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Phosphorus emitter profile control for silicon solar cell using the doss diffusion technique

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Abstract - *The Doped Oxide Solid Source (DOSS) diffusion technique is well suited for fine-tuning of the surface concentration. The dopant surface concentration is important during phosphorus emitter diffusion due to the opposite requirements of a lowly doped emitter for good blue response and a sufficiently high surface concentration for a good ohmic contact. The sources are made in the laboratory using the standard* $POCl_3$ *diffusion technique. DOSS Diffusions were carried out in the temperature range 850-1050°C using sources with different doping levels obtained by varying the* $POCl_3$ *partial pressure from 0.004 % to 4.28 %. The electrical profiles were measured using the Stripping Hall profiling technique. Phosphorus diffusion profiles with the complete elimination of the dead layer have been obtained over a large range of source concentrations for all investigated diffusion temperatures. The residual diffusion oxide thickness increased with both temperature and source doping level within the range 7.5-30 nm. XPS profiling indicated that the composition of the residual glass was a mixture of* P_2O_5 *and* SiO_2*.*

Résumé - *La technique de diffusion de l'oxyde dopé à source solide (DOSS) est bien adaptée pour le réglage fin de la concentration de surface. La concentration superficielle du dopant est importante lors de la diffusion de l'émetteur de phosphore en raison des exigences contraires d'un émetteur faiblement dopé pour une bonne réponse en bleu et une concentration de surface suffisamment élevée pour un bon contact ohmique. Les sources sont réalisées au laboratoire en utilisant la technique de diffusion standard* $POCl_3$*. Les diffusions d'oxyde dopé à source dopé ont été réalisées dans la plage de température 850-1050 °C en utilisant des sources avec des niveaux de dopage différents obtenus en faisant varier la pression partielle* $POCl_3$ *de 0.004 % à 4.28 %. Les profils électriques ont été mesurés en utilisant la technique de profilage Stripping Hall. Des profils de diffusion de phosphore avec élimination complète de la couche morte ont été obtenus sur une large gamme de concentrations de source pour toutes les températures de diffusion étudiées. L'épaisseur résiduelle d'oxyde de diffusion a augmenté avec la température et le niveau de dopage de la source dans la plage de 7.5 à 30 nm. Le profilage XPS indique que la composition du verre résiduel est un mélange de* P_2O_5 *et de* SiO_2*.*

Keywords: Doping – Silicon – Emitter - Dead layer - Residual diffusion oxide.

1. INTRODUCTION

The emitter design has a significant impact on the solar cell efficiency. In the photovoltaic industry, the solar cell emitter is homogeneously doped to 50-60 Ω/sq. for a good ohmic contact between the metal grid and the emitter most commonly using the $POCl_3$ diffusion technique [1]. The surface concentration is kept well above the solid solubility of phosphorus, leading to the occurrence of a layer of electrically inactive phosphorus precipitates called 'dead layer'. Yet, the illuminated surface area requires a lowly doped emitter for high blue response. A trade-off is achieved by the selective emitter doping [2] albeit with increased process complexity.

Recently attempts at reducing the surface concentration by finely tuning the phosphorus diffusion profile, without adding steps and therefore extra costs have been reported [3]. In $POCl_3$-based diffusion, however, it is difficult to achieve a shallower emitter with lower peak dopant concentration, for example by lowering the temperature, without incurring a higher emitter sheet resistance with poor homogeneity. The peak

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surface concentration and hence the profile can easily be tailored by using the Doped Oxide Solid Source (DOSS) diffusion technique which is similar to solid source doping except that the sources are made in the laboratory.

The DOSS technique has so far received little attention although it was first proposed in 1996 for the fabrication of high efficiency silicon solar cells with an efficiency of ~17% and ~20% for Cz and Fz silicon respectively [4] and industrial-type screen printed silicon solar cells [5, 6]. There are two main advantages over conventional diffusion techniques ($POCl_3$, spin on or spray). First, the source phosphorus content can be easily varied by changing the doping level. Second, the residual diffusion glass is thin and may serve as passivating layer.

