A Fast and Easily Implemented Method for Interstitial Oxygen Concentration Mapping Through the Activation of Thermal Donors in Silicon.

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Abstract

In this paper a method is presented to accurately and readily measure the interstitial oxygen concentration in silicon. This method relies on the modification of the Si resistivity after the generation of some oxygen-based Thermal Donors. The method is made very accurate due to the strong dependence of the thermal donors formation rate on the interstitial oxygen concentration. The presented procedure is non destructive and only requires a resistivity measurement setup and a standard 450°C air furnace. Very high spatial resolution mappings can be achieved using up-to-date resistivity measurement tools.

Keywords: Silicon, oxygen, thermal donors, resistivity

1. Introduction

Oxygen (O) is generally introduced unintentionally in silicon (Si) ingots during crystallisation. It can be already present in the Si feedstock used for crystal growth, or diffuse from the ambient or the crucible into the Si during crystallisation. O rearrangement into the crystal leads to various O-related defects which can influence the Si mechanical and electrical properties and alter the device performances.

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For instance, O precipitates are known to improve the mechanical strength of Si by inhibiting the glide of dislocations [1]. In solar cell processing, they also develop detrimental internal gettering effects counterbalancing the external gettering effect created by the phosphorus (P) diffusion. O (under the form of dimers) can also bind to boron (B) and form recombinating complexes responsible for the light-induced degradation of the carrier lifetime in B-doped wafers and solar cells [2]. The formation of oxygen-based thermal donors (TD) can also modify the carrier transport properties, as we shall discuss. All of these oxygen-related structures involve interstitial oxygen (O$_i$) as precursor. The knowledge of the interstitial oxygen concentration ([O$_i$]) is thus essential to better understand and control the macroscopic properties of Si wafers and solar cells. This is all the more true as high efficiency cells are generally made from Czochralski (Cz) Si substrates that contain high [O$_i$], usually in the range $5 \times 10^{17}$ cm$^{-3}$.

In this study, the extraction of [O$_i$] is made from the change in resistivity $\rho$ induced by the simultaneous changes in the majority carrier mobility ($\mu$) and in the charge carrier concentration ($n$ in n-type Si, $p$ in p-type Si) upon formation of TD during a 450°C annealing. Very high sensitivity has been observed, and an excellent agreement with Fourier Transform InfraRed (FTIR) spectroscopy measurements could be obtained. The presented method can be readily implemented with standard semiconductor tools. Interestingly there are no requirements regarding the surface polishing or the wafer thickness, which makes it very attractive in the current context of wafer thinning.

2. Thermal Donors properties

2.1. Generation and annihilation

Oxygen-based TD in Si have been very intensively studied since the pioneering work of Fuller et al. [3]. TD were found to be small oxygen-based aggregates formed during 350-500°C annealings, up to concentrations ([TD]) of a few $10^{16}$ cm$^{-3}$ for extended annealings [4]. Semi-empirical laws governing their formation kinetics were established by Wijaranakula as a function of [O$_i$] at 450°C [5], this temperature (T) constituting a good trade-off between amplitude and kinetics of formation. Interestingly the initial formation rate is highly dependent on [O$_i$] at 450°C [4], making [TD] highly sensitive to the spatial variations in [O$_i$]. This point is illustrated on Fig. 1 where [TD] is shown as a function of the annealing time ($t$) at 450°C, according to the model of Wijaranakula. While a sample with [O$_i$]=5×10$^{17}$ cm$^{-3}$ will contain [TD]=2×10$^{13}$ cm$^{-3}$ after a 1 hour annealing at 450°C, a sample with just three times more O$_i$ ([O$_i$]=15×10$^{17}$ cm$^{-3}$), will have 50 times more TD formed during the same annealing, close to [TD]=10$^{15}$ cm$^{-3}$.

![Figure 1](image.png)

Figure 1 Concentration of TD ([TD]) formed in silicon after a 30 minutes annealing at 450°C, as a function of the interstitial oxygen concentration ([O$_i$]) present in the sample.
In O-rich Si – such as Cz-Si – TD are efficiently generated during crystallisation (cooling of the ingot) and can lead to an alteration of $\rho = (pq\mu)^{-1}$ in p-type Si or $(nq\mu)^{-1}$ in n-type Si. To avoid these undesirable side-effects, a high temperature “TD killer” annealing (typically 650°C for 30 minutes [6]) can be used to leave the wafer TD-free and thus recover the initial electrical properties.

