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Hydrogen plasma and thermal annealing treatments on a-Si:H thin film for c-Si surface passivation

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Abstract

High efficiency solar cells can be fruitfully built using the amorphous/crystalline silicon technology, taking advantage of the high V_{oc} that occurs as a consequence of excellent c-Si surface passivation provided by a-Si:H films. Improvements of the interface quality can be obtained using post deposition treatments such as hydrogen plasma and thermal annealing. We propose the use of surface photovoltage technique, as a contact-less tool to evaluate the energetic distribution of the state density at amorphous/crystalline silicon interface, and FTIR spectroscopy of the same samples to appreciate the evolution of Si-H and Si-H_2 bonds. This approach leads to interesting applications for monitoring and improving the interface electronic quality, which is extremely susceptible to the different treatments adopted. We found that thermal annealing produces a metastable state which goes back to the initial state after just 48 hours, while the effect of hydrogen plasma post-treatment results more stable. Moreover H_2 plasma reduces the defect density of one order of magnitude with respect to thermal annealing and keeps it constant also after one month. The hydrogen plasma is able to reduce the defect density but at the same time increases the surface charge within the a-Si:H film due to the H^+ ions accumulated during the plasma exposure, leading to a more stable configuration.

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Keywords: Surface photovoltage; defect density; a-Si:H/c-Si heterojunction; solar cells; FTIR spectroscopy.

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1. Introduction

An effective opportunity to reduce PV cost of silicon based solar cell manufacturing is based on mono crystalline silicon (c-Si) wafers thinner than 100 μm. Moreover high efficiency silicon based solar cell can be achieved through the usage of amorphous/crystalline (a-Si:H/c-Si) silicon technology in which the thin a-Si:H layers are deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) systems at temperature below 300 °C. Indeed, to prevent thermal stress and wafer bowing due to substrates thickness, low temperature processes are recommended. The potentiality of this technology has recently been demonstrated, leading to very high efficiency n-type c-Si/intrinsic a-Si:H/ n-type a-Si:H solar cell [1]. This device has been the focus of a very strong line of research, and even if its most relevant aspects have been already addressed, investigations are still focusing on the treatments applicable to the c-Si surface before the deposition of the amorphous thin film as well as the deposition conditions of the intrinsic a-Si:H buffer layer deposited before the n-doped emitter layer [2]. In this work we analyze the use of H_2 plasma post treatment of a-Si:H layer used to passivate the c-Si surface. This treatment, indeed, has attracted interest due to its efficacy in enhancing the a-Si:H ability to passivate the c-Si surface without damaging the c-Si substrate [3, 4]. To evaluate the effectiveness of this treatment as well as thermal annealing, we compare the surface photovoltage (SPV) data with the Silicon - Hydrogen bonding characteristic peaks from FTIR spectroscopy both measured on the a-Si:H/c-Si interface, in order to estimate the correlation between density of states and different Si and H bonds. With the aid of these techniques we investigate the effect of hydrogen plasma treatment performed on a-Si:H/c-Si interface and its stability along the time.

2. Experimental details

2.1. Making of the sample

For the aim of this paper, many a-Si:H/c-Si interface were prepared depositing 5 nm of a-Si:H layer on 1 Ωcm 160 μm thick p-type doped <100> Cz-Si wafers by means of PECVD system with the following parameters: SiH_4 (5% in Ar) flow = 120 sccm, pressure = 750 mTorr, deposition temperature 250 °C, RF power = 35 mW/cm^2 (15W), electrodes distance = 3 cm. In these conditions the resulting growth rate is about 0.22-0.24 nm/s. Afterwards two different post-treatments were adopted to process samples:

- thermal annealing, in a ATV-PEO 603 static furnace at temperature of 250 °C for 10 minutes in nitrogen atmosphere [5];
- hydrogen plasma post-treatment, in the PECVD reactor according to the following conditions: H_2 = 77 sccm, pressure = 100 mTorr, temperature = 180 °C, electrodes distance = 1 cm, RF power density = 58 mW/cm^2, two minute process time.

