

Industrial diffusion of phosphorous n-type emitters for standard wafer-based silicon solar cells

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ABSTRACT

Formation of the pn-junction for charge carrier separation is one of the key processes of a modern high-volume solar cell production. In silicon wafer-based solar cell technology this is achieved by diffusion of phosphorus atoms in boron pre-doped wafers forming a sub-micron shallow n-type emitter in a 200 μm -thick p-type base. In this contribution we discuss both the characteristics of emitter doping profiles and the diffusion process itself as required for optimal solar cell conversion efficiencies. In addition we give an overview on state-of-the-art industrial diffusion technologies and conclude with a brief outlook on their evolution.

Introduction

In modern production lines for standard silicon solar cells, average energy conversion efficiencies of up to 16% and 17% are achieved on multi- and monocrystalline wafers, respectively. The word 'standard' denotes solar cells featuring a diffused front junction and screen-printed contacts on both sides. Other concepts like back junction

back-contacted solar cells can reach efficiencies exceeding 22%. This article focusses on diffusion for the standard solar cell. Though the process sequences and tools applied for the production of standard solar cells are very similar from case to case, there are small differences in the single process layout which can account for significant differences in the conversion efficiency produced. With

respect to diffusion, a bad process could lower the mean efficiency easily by 0.5% compared to that of one's competitors, whereas in turn a good process can yield a major advantage regarding cost per Wp. To understand what it takes to have a good emitter profile and corresponding process, let us have a look at a typical emitter profile and the manifold purposes it and the applied diffusion process serve.



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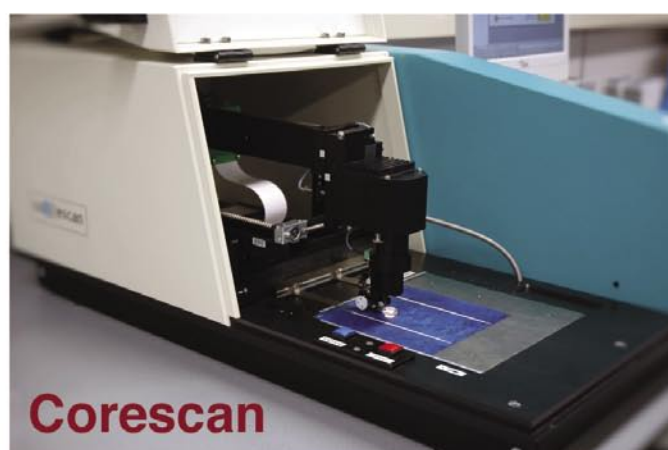


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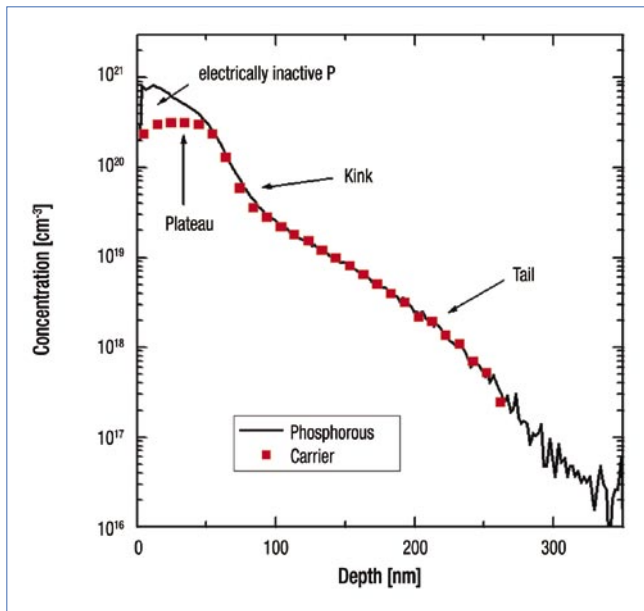


Figure 1. Charge carrier and chemical P profiles of an industrial-type 55Ω/sq emitter diffused by means of spin-on and in-line diffusion. The charge carrier concentration was measured by Stripping Hall Profiling; phosphorus concentration was determined by SIMS.

