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EDITED BY
Sergio Pizzini,
University of Milano-Bicocca, Italy

REVIEWED BY
Chu-Shou Yang,
Tatung University, Taiwan
Carlos Del Cañizo Nadal,
Polytechnic University of Madrid, Spain

*CORRESPONDENCE
Rabin Basnet,
rabin.basnet@anu.edu.au

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A review of defect mitigation strategies for UMG-Si wafers

Rabin Basnet* and Daniel Macdonald

School of Engineering, The Australian National University, Canberra, ACT, Australia

This review focuses on the challenges and potential pathways for utilizing upgraded metallurgical-grade silicon (UMG-Si) in the silicon photovoltaic industry. UMG-Si is an attractive low-cost alternative silicon feedstock, but its bulk quality is compromised due to the presence of defects and impurities. The review begins by identifying and discussing the various defects and impurities commonly found in UMG-Si wafers, drawing insights from a literature survey. The detrimental effects of these defects on solar cell performance are highlighted. Next, the review provides a summary of defect mitigation strategies that have been employed to improve the bulk quality of UMG-Si wafers. These strategies include *tabula rasa*, impurity gettering, and defect/impurity passivation through hydrogenation. The effectiveness of these strategies is evaluated by considering carrier lifetimes and comparing them with those of conventional silicon wafers. The review then examines the reported open-circuit voltages and efficiencies of solar cells based on UMG-Si wafers. A comparison is made between the performance of UMG-Si solar cells and those fabricated on conventional silicon. The impact of defect mitigation strategies on the performance of UMG-Si solar cells is discussed, emphasizing the improvements achieved through these strategies.

KEYWORDS

UMG silicon, tabula rasa, hydrogenation, phosphorus diffusion gettering, low-cost alternative silicon

1 Introduction

Upgraded metallurgical-grade silicon (UMG-Si) has long been considered as a viable alternative feedstock material for solar-grade silicon. The processing of UMG-Si involves several low-cost metallurgical techniques, in contrast to the energy-intensive Siemens process used in conventional polysilicon feedstock material. According to a recent estimate, UMG-Si boasts a 20% lower carbon footprint compared to chemically processed polysilicon (Méndez et al., 2021). Its low processing cost and capital expenditure (CAPEX) have positioned UMG-Si as a potential low-cost alternative to conventional polysilicon feedstock material. However, the dominance of Chinese polysilicon industries has resulted in a significant decrease in the spot price of standard polysilicon feedstock over the past decade, as shown in Figure 1. Recently, the spot price has experienced significant fluctuations due to an imbalance in supply and demand, reflecting the volatile nature of the market (Bernreuter, 2023), as shown in Figure 1. These current market conditions have posed a barrier to the adoption of alternative approaches, such as metallurgical purification, as feedstock materials for the Si-PV industry. Consequently, UMG-Si is facing challenges in establishing itself as a viable low-cost feedstock material.

Furthermore, it is widely known that UMG-Si contains significantly higher concentrations of metal impurities (iron, nickel, copper, etc.) and non-metal impurities (carbon and oxygen) compared to conventional electronic-grade silicon (EG-Si) (Bye and

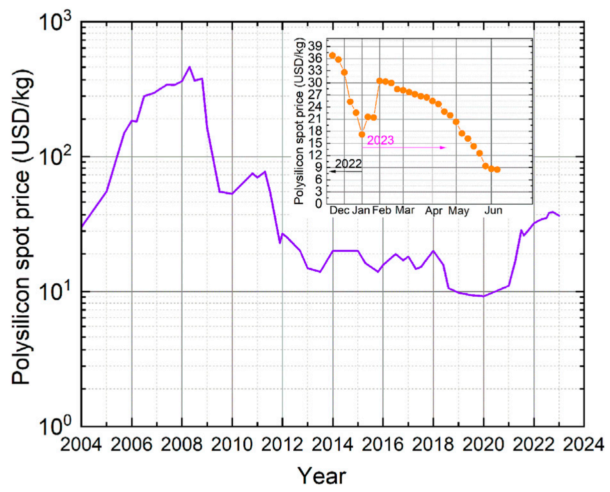

FIGURE 1
Monthly polysilicon spot price average from 2004 through 2023. The average monthly price of polysilicon in 2023 in shown in inset (Bernreuter, 2023).

Ceccaroli, 2014). Consequently, the adoption of UMG-Si is further limited in the current Si-PV market, which demands high electronic quality of silicon wafers due to the emergence of several high-efficiency solar cell technologies. To remain relevant and competitive in the Si-PV market, it is crucial to enhance the electronic quality of UMG-Si wafers. One of the most common methods employed to achieve this is by implementing appropriate defect mitigation strategies. In recent years, significant progress has been made in developing a variety of defect mitigation strategies that target a wide range of defects and impurities. Detailed information on the progress of defect strategies can be found elsewhere (Wright et al., 2021; Liu et al., 2022; Song et al., 2022).

This review will first examine a brief history and purification processes of UMG-Si. It will then identify the relevant defects reported in UMG-Si wafers, followed by an examination of common mitigation strategies used to enhance their electronic quality (based on carrier lifetimes and open circuit voltage (V_{oc}). Finally, the review will demonstrate the role of defect mitigation strategies in the evolution of solar cell performance based on UMG-Si wafers.

2 A brief update on UMG-Si purification

The detailed purification steps employed for producing polysilicon feedstock material is not the scope of this work, but can be found elsewhere (Delannoy, 2012; Li et al., 2017). Here we will only provide a brief overview of the process, as outlined in Figure 2. Metallurgical-grade silicon (MG-Si) are purified from silica ore by utilizing carbo-thermic reduction in submerged arc furnaces: $SiO_2 + 2C \rightarrow Si + 2CO$. The MG-Si is heavily contaminated, and typically contains 1wt% of impurities such as Fe, Al, Ti, Mn, C, B, P, Cu, Mg, etc. Thus, MG-Si must be further purified either by chemical or metallurgical routes to obtain the desired purity level of silicon feedstock material. For semiconductor industry, the high-purity level (9N) polysilicon feedstock material is produced by utilizing the standard Siemens process consisting of several chemical purification steps. However, the PV industry is cost-sensitive and can tolerate more impurities than semiconductor industry, therefore a dedicated purification steps were developed, and the product is commonly known as solar-grade silicon (SG-Si) feedstock. SG-Si can be purified from MG-Si either by using chemical or metallurgical routes.