The result of these processes on the a-Si:H/c-Si interface has been monitored evaluating the following properties:

- the minority carrier effective lifetime (τ_{eff}) by means of Quasi Steady State Photo Conductance Decay (QSS-PCD) measurements;
- the defect density D_{it} at the a-Si:H/c-Si interface by measuring the SPV as a function of applied bias voltage;
- the characteristics decay times (τ_1, τ_2 and τ_3) as deduced by SPV transient measurements as illustrated in detail in the following section;
- the presence and type of Si and H bonds as revealed by FTIR spectroscopy.

2.2. Surface Photovoltage Setup

SPV values were obtained measuring the evolution during time of the voltage induced by a laser beam pulsed on the a-Si:H/c-Si sample surface disposed in a Metal Insulator Semiconductor (MIS) structure formed by Glass/ITO/ Mica / a-Si:H/c-Si. An optical fiber was used to couple the light source with the sample, while the laser diode had its emission peak at 846.2 nm.

The surface potential SPV technique relies on the variation of the surface charge density and distribution as a direct effect of the radiation that causes the freedom of movement of the electrons into the conduction band [6]. The equation to obtain the interface density of states (D_{it}) from SPV measure is:

$$D_{it}(\phi_s) = \frac{C_i}{q}\left(\frac{dU_f}{d\phi_s} - 1\right) + \frac{1}{q}\frac{dQ_{sc}}{d\phi_s} \tag{1}$$

where $d\phi_s$ is the surface potential, C_i is the MIS structure capacitance, dU_f the variation of the bias voltage applied to the MIS and Q_{sc} is the charge present in the space charge region. Thus, knowing the capacitance of the MIS structure and the surface potential as a function of the applied bias voltage, it is possible to determine the density of states within the energy gap of the semiconductor.

Each SPV characteristic is obtained by transient technique, monitoring voltage variation as a function of time when a laser beam is pulsed on the a-Si:H/c-Si sample. Its modeling can provide information about carrier recombination velocity [7]. As a matter of fact, we found that it is possible to approximate the obtained experimental curves with a linear combination of three decreasing exponential curves:

$$SPV(t) = A_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) \tag{2}$$

where A_0, A_1, A_2 and A_3 parameters scale the experimental curves avoiding negative voltages. The characteristic time of the first exponential (τ_1) describes a fast decay of carriers, thus referring to the device regions with higher recombination velocity, typically the surface; τ_3 describes slower recombination rate and therefore is more correlated to carriers in the bulk, while τ_2 describes charges having an intermediate behaviour.

2.3. FTIR spectroscopy

The FTIR spectroscopy has been carried out on a-Si:H/c-Si samples using a Perkin Elmer FRONTIER system equipped with Attenuated Total Reflectance (ATR) in the range between 4000-600 cm^{-1} and analyzed with the aid of Perkin Elmer Spectrum software.

3. Results and discussion

It has been experimentally confirmed that both thermal annealing and hydrogen plasma treatment improve the passivation of c-Si surface with respect to an a-Si:H layer deposition.

Thermal annealing performed at temperature lower or equal to the a-Si:H layer deposition temperature and for prolonged time, usually in forming gas, has been proved to reduce the dangling bond density. Indeed, this process is useful to enhance the c-Si surface passivation because it re-arranges the bonding network and saturates the interface states thanks to hydrogen diffusion within the amorphous film [8]. Moreover it has been found that hydrogen plasma treatment can improve the silicon surface passivation leading to lifetime up to one order of magnitude higher, when performed as a part of a multistep a-Si:H deposition process [2].

Taking the moves from these results, in this work both treatments have been evaluated with the aid of SPV and FTIR measurements.

3.1. SPV measurements

To appreciate the effects of the post-treatments on our samples, we have measured the minority carrier bulk lifetime, calculated the defect density at the surface by measuring the SPV and derived the characteristics decay times from SPV transient measurements. In particular we extracted the minimum defect density values ($D_{it\,min}$) from the D_{it} ($eV^{-1}cm^{-2}$) distributions, reported in Fig. 1(a), as a function of energy within the forbidden bandgap at a-

Si:H/c-Si interface. These distributions have been deduced by the SPV measurement variation as a function of bias according to the equation (1) and shown in Fig. 1(b). A comparison between SPV measurements and D_{it} ($eV^{-1}cm^{-2}$) distributions of investigated samples, according to the thermal annealing and hydrogen plasma treatments listed in Table 1, is reported in Fig.1a) and Fig.1b) respectively.

