A technique is presented to simultaneously diffuse boron and phosphorus in silicon, and grow an in-situ passivating oxide in a single furnace step. It is shown that limited solid doping sources made from P and B Spin-On Dopant (SOD) films can produce optimal \( n^+ \) and \( p^+ \) profiles simultaneously without the deleterious effects of cross doping. A high quality passivating oxide is grown in-situ beneath the thin (~60 Å) diffusion glass, resulting in low \( J_0 \) values below 100 fA/cm\(^2\) for transparent (~100 Ω/□) phosphorus and boron diffusions. For the first time it is shown that impurities present in the boron SOD film can be effectively filtered out by employing separate source wafers, resulting in bulk lifetimes in excess of 1 ms for the sample wafers. The degree of lifetime degradation in the sources is related to the gettering efficiency of boron in silicon. This novel simultaneous diffusion, in-situ oxidation, impurity filtering and gettering technique was successfully used to produce 20.3% Fz, and 19.1% Cz solar cells, in one furnace step.

I. INTRODUCTION

High temperature thermal processing can limit the throughput of a cell manufacturing line and potentially reduce cell efficiency through bulk lifetime degradation. To fabricate high efficiency solar cells with minimal thermal processing, simultaneous diffusion techniques can be employed to co-diffuse the emitter and Back Surface Field (BSF). Researchers at Sandia National Laboratories [1] have demonstrated an aluminum and phosphorus diffusion technique in which one high temperature (>800 °C) POCl\(_3\) diffusion step is used to co-diffuse the emitter and pre-alloyed BSF, and grow a thick thermal oxide beneath the remaining phosphosilicate glass. Workers at IMEC have simultaneously diffused boron and phosphorus in an RTP using CVD doped oxides on opposite sides of a silicon wafer [2]. Using boron and phosphorus Spin-On Dopant (SOD) films in a conventional diffusion furnace, workers at UNSW have simultaneously formed the front and back groove diffusions for the double sided buried contact structure [3], reducing the number of thermal cycles from three to two. All of the above techniques result in a thick layer of diffusion glass on the wafer surfaces. This thick diffusion glass leads to a high reflectance when incorporated into a module and is therefore usually removed, thus eliminating any possibility for in-situ surface passivation.

In addition, POCl\(_3\) as well as the gasses typically used in CVD processes such as SiH\(_4\), B\(_2\)H\(_6\) and PH\(_3\) are highly toxic, and require significant expertise in handling and disposal. Our approach toward simultaneous diffusion, named the Dopant Oxide Solid Source (DOSS) technique [4], employs separate boron and phosphorus doping sources, which are interleaved with the solar cell wafers to simultaneously form a phosphorus emitter and boron BSF in a single furnace cycle. In the DOSS technique, the back sides of the solar cells (S) face the boron sources (B), and the front sides face the phosphorus sources (P) in a stacking arrangement shown in Figure 1. The B and P sources are fabricated in house from silicon wafers on which a controlled amount of the dopant oxide \( \text{POCl}_3\) or \( \text{B}_{2}\text{O}_3\) is deposited. The DOSS technique, which was first presented at the 25th Photovoltaics Specialists Conference [5], allows one to independently control the emitter and BSF doping profiles for a fixed thermal budget, by tailoring the concentration of \( \text{POCl}_3\) and \( \text{B}_{2}\text{O}_3\) on the source wafers. In our earlier work [4] sources were made by depositing \( \text{POCl}_3\) or \( \text{B}_{2}\text{O}_3\) on the source wafers using the liquid dopants POCl\(_3\) and BB\(_3\) respectively in a pre-deposition step. In contrast to conventional solid, liquid, CVD or spin-on doping techniques, the residual phosphorous glass on the solar cell wafers was extremely thin (~60 Å). This allowed for a thin thermal passivating oxide to be grown in-situ, while maintaining a total oxide thickness below about 150 Å, which will not significantly increase the reflectance of an
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AR-coated cell when incorporated into a module. This in-situ oxide was shown [5] to provide excellent surface passivation for light phosphorus diffusions (~90 Ω/□), resulting in virtually the same saturation current densities (Jsc's) for in-situ as well as re-grown thermal oxide passivation.

