

# Effects of conventional and rapid thermal annealing on minority carrier diffusion length in float zone and Czochralski silicon crystals

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## Abstract

Experimental results on the effects of various annealing cycles, needed in the fabrication of electronic devices, on the minority carrier diffusion length  $L_D$  in both Czochralski and float zone silicon crystals are presented and analysed. Particular attention is paid to the influence of the annealing mode, the heating ambient and the duration of the process. From discussion of the variations induced in  $L_D$  by each annealing system or thermal process, external contamination as well as residual metallic impurities are believed to be responsible for degradation of  $L_D$ . In Czochralski crystals, it was found that oxygen has an important role in determining the final  $L_D$ , and a gettering mechanism for metallic impurities is hypothesized.

## 1. Introduction

It is well known that the bulk minority carrier diffusion length  $L_D$  is the most important basic parameter determining solar cell performance [1]. Two major factors influence this parameter. The first is the quality of the starting material and the second is the various treatments which the sample undergoes until the solar cell is finished. In the starting material, it is not only important that the initial diffusion length is high, but also the presence of residual impurities and crystallographic defects which might interfere with subsequent processing steps has to be considered. In solar cell manufacturing, various thermal treatments intervene and usually lead to degradation of  $L_D$ . The mechanisms responsible for this degradation are, however, scarcely known. This is because the final results of the technological processes needed for cell fabrication are usually influenced by many parameters concerning the practical conditions, especially the annealing characteristics such as ambient gas, duration of heating, cooling rate etc., and accidental contamination resulting from handling and equipment during processing steps. Rarely can all these parameters be fully controlled. So, very different behaviours have been reported after similar thermal treatments. Cheng [2] found enhancement of lifetime in thermal annealed float zone (FZ) and Czochralski (CZ) crystals. Many other authors have reported a degrading effect of annealing at  $T > 700$  °C, but some attribute a

beneficial effect to oxygen [3] while others impute the degradation to oxygen precipitation [4]. These wide differences denote the presence of very complex phenomena and emphasize the need to attain tight control of the experimental conditions, so that it is possible to separate the effects of the different parameters.

The aim of this work was to carry out a systematic study of the effects of various thermal treatments on the minority carrier diffusion length  $L_D$ , on monocrystalline silicon, with close attention to the influence of the initial content of oxygen, considered to be the major residual impurity in such material.

## 2. Experimental details

The investigations were carried out on virgin n-type phosphorus-doped  $\langle 100 \rangle$  silicon of 1–5  $\Omega$  cm resistivity. Both float-zone growth (FZ) and Czochralski pulled (CZ) single crystals were used in order to observe the effects of heating on the simplest silicon material, and to look at the influence of the initial content of oxygen on the experimental results. The initial concentration of interstitial oxygen, obtained from IR absorption measurements was estimated at  $2.7 \times 10^{17}$  atoms  $\text{cm}^{-3}$  for CZ and below  $10^{16}$  atoms  $\text{cm}^{-3}$  for FZ crystals.

Samples of  $1 \times 1$   $\text{cm}^2$  were cut out from circular commercial wafers, 2 or 3 inches in diameter and

400  $\mu\text{m}$  thick, which were lapped on both sides. The samples were first degreased in boiling trichlorethylene for 5 min, cleaned in acetone, rinsed in running deionized water and dried in a nitrogen gas flow. When needed, the samples were chemically polished in a (57:18:25) 70% $\text{HNO}_3$ :50% $\text{HF}$ :100% $\text{CH}_3\text{COOH}$  etching mixture for 2 min which removed roughly 30  $\mu\text{m}$ , rinsed again in running deionized water and finally blow dried under nitrogen gas flux to be ready for the thermal treatments. These were generally done immediately after chemical preparation of the samples, at temperatures ranging from 450  $^\circ\text{C}$  to 1050  $^\circ\text{C}$  in steps of 200  $^\circ\text{C}$ . For each temperature value, four thermal cycles were carried out:

(i) fast thermal process under argon atmosphere for 10 s (RTA, argon, 10 s) to compare with recent literature data [5];

(ii) conventional thermal process under argon atmosphere for 30 min (CTA, argon, 30 min) to determine the influence of the annealing mode;

(iii) conventional thermal process under vacuum for 30 min (CTA, vacuum, 30 min) to observe the influence of the annealing ambient;

(iv) conventional thermal process under vacuum for 2 h (CTA, vacuum, 2 h) to observe the influence of the duration of annealing.