Preferred emitter profiles of solar cells

Figure 1 shows the chemical P and the resulting charge carrier profile of a 55Ω/sq emitter designed for standard silicon solar cells. The emitter was obtained by deposition of a highly concentrated P source on top of the silicon surface followed by a drive-in diffusion carried out in a lamp-heated in-line furnace [1]. Very similar profiles are obtained by classical quartz tube diffusion using phosphoroychloride (POCl₃) [2]. The main characteristics of such an industrial emitter are as follows. The charge carrier concentration corresponds to the solid solubility of P in Si at the applied diffusion temperature – in this case, 3.3 x 10²⁰cm³, which corresponds to the 900°C applied [3]. The P profile exhibits surface near concentrations even above the solid solubility. The chemical nature of this electrically inactive P is likely to be SiP clusters. Comparatively high doping concentrations > 5 x 10¹⁹ cm⁻³ are maintained down to roughly 100nm. The junction depth x_j is roughly 300nm. The resulting emitter sheet resistances are in the range of 40 to 60Ω/sq.

“With respect to diffusion, a bad process could lower the mean efficiency easily by 0.5% compared to that of one’s competitors.”

In order to understand why the presented profile is a well adjusted one and what it is that makes up a good emitter doping profile, let us have a look at the manifold purposes it serves:

- (1) separation of charge carriers
- (2) low carrier recombination within the emitter bulk at its surface
- (3) provision of lateral conductivity
- (4) provision of good Ohmic contacts to screen-printed Ag contacts.

(1) The main purpose of an emitter is, of course, separation of charge carriers by the strong built-in electric field within the space charge region formed in the transition region of n-type and p-type doping. This means that the hole of an electron hole pair generated by absorption of a photon in the emitter is transferred to the bulk once it encounters the space charge region (see Figure 2). Adversely, electrons are transferred from the wafer bulk to the emitter where

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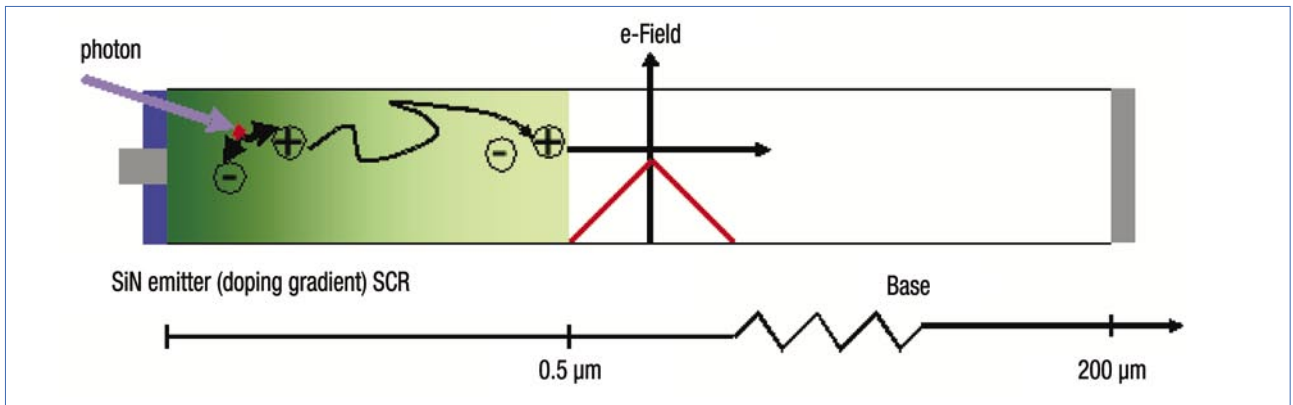


Figure 2. Solar cell cross-section showing the principle of charge carrier separation by the space charge region (SCR).

they become majority carriers. To serve the purpose of separation, the n-type doping only needs to overcompensate wafers' base doping, usually in the order of 10^{16}cm^{-3} .

“For doping densities exceeding 10^{18}cm^{-3} , Auger-induced recombination becomes the most dominating recombination channel.”

