INFRARED FURNACE EMITTER DIFFUSION FOR SOLAR CELLS

by

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Abstract

This thesis reports a method for controlling the phosphorus distribution of emitters for screen-printed solar cells diffused in an infrared conveyor belt furnace. The desired profile variation was obtained by varying the thickness of the phosphorus-doped source layer, diffusion time and diffusion temperature. Response surface methodology was used for mathematically modeling the relationship between the three design factors and each one of the three parameters characteristic of the emitter profile, namely, sheet resistance, junction depth and surface concentration. To obtain the latter two parameters, a method was developed based on TSUPREM-4 simulations and spreading resistance analysis. The software received, as input parameters, the sheet resistance measured with a four-point probe and the process conditions. Good agreement was obtained between measured profiles and TSUPREM-4 simulations. Analysis of the fitted models demonstrated the usefulness of response surface methodology in developing the emitter diffusion process and also the possibility of diffusing the emitter from a thinner source layer (< 65 nm) of higher phosphorus concentration ($\sim 3.5 \times 10^{21}$ P/cm³) than in common practice (thickness > 100 nm, concentration $< \sim 3 \times 10^{20}$ P/cm³), thus reducing material usage, among other benefits.

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List of Symbols and Abbreviations

Units

B/cm ³	boron atoms per cubic centimetre
cfh	cubic feet per hour
cm	centimetres
e/cm ³	free electrons per cubic centimetre
g	grams
in	inches
ipm	inches per minute
nm	nanometres
min	minutes
mA	milliamperes
mV	millivolts
P/cm ³	phosphorus atoms per cubic centimetre
rpm	revolutions per minute
s	seconds
sccm	standard cubic centimetres per minute
W	Watts
μm	micrometres
μA	microamperes
°C	degrees Celsius

Symbols

a	number of levels for each factor
A	name of the first factor
B	name of the second factor
C	name of the third factor
C	concentration
C_s	chemical surface concentration
$C_{s \text{ Fair}}$	C_s estimated using Fair's model
d	horizontal distance measured on bevelled sample
d_{fringes}	distance between interference fringes
D	diffusivity
erfc	complementary error-function
F	flux of diffusing atoms
F_{in}	F inside the volume
F_{out}	F outside of the volume
I	current
$I_{P \text{ max}}$	current at the maximum power point
I_{sc}	short-circuit current
J	current density
J_{sc}	short-circuit current density
k	number of factors
n_s	carrier surface concentration

$n_{s \text{ Fair}}$	n_s estimated using Fair's model
$n_{s \text{ suprem}}$	n_s estimated using TSUPREM-4 simulations
$n_{s \text{ suprem adjusted}}$	$n_{s \text{ suprem}}$ linearly transformed to match SRA profiles
P	phosphorus
R_{sh}	sheet resistance
Si	silicon
t	time
V	voltage
V_{oc}	open-circuit voltage
$V_{P \text{ max}}$	voltage at the maximum power point
x	direction of diffusion
$(x_1, x_2, \dots)$	independent variables
X_j	junction depth
$X_{j \text{ bevel and stain } 1e15}$	X_j measured using the method of bevel and stain
$X_{j \text{ suprem}}$	X_j estimated using TSUPREM-4 simulations
$X_{j \text{ suprem } 1e15}$	$X_{j \text{ suprem}}$ for background p-type doping of 10^{15} B/cm^3
$X_{j \text{ suprem } 1e17}$	$X_{j \text{ suprem}}$ for background p-type doping of 10^{17} B/cm^3
$X_{j \text{ suprem } 1e15, \text{ adjusted}}$	$X_{j \text{ suprem } 1e15}$ linearly transformed to match SRA profiles
$X_{j \text{ suprem } 1e17, \text{ adjusted}}$	$X_{j \text{ suprem } 1e17}$ linearly transformed to match SRA profiles
$y = f(x_1, x_2, \dots)$	response surface equation
α	distance from design centre to axial runs
Ω/sq	ohms per square

Θ angle of bevelled sample

Acronyms

ANOVA Analysis of Variance

CCD Central Composite Design

DOE Design of Experiments

HF Hydrofluoric Acid

IPA Isopropyl Alcohol

IR Infrared

PECVD Plasma-Enhanced Chemical Vapor Deposition

POCl_3 Phosphorus Oxychloride

PV Photovoltaic(s)

