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Exceeding 3 *m*s minority carrier lifetime in *n*–type non–contact crucible silicon

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Abstract

The presence of metal impurities and their interactions with structural defects (*e.g.*, dislocations) are deleterious to the performance of Si-based solar cell devices. To achieve higher minority carrier lifetimes that translate into higher solar cell efficiencies, novel growth methods with low dislocation densities and reduced metal impurity concentrations have recently been developed. These methods simultaneously aim to achieve low capital expense (capex), necessary to ensure rapid industry scaling. Monocrystalline Si grown by the non-contact crucible method (NOC-Si) has the potential to achieve high bulk minority carrier lifetimes and high efficiencies at low cost given its low structural defect density. Growth in large-diameter crucibles ensures high throughput consistent with low capex. However, high temperatures, coupled with conditions during Si growth (*e.g.*, crucible and ambient gas) can lead to the in-diffusion of impurities, compromising the potential to achieve high efficiency solar cell devices. Herein, we report high minority-carrier lifetimes exceeding 3 milliseconds (*m*s) in *n*-type NOC-Si material, achieved through a strict impurity-control procedure at the growth stage that prevents in-diffusion of impurities to the melt, coupled with a tailored defect-engineering process *via* optimized phosphorus gettering.

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Keywords: defects; impurities; minority-carrier lifetime; non-contact crucible; top-seeded solution growth; silicon; solar cells.

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1. Introduction

Metal point defects are known to be detrimental to solar cell performance [1, 2]. This detriment is exacerbated by the presence of structural defects (*e.g.*, grain boundaries and dislocations) [3, 4]. To maximize cell performance, new material growth methods have been developed to produce Si crystals with little or no grain boundaries and low dislocation densities [5, 6]. To ensure deployment, high quality material must be produced and at low cost [7].

A promising method that has recently gained attention is the non-contract crucible method (NOC-Si) [8, 9], which leverages the low cost structure of a cast-based growth method, while producing single-crystal Si material that enables high-efficiency solar cell devices [10]. However, as with all growth methods, the challenge to control metal point defect concentrations remains. High-temperatures required to grow Si enable incorporation of metal impurities into the melt as well as solid-state in-diffusion during growth. Strict control of the growth environment is therefore required for a material to achieve its entitled bulk minority-carrier lifetime [10].

We posit that as structural defect density is reduced, a cleaner bulk material is required to achieve higher minority-carrier lifetimes. Reducing impurities in the bulk can be achieved *via* two methods: (*i*) control of impurities in the growth environment (*e.g.*, contact interfaces, gas conditions), and (*ii*) through optimization of post-growth processing (*e.g*, Phosphorus gettering) which, in turn, drives impurities out of the substrate and into the Phosphor-rich layer.

In this contribution we build upon the results from Kivambe *et al*. [11] in which >1.8 ms lifetimes were achieved with NOC-Si material through a defect-engineering approach where different P-gettering time-temperature profiles were implemented to achieve high bulk minority-carrier lifetimes. Herein we first assess the impurity-related contributors to the 1.8 ms minority-carrier lifetimes measured after P-gettering. A feedback cycle to the crystal growers is then implemented. We observe reductions in impurity concentrations in the new generation of the material, which reveals a significant performance improvement.

2. Materials and methods

2.1. Material growth

Two *n*-type ingots, labeled *A* and *B*, are grown by the NOC-Si method, as detailed in Refs. [8, 9]. Ingots *A* and *B*, shown in **Fig. 1**, correspond to two growth runs completed under different environmental conditions. Ingot *A* (~1–2 Ω-cm), grown with a (100) crystal orientation, is cooled after melting at a rate of 0.2 K/min. Ingot *B* (~1–2 Ω-cm) is grown with a (100) crystal orientation and cooled after melting at a rate of 0.4 K/min. Ingot *A* is 26 cm in diameter and 6.2 cm in length with a weight of 4.04 kg, and ingot *B* is 33 cm in diameter and 7.0 cm in length, with a weight of 5.80 kg. These properties and growth characteristics are summarized in **Table I**.

