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Adequate method to study the surface passivation effectiveness in HEM multicristallin silicon wafers

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Abstract - *In this work we have examined the effectiveness of surface passivation on as-cut multicrystalline silicon (mc-Si) wafers using different techniques. The study is based on minority carrier lifetime measurements with quasi steady state photo-conductance, 'QSSPC'. Effective minority carrier lifetime (τ_{eff}) measured values of 12.4, 8.9, 4.9 and 3.1 µsec are obtained respectively with four silicon surface passivation techniques: 1- Shallow phosphorous diffusion emitter (n^+p), 2- Iodine-Ethanol (I-E), 3-Hydrofluoric acid (HF) emersion and 4- SiN_x layer deposition. These results suggest that the shallow n^+p emitter gives the τ_{eff} close to the bulk lifetime (τ_b) due to the better surface passivation quality. Simulations made with Hornbeck-Haynes model indicate that the τ_{eff} improvement can be correlated with the decrease of the surface recombination velocity (SRV) and the increment of bulk lifetime.*

Résumé – *Dans ce travail, nous avons examiné l'efficacité de la passivation des surfaces des plaquettes de silicium poly cristallin coupé (mc-Si) avec différentes techniques. Cette étude est basée sur des mesures de la durée de vie des porteurs minoritaires dans un état quasi statique de photo-conductance, 'QSSPC'. La mesure de la durée de vie effective des porteurs minoritaires (τ_{eff}) a donné lieu aux résultats suivants: 12.4, 8.9, 4.9 and 3.1 µsec qui ont été respectivement obtenus avec quatre techniques de passivation des surfaces de silicium: 1- Emetteur peu profond de diffusion de phospore (n^+p), 2- Iode -Ethanol (I-E), 3- Emersion de l'acide fluorhydrique (HF) et 4- SiN_x Disposition des couches. Ces résultats suggèrent que l'émetteur peu profond n^+p donne le τ_{eff} proche de l'allongement de la durée de vie en profondeur.*

Keywords: Lifetime measurement - Multicrystalline silicon - Surface passivation - Minority carrier.

1. INTRODUCTION

P-type multicrystalline silicon (mc-Si) wafers used in the photovoltaic (PV) industry represents 60 % of modules produced annually [1]. During the process fabrication of solar cells, the inspection of electrical charge carrier lifetime in the bulk of the mc-Si wafer is best tool for monitoring during wafer processing to predict and evaluate the impact of each technological step on this important physical parameter during the fabrication of the solar cell. Different techniques are used to measure effective lifetime by means of an averaged value over an area or a mapping of the wafer surface in the transient [2, 3] or the steady state 'SS' and quasi steady state 'QSS' modes [4, 5]. It is based on the decay photoconductance via the generation/recombination mechanisms of charge carriers. Techniques with the transient mode is more appropriate for high lifetime >200 µsec and are less sensitive to the surface recombination velocity 'SRV' of minority carrier. Techniques which use the SS and QSS modes like the QSSPC, the SRV factor affect heavily the measured values of τ_{eff} and for this reason the surface must be effectively passivated.

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Actually, two techniques are commonly used by the photovoltaic community to inspect the lifetime in silicon wafers; the Microwave photoconductance decay (MW-PCD) in the transient mode [6] and the QSSPC with the QSS mode [7]. This last are very fast and simple to use in a mc-Si bare wafers characterized by a low carrier lifetime (<200 µsec).

Before each measure step, the surface are chemically cleaned and passivated using a well-known technique such as thermally growth silicon dioxide (SiO_2) layer, floating n^+p junction, PECVD silicon nitride (SiN_x) layer and Iodine- Ethanol or Methanol (I-E solution) [7]. The I-E solution is not used systematically compared to thermally SiO_2, PECVD SiN_x layer and n^+p floating junction. In some cases, measurements are repeated a few times to reach the stability stage with an accuracy of 10% [9].

In the present work we have inspected the effective lifetime of P-type mc-Si wafers using QSSPC with a different surface passivation ways: Hydrofluoridric acid (HF), I-E solution, PECVD SiN_x layer and floating n^+p junction. To determine the SRV values from QSSPC lifetime curves and to identify the origin of τ_{eff} variation for each passivation way as a function of the charge carrier density injection level (Δn) we have used the Hornbeck-Haynes model.

