Effective impurity gettering by phosphorus- and boron-diffused polysilicon passivating contacts for silicon solar cells

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**ABSTRACT**

This paper presents direct experimental evidence for the strong impurity gettering effects associated with the formation of both phosphorus and boron doped polysilicon/oxide passivating contacts for silicon solar cells, doped via thermal diffusion from POCl3 or BBr3 sources. Ion-implanted iron is used as a marker to quantify the gettering effectiveness via carrier lifetime measurements. The process conditions for fabricating optimum polysilicon passivating contacts are found to remove more than 99.9% of the iron from the silicon wafer bulk. The gettering effects of POCl3 and BBr3 diffused polysilicon/oxide contacts mainly arise from the dopant diffusions, as opposed to gettering by structural defects in the polysilicon films. The thin oxide interlayer hinders the gettering effectiveness at low diffusion temperatures, although its blocking effect becomes small at the moderate temperatures used to fabricate optimum polysilicon contacts. The gettering effectiveness increases with increasing diffusion temperature. The gettering of iron from the silicon wafer bulk to the surface layers is found to have a negligible impact on their ability to suppress recombination at the interface with the silicon wafer. Therefore, the formation of polysilicon/oxide passivating contacts, via thermal diffusion from POCl3 and BBr3 sources, not only achieves high quality surface and contact passivation but also has the net additional benefit of achieving very effective gettering of unwanted impurities in the silicon wafer bulk.

**1. Introduction**

Passivating contacts for silicon solar cells reduce carrier recombination at the metal-silicon interface, leading to improved device efficiencies. Recently, doped polysilicon passivating contacts, formed by a layer of phosphorus- or boron-doped polycrystalline silicon film (commonly referred to as polysilicon, or poly-Si), together with an ultra-thin dielectric interlayer, have enabled significant gains in cell efficiencies. Examples include the world-records for both-side-contacted 25.7% single-crystalline [1] and 21.9% multicrystalline silicon (mc-Si) [2] solar cells, as well as a 25% interdigitated back contact (IBC) cell [3]. Given their compatibility with high temperature processes, polysilicon/oxide passivated contacts can be incorporated into current mass production of solar cells. Nevertheless, industrial silicon wafers have varying levels of purity and crystallinity, and they are subjected to different environments in terms of contamination control.

Impurities such as transition metals are commonly found in silicon wafers for solar cells, creating recombination centres in the silicon wafer bulk and therefore lowering device efficiencies. Phosphorus (P) diffusions are commonly used to achieve effective impurity gettering in silicon solar cell fabrication (see, for example, [4–8]). The gettering effects of boron (B) diffusions, on the other hand, rely on the specific process conditions [9–11]. Given the prominent role that impurity gettering has played in the development of silicon PV technology, and the potential for doped polysilicon/oxide contacts to replace P- and B-doped silicon layers for junction formation purpose, their potential impurity gettering effects need to be investigated and understood.

Gettering of silicon wafers by backside undoped (i.e. intrinsic) polysilicon films has been widely known and used in microelectronics for decades [12–16], and is attributed to a combination of impurity segregation and relaxation mechanisms [17]. Depending on the impurity solubility and diffusivity in silicon oxide, certain process conditions also result in backside polysilicon gettering in the presence of an oxide interlayer [18]. Recently, Krügener et al. reported minority carrier lifetime improvements upon the formation of phosphorus-doped polysilicon/oxide passivating contact structures by ex-situ doping of...
low-pressure chemical vapour deposited (LPCVD) polysilicon layers by ion implantation and subsequent annealing [3]. However, Krügener et al. did not find significant gettering during the fabrication of boron-doped polysilicon/oxide contacts by LPCVD and ion implantation.

This work aims to quantify the possible gettering effects of phosphorus and boron diffusion-doped polysilicon/oxide passivating contacts, via directly monitoring the changes in impurity concentration in the silicon wafer bulk. Iron (Fe) is used as a marker to quantify the gettering effectiveness, due to its pervasiveness in solar-grade silicon and its easy, accurate quantification techniques [15]. The polysilicon/oxide layers are doped by thermal diffusion using POCl3 or BBr3 sources. The intrinsic polysilicon films are formed by plasma-enhanced chemical vapour deposited (PECVD) amorphous silicon (a-Si) films, which partially recrystallise during the thermal diffusion step [19,20].