(2) However, the physical surface of the emitter gives rise to strong recombination of charge carriers due to a high density of inner band gap energy states caused by dangling silicon bonds. This recombination channel can be closed by a strong increase in n-doping within the emitter towards its surface, usually by introducing an n^+ front surface field (FSF). Literally speaking, the FSF deflects the holes from the emitter surface. The FSF is the analogy to the p^+ back-surface-field in the solar cell's backside. However, the FSF is not free. The heavy doping needed for a good FSF gives rise to carrier recombination via the Auger mechanism. For doping densities exceeding 10^{18}cm^{-3} , Auger-induced recombination becomes the most dominating recombination channel. For example, in n^{++} regions with doping concentration $>10^{20}\text{cm}^{-3}$, the carrier lifetime drops down to only 1 ns. Nevertheless, this lifetime corresponds to a diffusion length in the 300nm range giving the carriers a fair chance to reach the space charge region if the emitter is not too deep. The optimal doping of an emitter balances between a good FSF and little Auger recombination in the emitter bulk. It is important to note that the need for an FSF vanishes by provision of surface passivating layers like silicon nitride or thermally grown silicon oxide on top of the emitter. In this case, not only can the surface near doping be lowered, but the solar cells' performance even benefits from its lowering. Figure

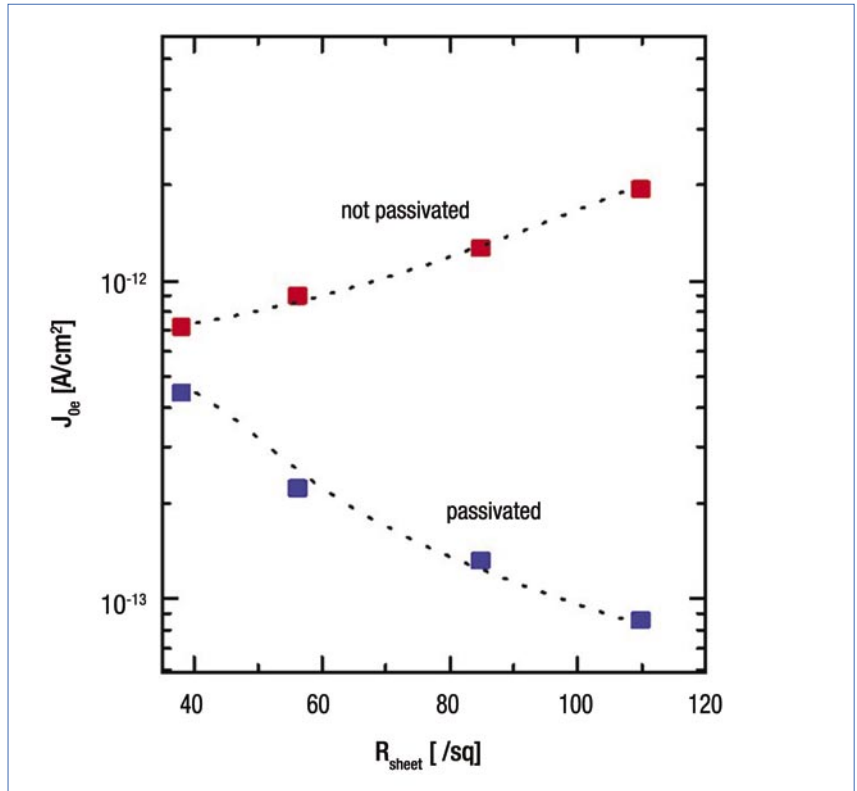


Figure 3. Emitter saturation current J_{oe} as a function of sheet resistance R_{sheet} for passivated and non-passivated emitter surfaces, respectively. Values have been determined experimentally. Surface passivation is provided by a 10-15nm rapid thermal oxide.

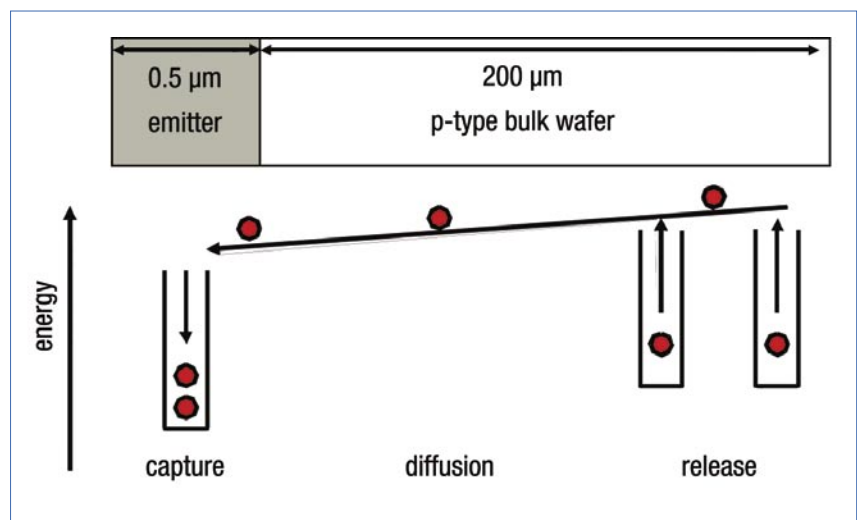


Figure 4. Sketch of the basic principle of diffusion-induced gettering of impurities.

