

STUDY ON THE DISSOCIATION OF GALLIUM-HYDROGEN PAIRS IN CRYSTALLINE SILICON DURING ILLUMINATED ANNEALING

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ABSTRACT: In this study, fundamental investigations are performed on gallium-doped Cz-Si samples with regard to the hydrogen content introduced from PECVD SiN_x:H layers in a firing step. The change in gallium-hydrogen (GaH) pair concentration was monitored with highly sensitive resistivity measurements since pair formation counteracts doping. It is found that GaH pairs form during dark annealing at elevated temperatures. In contrast, they partially dissociate within a few seconds at 240°C when excess charge carriers are generated by illumination. This fast dissociation is reversible such that GaH pairs form again during a subsequent dark anneal at 180°C. The dependence on excess charge carrier concentration suggests an electron-driven dissociation reaction.

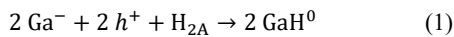
If illumination at elevated temperature is applied for days, even more GaH pairs dissociate as indicated by the change in resistance. Since it is not possible to form GaH pairs in a subsequent dark anneal, it is proposed that two different dissociation processes are taking place which might be independent or a cascade reaction.

Keywords: Hydrogen, Defects, Gallium-Hydrogen pairs

1 INTRODUCTION

The release of hydrogen from a dielectric layer is the most common method in solar cell production to use its ability to passivate dangling bonds and neutralize several defects and impurities in crystalline silicon. However, hydrogen has also a particular role in the generation of defects formed during light- and elevated temperature-induced degradation (LeTID), which can reduce solar cell efficiency significantly [1–2]. Since the underlying mechanisms of LeTID are still unclear and the direct microscopic impact of hydrogen is not tangible, quantifying hydrogen might be the key in the understanding of this defect. With only 10¹⁴ to 10¹⁵ cm⁻³, the total hydrogen concentration is fairly low, making it difficult to be observed directly. However, H tends to form acceptor-hydrogen pairs influencing bulk resistivity giving access to the hydrogen content. Therefore, the better accessible reaction of hydrogen with acceptors is a promising route for further investigations.

Such studies got some attention recently [3–6] on boron-doped silicon. This contribution focuses entirely on the study of gallium-hydrogen pairs (GaH) in Cz-Si. Adopted from the case of boron [3], the predominant overall reaction during annealing in the dark at elevated temperatures is



where this process consumes holes h^+ changing hole concentration p . The change in pair concentration $\Delta[\text{GaH}]$ can be derived from the change in (negative) hole concentration $-\Delta p$, thus $\Delta[\text{GaH}] = -\Delta p$. However, as Δp is only a measure of the change, it does not carry any information on the pair concentration already existent before annealing. Therefore, it is the aim of this study to clarify whether and under what circumstances the back reaction takes place so that (already existing) GaH pairs may be deliberately dissociated and thus quantified.

2 EXPERIMENTAL

Mono-crystalline Cz-Si:Ga (0.7 Ωcm) wafers were saw damage etched (KOH for 8 min at 80°C, final thickness 160 μm) and cleaned (surface oxidation by ozone followed by an HF dip). Subsequently, SiN_x:H

layers with thickness of 80 nm and index of refraction $n = 2.05$ were deposited on both sides using PECVD. The non-metallized samples were fired in a belt furnace with a measured sample peak temperature of 870°C to provide H-rich samples. Contacts were produced by thermal evaporation of aluminum and subsequent laser pulses to form laser fired contacts [7] allowing for direct contact resistance measurement. Resistivity measurements were performed in a four-terminal configuration on a temperature-controlled measurement setup as described in [8]. The negative change in hole concentration $-\Delta p = p_0 - p$ was calculated with respect to the hole concentration of a reference state p_0 from the resistance R of the sample. Hole mobilities for the respective hole concentration were taken from PVlighthouse mobility calculator [9].

To trigger formation of the pairs, the samples were dark annealed at 180°C on a hotplate (Prazitherm PZ-28, uncertainty ±0.5°C) until resistivity does not change any more. The dark anneal was repeatedly interrupted for ex-situ resistance measurements. To investigate the GaH pair dissociation, the samples were subjected to variable excess charge carrier concentrations Δn by illumination with a monochromatic, homogeneous light source ($\lambda = 808 \text{ nm}$) at $T = 240^\circ\text{C}$. In addition to the resistance, the effective lifetime τ_{eff} of excess charge carriers was determined via photoconductance decay measurements (WCT-120 lifetime tester, Sinton Instruments) regularly to allow for intensity adaptations in order to achieve constant

