GROWTH OF THIN <p> μc-Si:H LAYERS FOR n-i-p SOLAR CELLS: EFFECTS OF THE H_2- OR CO_2-PLASMA TREATMENTS

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ABSTRACT: Systematic investigations concerning the effects of an H_2-plasma or of a CO_2-plasma treatment of the surface of an <i>°a-Si:H layer are presented: it is known that these treatments favor the growth of a thin microcrystalline <p>° μc-Si:H layer. Auger Electron Spectroscopy (AES) measurements of untreated <i>°a-Si:H layers as compared to layers treated with H_2- or CO_2-plasmas show drastically different signatures of the Si or SiO_x species. In the case of CO_2-plasma treatment, a thin SiO_x layer can be observed. A previous study showed that the crystalline fraction of the <p> layer can be controlled by adjusting the duration of the H_2-plasma treatment acting on the surface of the <i>°layer [1]. These treatments were successfully implemented in n-i-p a-Si:H solar cells deposited on stainless steel. With H_2- or CO_2-plasma treatments, a V_{oc} value of 890mV can be obtained with values of FF close to 65% for undiluted <i>°a-Si:H. By subsequently using <p> layers with microcrystalline Si-C alloys, we obtained n-i-p a-Si:H solar cell deposited onto stainless steel with a V_{oc} value as high as 918mV and a value of FF of 74% with a <p>° μc-SiC:H window layer.

KEYWORDS: a-Si - 1: microcrystalline Si - 2: interfaces - 3

1. INTRODUCTION

In the case of n-i-p a-Si:H solar cells, the <p> layer and its interface with the amorphous <i> layer is known to be one of the most important issues when wanting to obtain high values of V_{oc} **and** FF. On one hand, the microcristalline <p> layer can easily (more easily than an amorphous <p> layer) form a tunnel junction with the overlaying TCO (which is <n> type for ZnO, ITO or SnO_2). Such a tunnel junction between the <p> layer and the TCO is needed to avoid losses in the FF and V_{oc}, due to a contact barrier. On the other hand, the <p> layer must be as thin as possible to minimize the losses by absorption in this "inactive" region of the cell. The problem is: how to grow a thin <p> microcristalline layer on an amorphous <i> layer?

Different studies have been undertaken with the goal of increasing the value of V_{oc} in n-i-p a-Si:H solar cells by using different methods to favor a microcrystalline growth of the <p> layer in the cell [2, 3, 4]. Other studies have been published, demonstrating that the latter is a) the characteristics of the <p> layers (i.e. the structure of the <p> layer) develop during the first 100-200° of the growth [5, 6]; that b) the structure of the <p> microcristalline layer depends on the structure of the substrate or of the underlying thin film [7]. One may, thus, conclude that the investigations of the optoelectrical characteristics of thick <p> microcristalline layers deposited onto standard laboratory substrates are of little relevance to the actual situation in the cell.

In a previous work [1] we had already reported on first investigations about the introduction of H_2- and CO_2-plasma treatments at the <i>-<p> interface to promote the microcrystalline growth of the <p> layer. In this paper we will focus more closely on the observable effects of these treatments on the surface of the <i> layer. We present Auger Electron Spectroscopy (AES) measurements of untreated <i>°a-Si:H layers or on which we applied H_2- or CO_2-plasma treatments.

In a second part, we present results on n-i-p a-Si:H solar cells deposited onto stainless steel sheets. For all cells (or "partial cells") presented in this paper, we used the same kind of substrate (stainless steel) and we kept the deposition parameters of the different layers directly involved constant so as to enable a straight forward comparison between the characteristics of the cells of these sub-systems. The <i> layers were deposited from undiluted silane and the <p> layer, when deposited onto glass, always shows microcristalline behavior ($\sigma_{dark} \ddagger 1S/cm$). The only difference between the samples is the nature and the duration of the plasma treatment at the <i>-<p> interface. The solar cells were deposited without back reflector and without back TCO so as to simplify the interpretation of cell measurements.