The conventional purification method employs a chemical routes as a modified Siemen's process routes (Block and Wagner, 2000; Tilg and Mleczko, 2000; Corp, 2005; Dornberger, 2005; Corporation, 2006; Braga et al., 2008). The major modification is performed by increasing the production rate of the decomposition reactor. In addition, several production procedures and quality control are relaxed in comparison to the standard Siemens process. As a result, the cost of purification is lower for the SG polysilicon. However, relatively high concentrations of impurities are present in the SG purified polysilicon feedstock compared to, EG polysilicon, as shown in Table 1. Further, similar to the Siemens process, this route produces harmful chlorosilane compounds as by-products (Sørensen, 1998).

As an alternative to chemical refinement techniques, several metallurgical techniques are used to obtain SG-Si from MG-Si, as shown in Table 2. Unlike chemical route, in metallurgical route a specific metallurgical purification technique is not enough to reduce all impurity concentrations to an acceptable level. Therefore, metallurgical route contains multi-step purification process targeting different impurities based on different chemical and thermodynamic properties. SG-Si feedstock obtained via a metallurgical process is termed as upgraded metallurgical-grade silicon (UMG-Si). Several groups have employed different combinations of metallurgical refinement techniques to obtain UMG-Si feedstock, as shown in Table 2.

Finally, silicon feedstock material is melted to crystalize silicon either to form multi-crystalline or mono-crystalline silicon ingots. Directional solidification or casting processes are used to grow multi-crystalline ingots. However, mono-crystalline silicon wafers are mostly grown using the Czochralski (Cz) method.

In the PHOTOSIL project (Einhaus et al., 2006; Margaria et al., 2010; Margaria et al., 2011), FerroPem, purified UMG-Si feedstock. This UMG-Si feedstock was then used to grow monocrystalline ingots through Czochralski silicon (Cz-Si) ingot growth as well as conventional multicrystalline silicon (mc-Si) by R&D companies like Apollon Solar and CEA-INES (France). Most of the reported works on UMG-Si wafers, such as from Apollon Solar, CEA-INES, The Australian National University (ANU), and University of New South Wales (UNSW), were based on PHOTOSIL project. Recently, the Aurinka PV group (Spain) has also reported some works on mc-Si based on 100% UMG-Si purified by FerroSolar group.

3 Defects and impurities in UMG-Si wafers

3.1 Oxygen precipitate-related defects

The incorporation of oxygen in Cz-Si is inevitable, and this leads to the formation of oxygen precipitate (OP) nuclei during the ingot cooling process. These OP nuclei act as recombination centers,

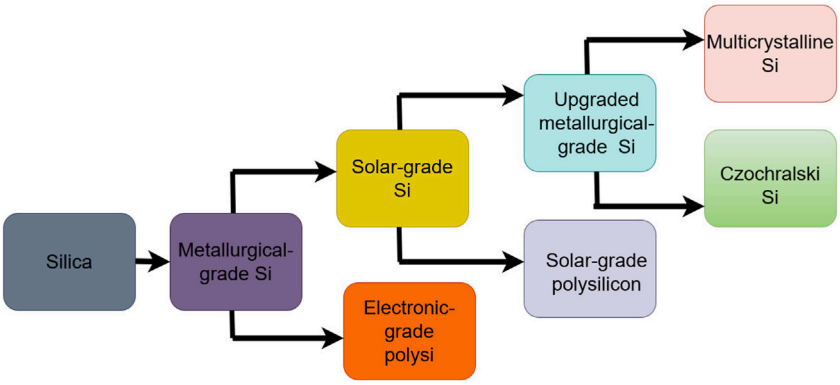

FIGURE 2
Schematic of process flows for the purification of polysilicon feedstock.

TABLE 1 Chemical characteristics of impurities in the different types of silicon feedstock material.

Impurity	MG-Si Pizzini, (1982) (ppm)	EG polysilicon Fornies et al. (2016) (ppm)	SG polysilicon Bernreuter, (2012) (ppm)	UMG-Si Bernreuter, (2012) (ppm)
B	15	4×10^{-5}	0.01	0.38
C	100–300	0.107	0.86	42.76
Na		0.006	0.04	3.27
Al	2100	0.01	0.02	0.96
P	30	3.3×10^{-4}	0.02	0.79
K		0.01	0.07	5.57
Ca	1800		0.07	5.71
Ti	180		0.09	0.34
Cr	30	0.001	0.09	0.37
Fe	4100	0.002	0.10	0.40
Ni	50	0.001	0.10	0.42
Cu	30	0.001	0.11	0.45
Zn		0.002	0.12	0.47
As			0.05	1.92
Mo	10		0.17	0.68
Sb			0.09	3.12

compromising the bulk quality even in the as-grown state. The recombination activity of OP further increases during subsequent high-temperature processing, such as dopant diffusions and oxidations. Several studies have indicated that the recombination activity of OP originates either from dangling bonds (Lang et al., 2012; Koizuka and Yamada-Kaneta, 2000), impurities decorating OP, or OP-induced secondary defects (dislocations, stacking faults) (Seifert et al., 1995; Kirscht et al., 1996; Mchedlidze and Matsumoto, 1998; Murphy et al., 2013; Murphy et al., 2014). Extensive research by Murphy et al. (2014); Murphy et al. (2013); Murphy et al. (2011); Murphy et al. (2012); Murphy et al. (2015) has provided comprehensive insights into the recombination activity of OP in both *n*- and *p*-types of solar-grade Cz-Si wafers. These studies suggest that the recombination activity of OP enhances with increased surface area and becomes more pronounced when impurities decorate the OP.