2. SURFACE PASSIVATION AND BULK LIFETIME MEASUREMENT

Generally the minority carrier lifetime spectroscopy in semiconductors is based on the generation-recombination mechanisms. Theoretically, there exist four mechanisms which monitor this physical parameter: Shockley-Read-Hall (SRH) recombination, Auger recombination, Radiative recombination and Surface recombination. Taking into account all this mechanisms, we can write the effective lifetime as follow [10]:

$$\frac{1}{\tau_{eff}} = \underbrace{\frac{1}{\tau_{SRH}} + \frac{1}{\tau_{auger}} + \frac{1}{\tau_{rad}}}_{\frac{1}{\tau_b}} + \frac{1}{\tau_s} \tag{1}$$

In the p-type silicon moderately doped by boron atoms ($Na \approx 1.5x10^{16}\ cm^{-3}$), the Auger component can be neglected. Also, the silicon is a semiconductor material characterized by an indirect band-gap which reduces the probability of the radiative optical transition and the recombination mechanism is negligible compared to SRH component. Considering these aspects and associating the SRH to the bulk component, the equation (1) can be simplified to:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_s} = \frac{1}{\tau_b} + \frac{1}{\tau_s} \tag{2}$$

The surface minority carrier lifetime τ_s can be related to the SRV and the wafer thickness W. If we assume that both front and rear surface recombination velocities have the same values ($S_{front} = S_{rear} = S$), the formulations below give τ_s depending on the surface recombination strength:

For low values of SRV < 250 $cm.s^{-1}$[10]

$$\tau_s = \frac{W}{2S} \tag{3.a}$$

For high values of SRV > 10^5 $cm.s^{-1}$ [11]

$$\tau_S = \frac{1}{D_n}\left(\frac{W}{\pi}\right)^2 \tag{3.b}$$

Where D_n is the diffusivity constant of minority carrier in the bulk. Generally D_n varies between 20 $cm^2.s^{-1}$ to 30 $cm^2.s^{-1}$ depending on the defect density in the silicon wafer.

In the range 250 $cm.s^{-1}$ < SRV < 10^5 $cm.s^{-1}$ τ_S are expressed as follow,

$$\tau_S = \frac{W}{2S} + \frac{1}{D_n}\left(\frac{W}{\pi}\right)^2 \tag{4}$$

We inject the term of {eq. (4)} in {eq. (2)}, the effective lifetime can be written,

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \left[\frac{W}{2S} + \frac{1}{D_n}\left(\frac{W}{\pi}\right)^2\right]^{-1} \tag{5}$$

Computing the {eq. (5)}, figure 1 illustrates the behavior of τ_{eff} as a function of the surface recombination velocity for different bulk lifetime τ_b values (1-50) µsec. The evolution of τ_{eff} curves suggests that the effect of SRV on effective lifetime are more pronounced in the intermediate range (10^2 $cm.s^{-1}$ < S < 5×10^4 $cm.s^{-1}$) for bulk lifetime values τ_b < 15 µsec. We can see also that $\tau_{eff} \approx \tau_b$ for S < 10^2 $cm.s^{-1}$ and for S > 5×10^4 $cm.s^{-1}$ as shown in Fig.1. For low SRV values, carrier lifetime is dominated by the term given in {eq. (3.a)} and then τ_{eff} is practically equal to the bulk life time τ_b. The dominance of this term decrease in high SRV values and then the surface recombination is governed by the second term described in {eq. (3.b)}. In the other hand when bulk lifetime is relatively higher τ_b > 15 µsec the τ_{eff} values are strongly dependent on the SRV values which correspond to S < 5×10^4 $cm.s^{-1}$. In conclusion, this study allow us to verify if τ_{eff} improvement is due only to the passivation quality or not, as discussed below.

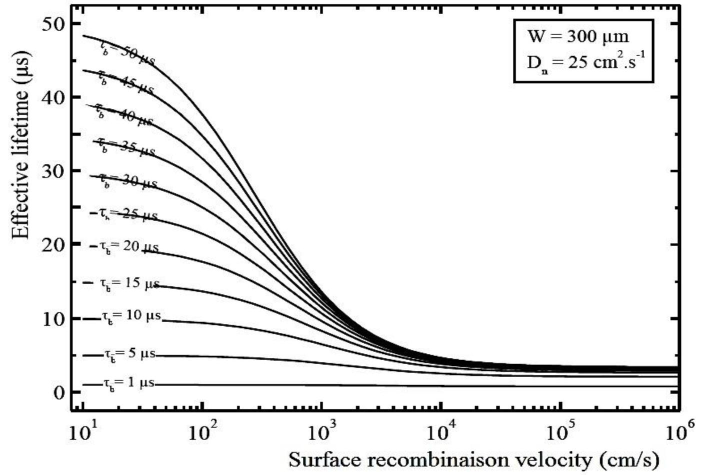

Fig. 1: Effective lifetime vs. minority excess carrier density depending on surface recombination velocity strength

