The Role of Silicon Interstitials in the Formation of Boron-Oxygen Defects in Crystalline Silicon

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Abstract. Oxygen-rich crystalline silicon materials doped with boron are plagued by the presence of a well-known carrier-induced defect, usually triggered by illumination. Despite its importance in photovoltaic materials, the chemical make-up of the defect remains unclear. In this paper we examine whether the presence of excess silicon self-interstitials, introduced by ion-implantation, affects the formation of the defects under illumination. The results reveal that there is no discernible change in the carrier-induced defect concentration, although there is evidence for other defects caused by interactions between interstitials and oxygen. The insensitivity of the carrier-induced defect formation to the presence of silicon interstitials suggests that neither interstitials themselves, nor species heavily affected by their presence (such as interstitial boron), are likely to be involved in the defect structure, consistent with recent theoretical modelling.

Introduction

Solar cells made with any boron-doped, oxygen-rich crystalline silicon material, such as Czochralski silicon (Cz-Si), suffer from a well-known carrier-induced defect which acts as a recombination centre [1-3]. The defect is known to occur only in the presence of both boron and oxygen, and is activated by the presence of excess carriers, arising either through illumination or carrier injection. A characteristic feature of the defect is that it may then be de-activated by annealing above 200°C. While the defect has been well characterised in terms of its electronic properties [4,5], its exact chemical make-up remains unclear. An early model was based on interstitial boron - interstitial oxygen pairs (B_iO_i) [6], while a more recent model suggests the defect may be composed of substitutional boron complexed with an interstitial oxygen dimer B_sO_{2i} [7]. This latter model can account for the approximately quadratic dependence of the relative defect concentration on the interstitial oxygen content [7,8]. While models involving interstitial boron have been promoted on the basis of molecular dynamics calculations [9], more recent density functional calculations have given strong support for the oxygen dimer model [10].

For any model involving interstitial boron, defect generation is likely to depend very strongly on the presence of intrinsic point defects, i.e. silicon self-interstitials and vacancies. An excess of silicon interstitials will tend to increase the interstitial boron concentration via a 'kick-out' mechanism, and hence increase the defect concentration, while an excess of vacancies will suppress it. It is also possible that silicon interstitials themselves directly form part of the defect. Recently, Rein *et al*. [8] showed that the presence of excess vacancies does not result in any significant change in the relative defect concentration N_t^*, at least for vacancy concentrations in the 10^{12} cm^{-3} range. These results suggest that vacancies are not likely to be involved in the defect, and
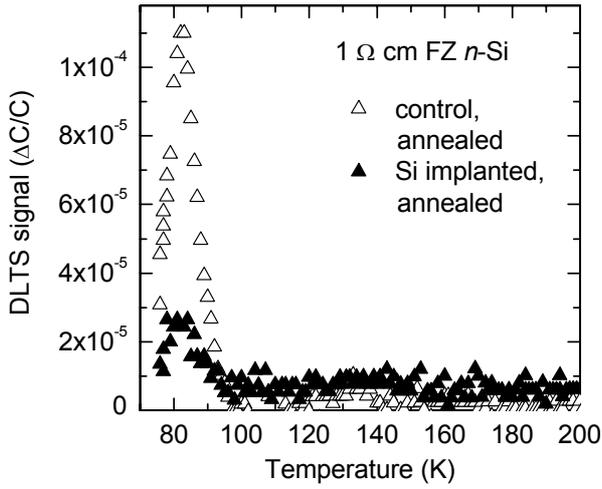
Figure 1. DLTS spectra of implanted and non-implanted n-type FZ samples, after annealing at 900°C. The peak near 80K is attributable to a vacancy-oxygen complex.
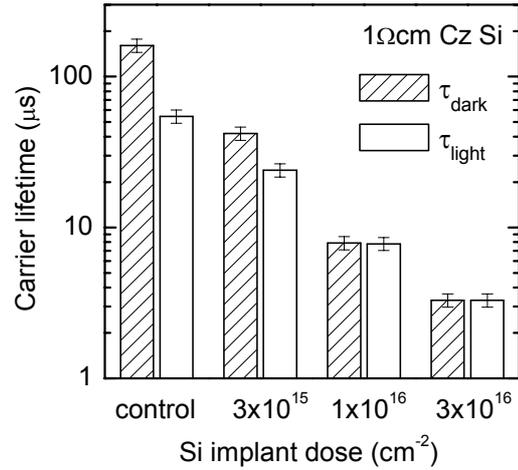

