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# Can hydrogenation mitigate Cu-induced bulk degradation in silicon?

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**Abstract**—Many defects can cause significant bulk degradation in crystalline silicon, which inherently limits solar cell efficiency. Perhaps the most well-known source of light-induced bulk degradation (LID) in Czochralski-grown silicon is the boron-oxygen defect. However, metal impurities, such as copper, can also cause severe degradation. Advanced hydrogenation processes incorporating minority carrier injection can effectively passivate boron-oxygen complexes, but their effect on copper-induced degradation has not been studied previously. Herein, we explore the effect of hydrogenation on LID in copper-contaminated silicon. Without hydrogenation the bulk lifetime decreases down to 5  $\mu\text{s}$  while in hydrogenated samples the bulk lifetime remains above 300  $\mu\text{s}$  during the whole degradation cycle. The results thus indicate that even in heavily copper-contaminated silicon hydrogenation can passivate Cu precipitates and mitigate Cu-LID.

**Keywords**—copper contamination, light-induced degradation, bulk defects, hydrogenation

## I. INTRODUCTION

Various light-induced degradation phenomena affect the minority charge-carrier lifetime in solar-grade crystalline silicon, which in turn leads to decreased solar cell efficiency. Czochralski-grown silicon (Cz Si) is known to suffer from bulk degradation caused by boron-oxygen complexes under illumination, often referred to as boron-oxygen light-induced degradation (BO-LID) [1]. BO-LID and ways to mitigate it have been studied extensively in the recent years, as reviewed by Niewelt *et al.* [2]. A successful method to eliminate BO-LID in Cz Si is advanced hydrogenation processing, in which hydrogen released from silicon nitride ( $\text{SiN}_x\text{:H}$ ) coatings passivates the lifetime-limiting bulk defects during subsequent illuminated annealing [3].

Other significant causes for light-induced bulk degradation in crystalline Si are metal impurities. Especially copper (Cu) is

a detrimental contaminant that causes severe and non-recoverable bulk degradation in silicon under illumination [4]. This phenomenon, dubbed Cu-LID, has been widely studied, and it is reportedly caused by Cu precipitation in Si bulk [5], [6].

Low Cu concentrations in the order of  $10^{10} \text{ cm}^{-3}$ , which can be present in commercial p-type Si, have been shown to cause significant Cu-LID [7]. Additionally, severe Cu contamination has been reported in slurry-based silicon wafer slicing [8], and electroplated Cu contacts have been proposed as alternative front contacts in Si solar cells [9]. Therefore, understanding Cu-induced degradation is especially important in the photovoltaic community. The success of advanced hydrogenation in the mitigation of BO-LID leads to the question if Cu-LID could also be passivated using hydrogenation. In this report, we study the degradation of bulk lifetime in intentionally Cu-contaminated Cz Si. We compare samples passivated with either thermal silicon dioxide ( $\text{SiO}_2$ ) or hydrogen-rich  $\text{SiN}_x\text{:H}$  deposited using plasma-enhanced chemical vapor deposition (PECVD) to explore the effect of hydrogenation on Cu-LID behavior.

## II. METHODS

Fig. 1 describes the processing and characterization of the samples. 156 mm  $\times$  156 mm solar-grade Cz Si wafers (thickness approx. 165  $\mu\text{m}$ , resistivity 2  $\Omega\cdot\text{cm}$ ) were used as substrates. The interstitial oxygen concentration was 13 ppma. After cleaning with RCA solutions and dilute HF (DHF), the wafers underwent dry thermal oxidation at 900°C. The resulting 15 nm  $\text{SiO}_2$  film was used as a surface passivation layer and a barrier layer against unintentional impurity contamination during the following Cu contamination, as only Cu can diffuse through the oxide [10]. After oxidation, the wafers were intentionally Cu-contaminated with dilute nitric acid solutions containing either 15 ppb or 100 ppb Cu ions. The wafers were spot-contaminated so that all wafers had an area contaminated with

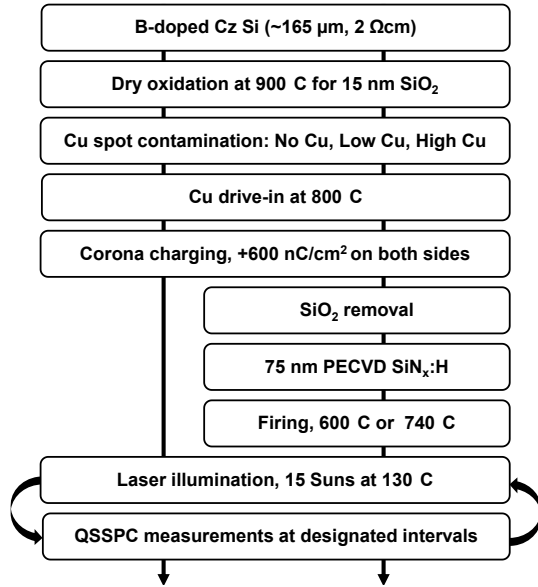


Fig. 1. Process flow describing the processing and characterization of the samples.