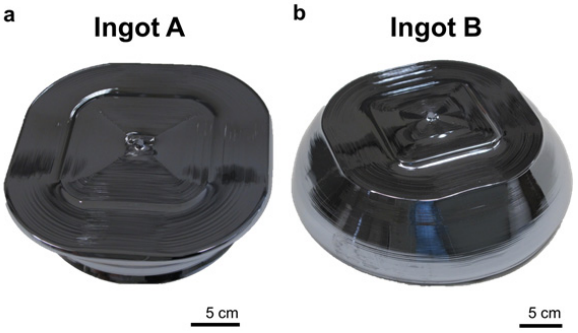

Fig. 1. Optical images of (a) NOC-Si ingot *A* with baseline impurity control, and (b) NOC-Si ingot *B* with improved impurity control.

Table 1. Measured properties and growth characteristics from Ingots *A* and *B*.

Material Properties and Growth Characteristics	Ingot *A*	Ingot *B*
Resistivity (Ω–cm)	1.1–2	1.2–2.2
Crystal Orientation	(100)	(100)
Cooling Rate (K/min)	0.2	0.4
Diameter (cm)	26	33
Length (cm)	6.2	7.0
Weight (kg)	4.04	5.80

Between the growth of ingot *A* and ingot *B*, the growth interface and crystal shape, which govern distribution of impurities, are modified. Besides implementing a cleaning of the environment between growth runs, a high-purity quartz shield is placed over the growth furnace to minimize metal point defect contamination from being transported into the liquid melt by gases.

2.2. Minority-carrier lifetime analysis

Wafers (12.5 × 12.5 cm^2, 200 μm thick) are sawn from both ingots and as-grown unpassivated minority carrier lifetimes are measured prior to laser-cutting the full size wafers into smaller samples (5 × 4 cm^2) for adequate handling and processing. Samples are subsequently saw-damage etched in a HNO_3:CH_3COOH:HF volumetric ratio mixture of 36:12:5 for five minutes to remove approximately 20 μm. Wafers are cleaned afterwards in an RCA chemical solution, eliminating metal and organic contaminants prior to surface passivation. Surface passivation is required to assess the bulk as-grown material quality and is performed by depositing 20 nm of Al_2O_3 via the atomic layer deposition (ALD) technique in a Cambridge NanoTech Savannah 200 tool at a 200 ºC temperature. Samples are subsequently annealed in a N_2 environment for 10 min at a temperature of 350 °C.

Lifetime maps are acquired with a Semilab WT-2000 microwave photoconductance decay (μ-PCD) tool, with a pixel resolution of 250 μm. The lifetime values from this technique are obtained by fitting a single time constant to a decay curve.

Injection-dependent lifetime curves are measured through the quasi-steady-state photoconductance (QSSPC) technique in a Sinton WCT-120 tool at room temperature.

2.3. Phosphorous diffusion gettering

Prior to gettering, wafer samples are first cleaned in RCA, followed by a 10% HF solution dip to remove the passivating Al_2O_3 layer. Phosphorous gettering is carried in a Tystar Tytan 2800 $POCL_3$ furnace. The time-temperature profile for P in-diffusion and gettering consists of loading the samples at 700 ºC, ramping up to 845 °C, plateauing for 25 min, followed by a 2 hour anneal at a temperature of 650 °C and immediate sample unloading, as reported in Ref [11]. This time-temperature profile has been reported to enhance the extraction of interstitial iron [12], and believed to be relatively effective in removing Cr species [13] in *p*–type Si materials.

After phosphorous gettering, samples are chemically etched in a HNO_3:CH_3COOH:HF volumetric ratio mixture of 36:12:5 for two minutes, removing 8 μm off of the wafer, including the phosphorus silicate glass (PSG) layer produced on the sample's surface after P in-diffusion. The samples are subsequently cleaned in an RCA chemical solution, and surface passivated with Al_2O_3 for a characterization of the post-gettered bulk minority carrier lifetimes.

2.4. Characterization process

The characterization process and feedback cycle to crystal growers is schematically represented in **Fig. 2**.

