CHARACTERIZATION OF SiN_X / a-Si:H CRYSTALLINE SILICON SURFACE PASSIVATION UNDER UV LIGHT EXPOSURE

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ABSTRACT: One of the most promising solution for crystalline silicon surface passivation in solar cell fabrication consists in a low temperature (<400°C) Plasma Enhanced Chemical Vapor Deposition of a double layer composed by intrinsic hydrogenated amorphous silicon (a-Si:H) and hydrogenated amorphous silicon nitride (SiN_x). Due to high amount of hydrogen in the gas mixture during the double layer deposition, the passivation process is particularly useful for multicrystalline silicon substrates in which hydrogenation of grain boundaries is needed. On the other hand the presence of hydrogen inside both amorphous layers can induce metastability. To evaluate this effect in this work we investigate the stability of the silicon surface passivation obtained by the double layer under ultraviolet light exposure obtained by a deuterium lamp filtering the spectrum to remove wavelengths below 330 nm. In particular we have verified that this double layer is effective to passivate both p and n-type crystalline silicon surface by measuring, via photoconductance decay, a minority carrier lifetime up to 0.5 msec. To investigate the passivation mechanisms, which is strongly connected to the charge laying inside the SiN_x layer, we have collected the FTIR spectra of the a-Si:H/SiNx/c-Si structures and we have monitored the capacitance-voltage profiles of Al/SiN_x/a-Si:H/c-Si (MIS) structures at different stages of UV light exposure. Finally we have verified the stability of the double passivation layer applied to the front side of solar cell devices by measuring their photovoltaic performances during UV light soaking.

Keywords: Silicon Nitride, Passivation, Capacitance, PECVD, Ultraviolet.

1. INTRODUCTION

Nowadays almost all photovoltaic industries adopt silicon nitride (SiN_x) as passivation layer of the emitter front surface, that can be deposited at low temperature (<400 C°) by plasma enhanced chemical vapor deposition (PECDV) system. This structure has led to an efficiency of 18% [1], [2] due to the effective antireflection coating and the good silicon surface passivation. The general trend is to reduce the cost of substrate to realize silicon solar cells; then thinner wafer also of multicrystalline silicon (mc-Si) are use, therefore low temperature process are needed to reduce the mechanical stress. Intrinsic amorphous silicon (a-Si:H) deposited by PECVD have been successfully used either as a buffer layer between SiN_x and the emitter of the cell, leaving antireflection effect almost unchanged, either for the rear side of the cell when a point contact is adopted, reducing the parasitic shunts that occur between inversion layer and local contact on p-type doped silicon based solar cell [5], [6]. On this base it has been demonstrated to have excellent passivation quality on both p- and n- type doped silicon substrate. Metastability effects are, however, inherent to any device every time that hydrogenation is employed.

In this paper we have analyzed the effect of ultraviolet (UV) exposure monitoring the passivation quality of a-Si:H/SiNx stacked layers for both p- and n-type doped silicon by means of effective lifetime τ_{eff} and impedance spectroscopy on metal insulator semiconductor (MIS) structure during the UV exposure. At the same time photovoltaic parameters of p-type silicon based solar cells, passivated by that double passivation layer have been collected. Finally we have verified the effect of annealing process on the a-Si:H/SiNx passivation stability.

2. EXPERIMENTAL

Sample P and N have been fabricated starting on 1 Ωcm <100> oriented CZ monocrystalline silicon wafer p- and n-type doped, having thicknesses of 350 μm and 530 μm respectively. They have been treated with a standard RCA cleaning process. Afterwards they have been placed in a 13.56 MHz PECVD reactor, in order to deposit the a-Si:H and SiN_x films on both side each at once. So they have been processed with the following parameters: 250 °C as substrate temperature; 0.75 Torr as working pressure; 15 W as RF power; 120 sccm of 5% SiH_4 diluted in Ar.; 250 °C as substrate temperature for a-Si:H layer; 0.75 Torr as working pressure; 110 W as RF power; 1.66 as NH_3/SiH_4 gas flow ratio for SiNx layer. Photo-conductance decay, to evaluate minority carrier effective lifetime τ_{eff} , has been measured on the samples, together infrared (IR) spectroscopy analysis performed in a Perkin Elmer 2000 FTIR in reflectance mode in the range 500 - 3000 cm^{-1}. Subsequently these samples have been cut in two parts, named P1, P2, N1, N2. The index 1 is referred to the samples not UV exposed, in order to use them as reference, instead the index 2 is referred to the exposed ones. The samples with index 2, have been irradiated with a UV light obtained by a deuterium lamp, filtered to reduce the spectrum to UV-A region, and focused to obtain a power density of 500 $\mu W/cm^2$. τ_{eff} measures have been collected at different exposure time.

