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THE TRADE-OFF BETWEEN PHOSPHORUS GETTERING AND THERMAL DEGRADATION IN MULTICRYSTALLINE SILICON

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ABSTRACT: The bulk recombination lifetime of multicrystalline silicon wafers is found to initially increase with phosphorus gettering, but then, for low resistivity wafers, to decrease after a certain optimum gettering time. This peak is attributed to a trade-off between the competing mechanisms of lifetime improvement through impurity removal, and lifetime reduction due to 'thermal degradation'. Such thermal degradation is found to be more pronounced in low resistivity samples. The physical cause of the thermal degradation has been attributed by some to the dissociation of impurity precipitates, resulting in a greater concentration of interstitial impurities. However, we find that a variable temperature gettering method, designed to circumvent the deleterious effects of precipitate dissociation, does not result in an increase in recombination lifetime, but instead results in a significant decrease. An observed increase in the dislocation density of low resistivity samples upon high temperature treatment is suggested as an alternative explanation for the thermal degradation effect.
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1. INTRODUCTION

Phosphorus gettering of multicrystalline silicon (mc-Si) wafers is known to increase bulk recombination lifetimes through the removal of mobile impurities, resulting in improved cell performance in terms of both current and voltage. However, mc-Si is also subject to bulk lifetime degradation when exposed to high temperature steps [1,2]. Any high temperature gettering process will necessarily involve both these competing mechanisms. Since gettering is most effective during the initial stages, when the concentration of impurities in the bulk is relatively high, it follows that there will exist an optimum gettering time which will result in a maximum bulk lifetime, after which the lifetime will decrease due to thermal degradation.

The aim of this work is to explore the nature of this trade-off between the beneficial effects of gettering and the detrimental effects of thermal degradation, particularly as it applies to samples of different resistivities. This latter point is important, since we find that the strength of the thermal degradation effect is strongly dependent on the dopant density, a dependence which can in principle affect the resulting optimum gettering time. The potential implications for incorporating a deliberate gettering step in commercial cell fabrication processes are discussed.

We also examine the physical origin of the thermal degradation. We find that high temperature oxidations resulted in a significant increase in the dislocation density in the low resistivity samples, suggesting a possible cause for the reduced lifetime. Previous workers have however suggested other mechanisms for this lifetime reduction, the most common being the dissociation of impurity precipitates at high temperature [1]. Plekhanov et. al. [3] modeled this dissociation, and concluded that certain variable temperature gettering regimes should result in an increase in lifetime by making use of the changing dissociation rates and impurity diffusivities at different temperatures. We performed such a gettering step and found no corresponding lifetime increase. Other aspects of the precipitate dissociation model which do not fit well with our results are also discussed.

2. EXPERIMENTAL METHODS

Gettering experiments were performed at 900°C for times of 20, 60, 120 and 180 minutes on mc-Si wafers with resistivities of 0.2, 0.4 and 1.4Ωcm. During gettering, $POCl_3$ vapour and O_2 comprised 0.1% and 7% of the gas stream respectively. The sheet resistances resulting from these gettering diffusions were 130, 25, 15 and 10Ω/□ for the four times above. Two wafers, taken from adjacent slices within the ingots, were processed for each resistivity and gettering time to provide confidence in the measurements.

The surfaces of the wafers must be sufficiently passivated to allow bulk recombination lifetime measurements. The gettering diffusions provide some surface passivation, although in all cases except the 20 minute gettering process, the resulting diffusion is so heavy as to limit the effective lifetime through emitter recombination. Consequently, in order to measure the bulk recombination lifetime, the heavily-doped phosphorus layer was etched off, and the samples re-passivated. This was achieved by a light phosphorus diffusion (20 minutes at 840°C ≈ 200Ω/□ sheet resistance) and thin in-situ oxidation, followed by a forming gas anneal. This etching and passivation step was not performed on the samples gettered for 20 minutes, since the gettering layer itself provided sufficient passivation. The quality of the surface passivation was monitored by including float zone (FZ) single-crystal silicon wafers of comparable resistivities in each batch of wafers.

