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Use of low-doped emitters in the characterization of silicon wafers

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ABSTRACT
This work has as main objective the qualification of the silicon used as a substrate in the manufacture of solar cells, through the technique of photoconductive decay (technique widely used in the sectors of research and industrial production of this type of devices).
The use of this technique together with the passivation of surfaces, through the formation of low doped phosphorus emitters (n+pn+ structure), allows the extraction of parameters that will assist the process engineer in the tasks of simulation and theoretical-experimental optimiza-tion of the steps that make up the complete manufacturing process.
The samples, processed in open tube furnaces through the pre-deposition of phosphorus (liquid source of POCl3) followed by oxidation in chlorinated environment (by means of TCA), are characterized with the WCT-100 "Lifetime Tester" equipment, for its effective lifetime (τ_{eff} - transient and quasi-static modes).
Using the data of the inverse of the lifetime as a function of the concentration of carriers, infor-mation is obtained regarding the volume of the material and the phosphorus emitters formed, thus enabling the analysis of the quality of the material and fundamental stages of the manufacturing process.

Keywords: Lifetime measurement, Photoconductance, Surface passivation, Material characterization, Emitter recombination current.

1 INTRODUCTION

The characterization and monitoring of the lifetime of minority carriers in silicon wafers are of fundamental importance for verifying the quality of the material to be used, optimizing the steps and controlling solar cell manufacturing processes. As described, in more detail by Cuevas et al. (2004), there are two basic methods to obtain the lifetime using the WCT-100 Lifetime Tester, depending on the way in which excess carriers (electrons and holes) are generated in semiconductor.

One of them consists in the analysis of photoconductance in wafers submitted to an extremely short light pulse (tens of microseconds, according to Sinton (1996), (1999)), called transient method, through which the decay rate of minority carriers is measured (Δn, in the case of a substrate of type p) obtaining its effective lifetime (τ_{eff}) through Eq. (1):

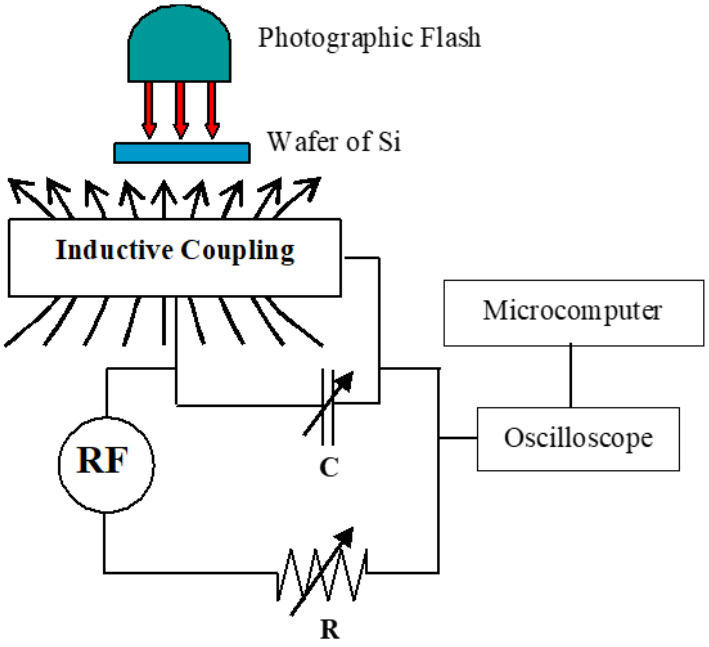
$$\frac{d\Delta n}{dt} = -\frac{\Delta n}{\tau_{eff}} \qquad (1)$$

Through a longer pulse (on the order of milliseconds), quasi-static method, a generation rate (G_L) constant or approximately constant so that the balance between generation and recombination allows the calculation of the effective lifetime, using the Eq. (2):

$$G_L = \frac{\Delta n}{\tau_{eff}} \qquad (2)$$

The determination of the excess concentration of minority carriers, Δn, is performed by measuring the photoconductance of the sample (σL) as a function of the incident luminous intensity. Through an RLC circuit, schematized in Fig. 1, fed by a radio frequency source (10MHz), with the sample located on the inductor, a voltage signal proportional to its conductivity in the dark is obtained. In this way the flash trigger, which generates an increase in the concentrations of carriers ($\Delta n = \Delta p$), causes a change in the conductivity of the wafer that, converted into voltage, can be measured, and collected through a digital oscilloscope and transferred to a microcomputer for further data processing. The measurement of the luminous intensity incident on the sample is obtained through a calibrated solar cell, located in the same plane and next to the wafer under study, through channel 2 of the oscilloscope.