the 15 ppb (referred to as Low Cu) and a different area contaminated with the 100 ppb (High Cu) solution. All wafers also had an area without Cu contamination (labeled No Cu). Cu ions were driven into Si bulk by a 20-min anneal in  $N_2$  at  $800^\circ C$ . After drive-in, both surfaces of the  $SiO_2$ -passivated samples were corona charged with  $+600 \text{ nC/cm}^2$  to ensure that the Cu ions stay in the Si bulk [10], [11]. Half of the wafers were used as control with  $SiO_2$  as the passivation layer, while in the other half the  $SiO_2$  layer was removed, and a 75-nm-thick  $SiN_x:H$  film (refractive index 2.08 at 633 nm) was deposited on both sides of the wafers using a Meyer Burger MAiA PECVD tool.

The  $SiN_x:H$ -passivated samples were fired to induce hydrogen into the silicon bulk with a measured peak temperature of either  $598 \pm 2^\circ C$  (labeled  $600^\circ C$  in the text) or  $740 \pm 2^\circ C$  (labeled  $740^\circ C$ ) using a belt furnace at belt speed of 550 cm/min. The accelerated degradation was carried out at  $130^\circ C$  with 15 suns laser illumination intensity (938 nm) for up to 500 s. The minority-carrier lifetime of all Cu-contaminated areas on the wafers was measured by the quasi steady-state photoconductance (QSSPC) method (Sinton Instruments WCT-120 tool) at designated illumination intervals. Bulk lifetime was determined from the injection-dependent carrier lifetime. First, the surface saturation current density  $J_0$  was fitted into the measurement data [13]. Then, the inverse bulk lifetime was calculated by subtracting the inverse lifetime corresponding to  $J_0$  from the inverse of the measured effective lifetime.

### III. RESULTS AND DISCUSSION

Fig. 2 shows an example of charge-dependent inverse effective carrier lifetime in a  $SiO_2$ -passivated Low Cu sample. The dots and continuous lines refer to measured data, while the dashed curves refer to the calculated Surface Defect Recombination (surface) component. The dashed lines with dots denote the calculated Shockley-Read Hall (bulk) component. These model components do not necessarily account for all bulk or surface recombination mechanisms. Moreover, the low-

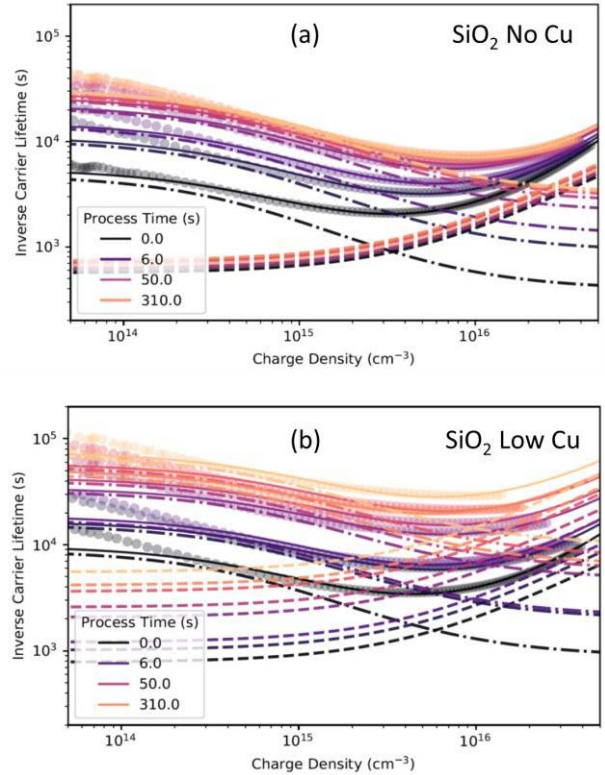


Fig. 2. Examples of charge density dependent inverse effective lifetime for a  $SiO_2$ -passivated No Cu (a) and Low Cu (b) samples. Dots and continuous lines denote measured lifetime data, based on which the surface (dashed lines) and bulk (dashed lines with dots) components were calculated.

injection tail of the lifetime data does not fit perfectly (as can be seen in Fig.2), which is likely due to the specific nature of the Cu-based defect. Nevertheless, the accuracy of the fit is sufficient for analyzing differences in bulk lifetime as a function of illumination time.