Effective recombination lifetimes were measured using the quasi-steady-state photoconductance (QSSPC) technique [4], which is well suited for obtaining area-averaged measurements on inhomogeneous material such

as mc-Si. Care needs to be taken when reporting recombination lifetimes on this type of material, as trapping effects can obscure the recombination lifetime at low carrier densities [5], resulting in anomalously high 'apparent' lifetimes, as described below.

Dislocation etches were performed using Yang's etch [6], which reveals such defects on crystals of various orientation.

3. RESULTS AND DISCUSSION

3.1 Interpreting the Lifetime Measurements

Figure 1 provides a good example of a typical injection-level dependent lifetime curve of a mc-Si wafer. This sample was a 1.4Ωcm wafer which had been gettered for 120 minutes and then passivated as described above. At carrier densities below about $5\times10^{14}cm^{-3}$ trapping effects are evident. In this region the photoconductance is distorted by a relative excess of majority carriers [5,7], hence we refer to 'apparent' effective lifetimes and carrier concentrations. Note that the term 'trap' refers to a state in the band-gap which temporarily holds minority carriers, but does not act as a recombination centre. Above $5\times10^{14}cm^{-3}$ however, the effect of the traps is swamped by the large number of excess carriers, and in this region we are able to associate the measured lifetimes with the recombination lifetime. All lifetimes reported in this work are measured at a carrier concentration of $2\times10^{15}cm^{-3}$ to avoid such trapping effects, and also to allow direct comparison between samples. Furthermore, since the quality of the surface passivation is sufficient to allow lifetimes about an order of magnitude larger to be measured on the FZ control wafers of comparable resistivities, the effective lifetimes can be interpreted as bulk recombination lifetimes.

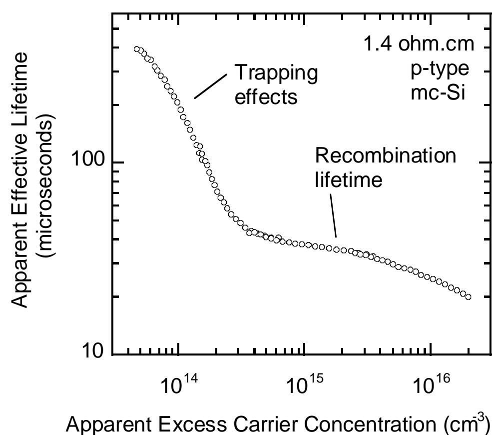

Figure 1: Apparent effective lifetime versus carrier concentration for a 1.4Ωcm mc-Si sample that had been gettered for 120 minutes at 900°C, and phosphorus passivated. The effect of traps is clear below about $5\times10^{14}cm^{-3}$. Accurate recombination lifetime measurements are only possible above this value.

3.2 Optimisation of the Gettering Time

Figure 2 shows the results of lifetime measurements on the mc-Si wafers of various resistivity subjected to various gettering times. During this gettering procedure, the two competing mechanisms of impurity gettering and thermal degradation are simultaneously at work. Initially, gettering is the dominant mechanism, due to the abundance of easily getterable impurities, and the recombination lifetime increases dramatically. This occurs similarly for all three resistivities, as shown in figure 2. However, as the efficacy of the gettering is reduced, after about 60 minutes, the behavior of the lifetimes is strongly resistivity-dependent. The effects of thermal degradation begin to impact significantly on the lower resistivity samples. However, for the higher resistivity wafers, the recombination lifetime becomes effectively constant.

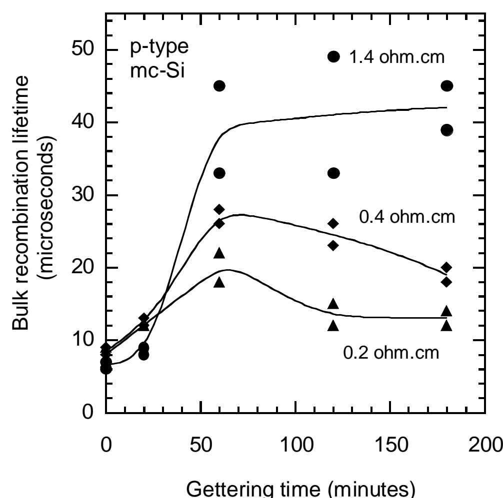

Figure 2: Bulk recombination lifetime versus gettering time for different resistivity mc-Si wafers. The lines are guides to the eye.