RSM Response Surface Methodology

RTP Rapid Thermal Processing

SIMS Secondary Ion Mass Spectrometry

SOD Spin-On Dopant

SOG Spin-On Glass

SRA Spreading Resistance Analysis

1.1 Background

The photovoltaic (PV) industry continues to expand rapidly. Annual production has increased fivefold since 1995, reaching over 350 Megawatt peak in 2001. The on-grid European and Japanese markets, supported by governmental incentives, account for much of today's demand. The growth of the rural electrification market in developing countries is slower, despite full economic and social justifications for PV technology in sunny, off-grid regions. In contrast, PV is rarely competitive in the grid-connected electricity sector. Photovoltaic technology thus faces market-related as well as technical challenges. The foremost research goal is to develop mass-production methods and thus reach the price levels required for widespread acceptance and sustainable growth. While the current market is dominated by crystalline silicon wafer-based and amorphous silicon technologies, the photovoltaics community is exploring numerous novel structures and materials for cost reduction.

Emitter diffusion is one of the crucial steps in the fabrication of industrial solar cells. All the usual emitter diffusion methods consist of the creation of a phosphorus-doped oxide layer on the silicon surface, release of phosphorus atoms from the oxide layer

and drive-in of phosphorus atoms into the silicon. An alternative method of forming the emitter, *in situ* doping during silicon deposition, is commonly used for the fabrication of thin-film solar cells. Emitter diffusion, however, will likely remain important for at least a few decades, as will solar cells made from crystalline silicon wafers.

In the traditional diffusion process, the phosphorus-doped oxide layer grows from a vapour made of POCl_3 , oxygen and nitrogen. The diffusion takes place in a quartz tube furnace and uses quartz wafer carriers, a high purity POCl_3 liquid source and high purity gases, thus eliminating the risks of metal contamination. However, the cycle time is long, typically one hour. The furnace also consumes high volumes of pure, expensive gases and lacks flexibility in handling various wafer sizes.

POCl_3 diffusion is universally used for the production of high-efficiency cells. Manufacturers of low-cost cells, however, often opt for conveyor belt furnaces in order to ease automation, increase throughput and reduce costs. In this case, the phosphorus-doped layer is simply applied, prior to diffusion, as a solution that solidifies to form an oxide-like structure.

Solar cell manufacturers started to diffuse emitters in belt furnaces in the early 1980's [1]. In the conventional type of belt furnace, resistors first heat the surrounding air in order to heat the wafers. Although this works well, convection heating has been surpassed by light heating. Light waves pass undisturbed through the air but excite the silicon atoms, thus rapidly heating the wafers by radiation. Some additional heat is transferred to the wafers from the belt by conduction and from the walls by convection. Light heating reduces energy consumption as well as the time required for the wafers to heat up and cool down. However, the risk of contamination is higher than in quartz furnaces. Metal atoms

evaporate from the belt and can diffuse into the wafers, thus degrading carrier lifetime. Possibilities for reducing this risk include placing the wafers on quartz holders or on quartz washers fixed to the metal mesh belt. A recently introduced conveyor belt furnace with a ceramic transport mechanism completely eliminates the problem [2].

Lamp-heated furnaces found in current solar cell manufacturing facilities use tungsten-halogen lamps that radiate mainly in the near-infrared range of the electromagnetic spectrum. The higher the process temperature, the shorter the dominant wavelength in Planck's distribution. No one knows exactly when an infrared (IR) furnace was first used for diffusion. Manufacturers first bought them for drying and firing screen-printed contacts and tried them out at some point for emitter diffusion. M.J.A.A. Goris *et al.* appear to have published in 1998 the first paper about emitter diffusion using an IR furnace [3]. However, Radiant Technology Corporation assured the author that manufacturers have diffused solar cell emitters in their IR furnaces for a much longer time, but preferred to keep this knowledge proprietary.

The newest type of diffusion furnace, the Rapid Thermal Processing (RTP) furnace, was first investigated for solar cell fabrication in the early 1990's [4]. Generally, the RTP furnace can only process one wafer at a time. The wafer rests on quartz pins inside a quartz chamber whose thermal mass is very low. Intense tungsten-halogen lamps shine light directly onto the wafer. Most of the lamp energy lies in the visible and ultra-violet (UV) regions of the spectrum. The wafer is primarily heated by radiation, with a very high heating rate up to a few hundreds of °C/s. The cooling rate is also very rapid once the lights are switched off.

