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REDUCED EFFECT OF B-O DEGRADATION ON MULTICRYSTALLINE SILICON WAFERS

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ABSTRACT: The quality of multicrystalline wafers is improving nowadays due to ingot and solar cell process optimisation. In the near future the effect of boron-oxygen (BO)-related light induced degradation could become perhaps as important for multicrystalline wafers as it currently is for monocrystalline Czochralski (CZ) wafers. In this paper boron-oxygen light induced degradation is investigated for multicrystalline silicon wafers. A special measurement procedure is required due to the presence of interstitial iron in mc-Si wafers. The degraded lifetime of the mc wafers in most cases is at the upper limit of the degraded lifetime experimentally determined by Bothe et al on CZ wafers. It is found that in mc-Si, in the presence of high carbon concentration (>8 ppma), this proposed lifetime limit is even exceeded. This implies a reduced effect of the BO defect and a new higher limit for the degraded lifetime, in the presence of carbon.

Keywords: lifetime, degradation, defect density.

1 INTRODUCTION

In the last decade several attentions are given to the light induced degradation (LID) of Czochralski (CZ) grown monocrystalline silicon wafers. The high oxygen content coming from the silica crucible together with the p-type Boron doping is responsible for the formation of Boron-oxygen (BO) compounds. These compounds form under illumination or when the samples are injected with charge carriers. The recombination activity of BO is enhanced respect to the one of the separate elements (oxygen and boron). The initial efficiency can be reduced up to 10% relative under illumination [1]. This is the reason why they are so detrimental under solar cell operation. Several studies have shown that this effect is the results of an increase recombination due to the formation of defect correlated to the interstitial oxygen and boron concentrations [2-4]. The initial efficiency can be fully restored with an annealing step at about 200 °C.

Also in case of multicrystalline silicon wafers the conditions for the happening of this detrimental effect are present: boron doping and oxygen presence. However there are other effects that make LID not dominant: i) the different growing technique, resulting in less oxygen concentration in multi wafers, and ii) the presence of other defects with higher recombination (i.e. metal impurities, carbon, crystal defect and grain boundaries).

The quality of multicrystalline wafers is improving nowadays due to ingot and solar cell process optimisation (gettering and hydrogenation). This mean that in the near future the effect of BO LID could became important also for multicrystalline wafers.

Another consideration is that new feedstock made of small particles can higher the concentration of oxygen in the ingot.

In this work we quantify the effect of BO LID in multicrystalline silicon wafers with different amount of oxygen and compare them to the effect created in monocrystalline Czochralski (CZ) wafers.

2 APPROACH

The appropriate parameter for the study of the BO defect formation is the normalised defect concentration N_t^*. N_t^* is defined as the difference between the inverse of the effective lifetimes before and after light degradation for a time t:

$$N_t^*(t) \equiv \frac{1}{\tau_{eff}(t)} - \frac{1}{\tau_{eff}(0)}, \qquad \text{Eq. 1}$$

For $t \to \infty$ $N_t^*(\infty) \equiv N_t^*$ represents the normalised defect density in a full degraded state.

All the samples investigated receives a polishing etch and a silicon nitride surface passivation at low temperature in order to study the recombination in the bulk. Before the LID the samples were annealed at 180 °C for 120 min in order to dissociate the BO complex eventually present.

The effective lifetime is measured by the QSS-PC method. The recombination in the bulk is the sum of different recombination. We schematised them as light sensitive recombination (τ_{LS}) and not light sensitive recombination (τ_{NLS}).

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{LS}} + \frac{1}{\tau_{NLS}}, \qquad \text{Eq. 2}$$

The recombination not light sensitive does not change after light soaking. Thus this term is annulled in the Eq.1.

In case of monocrystalline silicon wafers the LS recombination is due to the BO complex formation [4]. The number of defect is therefore determined from the Eq. 1. It has been shown that N_t^* is roughly proportional to the boron concentration N_{dop} and the square of the interstitial oxygen concentration O_i [4].