2. EXPERIMENTAL

The solar cells and the "partial cells" used were deposited with the VHF-GD technique at a plasma excitation frequency of 70 MHz within a single chamber system. The temperature of the electrodes was kept between 140¡C and 240¡C depending on the layer. The stainless steel substrates were 250 m thick, washed with organic solvents and pure water and dried with a N_2 flow jet.

For all cells, the top contact was an ITO layer deposited by sputtering through a mask, the apertures in the mask allowing us to define cells of $0.25cm^2$ area. A chromium-silver grid was deposited on the ITO to minimize the losses in FF due to series resistance. The residual silicon between the cells was removed by plasma etching (SF_6). The samples were annealed at 180¡C during 1hr30' before characterization.

The cells were characterized by measuring illuminated j-V curves under AM1.5 illumination; thereby, a two-source solar simulator was used. The values of V_{oc}

and FF were determined from the j-V curves. The Variable Illumination Measurements (VIM) were performed with the same simulator by adding gray filters for the low illumination measurements or by adding a Fresnel lens for the high illumination measurements.

For AES measurements, the samples were transferred from the system of deposition to the AES measurement system in airtight boxes under a N_2-atmosphere so as to prevent air contamination (especially oxygen contamination).

For the droplets photographs, the samples were cooled down to room temperature under N_2 atmosphere and the droplets of pure water were deposited with a syringe as soon as possible to minimize the oxidation of the surface due to air exposure.

To simplify the lecture of the next chapters, we use the convention described below:

Æ (a): No treatment of the <i>°a-Si:H surface (AES, droplets) or no treatment at the <i>-<p> interface (cells, VIM),

Æ (b): H_2-plasma treatment of the <i>°a-Si:H surface or of the <i>-<p> interface,

Æ (c): CO_2-plasma treatment of the <i>°a-Si:H surface or of the <i>-<p> interface.

3.   RESULTS AND DISCUSSION

3.1   AES measurements

The range of interest that lies between 50 and 120eV is shown in Fig. 1. When comparing <i> layers in cases (a) and (b) one notes a strong variation of AES intensity in the energy range corresponding to Si (86eV-90eV) and little variations of AES intensity in the energy range corresponding to SiO_x compounds (<75eV). On the other hand, in the case (c), a strong influence on the AES intensity in the energy range of SiO_x compounds is seen when variations in the energy range of Si are moderate. Note that no variation of AES intensity in the energy range of SiC compounds was found.
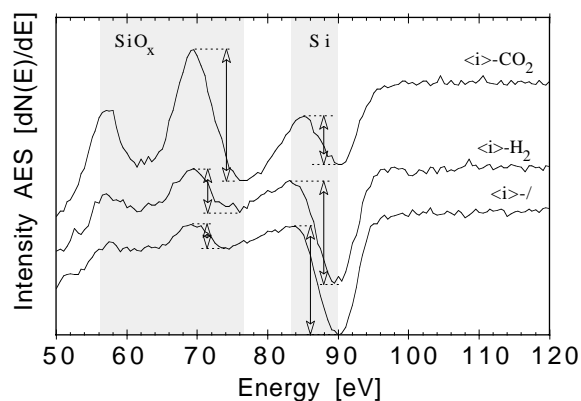

Figure 1: AES measurements of <i>°a-Si:H deposited onto stainless steel. Case (a) (<i>-/): untreated <i> layer; case (b) (<i>-H_2): H_2-plasma treatment of the <i> layer; case (c) (<i>-CO_2): CO_2-plasma treatment of the <i> layer. The curve are drawn separately to permit easier viewing.

For evidence, the CO_2-plasma treatment strongly oxidized the surface of the <i> layer. We conjecture that the Si-H bonds and/or the weak Si-Si bonds are broken by the effect of the CO_2-plasma, favoring, thus, the formation of new Si-O bonds.