3 shows the emitter saturation current J_{oc} as a function of sheet resistance. For the high doping case, i.e. low sheet resistances, the emitter J_{oc} is insensitive to surface passivation and hence it need not be applied. This explains why TiO_2 as a coating with almost no surface passivating characteristics can be used as an AR coating as long as sheet resistances are in the $30\Omega/sq$ range. However, for increasing sheet resistances, the emitter becomes sensitive to surface passivation allowing a significant gain in V_{oc} . Strictly speaking, it is the surface doping concentration C_s that drives V_{oc} in the passivated emitter case. The lower the C_s , the higher the V_{oc} . It is vital that solar cell manufacturers remain aware of their solar cells' front surface passivation quality if emitter doping is decreased.

(3) Being separated by the electric field in the space charge region, holes have to flow to the back contact through the silicon wafer, while electrons have to flow within the emitter layer to the nearest metal contact on the front. For standard solar cells featuring H-like contacts, the pattern metal fingers collect the current in the area while the busbars conduct the current. For low Ohmic resistive losses, a well conducting emitter layer is required, which purpose is served by using a rather high doping which in turn implies a low emitter sheet resistance. As a rule of thumb, we can say that the larger the finger spacing the lower the optimal sheet resistance. The roughly 2mm finger distance of standard solar cells usually yields 40 to $60\Omega/sq$.

(4) The biggest constraint on the emitter profile is placed by the screen-printed and fired-through silver pastes applied to the front. Due to the contact formation process, very high doping concentrations are required at the emitter surface. It has been proposed that chemical P concentrations in excess of the solid solubility are required by the pastes. In addition to this, high concentrations should be maintained down to approximately 100nm in depth. The reasons for these requirements are still under investigation. Initial studies on the underlying contact formation mechanisms have been published recently [4,5,6]. Furthermore, the emitters need to be rather deep ($>200nm$), as metal contamination stemming from the paste can penetrate into the space charge region and poison its electrical characteristics. With respect to lateral homogeneity of the sheet resistance, the screen-printing process requires a uniformity = $100\% \times (Max-Min)/2$ better than 5%. Missing this goal leads to poorly contacted wafer regions, thus reducing the overall cell performance.

From an engineering point of view it is important to know about these requirements as the resulting heavy and deep emitter doping massively downgrades the recombination properties. Relaxing these stringent requirements would yield significant gain in V_{oc} and J_{sc} (the latter due to improved blue response) and hence conversion efficiency. The good news is that all paste manufacturers are currently working hard to resolve this issue. However, the diffusion people need to be prepared. If the paste manufacturers succeed, they have to have the right emitters available for full exploitation of the potential.

Obviously, requirements (1) through (4) contradict each other, making fine-tuning the emitter profile a complex task. Table 1 illustrates a summary of the requirements with respect to the desired surface doping, junction depth and sheet resistance. It is up to the engineers to experimentally optimize the profiles with respect to solar cell efficiency.

Condition		C_s	x_j	R_{sheet}
low Auger recombination		↓	↓	↑
surface passivated?	no	↑	↑	↓
	yes	↓	↓	↑
contact material	Ag paste	↑	↑	↓
finger distance	large			↓
	small			↑

Table 1. Overview of the various requirements regarding surface concentration C_s , junction depth x_j and sheet resistance R_{sheet} of an emitter.

