

ON THE PHOTON-ENHANCED DIFFUSION OF PHOSPHORUS IN SILICON WAFERS DURING RAPID ISOTHERMAL PROCESSING

Stefan Peters^{1,+}, Pierre-Emmanuel Hicel², Jörg Horzel³, Sébastien Noël⁴, Ralf Preu¹

¹Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, D-79110 Freiburg,

²Qualiflow-Jipelec, 395, rue Louis Lepine, F-34935 Montpellier

³RWE SCHOTT Solar GmbH, Carl-Zeiss-Str. 4, D-63755 Alzenau

⁴CEA-GENEC, 17, rue des martyrs, F-38054 Grenoble

⁺Present address: Deutsche Cell GmbH, Berthelsdorfer Str. 111A, D-09599 Freiberg

E-mail: stefan.peters@deutschezell.de, Phone: +49-(0)3731-301-4445

ABSTRACT: For the diffusion of phosphorus in silicon it has been reported that rapid thermal processing (RTP) leads to an enhanced diffusion compared to conventional processing in quartz tubes (CFP). This enhancement has been attributed by several authors to photoelectrical or photochemical effects induced by visible and/or UV photons from tungsten halogen lamps (THL) used in RTP. In this work, we attempt to verify the proposed photon-enhanced diffusion of P in Si. An extensive study has been carried out using a special RTP reactor equipped with tungsten halogen lamps and additional excimer UV lamps. Various P sources such as spin-on dopants (SOD), APCVD P-doped SiO₂ and POCl₃ pre-diffused wafers have been tested. The experimental results show no evidence of photon-enhanced diffusion. For all dopant sources, additional irradiation of the dopant covered surface with high-energy photons causes neither a significant difference in the sheet resistance nor in the P profile compared to diffusion without photon irradiation. An important output of these experiments is that the implementation of excimer UV lamps in future RTP furnaces designed for PV applications is not necessary.

Keywords: Rapid Thermal Processing – 1: Diffusion – 2: Silicon – 3

1 INTRODUCTION

For the next generation of solar cell manufacturing rapid thermal processing (RTP) for diffusion (i.e. RTD) of P emitter is an option [1]. A frequently asked question about RTP is: why is RTP so fast compared to conventional processing in quartz tube furnaces (CFP)? Of course, the significantly higher heating and cooling rates used in RTP reduce the overall process time drastically compared to CFP. Also, the diffusion temperatures applied in RTP are generally higher than the ones feasible in CFP. This makes it possible to achieve the same kinetic results within shorter time. Additionally, in the case of diffusion of P in Si, highly P-doped SiO₂ layers are deposited on the wafer surface prior to RTP, whereas in CFP formation of the PSG takes place in the furnace by a chemical reaction of POCl₃ and O₂ with the Si surface. However, for the diffusion of P in Si it has been reported that RTP leads to shorter diffusion times than CFP even if heating and cooling times are neglected and identical diffusion temperatures and P sources are employed [2]. This enhancement has been attributed by several authors to photoelectrical or photochemical effects induced by visible and/or UV photons from the tungsten halogen lamps (THL) used in RTP [3,4]. The irradiation with additional photons from UV sources has been suggested to further reduce the diffusion time or alternatively to reduce the diffusion temperature necessary to obtain a desired emitter sheet resistance R_{sheet} [5,6]. With regard to solar cell processing this could be interesting because reduced diffusion times lead to increased throughput. Also, some of the widely used temperature sensitive multicrystalline Si materials might benefit from lower diffusion temperatures [1].

However, there is an intense discussion between researchers whether the observed enhancement is really due to photons or whether it is caused rather by thermal effects due to erroneous temperature measurements [7,8].

The purpose of this work is to verify the enhancement for two cases: First, when the surface covered with the P source is irradiated by photons from THLs. Second, when the surface covered with the dopant is illuminated by UV photons from excimer lamps. It is worth noting that we did not aim to prove that diffusion is generally enhanced in RTP compared to diffusion in CFP. There might be other effects accounting for it [9].

2 EXPERIMENTAL

The experimental procedure was well studied to avoid all problems concerning temperature measurements in RTP units. Unlike other researchers we did not rely on pyrometer and thermocouple (TC) measurements. This was done to enable us to clearly distinguish between non-thermal and thermal effects. This makes the difference between this work and other investigations on photon-enhanced diffusion. For this reason the diffusions were carried out using open-loop processes with pre-defined power profiles instead of temperature-regulated closed-loop processing. The wafer temperature was not regulated during the process.

