CONTROL OF DOPED LAYERS IN P-I-N MICROCRYSTALLINE SOLAR CELLS FULLY DEPOSITED WITH HWCVD

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Abstract

In this paper, the influence of the deposition conditions on the performance of p-i-n microcrystalline silicon solar cells completely deposited by Hot-Wire Chemical Vapour Deposition is studied. With this aim, the role of the doping concentration, the substrate temperature of the p-type layer and of amorphous silicon buffer layers between the p/i and i/n microcrystalline layers is investigated. Best results are found when the p-type layer is deposited at a substrate temperature of 125ºC. The dependence seen of the cell performance on the thickness of the i layer evidenced that the efficiency of our devices is still limited by the recombination within this layer, which is probably due to the charge of donor centres most likely related to oxygen.

Keywords: microcrystalline silicon, Hot-Wire CVD, solar cells, doped layers

1. Introduction

Microcrystalline silicon (μc-Si:H) is a heterogeneous material that consists of small

silicon crystallites embedded in a hydrogenated amorphous silicon (a-Si:H) matrix. This material has been effectively incorporated as the bottom cell in thin film silicon stacked pin/pin solar modules.

The most mature and widespread technique to deposit μc-Si:H is Plasma Enhanced Chemical Vapour Deposition (PECVD) [1], though best results have been achieved using high frequency, the so-called Very High Frequency Glow Discharge (VHF-GD). Lately, Hot-Wire CVD (HWCVD) has also been set as an alternative to grow μc-Si:H thin films. Initially, samples deposited with this technique at low substrate temperature suffered from poor stability due to dramatic post oxidation effects [2], and only those grown at much higher temperatures resulted in stable devices [3].

Recently, dense μc-Si:H has been obtained at low substrate temperatures (T_s ~ 150-300ºC) using tantalum wires and low filament temperatures (T_f ~ 1500-1700ºC) [4]. Efficiencies as high as 9% have been achieved in μc-Si:H p-i-n solar cells with the active layer deposited by HWCVD in the above-mentioned range of deposition conditions [5].

Nevertheless, despite the fact that it is possible to consider the production of solar modules using HWCVD to deposit the intrinsic layer and PECVD to deposit the doped ones, there are several technological aspects that make it interesting to develop completely Hot-Wire grown μc-Si:H photovoltaic devices. As much higher densities of atomic H are produced using HWCVD than PECVD, the former allows the investigation of deposition conditions for the doped layers that cannot be reproduced by PECVD. In addition, the lack of ion bombardment during Hot-Wire deposition permits the production of sharper and less defective interfaces. Moreover, HWCVD has no problem of inhomogeneities due to stationary waves and, therefore, the size of Hot-Wire industrial deposition systems can be much higher than that of PECVD ones,

especially if high frequency is used. Thus, the size of an industrial deposition system combining both techniques would be limited by the PECVD set-up properties.

In this paper we present progress in the deposition of completely Hot-Wire deposited p-i-n microcrystalline silicon solar cells regarding the effect of the different doped layers used and its correlation with the solar cell performance.

2. Experimental

All samples presented here have been deposited in a HWCVD multichamber set-up described elsewhere [6], using different chambers for the deposition of doped and intrinsic layers. Intrinsic layers, in all cases, have been deposited using the conditions leading to stable devices reported in [7], and only the deposition time has been changed in order to vary the i-layer thickness.

In this study of the effects of the doped layers on the performance of μc-Si:H solar cells, we have used three different types of contacts. Those cells labelled A contain heavily doped layers and have the p-type layer deposited at T_P = 125ºC (while the rest of the structure is deposited at T_s = 200ºC). Cells labelled B have the doped layers deposited using a doping gas phase concentration of 1% in all cases and the same set of deposition temperatures. In those labelled C, a-Si:H buffer layers have been included between the heavily doped microcrystalline doped layers and the active one. Finally, those devices labelled D also have heavily doped μc-Si:H layers, but the p-type one has been deposited at T_P = 200ºC. Technological aspects regarding the different cells considered are summarised in table 1.