3. EXPERIMENT

Samples used in this study are 1.5 Ω.cm p-type mc-Si as-cut wafers with 300 µm of thickness. All the wafers are adjacent and they were selected from the centre region of the same ingot. Firstly, they are chemically etched in NaOH: H_2O at 80 °C to remove the saw damage induced by slicing step followed by the Piranha etch clean process: H_2SO_4:H_2O_2 at 80 °C + HF and DI water rinse. Before lifetime measurements surface wafers were passivated by several ways: HF-dip and Iodine-Ethanol immersion passivation using a polyethylene bag, elaborating an n^+p floating junction through phosphorous diffusion characterized by a sheet resistivity of 250 Ω/□ and growing on the front and the rear surface sides of a 80 nm SiN_x layer in a Plasma Enhanced Chemical Vapor Deposition reactor. Lifetime measurements are performed using the quasi-steady-state photoconductance technique (*Sinton Consulting, WCT-120*). For the wet passivation measurements were implemented in the first 10 minutes.

4. RESULTS AND DISCUSSION

Measured apparent lifetime vs. minority excess carrier density curves obtained after each passivation method, are illustrated in the figure 2. We observe that the maximum excess carrier density (3.5×10^{15} cm^{-3}) has been reached with n^+p floating junction + 20 nm of thermally SiO_2 layer and the τ_{eff} at $\Delta n = 1\times10^{15}$ cm^{-3} reach 12.4 µsec. For I-E solution, HF Dip and SiN_x passivation, τ_{eff} measured values are respectively 8.2, 4.9 and 3.1 µsec. The maximum excess carrier density obtained with SiN_x is 7.5×10^{14} cm^{-3} and the given lifetime correspond to this value (Fig. 2).

On the other hand, the SiN_x layer does not give the best mc-Si surface passivation and regarding the shape of τ_{eff} (Δn) curves indicate that the traps activity is diminished for $\Delta n < 10^{14}$ cm^{-3} leading to a low apparent lifetime in low injection level region. To explain this behavior we suspect the formation of a new deep recombination centers at the Si/SiN_x interface during SiN_x deposition. The same behavior of τ_{eff} vs. Δn with SiN_x passivating layer was observed by Petres *et al*. [12], where the passivation quality of SiN_x layer was found lower than that of the thermally SiO_2.

The lifetime curve related to the SiN_x passivation (Fig. 2) cannot be explained by the recombination model described by Hornbeck-Haynes based on SRH recombination centers [13] which lead to a high apparent lifetime values in the region of low carrier injection as shown with samples passivated with n^+p junction (Blue curves). The lifetimes decrease in the carrier low injection level can be only attributed to another type of recombination centers. This phenomenon was observed and analyzed by Harder *et al.* and they propose a second type of trap states ‘recombination active trap’ [14].

In their study the lifetime measurements were performed using Photoluminescence (PL) technique compared by QSSPC one. In any case they not observed this behavior with QSSPC curves.

Using Hornbeck-Haynes model, the fit of measured lifetime curves allows us to estimate the SRV and the trap density of material after each type of passivation. In this model, the non recombinative traps N_t density is considered. The strength of the traps density alters the value of minority carrier injection level (Δn). In this case we obtain apparent carrier densities (Δn_{app}) which depend on several physical parameters: N_t, τ_t and τ_g which correspond to the traps density, trapping and emission time constants respectively. The carrier density related to the trapping phenomena is given by:

