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FeB and CrB pair reassociation kinetics in imperfect Si controlled by contactless lifetime scan maps

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Abstract. The kinetics of “metal-acceptor” pairing in boron-doped multicrystalline samples is investigated by means of contactless lifetime measurement. The case of FeB and CrB pairs is discussed and the influence of extended defect is evidenced for FeB. It is found that the reassociation of the “metal-acceptor” pairs is fast immediately after the dissociation and then slows down for several days. The results allow the identification of mixed contamination by Cr and Fe.

PACS. 61.72.-y Defects and impurities in crystals; microstructure – 61.72.Ss Impurity concentration, distribution, and gradients

1 Introduction

Transition metals (TM) are the most harmful impurities in silicon. Among the wide list of TM, Fe and Cr are commonly found because of the indispensable anneals required during device processing. They can be in precipitated forms, which are poorly recombinant, or associated with the acceptor atoms forming “metal-acceptor” pairs that are dissociated by a short anneal at about 210 °C [1,2]. However, if both these TM are strong killers of the minority carrier lifetime (τ_b), they have different behaviours in p-type silicon after the pair dissociation. In boron doped silicon, when the FeB and CrB pairs are broken, iron and chromium atoms become interstitial ones: Fe_i and Cr_i . In such a case and at low injection conditions the minority carrier recombination rate of Fe_i is about ten times larger than the one of FeB, whereas the recombination rate due to Cr_i is less intensive than that of CrB. This difference enables the identification of Fe or Cr when they are the main contaminants. This identification is not so easy if both contaminants are present due to a possible compensation of lifetime variations after the pair dissociation. A way to distinguish between these species could be the study of the kinetics of “metal-acceptor” pair reassociation. As reported by Istratov [3], numerous authors have given expressions to calculate the time of association for the FeB pairs but few works have been devoted to the reassociation kinetics of CrB pairs. In this paper, we investigate the qualitative reassociation kinetic of FeB and CrB pairs by means of τ_b variations determined by the contactless microwave phase-shift (μ W-PS) technique. This technique is suitable for as-grown samples and can also be used in

production line to check metal contaminations by the evolution of τ_b after each processing step.

2 Experimental

The samples investigated in the present work were multicrystalline p-type silicon wafers, cut from cast ingots, boron-doped, which were chosen in order to observe the influence of the extended defects on the reassociation kinetic of “metal-acceptor” pairs. They were doped in the range $1 - 3 \times 10^{16} \text{ cm}^{-3}$ and not voluntarily contaminated.

To obtain the Fe or Cr local concentrations, we used the method proposed by Lagowski [2] and Zoth [1], measuring the bulk lifetime before and after the pair dissociation. With this method the Fe concentration is given by expression (1) :

$$[F_e] = K(\beta, \eta) \left(\frac{1}{\tau_{\text{after dissociation}}} - \frac{1}{\tau_{\text{before dissociation}}} \right) \quad (1)$$

where K is a coefficient that depends on the dissociation rate β and on the injection level η . This coefficient has been determined in a previous work [4] by means of the deep level transient spectroscopy SULATM and lifetime measurements. For the determination of Cr concentration the coefficient K has been calculated using the capture cross section of Cr_i and CrB assuming a low injection level, as it is the case of our lifetime measurement technique. The Cr and Fe concentration were both found in the range $10^{10} - 10^{11} \text{ cm}^{-3}$.

However, the lifetime spectrum appears to be a more suitable parameter than metal concentration to study the kinetic pairing, and the use of lifetime spectra avoids

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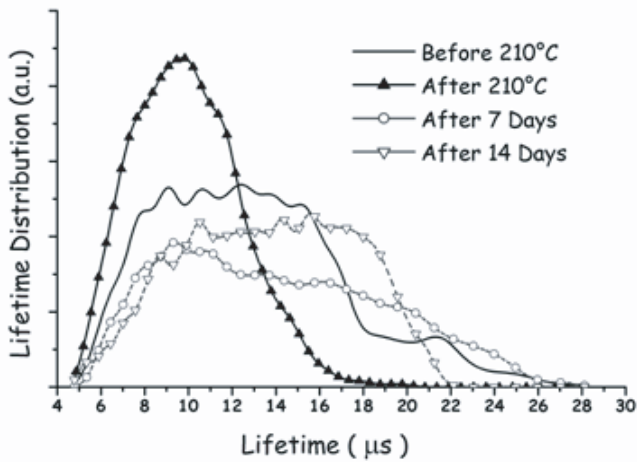


Fig. 1. Normalized lifetime spectra in iron contaminated mc-Si wafer. Straight line represents the initial state before the FeB pairs dissociation.

potential error coming from inaccurate coefficient $K(\beta, \eta)$. That is why we decided to base our analysis on such spectra.

