TEMPERATURE- AND INJECTION-DEPENDENT LIFETIME SPECTROSCOPY OF COPPER-RELATED DEFECTS IN SILICON

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ABSTRACT

Temperature- and injection-dependent lifetime measurements have been made on single-crystal silicon wafers containing deliberately introduced Cu precipitates. Applying the Shockley-Read-Hall model to the data from *p*-type samples gives an accurate characterisation of these recombination centres in the form of two independent levels – one shallow centre near the conduction band, and one deep centre. These two levels provide a useful approximation to the distributed defect band that is known to exist in the upper band half by previous DLTS studies. In *n*-type silicon the situation is complicated by the Fermi-level shifting through the defect energy band with increasing temperature, altering the charge state of the precipitates, and therefore imparting a strong temperature dependence to the capture cross sections.

1. INTRODUCTION

Copper is an important impurity in silicon, and occurs in many solar-grade silicon substrates. It is known to produce silicide precipitates with relative ease when present in high enough concentrations [1], and these in turn act as recombination centres. Deep-Level Transient Spectroscopy (DLTS) studies have shown that the precipitates form a continuous band of energy levels in the upper half of the band gap [2], from approximately E_C-0.2 to E_C-0.5 eV. Previous attempts at applying Injection- Dependent Lifetime Spectroscopy (IDLS) to such precipitates showed that the impact of this distributed band could be reasonably well approximated by modelling one deep level and one shallow level with the Shockley-Read-Hall model [3]. Since the combination of Injection- and Temperature-Dependent Lifetime Spectroscopy (IDLS and TDLS) allows, in principle, an unambiguous determination of defect parameters [4,5], the purpose of the present work is to apply both techniques for the first time to Cu precipitates in silicon.

2. EXPERIMENTAL DETAILS

2.1 Sample preparation

Both p-type (250 Ω cm) and n-type (20 Ω cm) copper-contaminated silicon samples were prepared by low-energy ion implantation. Implants were performed at 100 °C to reduce the formation of an amorphous layer, and the ion doses ranged between 2×10^{12} and 1×10^{15} cm^{-2}. The samples were then annealed in nitrogen at 900 °C for 56 minutes to drive the copper through. The surfaces were then etched back approximately 20 microns each side, cleaned, and passivated for lifetime measurement with silicon nitride films using plasma-enhanced deposition.

Although the solubility of Cu in silicon is very high at the anneal temperature used (>10^{17} cm^{-3}), the annealing is likely to result in extensive precipitation during cooling down. This is especially so considering the relatively slow quenching that our samples experienced as they were withdrawn from the quartz tube. Much of this precipitation will occur at the surfaces, especially in the p-type samples. These surface precipitates are subsequently removed during the pre-passivation etch. However, some precipitates will remain in the wafer bulk.

It is the recombination activity of these bulk precipitates that is of interest in this study. The uncertain extent of bulk versus surface precipitation does however mean that the bulk precipitate concentration is almost completely unknown, despite the fact that the implant dose is accurately measured. It should also be mentioned that presence of substitutional or interstitial Cu can not be excluded, and these may play a role in the reduced lifetimes. However, the ease with which Cu precipitates leads one to expect that their concentrations would be relatively low.

Control samples with no Cu implant were included in all cases to assess the limitation on lifetime caused by other mechanisms, such as Auger and surface recombination, and background furnace contamination.

2.2 Lifetime spectroscopy measurements

Temperature dependent lifetime measurements were performed at the Fraunhofer ISE using the microwave-detected photoconductance decay (μw-PCD) technique. The temperature range was generally 0-240 °C. In most cases, low-injection conditions were used, while being mindful to avoid trapping effects through the use of a bias light. For the *p*-type sample some high-injection measurements were also made at a fixed carrier density of around 1×10^{15} cm^{-3}.