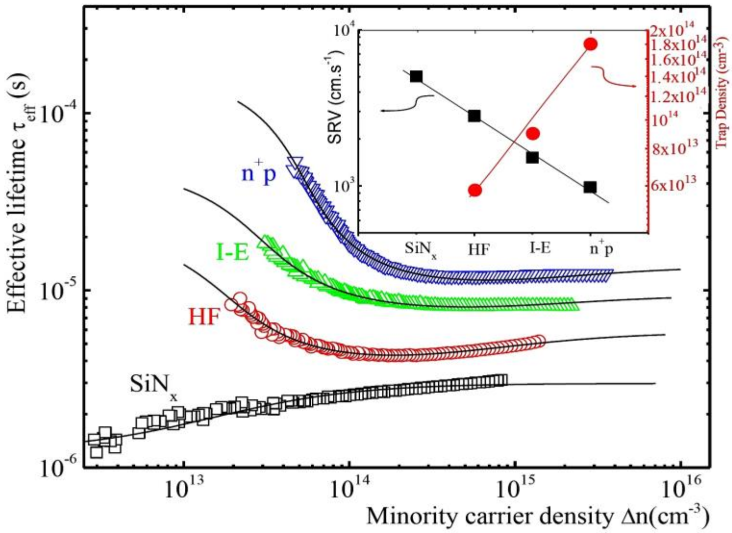

Fig. 2: Effective lifetime vs. minority excess carrier density corresponding to each passivation method

$$n_t = \frac{N_t \, . \, \Delta n}{\Delta n + N_t \dfrac{\tau_t}{\tau_g}} \tag{6}$$

And the apparent value off the excess carrier density is given by:

$$\Delta n_{app} = \Delta n_{av} + \frac{\mu_p}{\mu_n + \mu_p} n_t \tag{7}$$

During the measurement, the free electrons density and the conductivity are overestimated and the correct value of the effective lifetime vs. injection carrier density can be replaced by an apparent lifetime which is given by the following formulation taking into account the non-recombination traps:

$$\tau_{app} = \frac{1}{2N_t \, \tau_t/\tau_g} \left\{ \begin{array}{l} \tau_{eff} \left(N_t \dfrac{\tau_t}{\tau_g} + N_t \dfrac{\mu_p}{\mu_n + \mu_p} - \Delta n_{app} \right) + \\ \left\{ \left[\tau_{eff} \left(N_t \dfrac{\tau_t}{\tau_g} + N_t \dfrac{\mu_p}{\mu_n + \mu_p} - \Delta n_{app} \right) \right]^2 + 4 N_t \dfrac{\tau_t}{\tau_g} \tau_{eff}^2 \, \Delta n_{app} \right\}^{1/2} \end{array} \right\} \tag{8}$$

We can say that the term of the {eq. (6)}, play an important role in the determination of the measured lifetime and it is responsible on the high photoconductivity in the low carrier injection level as showed in the QSSPC measured curves. The electrons emission by the traps in P-type silicon wafer give a high photoconductivity in at low injection level regions ($\Delta n < 5\times10^{14}$ cm^{-3}). This behavior is not observed in the mono crystalline wafers which are traps free. In the case of the multicristallines substrates, this non-recombinative traps effect can be attenuated by using a bias light with a halogen lamp. Also someone use the photoluminescence PL light source to eliminate this phenomenon. In our experiment we have used the 2 msec. Xenon flash lamp and the obtained results are shown in the inset of figure 2. We note that the value of SRV decreases systematically with the passivation methods: SiN_x, HF, I-E and n^+p, while the trap density increases from 5.8×10^{13} to 1.8×10^{14} between the use HF and n+p method. QSSPC measurements with SiN_x layer show an excellent bulk neutralization of traps density and the apparent lifetime is not overestimated (Black curve) in the low injection region ($\Delta n < 10^{14}$ cm^{-3}) regarding the other passivation ways (Colored curves) which give lifetimes several orders greater than that measured at $\Delta n = 10^{15}$ cm^{-3} to avoid the traps effect on the photoconductivity.

A correlation between the measured lifetime and the calculated SRV indicates that the improvement lifetime is due to the good surface passivation. However, the measured lifetime is also a function of the bulk lifetime. So, to check if there is a change in the bulk lifetime with the performed passivation process, the {eq. (5)} was used to fit the four points of the apparent lifetime vs. SRV obtained for each passivation method; 9.4×10^2 $cm.s^{-1}$, with n^+p floating junction, 1.5×10^3 $cm.s^{-1}$ with I-E solution, 2.7×10^3 $cm.s^{-1}$ with HF immersion and 5×10^3 $cm.s^{-1}$ with SiNx layer (points in blue in figure 3).