AES measurements with different durations of the CO_2-plasma treatment to the surface of <i> layers is shown in Fig.2. With the increase in the duration of the CO_2-plasma treatment, we observe an increase of the AES intensity in the energy range corresponding to SiO_x compounds and a decrease in the energy range corresponding to Si. We conclude that the thickness of the SiO_x formed at the surface of the amorphous layer depends on the duration of the CO_2-plasma treatment and that the decrease of the Si range is explained by the substitution of the weak Si-Si bonds by Si-O bonds. Either in this serie, no carbon and no SiC compounds were found on the surfaces of the <i>°a-SiH layers with the AES measurements.
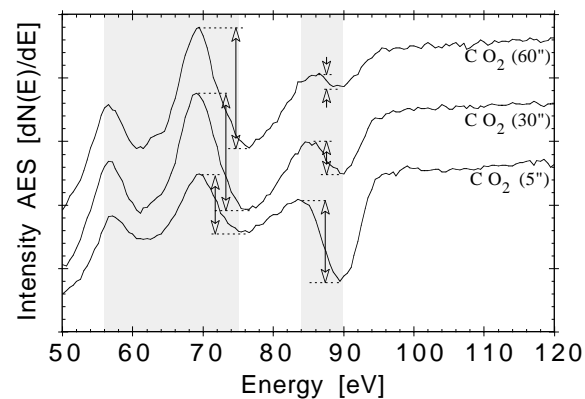

Figure 2: AES measurements of <i>°a-Si:H layers treated with a CO_2-plasma of different durations.

3.2   Droplets

A simple way to bring to the forefront the possible presence of a thin oxidized layer at the surface of <i>°a-Si:H layers is to deposit a small droplet of pure water directly on the surface of the layer [8]. Fig.3 shows that for the cases (a) and (b) the droplet stays round whereas, in the case (c), the droplet is completely flat: for cases (a) and (b), in which there is no oxidized layer, the surface can be considered hydrophobic whereas, in case (c), the surface becomes hydrophilic because of the presence of a thin oxidized silicon layer.
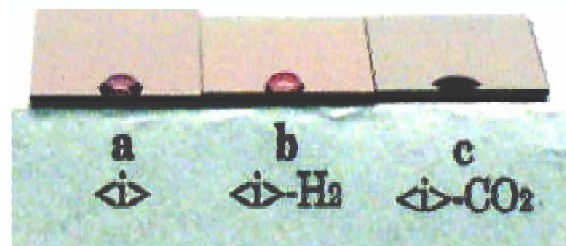

Figure 3: Photographs of small droplets deposited onto <i>°a-Si:H layers. In cases (a) and (b), the surface is hydrophobic whereas, in case (c), the surface is hydrophilic because of the presence of a thin oxidized silicon layer.

3.3 Rutherford Back Scattering (RBS) measurements

We performed RBS measurements on the series shown in Fig.2 with the goal to measure the thickness of the SiO_x layers but we found that it was not possible to determine the exact thicknesses because of the limited resolution of the RBS system. It means that the highest thickness value of SiO_x, obtained with 60" of CO_2-plasma treatment, is less than 30 .

With the RBS measurements we found that the hydrogen content of the a-Si:H layers slightly decreases with the increase in the duration of the CO_2-plasma treatment. This surprising observation has to be confirmed but the desorption of hydrogen in the underlying a-Si:H layer was partially confirmed by the measurement of pressure evolutions in the deposition chamber after different durations of CO_2-plasma treatments of <i> layers. We conjecture that the CO_2-plasma treatment creates species similar to H_2O vapor and then the source of hydrogen can only come from the a-Si:H layers previously deposited in the deposition chamber.

3.4 n-i-p a-Si:H solar cells

The last step of our study consisted in introducing these different plasma treatment in n-i-p a-Si:H solar cells. To focus our attention on the effects of the applied treatments and to minimize the variations due to other problems, we deposited the n-i-p structure directly onto stainless steel (i.e. without any particular back reflector or back TCO). Fig. 4 shows the j-V curves (active quadrant) of the three cells studied.

Let us repeat that the only difference between these cells is the plasma treatment at the interface between the <i> and the <p> layers. In the case (a), the solar cells show a poor value of V_{oc} and FF. With H_2- or CO_2-plasma treatments, the cells show improved values of V_{oc} and FF, the resulting j-V characteristics being quite the same in both cases, although the chemical effects of these treatments are drastically different on the surface of the <i> layers.