In this study, the source doping was controlled by changing the phosphorus partial pressure during $POCl_3$ diffusion. Phosphorus diffusion profiles without dead layer have been obtained over a large range of source concentrations for all investigated diffusion temperatures (850-1050°C).

2. EXPERIMENTAL

We used 4-inch Cz, (100) silicon wafers, 450 μm thick, p-type (boron doped), 0.5-2.5 Ω.cm in resistivity for both source wafers and processed wafers. A mirror-polished wafer was placed in the middle of each diffusion batch for characterization purposes. The sources were fabricated by P deposition from $POCl_3$, varying the partial pressure of $POCl_3$ from 0.004 % to 4.28 % and keeping all other process parameters constant. DOSS diffusion was carried out under a pure nitrogen flow using a configuration where the processed wafers are placed back to back between each pair of source wafers (figure1).

The diffusion temperature was varied from 850 to 1050 °C and the time fixed at 10 or 60 minutes. The electrically active concentration profiles were determined using the Stripping Hall (SH) technique (BIORAD HL5900) and the total chemical phosphorus concentration profile using Secondary Ion Mass Spectrometry (SIMS). The thin diffusion oxide was measured with ellipsometry at 632.8 nm and the sheet resistance with a four point probe. XPS spectra were measured in an ultrahigh vacuum system using a hemispherical analyzer (SPECS Phoibos 100 MCD-5).

A twin anode (Mg and Al) X-ray source was operated at a constant power of 300 W using Mg $K\alpha$ radiation. For depth profiling, Ar ion bombardment was carried out using a penning ion source (SPECS IQP 10/63).

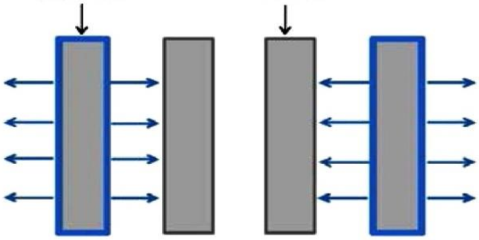

Fig. 1: Back to back stacking arrangement for DOSS diffusion in silicon

3. RESULTS AND DISCUSSION

The electrically active limit and the solubility limit for phosphorus in silicon at a given diffusion temperature were calculated from [7]. According to Solmi *et al.*, [7], the phosphorus concentration exceeding the electrically active limit, N_e, is electrically inactive, and appears as immobile phosphorus (SiP precipitates) for concentrations above the solubility limit, N_{sol}, and mobile interstitial phosphorus in the intermediate concentration region between N_e and N_{sol}.

Figure 2 shows the carrier concentration profiles obtained by the SH technique for a diffusion source doping of 0.004 % $POCl_3$, a diffusion time of 60 minutes and a diffusion temperature ranging from 850 to 1050 °C. At 850°C, the surface concentration is 2.5 x 10^{19} cm^{-3}. It increases up to 4.5 x 10^{19} cm^{-3} at 1000 °C and then drops to 2.4 x 10^{19} cm^{-3} at 1050 °C. The emitter sheet resistance varies from ~200 Ω/Sq. at 850 °C to ~24 Ω/Sq. at 1050 °C and the corresponding junction depth from about 0.3 to 2.0 μm.

For all investigated temperatures, the P surface concentration is too low to be useful for screen-printed solar cells. However, a surface concentration in the range of 10^{19} cm^{-3} is well-suited for high-efficiency laboratory solar cells with evaporated contacts. The phosphorus electrically active concentration limit, N_e, varies from 3.04 x 10^{20} cm^{-3} at 850 °C to 5.09 x 10^{20} cm^{-3} at 1050 °C. According to these results, the sources fabricated using a partial pressure of 0.004 % $POCl_3$ behave as finite sources and no dead layer occurs.