The most common manifestation of OP-related defects is in the form of ring or disc-like defects, often observed after high-temperature processing of Cz-Si wafers. Ring defects, known for their high recombination activity, can cause a significant loss of efficiency of solar cells. UMG-Si, characterized by relatively high concentration of impurities like carbon (as shown in Table 1), is more susceptible to enhanced oxygen precipitation during high-temperature steps (Basnet et al., 2018; Basnet et al., 2020a; Basnet

TABLE 2 Purification steps involved in the production of UMG-Si feedstock materials from different group.

Developer	Processes involved
Kawasaki Steel Corporation NEDO Project Weiss and Schwerdtfeger, (1994)	(1) EB melting (2) Directional solidification (3) Plasma treatment (4) Directional solidification
Apollon Solar PHOTOSIL Project Margaria et al. (2010)– Margaria et al. (2011)	(1) Directional solidification (2) Plasma treatment (3) Directional solidification
Elkem ASA Elkem Solar-investment decision-Skøyen Internal Report, (2023), Woditsch and Koch, (2002) Heliotronic Woditsch and Koch, (2002)	(1) Slag treatment (2) Acid leaching (3) Directional solidification
Bayer AG Woditsch and Koch, (2002)	(1) Acid leaching (2) Reactive gas blowing
	(3) Vacuum treatment (4) Directional solidification
University of Campinas Pires et al. (2005)	(1) Acid leaching (2) Electron-beam melting
SOLSILC Project Geerligs et al. (2002)	(1) Plasma treatment (2) Directional solidification
Ferroglobe and Aurinka PV group Forniés et al. (2019)	(1) Slagging (2) Vacuum purification (3) Directional solidification

et al., 2021). Consequently, ring defects readily form in UMG-Cz-Si compared to electronic-grade (EG) Cz-Si wafers, given the same thermal budget. This significantly hampers the applicability of UMG-Cz-Si wafers in solar cells (homo-junction) fabrication unless appropriate defect mitigation strategies are incorporated. However, recent advancements have resulted in significant progress in achieving better control over oxygen incorporation during Cz-Si ingot growth. Cz-Si in mass production can now achieve interstitial oxygen concentration [O_i] as low as 12 ppm in *n*-type and 16 ppm in *p*-type ingots. UMG-Si grown using the current Cz-Si process is expected to exhibit lower [O_i] and potentially fewer OP-related defects compared to ingots grown few years ago.

3.2 Metallic impurities

Metal impurities significantly limit the efficiency of silicon solar cells. They act as recombination centers both in the form of point defects (as interstitial or substitutional atoms, or metal-acceptor pairs) and as precipitates. Generally, metallic impurities in silicon ingots can originate from feedstock materials, crucible, or puller parts and during device processing. As ingot growth conditions and polysilicon feedstock material have improved, conventional silicon wafers tend exhibit better control over impurity incorporation (Basnet et al., 2023). UMG-Si feedstock contains high levels of metallic impurities compared to silicon feedstock obtained by conventional Siemens process, as shown in Table 1. It is worth noting that the improvement in metallurgical purification and ingot pulling processes is expected to decrease the impurities concentrations in UMG-Si. However, it's important to note that metallurgical purification involves multiple purification steps with different techniques, which may contribute to the variation in impurities concentrations. Nevertheless, the higher concentration of impurities in UMG-Si continues to reduce its electronic quality, making it unsuitable for current high-efficiency solar cells. This makes impurities-related defects are the most concerning for the adoption of UMG-Si in current the PV industry. Therefore, it is crucial to reduce impurity levels in UMG-Si by implementing appropriate gettering strategies.

3.3 Light-induced degradation (LID)

LID caused by the presence of boron-oxygen (BO) pairs is known to decrease the long-term stability of solar cell performance, resulting in approximately 2% relative efficiency loss within the first year of module operation (Wolny et al., 2013; Hallam et al., 2017). However, the Si-PV industry has recently shifted from using boron (B) as the main dopant for *p*-type wafers to gallium (Ga) in order to avoid LID caused by BO pairs (VDMA, 2023). As a result, LID due to BO pairs is no longer a relevant defect in the current Si-PV industry.

However, the metallurgical purification processes have limitations when it comes to effectively eliminating doping elements such as boron and phosphorus compared to chemical distillation and condensation used in Siemens process, as shown in Table 1. Due to the high concentration of both donors and acceptors, UMG-Si is considered a "compensated" material and is susceptible to LID caused by BO pairs. Therefore, this review also briefly discusses defect mitigation strategies employed to address BO pairs.

3.4 Crystallographic defects

Similarly, in the current Si-PV, there has been a shift away from cast-Si due to its inherent crystallographic defects, such as grain boundaries (VDMA, 2023). Therefore, any future developments related to UMG-Si should also focus on Cz-Si to remain relevant in the current market. However, some of the research, particularly from Spain-based Aurinka Solar are still primarily focused on UMG-mc-Si. The cost saving of over 40% per wafer offered by cast-Si compared to Cz-Si makes UMG-Si even more attractive material. Nevertheless, it is important to note that the perceived advantages of lower cost and environmental benefits will be negated if appropriate defect mitigation strategies are not applied to these wafers.

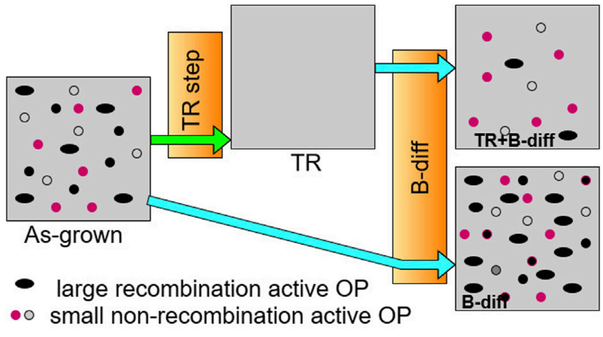

FIGURE 3
Schematic of *tabula rasa* process, which dissolves grown-in OP nuclei (as represented by middle block). Then, after subsequent high-temperature processing, OPs will grow lesser than in the sister sample without TR.