The goal of this paper is to present recent advances in the DOSS simultaneous diffusion technique in which the solid doping sources are fabricated using phosphorus and boron Spin-On Dopant (SOD) films in place of POCl3 and BBr3. It will be shown that in addition to forming optimal emitter and BSF profiles simultaneously, and providing in-situ oxide surface passivation, one can obtain high minority carrier lifetimes from a relatively impure boron SOD film through a powerful contamination filtering action. Several efficiency-enhancement features are combined in the DOSS technique to produce 19-20% efficient solar cells in one thermal cycle, using commercially available spin-on dopant films and a conventional diffusion furnace.

II. EXPERIMENTAL

Boron and phosphorus solid diffusion sources were made prior to each diffusion cycle by applying the same SOD film (B or P) to each side of a silicon source wafer. The source wafers are depleted after each diffusion cycle, and recycled (as sources) by a brief dip in 10% dilute HF to remove any residual glass. As shown below, the limited nature of these solid doping sources enables several high efficiency features to be realized in one furnace step using this simultaneous diffusion technique.

It should be recognized that at no point are the SOD films applied to the solar cell wafers. By applying the same SOD film to each side of a source wafer, as opposed to applying P and B films to opposite sides of a solar cell wafer, we eliminate the potential for cross doping during the film application process, and in addition reduce the handling requirements for the solar cell wafers. In production this would appear to be a distinct advantage over competing technologies since the sources could be made using high throughput techniques such as dip coating or spraying the dopants onto the sources, while the solar cell wafers are processed in parallel via cassette loading techniques.

III. RESULTS AND DISCUSSION

III-A Diffusion Profile Engineering Using DOSS Technique

To demonstrate the flexibility of the DOSS diffusion technique, a range of diluted phosphorus and boron SOD films were used to fabricate sources, followed by a 60 min diffusion cycle at 1000 °C in N2. All of the SOD films used in this work are commercially available, and were provided by Filmtronics Corporation, under the product name Boron-A for the boron films and the P500 series for the phosphorus films. Figure 2 shows the resulting sheet resistance dependence on % P2O5 in the phosphorus SOD film, and the % of concentrated Boron-A in the boron SOD film. As shown in figure 2 one can simultaneously achieve optimal emitter and BSF profiles, in the range of 20 to 300 Ω/□ by tuning the dopant concentration of the SOD film used to fabricate the source wafers.

The dependence of diffused sheet resistance on source concentration displayed in figure 2 is quite different than what is observed with conventional phosphorus or boron solid sources. Conventional solid sources deposit large quantities of the respective dopant compound (P2O5 or B2O3) so that the surface concentration is fixed by the solid solubility of the impurity at a given temperature. Thus one is severely restricted in designing a simultaneous diffusion process with conventional solid sources, since the surface concentration of both impurities are pinned at the solid solubility at the diffusion temperature.

The solid sources developed in this work are limited in the concentration of dopant oxides transferred from source to sample, and do not behave as “infinite” solid sources over a wide range of concentrations. This unique feature for solid doping sources allows one to tune the dopant surface concentration to produce optimal emitter and BSF profiles by simply adjusting the dopant concentration of the SOD film used to fabricate the sources. The upper limit for surface concentration is dictated by the solid solubility, at which point the sources behave as conventional solid sources.

III-B. Residual Oxide Thickness

Figure 3 shows the residual oxide thickness for boron and phosphorus diffused samples resulting from the limited solid doping sources developed in this work. The two sets of data are for boron and phosphorus diffusions at 1000 °C for 60 min in N2 only, with no in-situ oxide formation. From figure 3 it is clear that the residual glass thickness is very small, and is approximately the same value for both dopants, for sheet resistance (ρs) values greater than about 30 Ω/□. For ρs values below about 30 Ω/□, the glass thickness rises sharply with decreasing ρs, and the differences in glass thickness between boron and phosphorus diffused samples becomes more pronounced. For most phosphorus emitters of interest, having ρs values in the range of 40-
100 Ω/□, the residual glass thickness ranges from 65–90 Å. This is about an order of magnitude lower than what is obtained when using conventional solid, liquid, CVD or spin-on doping sources.

