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NEUTRON ACTIVATION ANALYSIS IN A SOLAR CELL FABRICATION PROCESS

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ABSTRACT

In the last decade the photovoltaic market presented an exponential growth causing an increase in the silicon demand. Silicon solar cells have been obtained in most cases in crystalline wafers, either multicrystalline or monocrystalline. However, the shortage in the silicon feedstock has imposed the necessity of development of new materials such as solar grade silicon (higher impurity concentration) and of improvement of the fabrication process technology, becoming imperative the development of initial material characterization techniques.
In this work, samples of FZ silicon with 25Ω.cm resistivity were characterized just after two steps of the solar cell fabrication process: the initial cleaning and oxidation using two different techniques of analysis: Photoconductive Decay (PCD) and Instrumental Neutron Activation (INAA).
The PCD technique characterization allowed to qualify the bulk lifetime of oxidized samples, τ_{bulk}, about 1ms and the surface recombination surface velocity, $S_{eff-max}$, about 10.8 cm/s, showing the good quality of the initial material and the obtained passivation layer.
In sequence, the Instrumental Neutron Activation Analysis (INAA) characterization showed that the impurity concentrations were kept practically the same just after cleaning and just after oxidation, corroborating the found results of the PCD characterization, and therefore, showing the suitability of the application of INAA, a nuclear analytical technique, which allows a qualitative monitoring of a solar cell fabrication step.

1. INTRODUCTION

The growing energy world demand, the oil price variations due to economical and geopolitics interests, and the higher concerns on pollutant residues launched to atmosphere have increased the use of renewable energy sources. The photovoltaic energy is among the most important sources, presenting an exponential growth of photovoltaic installations in the last ten years [1].

Considering the photovoltaic installed systems, it can be noticed that about 90% of the used solar cells are processed with crystalline silicon, being either multicrystalline (53% mc-Si) or Czochralski monocrystalline (37% Cz - Si) [2]. However, as a consequence of the increase in the demand, there has been a shortage in the silicon feedstock, forcing the industries to find out new alternatives such as working with thinner crystalline wafers [3], developing materials as “solar grade silicon” (SoG-Si) and others. In turn, the use of materials with

different characteristics and different purity grades (float zone - FZ, Cz, mc, SoG) have also required research investments and developments in the solar cell fabrication processes, becoming a virtuous cycle where the main objective is cost reduction [3] keeping the efficiency at acceptable values for photovoltaic applications.

At this work the starting material characterization is performed using two different techniques: Photoconductive Decay (PCD) and Instrumental Neutron Activation Analysis (INAA). Firstly, high quality material, FZ and p-type silicon, with 25Ω.cm resistivity and 270μm thickness, was chosen in order to put into evidence the bulk lifetime degradation due thermal treatments.

The photoconductive decay technique (PCD) has been performed allowing evaluating the quality of surface passivation and the bulk lifetime before and after thermal oxidation.

However, as widely known, the bulk lifetime is straightforwardly related to the recombination centers introduced by impurities, which come either from the initial material or from the several steps required for the solar cell fabrication (RCA initial cleaning, oxidation, phosphorus diffusion, aluminum evaporation annealing and others). Specially, during the oxidation process, when silicon is submitted to high temperatures for a long period, some impurities can migrate to the bulk due to their high diffusion coefficients [4,5], consequently degrading $\tau_{bulk.}$ Meanwhile, some of them can remain on the surface, and other ones are trapped at the oxide interface, increasing the interface state density and therefore, the surface recombination velocity [6].

Thus, in order to analyze the impurities that were incorporated during the thermal oxidation step, the samples were also characterized by Instrumental Neutron Activation Analysis (INAA) before and after the thermal treatment.

2. EXPERIMENTAL

2.1. Sample processing

Aiming to remove possible contaminants on the surface, the samples were undergone to an optimized chemical etching [7], and characterized by PCD technique using a chemical passivation (HF).

Then, the samples with different areas 8.41cm^2 (for PCD measurements) and 2.25cm^2 (with about 150mg mass for INAA analysis) were cleaned with the standard initial RCA cleaning using upper grade chemical reagents [8]. In sequence, the samples, E-10-2 and EP2, were oxidized together in chlorine ambient (TCA) under 1150°C temperature, providing suitable films, not only for passivating surfaces, but also for oxide mask use in the solar cell fabrication with planar technology. In order to minimize the contribution of the surface recombination, the samples were also submitted to a hydrogenation process known as alneal.