To get more inside the behavior of the passivation layers, Metal Insulator Semiconductors (MIS) structure have been fabricated on the described samples as reported in Table 1. These MIS have been characterized by capacitance-voltage (C-V) and conductance-voltage (G-V) measurements, performed in dark and room temperature conditions, in the range of 0.1-10 KHz frequency and ±40 V gate voltage. The flat band voltage V_{FB} from C-V profile [7], [8], the charge within the insulator Q_f from the V_{FB} [8], the interface trap density D_{it} from G-V measurements [9] are the main parameters we have obtained by these measures.

A p-type doped silicon based solar cell, described elsewhere [10], has been used to deposit on top side the experimented amorphous passivation double layer, in order to verify the any metastability effect of passivation. At different time of UV exposure, the photovoltaic parameters, short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and efficiency (Eff), have been monitored by current-voltage measurements (I-V) under AM 1.5G and dark, room temperature conditions.

To overcome metastability effects on double amorphous layer, thermal annealing has been experimented. Several silicon FZ substrates, 260 μm thick, 40 Ωcm resistivity, p-type doped, 4 cm^2 area, have been passivated by a-Si:H/SiN_x and annealed at 215 °C for 40 minutes ant then at 250 °C for subsequent 40 minutes. Afterward they have been exposed to UV light for 25 hours and τ_{eff} has been monitored.

3. RESULTS AND DISCUSSION

Figure1 shows the IR spectra of sample P1 and N1 before UV irradiation. From comparison of two different spectra, it can be seen that that the peaks at 820 cm^{-1}, 614 cm^{-1}, 1550 cm^{-1}, related to N-Si_3 (asymmetric stretching mode [11]) , Si-Si (stretching mode [12]), NH_2 (wagging mode [13]) respectively are higher in sample P; while the 2170 cm^{-1}, relative to H-Si-HN_2 (stretching mode [14]) are higher in sample N1. It can be deduced that the a-Si:H/SiNx double layer composition is influenced by the doping type of silicon substrates on which it has been grown.

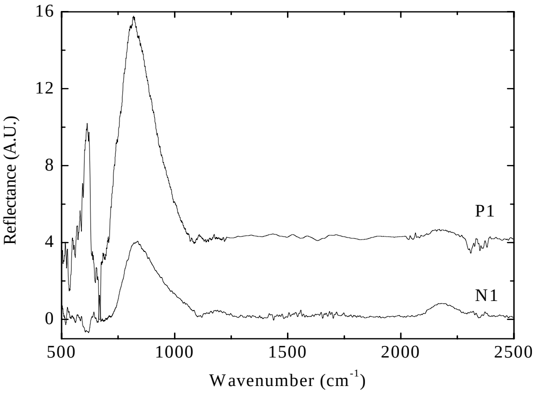

Figure 1: IR spectra of samples P1 and N1 measured before UV light exposure.

As a first result of a-Si:H buffer layer between SiN_x and Si introduction, the τ_{eff} value grows up to one order of magnitude with respect to the single SiN_x passivation layer on both doping substrates type.