3.5 Variable Illumination Measurements (VIM)

The authors have further analyzed the fabricated solar cells having different treatments at the <i>-<p> interface by measuring the V_{oc} at different illumination levels (AM1.5 spectrum). The results are plotted in Fig.5. The curvatures observed for high values of light intensity (>5ÆAM1.5) are due to heating effects during the measurements and will not be considered in the following.

The current-voltage characteristics of a p/n junction is given by [9]:

$$j(V) = j_L - j_0[exp(\frac{qV}{nkT})-1] = j_L - j_{dark}$$

where $j(V)$ is the current j at voltage V, j_0 is the reverse saturation current, q is the electronic charge, n is the quality diode factor, k is Boltzmann's constant, T is the temperature and j_L is the light generated current.

It is generally accepted that the current is simply the superposition of the dark current (j_{dark}) and the photogenerated current (j_L) (hypothesis of superposition) and then, in open-circuit condition, the V_{oc} is given by:

$$V_{oc} = \frac{nkT}{q} ln(\frac{j_L}{j_0}+1) - \frac{nkT}{q} ln(\frac{j_L}{j_0})$$

The semi-log plot of the V_{oc} vs. illumination intensity is then a straight line with a slope given by:

$$slope = \frac{nkT}{q}Æln(10)$$

For the p-i-n (or n-i-p) diode, Merten et al [10] have postulated that an additional recombination current loss (j_{rec}) have to be taken into account:

$$j(V) = j_L - j_{dark} - \mathbf{j_{rec}}$$

and that j_{rec} depends on the illumination level. This additional current affects the aspect of the plot of the V_{oc} vs. illumination intensity by curving the "straight line" similarly as those observed experimentally in cases (b) in the Fig.5. Note that similarly curved plots have been found by Lee et al [11], when studying n-i-p solar cells using the H_2 dilution method.
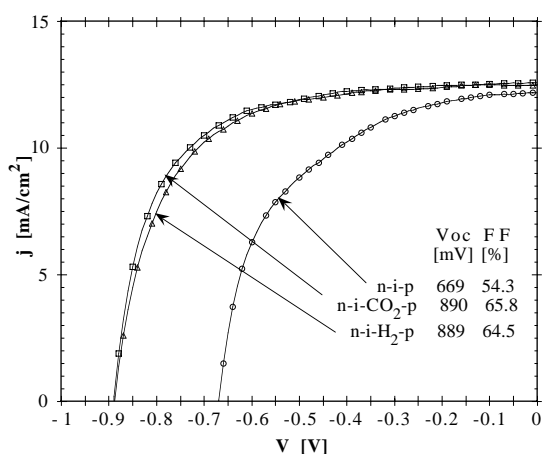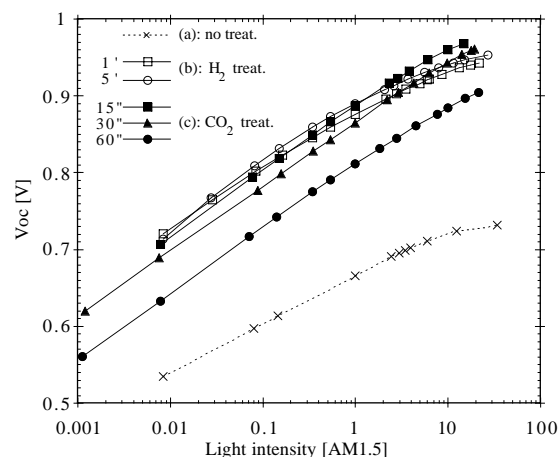
Figure 4: j-V curves of n-i-p a-Si:H solar cells deposited onto stainless steel. The parameters of deposition of the <n>, <i> and <p> layers are kept constant. The only difference between these cells is the H_2- or CO_2-plasma treatment applied at the <i>-<p> interface.

Figure 5: Variable illumination measurements of the values of V_{oc}. Open symbols: Different durations of H_2-plasma treatment. Filled symbol: Different durations of CO_2-plasma treatment. Crosses: No plasma treatment

This lead to the following speculations:

— For cases (a) and (c), the interface recombination dominates and the behavior of our n-i-p diodes approach that of a "bad quality" p/n diode (with the quality diode factors $n_{(a)}$=1.07; $n_{(c)}$=1.4).