![Diffusion Glass Thickness vs Sheet Resistance](image)

Figure 3. Residual oxide thickness for P and B diffused wafers with no in-situ oxidation.

A physical model is presented below to explain two unique features of the DOSS technique; the tunability of the surface concentration below the solid solubility, figure 2, and the resulting thin diffusion glass shown in figure 3. These attributes are used to obtain optimal profiles and in-situ surface passivation resulting in low J0 values.

### III-C. Proposed Model for DOSS Diffusion

The phosphorus SOD used in this work is an industry-standard solution of P2O5, H2O, tetraethylorthosilane (TEOS), and ethanol. The hotplate bake prior to diffusion serves to drive off the ethanol solvent leaving a glassy film of P2O5, H2O and TEOS. At diffusion temperatures above about 700 °C, TEOS reacts to form SiO2, H2O and C2H4 [6,7]. It is well known that P2O5 is extremely hygroscopic [8], and will react with H2O intentionally added to the SOD film, as well as with moisture in the laboratory environment and trace amounts of moisture in the process gasses, to form the volatile species H3PO4 (phosphoric acid), which has a boiling point of about 400 °C. It is assumed that this is the phosphorus containing species that is transported from the source to the sample wafer. The reverse reaction takes place on the sample wafer resulting in a film of P2O5 on the sample surface with H2O as a by-product; a process which was found to occur during the direct vaporization of H3PO4 at elevated temperatures [9];

\[
P_2O_5 + 3H_2O \xrightarrow{\text{Source}} 2H_3PO_4 \quad (1)
\]

The oxide of phosphorus, P2O5, deposited on the sample surface proceeds to react with silicon to form SiO2 and P, which preferentially diffuses into silicon:

\[
2P_2O_5 + 5Si \rightarrow 5SiO_2 + 4P \quad (2)
\]

For the case of limited doping sources, we propose that the starting thickness of P2O5 formed on the sample surface is extremely thin, and is limited by the dose of H3PO4. During the diffusion cycle reaction (2) is essentially driven to completion, resulting in a thin layer of SiO2 rich glass on the sample surface, and the surface concentration of P below the solid solubility. Thus by controlling the concentration of P2O5 in the SOD film, we can limit the dose of H3PO4, and thus the thickness of P2O5 on the sample, allowing the underlying silicon to consume virtually all of the available phosphorus for concentrations below the solid solubility. This result is notably different than conventional SiP2O7-based solid sources which are designed to be reused for hundreds of hours. These conventional solid sources continually deposit a stream of P2O5 on the sample wafers, which results in a thick layer of diffusion glass on the surface [10], and thus provides a supply of phosphorus which exceeds the solid solubility. In this case the surface concentration is dictated by the solid solubility of P in Si, and thus the only degrees of control is the diffusion temperature and time. But by fabricating solid doping sources in the limited source regime we now have a third degree of control in addition to temperature and time; the source concentration.

The situation for boron sources fabricated from a boron SOD film is analogous to phosphorus: The Boron-A film used in these experiments is a proprietary boron-based polymer dissolved in cyclohexane and diluted with toluene, which converts directly to B2O3 at about 450 °C [11]. It is likely that B2O3 is directly transported from the source to sample wafer, although HBO2 which has a much higher vapor pressure than B2O3 is known to form in the presence of even trace amounts of moisture [12]. For the case of limited boron diffusions, the reactions on the sample surface proceed as in the case of phosphorus:

\[
2B_2O_3 + 3Si \rightarrow 3SiO_2 + 4B \quad (3)
\]

resulting in a thin SiO2-rich glass layer and a boron concentration below the solid solubility.

To test the above hypothesis; that the emitter surface concentration depends on the starting thickness of P2O5 on the sample wafers, diffusions were carried out using planer and textured sample wafers which face opposite sides of the same phosphorus source. By etching [111] oriented pyramids in the [100] sample surface, the surface area is increased by a factor of \(1/cos45°=1.73\) over a planer surface. Thus for a limited dose of H3PO4, the resulting thickness of P2O5 on the textured sample will be less than the planer sample since the available quantity of P2O5 is spread out over a larger surface area. According to the proposed model this should result in a lower surface concentration on the textured wafers or equivalently a higher sheet resistance. As shown in figure 4 this is indeed the case.