Figure 2 suggests that all samples reach a maximum lifetime, or close to it, after 60 minutes. However, it seems reasonable to suppose that the optimum gettering time would exhibit some dependence on the substrate resistivity, considering the stronger thermal degradation in the lower resistivity samples. More experiments close to the 60 minute point may reveal such a weak dependence, with more heavily doped samples requiring slightly shorter gettering times.

After gettering for 60 minutes, recombination lifetimes were typically two to three times higher than in the untreated wafers. Of particular note are the results for the 0.2Ωcm material, which exhibited lifetimes above 20µs in one case. Such a bulk lifetime corresponds to an open-circuit voltage of around 670mV for a 180µm thick cell. Of course the challenge with achieving such voltages in practice lies in reducing the thermal degradation of the lifetime during subsequent cell processing. Stocks et. al. [8] and Kerr et. al. [9] have measured $V_{OC}\approx655mV$ in cells made with this material.

The results are of relevance for any attempt to introduce gettering steps into commercial cell fabrication processes, which has previously been seen as undesirable due to the perceived long gettering times required. This work shows that, particularly for low resistivity wafers, long gettering times (more than one hour), are not only unnecessary but actually detrimental. Further reductions in gettering time can potentially be achieved as industry moves towards thinner substrates. However, there still remains the challenge to develop an industrially feasible cell fabrication process that is capable of fully exploiting

high bulk recombination lifetimes. By contrast, despite their relatively lower bulk lifetimes, current commercial mc-Si cells are largely limited by recombination in the emitter and at the rear surface (Al BSF) [10].

3.3 Further Evidence of Thermal Degradation

The extent to which thermal degradation of the recombination lifetime occurs is strongly dependent on the dopant density, as suggested by figure 2, with more highly doped samples more severely affected. Figure 3 shows results which reveal this dependence in a more explicit way. Several mc-Si wafers of varying resistivity were subjected to either a 900°C or a 1050°C dry oxidation step for 30 minutes. Lifetimes before and after oxidation were all measured at a carrier concentration of 2×10^{15}cm^{-3}, to avoid trapping effects. Surface passivation was provided by the oxide, which was given a forming gas anneal prior to lifetime measurement. Control FZ wafers of similar resistivity were included to ensure the surface passivation was sufficient to allow the lifetimes measured on the mc-Si samples to be interpreted as bulk recombination lifetimes. The data is presented as the ratio of these lifetimes post- and pre-oxidation. Prior to oxidation, the samples were phosphorus gettered for 60 minutes in order to maximise the recombination lifetime, and hence increase the sensitivity of the experiment.

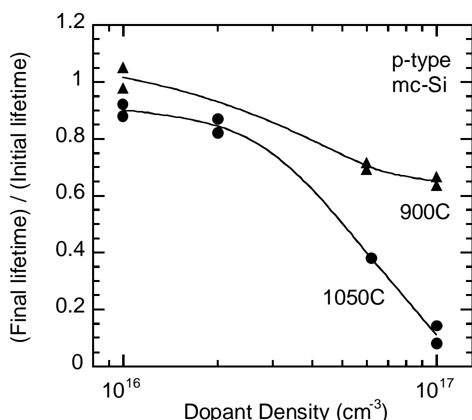

Figure 3: ratio between final and initial recombination lifetimes in mc-Si before and after a 900°C and 1050°C oxidation for 30 minutes, versus dopant density. The solid lines are guides to the eye.

Clearly the higher temperature oxidation results in greater thermal degradation. In fact, the more highly doped samples experience a massive reduction in lifetime, losing about 90% of the pre-oxidation value, for the 1050°C oxidation. However, the more lightly doped wafers are much more resilient. These results are consistent with those presented in the previous section, in which the high resistivity wafers did not noticeably suffer from thermal degradation during any of the 900°C gettering steps. This resilience offers an explanation for the success of high efficiency cell processes when applied to higher resistivity mc-Si material [11]. Standard PERL designs involve a large number of high temperature oxidations and diffusions, which would severely degrade low resistivity material but leave high resistivity substrates relatively unchanged.