4 Mitigation strategies

4.1 Tabula rasa

Tabula rasa (TR) is a high-temperature annealing process that has been used in the microelectronic industry to defect engineer OP-related defects by creating a "magic denuded zone" (Falster et al., 1997). However, this step has also been slowly used in solar cells research to mitigate bulk degradation (Basnet et al., 2018; Ochoa et al., 2020; LaSalvia et al., 2019). It is commonly used as a pre-fabrication process to improve bulk quality by minimizing thermal history (dissolving grown-in OP nuclei or metal precipitates) in Cz-Si wafers (Basnet et al., 2018; Basnet et al., 2019; LaSalvia et al., 2019; Basnet et al., 2020b), as shown in Figure 3. The schematic illustrates that the TR step dissolves grown-in OP nuclei, making the samples free of OP nuclei, as represented by the middle block. Following subsequent high-temperature processing, the sample subjected to Tabula Rasa shows reduced growth of OPs compared to the one without the TR treatment.

The application of the TR step had a significant impact on the carrier lifetime of the *n*–type UMG-Cz-Si wafers from the PHOTOSIL project, as shown in Figure 4. The as-grown samples, which did not undergo any TR step (t = 0 min), exhibited much lower carrier lifetimes $(100 - 200)\ \mu s$ at an injection level of 1×10^{15} cm^{-3}) across all three sections (seed, middle, and tail) of the UMG-Cz-Si ingot compared to *n*-type EG-Cz-Si sample (>2 *ms*). However, after the TR step, the carrier lifetimes of the UMG-Cz-Si samples improved significantly, particularly from the middle of the ingot, reaching carrier lifetimes (>2 *ms*) comparable to those of the EG-Cz-Si samples. These results highlight the importance of implementing appropriate defect mitigation strategies to enhance the bulk quality of UMG-Si wafers. Moreover, the UMG-Cz-Si samples were found to be more sensitive compared to the EG-Cz control samples to the TR conditions, such as duration, temperature and ambient, as shown in Figure 4. There is only a small range of temperature and duration of TR, which provides a beneficial impact of a TR step. Therefore, careful optimization of the TR step is essential, especially for UMG-Cz-Si samples.

Figure 5A demonstrates the benefits of a TR step when samples underwent boron diffusion, which is necessary for junction formation in *n*-type UMG-Si wafers. Two sets of the UMG-Cz-Si and EG-Cz-Si samples, consisting of as-grown (no TR) and TR-treated, were subjected to boron diffusion. After boron diffusion process, the effective carrier lifetimes of both the as-grown samples reduced ($\tau_{\text{as-grown}} > \tau_{\text{B-diff}}$). However, a reduction in lifetime was significantly higher in UMG-Cz-Si compared to EG-Cz-Si samples, indicating that UMG-Cz-Si wafers were more prone to degradation than EG-Cz-Si under the same high-temperature processes. Nonetheless, when the samples were treated with TR prior to boron diffusion, the degradation was significantly reduced ($\tau_{\text{as-grown}} < \tau_{\text{TR+B-diff}}$), particularly in UMG-Cz-Si samples.

Additionally, interstitial oxygen concentration [O_i], measured by Fourier-transform infrared spectroscopy (FTIR) showed a significant increase after TR step in UMG-Cz-Si compared to EG-Cz-Si, as shown in Figure 5B. This suggests that UMG-Cz-Si initially had high concentrations of grown-in OP nuclei, which further grew and became more recombination active during boron diffusion, resulting in reduced effective lifetimes. The dissolution of grown-in OP nuclei through TR helped to improve bulk quality of UMG-Cz-Si, making it more resilient to degradation during subsequent boron diffusion. This concept of employing TR as a pre-fabrication treatment was utilized to fabricate tunnelling oxide passivated contact (TOPCon) solar cells based on *n*-type UMG-Cz-Si wafers, achieving a record solar cell efficiency of 22.6% (Basnet et al., 2019), also refer Table 4. In the same batch, cells without the TR step, highly recombination active ring defects appeared and experienced a loss of over 50 mV of implied open-circuit voltage (iV_{oc}).

It has been observed that the benefit of the TR step is not permanent but only delays the onset of ring defects during subsequent high-temperature processes (Basnet et al., 2020a). The incubation duration for ring defects formation depends on the bulk quality of samples and the thermal conditions. Generally, the onset of ring defects occurs faster in UMG-Cz-Si samples than in EG-Cz-Si samples with the same thermal budget. The presence of high concentrations of impurities, such as carbon and metal impurities enhances the growth of OP (Zhang et al., 2015; Shimura, 1986) and accelerates the formation of ring defects in the UMG-Cz-Si. TR poses challenges due to requirement of high temperature (>1,000°C), leading to increased processing costs and introducing a notable risk of contamination for industry. Therefore, optimization of the thermal budget during the fabrication process is crucial for maintaining the bulk quality of any UMG-Cz-Si wafers than adapting a TR step in industrial application.

4.2 Gettering

Gettering is the one of most common form of defect mitigation method which helps to relocate mobile metal impurities, such as interstitial iron from the bulk of silicon to a region in the device where they have a less harmful impact on the device performance. Typically, phosphorus diffusion performed to form an n^+ region in traditional *p*-type passivated emitter and rear cells (PERC) or aluminium back surface field (Al-BSF) solar cells, provides gettering effect that can reduce interstitial iron concentration by more than two orders of magnitude. Additionally, recent works have demonstrated that passivating contacts based on doped polysilicon

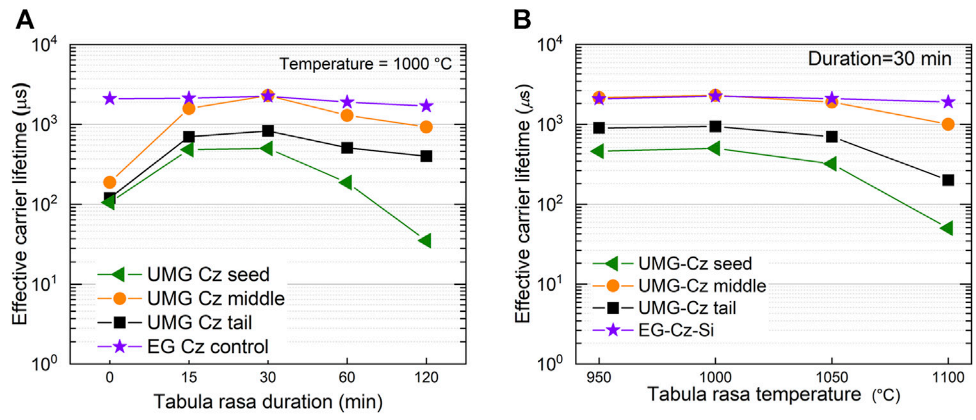

FIGURE 4
Effective carrier lifetimes at an injection 1×10^{15} cm^{-3} for the UMG-Cz-Si wafers from three different positions of the ingots and the EG-Cz-Si control samples. **(A)** Isothermal TR treatment of 1,000°C as a function of duration, with as-grown lifetimes shown as 0 min. **(B)** Isochronal TR treatment of 30 min as a function of temperature. Samples were passivated by SiN_x:H layers (Basnet et al., 2018).