Figure 4 shows that for low concentrations of P2O5 in the SOD films used to fabricate the sources, the textured wafers have a higher sheet resistance than the planer wafers by a factor of about 2 when facing the same sources. As the % P2O5 in the SOD film is increased, the difference in pS is reduced until the pS's for the textured and planer wafers approach the same value for the "infinite" P2O5 case, which corresponds to that of conventional solid sources.
For comparison, diffusions were carried out using POCl₃ and conventional SiP₂O₇-based solid sources, with textured and planer wafers diffused simultaneously. As shown in the inset table of figure 4, the values of $p_e$ for textured and planer wafers is nearly identical when using POCl₃ and conventional solid sources. However, in the case of limited solid sources used in the DOSS technique, the same source can produce an 88 $\Omega$·cm textured emitter and a 46 $\Omega$·cm planer emitter. This feature can be used to obtain an in-situ selective emitter for screen-printed contacts: By selectively texturing the field region of an emitter using a SiN texture mask, one can simultaneously diffuse a flat grid region of 46 $\Omega$·cm, and a textured field region of 86 $\Omega$·cm, taking full advantage of the in-situ oxide passivation found in the DOSS technique.

### III-D. In-Situ Oxide Surface Passivation

Table 1 shows the results of emitter saturation current density ($J_0$) measurements at 25 °C [13], made on heavy and light boron and phosphorus diffusions, with in-situ oxide passivation. As shown in table 1, a heavy (25 $\Omega$·cm) boron BSF typically used in high efficiency cell designs results in a $J_0$ value of 417 fA/cm². By forming a lighter boron diffusion of 110 $\Omega$·cm, coupled with in-situ oxide passivation this $J_0$ value can be reduced to 92 fA/cm². This value for $J_0$ is a factor of two higher than reported by King [ref] for 126 $\Omega$·cm boron BSF using CVD doped oxides, but is still capable of producing low values of effective recombination velocity at the high-low ($p^+$) junction. For a 2 $\Omega$-cm (p-type) material, the effective surface recombination velocity at the $pp^+$ junction can be expressed as:

$$S_{pp^+} = \frac{N_A}{g_n^2} \left( 1 + \frac{\alpha}{N_A} \right) J_0$$

which corresponds to an $S_{pp^+}$=556 cm/s under low level injection ($\Delta n<<N_A$). In practice the true value of $S_{pp^+}$ will be higher due to additional recombination at the ohmic contacts to the (full) $p^+$ BSF. But, by reducing the metal coverage by forming point contacts or screen-printing an Al/Ag grid, the effects of contact recombination can be reduced.

### Table 1. $J_0$ measurements for heavy and light boron and phosphorus diffusions.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Sheet Resistance</th>
<th>$J_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>25 $\Omega$·cm</td>
<td>417 fA/cm²</td>
</tr>
<tr>
<td>Boron</td>
<td>110 $\Omega$·cm</td>
<td>92 fA/cm²</td>
</tr>
<tr>
<td>Phos. (with Ox.)</td>
<td>90 $\Omega$·cm</td>
<td>607 fA/cm²</td>
</tr>
<tr>
<td>Phos. (w/o Ox.)</td>
<td>90 $\Omega$·cm</td>
<td>809 fA/cm²</td>
</tr>
<tr>
<td>Phos. (with Ox.)</td>
<td>43 $\Omega$·cm</td>
<td>130 fA/cm²</td>
</tr>
</tbody>
</table>

The benefits of in-situ oxide passivation of phosphorus diffused emitters formed using SOD-coated source wafers are shown in Table 1. As shown in Table 1, for a 90 $\Omega$·cm n⁺ diffusion with in-situ oxide passivation, the resulting $J_0$ value is low, resulting in $J_0$=67 fA/cm². By removing the in-situ oxide, the $J_0$ value increases to 809 fA/cm², demonstrating the superb passivating qualities of the in-situ oxide provided by the DOSS technique. By forming a heavier n⁺ diffusion (~43 $\Omega$·cm) which is appropriate for screen printed contacts, we have found that the $J_0$ value shows only a moderate increase to 130 fA/cm², which is still capable of producing high open circuit voltages. That we can obtain a low $J_0$ of 130 fA/cm² for a (semi-opaque) 43 $\Omega$·cm phosphorus diffusion is most likely due to the fact that the diffusions are carried out well below the solid solubility. This reduces the probability of introducing significant surface damage, commonly referred to as a “dead layer” [14], allowing the device to take advantage of the high-quality in-situ oxide passivation.