2.2. Model for the influence of TD formation on the free carrier density

Unlike standard doping impurities, TD introduce two distinct energy levels $E_1$ and $E_2$ in the Si gap, located respectively 75 and 170 meV below the conduction band edge [7]. As a consequence, TD are double donors (TD$^{2+}$) in p-type Si whatever the hole concentration (p) and in n-type Si up to an electron density (n) of around $5 \times 10^{15}$ cm$^{-3}$. In this case ($[TD]= [TD^{2+}]$), the carrier density after TD formation in a Si sample possessing an acceptor (N$_A$) or donor concentration (N$_D$) is given by the following expressions, where the factor 2 arises from the double donor character of TD:

$$n = N_D^{+} + 2\times[TD] \quad \text{in n-type Si} \quad (1)$$

$$p = N_A^{-} - 2\times[TD] \quad \text{in p-type Si} \quad (2)$$

where $N_D^{+}$ and $N_A^{-}$ are the ionized dopant concentrations. For standard dopants such as B and P, all dopants are ionized at room T for the doping levels considered here, i.e. $[B^-] = [B]$ and $[P^+] = [P]$.

In more heavily doped n-type Si ($n > 5 \times 10^{15}$ cm$^{-3}$), a non negligible fraction of TD can be either single donor (TD$^+$), or even neutral (TD$^0$) at very high n, due to the shift of the Fermi level ($E_F$) towards $E_1$ and $E_2$. The concentrations of each population can be calculated for given $N_D$ (or $N_A$) and [TD] by solving the charge neutrality equation with respect to the Fermi level $E_F$. The computed $E_F$ is then inserted back into the expressions giving the concentration of each population, as derived from the Fermi-Dirac statistics. Eq. (1) is also slightly changed to $n = N_D^{+} + 2\times[TD^{2+}] + [TD^+]$ to include all the TD populations (Eq. (2) remains unchanged since TD are all double donors in p-Si). These more complex cases have been treated and will be presented in a separate forthcoming contribution. In the present paper we will focus on the most common cases for which $[TD]= [TD^{2+}]$, in order to outline the key points of the method.

2.3. Model for the influence of TD formation on the majority carrier mobility

$\mu$ in Si is mainly limited by ionized impurities and lattice scattering in virtually all Si [Arora]. The ability of an impurity N times ionized to scatter a charge carrier is proportional to $N^2$ [8]. As a consequence a TD$^{2+}$ will scatter 4 times more efficiently than a singly ionized impurity such as $P^+$ or $B^+$, or TD$^+$. In this work, $\mu$ in samples containing TD was modeled with the help of the empirical model of Arora [9] which gives $\mu$ as a function of T and the total impurity content (N). To include the influence of TD on $\mu$, we set N as the sum of $N_D^{+}$ (or $N_A^-$) and [TD] weighted by their respective scattering power, i.e. for instance $N = N_D^{+} + 4\times[TD]$ for an n-type wafer. In the highly doped n-type samples, where TD can also be neutral or singly ionized, N has to be changed to $N = N_D^{+} + [TD^+] + 4\times[TD^{2+}]$, assuming that the carrier scattering on neutral TD$^0$ is negligible.

3. $[O_I]$ mapping procedure

The presented method links the values of $\rho$ measured before and after a 450°C annealing to the amount of generated TD, from which is then extracted the value of $[O_I]$. First of all, a TD-killer annealing can be carried out to ensure that no TD are present at the initial stage. Then, N$_D$ (or N$_A$) is determined everywhere across the sample using the first $\rho$ mapping ($\rho_1$). After the annealing step, a second $\rho$
mapping ($\rho_2$) is carried out, which reflects the effects of the TD formation on both $\mu$ and $n$ (or $p$). Then, at each point of the sample, the value of $N_D$ (or $N_A$) is entered in the model for $\rho$ described above, and $[TD]$ is determined as the unique solution giving a calculated $\rho$ equal to the experimental $\rho_2$. Eventually, the model of Wijaranakula is used to transform the $[TD]$ mapping into an $[O_i]$ mapping.

![Diagram](image.png)

**Figure 2** Principle of the method for $[O_i]$ mapping.

The method is illustrated step-by-step with the experimental results obtained on an as-cut, 300 $\mu$m thick, 19 $\Omega$.cm n-type P-doped Cz-Si wafer ([P]=2.2×10^{14} cm^{-3}) of area 125×125mm². For this example, the $\rho$ mappings were carried out using a 4 point-probe setup. The case of TD activation in p-type Si can be analysed in a similar fashion and its specificities are briefly discussed when necessary.

### 3.1. Mapping of the initial dopant density

Prior to any TD generation and in non-heavy doping conditions ([P]<10^{17} cm^{-3}), [P']=[P] and therefore $\rho$ is given by $\rho = ([P]q\mu([P]))^{-1}$ where $\mu$ is calculated with Arora’s model setting $N=[P]$. [P] being the only unknown in the expression of $\rho$, the value of [P] can be calculated everywhere on the wafer, as shown in Fig. 3.