Injection-dependent lifetime measurements were taken at ANU with the Quasi-Steady-State PhotoConductance (QSSPC) technique [6] at room temperature. In some cases a 'bias correction' [7] was applied to reduce the effect of traps, therefore

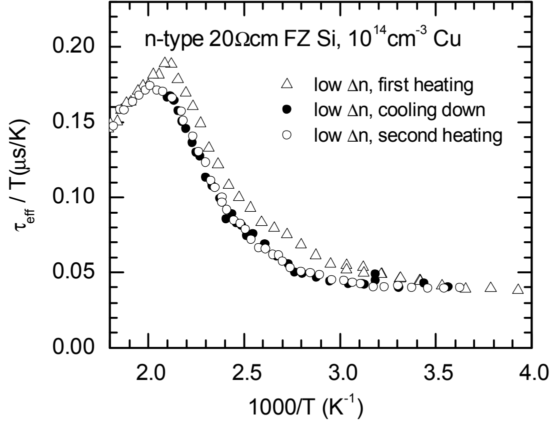

Fig. 1. *Temperature-dependent, low-injection, lifetime measurements for the n-type sample.*

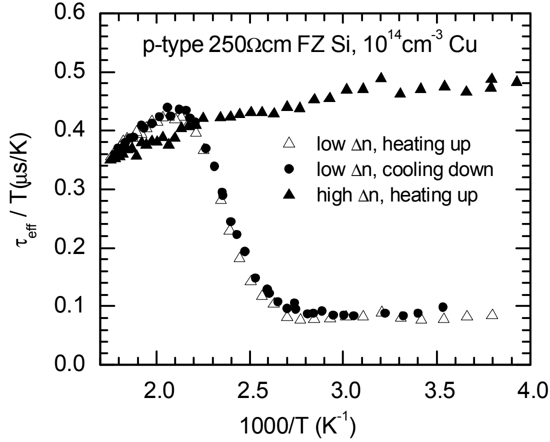

Fig. 2. *Temperature-dependent, low-injection and high-injection, lifetime measurements for the p-type sample.*

extending the range of lifetime data to lower injection levels.

Control samples containing no Cu were also measured with the QSSPC technique across a broad range of injection levels. Some Cu-implanted samples that received lighter doses exhibited lifetimes close to these controls. Only samples that had lifetimes an order of magnitude or lower than the control samples are presented in this work, since only in these cases can we be sure that the measurements reflect almost entirely the effect of the Cu precipitates.

3. RESULTS AND DISCUSSION

Fig. 1 shows the temperature-dependent low-injection lifetime for the *n*-type 20 Ω cm sample. Three curves are shown, corresponding to the initial heating, cooling, and a second heating step. The change in the lifetime after the first heating is most likely due to incomplete precipitation. The second heating revealed no further change, suggesting the initial cycle was sufficient to complete the process. The *p*-type sample showed no such behaviour, indicating that the Cu was already fully precipitated. Fig. 2 shows the low-injection and high-injection results for the *p*-type 250 Ω cm sample. Note that the high-injection carrier density used is almost two orders of magnitude greater than the dopant density, meaning that the SRH lifetime is independent of the exact injection level.

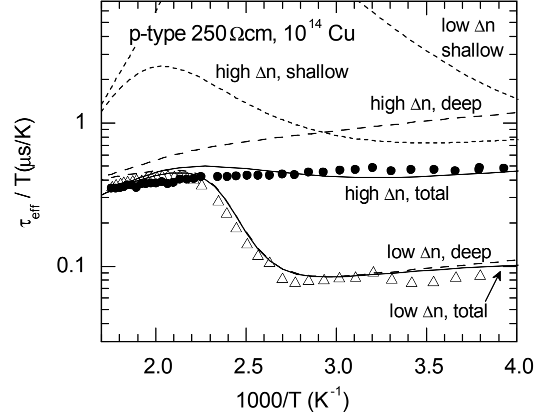

Fig. 3. *Fitting two independent SRH centres to the temperature-dependent lifetime data for the p-type sample. The impact of the shallow and deep levels is shown separately, as well as their combined effect, for both the low- and high-injection conditions.*