Figure 2. Measured excess carrier lifetimes (at an excess carrier density of $\Delta n = 10^{15}$ cm^{-3}) as a function of silicon implant dose, before and after defect activation (τ_{dark} and τ_{light}), for the Cz samples.

furthermore, hint that interstitial boron is not involved either, since its concentration would be suppressed by the presence of vacancies. In this work, we study the effect of the other important intrinsic point defect - silicon interstitials - and their role in the formation of the boron-oxygen defect.

Experimental Details

Silicon interstitials were introduced into 1Ωcm boron-doped Cz and low-oxygen float-zone silicon (FZ-Si) by Si-ion-implantation in the dose range 3×10^{15} to 3×10^{16} cm^{-2}. Implantation was performed at an energy of 36keV and a temperature of 100°C to reduce amorphisation of the surface. The samples were then annealed at 900°C for 1 hr. For these high doses, this causes dislocation loops to form near the surface, which slowly dissolve and inject silicon interstitials deep into the bulk, as discussed in Refs. [11,12]. However, some dislocation loops will remain in the sub-surface region, and these cause an increase in recombination. To avoid these extended defects masking the effects of the interstitials diffused deeply into the samples, the surface region was etched off prior to any measurements.

The presence of the deep-lying extra interstitials is detected indirectly via a reduced vacancy-oxygen concentration as measured by DLTS [12], as shown in Figure 1. Note that in this plot, the control sample was co-annealed with the implanted sample, and therefore the dramatic reduction in the vacancy concentration must be due to the implantation, rather than simply due to changes caused by the annealing process itself. From these measurements, the interstitial concentration is estimated to be in the 10^{12} cm^{-3} range.

For the carrier lifetime measurements, plasma-enhanced chemical-vapour-deposited (PECVD) SiN films were applied to provide surface passivation [13], while lifetimes were measured using the quasi-steady-state photoconductance technique [14]. These were performed before and after (τ_{dark} and τ_{light}) activation of the boron-oxygen defects by illuminating the samples for 16 hours under white light of approximately 1 sun intensity (100 mW/cm^2). The change in recombination rate at a given excess carrier concentration is then proportional to ($1/\tau_{light}$ - $1/\tau_{dark}$). Since the Shockley-Read-Hall model states that the recombination rate is proportional to the defect concentration, this parameter is also proportional to the concentration of light-induced recombination centres activated by the illumination. Hence, the relative light-induced recombination centre density, labelled N_t^*, is
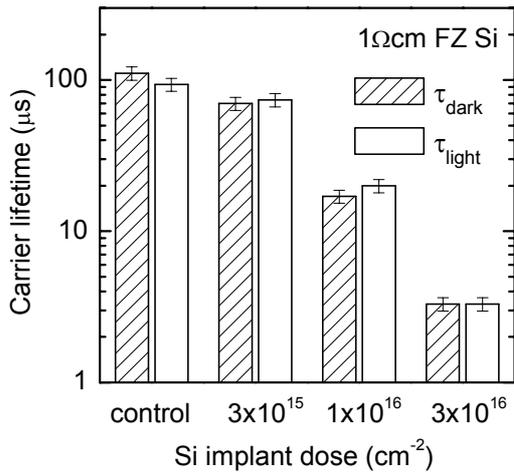
Figure 3. Measured excess carrier lifetimes at $\Delta n = 10^{15}$ cm^{-3} as a function of silicon implant dose, before and after defect activation (τ_{dark} and τ_{light}), for the FZ samples.
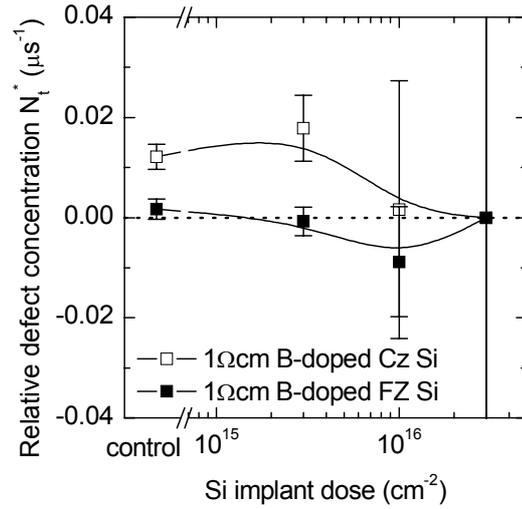
Figure 4. Relative defect concentration as a function of Si implant dose for the Cz and FZ samples. The error bars are calculated assuming a relative lifetime uncertainty of 10%.