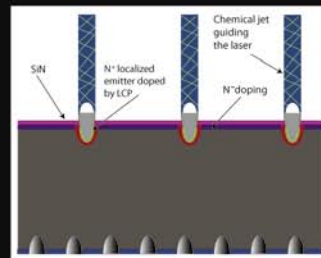
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The selective emitter concept

Thus far we have discussed emitters with a laterally homogeneous doping. Why not provide different parts of the solar cell area with different doping and dissolve the contradicting requirements? This approach is commonly called the selective emitter concept. Selective means provide a highly doped, deep emitter below the metal contacts for good contact properties but a lowly doped, shallow one for improved recombination characteristics. Regarding the solar cells' characteristics, this concept promises high fill factors and high V_{oc} , as well as a good blue response (high J_{sc}). From a physical standpoint, this is the best possible emitter. In literature written on this topic, efficiency enhancements between 0.2% and 1% absolute have been demonstrated, simulated or calculated over the past decades. An estimated 20-plus different approaches and process sequences have been presented on how best to actually manufacture selective emitter solar cells. Some are feasible only in a laboratory environment; others are ready for production. However, so far the selective emitter concept has made it only in one or two solar cell production lines. Supposedly this is due to the higher cost and complexity brought to the table by additionally needed process steps and equipment. Obviously, these negative factors are not weighted off by a decent increase in conversion efficiency.

Interestingly, the old-fashioned idea of a selective emitter has seen a revival recently; many new technological approaches have been proposed of late. For example, local doping by a chemical liquid jet-guided laser [7], highly doped semiconductor fingers with perpendicularly crossing metal fingers [8] or local wet chemical etch back of originally highly-doped emitter [9] were presented at recent PV conferences. Solar cell manufacturers are continuously assessing whether any of the new concepts could actually bring a clear cost per Wp advantage.

Preferred diffusion processes of solar cells

Having discussed the correct emitter characteristics, let us now have a look at the diffusion process itself. In general, diffusion is a physical process transporting particles, e.g. atoms, from a region of higher concentration to one of lower concentration by random molecular motion. The latter relates to temperature and hence temperature is the biggest knob to manipulate the speed of a diffusion process. Eventually, diffusion will result in complete mixing or a state of equilibrium that for most practical applications is neither needed nor desired. Hence, temperature which was ramped up in the first place to make the diffusion process start is ramped down after a certain amount of time, practically ceasing

diffusion. In fact, it would be desirable to freeze the concentration distribution as obtained at the diffusion temperatures.

In silicon, diffusion of many species can be well described phenomenologically, yet some of the underlying physics is not fully understood from a microscopic point of view. For example, the theory of P diffusion in Si is still under investigation. Kveder et al [10] propose a model where the main contribution to phosphorus diffusion at $[P] < 2 \times 10^{19} \text{cm}^{-3}$ comes from the kick-out mechanism, while at higher P concentrations the diffusion is dominated by phosphorus vacancy complexes. Their model nicely predicts the development of the well-known kink-and-tail profile for P diffusion as shown in Figure 1. It does, however, not predict the surface near supersaturation with electrically inactive P.

It is worth noting that their model enables the prediction of phosphorus diffusion-induced gettering (PDG) of (substitutional) metal impurities. For block-crystallized multicrystalline silicon wafers, proper gettering is important for achieving high efficiencies since it effectively removes reminiscent contaminations like Fe, Cr and Cu from the wafer bulk [11]. Gettering helps to increase the carrier lifetime, thus enhancing the solar cell efficiency. As sketched in Figure 4, a gettering process consists of three steps: impurity release from its energetic binding, travel through the wafer by diffusion, and finally capture of the impurity where the emitter acts as a sink. From a solar cell's perspective, two things should be kept in mind. First, though the impurities gather inside the phosphorus emitter they are less harmful there than in the p-type bulk since its carrier lifetime is limited by Auger recombination anyway. Secondly, a proper gettering process asks for comparatively moderate temperatures. This is because the emitter capabilities of acting as a sink strengthen with decreasing temperature. On the other hand, the impurities make their way to the sink by diffusion which takes quite some time if temperatures are low. As a rule of thumb, proper gettering of multicrystalline silicon wafers should be performed below 900°C for several minutes to hours. In support of this statement, Figure 5 shows the mean bulk carrier lifetime of neighbouring block-cast multicrystalline wafers after phosphorous diffusion gettering at different temperature and time conditions. Following a 15-minute gettering process at 870°C, the carrier lifetime can be tripled compared to the as-grown wafer. However, for RTP-diffused samples where very short gettering times down to a few seconds were applied, little or no lifetime improvement is observed. Remarkably, for temperatures exceeding 900 to 950°C, a thermally-induced degradation of the carrier lifetime occurs. We suspect this to be caused by the dissolution of metal precipitates at elevated temperatures and their

subsequent decorating of intrinsic defects like dislocations [1]. The temperature and time combination of an optimal gettering process depends on the specific defect spectrum of the multicrystalline silicon material to be improved and has to be found experimentally.