Figure 1 - Schematic diagram of the WCT-100 apparatus with data acquisition system.



The relationship between the photoconductance, measured by the circuit, and the excess of photogenerated carriers in the volume of the wafer is given by the Eq. (3):

$$\Delta\sigma_L = (\mu_n \Delta n + \mu_p \Delta p) qW = qW\Delta n(\mu_n + \mu_p) \quad (3)$$

where q, W, μ_n and μ_p *represent, respectively, the electric charge, the thickness of the sample and the mobility of the carriers (electrons and holes).*

The total flux of photons incident on the surface of the sample (N_{ph}), measured through the solar cell, converts to generation by volume through the Eq. (4), considering the absorption coefficient (f_{abs}) of silicon and the intensity transient of the light source:

$$G_L = N_{ph} f_{abs} - W \frac{d\Delta n}{dt} \quad (4)$$

Thus, from the Eq. (2) one can obtain a single generalized expression (Eq. (5)) which includes the two traditional definitions for determining lifetime, the transient and the quasi-static:

$$\tau_{QSSPC} = \frac{\Delta n W}{N_{ph} f_{abs} - W \frac{d\Delta n}{dt}} \quad (5)$$

The validity of Eq. (5), as described by Nagel et. al (1999), does not depend on the duration of the light pulse, in transient or quasi-static mode, and the lifetime of the minority carriers in the sample volume. Still, one should consider the assumption of a uniform generation within the volume of the wafer that can be obtained through high-quality surface passivations or thicknesses smaller than the diffusion length of the carriers ($W << L_{dif}$). Measurements outside this condition can lead to a decoupling between the transient and quasi-static curves, obtained for various injection levels.

1.1 LIFETIME COMPONENTS

The effective lifetime obtained through the procedure described above can then be analyzed for its volumetric and surface components (Eq. (6)) as described in the works of Kane et. al (1985) and Cuevas (1999), for samples passivated by means of light phosphorus depositions:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + 2\frac{J_{0e}(\Delta n + N_A)}{qni^2 W} + (B\Delta n + C_A \Delta n^2) \quad (6)$$

where τ_{bulk} is the lifetime, at low injection, of the minority carriers in the sample volume, $2J_{0e}$ the component of the recombination current density of the formed emitters (front and posterior surfaces), N_A *the* doping of the material, in this case p type, C_A *and* B the *coefficients related to the Auger and radiative recombination respectively.*

Through Eq. 6, a chart of $1/\tau_{eff}$ as a function of Δn, after subtraction of the components (Auger + Radiative), under conditions of high injection at the base presents a line, whose angular coefficient is related only to the recombination in the diffused regions, revealing the value of the recombination current density produced by the formed emitters.

2 EXPERIMENTAL PROCEDURE

The precise determination of the lifetime of the material volume from the components of the effective lifetime (volume, surface(s) – if not doped, emitter(s)), through the QSSPC/PCD technique requires minimization of surface recombination. Among the passivation techniques we can mention those obtained by means of thermal steps (oxidations or light diffusions), wet chemical passivation, nitriding, etc.

However, the realization of thermal steps, necessary in the manufacture of devices and the formation of passivating layers, can lead to degradation of the material used.

As an alternative to thermal passivation processes, one can use dilute hydrofluoric acid, an effective passivator of surfaces, according to Yablonovitch et. al (1992). Thus, we opted for the use of HF to characterize the lifetimes in the sample volume, according to the procedure described by Lago et. al (2000 and 2001) for measurement and calibration of WCT-100 equipment, in this new condition. Although destructive in manufacturing stages other than the initial one, and relatively dangerous, this method can be used to evaluate the condition of the material before high-temperature processes.