given by $(1/\tau_{light} - 1/\tau_{dark})$. Here we have extracted the lifetimes at an excess carrier concentration of 1×10^{15} cm^{-3}. Consistent with previous work, we have calculated N_t^* in units μs^{-1} [8].

Results and Discussion

The carrier lifetimes prior to illumination were found to decrease significantly with increasing Si dose in both the Cz and FZ samples, as shown in Figures 2 and 3. This reflects the presence of the excess interstitials deep in the wafer bulk. Previous measurements of the spectral response of similarly prepared samples have revealed that these interstitial-related defects indeed diffuse hundreds of microns deep during the annealing [11]. They may then react with other defects or impurities within the wafer, or possibly act on their own, to introduce recombination centres. In this case, we are interested in a possible interaction with oxygen that may produce the well known carrier-induced boron-oxygen defect, characterised by the relative defect concentration N_t^*.

The calculated N_t^* values for all samples are shown in Figure 4, with corresponding error bars calculated by assuming a conservative 10% relative uncertainty in the lifetime measurements. The FZ samples have N_t^* values around zero in all cases, as expected due to the low oxygen content of this material. The Cz control (not implanted, but annealed) suffered a drop in lifetime after illumination corresponding to a relative defect concentration of $N_t^* = 1/\tau_{light} - 1/\tau_{dark} = 0.012$ μs^{-1}, which is typical for this material [8]. After implantation, the N_t^* values for the Cz samples are, within uncertainty, unchanged, as shown in Figure 4. Unfortunately, the uncertainty increases with Si dose due to the masking effect of other recombination centres, unrelated to the boron-oxygen defect, introduced by the implantation process. As such, the sensitivity of the experiment is reduced at higher doses. Nevertheless, the fact that the N_t^* values are close to zero for the higher doses, albeit with large uncertainties, indicates quite strongly that the boron-oxygen defect concentration has at least not *increased* due to the presence of the interstitials.