It should be noted here that for wafers made of monocrystalline silicon, gettering is far less important as it features significantly fewer harmful metal impurities. This eases the restrictions on diffusion temperature and time. In general, monocrystalline can be diffused at any temperature and time, giving you the chance to speed up the diffusion process and thus increase the throughput of a diffusion system [1].

Manufacturer's choice: diffusion equipment

Making use of solid-state diffusion of impurities for doping purposes has been one of the old-fashioned processes applied in semiconductor device fabrication for many decades. While in memory and logic chip fabrication diffusion has been replaced by ion implantation plus activation step (where no diffusion must occur), it is still the state-of-the-art doping technique used in silicon solar cell production lines. According to the author's view, this is likely to remain so for the next few years. With modern equipment, the cost of ownership is well below 10 €cent per wafer. In general, two technological solutions are available for emitter diffusion.

The traditional solution is the resistance heated quartz furnace utilising POCl_3 as a source of phosphorus. This approach was borrowed from the semi industry many years ago and has been elaborated ever since according to the PV industry's requirements. The throughput of modern five-stack furnaces has been increased up to 1500 wafers (6-inch) per hour sorting the wafers in a back-to-back mode into boats made of quartz or SiC. Currently, the boats' slot spacing is 4.76mm in order to obtain the desired <5% lateral doping homogeneity. However, by the application of diffusion at reduced process pressure, the slot spacing can be halved without sacrificing lateral homogeneity [12,13]. Theoretically this enables twice the throughput. Special wafer handling equipment has been developed for boat loading that minimises handling-induced wafer breakage.

In contrast to the batch-type quartz tube furnaces, dedicated in-line equipment was developed in recent years to meet the industries' demands of highest throughput, low breakage rates and improved lateral doping homogeneity. Any in-line diffusion system consists of two units. One unit is meant for deposition of the phosphorous source on the silicon wafers' surface, e.g. spray-on of P-containing liquids. The second unit serves for the actual diffusion of P from

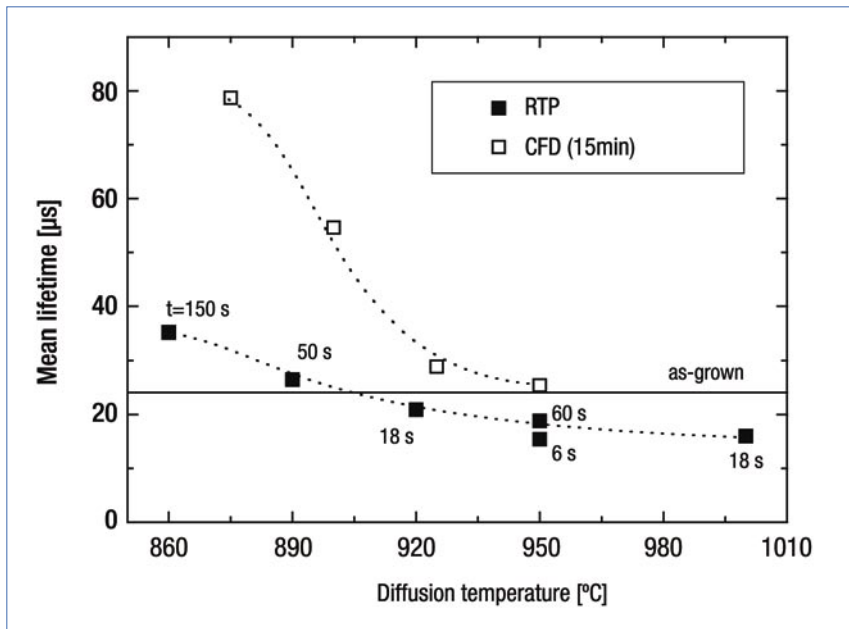


Figure 5. Mean bulk carrier lifetime of neighbouring block-cast multicrystalline wafers before and after phosphorous diffusion gettering at different temperature and time conditions. RTP was carried out applying a P spin-on source. The diffusion times are given next to the measurement points. Conventional diffusion was performed in a quartz tube furnace using POCl_3 for 15 minutes. Prior to lifetime measurement, the diffused layers were etched off and the wafer surfaces were passivated by SiN .