3. Results and discussion

There are two technological aspects that mainly influence the process of optimisation

of the deposition conditions of doped μc-Si:H layers to be used in a solar cell. One is the fact that the properties of very thin microcrystalline layers can be different than the bulk ones of thicker layers commonly used to evaluate the material properties. The second aspect that needs to be taken into account is the dependence of the resulting properties on the nature of the substrate on which they are grown [8]. Therefore, in order to avoid misinterpretations originated by these effects, we deposited full p-i-n structures so that a direct correlation between the device performance and the deposition conditions could be made.

Figure 1 shows the open circuit resistance (R_{oc}) as a function of the short circuit current (J_{sc}), i.e. the slope of the J-V curve in open circuit conditions as obtained from Variable Illumination Measurement (VIM) measurements [9]. This plot is usually a straight line for moderate illuminations and can exhibit a moderate saturation for high illumination levels [9]. The expected linear behaviour could be seen in all samples labelled A, C and D. On the contrary, the series resistance (the limit of R_{oc} at high illumination levels) of sample B was much higher and no saturation was observed at high J_{sc} values. Such behaviour could not be interpreted with an ohmic resistance and was attributed to a space charge limited transport between the p-layer and the ZnO:Al contact. Samples having the p-type layer deposited at 125ºC (A) showed an almost undetectable series resistance, regardless the presence or not of an a-Si:H buffer layer. On the other hand, those samples deposited at 200ºC presented some saturation at high short circuit current values, corresponding to a contact resistance of 4±1 Ω·cm.

A more surprising result is that of the dependence of the short circuit current with the thickness of the active layer of the device, which is shown in figure 2a. It is clearly observed that, regardless the doped layers considered, J_{sc} in all cases was higher for thinner i-layers. This behaviour could be imputed to an increase in the recombination

with increasing i-layer thickness. Further analysis of this fact was done from the spectral response measurements of the devices, which are plotted in figure 3. In this figure, it was observed that cells with thinner active layers presented wider responses. Moreover, it could also be seen that the cells with the p-type layer deposited at lower T_P showed better collection at short wavelengths than those deposited at higher temperature. Besides, those devices including buffer layers (B) exhibited the worst collection at short wavelengths. As the thickness of the p μc-Si:H layers was the same in all the studied devices, this different behaviour was attributed to different degree of recombination within the i-layer, close to the p/i interface. The increased recombination in the case where the p layers were deposited at 200ºC could be due to boron contamination of the intrinsic layer, causing a decrease in the electric field in this region and, thus, enhancing recombination. This results were in agreement with reported enhanced boron diffusion due to atomic hydrogen [10]. It is also worth noticing that the short wavelength response of cells where T_P was 125ºC was similar to the best ones reported for microcrystalline silicon solar cells deposited by PECVD and is not limiting the efficiency of the device.

Additionally, whereas J_{sc} of the best A cell (T_P = 125ºC), that having a 660 nm thick intrinsic layer, is nearly identical to that reported in [5] using PECVD-deposited doped layers, this parameter was clearly worse in the case of the thicker cell, indicating significant recombination even under short circuit conditions. This behaviour was attributable to a screening of the electric field due to the presence of undesired donor impurities inside the intrinsic layer.

The behaviour observed for the open circuit voltage (V_{oc}) with the different i-layer thicknesses and types of contacts was also in agreement with the above-mentioned interpretation. In figure 2b, the V_{oc} of the different devices as a function of the active

layer thickness is presented. There it can be observed that the cell having the lowest doping level (B) had a much lower V_{oc}. This fact was consistent with the above-mentioned existence of a space charge in the p/ZnO:Al interface that could provoke a significant voltage drop in this junction. A low built-in potential due to reduced doping level could also be considered. Nevertheless, the conductivity of samples with this doping level and thickness was of about 0.1 S/cm, which should cause a built-in potential higher than 1.0 V.

From the results in figure 2.b, it was also clear that the V_{oc} was not strongly dependent on the i-layer thickness. The increase in this parameter for lower intrinsic layer thicknesses observed in [5] is expected for a solar cell with a nearly uniform field across the active layer, but not in the case of cells with non-uniform fields in the i-layer.