The investigation of the BO-related defect in multi-crystalline silicon (mc-Si) is complicated by the presence of interstitial iron Fe_i (typical concentrations are ~10^{11}-10^{12} cm^{-3}). At room temperature, the Fe_i forms meta-stable pairs with substitution boron. Illuminating or heating the sample will cause the FeB pairs to dissociate, resulting in an additional change of the effective lifetime [5]. The combined effect of FeB dissociation and BO-defect formation is shown in Fig. 1, where the injection-dependent lifetime curves are presented for a mc-Si wafer before and after optical dissociation steps of increasing

duration. The change in the $\tau_{eff}(\Delta n)$ dependence before illumination and after 2 min of illumination is the result of the dissociation of FeB pairs, leading to an increase of τ_{eff} for $\Delta n > 2\times10^{14}$ cm^{-3}. The decrease of τ_{eff} with increasing illumination time results from the BO-defect formation.

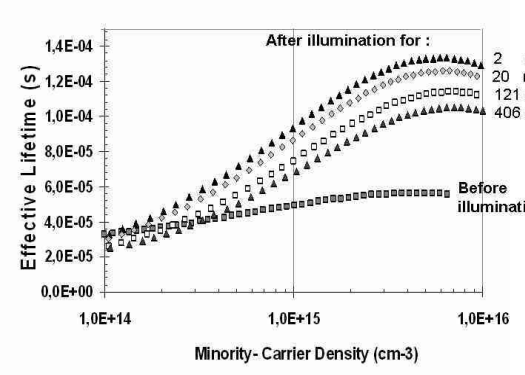

Figure 1: Effective lifetime versus the injection level Δn before and after illumination for different duration.

Since τ_{eff} results from the contribution of all the recombination channels present in the sample:

$$\frac{1}{\tau_{eff}}(t) = \frac{1}{\tau_{other}} + \frac{1}{\tau_{Fe_i}} + \frac{1}{\tau_{FeB}} + N_t^*(t), \qquad \text{Eq. 3}$$

It is very important to keep the contribution of the first three terms the same for all the measurements. This was done by measuring τ_{eff} after a fixed time interval of 45 seconds after switching-off the lamp. In this case the FeB and Fe_i concentration is kept constant and thus the corresponding recombination (lifetime). Furthermore, the assumption was made that the term $1/\tau_{other}$ was not affected by the illumination step.
In the curves presented in Fig. 1, which were all taken with this fixed delay time of 45 seconds after switching off the lamp, a clear decrease in τ_{eff} with increasing illumination time can be observed, resulting from the formation of the BO defect. The influence of illumination on both the FeB and BO related defects are demonstrated in Fig 2.

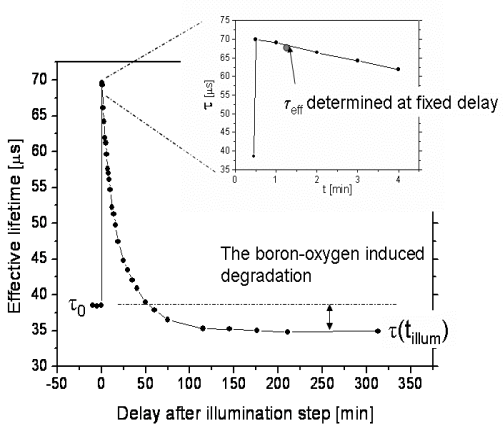

Figure 2: Effective lifetime versus the delay time after switching off the lamp, determined at an injection level $\Delta n = 1\times10^{15}$ cm^{-3}. At t=0 the sample has been placed in the dark after having been illuminated with a halogen lamp with intensity I=330 mW/cm^{-2} for 100 min.