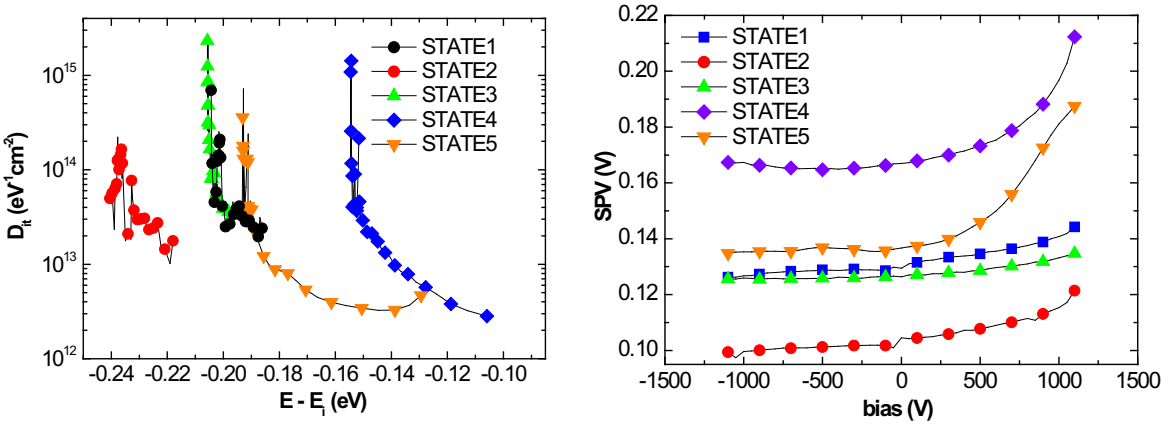

Fig. 1. (a) Density of state D_{it} ($eV^{-1}cm^{-2}$) distribution as a function of energy within the forbidden bandgap at a Si:H/c-Si interface, (b) SPV measurements as a function of bias voltage in the different states.

Indeed in Table 1 the results of the different measurements before, immediately after and 48 hours after the thermal annealing process are reported; each of these conditions, with all the characterizing parameters, are here defined as STATE of the samples; thus we refer to the "as grown" as STATE1, the "thermally annealed" as STATE2, and the condition "after 48 hours" as STATE3. The thermal annealing produces beneficial effect on $D_{it\ min}$ and lifetimes. This effect is evident from the parameters values in STATE2. However, performing the lifetime and SPV measurements 48 hours after the thermal annealing treatment (STATE3) we have seen that both lifetime and density of states have recovered to levels close to STATE 1, showing a decay of the c-Si surface passivation.

Table 1. Key parameter values in the defined states.

	STATE1	STATE2	STATE3	STATE4	STATE5
τ_{eff} (μs)	78	339	80	-	-
$D_{it\ min}$ ($eV^{-1}cm^{-2}$)	2.4 10^{13}	1.0 10^{13}	3.2 10^{13}	2.8 10^{12}	3.3 10^{12}
Offset (V)	0.136	0.104	0.126	0.167	0.130
Q_s (cm^{-2})	2.07 10^{11}	1.8 10^{11}	1.99 10^{11}	2.29 10^{11}	2.02 10^{11}
τ_1(10^{-5}s)	2.06	4.08	3.31	2.10	2.15
τ_2(10^{-4}s)	2.35	4.79	2.00	2.37	4.05
E_f (eV)	0.362	0.327	0.358	0.410	0.371

In Table 1 we refer to the hydrogen plasma post-treatment as STATE4, STATE5 is the same sample measured one month later. It is evident that plasma post-treatment improves the silicon surface passivation leading to a more stable condition with respect to thermal annealing treatment. Indeed, after one month the density of states does not increase.