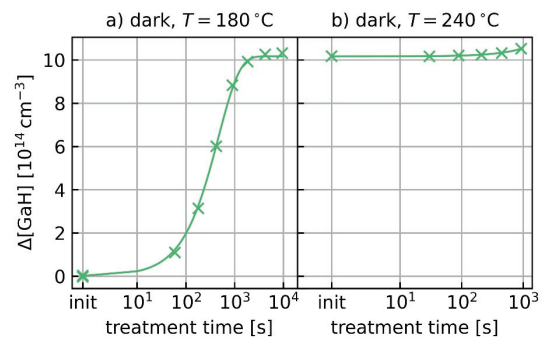


Figure 1: Change in [GaH] derived from negative change in hole concentration $-\Delta p$. a) Formation of GaH pairs during dark anneal at 180°C. b) Subsequent treatment at 240°C. Lines are guide to the eye only.

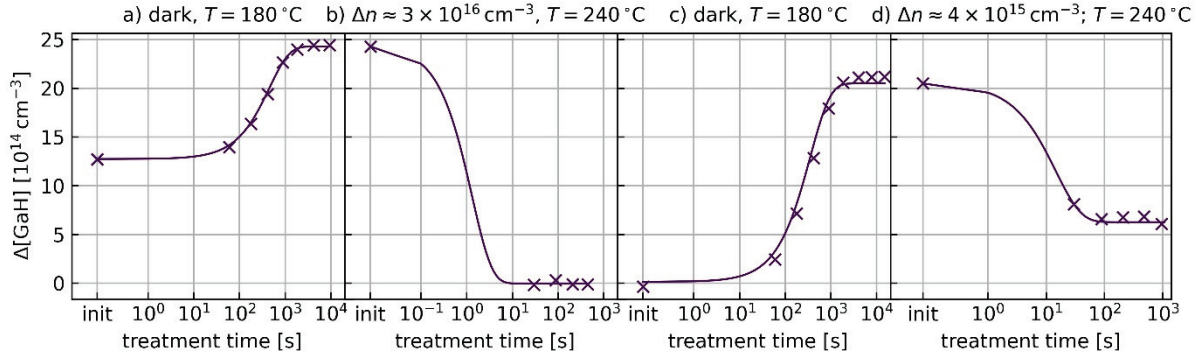


Figure 2: Change in [GaH] derived from negative change in hole concentration $-\Delta p$. a) Formation of GaH pairs during dark anneal at 180°C. b) Subsequent illuminated anneal at 240°C. c) Formation of pairs in the dark. d) Dissociation again with different excess charge carrier concentration Δn . Lines are guide to the eye only.

excess charge carrier concentration despite changes in τ_{eff} . It should be mentioned that samples were at 30°C during lifetime measurement. Due to the temperature dependence of τ_{eff} , an uncertainty in Δn is expected, since the illuminated anneal takes place at 240°C.

Three experiments were conducted: dark annealing only (Fig. 1), a sequence of dark and “short” illuminated annealing steps (Fig. 2), and a sequence of dark and “long” illuminated annealing steps (Fig. 3). Note that the first dark annealing step is the same for all experiments and is intended to form GaH pairs for later dissociation steps.

3 RESULTS

The relative change in pair concentration $\Delta[\text{GaH}]$ derived from resistance measurements during dark anneal at 180°C in three experiments is plotted in Fig. 1 a), 2 a) and 3 a). The scaling of $\Delta[\text{GaH}]$ is different in each figure, since the reference state p_0 was deliberately set to the minimum value for each sample in the course of the experiment.

The concentration of GaH pairs is rising until ~ 2 h, after which a saturation value seems to be reached.

In order to check whether annealing at 240°C even without illumination already leads to a dissociation of GaH pairs, the change in charge carrier concentration Δp during a subsequent anneal at $T = 240^\circ\text{C}$ and $\Delta n = 0$ was studied (Fig. 1 b). There is no significant change despite a small increase which is likely to be attributed to the formation of thermal donors [5]. Things change drastically if

illumination is applied, as shown in Fig. 2 b). A fast change in resistance which translates into a steep decrease of $\Delta[\text{GaH}]$ is visible for treatment times below 1 min. Note that due to the lack of data in the first minute the shown line does not necessarily reflect the true progression. The change in resistance is partially reversible as shown in Fig. 2 c) and 2 d), where dark annealing followed by illuminated annealing reproduces the temporal behavior observed before. This gives strong evidence that the aforementioned reaction runs forward without excess charge carriers and backwards with charge carrier injection. Since the extent of the decay is higher with higher injection, it is reasonable to assume that the equilibrium of formation and dissociation can shift with excess charge carrier concentration.

