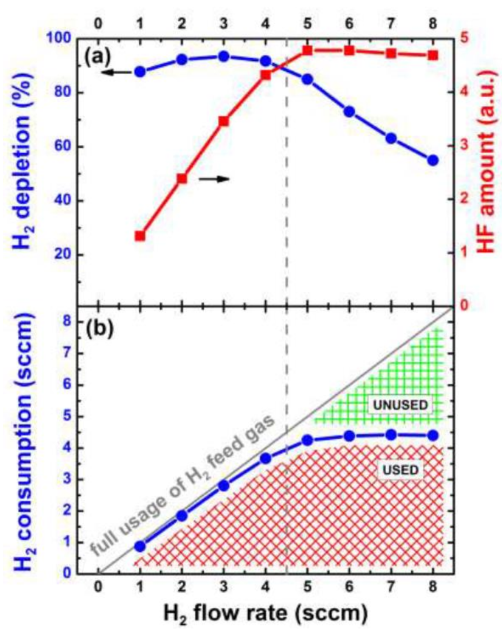

Figure 1 (from Ref.[3])

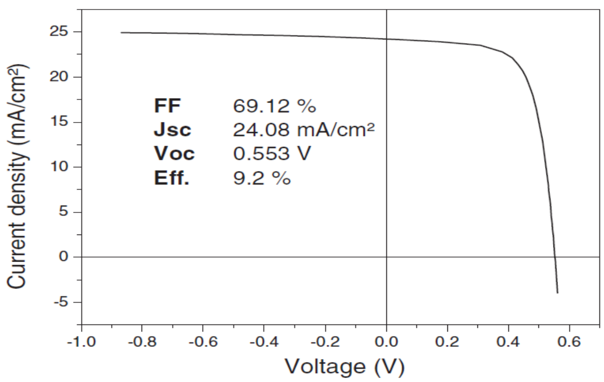

Figure 2 (from Ref. [2])

Material characterizations have shown a complex structure of the µc-Si:H films deposited with $SiF_4/H_2/Ar$ plasma: amorphous tissue, crystallites, and grain boundaries. For fully crystallized absorber layers, we found that V_{OC} increases with the grain boundaries fraction which leads us to suggest that an amorphous tissue is not necessary to passivate the crystallites. PIN µc-Si:H single junction solar cell with fully crystallized absorber layer has achieved an efficiency of 9.2%, and due to the defect density as low as $5.1x10^{14}cm^{-3}$ [2], V_{OC} as high as 536mV was got [6].

Tailored Voltage Waveform

A non-sinusoidal waveform, called Tailored Voltage Waveform (TVW), with a period equivalent to RF frequencies has been shown to be an effective technique to decouple maximum (and mean) Ion Bombardment Energy (IBE) from the ion flux at the electrodes within the CCP discharge [7]. The idea of TVW source used are a sum of harmonic frequencies with varied phase shift ϕ between them. By keeping V_{PP} constant, one can change the waveform by varying ϕ from 0 to π, thus the waveform type goes through 'Peak' (ϕ=0π), 'Sawtooth' (ϕ=0.5π) and 'Valley' (ϕ=π) (Figure 3). When doing so, the DC bias (V_{DC}) goes from a minimum, in relative value, to a maximum. Thus, the mean IBE can be almost continuously increased. When this technique is used in a plasma enhanced chemical vapor deposition (PECVD) system for the growth of µc-Si:H, the control over IBE is directly translated into the growth mechanism [8] and material properties [9]. This technique has also been used to deposit the absorber layer of µc-Si:H solar cells using SiH_4/H_2 plasma, and the control over IBE was shown to impact device performance [10]. Furthermore, the 'Sawtooth' type of waveform, which presents different rising and falling slopes over one cycle, has been demonstrated, both theoretically and experimentally, to be able to induce different ionization rate in the front of different electrodes, thus the ion flux to different electrodes. This phisycs will be further discribed in the section of '*Tailored Voltage Waveforms*'.

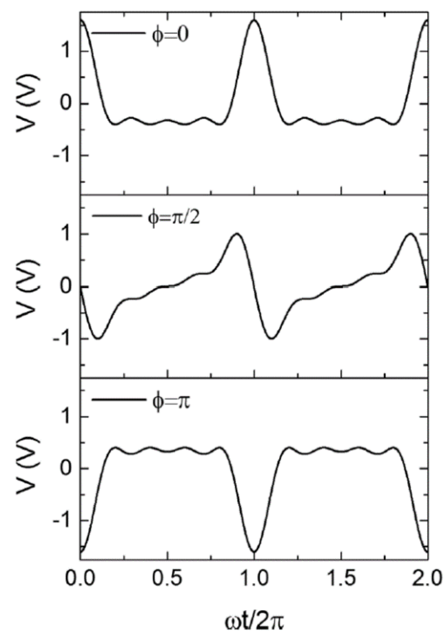

Figure 3 (from Ref, [8])

Currently, we are trying to make a combination of the $SiF_4/H_2/Ar$ plasma and the TVW excitation source. Investigation of materials properties (optical and electrical) of the µc-Si:H films with the influence of IBE, as well as the photovoltaic application of plasma chemistry asymmetry induced by the 'Sawtooth' type of waveform are underway.