Transient SPV measurement provides a further analysis of the post-treatment effect of surface passivation, providing a key to better understand the evolution between the defined states. Results in Table 1 shows that the

thermal annealing leaves the a-Si:H/c-Si interface in a metastable state (STATE2), which rapidly decays towards a state (STATE3) whose parameters look almost similar to those of STATE1; on the other hand the H_2 plasma treated sample appears more stable, since we observe that STATE5 keeps the minimum defect density values $D_{it\ min}$ at an order of magnitude lower than STATE1 and very close to the values of STATE4. Secondly it is worth to note that the samples treated with the H_2 plasma have the density of surface states one order of magnitude lower than that of both untreated and thermally annealed samples. Therefore hydrogen plasma treatment effectively improves the interface quality, saturating the silicon dangling bonds. Moreover at 0 V of bias condition the transient characteristic (depending on τ_1 and τ_2) of STATE4 is similar to that of STATE1. Instead thermally annealed sample has a similar $D_{it\ min}$ of untreated sample (STATE1), but the transient τ_1 and τ_2 are almost double longer. This situation however is not stable, since just after 48 hours the $D_{it\ min}$ increases and τ_1 and τ_2 decrease to their initial values.

To summarise the evolution of the a-Si/c-Si interface due to post deposition treatments of the a-Si:H layer, in Fig. 2 we report a flowchart of the STATES, each of them characterized by relevant parameters.

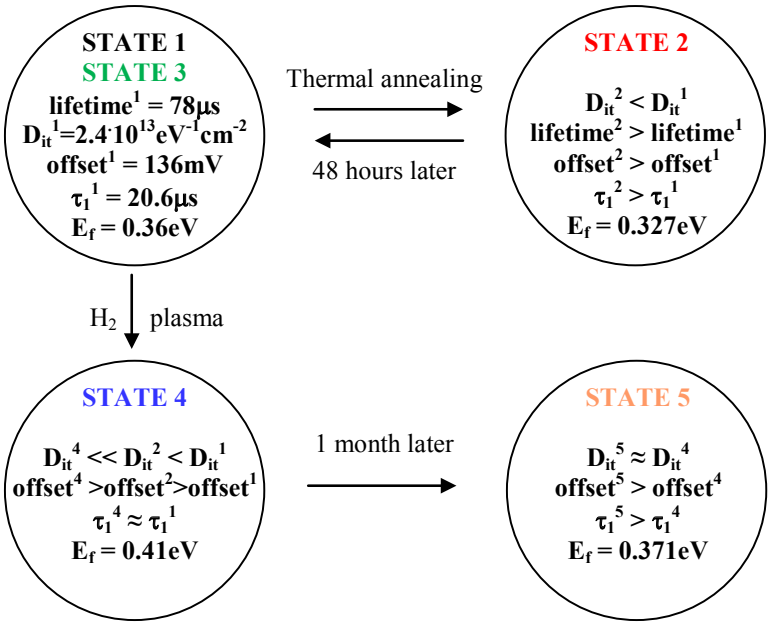

Fig. 2. Flow chart of the STATES characterized by relevant parameters. Each STATE characterizes the a-Si:H/c-Si interface. Post deposition treatments of the a-Si:H/c-Si sample induce evolution between the STATES.

3.2. FTIR spectroscopy

To investigate the bonds between Si and H we used FTIR spectroscopy on a-Si:H/c-Si samples, benchmarking the FTIR spectra acquired in all considered states with the "as grown" sample.

In this analysis our attention was focused on:

- the peaks positioned at 630cm^{-1} and 670cm^{-1} related to Si-H and Si-H_2 respectively wagging [9, 10];
- the peaks positioned at 2080cm^{-1} and 2114cm^{-1} related to Si-H and Si-H_2 respectively epitaxial [11];
- the peaks positioned at 2005cm^{-1} and 2088cm^{-1} related to Si-H and Si-H_2 respectively interface [11].