2.1 Design of the UV RTP reactor

Fig. 1 shows a schematic drawing of the RTP reactor used for the experiments. THLs are located below the sample in two perpendicular rows. In addition, excimer UV lamps emitting at a wavelength of 222 nm are located above. The density of UV power incident on the top wafer surface is in the range of 60 mW/cm². This is 2 orders in magnitude lower than the power coming from the THLs. However, according to publications, this intensity would definitely suffice to observe UV-enhanced diffusion [6]. The wafer is surrounded by a cold-wall chamber. A pyrometer is located above the wafer allowing to monitor the process.

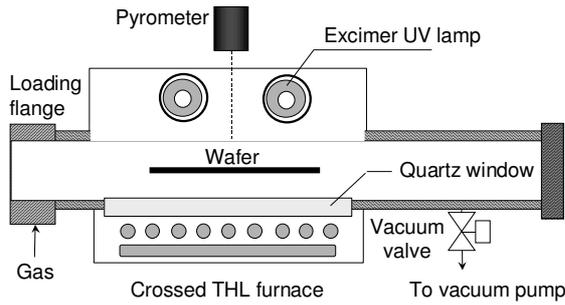


Figure 1: Drawing of the UV-RTP reactor used for the experiments on the photon-enhanced diffusion of P in Si. Drawing courtesy of Qualiflow-Jipelec.

2.2 Open-loop processing

In open-loop processing the heating parameters are fixed by pre-programmed power profiles. There is no feed-back of the wafer temperature as measured by TC or by pyrometer. Fig. 2 shows the standard open-loop process developed for the diffusion experiments. At first, the chamber is evacuated below 1 mbar and N_2 ambient is established. Then, the power of the THLs is ramped to a plateau power. A THL power of 66 % has been set for most of the experiments described in this publication and corresponds to a wafer temperature of roughly 900°C if a double-side polished Si wafer is heated (see Fig. 2). A THL power of 73 % accounts for a wafer temperature of roughly 950°C . It takes about 1 min until the wafer reaches a constant temperature. After a plateau of 240 s the wafer is cooled rapidly by switching off the THLs. Additionally, atmospheric pressure is re-established. In the case of diffusions with extra UV light illumination, the excimer lamps are switched on along with the THLs. We have checked that switching on the UV lamps does not increase the wafer temperature significantly (Fig.3).

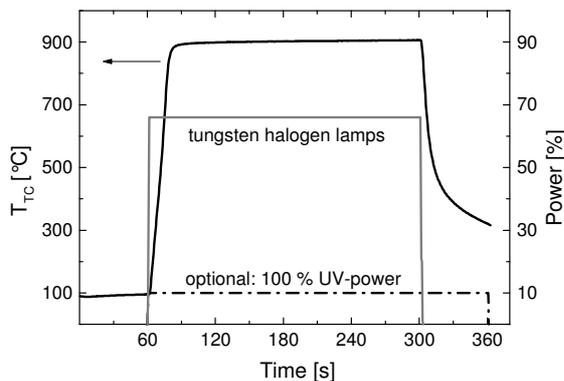


Figure 2: Open-loop process used for the experiments and corresponding temperature profile of a double side polished wafer. Wafer temperature was measured by a TC embedded into the wafer surface not facing the THLs.

Reproducible open-loop processing requires identical starting conditions for each wafer. Therefore, at least one test wafer was heated prior to the actual diffusion and the time between successive runs was kept constant. We have thoroughly verified that the run-to-run repeatability for this kind of open-loop processing is better than 3°C regardless of whether the excimer UV lamps are switched on or off. This temperature uncertainty is definitely lower than any reported diffusion enhancement that would translate to a temperature difference larger than 20°C .

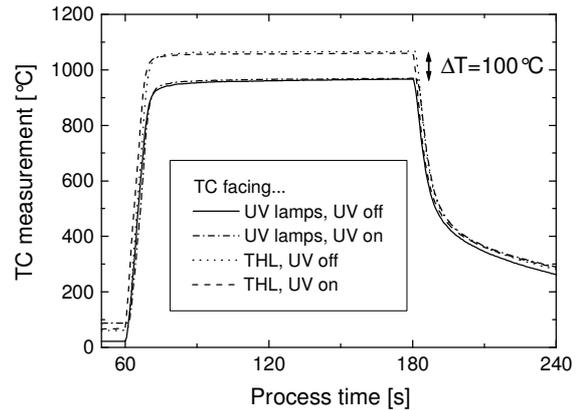


Figure 3: Experiment to demonstrate that temperature measurements with a TC can easily yield erroneous results when the TC is subjected to direct irradiation.