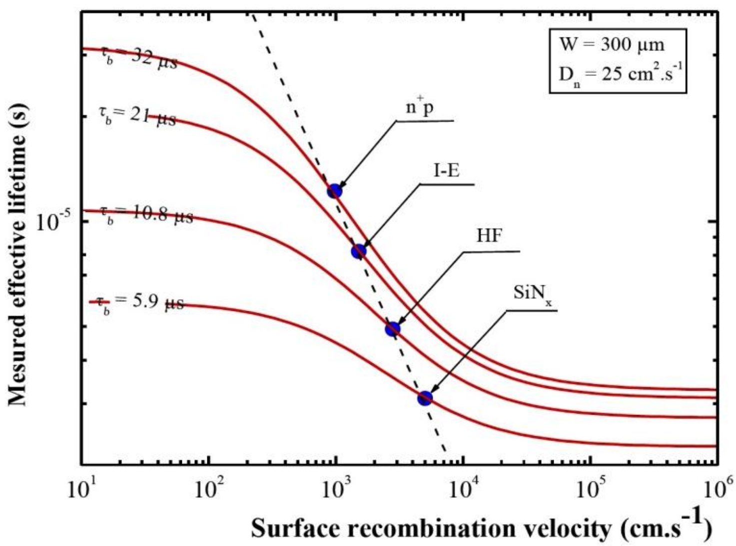

Fig. 3: Bulk lifetime values obtained from the fit of the four points of the effective lifetime vs. SRV for each passivation technique

The corresponding τ_b values of the processed mc-Si wafers are: 32 µsec, 21 µsec, 10.8 µsec and 5.9 µsec respectively. We found that is not possible to fit the four points with only one curve. Therefore, we have plotted a curve for each point associated to a fixed value of bulk lifetime, indicating that the bulk lifetime also changes with the SRV according to the passivation method. As a result, surface passivation has a direct impact on the SRV and the bulk lifetime as well as the trap density.

From the performed QSSVoc measurements on the mc-Si wafers with the different passivation ways, we have observed that the implied open circuit voltage values follow the effectiveness of the surface passivation during the lifetime measurements. For the SiN_x sample, the corresponding optical constant of 0.9 was considered. As illustrated in figure 4 and by extrapolation, the values of the implied voltage are respectively: 552, 582, 592 and 611 mV obtained with SiN_x, HF dip, I-E solution and n^+p floating junction passivation methods.

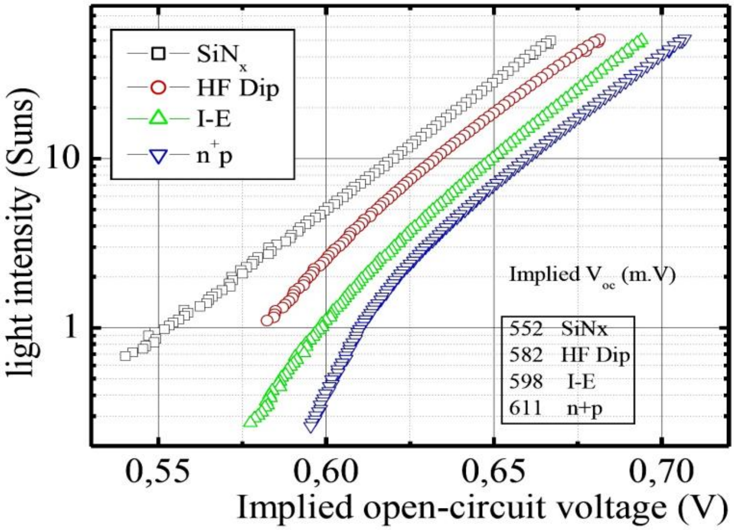

Fig. 4: Measured Implied voltage values correlated with passivation technique

These results prove the effectiveness of the used processes as shown in figure 2 and correlate between the increases of τ_{eff} from 3.1 µs to 12.4 µs. The physical meaning of the implied voltage is the electrical potential which can produce each wafer in the finished solar cell.

5. CONCLUSION

In this work we have examined the behavior of the carrier minority lifetime vs. excess carrier on the HEM multi crystalline wafers using the QSSPC technique under different surface passivation conditions. The chemical surface pre-clean of the silicon wafer is a critical parameter and affects the τ_{app} measured values via the passivation quality.

We have observed that the wet chemical surface passivation like the Iodine Ethanol solution and the HF Dip are considerably altered by the surface clean with and without piranha etch step. In such case the I-E solution gives the correct τ_{app} value for the bare Mc-Si wafers.

Also bulk lifetime of the processed wafers is determined using QSSPC τ_{app} measurement and the τ_b values corresponding to 32 µsec (n^+p floating junction), 21 µsec (I-E), 10.8 µsec (HF dip) and 5.9 µsec (SiNx) are extracted using fitting curves of the effective lifetime vs. surface recombination velocity.

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