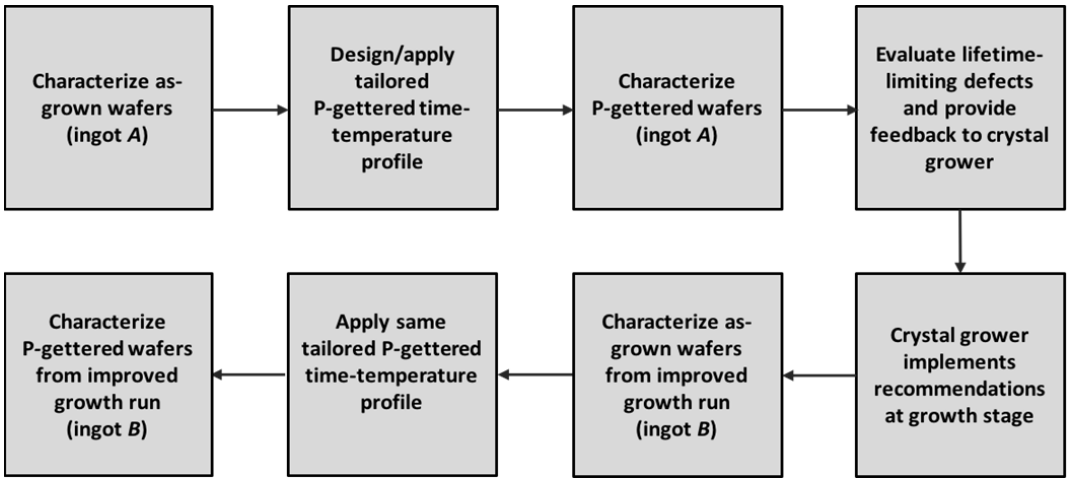

Fig. 2. Schematic representation of steps involved in the characterization and feedback to crystal growers process. Materials are initially characterized after their usual growth process (ingot *A*). Based on the defects identified, a tailored P-gettered time-temperature profile is designed and applied to improve bulk minority lifetimes. After post-P-gettering characterization, recommendations are provided to crystal growers to be implemented at the growth stage. Characterization is then performed on the wafers after environment conditions are modified during growth (ingot *B*) both at the as-grown state, and after P-gettering, while controlling for the P-gettered time-temperature profile.

3. Results and discussion

A comparative assessment of the bulk minority carrier lifetime responses from the P-gettered samples demonstrates a noticeable difference between growth cycles. By using the same P-gettering time-temperature profiles and implementing a stringent impurity control during growth (*i.e.*, cleaning of the growth environment, and placing a high-purity quartz shield over the growth furnace area), improvements in bulk minority carrier lifetime values were performed and quantified between growth runs.

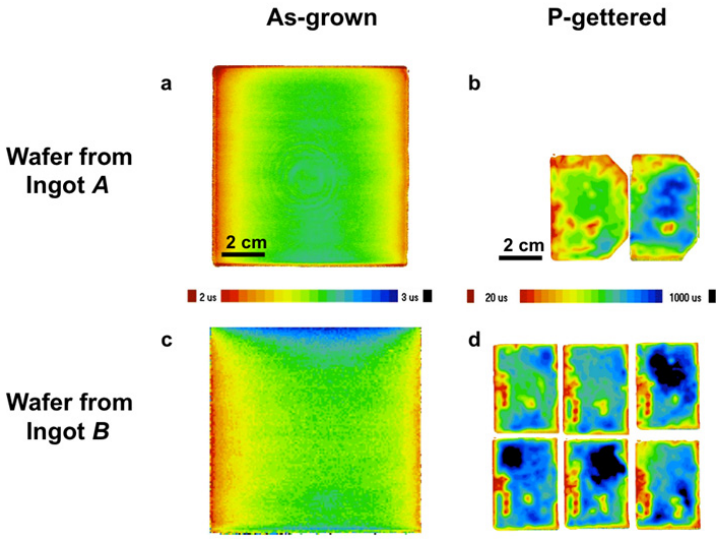

Fig. 3. µ-PCD Lifetime maps of the NOC-Si as-grown wafers from (b) ingot *A* and (c) ingot *B*. P-gettered µ-PCD lifetime maps of samples from the wafers in (a) and (d) are shown in (b) and (d) for ingot A, and B, respectively. Red continuous dots on (b) and (d) correspond to the laser scribing on each sample.