We have carried out an experiment to demonstrate that temperature measurements with TCs in RTP can easily yield erroneous results. A TC was embedded in the middle of a wafer with polished and hence optically identical surfaces. The wafer was heated with our open-loop process featuring a 120 s plateau of 73 % THL power. In one case the TC faced the UV lamps and in the other case the wafer was turned over, now with the TC facing the THLs. For both cases two runs were performed, first with the UV lamps off and then with the UV lamps on. As shown in Fig. 3 the influence of the UV lamps is very small. However, when the TC directly faces the radiation from the THLs a much higher temperature is measured than for the case that the TC is facing the UV lamps. The difference to the non-irradiated case is as much as 100°C . The actual wafer temperature could not possibly increase in the same way because the two wafer surfaces are optically identical. Neither a temperature gradient between the two wafer surfaces could cause such a difference. The experiment justifies our approach to use open-loop processing.

2.3 Dopant sources and silicon wafers

For the first time, we used wafers with the P source deposited on both surfaces. But only one surface was exposed to photon irradiation. During RTP, the temperature difference between the two surfaces is negligible. Hence, a difference in R_{sheet} or P profile would unambiguously prove photon-enhanced diffusion. In order to assess whether the enhancement depends on the type of P source, we studied the diffusion from various P sources. As external sources the Filmtronics spin-on dopants P507 and P508 were applied, featuring a medium and a high P concentration, respectively. The first one had shown to yield emitters with completely electrically active P whereas the latter one yields inactive interstitial P of up to 10^{21} cm^{-3} . Alternatively, $\text{SiO}_2\text{:P}$ was deposited by APCVD with 20% P. Additionally, an internal P source was prepared by CFP using POCl_3 . The wafers were diffused at 900°C for 10 min in air yielding R_{sheet} of $58 \Omega/\text{sq}$. The PSG was etched in HF prior to RTD.

P diffusion was performed on B-doped (100)-oriented, 4 inch Cz-Si wafers. Wafers were either $7\text{-}21 \Omega\text{cm}$ doped and single-sided polished or $0.5\text{-}2.0 \Omega\text{cm}$ doped and double-sided polished.

2.4 Experimental procedure

RTD was performed using the open-loop recipe of Fig.2. One sample was diffused without UV light and subsequently an identically prepared one with UV light from the front. This was done for all P sources which were sometimes deposited on both surfaces. The front of a wafer is defined as the one facing the UV lamps regardless of whether they were on or off. After RTD the PSG was etched and R_{sheet} was measured by four point probing on 25 spots in the wafer centre. P profiles were measured by secondary ion mass spectroscopy (SIMS).

3 RESULTS

Tab.1 reports the mean R_{sheet} for the different P sources after RTD. For the P508, comparison of R_{sheet} of the one-sided diffused samples 8P-3 and 8P-4 gives no indication of UV-enhanced diffusion. The same holds for samples 8P-5 and 8P-6 which were subjected to a higher diffusion temperature due to increased THL power. For both sets the difference in R_{sheet} between the case without UV and the case with UV is extremely small. The temperature difference which would explain this R_{sheet} difference can be estimated roughly. It was shown that increasing the THL power from 66 to 73% leads to an increase in wafer temperature of about 50°C. R_{sheet} of sample 8P-5 is 23.6 Ω/sq lower than R_{sheet} of sample 8P-3. In first approximation we assume that R_{sheet} varies linearly with temperature in the relevant range. This means that 1 Ω/sq difference in R_{sheet} corresponds to a temperature difference of roughly 2°C. Thus, the small differences in R_{sheet} can be explained by just 3 to 5°C. It was shown earlier that the comparison of open-loop diffusion without UV with open-loop diffusion with UV leads to an uncertainty in wafer temperature of less than 3°C as long as optically identical wafers are used. Taking into account that the spin-on procedure yields comparable but not identical optical properties one can conclude that the observed variations in R_{sheet} are within the limits of experimental error and do not point to UV-enhanced diffusion. The same conclusion can be drawn from the atomic P profiles in Fig.4a. The profile diffused

without UV coincides perfectly with the one diffused with UV. Remarkably, for the double-sided diffused wafer 8P-7 both sides exhibit similar R_{sheet} . This means that THL illumination alone does not in any case yield photon-enhanced diffusion.