3.1 p-type samples

Fig. 3 shows the result of fitting two SRH recombination centres to the temperature dependent data of the *p*-type sample. The energy levels and capture cross-section ratios (also known as the k-factors, $k = \sigma_n/\sigma_p$) [5] determined in this way are shown in Table I. Note that the ratio of the density of the two levels is kept fixed in all the modelling, as is required physically. The low-injection curve is almost completely dominated by the deep centre, while at high injection both centres play a role.

Fig. 4 shows the fitting of these same two centres to the injection-dependent data of the sample from Fig. 3, plus another wafer of the same resistivity with a higher Cu dose. The good agreement between the low-injection TDLS, the high-injection TDLS, and the two room temperature IDLS curves, using the same energy levels and cross-section ratios, is quite remarkable. It serves to show that the use of only one shallow and one deep level as an approximation to a distributed band of states is, at least in the case of Cu precipitates, a reasonable one.

It should be emphasised that the parameters determined in this way are only *effective* parameters that, in a sense, lump together the combined impact of the distributed states associated with Cu precipitates.

The resulting defect parameters are considered more accurate than those published in the earlier IDLS-only analysis [3]. Also, the previous IDLS analysis could not specify if the shallow level was in the upper or lower band half. The TDLS analysis here establishes that it must indeed be in the upper

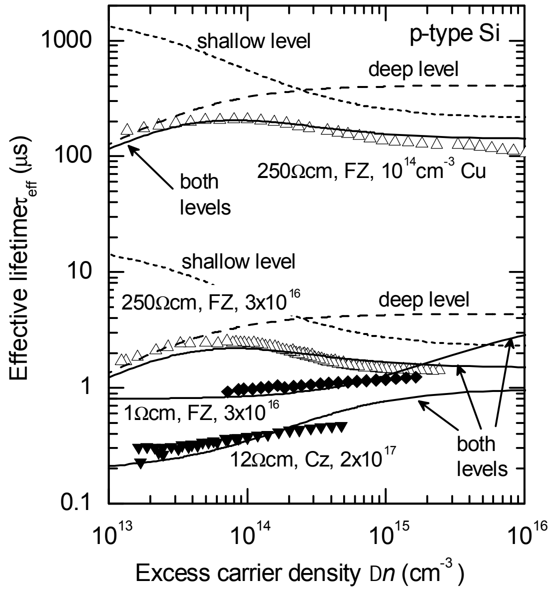

Fig. 4. *Fitting the same two independent SRH centres of Table I to the injection-dependent lifetime data for the p-type sample of Fig. 3, as well as a second 250 W cm sample with a greater Cu dose, and 1 and 12 W cm samples from Ref. [3]. The impact of the shallow and deep levels is shown separately (for the 250 W cm samples), as well as their combined effect (for all samples).*

band half, in agreement with Schroter's DLTS results.

Given that the TDLS and IDLS fits for the 250 Ω cm *p*-type sample are self-consistent, and that for all *p*-type samples the Fermi level should be far away from the defect band, it is reasonable to hope that the same parameters should be valid for *p*-type samples of other resistivities. Such data has been taken from previous studies [3] and is also shown in Fig. 4 and Table I. It can be seen that the parameters determined by TDLS for the *p*-type case here do indeed provide a reasonable description of the injection-dependent lifetimes for samples with very different dopant densities. For the 12 Ω cm case, however, the fit is somewhat imperfect. This could be due to the high Cu concentration potentially altering the effective dopant