Spatial distribution differences in lifetime were quantified with μ-PCD (as-grown and P-gettered for samples from ingot *A* and *B*) as shown in **Fig. 3a–d**. The as-grown state lifetime distribution for samples from Ingot *A*, and *B*, are shown in **Figs. 3a** and **3b**, respectively. A homogeneous distribution can be observed in both cases, with the distinction that slight swirls can be observed in the wafer from ingot *A* causing slight lifetime variations in the center of the wafer. The lifetime response for samples from ingot *A* and *B* upon P-gettering are shown in **Figs. 3b** and **3d**, respectively. Larger areas and with higher bulk minority carrier lifetimes (denoted as dark blue and black color) can be observed for the samples from ingot *B*, as compared to the samples from ingot *A*.

Injection-dependent carrier lifetimes for the best-performing samples from ingots *A* and *B* are shown in **Fig. 4**. The effective lifetime improvements after P-gettering and adopting defect-control measures resulted in a 77% increase from 1.8 ms (ingot *A*) to 3.2 ms (ingot *B*) at $\Delta n=10^{15}$ cm^{-3}.

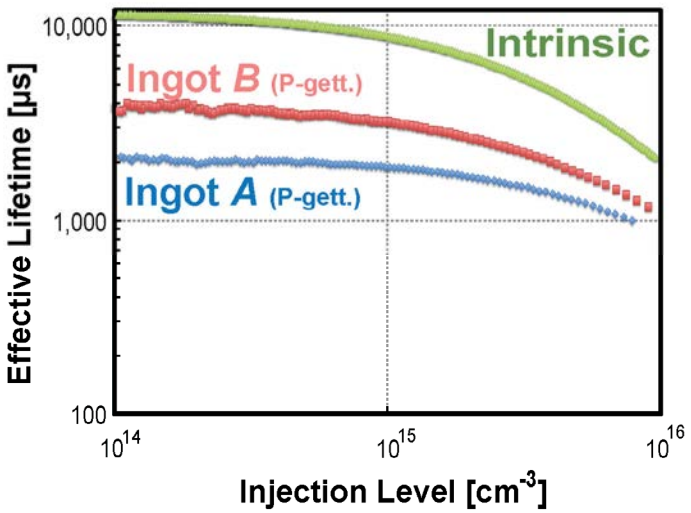

Fig. 4. Effective minority-carrier lifetime values of samples after an extended P-diffusion gettering process for samples from ingots *A* and *B*.

By analyzing the Shockley-Read-Hall contributions to the effective lifetime after modifications performed between growth runs, we deduce that the concentrations from potential slow diffusers, such as chromium, must be at or below 5×10^{9} cm^{-3} to achieve the measured 3.2 ms lifetime at $\Delta n=10^{15}$ cm^{-3}. With the improvements implemented while producing ingot *B*, the material was able to achieve low metal concentrations that we are unable to detect with current characterization techniques. Further informed optimization of growth and processing conditions is limited by the availability of techniques that can detect low metal concentrations.

4. Conclusion

Through an extended characterization process and informed feedback loop to the crystal growers, we are able to demonstrate that silicon materials grown by the non-contact crucible Si method (NOC-Si) have the potential to achieve high bulk minority carrier lifetimes exceeding 3 *m*s in n–type Si. We attribute this improvement to the strict environmental control implemented prior to the growth of ingot *B*, and informed by learning from ingot *A*.

The analysis presented herein suggests that that (*i*) NOC-Si produces material that can enable high efficiency devices and (*ii*) as industry moves towards higher quality materials, advanced characterization techniques that allow for characterization of low concentrations of metal impurities are necessary.

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