The FF as a function of the i-layer thickness showed a similar behaviour to that of the V_{oc}, showing almost no variation with the device thickness. This parameter had also a much lower value in the case of the B sample. Nevertheless, the FF values had a dramatic relation with the dry-etching process carried out to reduce lateral leakages. Thus, despite the fact that sample A1 (660 nm thick i-layer) showed the most promising results (J_{sc} = 20.5 mA/cm^2 and a wider spectral response), best efficiency of 5.3% was achieved for cell A2 (990 nm thick i-layer) after dry-etching (J_{sc} = 17.5 mA/cm^2, V_{oc} = 0.48 V and FF = 0.63).

Surprisingly, the main difference between the results of the cells presented in this paper, which have Hot-Wire deposited doped layers, and those reported in [5], where the doped layers are deposited by PECVD, cannot be attributed to the doped layers but to the presence of donors within the active layer of our devices.

p-i-n solar cells having its active layer deposited under the same conditions than those

analysed here ($X_c \sim 0.45$) result in stable devices, with no trace of meta-stability after 2400 hours of AM1.5 light exposure. Material with higher amount of amorphous phase ($X_c \leq 0.4$) has a lower initial defect density, but this defect density increases after long light exposure [7]. Oxygen concentration in these samples measured by SIMS was of approximately $6 \cdot 10^{18}$ cm^{-3} and mainly imputable to impurities coming from the walls of the deposition chamber. The crystalline volume fraction, the impurity content or passivation of oxygen-related donors [11] are the most likely parameters to affect the recombination within the active layer of a μc-Si:H solar cell.

4. Conclusions

From the study of the performance of completely Hot-Wire deposited p-i-n microcrystalline silicon solar cells with different sets of doped layers, it can be concluded that p-type layers deposited at a substrate temperature of 125ºC and a high doping level are most suitable to result in high efficiency devices. Best efficiency of 5.3% has been achieved in a completely Hot-Wire grown solar cell with the p-type layer deposited at such low temperature.

On the other hand, it was also observed that the main factor limiting the efficiency of the solar cells presented in this work can be attributed to recombination within the intrinsic layer, most likely due to a screening of the electric field induced by the undesired presence of a significant donor density imputable to oxygen contamination during deposition.

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Figure captions

Table 1 - Solar cell technological information: gas phase relative concentration of boron in p-type layer ([B]/[Si]) and of phosphorous in n-type one ([P]/[Si]), substrate temperature during the deposition of p-type layer (T_P), thickness of buffer layer (d_{BL}), and thickness of intrinsic layer (d_i).

Fig. 1 – Open circuit resistance (R_{oc}) obtained from VIM measurements as a function of the short circuit current (J_{sc}) for the different kind of doped layers used.

Fig. 2 – J_{sc} (a) and V_{oc} (b) as a function of the thickness of the intrinsic layers for the different kind of contacts used.

Fig. 3 – Spectral responses of the different p-i-n solar cells.

Cell	[B] /[Si]	[P] /[Si]	T_P (ºC)	d_{BL} (nm)	d_i (nm)
A1	5%	2%	125	0	660
A2	5%	2%	125	0	990
B1	1%	1%	125	0	660
C1	5%	2%	125	4	1730
C2	5%	2%	125	11	720
D1	5%	2%	200	0	900
D2	5%	2%	200	0	660