Matrix Distributed Electron Cyclotron Resonance

Besides, an alternative way to deposit µc-Si:H films in our laboratory is to use the *Matrix Distributed Electron Cyclotron Resonance (MDECR)* PECVD. Figure 4 [11] shows the general view of the system.

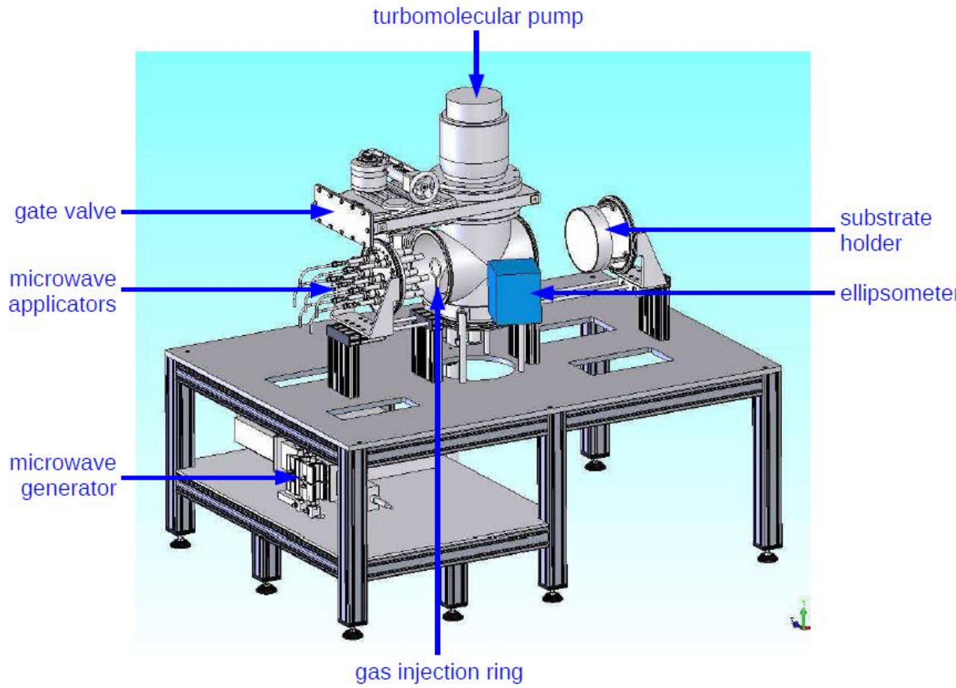

Figure 4 (from Ref. [11])

Compared with standard RF-CCP system, high plasma density achievable (10^{10}-10^{12}cm^{-3}) in MDECR case ensures the large increase of the films deposition rate. With SiH_4/H_2 plasma, deposition rate of µc-Si:H films as high as 28 Å/s was achieved [12]. Besides, due to the special design of the system, its dimension could be easily extended to the desired scale without physical or technique obstacles, just by repeating the power injection array, which are of great interest to both laboratory and industry.

In addition, there is much less concern about the powder formation within the chamber during the process of µc-Si:H growth, which usually happens in the standard RF-CCP system, due to the rather low working conditions (<10 mTorr). Moreover, such a low pressure condition also ensures that, before striking on the growing surface, the ions acceleration within the plasma sheath is much less collisionless, which means that the IBE can be monitored if the V_{DC} on the substrate electrode is known (bulk plasma potential V_{pl} is always several volts higher than V_{DC}). In fact, this V_{DC} can be tuned by varying another RF power supply on the substrate side (power negligible compared to the microwave power injection). In other words, the IBE can be more precisely controlled just by varying the RF power injection, which is of great importance for the optimization of µc-Si:H films properties. For µc-Si:H deposited with SiH_4/H_2 plasma, effect of IBE on structural and electrical properties has already been studied[13] [14][15][16].
Currently, the transfer of the promising $SiF_4/H_2/Ar$ plasma to MDECR-PECVD system for the µc-Si:H films deposition and its application on photovoltaic are underway.

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