The C-V profiles normalized to the insulator capacitance C_i (listed in Table I) for sample P1 and N1 in Figure 2 are reported. These curves describe a step function from depletion to accumulation positioned on the flat band voltage (V_{FB}). The distortion of the step function can be put in relation with voltage stretch-out of interface trap charge distribution. Depending on the probe frequency, different shape in the capacitance step function can be found. The presence of fixed positive charge Q_f., can be found observing that, on both p- and n-type doped silicon, the V_{FB} position shifts toward negative values with respect to the an ideal one. This can be evaluated taking into account the accumulation regime or by means of thickness of the insulator as in sample P1 and P2. This charge is in relation with the silicon dangling bonds composed of a silicon atom bonded to three nitrogen atoms, having an unpaired electron [15], [16]. Depending on the substrate doping type, the presence of this positive charge within the SiN_x produces a different passivation mechanism. As can be seen from low frequency C-V profile, on p-type doped silicon sample P1, the electrons are attracted close to the interface and an inversion layer occurs. Instead, in the case of the n-type doped silicon, sample N1, the electrons are pushed close to the silicon surface side where produce an accumulation, due to the positive charge that laying within the dielectric layers. Therefore there is no evidence of inversion layer even if a low frequency probe is used. The accumulation status still remains when the MIS is biased toward negative gate voltage.

Sample	MIS structure	C_i (nF)	V_{FB} (V)	Q_f/q (cm^{-2})	D_{it} ($cm^{-2}eV^{-1}$)
P1	SiN_x/ a-Si:H /p-Si	0.397	-33.5	$1.0 \cdot 10^{13}$	$2.8 \cdot 10^{11}$
P2	SiN_x/ a-Si:H /p-Si	0.397	-39	$1.2 \cdot 10^{13}$	$4.2 \cdot 10^{11}$
N1	SiN_x/ a-Si:H /n-Si	0.31	-0.5	$1.1 \cdot 10^{11}$	$1.2 \cdot 10^{10}$
N2	SiN_x/ a-Si:H /n-Si	0.365	-5.5	$1.6 \cdot 10^{12}$	$1.6 \cdot 10^{10}$

Table I. Structure, C_i, V_{FB}, Q_f, D_{it} of MIS samples before (sample P1 and N1) and after 20h UV light exposure (sample P2 and N2).

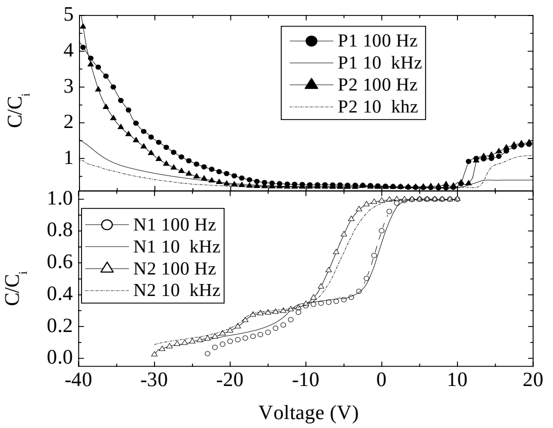

Figure 2: C-V measurements at 100 Hz and 10 KHz of samples P1 and N1 before UV light exposure and samples P2 and N2 after 20 hours UV light exposure .

The silicon surface passivation is affected by the presence of interface states, arising from plasma deposition of the amorphous layers related to dangling bonds at the interface and hydrogen diffusion into the silicon substrate [17]. G-V measurements supplies a quantification of their amount and energy position in the gap. The plot of G(ω)/ω in Figure 3 is reported. In case of sample N1 a peak appears, weakly bias dependent in amplitude, positioned at 1 kHz that does not vary with the gate voltage. This reveals two main topics:

1) a level of traps lays at energy position $E = KT \cdot \ln(\nu/\omega)$ of 0.37 eV from the valence band within the silicon band-gap, calculated assuming an escape frequency of $\nu = 10^{10}$ for c-Si;

2) the level extends inside the silicon substrate at the same energy reducing its density and the Fermi level crosses it always at the same distance from the depletion edge.

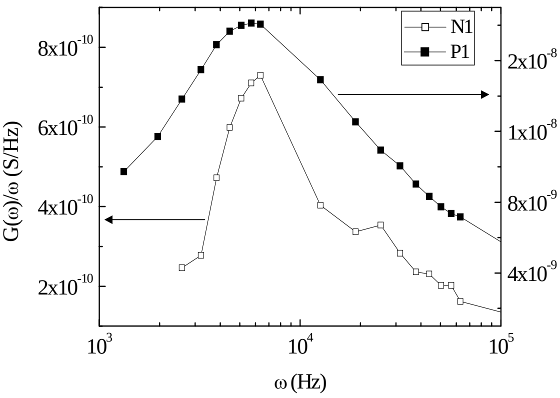

Figure 3: G(ω)/ω vs ω of samples P1 and N1.