In this graph, τ_{eff} at a fixed injection level $\Delta n = 1\times10^{15}$ cm^{-3} is presented versus the delay time after a 100 minute illumination step. The sharp increase in the lifetime is due to the FeB pair dissociation. As the FeB pairs start to re-pair, the lifetime decreases. The formation of the BO-defects during the 100-minute illumination, however, causes the lifetime to stabilize at a new lower value τ_{eff} (t), where t is the illumination time. For highest sensitivity in measuring the change in the effective lifetime as a result of the formation of the BO-related defect, the offset given by $1/\tau_{other}$ (in Eq. 3) is kept as small as possible. To this end, τ_{eff} (t) was determined at an injection level of $\Delta n = 1\times10^{15}$ cm^{-3}, where τ_{eff} is much higher than for instance at the cross-over point $\Delta n \sim 1\text{-}2\times10^{14}$ cm^{-3} (see Fig. 1).
The surface of the Si wafers was passivated with a PECVD-deposited silicon-nitride layer. This layer is optimised for as deposited surface passivation. The passivation properties under illumination were investigated with the use of a FZ wafer. This FZ wafer showed a lifetime decrease under illumination that was much larger than what can be expected on the basis of its maximum oxygen content ($[O_i]$ max ~0.5×10^{17} cm^{-3}) and the lifetime did not recover after an annealing step around 200 °C. Therefore the decrease in τ_{eff} was attributed to a degradation of the SiNx . This surface degradation was used to correct the BO defect density calculation for mc-Si and CZ samples Fig.3.

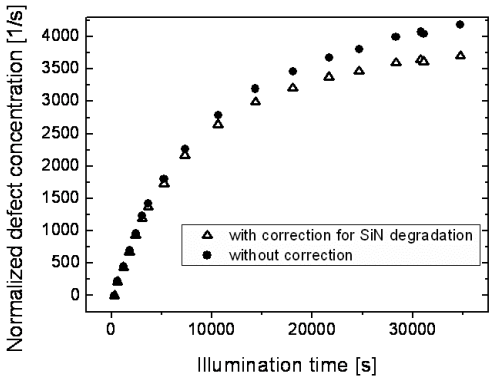

Figure 3: $N_t^*(t)$ for a mc-Si wafer. The correction for the degradation of the silicon nitride is also shown.

2.1 Sample selection

A set of multicrystalline silicon wafers with interstitial oxygen concentration in the range 1.5-5.6×10^{17} cm^{-3} and different carbon concentration (2-10 ppma) is used for this investigation. The oxygen and carbon concentration was determined with FTIR spectroscopy. The boron concentration was calculated by resistivity measurements. Neighbouring samples were used to verify the presence of thermal donor (TD). Since thermal donor can be electrically active, the dopant concentration N_{dop} determined by resistivity measurements is equal to the substitution boron concentration $[B_s]$ in absence of TDs. To check for the presence of TDs, the resistivity was measured before and after an annealing step at 700 °C for 30 min. Since a significant effect from thermal donors has not been observed the substitution boron concentration was taken to be equal to the doping concentration. In the samples

analysed the doping concentration (N_{dop}) is in the range $0.8\text{-}1.3\times10^{16}$ cm^{-3}.

In order to verify this approach two CZ samples were prepared and measured in the same conditions.

3 BO-DEFECT CONCENTRATION

In Fig. 4 N_t^*/N is plotted versus the oxygen concentration. The solid line represents the inverse degraded lifetime derived from the empirical equation as described by Bothe et al [2] for monocrystalline CZ wafers. It is calculated with the average doping concentration of the mc samples investigated. The inverse degraded lifetime represents the metastable defect density in case other recombination can be considered negligible. The measured defect densities determined for multicrystalline wafers show nearly a quadratic increase with the oxygen concentration, in agreement with the theory involving the oxygen dimer in the BO complex formation [4].

The monocrystalline CZ wafers, measured applying the same method described in the previous section, are also shown in Fig. 4. The normalised defect density is in agreement with results presented by Schmidt et al [4].