![Diagram](image.png)

**Figure 3** [P] mapping extracted from the first $\rho$ mapping measured by 4 point-probe. X and Y are the geometrical coordinates.
3.2. Annealing at 450°C

The second step involves an annealing at 450°C followed by a quenching in air. \( t \) varies typically between a few minutes to a few hours, and should be enough to induce a measurable variation of \( \rho \). In the example shown, \( t \) was about 1 hour and led to a change in \( \rho \) close to 50%. Much shorter \( t \) can be used, provided that the change in \( \rho \) is measurable. Based upon our experience, changes of \( \rho \) of only 3% enable the procedure to be successful.

In more heavily-doped n-type samples, where the TD can exist under other charge states than TD\(^{2+}\), the \( \rho \) variation should be maintained below 5%. Indeed it is necessary to assume that between the first and the second \( \rho \) measurements, \( E_F \) remains constant (within a few percent), to be able to calculate the concentrations of all TD populations.

3.3. Mapping of \([O_i]\)

After TD formation, \( n \) is increased to \( n=[P]+2\times[TD] \) and \( \mu \) is reduced as predicted by Arora’s model when \( N \) is set to \( [P]+4\times[TD] \). In the case of an initially B-doped wafer, the generation of TD leads to dopant compensation. Although Arora’s model was initially designed for uncompensated Si, it was recently shown to provide correct \( \mu \) in low and moderately compensated Si \([10,11]\). The treatment presented here should therefore apply to B-doped Si as long as \([TD]\) remains significantly smaller than \([B]\) (in this case, \( N \) has to be set to \([B]+4\times[TD] \)). In practice, it means that the change in \( \rho \) before/after annealing should be kept below around 30%, based on estimations from our previous results \([10]\).

In turns these changes in \( n \) and \( \mu \) influence \( \rho \), according to:

\[
\rho = \left(\frac{[P]+2\times[TD]}{[P]+4\times [TD]}\right)^{\frac{q \times \mu}{[P]+4\times [TD]}}
\]  

(3)

Since \([P]\) has been determined beforehand across the wafer, the only unknown in Eq. 3 is \([TD]\) which can therefore be calculated everywhere on the wafer (see Fig. 4a)).

Eventually \([O_i]\) is calculated using the model of Wijaranakula, but in a reverse way. Indeed the model was designed to calculate \([TD]\) when \([O_i]\) and \( t \) are entered. Thanks to an iterative procedure, the model was this time used to provide \([O_i]\) when the input parameters are \([TD]\) and \( t \). The resulting mapping is shown in Fig. 4b). For information, the time necessary to perform the full wafer analysis was around 30 minutes. For comparison, FTIR measurements were also carried out at some positions across the wafer. Before measurements, the wafer underwent a HF:HNO\(_3\):C\(_2\)COOH chemical etching to achieve a sufficiently low surface roughness. \([O_i]\) was determined from the peak height (h) extracted from the FTIR spectra, and calculated with the expression \([O_i]=3.3\times10^{17}\times2.3\times h/d \) where \( d \) is the sample thickness. The obtained values show an excellent agreement between the mapping, both qualitatively and quantitatively. Also note that the developed method is very sensitive due to the strong dependence of \([TD]\) on \([O_i]\). It can be seen in Fig. 4a) and Fig. 4b), where strong variations of \([TD]\) (nearly 100% variation across the wafer) help determine with high accuracy minor changes in \([O_i]\) (less than 20% variations). At the end of the mapping, a “TD-killer” annealing can be done to restore the initial wafer properties.
4. Conclusions and outlook

A new method for accurately measuring [O\textsubscript{i}] in Si was presented, based upon the change in \(\rho\) as measured at room T, before and after a TD-generating 450°C annealing. We showed that standard \(\rho\)-mapping tools allow [O\textsubscript{i}] mappings to be performed easily. As demonstrated, the method is highly sensitive due to the strong dependence of the TD generation rate on [O\textsubscript{i}]. The method can be directly applied to as-cut samples, and there is not limit for the sample thickness, since \(\rho\) is measurable whatever the thickness. Additionally, high-resolution (less than 100\(\mu\)m) \(\rho\) measurement tools are now available, and enable highly resolved [O\textsubscript{i}] mappings to be achieved.

We are currently investigating the transposition to multicrystalline and Upgraded Metallurgical Grade (UMG)-Si. Especially in UMG-Si, the presence of impurities such as germanium, carbon or hydrogen could influence the TD formation kinetics. Therefore the applicability of the method to UMG-Si is not straightforward and needs verification. Also an alternative method that does not involve \(\mu\) considerations, and thus avoids the uncertainties on \(\mu\) in compensated Si, is currently being tested.

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References