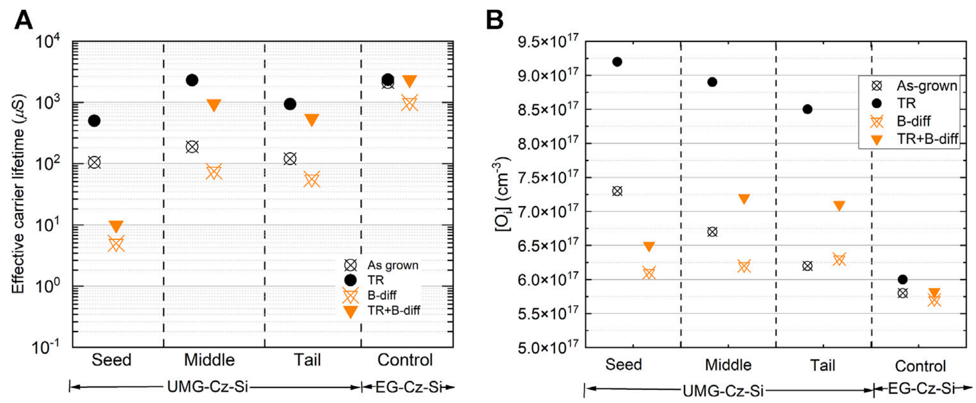

FIGURE 5
Evolution of the effective lifetimes (at an injection level of 1×10^{15} cm^{-3}) and **(B)** [O_i] of the UMG-Cz-Si from three different positions of the ingot and EG-Cz-Si samples for combinations of TR and boron diffusion steps. Samples were passivated by SiN_x:H layers (Basnet et al., 2018).

layers (both polarities) are known to provide strong gettering effects (Yang et al., 2023; Hayes et al., 2019).

The effectiveness of gettering depends on finding a balance between impurity diffusion and their segregation to the sink layer (diffused layers). Higher temperatures promote impurity diffusion towards the sink layer but reduce segregation, while lower temperatures enhance segregation to the sink. It is important to optimize the gettering thermal budget not only for impurity removal but also to mitigate other forms of bulk degradation. In some cases, high-temperature gettering processes can activate grown-in defects such as OP, leading to a severe reduction in carrier lifetime. As result, most works on UMG-Si wafers have used a lower temperature range (around 780°C) compared to conventional phosphorus diffusion (≥800°C) (Basnet et al., 2018; Catalán-Gómez et al., 2022). Additionally, the gettering effectiveness in UMG-Si wafers have been found to be enhanced by extending the duration or employing a two-step PDG process (Dasilva-Villanueva et al., 2023), as shown in Figure 6. Dasilva-Villanueva et al. (2023) reported an effective carrier lifetime values up to 645 μs (at an injection level of 1×10^{15} cm^{-3}) in *p*-type UMG-mc-Si samples after utilizing two consecutive PDG processes. The benefit of the sequential PDG processes were uneven, with a major impact resulting from the first PDG carried out at a lower temperature and a subsequent moderate but still significant contribution from the second PDG process. Interestingly, the samples were found to be more tolerant to relatively wide range of temperature and durations of second PDG process and can be performed at high temperatures compatible with emitter formation.

Therefore, optimization of the gettering process for UMG-Si wafers should consider a trade-off between the process parameters and impurity behaviour. Furthermore, the bulk degradation during phosphorus diffusion getterting can be mitigated by combining with it with either a TR or H to achieve the most effective improvement in bulk quality, known as a TR+PDG or PDG+H steps, respectively, as shown in Table 3.

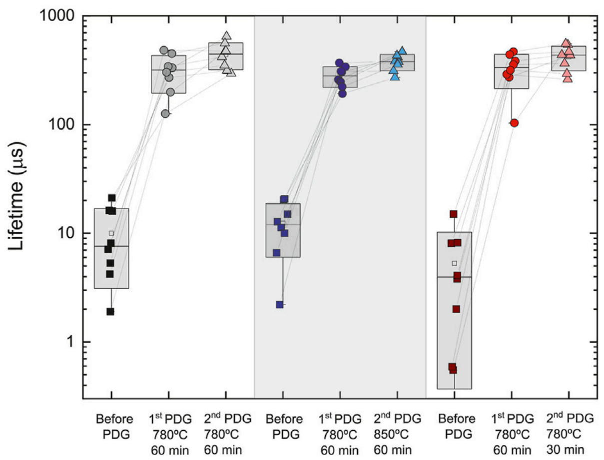

FIGURE 6
Effective lifetime variation of the samples [at an injection level of 1×10^{15} cm^{-3})] from different sections of UMG-mc-Si ingot grown by FerroSolar (Forniés et al., 2021) based on UMG-Si feedstock manufactured by FerroGlobe after one and two PDG processes passivated by iodine-ethanol. In the box-type plot whiskers represent max-min variation, the height of the box represents the standard deviation, the non-filled square corresponds to the mean value and the middle line represents the median value. Connection dashed lines are included to identify the change of individual samples (Dasilva-Villanueva et al., 2023).