The lifetime measurements were carried out with the microwave phase-shift (μ W-PS) technique. As the microwave photoconductive decay (μ PCD), this technique is contactless and takes the additional advantage to work at practically constant injection level because of the excitation light which is weakly sine modulated. The μ W-PS measures the phase shift Φ between the modulated exciting light and the microwaves reflected power by the sample. From the Φ measured the bulk lifetime is deduced using the procedure detailed in reference [5]. Moreover, the major advantage of the μ W-PS is that it enables the determination of the actual bulk lifetime and the actual surface recombination velocity [5], independently of the surface states. Then the metal concentration involved in pair formation is determined from the actual bulk lifetime and its determination does not require surface passivation.

Notice that μ W-PS does not need bias light that could dissociate “metal-acceptor” pairs [6] inducing error on pairing kinetics evaluation.

3 Results and discussions

As multicrystalline samples are inhomogeneous, it is useful to analyse the lifetime spectra in order to identify the dominant τ_b values. Figure 1 shows the normalized lifetime spectra obtained in mc-Si wafers before the thermal treatment at 210 °C for 10 min and the evolution immediately after, as well as some days after. We see clearly that lifetime decreases in the range 8–10 μ s after the dissociation of the FeB pairs due to the appearance of interstitial iron atoms. A few hours later, a wide amount of Fe_i disappears but then the kinetics slows down when the sample is

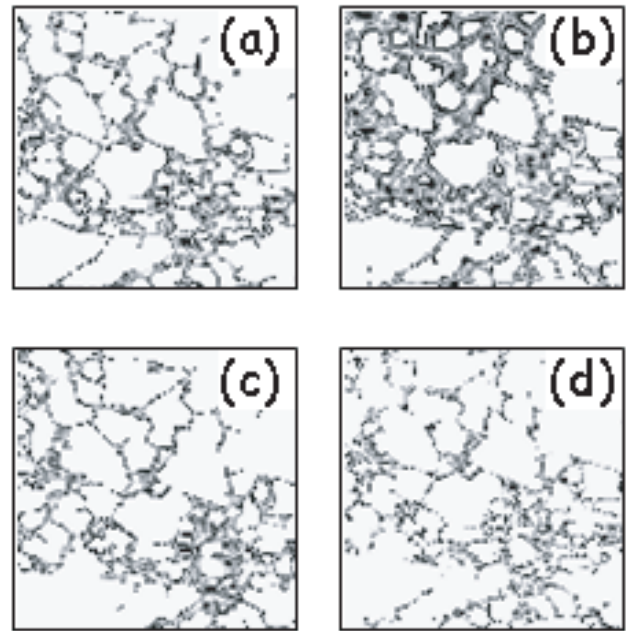


Fig. 2. Monochromatic lifetime mapping centred on 8μ s \pm 20% of mc-Si sample of Figure 1

stocked in the dark at room temperature. Seven days after the dissociation the spectrum is progressively reverted to its original position, which is practically reached 14 days after, meaning that almost all the FeB pairs are reconstructed. However, we can observe a slight improvement of lifetime compared to the first measurement. That could be explained if a part of Fe_i has disappeared, maybe in form of precipitates, in the vicinity of the grain boundaries (GBs). Effectively Figure 2a and Figure 2b show that the interstitial iron is essentially concentrated close to the GBs, and the effect of the dissociation is quite less visible in grains. When the samples are stocked, the pairing occurs and lifetime mapping shows that τ_b increases everywhere (Figure 2c and 2d). Observing Figure 2d, we remark that the GBs are less recombinant 14 days after the dissociation than before, confirming that a part of Fe_i has precipitated close to the GBs, which become less recombinant.

Similar investigation in others mc-Si wafers boron-doped and coming from another ingot, leads to different variations of lifetime. For these samples the thermal treatment at 210 °C increases the lifetime, indicating that CrB pairs are broken and that Cr_i atoms are produced, which are less recombinant. The presence of Cr in these samples was confirmed by SIMS analysis. We see in Figure 3 that before the dissociation there are two peaks, a large one at 9.10 μ s and a smaller one at 9.69 μ s. Immediately after the treatment at 210 °C the first large peak disappears totally, the peak at 9.69 μ s increases strongly and a second one appears at 10.32 μ s. The lifetime scan maps before and after the dissociation, given by Figure 4a and 4b, respectively, indicates that in opposition to the iron