The trap level assumes its maximum value density (D_{it}) at the a-Si:H/Si interface and it can be calculated directly from the maximum of G(ω)/ω [9]. This level reduces the possibility of an inversion layer at the silicon surface, since the Fermi level cannot easily move beyond the energy of that trap level toward the valence band edge. On the other hand if holes would be attracted at the silicon surface they would be trapped and released into the amorphous silicon band tail, leading to a new G(ω)/ω broaden distribution. Sample P1, in depletion regime, show a higher peak positioned at 1 kHz, that still remains evident in inversion regime, confirming that it exchanges with electrons. Moreover when the sample P1 is in accumulation regime a trap of holes within the a-Si:H band tail occurs, corresponding again to a G(ω)/ω broadening. Therefore the D_{it} are always calculated at a gate bias at which the Fermi level crosses 0.37 eV. The whole of charge and traps are affected by UV light exposure of the double insulator layer. Indeed, like the C-V profile reveals (see Figure 2), the V_{FB} of both P2 and N2 assumes more negative values, from which an increase of positive charge can be revealed. The UV radiation enhances the traps induced during plasma deposition at interface with the silicon wafer, giving place to a rice of G(ω)/ω at 1 kHZ.

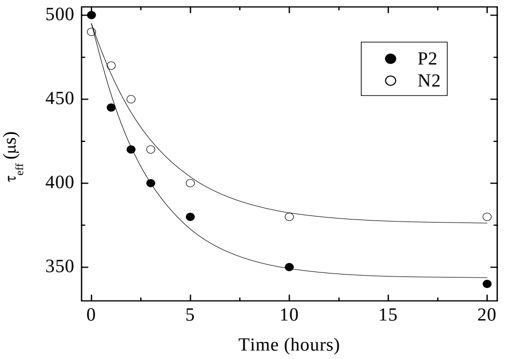

Figure 4: Effective minority carriers lifetime τ_{eff} of sample P2 and N2 at different time of UV light exposure.

In Table I the V_{FB}, Q_f and D_{it} of sample P2 and N2 after 20 hours of UV light exposure are summarized; higher the increment of positive charge, lower the traps effect on the surface recombination velocity, leading to a better stability of passivation of silicon surface, like shows the τ_{eff} decay of sample N2 reported in Figure 4.

To check the efficacy of the a-Si:H/SiN$_x$ as passivation layer, an n-type emitter solar cell has been covered with the double passivation layer. Of course its photovoltaic parameters have been grown after both passivation and antireflection effects. In particular Voc is increased from 598 to 618 mV.

During the UV light exposure, the photovoltaic parameters show different behavior as depicted in Figure 5. While Jsc and Voc remain almost unchanged FF decreases of about 3% and then the efficiency loses 0.5%. This effect is due to an increase of defects at a-Si:H/Si interface that enhances the surface recombination velocity, as confirmed by the reverse bias I-V characteristics in dark reported in Figure 6. Indeed if at a-Si:H/Si interface the density of traps increases, a reduction of minority carriers occurs and then a decrease of injected current in reverse bias takes place. In the inset of Figure 6 the current density collected at -1V of bias is reported as a function of UV exposure time. A decay of about 20% of current density occurs very similar to that of τ_{eff} of sample N2 seen in Figure 4.