Table 1

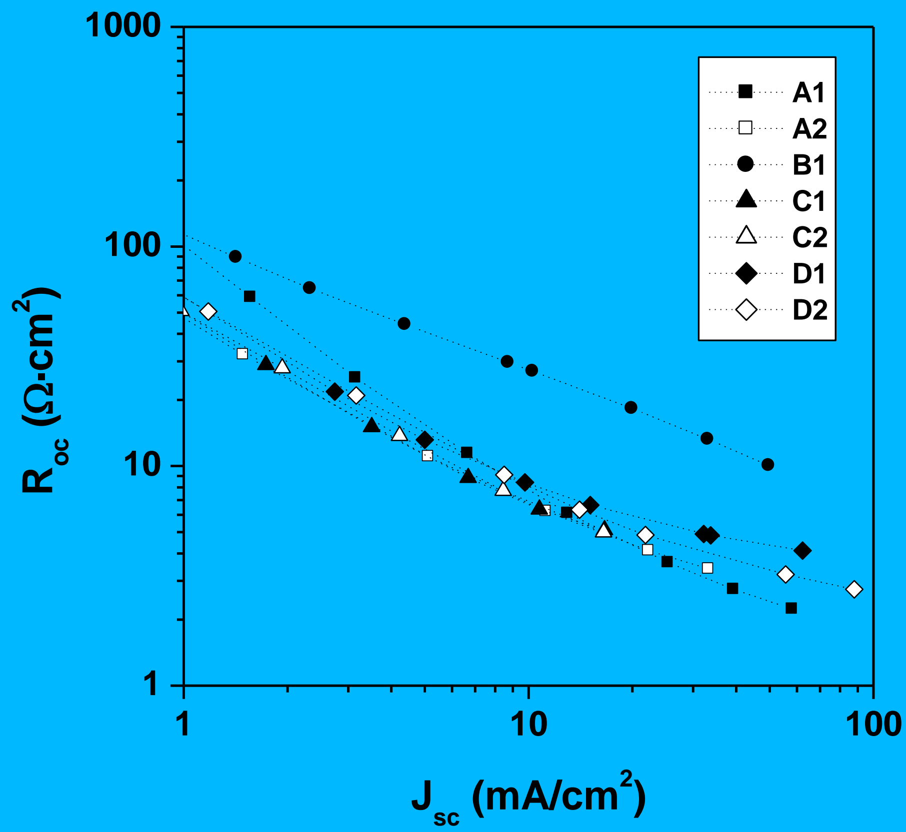

Figure 1

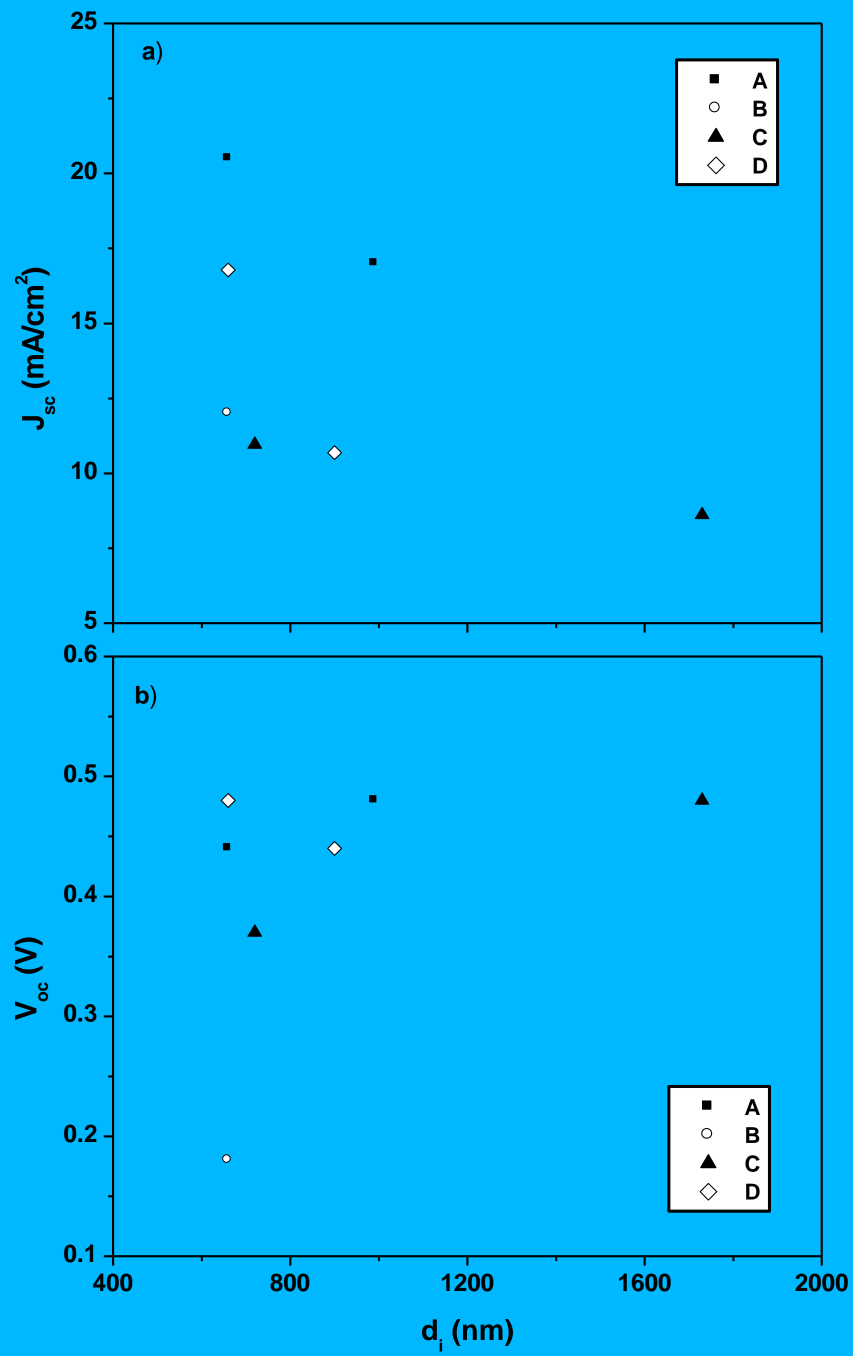