As a matter of fact both Si-H and Si-H_2 groups reveal their presence in the "as grown sample", and they modify depending on the subsequent treatment. Taking into account that the higher is the Si-H content at the a-Si:H/c-Si interface, with respect to Si-H_2, the better is the c-Si passivation [12], we have observed interesting correlations between the evolution of Si-H / Si-H_2 groups and the c-Si surface quality. In particular we have found that 10 min of

thermal annealing at 250°C initially reduces the Si-H_2 groups centred at 670cm^{-1}, 2088cm^{-1} and 2114cm^{-1}, while increases the Si-H content at 2080cm^{-1} and reduces the Si-H signature at 630cm^{-1}. This effect promotes an enhancement of the c-Si surface passivation, as previously noted, moving from STATE1 toward STATE2. Nevertheless, after one month from the thermal annealing treatment, the amount of Si-H and Si-H_2 almost recovers the "as grown" conditions, as evident comparing the two FTIR spectra reported in left and right picture of Fig. 3. This effect confirms the c-Si surface passivation metastability produced by thermal treatment. This is in agreement with the already seen statement: STATE2 → STATE3 ≈ STATE1. The corresponding FTIR spectroscopy Gaussian peaks of Si-H and Si-H_2 groups are reported for comparison in left and right pictures of Fig. 3.

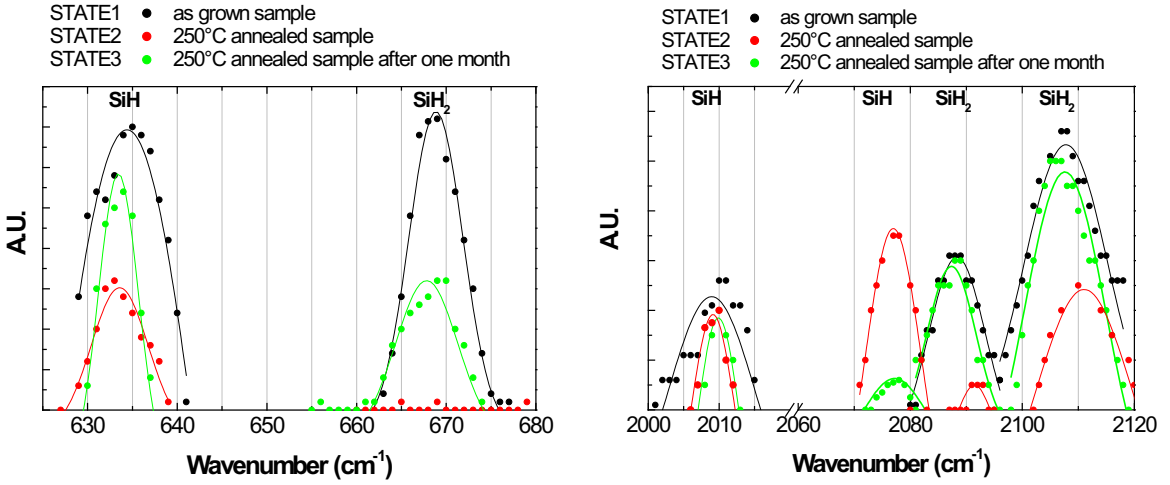

Fig. 3. FTIR Spectra related to the thermal annealed sample. Gaussian peaks are reported for as grown condition STATE1, after thermal treatment STATE2 and after one month from the thermal treatment STATE3 respectively.