For CTA treatments, the samples were inserted into the cold zone of the furnace, and then pushed into the hot zone at the predetermined temperature. After heating, the power was switched off and the samples cooled in the same ambient prior to removal from the furnace. RTA was carried out in a halogen-lamp heated furnace, model FAV4 from JIPELEC (France). This new furnace is characterized by "cold walls" and is programmable for temperature ramps and steps. The cooling rate was typically around 100  $^\circ\text{C s}^{-1}$  and was limited by the thermal inertia of the furnace.

After the heat treatments at 450  $^\circ\text{C}$  or 650  $^\circ\text{C}$ , the resistivity of CZ samples was systematically measured, but no noticeable change was revealed. So, we can conclude that no significant concentration of thermal donors was created in our material.

The minority carrier diffusion length  $L_D$  was determined using surface photovoltage (SPV) measurements [6]. The relative error in measurement of  $L_D$  is estimated at  $\pm 10\%$ . To obtain a correct SPV signal and take accurate  $L_D$  measurements, all samples, being n-type, were boiled in deionized water for 1 h to ensure correct band-bending at the surface. Next, their backside was lapped to ensure the same backcontact on all of them, and to prevent the creation of a surface space charge on the back. It is important to point out that, because of the thickness  $W$  of our samples ( $W \approx 350 \mu\text{m}$ ), the real value of the minority carrier diffusion length could only be correctly measured when  $L_D \leq W/4$ . Otherwise, we obtain a value which is less than the true value [7].

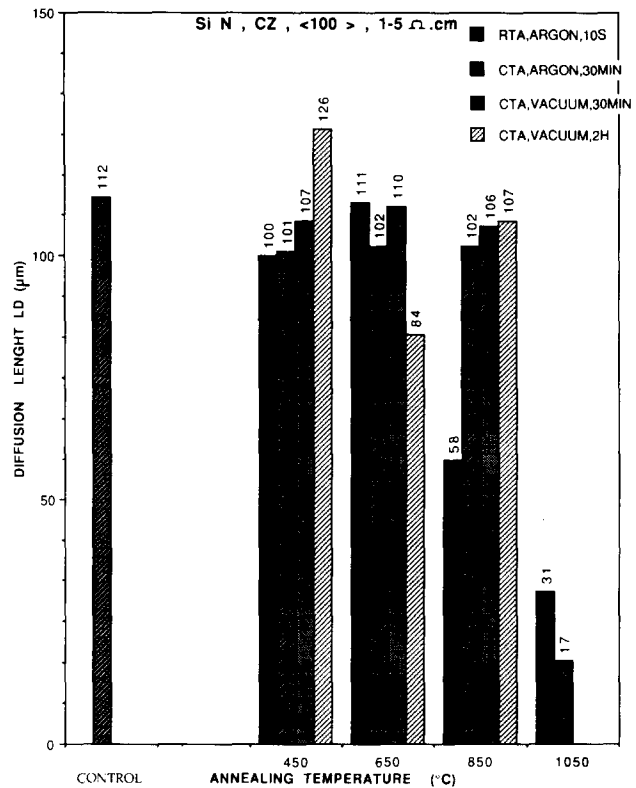


Fig. 1. Functional dependence of the minority carrier diffusion length on processing temperatures, and its evolution according to four selected thermal cycles, in CZ silicon crystal.

### 3. Experimental results and discussion

Figures 1 and 2 show the dependence of  $L_D$  on the processing temperature for the four selected thermal cycles. It is worth noting that each  $L_D$  value reported here represents an average measure repeated many times on at least two samples.