In Fig. 4 a different level of BO defects is observed in wafers with similar O_i concentration. This seems to be related to the presence of C. In Fig.4 the wafers with a higher carbon concentration (8-10 ppma) show less BO-defects than the wafers with corresponding oxygen but lower (2-4 ppma) carbon concentration. This effect can be associated with the formation of carbon-oxygen dimers (O_{2i}) complex [6]. This complex formation is in competition with the formation of BO complex. This effect was recently shown on CZ samples by Schmidt et al [4]. Compared to mc wafers with lower carbon, the metastable defect formation is reduced by about a factor 2 in carbon rich mc-Si wafers.

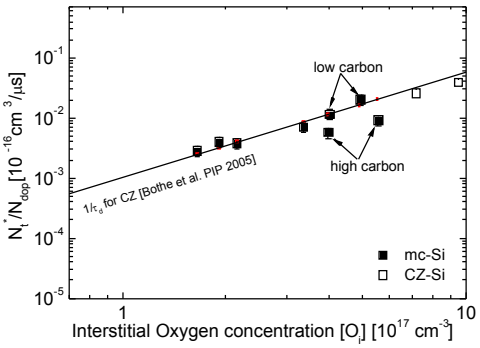

Figure 4: N_t^*/N_{dop} as a function of the interstitial oxygen concentration. The solid line represents the inverse degraded lifetime derived from the empirical equation as described by Bothe et al [2].

4 LIFETIME AFTER DEGRADATION

In Fig. 5 the effective lifetime after complete degradation (solid square) is plotted as a function of the oxygen concentration. The solid line is the degraded lifetime as calculated from the empirical equation found for Cz samples [2]. The empirical equation is considered as the lifetime limit for mc-Si wafers.

Fig. 5 shows also the bulk lifetime (open squares) of the wafers, calculated by correcting for the surface recombination velocity as measured on FZ wafers. The effective lifetime and even more the bulk lifetime are very close to, and in some case exceed, the lifetime limit. It is important to remark that the bulk lifetime of the mc wafers is still affected (reduced) by the recombination via Fe_i defect and by other recombination (i.e. grain boundaries, other metal impurities). In order to exclude the contribution of this additional recombination the lifetime from the BO-defect is also shown in Fig. 5. This lifetime is given by the inverse defect concentration $1/N_t^*$. The BO lifetime is in agreement with the lifetime limit for all except for the two wafers with highest carbon concentration. The $1/N_t^*$ can be regarded as the new higher limit in presence of carbon.

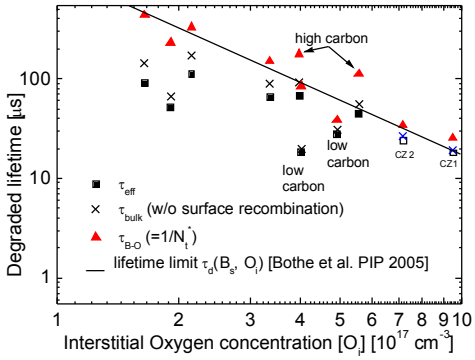

Figure 5: Degraded lifetime as a function of the interstitial oxygen concentration. The solid line represents the degraded lifetime derived from the empirical equation as described by Bothe et al [2].

5 CONCLUSIONS

The boron-oxygen light induced degradation has been studied for mc-Si wafers. The normalised defect density N_t^* determination requires special procedure due to the presence of Fe_i in mc. The procedure was tested using CZ wafers and the results were in agreement with data already available in literature. The surface passivation degradation during illumination was taken in consideration. The degraded lifetime of the mc wafers in most cases has reached the fundamental upper limit of the BO related lifetime (as proposed by Bothe et al [2]). In presence of high carbon concentration (>8 ppma) the proposed limit is even exceeded. The $1/N_t^*$ can be regarded as the new fundamental limit in presence of carbon and excluding the recombination via other defects.

6 ACKNOWLEDGEMENTS

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