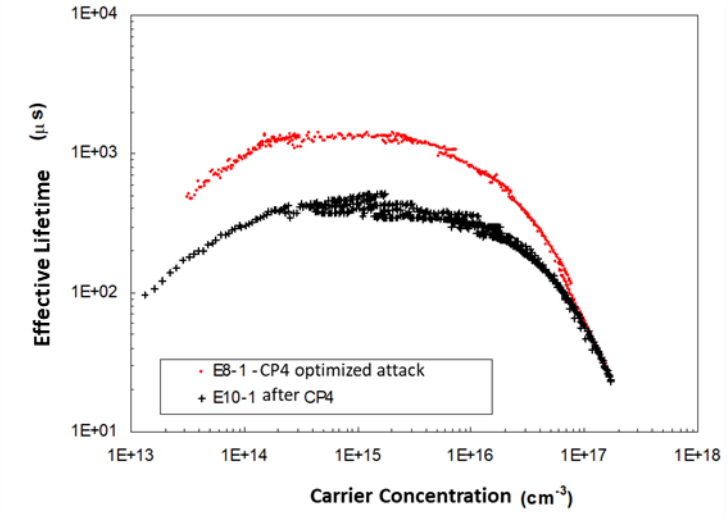
On the other hand, high-quality surface passivations, through light phosphorus diffusions, prepare the way for the characterization of several fundamental steps in the manufacture of high-efficiency solar cells.

Thus, in the work developed here we used a silicon wafer of 4" diameter, FZ, with resistivity of 25Ωcm doped with boron and orientation <1 0 0>. The wafer had one of the surfaces polished and the other chemically etched with an initial thickness of 300μm. After the CP4 attack procedure, aiming to reduce superficial imperfections, the E10-1 sample of area (3.9 x 3.9)cm^2 presented a thickness of 272μm. Most of the times, and depending on the manufacturer of the silicon wafer, this polishing step, although not optimized, becomes necessary in the characterization of the lifetime using HF as a passivating agent.

Before each process, including measurement in HF, samples are subjected to complete RCA cleaning (removal of organic and metallic compounds) using MOS grade or higher chemicals.

The graph in Fig. 2 shows the results of the measurement of the effective lifetime of samples E8-1 and E10-1 passivated in HF, after attack optimized in CP4 and not optimized, respectively. It can be observed that higher values of lifetime (~1ms), can be obtained through an optimization of the attack time in CP4.

Figure 2 - Measurement of the effective lifetime of the samples E8-1 and E10-1 (FZ, p-type, ρ = *25Ωcm)*, immersed in HF.



After this measurement, the sample was submitted to a pre-deposition of phosphorus at 850ºC, resulting in a leaf resistance of 1.4kΩ/□, followed by removal of PSG in HF and redistribution of phosphorus/passivating oxidation in chlorinated environment (TCA) at 1050ºC. An R□ = 400Ω/□ was obtained under an oxide with a thickness of 226nm.

In the last step of the process, 107nm of aluminum was deposited on each side of the sample with subsequent annealing at 450ºC, in an 8% hydrogen environment in nitrogen ("forming gas alneal "). The "alneal" technique allows to improve passivation by decreasing the density of interface states (dangling bonds) due to the release of atomic hydrogen, from a reaction with residual water molecules, present in the oxide, and Al according to Aberle (1999).

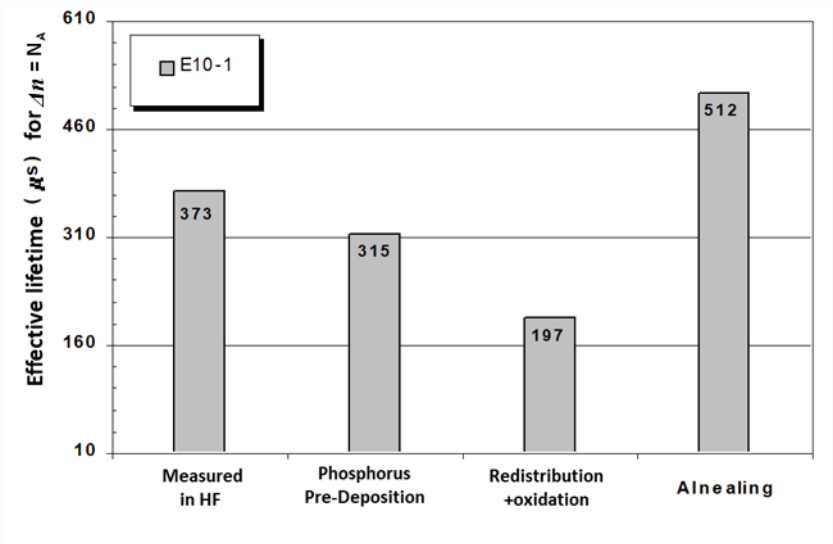
It is noteworthy that during the pre-deposition stage of phosphorus, low-cost oxygen, industrial standard (without qualification), and nitrogen obtained from a liquid N_2 storage tank were used. In the oxidation step with TCA, special, higher cost oxygen 2.8 (99.8% purity) was used.