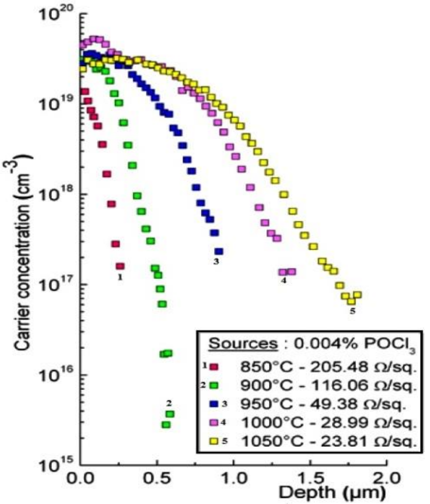

Fig. 2: SH doping profiles using a source doping level of 0.004% $POCl_3$ and a diffusion time of 60 minutes

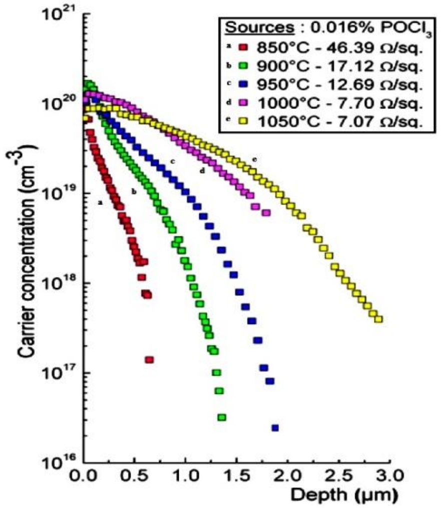

Fig. 3: SH doping profiles using a source doping level of 0.016% $POCl_3$ and a diffusion time of 60 minutes

The carrier profiles obtained for a diffusion source doping of 0.016 % $POCl_3$ and 60 minute diffusions are illustrated in figure 3. At 850°C, the surface concentration reaches 1.15 x 10^{20} cm^{-3} and increases to 1.44 x 10^{20} cm^{-3} at 900°C. Beyond this temperature, the surface concentration diminishes gradually to about 1.0-1.1 x 10^{20} cm^{-3} at 950-1000 °C and 6.9 x 10^{19} cm^{-3} at 1050 °C. Again, the phosphorus electrically active concentration limit N_e is well above these values for all investigated temperatures and therefore it can be concluded that these emitters exhibit no dead layer.

In the range 850-1050 °C, the sheet resistance varies from 46 to 7 Ω/Sq. and the junction depth from ~0.7 to ~3.5-4 μm. It is now possible to contact emitters with surface concentration as low as 1 x $10^{20}$$cm^{-3}$ using recently developed new silver screen printing pastes [8]. Thus, the emitter obtained at 850 °C with a sheet resistance of 46 Ω/Sq. should be adapted to industrial type screen-printed solar cells.

Similar results are obtained with a source doping level of 0.16 % $POCl_3$ and a diffusion time of 60 minutes (figure 4). The surface concentration diminishes gradually from 1.5 x 10^{20} cm^{-3} at 850 °C to 4.5 x 10^{19} cm^{-3} at 1050 °C. The corresponding sheet resistances are 53 to 8 Ω/Sq.

Such decrease in surface concentration with increasing temperature is indicative of finite source diffusion. From 900 to 1050 °C, the surface concentration is in the range of 10^{19} cm^{-3} which too low for screen-printed contacts. In this case also the surface concentration is well below N_e which implies that no dead layer exists for the entire investigated temperature range.

Figure 5 shows the concentration profiles obtained for 10 minutes diffusions using a source doping level of 4.28 % $POCl_3$. The diffusion temperature was varied from 900 to 1050 °C. The surface concentration increases from 1.5 x 10^{20} cm^{-3} at 900 °C to 2 x 10^{20} cm^{-3} at 925 °C and changes little from 2.15-1.92 x 10^{20} cm^{-3} as the temperature was increased further to 1050 °C.