Work is currently under way to introduce screen-printed contacts to the cell fabrication process using the 43 $\Omega$·cm phosphorus emitter and 110 $\Omega$·cm boron BSF shown in Table 1. Measurements of the specific contact resistance ($p_c$) by the transmission line method have resulted in average $p_c$ values of 2.9 mΩ-cm² for 46 $\Omega$·cm phosphorus diffusions and 4.3 mΩ-cm² for 85 $\Omega$·cm boron diffusions using Ag/P and Ag/Al pastes respectively. Computer modeling indicates that greater than 18% Cz screen-printed cells should be feasible if effective surface passivation can be maintained and the metal area coverage kept to a minimum (≤10%).

### III-C. Impurity filtering and Gettering Using DOSS Technique

Historically it has been difficult to obtain high minority carrier lifetimes when using a boron SOD film as a dopant source, when spun directly onto a wafer. The impurity levels of contaminants such as Fe, Cr, Cu and Ni are typically present in the 10 ppb range for the SOD films used in this work [11], which can lead to significant bulk lifetime degradation. In the present work it was discovered that by fabricating separate boron sources using a relatively impure boron SOD film, one could filter out much of the contaminants present in the film, liberating a relatively “pure” flux of $B_2O_3$ from the film-coated source wafer.
The effectiveness of this impurity filtering action is seen in figure 5, in which the boron-diffused bulk lifetime, $t_b$ is shown as a function of injection level, $n$. Two sets of source/sample wafers were used in these experiments, in which a 100% Boron-A film was applied to a p-type 2.3 cm float zone silicon wafer which was then used as a source for an adjacent 2.3 cm sample wafer. Special care was taken in these experiments to insure cleanliness of the spin-on process. The first set of wafers, labeled Sample 1 and Source 1 respectively in figure 5 were diffused at 1000 °C for 60 min in $N_2$, with no in-situ oxide grown. The second set of source/sample wafers were subjected to an additional 66 min in-situ oxidation at 1000 °C to grow a thick thermal oxide and are labeled Sample 2 and Source 2. As shown in figure 5, the difference in bulk lifetime between the source and sample wafers is large for the cases with and without the thick in-situ oxide. In both cases the impurity filtering action resulted in high bulk lifetimes in excess of 1 ms for the sample wafers, but degraded the source wafers to a lifetime of 227 µs and 5.9 µs for the non-oxidized (case 1) and oxidized cases (case 2) respectively. We have observed this behavior numerous times using 5 different lots of boron SOD film manufactured over the past 2 years. By indirectly doping the samples via film-coated source wafers, impurities in the boron SOD film are diffused into the sources but are not transported to the samples, resulting in lifetimes in excess of 1 ms for these high-quality Fz-Si wafers. Thus the sources act to filter out impurities from the boron SOD film, allowing a relatively pure layer of $B_2O_3$ to deposit on the sample surface.

$$\frac{[X^+_i]}{[X^+_t]} = \frac{\Delta E_f}{kT}$$

where $X^+$ is the ionized interstitial metal concentrations and $\Delta E_f$ is the Fermi-level offset between the $p^+$ and $p^-$ regions.

While we have not attempted to identify the lifetime limiting impurities in this work, our results are consistent with those reported in the literature for boron gettering of the metallic impurities present in the Boron-A SOD film. These results suggest that clean boron diffusions resulting from the impurity filtering mechanism in the DOSS technique, coupled with effective boron gettering can be used to significantly enhance the minority carrier lifetime of solar grade materials. The simplicity and flexibility of the DOSS diffusion technique makes this an ideal approach to study boron and phosphorus (co)gettering phenomena while maintaining the ability to produce high efficiency solar cells in one furnace step.