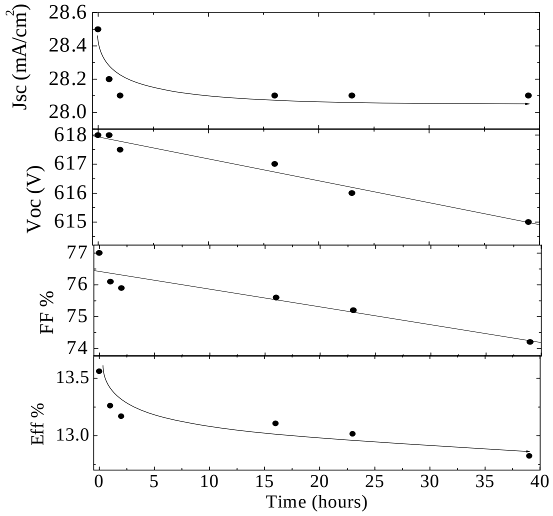

Figure 5: Evolution of photovoltaic parameters during UV light exposure.

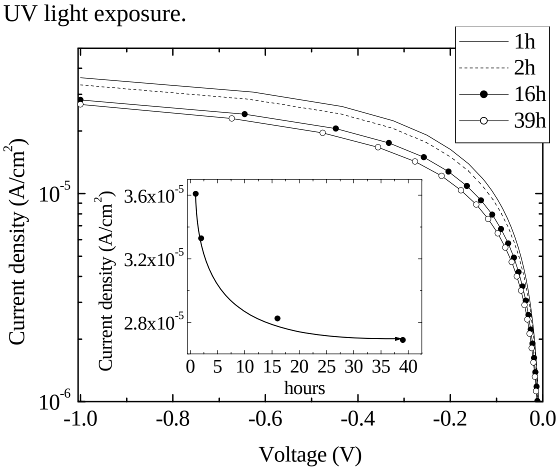

Figure 6: I-V characteristics in reverse bias and dark conditions at different time of UV light exposure. In the inset, the current density at -1V of bias is reported as a function of exposure time.

Finally the minority carrier effective lifetime, normalized to the initial value, of the p-type doped FZ a-Si:H/SiNx passivated samples in Figure 7 is reported.

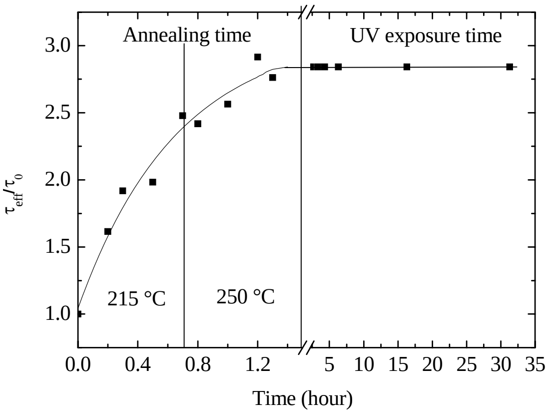

Figure 7: Normalized τ_{eff}, of the p-type doped FZ a-Si:H/SiNx passivated samples during thermal annealing and UV light exposure.

We have found that during the thermal annealing the τ_{eff} increases almost three times and after a prolonged UV light exposure remains unchanged. Very similar results has been carried out on analogous p-type doped silicon FZ substrate, n-type diffused at 60Ω/□ and passivated by a-Si:H/SiN$_x$ on both sides. In this experiment the recombination current in the emitter region J_{oe} has been monitored at different stage of annealing treatment and during the UV light exposure. As a result a stability of J_{oe} has been found.

Then we can conclude that thermal annealing reduces the metastability effect of UV light exposure on the amorphous passivation layers.

4 CONCLUSION

In this paper the functionality of silicon surface passivation using a-Si:H/SiNx double layer has been evaluated for both doping type of crystalline silicon and has monitored during the UV light exposure. IR spectroscopy has shown that the bonding composition of passivation layer depends on doping type of silicon substrate. Impedance measurements have been confirmed the role of positive charge in the passivation mechanism of both doping type of silicon substrate and have been established that UV light exposure produces an increment of positive charge as well as interface traps. During UV light exposure the passivation of silicon surface obtained by a-Si:H/SiNx layer has degraded less when this layer has been deposited on n-type rather than grown on p-type silicon. Finally A-Si:H/SiNx has been resulted in an effective passivation layer and antireflection coating of a p-type based solar cell. The UV light exposure of this cell has been produced an efficiency loss of 0.5%, due to the increment of traps close to the a-Si:H/Si interface.

Thermal annealing enhance the amorphous double layer stability to UV light exposure.

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