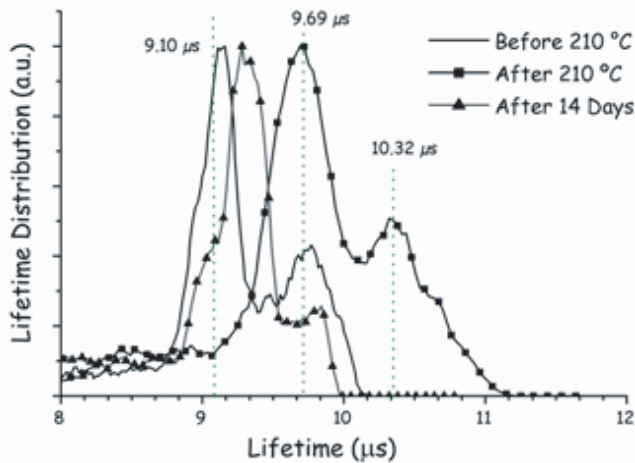


Fig. 3. Normalized lifetime spectra in chromium contaminated mc-Si wafer. Straight line represents the initial state before the CrB pairs dissociation.

contaminated samples, a great variation occurs in grains, with very weak modifications in the vicinity of the GBs. To observe the pairing kinetics of the CrB pairs, the sample was also stocked in dark at room temperature. A new lifetime mapping after 14 days indicates that the peak at $10.32 \mu\text{s}$ has totally disappeared and that the new spectrum is very close to the initial one (straight line in Figure 3). Intermediate measurements between the dissociation and 14 days after, show first a fast kinetic pairing at the beginning of the reassociation and then a slackening, that is in agreement with K. Mishra [7]. Another difference between Fe and Cr is that in the case of chromium contaminated samples the dissociation is more reversible, probably due to the weak influence of extended defects.

The case of samples with mixed contamination leads to use equation (1) carefully. Indeed, as Fe and Cr have opposite effects on lifetime, compensations can occur after the thermal treatment at $210 \text{ }^\circ\text{C}$ minimising the concentration of [Fe] or [Cr].

However, two additional indications enable us to identify the nature of contaminants. If variations of lifetime occur essentially close to the extended defects it could be concluded that iron is the major impurity. This behaviour has been still observed by M. Kittler [8] using EBIC characterisations. In opposition, when the main variations take place in grains, Cr is certainly present. Consequently, a sample showing clear variations close to GBs as well as in grains is probably contaminated by both Fe and Cr. In this last case, only the lifetime spectra analysis makes possible the separation of the effects due to Fe from those due to Cr.

4 Conclusions

Determination of lifetime spectra lead to the kinetics of FeB and CrB pairing in mc-Si wafers. For both

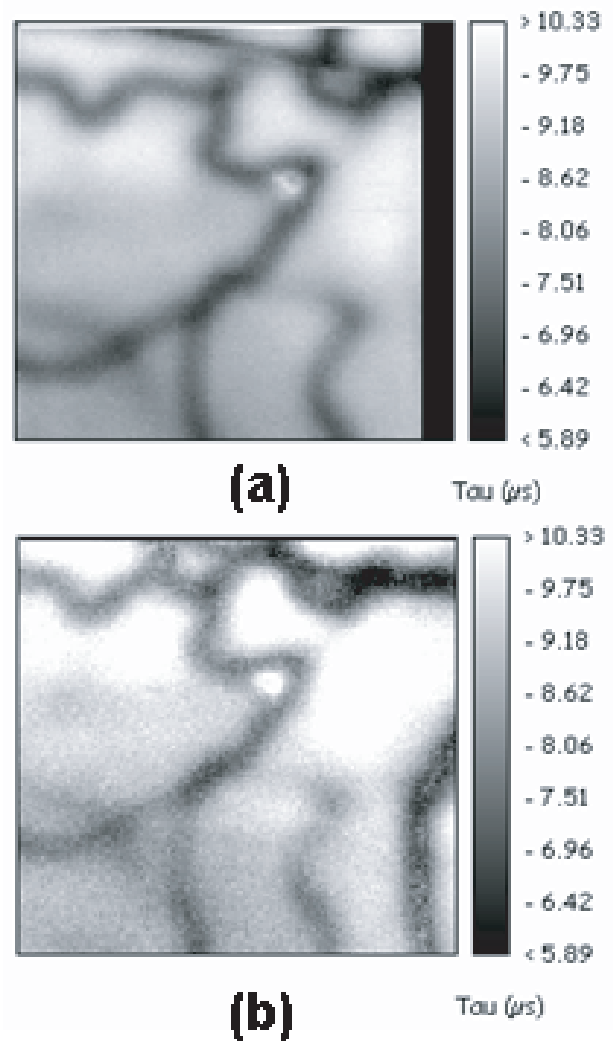


Fig. 4. Lifetime mapping of a Cr contaminated mc-Si wafer: (a) before dissociation of CrB pairs and (b) immediately after.

contaminants the pairing kinetics is fast few hours after the dissociation of the pairs and then slows down, taking several days, to be reverted to the initial state. In the case of contamination by Fe, the dissociation is not totally reversible and a slight improvement occurs in the vicinity of extended defects after two weeks, whereas in the case of Cr contamination, the larger variation takes place in grains and is totally reversible. This difference enables the identification of samples contaminated by Fe, as well as by Cr, using only the non destructive $\mu\text{W-PS}$ technique.

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