— In the cases (b), the interface recombination is further reduced and bulk recombination starts to be the dominating factor. The behavior of our n-i-p diodes approach that of an "ideal" diode as described by Merten et al [10].

Further investigations, both experimental and theoretical, are necessary to substantiate these speculations and also to explain the differences in the observed values of the quality factors $n_{(a)}$ and $n_{(c)}$.

3.6 H_2-plasma treatment in a n-i-p a-Si:H solar cell with <p>° c-SiC:H "window" layer

Considering that the hydrogen plasma treatment of the <i> a-Si:H can favor the density of centers of nucleation for a microcristalline growth of the <p> layer, we deposited a n-i-p a-Si:H solar cell onto stainless steel using a silicon-carbide <p>° c-SiC:H "window" layer ($CH_4/[SiH_4+CH_4]$=50%). The incorporation of carbon is known to penalize the microcristalline growth of a layer and, to compensate this "amorphization", we increased the duration of H_2-plasma treatment of the <i>°a-Si:H layer before the deposition of the <p>° c-SiC:H layer. Fig.6 shows the resulting j-V curve of a n-i-p a-Si:H solar cell deposited onto stainless steel without back reflector or back TCO. The observed increase of V_{oc} is partially due to a slightly lower deposition temperature of the <i> layer (diluted) as well as the incorporation of carbon into the <p> layer. The high value of FF is due to an increase of the doping level of the <p> layer and an increase of the H_2-plasma treatment at the <i>-<p> interface so as to compensate the "amorphization" of the <p> layer due to both the increase of doping level and the incorporation of carbon in the <p> layer. Without this treatment, the <p>° c-SiC:H "window" layer will certainly grow with an amorphous structure and have a poor quality of contact with the ITO.
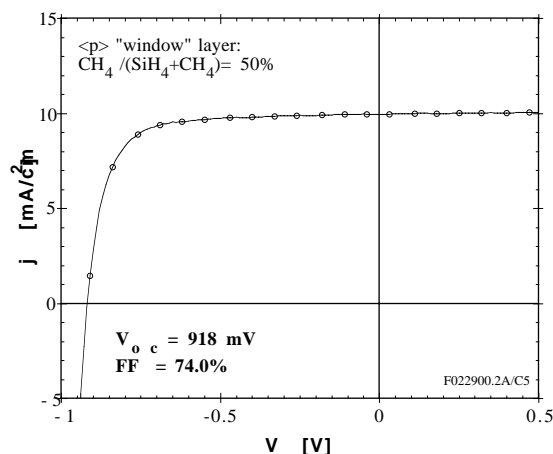

Figure 6: Incorporation of H_2-plasma treatment of the <i>/<p> interface for n-i-p a-Si:H solar cell with <p>° c-SiC:H "window" layer. The microcristalline growth of the carbide <p> layer is enhanced by the increase of duration of the H_2-plasma treatment.

4. CONCLUSIONS

In this paper, the authors present results concerning n-i-p a-Si:H solar cells deposited onto stainless steel. To favor the growth of a thin <p>° c-Si:H layer on a <i>°a-Si:H layer, we introduced H_2- and CO_2-plasma treatments at the <i>-<p> interface. From a systematic study of the effects of these treatments, we can conclude that the CO_2-plasma treatment oxidized the surface of the <i>°layer. We found that the microcrystallinity of the <p> layer can be controlled by the duration of the H_2-plasma treatment of the <i> layer. From the Variable Illumination Measurements (VIM) of the values of the V_{oc}'s, we found that the behavior of the cells are significantly different due to the applied plasma treatements. With this useful method, further investigations will be carried out to a better understanding of the recombination effects at the <i>-<p> interface or in the bulk of the <i> layer. Finally, we successfully introduced these plasma treatments in complete n-i-p a-Si:H solar cells deposited onto stainless steel obtaining thereby a V_{oc} of 918mV with a FF of 74%.

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