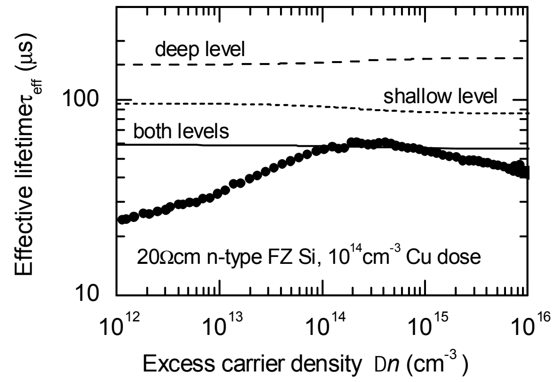

Fig. 5. *Injection-dependent lifetime data for the 20 W cm n-type sample. The lines are the deep, shallow and combined SRH curves for the parameters in Table I determined for the p-type sample.*

concentration, or could represent an effect of the strongly non-uniform carrier profiles due to the very short lifetimes (and hence diffusion lengths).

3.2 n-type sample

Applying TDLS to the case of the *n*-type sample is considerably more complicated, since the Fermi-level then lies within the defect band (also shown in Table I). As the Fermi-level changes with temperature, so does the amount of charge on the precipitates, which will in turn cause changes to the capture cross-sections through coulombic attraction/repulsion. A strong temperature dependence of the cross-sections would then need to be included in the model, and it is not entirely clear which type of dependence would be appropriate. It was not possible to obtain any satisfactory fit to the data using the standard capture cross section models.

In addition to the temperature dependence, *n*-type samples of different resistivities will of course have different Fermi-levels at a *given* temperature. This means that even injection-dependent curves at room temperature for different resistivity *n*-type samples cannot, in principle, be described by a single set of cross sections.

Fig. 5 shows the injection-dependent lifetime curve for the 20 Ω cm sample. Also shown are SRH

Resistivity (Ω cm)	Type	N_A or N_D (cm^{-3})	Fermi level E_C-E_F (eV)	Cu dose (cm^{-3})	N_{SRH} (relative)	E_C-0.2eV level k-factor	E_C-0.58eV level k-factor
250 FZ	p	5×10^{13}	0.78	3×10^{16}	95	0.015	10
"	"	"	"	1×10^{14}	1	"	"
12 Cz	"	1×10^{15}	0.86	2×10^{17}	140	"	"
1 FZ	"	1.5×10^{16}	0.93	3×10^{16}	35	"	"
20 FZ	n	2×10^{14}	0.31	1×10^{14}	2	"	"

Table I. Parameters for the various Cu-contaminated samples. The Cu dose represents the amount of Cu introduced, which may be much greater than the final Cu precipitate density in the wafer bulk. The final two columns represent the parameters used in the SRH modelling. The relative recombination centre density is the normalised density of these centres required to achieve a reasonable fit. For the n-type sample this is indicative only, since the cross sections are not valid in this case.

curves calculated with the recombination parameters determined for the *p*-type samples. Although changing the value of N_{SRH}, which is unknown, can alter the vertical position of the curves, their *shape* is clearly incorrect. In fact it is only possible to get a reasonable fit for this sample if the effective k-factor of the deep level is *reduced*, meaning it is less attractive for electrons. This is consistent with the precipitates becoming more negatively charged as the Fermi level rises into the defect band. As mentioned above however, the k-factor would be different for other *n*-type resistivities.

4. CONCLUSIONS

The recombination activity of Cu precipitates in *p*-type crystalline silicon can be reasonably well described using a set of two *effective* energy levels and capture cross section ratios. These levels occur near the edges of the defect band known from DLTS studies. For *n*-type silicon on the other hand, the shifting of the Fermi level through the defect band causes the capture cross section ratios to change strongly with both temperature and dopant density. These conclusions are also likely to be valid for other types of metallic precipitates that exhibit band-like states in either half of the energy gap.

ACKNOWLEDGEMENTS

This work has been supported by the Australian Research Council and the Australian-German Joint Research Co-operation Scheme. The authors acknowledge the assistance of J. Williams, M. Conway and H. Tan of the Research School of Physical Sciences, ANU, and W. Brendle, University of Stuttgart.

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