Details of the fabrication technique and optimisation processes for the doped polysilicon/oxide contacts used in this study were previously published in Refs [21–23].

2. Experimental methods

A flowchart outlining the experimental procedures is shown in Fig. 1. Details are described below.

High quality float-zone silicon (FZ-Si) wafers with precise amounts of intentional iron contamination were used in this work. The boron-doped p-type silicon wafers had a resistivity of 0.9 Ω·cm and a thickness of 180 ± 5 μm after saw damage etch. The silicon wafers were implanted with 56Fe using a relatively low ion implantation energy of 70 keV. The implantation dose was 1.8x10¹⁴ cm⁻², which corresponds to a volumetric Fe concentration of 10¹³ cm⁻³ for the 180-μm thick wafers. The implanted wafers were then annealed at 1000 °C in dry oxygen for a total of 2 h to uniformly distribute Fe throughout the wafer thickness.

The implantation energy and doses used here, combined with an 1000 °C post-implantation anneal, are expected to result in negligible residual damage in silicon wafers [24]. The solubility of Fe in silicon at 1000 °C is 4 × 10¹⁴ cm⁻³ [25], which is well above the implanted Fe concentration of 10¹³ cm⁻³, meaning that the implanted Fe remains dissolved in silicon, i.e. as interstitial Fe (Fe⁺) in the silicon wafer bulk. The amount of Fe precipitation during the 10 °C/min cool-down to 800 °C is negligible, as was previously found for Fe-implanted FZ-Si samples [26], and is also confirmed via lifetime-based measurements of the interstitial Fe concentrations ([Fe⁺]) using the FeB pair-breaking technique [27–28]. The bulk Fe⁺ concentrations were found to be (1 ± 0.1) × 10¹³ cm⁻³. After lifetime measurements, the thermally grown silicon oxide layers were removed in dilute hydrofluoric acid (HF).

The Fe-implanted wafers with the same initial Fe⁺ concentration of 10¹³ cm⁻³, together with a control group of non-implanted FZ-Si wafers of the same resistivity and thickness, were subjected to the fabrication of doped polysilicon/oxide contacts on both sides of the wafers (symmetric structure). In order to study the gettering effects, variations in the fabrication steps were experimented, as shown in Fig. 1. These include, varying the interlayer oxide properties (chemical oxide, thermal oxide of different thicknesses, and no oxide), and replacing the dopant diffusions with nitrogen anneals. The same phosphorus and boron diffusions were also performed on silicon wafers without the polysilicon/oxide layers, i.e. the conventional POCl3 and BBr3 diffusions for forming heavily doped silicon surface layers were included. Each process step is described as follows.

Thin chemical silicon oxide layers were grown by immersing silicon wafers in a 60 wt% nitric acid bath at a temperature of ~90 °C for 30 min. Thermal oxide layers were grown by annealing silicon wafers in dry oxygen at 600 °C and 850 °C respectively for 5 min. Previous ellipsometry measurements show that the oxide thicknesses are ~1.3 nm for the chemical and 600 °C thermal oxide layers, and ~4 nm for the 850 °C oxide [19,21–23].

Intrinsic a-Si layers of 30–40 nm were deposited by PECVD, at a reactor set temperature of 500 °C and an on-sample temperature of ~250 °C. Phosphorus or boron diffusion doping was achieved by using POCl3 or BBr3 as diffusion sources in quartz tube furnaces. Phosphorus diffusions were carried out at 780 °C, 820 °C and 890 °C for the same total time of 40 min. Boron diffusions were at 860 °C, 930 °C and 1000 °C for 80 min. The loading and unloading temperature was 700 °C, and the ramp-up and cool-down rate was 10 °C/min. No forming gas anneal was conducted after the diffusion steps. A subset of the samples underwent nitrogen anneals for the same temperature profiles as POCl3 diffusions. The high temperature processes also enable the partial recrystallisation

![Sample preparation flowchart](image-url)
of the a-Si films [19,20]. Although the exact fraction of polycrystalline and amorphous silicon in the high-temperature annealed films requires further investigation, in this work we will refer to the annealed a-Si as polysilicon, to be consistent with previous reports [20,22,23].