the source into the wafer. It consists of a more or less thermally isolated channel heated either by means of tungsten IR

lamps or resistively. The majority of the transportation of the flat lying wafers through the furnace is achieved by a

metal belt. As alternatives, metal-free and low-mass techniques featuring ceramic rollers or strings working according to the walking beam principle have been developed [14]. These novel transport systems minimise metal contamination and allow the realization of high heating and cooling rates, which help to reduce the length of such systems. It is up to the customer to decide on the appropriate combination of P source, heating method and transportation system. The throughput of current in-line diffusion systems is in the range of 1500 wafers per hour depending on furnace length and the number of tracks [15]. It has to be noted that for in-line systems, throughput is driven mainly by the required diffusion time. Increasing the diffusion time of a given system, for example for gettering reasons, will inevitably lower throughput.

This is a close competition between batch and in-line systems. Taking the pros and cons into account does not present any clear favourite for this process. It seems that deciding for either of them depends on a company's history and philosophy regarding automation.

Summary

Formation of the pn-junction by phosphorus diffusion is one of the key processes of modern solar cell production. The phosphorus emitter serves many

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purposes: separation of charge carriers, provision of lateral conductivity and provision of good contacts to screen-printed Ag contacts. All of this has to be achieved with an emitter profile exhibiting low carrier recombination characteristics within the emitter bulk and at its surface. For multicrystalline silicon solar cells, the applied diffusion process also needs to provide efficient gettering of impurities. Elaborated diffusion equipment and optimized processes are available to fulfil these requirements.

Nevertheless, current diffusion equipment needs to be improved continuously in order to meet the 10% cost of ownership reduction per year target as imposed by the German feed-in tariff. Therefore, scaling-up of such systems to the limits is the right way to go. However, in doing so, the electrical quality of the diffused emitter must not suffer and has to be monitored carefully. Additionally, future diffusion equipment must be suited for the formation of high Ohmic emitters exhibiting low surface near doping concentration while maintaining excellent cross wafer and wafer-to-wafer uniformity.

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References

- [1] Peters, S. 2004, 'Rapid Thermal processing of Crystalline Silicon Materials and Solar Cells,' Ph.D. thesis, University of Constance.
- [2] Negrini, P. et al 1975, in: *J. Electrochem. Soc.* 122(9), p. 1254.
- [3] Nobili, D. 1988, in: *Properties of silicon*, INSPEC, p. 394.
- [4] Ballif, C. et al 2003, in: *Applied Physics Letters* 82, p. 1878.
- [5] Schubert, G. et al 2006, in: *Solar Energy Materials and Solar Cells* 90, p. 3399.
- [6] Mette, A. 2007, Ph.D. thesis, University of Freiburg.
- [7] Kray, D. et al 2008, *33rd IEEE PV Specialist Conference*, St. Diego.
- [8] Wenham, S. et al 2005, *Conf. Rec. PVSEC-15 Conf.*, Shanghai.
- [9] Haverkamp, H. et al 2008, *33rd IEEE PV Specialist Conference*, St. Diego.
- [10] Kveder, V. et al 2000, *Materials Science and Engineering* B 71.
- [11] Istratov, A. A. et al 2000, *Applied Physics A: Material Science & Processing* 70, p. 489.
- [12] Ritzi, T. et al 2008, *23rd European PV Solar Energy Conference*, Valencia.

[13] Web reference [available online at <http://www.semco-engineering.com>].

[14] Biro, D. et al 2002, *Solar Energy Materials and Solar Cells* 74, p. 35

[15] Web reference [available online at <http://www.despatch.com>].

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Dr. Stefan Peters studied physics at the Universities of Bielefeld, Edinburgh, Freiburg and Constance. In 1997 he chose the Fraunhofer ISE in Freiburg for preparation of his diploma and Ph.D. theses, both on the application of Rapid Thermal Processing (RTP) to silicon solar cell fabrication. In 2003 he joined Deutsche Cell, Freiberg, as a technologist where he was responsible for phosphorus diffusion and PECVD of silicon nitride. Since 2006 Dr. Peters has been with Q-Cells heading the department for thermal and vacuum processes within Q-Cells' technology division. His duties comprise the development of processes and equipment for doping, surface passivation and antireflective coatings.

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