Comparing the single-sided diffused samples 7P-3 and 7P-4, no influence of the additional UV illumination can be observed for the P507. R_{sheet} is identical within the limits of experimental error. The corresponding SIMS P profiles (Fig.4b) match each other perfectly. There is neither a difference in the plateau nor in the tail region. The near-surface P concentration matches well the solid solubility of P in Si at the diffusion temperature of approximately 900°C. As mentioned, for the P507 the profiles of the electron and the P concentration always coincide. Hence, in contrast to the SOD P508, the P507 does not yield near-surface electrically inactive SiP precipitates. This indicates substantial differences in the chemical composition of the two SODs.

For samples diffused with the APCVD $\text{SiO}_2:\text{P}$ no conclusion towards photon-enhanced diffusion can be drawn either. The R_{sheet} difference between the sample diffused with UV (20P-8) and the one without UV (20P-7) can be explained by a temperature difference definitely smaller than 3°C. This lies within the limits of experimental error. Also, the P profiles (Fig.4c) perfectly agree. In addition, the double-sided diffused wafer (20P-5) shows no significant deviation in R_{sheet} between the non illuminated front and the back which was irradiated by the THLs. Hence, there is no indication of enhanced diffusion caused by THL photon irradiation.

R_{sheet} of the CFP pre-diffused wafers decreases upon RTD. According to the P profiles (Fig.4d) this is caused by a drive-in and activation of P which was inactive after pre-diffusion. Before RTD the profile exhibits a surface concentration up to $7 \times 10^{20} \text{ cm}^{-3}$ which is nearly a factor of two higher than the solid solubility at the CFP pre-diffusion temperature of 900°C. After RTD the surface concentration decreased and the complete P profile penetrates deeper in the Si. The profiles after RTD do not depend on whether the surface was irradiated by photons from THLs, UV lamps or not at all. There is no evidence of enhanced diffusion of P within the bulk of a Si wafer.

Table 1: Sheet resistance after RTD using the open-loop process of Fig.1, once with and once without UV light. For some samples the P source was deposited on both surfaces to test on enhanced diffusion under irradiation with photons from THLs.

Sample ID	P source	Front (side facing UV lamps)		Back (side facing THL lamps)	
		UV lamps	R_{sheet} [Ω/sq]	THL power [%]	R_{sheet} [Ω/sq]
8P-3	Spin-on P508	off	47.0 ± 1.1	66	no source applied
8P-4	Spin-on P508	on	45.3 ± 1.1	66	no source applied
8P-5	Spin-on P508	off	23.4 ± 0.5	77	no source applied
8P-6	Spin-on P508	on	21.6 ± 0.5	77	no source applied
8P-7	Spin-on P508	off	25.5 ± 0.6	66	27.3 ± 0.6
8P-8	Spin-on P508	on	24.9 ± 1.0	66	25.8 ± 1.5
7P-3	Spin-on P507	off	54.7 ± 1.7	73	no source applied
7P-4	Spin-on P507	on	55.5 ± 1.1	73	no source applied
20P-5	APCVD $\text{SiO}_2:\text{P}$	off	38.8 ± 1.7	66	39.1 ± 1.9
20P-6	APCVD $\text{SiO}_2:\text{P}$	on	37.3 ± 1.6	66	38.5 ± 1.4
20P-7	APCVD $\text{SiO}_2:\text{P}$	off	60.5 ± 2.5	66	no source applied
20P-8	APCVD $\text{SiO}_2:\text{P}$	on	59.2 ± 2.3	66	no source applied
5-4	CFP pre-diffused	no RTP	58.4 ± 0.7	no RTP-	58.5 ± 0.6
5-2	CFP pre-diffused	off	49.8 ± 0.3	73	49.2 ± 0.6
5-3	CFP pre-diffused	on	49.6 ± 0.6	73	51.7 ± 0.6