Samples without the complete doped polysilicon/oxide structures (i.e. polysilicon samples without oxide interlayers, polysilicon samples undergoing N<sub>2</sub> anneals instead of dopant diffusions, and diffusion doped crystalline silicon wafers) lack effective surface passivation, and hence they required additional surface etching and coating with double-side PECVD silicon nitride films to enable bulk lifetime measurements. The loss of Fe<sub>e</sub> via gettering to the PECVD nitride films was estimated to be 20% for the given reactor [29], and this has been accounted for in the reported bulk Fe<sub>e</sub> concentrations in this paper.

The effective minority carrier lifetime of the samples was measured by a WCT-120 tool from Sinton Instruments, using either quasi-steady-state photovoltaic current (QSSPC) or transient photocurrent decay (PCD) modes [30]. Implied open circuit voltage under 1-sun was also estimated from the measured lifetime curves using the same tool, as well as the sheet resistance from conductance measurements. The interstitial Fe concentration in the silicon wafer bulk was determined from effective lifetimes measured in the interstitial Fe and Fe-B paired states [27,28,31], and strong illumination was used to dissociate the FeB pairs [32]. The reported uncertainties in [Fe<sub>e</sub>] arose from assuming a 10% uncertainty in the measured effective lifetimes before and after FeB pair breaking.

3. Results and discussion

3.1. Gettering effectiveness of the doped polysilicon/oxide contacts

As shown in Fig. 2, very effective gettering is achieved through the formation of diffusion-doped polysilicon/oxide passivating contacts, for both phosphorus and boron doped polysilicon. Note that the two samples in Fig. 2 underwent process conditions that result in the optimum polysilicon contact properties, in terms of the passivation and carrier transport qualities, and they were not designed to optimise the gettering effectiveness. These samples are coated with 30–40 nm polysilicon layers with ~1.3 nm chemical oxide interlayers, and were subjected to either POCl<sub>3</sub> or BBr<sub>3</sub> diffusion at moderate temperatures of 820 °C and 930 °C, respectively. As will be shown later in Section 3.2.2, the gettering effectiveness increases with increasing diffusion temperature. Nevertheless, the moderate diffusion temperatures used to achieve the best passivating contact properties (detailed in Ref [21,22] and also shown in Section 3.3) already enable very effective gettering of bulk impurities, removing more than 99.9% of bulk iron during the contact formation processes. This indicates that effective gettering can be achieved concurrently with the formation of high performance polysilicon passivating contacts.

The strong gettering effect of phosphorus doped polysilicon contacts is consistent with the reported bulk lifetime improvements upon the formation of P-doped polysilicon contacts via ion implantation and annealing [3,31]. However, boron implantation-doped polysilicon contacts were found to generate no such gettering effect [3], while significant gettering by boron diffusion-doped polysilicon is evident in this work (Figs. 2 and 3). As will be shown later in Section 3.2.1, the gettering effect of polysilicon contacts mainly comes from dopant diffusions. The very different gettering efficiencies of implanted and diffused boron-doped polysilicon/oxide structures are therefore related to the different doping processes.

The following mechanisms have been reported in the literature for the gettering of Fe in heavily boron-doped silicon (without other crystal defects): i) Fe segregation into heavily doped silicon due to higher solubility [11,33], ii) enhanced Fe surface precipitation in boron-doped silicon [34,35], iii) Fe segregation into boron-silicide precipitates [10,36], and iv) Fe gettering by boron-rich layers [9,37]. Based on the known Fe solubilities in heavily boron-doped silicon [11] and moderately doped silicon [25] at 700–1000 °C, the first two gettering mechanisms are unlikely to cause significant gettering effects, which explains the commonly observed poor gettering effects of boron-doped silicon on its own [9]. The third mechanism relies on the nucleation and growth of boron-silicide precipitates in the boron-doped region, which requires long annealing hours as shown in Refs [10,56]. The diffusion temperature-profiles used in this work, as well as in Krügener et al. [3], are not expected to result in significant formation of boron-silicide precipitates.