Single-wafer RTP furnaces found in microelectronics facilities severely limit the throughput of a solar cell manufacturing line. Therefore, for RTP to become a viable alternative, affordable high-throughput machines need to be built. Commercial multiple-wafer quartz RTP machines exist [5], but their high price discourages most solar cell manufacturers. Some research teams have instead adapted regular conveyor furnaces with metal belts by equipping them with RTP lamps [6][7]. More recently, infrared furnaces with additional UV lamps have become commercially available [8]. Short-wavelength light heating gives the fastest diffusion processes, but the lamps are very expensive and have a short service life.

This study presents results of emitter diffusions performed in a conventional infrared belt furnace. This established type of furnace has proven reliable and cost effective. Before the newer methods of optical heating become common in industrial solar cell processing, it must be shown that the saved time justifies their higher cost and that they can easily give the same good results as conventional infrared diffusion, despite fast cooling rates that can deteriorate material quality [9].

1.2 Thesis Objectives

The main objective of this thesis is to gain control over the phosphorus distribution of an emitter diffused in an infrared conveyor belt furnace or, in other words, to know how to select the process parameters to obtain a given emitter profile. The accomplishment of this step greatly facilitates optimizing the emitter when making complete solar cells and fixing all parameters. In addition, the ability to control the emitter profile is becoming increasingly important as solar cells become thinner; screen-printing metallization is

becoming more delicate and thus increasingly relies on the optimization of the emitter profile. The results of this thesis cover emitter diffusion profiles suitable for homogeneous screen-printed cells made today and in the foreseeable future.

A secondary objective is to find the simplest, quickest and least expensive way to gain control over the profile, since the procedure needs to be repeated if any of the fixed factors changes, such as the wafers, furnace or phosphorus source. The present work also aims at helping experimenters understand the influence of the main process parameters and choose a starting point when repeating the procedure. Finally, since emitter diffusion using an infrared furnace is already common in the photovoltaics industry, this project aims at exploring a slightly different avenue that might improve the process: infrared diffusion is performed with phosphorus-doped layers thinner and more heavily doped than in previous research.

A Design of Experiments (DOE) approach is very useful for dealing with the several factors that influence infrared emitter diffusion. In this experimental strategy, process parameters are varied together, instead of one at a time as is extensively done in practice. The DOE approach makes a very efficient use of the collected data and permits an objective analysis by statistical methods.

The first objective of the experiments was to fix the values of the factors held constant and to select the design factors, i.e. the process parameters varied in order to control the emitter profile. Design factors must have a strong influence on the profile within the controlled range. Diffusions in this phase of the project were performed using a quartz tube furnace. Subsequent experiments served the purpose of plotting the parameters that characterize the emitter profile as a function of the design factors. These experiments were

conducted in an infrared furnace as well as in a quartz tube furnace in order to compare diffusions using resistance- and lamp-heating.

1.3 Thesis Outline

This introductory chapter has outlined the main diffusion techniques presently used for solar cell fabrication, stated the objectives of the project and briefly mentioned the steps taken to accomplish them. Chapter 2 provides some information on the emitter formation process presented in this thesis. Chapter 3 reviews useful results found in the scientific literature. Chapter 4 details the experiments conducted and Chapter 5 presents and discusses the results. An example of solar cell fabrication is given in Chapter 6. Finally, conclusions and suggestions for future work are presented in Chapter 7.

Emitter Formation Process

2.1 Introduction

The emitter formation process presented in this thesis consists of two steps: the application of a phosphorus-containing layer onto the wafer and the diffusion of the phosphorus atoms into the silicon. The resultant emitter profile must satisfy certain conditions in order to help the solar cell reach a useful energy conversion efficiency. This chapter gives information on the phosphorus source layer applied onto the wafer, on phosphorus diffusion in silicon and on the requirements placed on emitters for screen-printed cells.

2.2 Spin-On Dopant Sources

Liquid diffusion sources used in the PV industry belong to a family of spin-on glass materials widely utilized in microelectronics for diffusion and planarization. A spin-on glass material is a solution of particles in colloidal suspension in a single-phase liquid. The solution is applied to a substrate by spin coating, spraying, dipping, screen printing or vapor deposition. Once solidified, spin-on glass layers are similar to silicon oxides. Spin-on glass (SOG) materials containing atoms to be diffused into a substrate are called spin-

on dopant (SOD) sources. Phosphorus SOD sources are made of phosphosilicate polymer molecules dissolved in organic solvents.