Similar analysis was done for all samples. A general trend in effective lifetime in the  $SiO_2$ -passivated samples is that they degrade with all Cu levels and that degradation is more pronounced with a higher Cu concentration. In the  $SiN_x:H$ -passivated samples, on the other hand, the degradation is much smaller and also a clear recovery is observed after degradation. Furthermore, the Cu dependency is not as clear as in the  $SiO_2$  samples. An interesting observation is that the  $SiO_2$ -passivated Cu-contaminated samples exhibit clear surface degradation in addition to bulk degradation, but this phenomenon is discussed in detail elsewhere [13].

To further study the influence of hydrogen on the passivation of possible Cu defects, the bulk lifetime at  $\Delta n = 1.5 \cdot 10^{15} \text{ cm}^{-3}$  for both passivation layers and all Cu levels is presented in Fig. 3: (a) for  $SiO_2$ -passivated samples, (b) for  $SiN_x:H$ -passivated samples fired at  $600^\circ C$ , and (c) for samples fired at  $740^\circ C$ . In the  $SiO_2$ -passivated samples, the bulk lifetime decreases as a function of the contamination level so that the extent of degradation is clearly higher for the samples with higher Cu concentration. It is worth to point out that in heavily Cu contaminated sample, the degradation is really significant as the

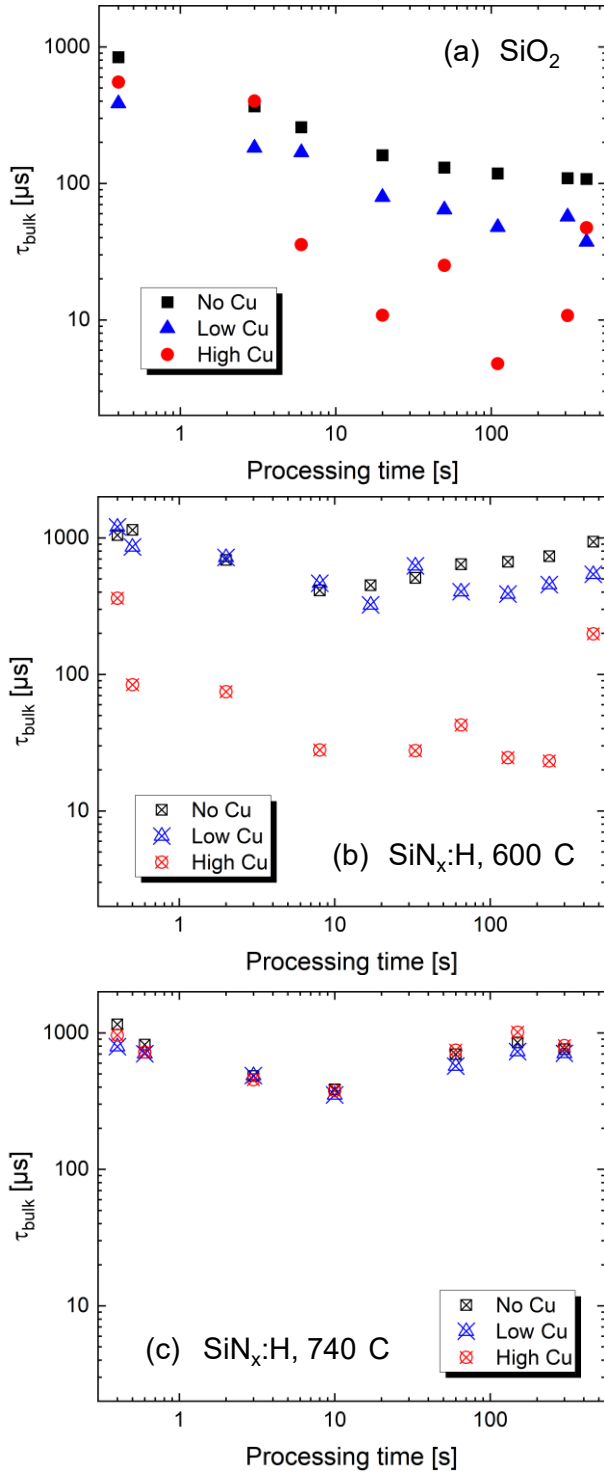


Fig. 3. Bulk lifetime for (a)  $\text{SiO}_2$ -passivated, (b)  $\text{SiN}_x\text{:H}$ -passivated samples fired at  $600^\circ\text{C}$ , and (c)  $\text{SiN}_x\text{:H}$ -passivated samples fired at  $740^\circ\text{C}$  with all Cu levels.

bulk lifetime decreases from nearly a millisecond to less than  $10 \mu\text{s}$ . This was expected behavior based on literature although Cu-LID has not been studied earlier with such accelerated conditions [14]. The dominating degradation mechanism in the Cu-contaminated samples is likely Cu precipitation in the bulk,

while the decrease in bulk lifetime in the No Cu area can be explained by conventional BO-LID. As the  $\text{SiO}_2$  passivation layer does not contain a significant amount of hydrogen, the BO defects are not passivated in the bulk nor is Cu-LID recovered even after prolonged illumination.