Again, these values are well below the active concentration limit N_e at all investigated temperatures. From these results, it can be inferred, as noted previously for lower $POCl_3$ partial pressures, that no dead layer occurs. Note that the profiles shown in figure 5 are too deep for efficient solar cells and need further adjustments by reducing the diffusion temperature and/or diffusion time.

According to the above results, it can be concluded that under our experimental conditions, the sources behave as finite sources and the formation of a dead layer is avoided.

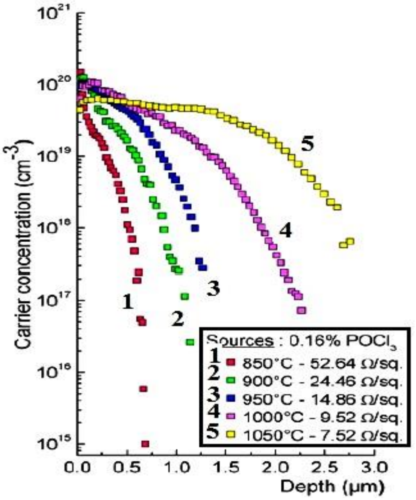

Fig. 4: SH doping profiles using a source doping level of 0.16% $POCl_3$ and a diffusion time of 60 minutes

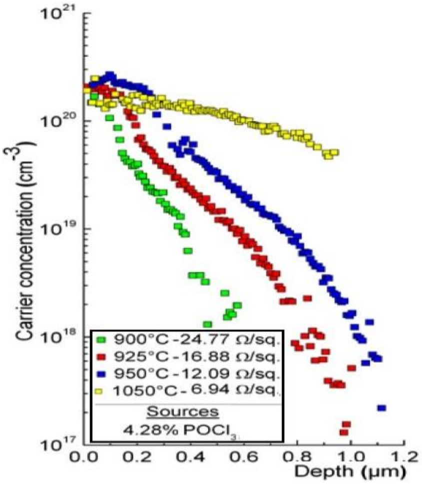

Fig. 5: SH doping profiles using a source doping level of 4.28% $POCl_3$ and a diffusion time of 10 minutes

Using a source doping level of 4.28 % $POCl_3$, the total P concentration SIMS profile was compared to the SH profile for a diffusion performed at 925 °C for 10 minutes (figure 6). The surface concentrations are 2.08 x 10^{20} cm^{-3} and 3.4 x 10^{20} cm^{-3}

for the SH and SIMS profiles respectively, but away from the surface region below a concentration of ~2 x 10^{20} cm^{-3} both profiles coincide.

Both values are well below the electrically active limit (3.76 x 10^{20} cm^{-3}) and the solubility limit (6.17 x 10^{20} cm^{-3}) at this temperature thus confirming the absence of a dead layer. The surface discrepancy may be attributed to an overestimation of the P density caused by SIMS measurement sputtering artifacts in the near-surface region.

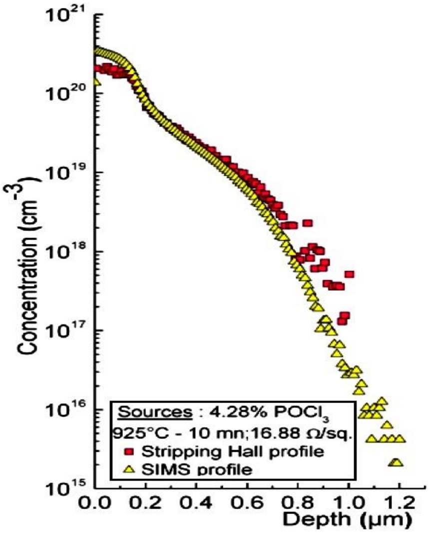

Fig. 6: SIMS and SH doping profiles for a diffusion performed at 925°C for 10 minutes using a source doping level of 4.28% $POCl_3$

The variation of the residual diffusion oxide thickness as a function of diffusion temperature and source doping level is plotted in figure 7. It can be seen that the oxide thickness increases with both temperature and source doping level within the range 7.5 to 30 nm.