On CZ silicon, the results obtained (Fig. 1) lead us to conclude that for temperatures ranging from 450  $^\circ\text{C}$  to 850  $^\circ\text{C}$ , CTA treatments have practically no negative effect on  $L_D$  whatever the ambient used (neutral gas or vacuum) and the duration (30 min or 2 h). Indeed, except for the low decrease ( $-25\%$ ) observed after 2 h in the furnace at 650  $^\circ\text{C}$ , all  $L_D$  variations remain generally within the margin of experimental error, estimated to be around  $\pm 10\%$ . For temperatures larger than 850  $^\circ\text{C}$ ,  $L_D$  drops abruptly and reaches a very low value ( $-85\%$ ) at 1050  $^\circ\text{C}$ . This strong degradation, which very often occurs at such temperatures, can be related to dislocations and to other defects thermally induced in the material, as has been revealed by the etch-pit method [8].

Compared with the CTA cycles, the degradation of  $L_D$  after the RTA mode starts earlier (at approximately 650  $^\circ\text{C}$ ) and undergoes progressive worsening up to the

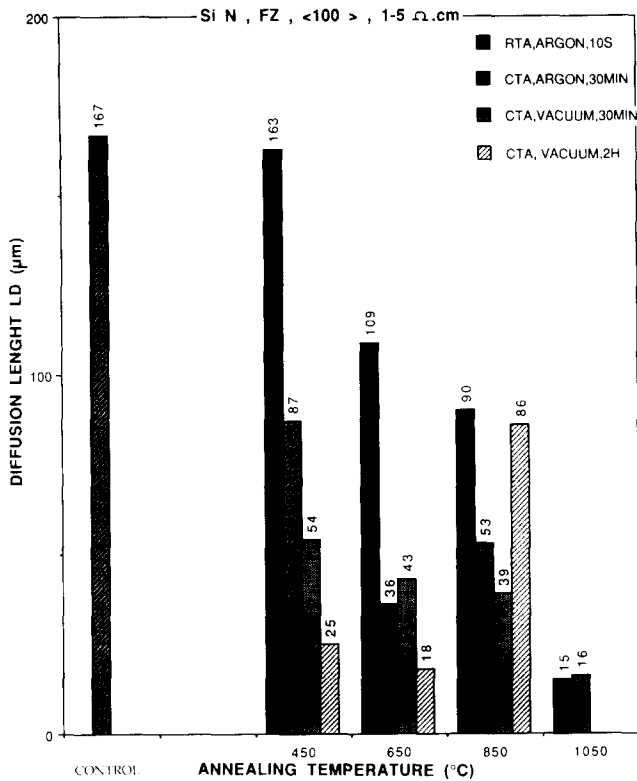


Fig. 2. Functional dependence of minority carrier diffusion length on processing temperatures, and its evolution according to four selected thermal cycles, in FZ silicon crystal.

highest temperatures. However, at 1050 °C,  $L_D$  is larger than that obtained with CTA at the same temperature. It is worth noting that the functional dependence of  $L_D$  on  $T$  in the RTA cycle is very similar to that already observed in the case of p-type CZ silicon [5]. This indicates that there is no significant interaction between dopants and the defect responsible for the degradation of  $L_D$ . Quat *et al.* [9] reached the same conclusion.

On FZ silicon, Fig. 2 shows that almost all thermal treatments degrade  $L_D$  strongly. For the RTA mode, this degradation seems to begin at around 500 °C, while for CTA treatments it starts at  $T < 450$  °C where it already attains dramatic levels. Generally, it seems that whatever the thermal cycle,  $L_D$  decreases progressively when the temperature increases, and at 1050 °C it is close to the sensitivity limit of the technique. If we classify the four thermal cycles selected according to the decrease in  $L_D$ , RTA is first, followed by CTA argon 30 min, followed by CTA vacuum 30 min and CTA vacuum 2 h comes last. On the basis of this classification, we can conclude that at least in the case of FZ silicon, the RTA treatment appears to be more promising than CTA, because the degradation induced in  $L_D$  is lower. This conclusion confirms the earlier results of our previous works [10, 11]. If one must apply the CTA mode, then it is better to do it under neutral gas

ambient rather than vacuum. Moreover, the duration of heating time must be relatively short, except if some propitious conditions for gettering arise, in which case the thermal treatment may have beneficial effects.