On the other hand, the bulk lifetime in the  $\text{SiN}_x\text{:H}$ -passivated samples shows clearly different behavior than in the  $\text{SiO}_2$ -passivated samples. The  $\text{SiN}_x\text{:H}$ -passivated reference and Low Cu samples fired at relatively low temperature ( $600^\circ\text{C}$ ) show clear signs of successful hydrogenation: the degradation is much smaller and is even followed by almost a full recovery, which is characteristic behavior for BO-LID. However, the bulk lifetime in the High Cu samples drops to below  $30 \mu\text{s}$  already after 10 s of illumination and does not show a similar recovering trend. Thus, Cu-LID appears to be mitigated in the Low Cu samples, while Cu precipitation is still the dominant bulk lifetime-limiting mechanism in the High Cu samples.

In the samples fired at  $740^\circ\text{C}$ , the behavior is again different. As contrary to the lower firing temperature, recovery of the bulk lifetime is observed also in High Cu samples so that the lifetime remains above  $400 \mu\text{s}$  during the whole illumination cycle. Actually, all the samples seem to become identical after the hydrogenation treatment and show only BO-LID defect characteristics. Consequently, Cu-LID seems to be completely eliminated in the samples fired at  $740^\circ\text{C}$ . This suggests that the species that passivates the Cu-related defects is not the limiting factor: Cu-LID was recovered at a similar rate despite the Cu concentration.

Based on the results by Nampalli *et al.* [14], Cu-LID should be more pronounced with the higher firing temperature. This is because firing was shown to dissolve possible Cu precipitates and drive mobile Cu atoms into the bulk making them more harmful for the bulk lifetime during subsequent illumination. Therefore we can assume that the samples that experienced higher temperature firing should have at least the same amount (or even more) of harmful Cu atoms in the bulk than the ones fired at  $600^\circ\text{C}$  or those without firing at all ( $\text{SiO}_2$  samples). Consequently, it was rather surprising to see that Cu-LID dominated in the samples that were fired at low temperature – but not at high temperature. This can be explained by that the lower firing temperature potentially leads to a smaller concentration of hydrogen in the Si bulk, not providing enough hydrogen to passivate a high amount of Cu defects. This leaves the LID caused by the higher Cu concentration unrecovered. The higher firing temperature, on the other hand, introduces more hydrogen into the Si bulk, which leads to the efficient passivation of Cu precipitates even when the samples are highly Cu contaminated.

#### IV. CONCLUSIONS

Cu-contaminated  $\text{SiO}_2$  and  $\text{SiN}_x\text{:H}$  passivated samples showed significantly different bulk degradation behavior under high-intensity illumination (15 suns) at elevated temperature. In the  $\text{SiO}_2$ -passivated samples the extent of the bulk degradation had a direct correlation with Cu concentration. Without Cu contamination bulk lifetime remained above  $100 \mu\text{s}$  and was dominated by BO-LID, while in the Cu contaminated samples the lifetime was significantly lower decreasing even below  $5 \mu\text{s}$ . On the contrary, in the  $\text{SiN}_x\text{:H}$  samples fired at  $740^\circ\text{C}$  the bulk

lifetime remained above 300  $\mu$ s during the illumination in all samples regardless of Cu concentration showing to our surprise no more traces of Cu-LID. However, when the firing was done at lower temperature, at 600°C, only the samples with low copper concentration could be successfully hydrogenated and severe bulk degradation was still present in heavily contaminated samples. This is a clear indication that in the latter case there was likely not enough hydrogen released into the bulk to passivate all possible Cu defects. The results presented here thus lead to the conclusion that hydrogen released from the SiN<sub>x</sub>:H film can passivate recombination-active Cu precipitates even in heavily Cu-contaminated silicon and mitigate Cu-LID, provided that the firing step is done at a sufficiently high temperature. In the future, it should be investigated whether the successfully hydrogenated copper samples maintain the high lifetime also under field operation conditions.

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