In microelectronics, SOG is practically always applied by spin coating. PV manufacturers prefer higher throughput techniques, with spraying being the most common one. Compared to spin coaters, sprayers give lower uniformities and poorer control over thickness. Hence, a thick SOD layer that acts like an infinite source of dopant material is sprayed onto the wafer. The final emitter profile is then independent of SOD thickness.

During the spin coating cycle or after source application by another method, the liquid begins to vaporize, leaving behind a semi-solid thin film. As viscosity rises, the coating undergoes a so-called “sol-gel transition” from a solution to a rigid two-phase system of solid particles and solvent-filled pores.

After deposition of the SOD layer, diffusion may be performed directly or following a low-temperature baking step. Baking modifies the SOD composition and structure due to solvent and phosphorus compound evaporation, cross-linking of polymers and water release. The phosphorus-doped layer is very hygroscopic and, therefore, moisture absorption affects the results if the wafers are stored for a period of time after film application and prior to diffusion. Baking alleviates this problem since the resultant polymer cross-linking densifies the film, thus reducing moisture trapping.

After diffusion, the SOD layer is stripped off in a dilute HF solution. The film may be difficult to remove if the diffusion treatment has caused some remaining organic solvent to strongly adhere to the silicon surface [10]. Baking so as to evaporate all solvents prior to diffusion solves this problem. Adjusting the percentage of oxygen in the ambient

so as to grow a thin oxide layer at the silicon surface also facilitates the removal of the SOD layer.

2.3 Phosphorus Diffusion in Silicon

In the mid-1800's, Adolph Fick introduced two differential equations to quantify diffusion, referred to as Fick's first and second laws. Fick's first law states that diffusion is driven by the concentration gradient. This law is described by:

$$F = -D \frac{\partial C}{\partial x}$$

where F is the flux (atoms/(cm²·s)), D is the diffusivity (cm²/s), C is the concentration (atoms/cm³) and $\frac{\partial C}{\partial x}$ is the concentration gradient.

Fick's second law expresses the conservation of matter and says that the increase in concentration with time in a cross section of unit area and thickness Δx is the difference between the flux into the volume and the flux out of the volume.

$$\frac{\Delta C}{\Delta t} = \frac{F_{in} - F_{out}}{\Delta x}$$

Substituting Fick's first law and taking the limit gives:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right)$$

These equations can be solved analytically if the diffusion coefficient is assumed constant. One analytical solution requires that a fixed dopant dose be introduced at the wafer surface prior to diffusion. This solution gives a Gaussian distribution of dopant atoms in the wafer. Another case of interest arises when diffusion occurs from an infinitely thick layer that initially contains a uniform dopant concentration. The diffusion profile then follows the complementary error-function (erfc) and surface concentration remains

constant over time. The diffusion profile obtained when diffusing phosphorus into silicon from a thick SOD layer is often approximated to an erfc distribution [11][12].

At high concentrations, the diffusion of phosphorus in silicon produces an impurity atom distribution that differs considerably from the Gaussian or erfc distributions [13] [14]. Figure 2.1 shows the plateau, kink and tail of a typical profile. The tail profile approximates a complementary error function with a surface concentration, C_k , occurring at the profile kink. The plateau seems to disappear when surface concentration is below $2 \times 10^{20} \text{ P/cm}^3$ [15].

Figure 2.1: A typical high concentration phosphorus diffusion profile in silicon.
Reference: [13]

In order to describe the dopant profiles of real devices accurately, process simulators incorporate modifications to Fick's laws and solve the resultant equations with numerical methods. Richard B. Fair was among the first scientists to study the modeling of phosphorus diffusion into silicon. He presented curves [13], reproduced below and

referred to later in the thesis, of the surface concentration as a function of the $R_{sh} \cdot X_j$ product. The curves stop at the solid solubility limits.

Figure 2.2: Total and electrically active P surface concentration vs. average resistivity for the 800-1050°C temperature range. Reference: [13]

The thesis uses the process simulation software TSUPREM-4 to simulate the diffusion of phosphorus into silicon. The software includes several models to take into account the dependence of diffusivity on the impurity, point defect and carrier concentrations. Explanations on the modeling capabilities of TSUPREM-4 for the simulation of diffusion can be found in [16] and [17].