If we compare CZ and FZ materials, a noticeable difference in behaviour with respect to the annealing cycles can be easily observed. Indeed, whatever the thermal cycle and temperature chosen, the degradation of  $L_D$  in FZ silicon is systematically larger than that observed in CZ crystal. This difference in  $L_D$  behaviour stems from the oxygen content of the as-grown material. In CZ silicon, oxygen is known to form complex defects with vacancies and with metallic impurities. Since surfaces are known to be sources of vacancies, it is possible that recombination centres which degrade  $L_D$  are related to vacancy complexes. Thus by pairing off with vacancies and gettering metallic impurities, oxygen competes with the formation of defects and leads to lower degradation of  $L_D$ , as observed here in CZ material.

If we correlate all the experimental results we have obtained, and the various literature data that we have consulted (for a comprehensive review see ref. 5), we believe that the recombination centres introduced in our annealed samples are essentially due to activation of metallic impurities, very probably transition metals. Some of these impurities exist in the starting material (residual content of metallic atoms), but the major part might be a result of contamination of the samples from handling and equipment (external contamination). Indeed, it has been proved that handling a bare silicon wafer with metal tweezers introduces a large number of metallic impurities which exceeds the initial content [12].

In CZ silicon material, the classical thermal treatments appear to act less unfavourably on  $L_D$  in comparison with treatment using a rapid anneal system. This could be due to the fact that, with the RTA mode, slow diffusing metallic impurities, of internal (residual atoms) and external (contamination) origin, are frozen in electrically active sites in the quenching step inherently included in the annealing cycle. In the case of classical cycles, the samples are slowly cooled off. So, during the cooling step, the metallic impurities can be electrically deactivated, either by precipitation on as-grown nucleation centres, or by an intrinsic gettering mechanism exerted by oxygen microprecipitates pre-existing in the bulk of the wafers. So, at the end of the thermal cycle, the samples can be extracted from the furnace without recombination defects.

In FZ silicon, neither the as-grown nucleation centres which allow precipitation, nor the sites favourable for the intrinsic gettering process are generally present. Therefore, the metallic impurities cannot get rid of their electrical activity. In this case, either they keep their

active form, or they form more stable defects in the material. The concentration and the nature of these defects depend on the number of external impurity atoms which diffuse towards the bulk of the sample during its stay in the furnace. As this number increases, the electrically active defects, resulting from metallic impurities which have not been deactivated, can increase, develop or exist under many forms. We understand, therefore, why more prolonged heating or a higher annealing temperature lead to a more significant degradation of  $L_D$  in this material. In the first case, the duration of heating affects directly the number of external impurities diffusing towards the bulk of the material. In the second case, the more the annealing temperature increases, the longer the cooling step, and consequently the time the samples remain in the furnace is prolonged. This has positive consequences on the number of external impurities diffusing in the samples. For treatments under argon flux, the risks of contamination by metallic impurities are relatively reduced and  $L_D$  remains less degraded. To develop this discussion and justify the conclusions, we refer to comprehensive reviews [5, 13] and our previous publications [14, 15] in which we give proof that external contamination by metallic impurities is at the origin of the  $L_D$  degradation.

#### 4. Conclusion

In this work, we carried out a systematic study of the effects of various thermal treatments needed in the fabrication of electronic devices, on the minority carrier diffusion length  $L_D$ . To perform this study, commonly available quality monocrystalline silicon was used and close attention was paid to the influence of the oxygen content in as-grown material. By varying the physical parameters characterizing the annealing cycles such as heating mode, ambient and duration, we have been able to classify the various thermal treatments as a function of their harmful effects on  $L_D$ . From the discussion of

our results and based on recent literature data, it seems that residual metallic impurities, external contamination, and oxygen content play an important role in determining the final  $L_D$ . The mechanism of interaction and their influence, as we have tried to present in this paper, will be helpful in understanding the complex problem of thermal process-induced recombination centres in heat-treated silicon.

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