2.2. Photoconductive Decay Technique

The photoconductive decay technique is a contactless technique able to measure the effective minority carrier lifetime (τ_{eff}) as function of the excess carrier density Δn, generated by optical excitation.

In order to perform the measurements the WCT-100 Lifetime Tester equipment from Sinton Consulting [9] was used. In this equipment, a flash lamp pulse insides over the sample and a calibrated solar cell at the same time, then the carrier concentration decay in the sample is measured as voltage variations of a RF bridge (10MHz), while the calibrated solar cell is used to determine the light intensity over the sample. An oscilloscope registers the data that are stored in a computer for future analysis.

The measured effective lifetime, τ_{eff} as function of the excess carrier concentration is known to be dependent on frontal and rear surface recombination velocities, $2S_{eff}$, sample thickness, W, and bulk lifetime, τ_{bulk}, determined by the expression (1).

$$\frac{1}{\tau_{eff}} = \frac{2S_{eff}}{W} + \frac{1}{\tau_{bulk}} \quad (1)$$

Thus, in order to extract some information about the bulk lifetime in the analyzed sample, it is imperative to minimize the surface recombination velocity by passivating the surfaces, either using chemical passivation with HF [7], thermal oxidation [8], light diffusion (n^+pn^+ structures) [7] or silicon nitride.

At this work two types of surface passivation were chosen: chemical passivation with HF and thermal oxidation. The former type allowed the qualification of the effective lifetime of the starting material, τ_{eff}, with no thermal process, and the latter one allowed obtaining information about the effective lifetime just after the thermal process (oxidation) and just after the hydrogenation technique (alneal).

2.3. Instrumental Neutron Activation Analysis

In the INAA technique, samples and elemental standards are irradiated in a reactor thermal neutron flux and the induced gamma ray radioactivities is measured by gamma ray spectrometry in order to qualitative and quantitatively determine the elements of interest.

In this study, the elements As, Br, Ca, Co, Cr, Fe, Na, Se, W and Zn were investigated as trace impurities in FZ silicon, before and after the thermal treatment typically used for solar cell fabrication.

The INAA characterization was performed in two samples: just after the initial cleaning and just after oxidation. About 150 mg sample mass was irradiated with elemental standards and blanks at the IEA-R1 Nuclear Research Reactor of IPEN under a thermal neutron flux of 1.5 x 10^{12} n cm^{-2} s^{-1} for a 16 h period. The induced radioactivity was measured using a CANBERRA GX 2020 detector with associated electronics. The resolution for the 1322 keV gamma ray of ^{60}Co was 1.70 keV.

After a 3-day decay period, the induced radiation in samples and standards was measured in a gamma ray spectrometer for 1 h (standards) and 4 h (samples). In this first measurement, the elements As, Br, Ca, Na, and W were analyzed.

After a 15-day decay period, a new measurement was performed. Standards and samples were measured for 2 h and 10 h periods, respectively. In this second measurement, the elements Co, Cr, Fe Se e Zn, with longer half-lives were evaluated.

Limits of detection (LDs) were calculated taking into account the background baseline of gamma ray spectra in the energy region of each element, according to Currie [10] for the irradiation and measurement conditions described above.

3. RESULTS AND DISCUSSION

3.1. PCD Characterization

Figure 1 shows a comparison of the effective lifetimes measured for the carrier excess concentration ($\Delta n=5.4x10^{14}cm^{-3}$) measured in sample E-10-2 in three different conditions: a virgin sample, just after oxidation and just after alneal process.

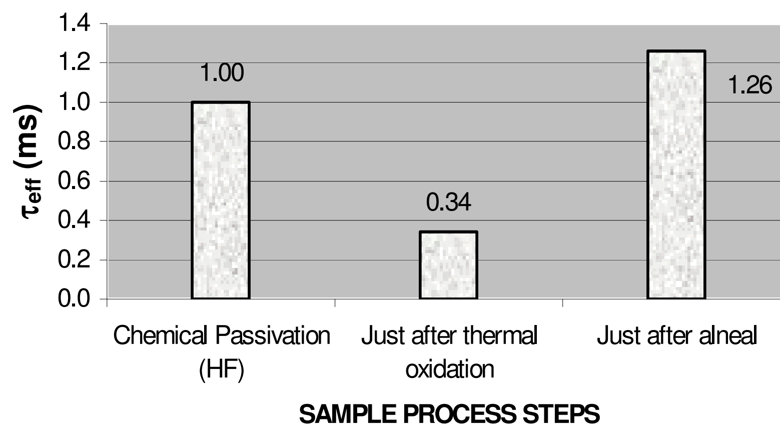

Figure 1: Comparison between the measured effective lifetimes, τ_{eff} measured in sample E-10-2 before and after thermal treatment.