The most likely explanation for the different gettering efficiencies of ion implanted and BBr<sub>3</sub>-diffused boron-doped polysilicon is the formation of boron-rich layers (BRLs) during the BBr<sub>3</sub> diffusion process [38–40]. A thin BRL is known to reside in between the boron silicate glass (BSG) and the boron-doped silicon region [38–41]. Samples doped via ion implantation and subsequent annealing in inert gas do not have such BRLs. BRL has been shown to be a very effective gettering site, and once removed via post-diffusion oxidation, as is commonly done in cell fabrication, a poor gettering effect is observed for the sole presence of boron doped silicon [9,37]. The physical gettering mechanism of BRLs, however, is unknown at this stage. We confirmed the presence of BRLs on our BBr<sub>3</sub>-diffused polysilicon samples via a simple HF dipping test. The sample surfaces were found to remain hydrophilic after long-time immersion in HF, which is a clear indication of the presence of BRLs on sample surfaces, as BRL is known to be insoluble in HF [38].

Boron-rich layers are detrimental for the surface passivation of boron-doped silicon [9]. However, removal of the BRL via post-diffusion oxidation is not necessary for the doped polysilicon/oxide contacts, as a good surface passivation is already achieved via the polysilicon/oxide structure. BRL can therefore be retained in BBr<sub>3</sub>-diffused polysilicon/oxide for substantial gettering effects, highlighting the advantage of BBr<sub>3</sub>-diffused polysilicon/oxide contacts over both direct
BBB₃ diffusion on silicon wafers and ion implanted boron-doped polysilicon/oxide contacts.

3.2. Understanding the gettering effects: Impact of dopant diffusion, temperature, and oxide interlayer

3.2.1. Separating the gettering effects of intrinsic and doped polysilicon

The observed strong gettering effects of doped polysilicon/oxide layers (Fig. 2) could arise from the polycrystallinity of the films [12–16], the heavy doping present in them [4–8], or a combination of both. To investigate this, we compare the gettering effects of intrinsic polysilicon films to those of dopant-diffused ones. The results are presented in Fig. 3.

Fig. 3(a) shows that the intrinsic polysilicon films used in this work do not have a significant gettering action, removing only half of the initial bulk Fe concentrations. The gettering ineffectiveness is similar for samples with and without the oxide interlayer, and is also similar for intrinsic polysilicon films annealed at different temperatures in 780–890 °C.

The inability of these intrinsic polysilicon films to getter bulk impurities may be related to their structural configuration and/or thickness. The polysilicon films used in this work come from partially recrystallised a-Si films deposited by PECVD at a low temperature of ~250 °C, while those used in microelectronics for backside gettering purposes consist of polysilicon deposited by CVD at much higher temperatures of 600–800 °C [12]. In addition, the recommended film thickness for backside polysilicon gettering is 500 nm to 3 µm [12], which is much thicker than our 30–40 nm deposited a-Si films, offering more grain boundary area for impurity segregation and relaxation. Moreover, the segregation coefficient of Fe between polysilicon and crystalline silicon (c-Si) is only 2–16 at 1175–1020 °C [17]. Therefore, the provision of a sufficient amount of grain boundaries is important for the gettering action of intrinsic polysilicon layers, that is, the thickness ratio of the polysilicon film to the bulk crystalline silicon substrate, where impurities are gettered from, should be considered.

It is interesting to note that the 225-nm thick LPCVD polysilicon films used in Krügener et al.’s work also have poor gettering effects, even after having been boron-implanted [3]. This again may be related to the different film compositions, thicknesses (especially thickness ratios), and perhaps the higher thermal budgets used in fabricating integrated circuits (IC) devices compared to silicon solar cells.

Phosphorus diffused polysilicon layers, on the other hand, show a very strong gettering action (see Fig. 3(a)). Note that the seemingly missing [Feₓ] data represent cases where the remaining Fe concentrations are below the detection limit. In these cases only upper limits are shown, which are estimated based on assuming a conservative 10% uncertainty in the measured lifetimes before and after Feₐ pair-breaking.