4.3 Hydrogenation

Hydrogen passivation, also known as hydrogenation, is widely used defect engineering process in silicon solar cell fabrication. It involves annealing hydrogen-rich dielectric films, such as SiN_x:H, AlO_x:H, and a-Si:H, at a moderate temperature range (typically 500 – 700°C for few seconds to minutes) to release hydrogen and passivate defects either in bulk or interfaces. Hydrogenation is effective in passivating various defects relevant to silicon solar cells, including OP, BO pairs, and grain boundaries (Park et al., 2009; Wilking et al., 2014; Hallam et al., 2015). The conditions of hydrogenation need to be optimized to effectively passivate the specific targeted defects.

Hydrogenation is typically performed by annealing the samples in a tube furnace, hotplate, or rapid thermal annealing, with or without illumination. Its passivation effectiveness is highly dependent on whether it is used in isolation or in combination with other methods such as TR and PDG.

In the case of UMG-Cz-Si wafers, hydrogenation is commonly used for passivating OP-related defects. It can effectively passivate ring defects that are formed during high-temperature processing, as shown in Figure 7. Generally, hydrogenation is most effective when combined with TR and PDG for the passivation of ring defects and grown-in OP nuclei in UMG-Si wafers (Basnet et al., 2018). It is important to note that the impact of hydrogenation also depends on the ingot position. Additional optimization of hydrogenation conditions may be required when dealing with higher defect densities of different types of defects. It is believed that in the seed-end of Cz ingot, vacancy-related defects are also present along with OP-related.

Hallam et al. (2015) proposed an advanced hydrogenation process that involves laser illumination. This process can manipulate hydrogen charge states, enhancing the passivation effectiveness of defects such as BO pairs, oxygen precipitates and grain boundaries. This advanced hydrogenation process offers improved passivation capabilities compared to traditional hydrogenation methods.

Vicari Stefani et al. (2019) conducted a study on the utilization of advanced hydrogenation combined with a PDG step (PDG+H) to improve the bulk quality of *p*-type UMG-mc-Si wafers. They found that hydrogenation alone did not significantly improve the bulk quality. However, when combined with a PDG step (PDG+H), a remarkable improvement in carrier lifetime was achieved, as illustrated in Figure 8A. When the hydrogenation process was applied to a previously gettered sample, the recombination activity of most grain boundaries decreased significantly. Additionally, an improvement in the intra-grain regions was observed, as well as the passivation of a fraction of defects gettered to the dislocation clusters during gettering. The increased effectiveness of hydrogenation after the gettering treatment can be attributed to the removal of metallic impurities, including interstitial iron (Fe_i), and complexes such as iron-oxygen (Fe–O) and iron-boron (Fe–B) during the gettering step. By eliminating these impurities, more hydrogen became available for passivating the grain boundaries during the subsequent hydrogenation process. Further, the carrier lifetimes of UMG-mc-Si samples were compared after normalizing to their resistivity. After normalization, UMG-mc-Si samples exhibited similar carrier lifetimes to conventional mc-Si samples, as shown in Figure 8B. Furthermore, in the same study, the PDG+H process was employed as a pre-fabrication step to fabricate a silicon heterojunction (SHJ) solar cell based on *p*-type UMG-mc-Si wafers. This approach resulted in a record V_{oc} of 690 mV, demonstrating the effectiveness of the combined PDG+H process in enhancing the performance of solar cells fabricated from UMG-mc-Si wafers. This achievement is also presented in Table 4, which summarized the V_{oc} and efficiencies of solar cells based on UMG-Si wafers from various studies. Consequently, gettering and hydrogenation emerge as the two most promising strategies for enabling high-efficiency UMG-Si solar cells. Although these strategies are standard processes in current industrial cells, the need for extended gettering steps (such as 2-step or slow ramp-down) may be constrained by the current throughput rate of the industry.

Hydrogenation has been also employed to permanently deactivate BO pairs in compensated UMG-Cz-Si solar cells. Previous works on the deactivation of BO pairs in compensated silicon had shown inconsistent until Sun et al. (2018) demonstrated the complete regeneration of BO defects in *n*-type UMG-Cz-Si based SHJ solar cells. In their study, hydrogen from a-Si:H layers was utilized to deactivate BO pairs in compensated UMG-Cz-Si cells, resulting in a fast and complete regeneration of BO pairs under 93 suns at 220°C.

Table 3 provides a summary of various defect mitigation strategies used either in isolation or in combination to improve the material quality of UMG-Si (Cz and mc) wafers. The improvement in bulk quality is quantified by effective lifetimes measured at an injection level of 1×10^{15} cm^{-3}. Wherever available, the effective lifetimes of control samples (EG-Si) are

TABLE 3 Elucidation of impact of the defect mitigation strategies on carrier lifetimes of UMG-Si wafers used in different works with corresponding EG-Si used as a control.

	Defects	Mitigation strategies	τ_{EG}	τ_{umg}	Res.	Type	Passivating films
			μs	μs	Ω·cm		
Hallam et al. (2012)		None		1		p-Cz	SiN_x:H
	BO	H		40–440			
Basnet et al. (2018)		None	2,100	196	2.4	n-Cz	SiN_x:H
	OP	TR	2,350	2,300			
	Impurities	PDG	4,000	1,700			
		TR+PDG	4,600	4,490			
		PDG+H	4,200	3,200			
		TR+PDG+H	4,700	3,957			
Basnet et al. (2020b)		None	1,240	294	2.4	n-Cz	a-Si:H
	OP	TR+PDG	3,080	1,130			
	Impurities	PDG+H	2,860	971			
Dasilva-Villanueva et al. (2023)		None		5	1–1.5	p-mc	SiN_x:H
	Impurities	2-PDGs		100			
Yoon et al. (2013)		None		1		p-mc	
	Impurities	1 PDG		1.5			
		2 PDG		3			
Dasilva-Villanueva et al. (2023)		None		10–20		p-mc	Iodine-ethanol
	Impurities	2 PDGs	645				
Vicari Stefani et al. (2019)		None	90	11		p-mc	a-Si:H
	BO	H	92	26			
	Impurities	PDG	128	58			
		PDG+H	270	70			

included for comparison. The results clearly demonstrate that defect mitigation strategies have successfully enhanced the carrier lifetimes of UMG-Si wafers, regardless of dopant type (p- or n-type) and whether based on Cz and mc-Si wafers.