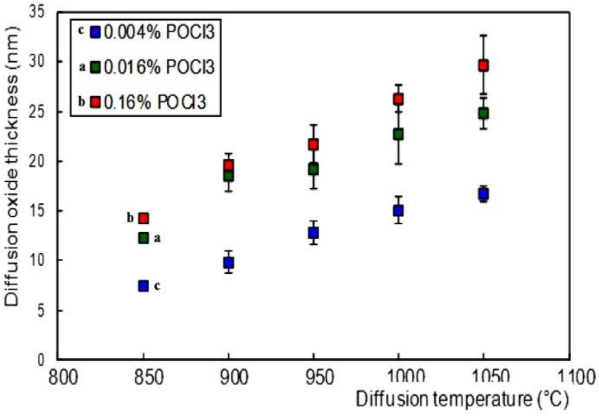

Fig. 7: Residual DOSS oxide variation with diffusion temperature and source doping level represented by the $POCl_3$ partial pressure

Figure 8 shows the concentration depth profiles of the elements P, O, Si and C in the residual oxide for a wafer diffused at 900 °C for 10 minutes using a source doping level of 4.28 % $POCl_3$. The detected Carbon may be attributed to organic contamination of the silicon wafers which was not completely removed by the saw damage etching and cleaning steps prior to diffusion [9]. No B was detected since the concentration of the p-type silicon substrates ($\approx 10^{16}\,\mathrm{atoms/cm^3}$) should lead to a surface concentration of 10^{13} atoms/cm^2 which is well below the XPS detection limit. Figure 8 shows that the Si concentration continuously increases from the surface to the bulk. To calibrate the depth scale, the oxide thickness determined by ellipsometry (19.07 nm) was used and it was assumed that the sputter rate is constant through the whole profile. An interesting point is related to the P concentration distribution.

Figure 9 shows the expanded P depth profile of figure 8. The P accumulated in an external film of thickness roughly a half of the total thickness ($\approx 10\,\mathrm{nm}$) as well as at the oxide/Si interface (see the local maximum of the P concentration around 20 min). The pile-up at the oxide surface is attributed to the continuous supply of P_2O_5 which is transferred directly from the adjacent diffusion source to the silicon wafer. A compound ratio between SiO_2 and P_2O_5 can be calculated from the atomic ratios between P, Si and O [10].

For example, at the 3rd measurement point, the atomic P, Si, O and C concentrations are equal to 3.0%, 29.6%, 66.3% and 1.0% respectively. Neglecting the C concentration leads to a residual diffusion glass having a composition of 90% SiO_2 and 10% P_2O_5. The pile-up at the oxide/Si interface is probably due to the accumulation of elemental P generated by the reduction of P_2O_5 at the Si wafer surface.