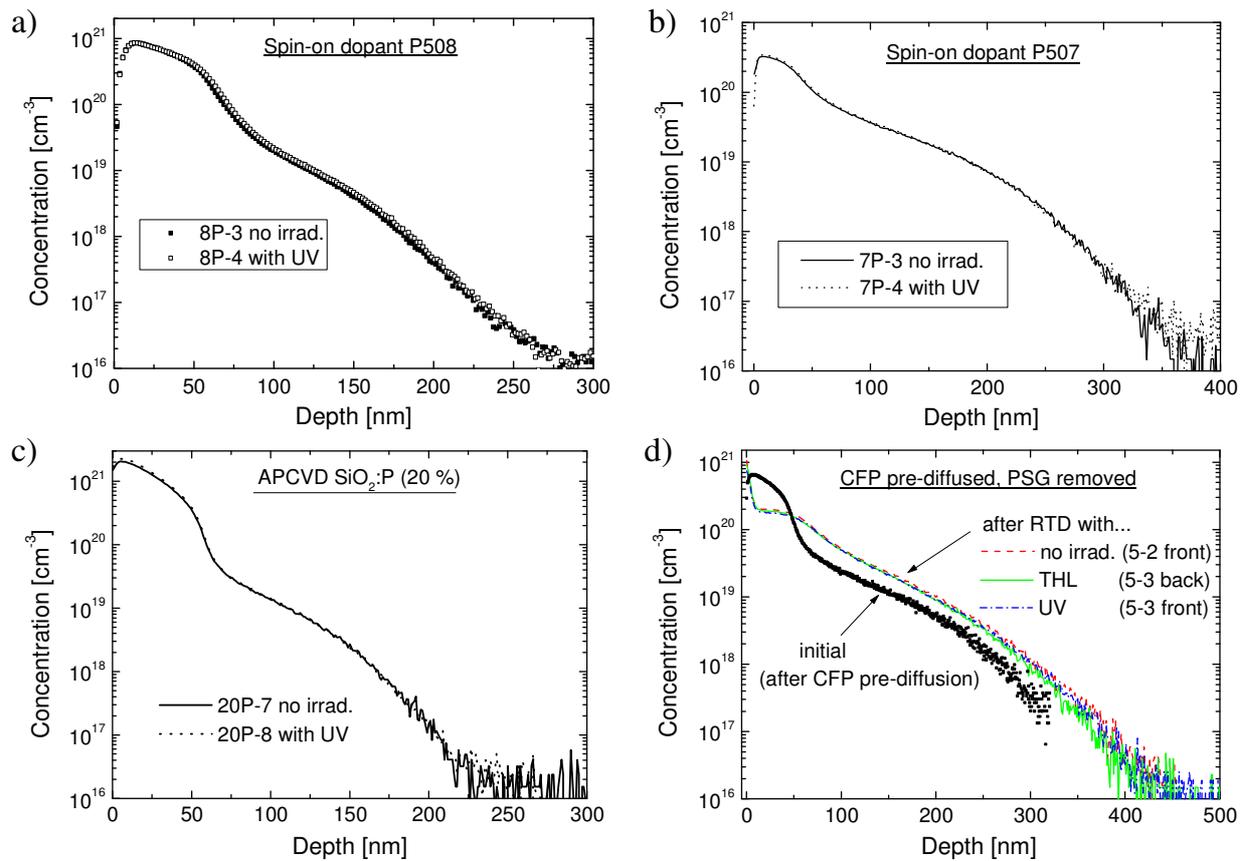


Figure 4: P profiles as measured by SIMS after rapid thermal diffusion from chemically different P sources without and with UV photon irradiation impinging on the dopant covered side (compare Tab.1).

4 SUMMARY AND CONCLUSIONS

In this work we attempted to verify the proposed photon-enhanced diffusion of P in Si. An extensive study was carried out using an RTP reactor equipped with THL and additional excimer UV lamps. Spin-on dopants, APCVD P-doped SiO₂ and CFP POCl₃ pre-diffused wafers were tested. The experimental results show no evidence of any photon-enhanced diffusion. For all studied dopant sources the additional UV irradiation from the excimer lamps during diffusion caused neither a significant difference in sheet resistance nor in the P profile compared to diffusion without additional UV photons. Hence, the use of additional UV lamps in RTP reactors for diffusion purposes seems to offer no advantage. Additionally, no enhanced diffusion under irradiation of photons from the THLs could be measured.

Some of the reported diffusion accelerations which have been interpreted as photon-effects, may in fact be pure thermal effects caused by inaccurate determination of the process temperature. We have demonstrated that relying on thermocouple readings can yield erroneous temperature values with deviations as high as 100°C.

However, the absence of photon-enhanced effects in this study does not mean that the dopant diffusion in RTP is not enhanced compared to CFP. There are other possible explanations which could account for enhanced diffusion in RTP. For example, non-equilibrium conditions could lead to increased anomalous phosphorus diffusion.

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