**III-D. High Efficiency Solar Cell Fabrication**

The ability of the DOSS technique to produce optimal emitter and BSF profiles, in-situ oxide surface passivation and maintain high bulk lifetimes is demonstrated by high efficiency solar cell fabrication. The cell structure used is referred to as a Simultaneously diffused, Textured, in-situ oxide AR-coated solar cell (STAR cell). Figure 6 shows the light IV, IQE and reflectance measurements confirmed by Sandia National Laboratories of two STAR cells made on (boron) source and sample wafers, in order to illustrate the power of impurity filtering in this technology. The 4.2% random textured cells were fabricated on 2.3 cm float zone silicon, in a 60 min simultaneous diffusion process at 1000 °C in $N_2$ followed by a 66 min in-situ oxidation to grow a ~1070 Å $SiO_2$ single layer antireflection coating. Photolithography was used for the front and back contacts, with point contacts made to a full boron BSF in order to use the (back) in-situ oxide as a dielectric for a back side reflector. This type of structure has recently produced (confirmed) efficiencies as high as 20.1% in one furnace step [17] using the DOSS diffusion technique.

Figure 6 illustrates the merit of using separate boron source wafers, which resulted in an efficiency of 19.4% for the cell adjacent in the diffusion furnace to the 15.2% cell to which the boron SOD film was applied. Both cells were fabricated out of the same float zone silicon material and had the same emitter and BSF sheet resistances. The 4.2% boost in absolute efficiency by using a separate boron source is attributed to the filtering of impurities present in the boron SOD film, a process
which according to figure 5 results in bulk minority carrier lifetimes in the vicinity of 1 ms for this material.

In order to reduce the processing temperature from 1000 °C and improve the surface passivation and AR coating properties, a second generation (STAR-II) process is currently under development. In the STAR-II design, the diffusion temperature is reduced to 925 °C and the oxidation time reduced to 10 min. These process changes produce a lighter boron BSF (~100 μm) and a thinner oxide so that a ZnS/MgF2 DLAR-coating can be used with the textured emitter. PECVD SiO2 is deposited on the back \textit{in-situ} oxide as a dielectric for a back side reflector, and point contacts made to the (full) transparent boron BSF. Initial STAR-II results are encouraging, giving efficiencies of 20.3% on 4 cm² Fz (2.3 Ω-cm) cells and 19.1% on 200 μm thick Cz (10 Ω-cm) cells. Internal quantum efficiency measurements are shown in figure 7 for the 19.1% Cz STAR-II cell. The high long wavelength quantum efficiency demonstrates that in addition to good surface passivation and bulk lifetime, effective light trapping is achieved in this 200 μm thick device, due to the Si/SiO2/Al back side reflector. In comparing STAR-I and STAR-II Fz cells, a 10 mV increase in Voc is obtained which can be largely attributed to the transparent, oxide passivated boron BSF. Further improvements are expected through optimization of the surface passivation and AR coating properties, in order to reach the goal of producing 20% Cz cells in one furnace step using the STAR-II process. Research is also underway to integrate screen printing with the STAR technology to produce manufacturable, high efficiency solar cells.

IV. CONCLUSION

In conclusion, we have made significant advances in the DOSS simultaneous boron and phosphorus diffusion technique. It is shown that the boron and phosphorus source wafers can be fabricated from SCD films, which provide a high degree of flexibility in process design and eliminate the need for separate POCl₃ and BBr₃ diffusion furnaces. Several efficiency-enhancing features of the DOSS technique, such as \textit{in-situ} oxide surface passivation, impurity filtering and boron gettering are presented and quantified. These efficiency enhancement techniques are combined to produce 19-20% efficient Fz and Cz solar cells in a single thermal cycle, using sources and equipment which are completely compatible with the current PV technology base of conventional diffusion furnaces.

![Figure 6. Impact of impurity filtering action on solar cell efficiency, showing a 4.2% increase in (absolute) efficiency for the sample device as compared to the corresponding source device.](image)

![Figure 7. IQE of 19.1% STAR-II cell on 200 μm thick Cz-Si.](image)

V. REFERENCES


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