3.2.2. Comparison to gettering from direct dopant diffusions

Compared to the POCl₃-diffused polysilicon without the oxide interlayer, POCl₃-diffused crystalline silicon demonstrates better gettering effects, as shown in Fig. 3(a) for the bare Si samples. The residual bulk Fe concentrations of the bare c-Si wafers are all below the [Feₓ] detection limit. This probably relates to the different effective phosphorus doping in crystalline silicon and polycrystalline silicon, as dopants tend to segregate into grain boundaries [42–44] in polysilicon. Sheet resistances of the diffused bare Si wafers are found to be consistently lower than those with the polysilicon contacts, for both POCl₃ and BBB₃ diffused samples, indicating a higher concentration of electrically active dopants in the bare c-Si samples.

Similar to the results in Fig. 3(a), boron-diffused c-Si offers better gettering effects than boron-diffused polysilicon/oxide layers under the same diffusion conditions, as shown in Fig. 3(b). Results in Fig. 3 therefore clearly indicate that, the dominant gettering mechanism of these P and B diffusion-doped polysilicon/oxide layers is related to the POCl₃ and BBB₃ diffusions. Polysilicon alone offers poor gettering effects. The blocking effect of the oxide interlayer, and its dependence on the diffusion temperature, will be discussed later in Section 3.2.3.

The gettering effectiveness of both polysilicon contacts and diffused c-Si wafers is found to increase with increasing diffusion temperature, for both POCl₃ and BBB₃ diffusions (see Fig. 3). As the gettering action of polysilicon contacts is dominated by the dopant diffusion processes, this dependence of the gettering effectiveness on the diffusion temperature can be explained by the well-studied gettering effects of dopant diffusions.

Higher diffusion temperatures lead to more heavily doped silicon layers, which are known to achieve better gettering effects [33]. However, the segregation coefficient of metals in heavily doped silicon
generally decreases with increasing temperature (iron as an example in Ref [8]), which may offset the increased gettering effectiveness of heavier doping, as experimentally shown in Ref [7] for samples unloaded from the furnace at the respective diffusion temperatures. All samples used in this work experienced the same rate of 10 °C/min cool-down to 700 °C before being unloaded, meaning that more effective gettering could be achieved in more heavily doped samples during the cool-down phase, giving rise to higher overall gettering efficiencies for samples diffused at higher temperatures. For BBr3-diffused silicon where the BRL acts as the main gettering site, BRL thickness was found to increase with increasing diffusion temperature [41], which may explain the stronger gettering effects at higher temperatures.

3.3.2.3. Effect of interlayer oxide on gettering effectiveness

Fig. 3(g) also illustrates the impact of the interfacial oxide on the gettering effectiveness. Samples with no oxide, chemically grown oxide of ~1.3 nm, and thermally grown oxides of ~1.3 nm and ~4 nm underwent the same PECVD deposition and POCl3 diffusion processes. Comparing the remaining bulk [Fe0] for each diffusion temperature, it can be seen that the presence of an oxide interlayer hinders the gettering action, and that the gettering effectiveness decreases with increasing oxide thickness. At lower diffusion temperatures, the samples with no oxide show the best gettering efficiency, but a similar efficiency can be achieved in the presence of a thin chemical oxide by increasing the diffusion temperature, as evidenced by a residual [Fe0] below the detection limit. The different gettering effectiveness of the chemical and thermal oxides of the same thickness likely relate to the different oxide density achieved by the two growth methods.

For samples with a 4-nm thick thermal oxide interlayer, ineffective gettering is observed for all diffusion temperatures, reducing the bulk [Fe0] by only about a half. In addition, there is no temperature-dependence of the gettering effectiveness. The diffusivity of iron in SiO2, however, is known to increase with increasing temperature, although the reported diffusivities in the literature vary by a few orders of magnitude (as summarised in Ref [18]). Discrepancies in the reported iron solubility in SiO2 are even larger and the results are contradictory. While Ramappa and Henley reported a strong segregation of Fe into the SiO2 [45], Smith et al. found that the ratio of Fe concentrations in SiO2 to Si is only 1.3 [46], and Istratov et al. observed reduced Fe concentrations in SiO2 compared to the Si [18]. These conflicting data make it difficult to assess and quantify the blocking mechanisms of the oxide interlayer. The blocking effect of the 4-nm oxide may result from low Fe solubility and diffusivity at the diffusion temperatures and times. It may also be caused by the insufficient doping through the oxide into the substrate silicon, which has been found to be important for achieving good passivating contact properties, and for the given diffusion conditions a 4-nm oxide interlayer is too thick to allow dopants to diffuse through [21,22]. Further investigations are required to understand the poor gettering associated to thick oxides, even though such oxides have little practical interest, since they also block the transport of electrical current [21,22].