An interesting observation made during the lifetime measurements of these samples was that the trapping effect was noticeably more pronounced after the 1050°C oxidation step for the most highly-doped wafers.

3.4 Physical Origin of Thermal Degradation

It is interesting to consider what might be physically responsible for such thermal degradation. It has been suggested that impurity precipitates are dissociated at high temperatures, allowing the impurities to diffuse throughout the bulk [1,3]. Modeling of such dissociation behavior, by Plekhanov et. al [3], has revealed that a *decrease* in the recombination lifetime can be expected for gettering treatments at constant temperatures, if the dissociation rate and solubility are high enough, and subsequent cooling fast enough, to result in more interstitial impurities than were initially present. Such an effect provides a potential explanation for the observed decrease in lifetimes in figure 2. However, according to the modeling, this reduction is expected to be completed within a matter of seconds at most, as opposed to many minutes as the data in figure 2 suggests. Hence it seems unlikely that the thermal degradation encountered in this work is caused by the type of precipitates considered by Plekhanov et. al.

Those authors proceed to suggest that a significant improvement in lifetime can be gained if variable temperature gettering is used instead of constant temperature gettering. This conveniently provides a method of experimentally testing the applicability of their model to the samples studied here. The initial gettering temperature suggested is 1200°C, followed by ramping down in steps of 100°C, and remaining at each temperature for increasing periods of time. The high initial temperatures allow for rapid and near-complete precipitate dissociation, and the calculated ramping down allows the freed impurities to be gettered whilst their solubility and diffusivity are sufficiently high.

We performed a variable temperature gettering procedure, on two 0.2Ωcm mc-Si wafers, according to the recipe of Plekhanov et. al.. The resulting bulk recombination lifetimes of 7 and 9μs, as measured at a carrier concentration of 2×10^{15}cm^{-3}, were almost as low as those in non-gettered material (see figure 2). This indicates that these wafers were subject to thermal degradation not related to the type of precipitate dissociation considered by Plekhanov et. al. It is of course possible that there are precipitates present with a dissociation energy much larger than those authors used, but if this were true, a vastly longer gettering time, possibly even for variable gettering procedures, would be required. Note also that an explanation involving dissociating precipitates does not provide an insight into the cause of the dopant density dependence of the thermal degradation

As a possible alternative explanation for the observed thermal degradation, we present evidence that high temperature steps cause an increase in the dislocation density. Figure 4 shows optical images of a section of a 0.2Ωcm mc-Si wafer before and after a 1050°C oxidation. Initially, the sample was bright etched in a HF/HNO_3 solution to obtain a smooth surface, and then dislocation etched. The first image reveals grain boundaries and a few dislocations distributed within the grains on the sample before oxidation. The wafer was then HF/HNO_3 etched again to obtain a fresh surface, and oxidised. After oxidation and lifetime measurement, the oxide was etched off, and about 20μm of silicon etched from the surface

with HF/HNO_3 to remove any surface damage acquired during oxidation, and then dislocation etched again. The silicon etches did not completely remove the initial etch pits along the grain boundaries, resulting in trenches being formed along them. These trenches are evident in the second image, which was taken after the final dislocation etch. Nevertheless, there is a clear increase in the concentration of dislocations within the grains, and in several places new grain boundaries have propagated into the grains.