The simulations performed for this work used several of the models made available by TSUPREM-4. For instance, the simulations accounted for concentration-dependent diffusion. All common dopants in silicon diffuse faster in regions of higher concentration and hence tend to create profiles with smaller concentration gradients in more heavily doped regions. This dependence of diffusivity on the doping level arises because the concentrations of point defects in their various charge states depend on the concentration of

electrons. On an atomic scale, diffusion takes place because impurity atoms interact with vacancies and interstitials. In the case of phosphorus, diffusion is thought to occur due to interactions with interstitials only. The overall diffusivity is composed of terms due to pairing of the dopant atoms with neutral, positive, negative and doubly negative point defects. Each term is function of a pre-exponential factor, an activation energy, and temperature. Since the relative importance of each term (of each point defect charge state) is determined by the doping level, diffusivity is also function of the electron concentration.

TSUPREM-4 also accounts for the presence of an internal electric field generated by the diffusing phosphorus. This field is set up when electrons from the donor atoms diffuse ahead because of their higher mobility. In steady-state condition, the field prevents the electrons from diffusing further and drags the phosphorus atoms deeper into the bulk. In order to simulate the enhancement of dopant diffusivity, TSUPREM-4 adds field terms to the equations describing the impurity fluxes.

Besides the diffusion coefficients and the electric field terms, the mathematical description of the impurity fluxes also includes factors that model the enhancement (or retardation) of diffusion due to non-equilibrium point defect concentrations. The software provides a choice of three point defect enhancement models. If the PD.FERMI model is selected, then the point defect concentrations are assumed to be at their thermal equilibrium levels and the enhancement factor is unity. If instead the PD.TRANS model is selected, then the calculation of the enhancement factor takes into account the generation of point defects at interfaces, the diffusion of point defects into the substrate, and recombination at interfaces and in the bulk. The diffusions conducted for this project took place in an ambient that contained oxygen. Oxidation of the silicon surface injects interstitials into the bulk

as it causes an expansion of 30% to form the SiO_2 structure. The resultant supersaturation of interstitials and enhancement of phosphorus diffusion are simulated by the PD.TRANS model. The third option, the PD.FULL model, includes all the effects of the PD.TRANS model plus the effects of dopant diffusion on point defect concentrations. These make an important contribution to high-concentration diffusion modeling. They come about because of the interactions between dopant atoms and point defects. Near the wafer surface, substitutional phosphorus atoms interact with silicon interstitials to form phosphorus-interstitial pairs. Mobile (paired) phosphorus atoms diffuse, regain substitutional lattice positions deeper into the substrate and thus release silicon interstitials in the interior region. In this way, the deeper portion of the profile becomes supersaturated with interstitials, and the concentration of interstitials near the surface decreases. The non-equilibrium interstitial concentrations enhance dopant diffusion in the interior region and reduce diffusion close to the surface, thus creating the kink and tail of the profile. Although PD.FULL appears to be the most appropriate model to simulate the diffusion of heavily doped emitters, it was found to give junctions deeper than the measurements by a factor of at least two, whereas PD.TRANS gave results relatively close to the measured profiles. PD.TRANS was therefore selected as the point defect enhancement model.

The previous paragraphs mentioned modifications made to Fick's laws to better simulate the diffusion process. The simulations involved a number of other models to take into account solid solubility, activation of impurities, segregation of impurities at the interface, equilibrium concentration of point defects, surface oxidation, and others. The simulations performed for this work used all default models, with the exception of PD.TRANS, and did not change any of the equations modeling the physical processes. However, the

software contains many adjustable parameters, and if many precisely measured profiles were available, then the exploration of how to adjust the physical parameters to fit the simulations to the experimental data could be worthwhile.

2.4 Emitter Profile For Screen-Printed Cells

There is no optimum emitter profile universal to all solar cells, since cell efficiency also depends on other parameters, such as the metallization and anti-reflection technologies. This thesis does not attempt to develop an optimized solar cell process, but rather covers a range of emitter profiles, including those that yield the current best efficiencies for screen-printed cells with homogeneous emitters.

2.4.1 Surface Concentration

The trade-off between high and low phosphorus surface concentration reconciles two important cell parameters, namely low front surface recombination and low front contact resistance. A low surface concentration favors the former to the detriment of the latter.

For cells metallized using photolithography, Noel *et al.* [18] recommended a surface concentration of 10^{20} P/cm³ or lower in order to reach low front surface recombination velocities. Screen printing is not capable of the low finger widths and spacings possible with photolithography and hence necessitates larger surface concentrations to achieve low contact resistance. Carrier surface concentrations of screen-printed cells appear to always exceed about 2×10^{20} e/cm³ [5][7][19][20].