According to the obtained results the effective lifetime, τ_{eff} found in the virgin samples could be totally recovered in the samples with thermal oxidation followed by alneal process. This fact allows inferring that the thermal treatment is not degrading significatively the bulk lifetimes of the samples after the high temperature process.

On the other hand, aiming to qualify the surface passivation, an upper bound for the surface recombination velocity, $S_{eff-max}$ was calculated by the assumption that the τ_{bulk} is high enough, so that the surface recombination is the main component in the measured τ_{eff} ($S_{eff-max}=W/(2x\tau_{eff})$). This calculus could demonstrate a high quality surface passivation showing that the maximum surface recombination velocity that could be attributed to the sample after oxidation was about 10.8m/s (typically obtained in high efficiency solar cells).
Meanwhile, taking into account that a p-type silicon with 25Ω.cm resistivity due to Auger

and Radiation effects in the semiconductor presents a 85ms lifetime, a lower bound to the bulk lifetime ($1/\tau_{bulk}=1/\tau_{Auger}+1/\tau_{radiation}+1/\tau_{SRH}$) could be extracted considering only the Shockeley-Read-Hall (SRH) contribution. The lower bound bulk lifetime, $\tau_{bulk-min}$ found at the last step of the sample processing (oxidation followed by alneal) was about 1.28ms, representing the lower value that can be associated to the effective lifetime, τ_{eff} measurement, and therefore, showing a high potentiality for solar cell fabrication.

Thus, the initial cleaning and thermal oxidation steps were characterized by PCD being demonstrated that it is possible to obtain high quality passivation of the p-type silicon surface and the bulk lifetime could be preserved after the thermal treatment (in chlorine ambient) followed by alneal technique.

3.2. Instrumental Neutron Activation Analysis Results

As mentioned previously, in order to evaluate the impurity traces before (sample EP1) and after thermal treatment (sample EP2, oxidized together to E-10-2), the Instrumental Neutron Activation Analysis characterization was performed. A list of the analyzed elements and their correspondent limit of detection, LD is presented at Table 1.

Table 1. Impurity content and LD in two FZ-Si samples obtained by INAA, $\mu g\ g^{-1}$

Element	EP1 (after cleaning)	EP2 (after oxidation)	LD
As	ND[a]	ND	1.5×10^{-3}
Br	0.10 ± 0.01	0.16 ± 0.01	7.6×10^{-3}
Ca	ND	ND	1.6
Co	ND	ND	2.6×10^{-3}
Cr	ND	ND	13×10^{-3}
Fe	ND	ND	1.6
Na	ND	ND	1.4
Se	ND	ND	1.6×10^{-4}
W	ND	ND	6.2×10^{-3}
Zn	ND	0.13 ± 0.02	0.066

[a.] non detected, concentration lower than LD.

According to this table, most of the analyzed element concentrations were practically not altered after the thermal treatment, corroborating the PCD results where the initial effective lifetime could be completely recovered, as shown in Figure 1. Meanwhile, the small changes in Zn and Br concentrations detected at sample EP2 by INAA did not cause significant changes in the bulk lifetime, as shown by the PCD characterization (see Figure 1).

Another remarkable point is that due to the low concentration of the analyzed elements in the starting material only a qualitative analysis of the process was performed since most of element concentrations are lower than the respective limits of detection. However, if a starting material with lower grade of purity such as multicrystalline and solar grade silicon was considered instead of FZ silicon, this technique could help monitor the development of the devices more accurately.

4. CONCLUSIONS

By using the PCD characterization it was demonstrated that even after thermal oxidation in chlorine ambient the wafer had a high quality surface passivation and the bulk lifetime preserved.

Aiming to associate the measured bulk lifetime with PCD to the impurity concentrations incorporated during the process, the INAA was performed, showing no significant changes after the thermal process, as predicted by the PCD characterizations.

Despite, the impurities in the FZ-Si samples have been analyzed only qualitatively by the INAA; it would be possible to determine the impurities by changing the experimental conditions such as use of longer irradiation periods and gamma ray detectors of higher efficiency. Moreover, this analysis is an important tool for starting materials with higher impurity concentrations such as multicrystalline and solar grade silicon.

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