From the transient and quasi-static techniques (QSSPC/PCD), and aiming at a better characterization of the recombination parameters and consequently the analysis of the process, a scan was performed in a wide range of injection levels, $\Delta n = 3x10^{12}cm^{-3}$ up to $7x10^{16}cm^{-3}$.

2.1 RESULTS

Fig. 3 shows a graph with the evolution of the effective lifetimes of sample E10-1, obtained after each processing step for a level of injection of carriers equal to the doping of the base ($\tau_{eff} \rightarrow \Delta n = N_{A=5,4x10^{14}cm^{-3}}$).

3 – Evolution of the lifetime of the sample E10-1 (FZ, *type p*, ρ = 25Ωcm), collected at the injection level equal to the doping of the base.



As expected, a decrease in the value of the effective lifetime can be observed along the stages of pre-deposition and redistribution of phosphorus in relation to the initial measure, with passivation in HF.

It is worth mentioning here, although evident due to the very process of formation of the emitters, the increase in recombination between the stages of pre-deposition of phosphorus ($J_{0e}=2.09x10^{-14}$A/cm^2) and after redistribution/oxidation ($J_{0e}=12.10x10^{-14}$A/cm^2), situation in which the emmiters are formed. At the same time, a value of $J_{0e}=4.56x10^{-14}$A/cm^2 for each emitter after the annealing step ("alneal").

As can be observed using a passivation process based on light phosphorus diffusions, 512us of lifetime is obtained at the end of the procedure, a value higher than that initially obtained with the sample immersed in HF. It is worth mentioning from the result obtained, the excellent quality of the process used, considering the various thermal and chemical cleaning steps to which the sample was submitted, combining with the use of industrial oxygen during the stage of pre-deposition of phosphorus.

This result configures, therefore, the use of light phosphorus diffusions as an excellent procedure for the characterization of initial material, in addition to providing conclusive information on the preservation of the lifetime throughout manufacturing processes of high-efficiency devices

using technologies not dependent on mechanisms of trapping impurities (gettering) through phosphorus or aluminum.

3 CONCLUSIONS

A material characterization method based on passivation of surfaces through light phosphorus diffusions is used, together with QSSPC/PCD analysis techniques. The information obtained allows an evaluation of the material as well as its behavior throughout a 'simplified' manufacturing process, since procedures like those that make up the manufacturing process of complete devices are used. This includes: chemical cleanings, pre-deposition and redistribution of dopants, oxidation, metallization and annealing, (although some are limited to intermediate values, as in the case of the leaf resistance of the emitters).

The maintenance of the lifetime at high values, after each thermal process, assumes fundamental importance in the development of high-efficiency cells without the need to trap impurities, such as PERL devices, PERC, and bifacial cells.

The achievement of a high final effective lifetime (τ_{eff} = 512μs, for $\Delta n = N_A$), higher than that obtained in HF and prior to the thermal steps, proves the effectiveness of the processes involved and previously mentioned.

Although the structure analyzed does not correspond to that of a finished solar cell (however very close) one can use the implied open circuit voltage as a figure of merit of the material/process set. So under conditions of 1 Sun illumination, the analysis of the effective lifetime curve ($\tau_{eff} = \tau_{bulk}$)| 1 sun allows to obtain an open circuit voltage of Voc = 642mV (implied Voc).

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