It turns out that not only the equilibrium value as a result of formation and dissociation but also the dissociation rate constant is dependent on injection level Δn and temperature [10]. This is probably the reason behind the different limiting values in Figs. 2 b) and 2 d) obtained under different illumination conditions.

While most of the effect seems to occur in several seconds for the presented combinations of temperature and injection, this process can take up to an hour at temperatures of 180°C [10]. It is likely that the aforementioned dependence of the reaction rate on injection is caused by the fraction of different charge states of hydrogen. The fraction depends on Fermi level [11,12] which in turn is determined by excess charge carrier concentration. As described elsewhere in more detail [10], the fraction of negatively charged hydrogen can explain

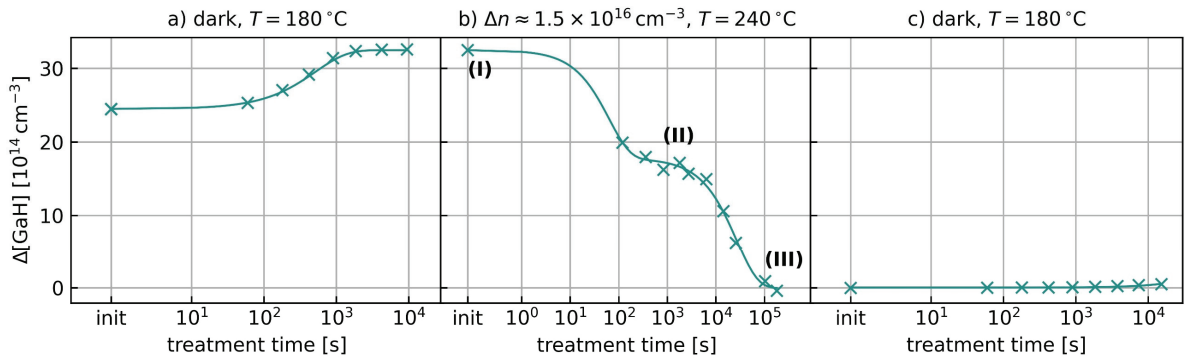


Figure 3: Change in [GaH] derived from negative change in hole concentration $-\Delta p$. a) Formation of GaH pairs during dark anneal at 180°C. b) Subsequent extended illuminated anneal at 240°C. c) No pair formation in the dark. Lines are guide to the eye only.

the dependence of the reaction rate on injection Δn .

However, cycling between formation and dissociation in Fig. 2 does not seem to be perfectly reversible as the limiting values in Figs. 2 a) and 2 c) are not the same. The reason behind this might be explained by the third experiment (Fig. 3). For illuminated annealing for more than 1 day, another increase in hole concentration indicates a second, slower decrease in GaH pair concentration. This behavior is depicted in Fig. 3 b) as transition between (II) and (III). After the state indicated by (III) is reached, pair concentration $\Delta[\text{GaH}]$ does not change significantly under dark annealing conditions (Fig. 3 c) making this an irreversible process. Hence, the difference in limiting values in Figs. 2 a) and 2 c) might indicate that some irreversible dissociation already occurs there as well.

Due to the difference in time constants of these two effects and their different behavior (reversible vs. irreversible), there are probably two processes ongoing. However, the presented data are not sufficient to tell whether a cascade reaction takes place or two independent reactions. However, it is plausible that the first, reversible dissociation of GaH under illumination pairs shifts reaction (1) towards its precursors $\text{H}_{2\text{A}}$ and unpaired Ga^- . The second drop in pair concentration may be attributed to a transition of hydrogen into a more stable configuration. Effusion cannot be excluded as well.

3 CONCLUSIONS

The formation and dissociation of GaH pairs in Ga-doped Cz:Si has been investigated successfully via resistivity measurements.

The formation of these pairs can be triggered in hydrogen-rich samples by dark annealing, the dissociation only occurs in presence of excess charge carriers. If injection is applied, a balance between formation and dissociation is established. Since the dissociation only takes place in the presence of excess charge carriers, the assumption of an electron-driven process is obvious. GaH pairs form again during a subsequent dark anneal.

In contrast, illuminated annealing durations of days lead to the dissociation of additional GaH pairs. This dissociation is reversible in a sense that these pairs do not form again during a subsequent dark anneal.

The results presented here open the way for concise hydrogen determination in Ga-doped silicon and the insight into the behavior of GaH pairs can help in the understanding of the LeTID effect.

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