Figure 2

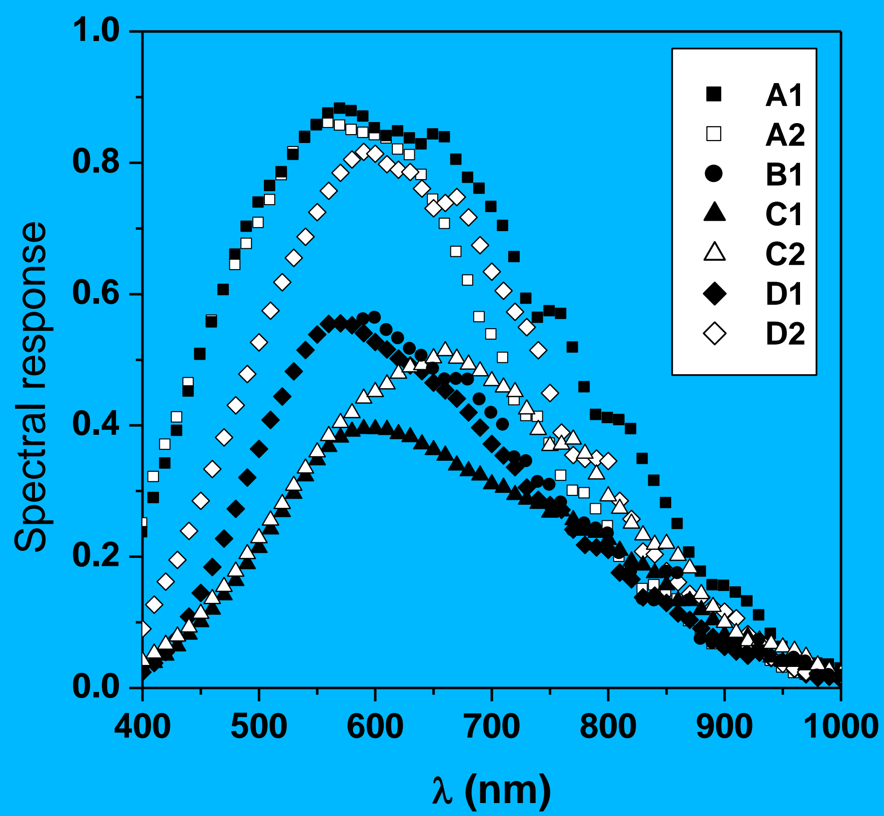

Figure 3