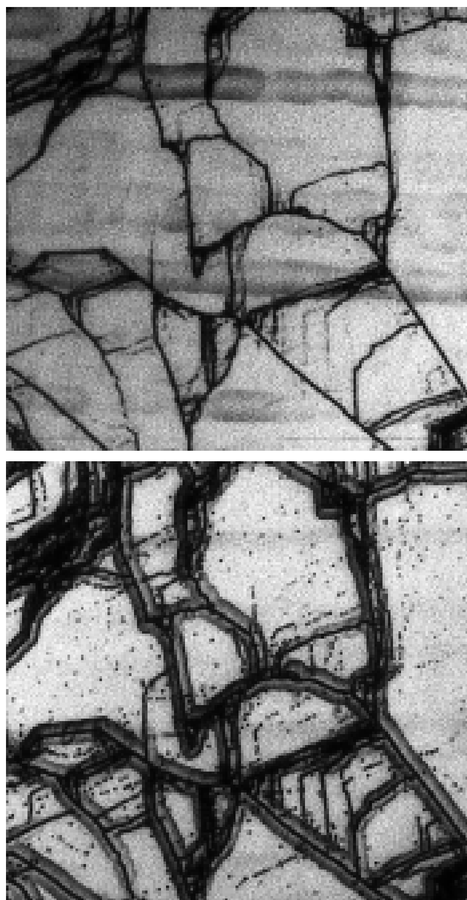

Figure 4: Optical images of a section of the same 0.2Ωcm mc-Si wafer before (top) and after (bottom) a 30 minute 1050°C oxidation. The wafer has been dislocation etched to reveal dislocations as small pits. The trenches in the bottom figure are due to a previous silicon etch. Magnification is about 50×.

A 1.4Ωcm sample was subjected to the same treatment as above, and although in some places the dislocation density increased, in general there were much fewer new dislocations than in the 0.2Ωcm case. A tentative explanation then of the source of these dislocations would be the large mis-match factor of boron in silicon, which may result in dislocation creation at high temperatures. Considering that these thermal degradation effects were not observed in FZ silicon, it seems that grain boundaries and other crystallographic defects in mc-Si also act in some way as seeding sites for dislocation creation.

Further indirect evidence in support of an increase in dislocations comes from the fact that the trap density increases in the heavily degraded 0.2Ωcm samples. Previous work has established a correlation between the presence of trapping states and dislocations [5].

4 CONCLUSIONS

Phosphorus gettering of mc-Si wafers is a useful method for improving bulk recombination lifetimes. However, the simultaneous effect of a different physical mechanism, referred to as thermal degradation, results in a net decrease in lifetime for long gettering times, particularly for samples of lower resistivity. We find that the trade-off between these two effects results in an optimum gettering time of about 60 minutes for gettering at 900°C under the $POCl_3$ conditions used. Such a gettering step generated maximum or very near maximum lifetimes in all three resistivities studied, although there may be a weak dependence on resistivity which favours slightly shorter gettering times for lower resistivity samples.

The physical source of the thermal degradation has been investigated also. Previously, this effect has been attributed to the dissociation of impurity precipitates. However, we find that the time scale of the thermal degradation investigated here is inconsistent with that previously modeled for precipitate dissociation. Such a model also does not provide a direct explanation for the resistivity dependence of the thermal degradation effect. Furthermore, a variable temperature gettering treatment which has been advocated as overcoming the deleterious effects of precipitate dissociation, and consequently should significantly improve the recombination lifetime, was found to actually result in a worsened lifetime.

As an alternative possible explanation for the thermal degradation, we present evidence which shows an increase in the dislocation density, particularly on lower resistivity wafers. It may be that this increase, due to thermal stress at high temperature coupled with existing strains in the crystal (dopant sites and grain boundaries etc.), causes the observed decrease in lifetime.

REFERENCES

[1] I. Hanke, M. Apel and W. Schroter, Proceedings 14th European Photovoltaic Solar Energy Conference, Barcelona (1997) 735.

[2] M. Mimura, S. Ishikawa and T. Saitoh, Technical Digest 11th Photovoltaic Science and Engineering Conference, Sapporo (1999) 357.

[3] P. S. Plekhanov, R. Gafiteanu, U. M. Gosele and T. Y. Tan, J. Appl. Phys. **86** (1999) 2453.

[4] R. A. Sinton and A. Cuevas, Appl. Phys. Lett. **69** (1996) 2510.

[5] D. Macdonald and A. Cuevas, Appl. Phys. Lett. **74** (1999) 1710.

[6] K. H. Yang, J. Electrochem. Soc. **131** (1984) 1140.

[7] R. A. Smith, *Semiconductors*, Cambridge University Press, Cambridge (1959).

[8] M. Stocks

[9] M. Kerr, J. Schmidt and A. Cuevas, this conference.

[10] A. Cuevas, to be published.

[11] J. Zhao, A. Wang, M. Green and F. Ferrazza, Appl. Phys. Lett. **73** (1998) 1991.