Hydrogenation passivation can be sensitive to subsequent high temperature (>650°C) processes, as the elevated temperatures can cause hydrogen effusion from the bulk of the material (Sopori et al., 2002), leading to a loss of passivation efficacy. Therefore, it is important to perform hydrogenation after all the high-temperature processes to ensure its stability.

To address the issue of hydrogenation stability at higher temperatures, some recent works have proposed fluorination as an alternative passivation method. Fluorine-containing films, such as magnesium fluoride (MgF_x) have been used for fluorination (Sio et al., 2023; Basnet et al., 2022). Fluorination has shown promise in passivating ring defects in n-type UMG-Cz-Si, and it has been observed that fluorine passivated ring defects exhibit slower de-passivation kinetics compared to hydrogen-passivated ring defects. This suggests that fluorine passivation can offer greater stability than hydrogen passivation of ring defects during subsequent heat treatments.

5 Impact of defect mitigation and solar cells performance

Table 4 summarizes the V_{oc} and efficiency (η) of UMG-Si solar cells obtained from various studies, including comparisons with EG-Si solar cells used as controls in the corresponding batches. In earlier works, solar cells based on UMG-Si wafers were primarily aluminum back surface field (Al-BSF) structure, which has inherent limitations in efficiency. As a result, the cell efficiencies were low, and the V_{oc} for both control and UMG-Si cells were similar.

However, when a high efficiency solar cell structures such as passivated emitter and rear totally diffused (PERT) and passivated emitter with rear locally diffused (PERL) were employed, the

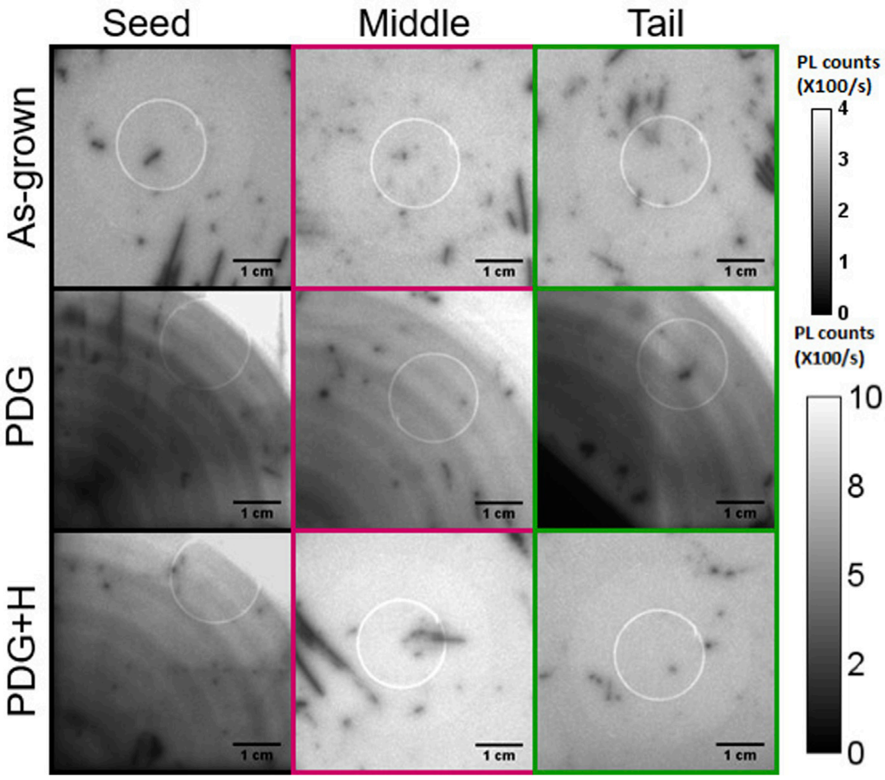

FIGURE 7
PL images of the UMG-Cz-Si wafers from three different positions of the ingot which show the effect of PDG and PDG+H compared to the as-grown state. A scale bar shown in the first row is for the as-grown samples and in the second row is for all other samples. All of the images were captured at constant illumination intensity of 0.5 suns and normalized to PL counts/second. The bright circle in the images is an artefact due to the conductance coil in the PL imaging tool (Basnet et al., 2018).

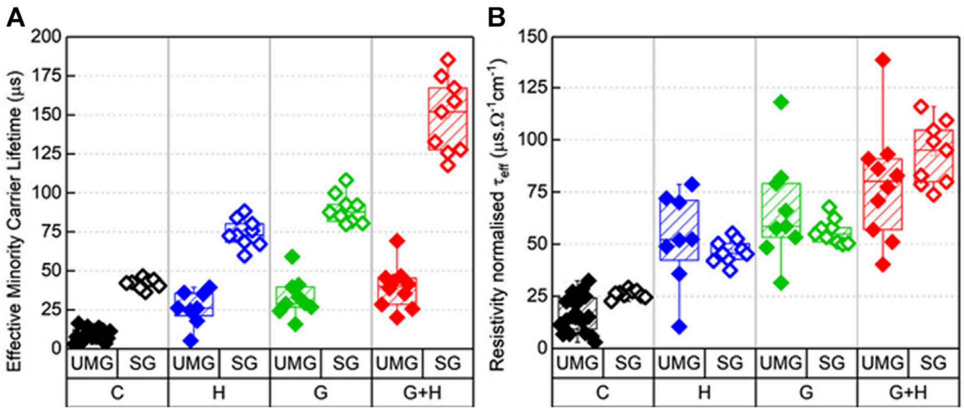

FIGURE 8
Impact of the defect mitigation strategies in **(A)** the effective minority carrier lifetime and **(B)** resistivity normalized effective minority carrier lifetime on both p-type UMG-mc-Si and solar-grade multi-crystalline silicon (SG-mc-Si) wafers. The wafers are divided in four groups, according to the defect mitigation strategies processes applied: non-gettered and non-hydrogenated control wafers (C), gettered (G) wafers, hydrogenated wafers (H), and gettered + hydrogenated wafers (G + H) (Vicari Stefani et al., 2019).

efficiency of UMG-Si solar cells also increased (Zheng et al., 2017), Rougieux et al. (2016). Zheng et al. (2017) achieved a record UMG-Si solar cell efficiency of 21.1% in 2017. In these works, the V_{oc} of the UMG-Cz-Si cells were nearly 20 mV lower than the control solar cells, resulting in >0.8% (abs) loss in efficiencies. This indicates that the bulk quality of UMG-Cz-Si wafers is a significant limiting factor for achieving higher efficiencies when used in the high-efficiency solar cell structures.

