

Effective lifetime of minority carriers in silicon: the role of heat- and hydrogen plasma treatments

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1. Introduction. The problem of the bulk minority carrier lifetime of silicon calls for a better fundamental understanding, since a number of silicon-based devices (such as detectors and solar cells) requires as high as possible values of the minority carrier lifetime in high-purity and low-cost material, respectively. In both cases this material parameter can be influenced by thermal treatments during the device processing and also by an incorporation of hydrogen. Moreover the growing importance of low-cost silicon for terrestrial solar cell applications needs a development of techniques for the improvement of the material. In a certain sense such techniques as gettering or hydrogenation are the penalty for the low-cost production. The advantage of this approach comes from the possibility to improve the material properties by using a low-temperature budget.

One of the effective methods to realize this strategy is the hydrogen plasma treatment, which is usually regarded as hydrogen bulk passivation. The present understanding of this phenomenon attributes the improvement of the minority carrier lifetime to the passivation of dangling bonds of structural defects. At the same time it is well established that mainly the oxygen-related defect centers are responsible for the bulk lifetime value in p-type silicon. Most of these defects are thermally dissociated during the solar cell processing in the case of the conventional high-temperature technology based on diffused p-n junction silicon solar cell fabrication. At the same time, only limited information concerning the interaction between hydrogen and oxygen-related centers and the resulting influence on the effective lifetime of minority carriers in silicon is known from the literature.

This paper reports the results of lifetime measurements of different silicon (both n and p-type) materials (Cz Si, FZ Si, mc-Si (Baysix)) after heat treatments at 700°C and below, using a microwave photoconductivity decay (μ -PCD) set up. An effective lifetime, which depends on the bulk lifetime and the surface recombination velocity, can be obtained in this way.

2. Experimental. Hydrogenation was done by two different methods. The one-step hydrogenation was done using a remote-plasma set up at 200-400°C. For the two-step hydrogenation process samples were exposed to a RF hydrogen plasma at ~260 °C in a standard PECVD set-up at 13.56 or 110 MHz (first step). The post-hydrogenation annealing was done at temperatures around 400 °C in forming gas or in flowing nitrogen (second step). To extract the bulk lifetime values a surface passivation was performed. The influence of surface recombination was minimized by a hydrogen termination using an HF treatment; α -Si:H or SiN_x layer deposition was used for the surface passivation. The deposition of α -Si:H and

SiN_x layers were done in a conventional PECVD reactor.

3. Results and Discussion. It is found that the hydrogen incorporation into the high-purity FZ silicon leads to a *decrease* of the value of the lifetime. By using a comparative analysis of high-purity oxygen-free and oxygen-rich FZ Si it is established that the presence of both oxygen-related centers and hydrogen leads to a decrease of the minority carrier lifetime in Si. It is concluded that the formation of lifetime killer centers can be attributed in this case to the hydrogen-oxygen-related complexes in Si.

It will be demonstrated that the presence of hydrogen in p-type mono-crystalline Si is not desirable since it leads to the formation of lifetime killer centers. In case of multi-crystalline Si the same mechanism is active but it is competing with the hydrogen passivation of grain boundaries and could eventually be positive for the enhancement of the minority carrier lifetime in this material. The application of the developed method for the enhancement of the efficiency of Hetero Junction (HJ) solar cells on p-type Si substrates will be demonstrated.

At the same time it is established that the thermal donor formation process, which occurs at temperatures around 400 °C leads to the enhancement of the minority carrier lifetime especially in Cz Si (Fig. 1). It is found that the absolute lifetime value can be enhanced up to one order of magnitude in this case. This result can be explained by an effective low-temperature gettering process by oxygen-related centers.

All substrates had an unknown preparation pre-history and were measured after the surface passivation by HF-dip hydrogen termination. One can see a low lifetime for as-received Si, and a strong increase after the heating. It is speculated that unintentional incorporation of hydrogen during the wafer preparation steps might be responsible for the lifetime decrease in as-received substrates before and after the heating. Moreover, it was found that hydrogen termination by an HF-dip is as good a passivation as by an α -Si:H layer and can be used for lifetime measurements by the μ -PCD method.

It will also be shown that the deposition temperature of the α -Si:H or SiN_x passivation layers is an important parameter to provide a good effective minority carrier lifetime. In other words, not only the quality of the surface passivation but also the evolution of the impurity system (mainly oxygen and hydrogen) in all investigated silicon-based samples by the heat treatment during the passivation procedure (α -Si:H, SiN_x layer deposition) controls the effective minority carrier lifetime. Finally, it is shown that a degradation of the effective minority carrier lifetime with time for all investigated kinds of surface passivation was observed.

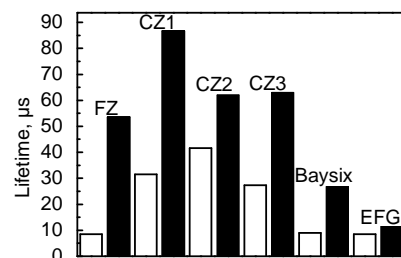


Figure 1: Lifetime of as-received (white) and annealed (black) at 450°C for 20 min Si samples: **CZ1** – CZ Si, 1.5 Ω cm; **CZ2** – Cz Si 3 Ω cm; **CZ3** – CZ Si, 10 Ω cm. All samples before measurements were terminated by hydrogen using the HF-dip treatment.