Notwithstanding these large uncertainties, it is tempting to conclude that the defect formation may even be *suppressed* by the presence of excess interstitials for the highest doses. One very speculative explanation is, assuming the oxygen dimer model is correct, that the interstitials may somehow impede the creation or diffusion of oxygen dimers.
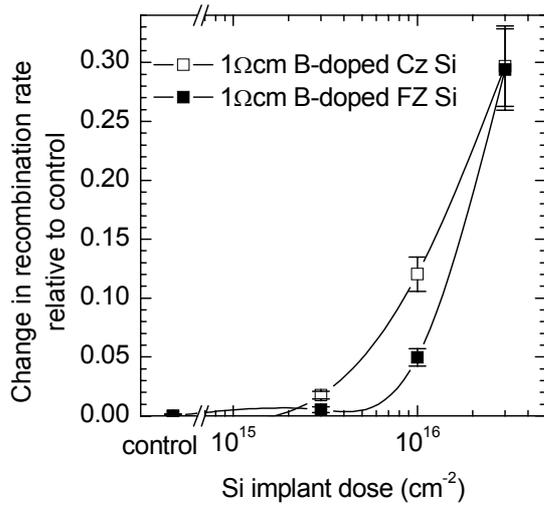
Figure 5. Change in the recombination rate U at an excess carrier density of $\Delta n = 10^{15}$ cm^{-3} relative to control samples for the FZ and Cz (annealed state) samples as a function of implant dose.
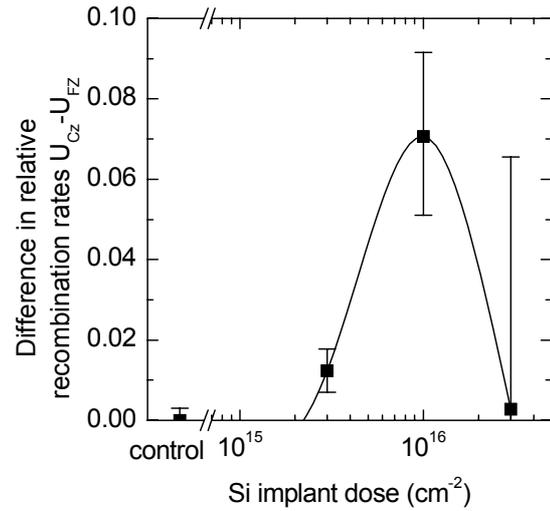
Figure 6. Difference in relative recombination rates U_{Cz}-U_{FZ}, which is proportional to the density of additional recombination centres attributable to interactions between silicon interstitials and oxygen.

Although the results indicate that there is no positive correlation between the presence of silicon interstitials and the carrier-induced boron-oxygen defect, other interactions between oxygen and interstitials are certainly possible. Figures 2 and 3 show that the lifetime decrease is more rapid in the Cz samples for the lighter doses, hinting that such an interaction may exist. This is shown more explicitly in Figure 5, where we have plotted the change in the relative recombination rate U for both the Cz and FZ samples, via $U = 1/\tau_{implant} - 1/\tau_{control}$, with the lifetimes measured at an excess carrier density of 1×10^{15} cm^{-3}. In calculating U for the Cz samples, we have used the non-degraded lifetimes τ_{dark}, although the results are very similar if τ_{light} is chosen instead.

The recombination rates increase with the Si dose for both the Cz and FZ wafers, reflecting the introduction of extra recombination centres. However, it is apparent that the increase in recombination rate is greater for the Cz samples for the lower doses. This is revealed further by plotting the difference in the rates U_{Cz}-U_{FZ} in Figure 6. This difference represents any additional recombination, over and above that due to interstitials alone, in the Cz samples, and is presumably due to the presence of interstitial oxygen. Hence the results suggest that there is indeed an interaction between the interstitials and oxygen, and that this generates additional recombination centres which significantly affect the lifetime for the lower doses. At the highest dose, other defects related to the interstitials, but not involving oxygen, apparently dominate the recombination rates in both Cz and FZ material.

Note that despite the interaction between oxygen and interstitials for the lower doses, the relatively low concentrations of defects generated means that any change in the interstitial oxygen concentration is not detectable, since this is typically above 10^{17} cm^{-3} in Cz material. Consistent with this, Fourier Transform Infrared (FTIR) spectra revealed that the interstitial oxygen peak at 1107 cm^{-1} was indistinguishable between the implanted and non-implanted Cz samples.

Conclusions

Silicon self-interstitials appear to interact with oxygen in Cz silicon, generating additional recombination centres. However, it is clear that these centres are not those responsible for the well known carrier-induced boron-oxygen defect. In fact, the evidence reveals that there is no strong positive correlation between boron-oxygen defect formation and the presence of excess interstitials, at least for the interstitial concentrations achieved here. Therefore the results count against a possible role of interstitial boron or silicon interstitials in the carrier-induced defect, and thus indirectly support the substitutional boron – oxygen dimer model.

Acknowledgements

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