TABLE 4 A comparison of reported performance of solar cells based on UMG-Si (Cz and mc) wafers and corresponding conventional silicon wafers used as a control. It also includes V_{oc}, resistivities of wafers, cell structure, and any defect mitigation strategies employed.

Authors		Cell type	Type	Size	V_{oc} UMG	η umg	V_{oc} EG	η EG	Institute	Year
				mm^2	mV	%	mV	%		
De Wolf et al. (2002)			*p*-mc		612.8	12.4	624	14.7	*IMEC	2002
Kohler et al. (2009)		Screen printed	*p*-mc	125*125	622	16.2			Uni Konstanz	2009
Kraiem *et al.*		Screen printed	*n*-Cz	125*125	617.5	17.6			Apollon solar	2010
Engelhart et al. (2011)		PERC	*p*-mc	156*156	650	18.4	647	18.4	Q-cells	2011
Chang, (2011)	no	Al BSF	*p*-mc	156*156		14			**KICET	2011
	HPHA				615	15.6				
Einhaus et al. (2012)		SHJ	*n*-Cz	125*125	725	19	729	19.6	Apollon Solar	2012
Schiele et al. (2013)		PhosTop	*n*-Cz	125*125	648	19			Uni. Konstanz	2013
Doris Lu et al. (2015)		LDSE-AlBSF	*p*-mc		650	19.1			UNSW	2015
Rougieux et al. (2016)		PERT	*n*-Cz	20*20	649	19.8	665	21.3	ANU	2015
Zheng et al. (2017)		PERL	*n*-Cz	20*20	666	21.1	686	21.9	ANU	2017
Forniés et al. (2018)		Al-BSF	*p*-mc	156*156		18.5		18.6	Aurinka PV	2018
Basnet et al. (2019)	TR	TOPCon	*n*-Cz	20*20	679	22.6	683	22.4	ANU	2019
Vicari Stefani et al. (2019)		SHJ	*p*-mc	156*156					UNSW	2019
	PDG+H				690	18.7				
Forniés et al. (2019)	Extended PDG	PERC	*p*-mc	156*156	649	20.1	651	20.4	Aurinka PV	2019
Basnet et al. (2020b)	no	SHJ	*n*-Cz	20*20	678	18	708	21.2	ANU	2020
	TR+PDG				717	21	721	22.7		
	PDG+H				715	21.2	720	22.4		

Note; *IMEC: interuniversity microelectronics centre, Belgium, **KICET: korea institute of ceramic engineering and technology.

To address the low bulk lifetime and mitigate bulk degradation of UMG-Cz-Si wafers, appropriate defect mitigation strategies such as TR, PDG and hydrogenation have been employed. These strategies have been instrumental in achieving a current record efficiency for UMG-Cz-Si solar cells based on TOPCon and SHJ structures (Basnet et al., 2019), Basnet et al. (2020b). In the case of TOPCon structure, TR was incorporated as a pre-treatment step to mitigate the bulk degradation during subsequent high temperature processes, such as boron diffusion and TOPCon layers formation. Further, gettering effect provided by phosphorus doped polysilicon layers helped to mitigate the impact of metal impurities (Yang et al., 2023), Hayes et al. (2019). The combined effect of TR and gettering effects and better passivation by TOPCon layers helped to achieve a similar V_{oc} of 679 mV and 683 mV for solar cells based on UMG-Cz-Si and EG-Cz-Si, respectively.

For the SHJ structure, pre-fabrication treatments such as such as TR+PDG and PDG+H were utilized to enhance the bulk quality of UMG-Cz-Si, resulting in significant improvements in V_{oc} (>30 mV) and efficiency (>3% absolute) compared to the as-grown cells. Interestingly, EG-Cz-Si also exhibited improvements with pre-fabrication treatments. Nevertheless, the V_{oc} of UMG-Cz-Si solar cells were comparable to those of the EG-Cz-Si solar cells. This indicates that UMG-Cz-Si can be a competitive alternative to EG-Cz-Si, if appropriate defect engineering steps are implemented during solar cell fabrication.

Furthermore, Forniés et al. (2019) demonstrated a record efficiency of *p*-type UMG-mc-Si utilizing PERC technology. The work had employed an extended PDG step to improve the gettering effectiveness. UMG-mc-Si solar cells achieved 20.1% efficiency and the control cells based on conventional mc-Si achieved 20.4%. However, the study did not mention the gain in efficiency achieved by using extended PDG step.

6 Conclusion

In summary, the development and implementation of defect mitigation strategies has shown promising results in improving the bulk quality of current UMG-Si wafers. Several methods such as *tabula rasa*, gettering and hydrogenation have been utilized and optimized to mitigate various defects and impurities present in UMG-Si. These strategies have led to improvements in carrier lifetime, V_{oc} and efficiency of solar cells based on UMG-Si wafers. While UMG-Si wafers are low quality compared to conventional silicon wafers, advancements in UMG-Si purifications and ingot growth processes are expected to further enhance the quality of UMG-Si in the future. By optimizing defect mitigation strategies, the performance of UMG-Si based solar cells are expected to further improve to be competitive with conventional silicon solar cells, indicating the potential of UMG-Si as a viable alternative. However, it is important to conduct detailed techno-economic studies to evaluate true advantages of defect mitigation strategies and fully exploit the cost and environmental benefits of UMG-Si. Continued research and development efforts in purification steps and defect mitigation strategies will contribute to the advancement and wider adoption of UMG-Si in the Si-PV industry.

Author contributions

RB: Conceptualization, Data curation, Investigation, Methodology, Resources, Visualization, Writing–original draft, Writing–review and editing. DM: Funding acquisition, Supervision, Writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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