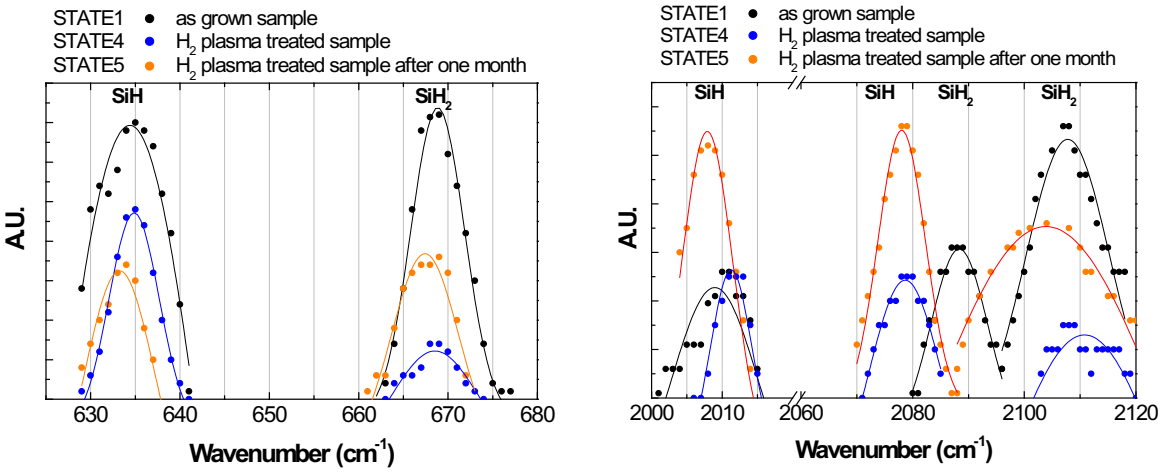

Fig. 4. FTIR Spectra related to the H_2 plasma treated sample. Gaussian peaks are reported for as grown condition STATE1, after H_2 plasma treatment STATE4 and after one month from the H_2 plasma treatment STATE5 respectively.

On the other hand, the H_2 plasma post treatment performed after a-Si:H buffer layer deposition, reduces the Si-H_2 content of both a-Si:H layer and a-Si:H/c-Si interface. A reduction of Gaussian peaks centered at 670 cm^{-1}, 2088cm^{-1} and 2114cm^{-1} is evident from the FTIR spectra reported in upper and lower picture of Fig. 4. Contemporary the H_2

plasma post treatment increases the Si-H content, as evident comparing the FTIR peaks before and after H_2 plasma treatment (STATE1 and STATE4), centered at 2005cm^{-1} and 2080cm^{-1} reported in the right picture of Fig. 4. Whereas the FTIR peak centered at 630cm^{-1} slowly reduces respect to the as grown sample, as reported in the left picture of Fig. 4. All these effects are in agreement with the D_{it} reduction and the c-Si surface passivation enhancement, as already stated in Fig. 2 and Table 1. After one month from the H_2 plasma treatment the Si-H Gaussian peaks centered at 2005cm^{-1} and 2080cm^{-1} are higher than the beginning of the treatment. Whereas the both Gaussian peaks of Si-H_2 groups centered at 2114cm^{-1} and 670 cm^{-1} show an increment not sufficient to recover the FTIR spectra related to the as grown sample as in case of one month after thermal annealing. This suggest a helpful evolution of hydrogen within the a-Si:H layer and a-Si:H/c-Si interface indeed it leads to a more stable surface passivation (STATE4 and STATE5). These results are in good agreement with what observed by previously seen SPV analysis. The FTIR spectroscopy analysis confirms that the thermal annealing can produce metastable surface passivation, while suggest H_2 plasma post treatment as an interesting way to enhance the c-Si surface passivation leading to a more stable effect on c-Si surface also after prolonged time from the plasma process.

4. Conclusions

In this paper we adopted SPV and FTIR techniques to evaluate the effects of post deposition treatments of a-Si:H/c-Si interface performed to improve its quality. Hydrogen plasma post processing has been compared with thermal annealing also after long time from the treatment.

SPV measurements were used to appreciate the density of states D_{it} as well as the decay times τ_1 and τ_2 of the SPV transient, related to the recombination at the heterojunction. FTIR spectra allowed investigation on the evolution of hydrogen within the a-Si:H layer and a-Si:H / c-Si interface. Leveraging on these techniques we have gave evidence that thermal annealing drives the a-Si:H / c-Si interface in a metastable state, which goes back to the initial state after just 48 hours, while the effect of hydrogen plasma post-treatment results more stable and enduring in time, presenting no substantial change after one month. Moreover, with respect to thermal annealing treatment, H_2 plasma reduces the D_{it} of one order of magnitude. The hydrogen plasma is also able to reduce the D_{it} but at the same time increases the surface charge within the a-Si:H film due to the H^+ ions accumulated during the plasma exposure. Investigation with FTIR spectroscopy measurements confirms the evolution described by SPV measurements.

Measures performed both with SPV and FTIR spectroscopy suggest that H_2 plasma treatment after a-Si:H deposition represents a valid technique to enhance c-Si surface passivation as well as its stability.

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