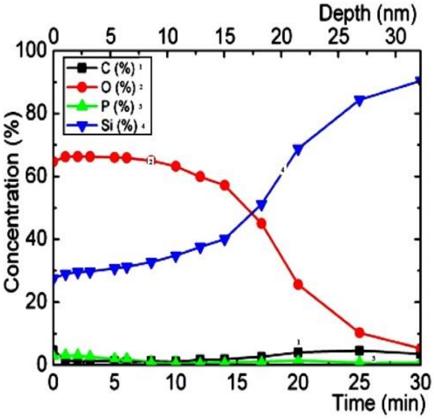

Fig. 8: XPS profiles for the elements P, Si, O and C

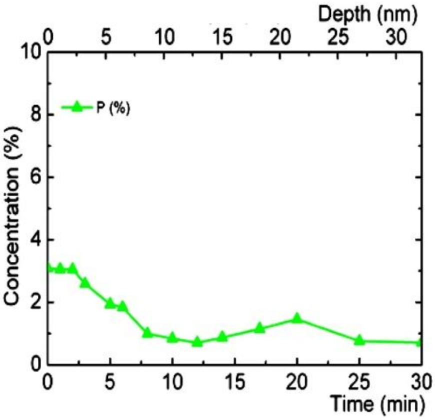

Fig. 9: Expanded plot of the XPS profile of P

4. CONCLUSION

In this study, we have demonstrated the suitability of the DOSS diffusion technique for control of the phosphorus emitter profile and the complete elimination of the dead layer. Using a partial pressure of 4.28% during the source fabrication step leads to a surface concentration around 2 x 10^{20} cm^{-3} which is suitable for a low resistance contact. XPS profiling showed that the residual diffusion oxide was composed of P_2O_5 in a SiO_2 matrix. The P distribution is not homogeneous. It shows a pile-up near the oxide surface and also at the oxide/Si interface.

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REFERENCES

[1] D. Neuhaus and A. Münzer, '*Industrial Silicon Wafer Solar Cells*', Advances in OptoElectronics, Vol. 2007, ID24521, 15 p., 2007.

[2] G. Hahn, '*Status of Selective Emitter Technology*', Proceedings 25th European Photovoltaic Solar Energy Conference, Valencia, Spain, 1091, 2010.

[3] *Y. Komatsu, J. Anker, H. Geerman, P. Venema and A. Stassen, 'Emitter Performance Improvement of Multicrystalline Si Solar Cells by Controlling the* N^{++} *Layer'*, Proceedings 26th European Photovoltaic Solar Energy Conference, Hamburg, Germany, pp. 1340 - 1344, 2011.

[4] T. Krygowski, P. Sana, G. Crotty and A. Rohatgi, '*A Novel Technology for the Simultaneous Diffusion of Boron, Aluminum and Phosphorus in Silicon*', Proceedings 25th IEEE Photovoltaic Specialists Conference, Washington D.C., 393, 1996.

[5] R. Chaoui, A. Messaoud, M.L. Zitouni and M.R. Charif, '*Development of an Emitter for Industrial Silicon Solar Cells Using the Doped Oxide Solid Source Diffusion Technique*', Renewable Energy, Vol. 23, N°3-4, pp. 417 - 428, 2001.

[6] R. Chaoui, A. Messaoud and M.L. Zitouni, '*Fabrication of Large Area Screen - Printed Monocrystalline Silicon Solar Cells Using the Doped Oxide Solid Source Diffusion Technique*', Proceedings 17th European Photovoltaic Solar Energy Conference, Munich, Germany, 1942, 22-26 Oktober, 2001.

[7] S. Solmi, A. Parisini, R. Angelucci, A. Armigliato, D. Nobili and L. Moro, '*Dopant and Carrier Concentration in Si in Equilibrium with Monoclinic Sip Precipitates*', Physical Review B, Vol. 53, N°12, 7836, 1996.

[8] I. Cooper, K. Tate, A. Carroll, K. Mikeska, R. Reedy, and A. Rohatgi, '*Low Resistance Screen-Printed Ag Contacts to* $PoCl_3$ *Emitters with Low Saturation Current Density for High Efficiency Si Solar Cells*', In Proceedings 38th IEEE Photovoltaic Specialists Conference, Austin, Texas, pp. 3359 - 3364, 2012.

[9] U. Gangopadhyay, S.K. Dhungel, P.K. Basu, SK. Dutta, H. Saha and J. Yi, '*Comparative Study of Different Approaches of Multicrystalline Silicon Texturing for Solar Cell Fabrication*', Solar Energy Materials & Solar Cells, Vol. 91, N°4, pp. 1147 - 1151, 2007.

[10] C. Voyer, D. Biro, T. Buettner and R. Preu, '*Mechanisms Involved in the Formation of Phosphosilicate Glass by Dehydration of Sprayed Phosphoric Acid in an In-Line Diffusion Furnace*', Proceedings 22nd European Photovoltaic Solar Energy Conference, Milan, Italy, pp. 1630 - 1633, 2007.