3.3. Impact of gettering on the passivation quality of polysilicon contacts

This section investigates the possible impact of impurity gettering on the passivation quality of the polysilicon contacts via comparing the measurements of 1-sun implied open circuit voltage (iVoc) on samples that underwent the same contact formation processes with and without an initial bulk Fe concentration of 10^{19} cm^{-3}. The results are presented in Fig. 4. Note that the iVoc values are determined from the measured effective lifetime curves of the samples with symmetrical double-side polysilicon contact structures.

As shown in Fig. 3, an effective gettering of iron to a remaining bulk Fe concentration of 10^{19} cm^{-3} (i.e. removal of 99.9% bulk Fe) requires diffusion temperatures above 820 °C for the P-doped polysilicon/chemical oxide structure, 890 °C for the P-doped polysilicon/thin thermal oxide (~1.3 nm), and 860 °C for the B-doped polysilicon/chemical oxide. Fig. 4 shows that, for samples with low residual [Fe0] below 10^{16} cm^{-3}, similar iVoc is measured on Fe-implanted and no-Fe control samples. The even lower iVoc of some of the no-Fe control samples in Fig. 4(c) (860 °C and 1000 °C) are likely caused by some unknown bulk defects in these two wafers.

A more direct approach for assessing the surface passivation quality is via measuring the saturation current density J0 on high resistivity silicon wafers. However, low resistivity silicon wafers were used in this work to enable convenient bulk Fe measurements using the FeB pair-breaking technique. Nevertheless, J0 can be estimated from the implied Voc based on the known bulk properties (radiative, Auger, and Fe-dominated Shockley-Read-Hall recombination channels). An iVoc of 720 mV corresponds to a J0 of 12 fA/cm² per side for the POCl3-diffused polysilicon contacts in Fig. 4(a) and (b), and an iVoc of 704 mV corresponds to a J0 of 23 fA/cm² per side for the BBr3-diffused polysilicon in Fig. 4(c). Lower J0 values are possible through fine-tuning the optimization process, in some cases combined with a post-diffusion forming gas anneal, as demonstrated in Refs [21,22].

In summary, the iVoc results in Fig. 4 indicate that the presence of gettered iron in P and B doped polysilicon/oxide layers does not affect the passivation quality of the polysilicon contacts, further strengthening the advantage of using doped polysilicon/oxide structures to achieve both passivating contact formation and impurity gettering effects.
4. Conclusion

Moderate diffusion temperatures, which are required to achieve optimum surface passivation and low contact resistance for the polysilicon/oxide structure, have been found to also result in significant gettering of bulk metallic contaminants, for both phosphorus and boron diffused polysilicon/oxide contacts. The strong gettering effect of the polysilicon passivating contacts mainly comes from the efficient gettering capabilities of heavily phosphorus doped silicon in the case of POCl$_3$-diffused polysilicon/oxide contacts, and from the gettering action of boron-rich layers in the case BBr$_3$-diffused polysilicon/oxide contacts. The gettering effectiveness increases with increasing diffusion temperature for samples removed from the furnace at moderate or low temperatures. The presence of the oxide interlayer hinders the gettering effectiveness, although at optimum polysilicon fabrication conditions (very thin oxides combined with sufficiently high diffusion temperatures), the blocking effect is small, enabling the removal of more than 99.9% of the bulk iron.

Lastly, the passivation quality of the doped polysilicon/oxide contact structures is not compromised by the gettering action. This means that a separate gettering step or a trade-off between gettering and passivation are not required, and hence impurity gettering is an added benefit of diffusion-doped polysilicon/oxide passivating contacts. Particularly, BBr$_3$ diffusion-doped polysilicon contacts can achieve very efficient gettering of bulk impurities thanks to the formation of a boron-rich layer, offering an advantage over boron implanted polysilicon contacts and BBr$_3$ diffusion-doped silicon substrates (where the boron-rich layer has to be removed to allow adequate surface passivation), which have poor gettering efficiencies.

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References