At normal diffusion temperatures (around 900°C), the chemical solid solubility of phosphorus in silicon is about 7×10^{20} P/cm³, whereas the maximum electrically active concentration is about 3×10^{20} P/cm³ [13]. The lower the chemical surface concentration,

the lower the carrier surface concentration and the smaller the difference between the two. Hence, the lower the chemical surface concentration, the lower the inactive phosphorus population. When the chemical surface concentration is only 10^{20} P/cm³, the electrically active surface concentration is very close to the same value. For today's screen-printed cells, carrier surface concentrations of 2×10^{20} e/cm³, corresponding to chemical surface concentrations of 4×10^{20} P/cm³, can give satisfactorily low contact resistance values [7][19][3]. Higher surface concentrations unnecessarily degrade the short-wavelength response and should in general be avoided.

2.4.2 Junction Depth

A shallow junction improves short-wavelength current collection efficiency but increases the susceptibility to shunting by the metallization. The shallowest junction that can currently accommodate screen-printed contacts fired through PECVD hydrogenated silicon nitride is around 0.25 μ m [21].

2.4.3 Sheet Resistance

Given the diffusion temperature, substrate background doping, surface concentration and junction depth, the sheet resistance is fixed [13]. The solar cell design must consider, in addition to the previously mentioned factors, the emitter lateral series resistance. The optimum sheet resistance for homogeneous emitters of cells screen-printed through silicon nitride was reported as being in the 40-55 Ω /sq range [22]. According to Figure 2.2, this range of values agrees well with a minimum junction depth of 0.25 μ m and a carrier surface concentration of 2×10^{20} e/cm³, at 900°C. Improvements in future metallization schemes will permit higher sheet resistances.

Previous Diffusion Experiments and Results

3.1 Introduction

Doping of silicon by phosphorus diffusion from spin-on dopant oxide layers is a well-established technique in microelectronics and photovoltaics technologies. However, only photovoltaics manufacturers perform this diffusion using an infrared belt furnace, and literature on this subject is scarce. Therefore, most of the background information presented here comes from research dealing with resistance-heated and RTP furnaces.

3.2 Influence of Type of Furnace

As outlined in the introductory chapter, a few types of diffusion furnaces exist, with the newer ones speeding up the process and consuming less energy. A comparison between emitters diffused in an IR- and in a resistance-heated belt furnace showed that IR heating can give the same profile in less time at the same peak temperature. The time is reduced by 25-65% at 935°C and by 10-35% at 920°C when sheet resistance is in the 30-50 Ω/sq range [3]. The POCl_3 process was also compared with infrared diffusion [20]. Cells with emitters diffused with the POCl_3 or IR processes had comparable I-V charac-

teristics when the substrate was of high quality. However, IR diffusion resulted in higher carrier lifetimes and efficiencies for cells made of lower quality material.

Rapid thermal diffusion of screen-printed cells was first presented in the mid-1990's [22]. Soon afterwards, emitter diffusion in a belt furnace equipped with RTP lamps was demonstrated [7][6]. Rohatgi *et al.* [6] compared emitter diffusion from a SOD layer in a single-wafer quartz RTP furnace, in an RTP belt furnace and in a tube furnace. Diffusion of a 40 Ω/sq emitter at 880°C required three, six and thirty minutes respectively. This clearly shows that RTP speeds up the diffusion process, due not only to steeper temperature ramps but also to faster phosphorus diffusion at a given temperature.

Diffusion enhancement by RTP lamps is attributed to the short-wavelength photons seen by the wafer. Evidence of optical effects in rapid thermal diffusion of phosphorus in silicon was reported many times [23]-[28]. Pyrometers or thermocouples monitor temperature to ensure that the diffusion enhancement does not simply occur because of thermal effects. To prove beyond doubt the presence of optical effects, short-wavelength illumination was shown to yield lower sheet resistances even at lower temperatures [28]. The diffusion enhancement is not yet explained. A suggestion that short-wavelength photons only affect the structure of the SOD layer rather than changing the diffusion kinetics in silicon [23] was refuted by experiments that showed a diffusion enhancement even in the absence of a SOD layer [24]. A plausible idea is found in a publication reporting measurements of the non-thermal influence of photon illumination on diffusion of germanium and indium in silicon [29]. The diffusion coefficient changed substantially in response to illumination by photons with energies higher than the bandgap, in opposite directions for n- and p-type silicon substrates. The experiments therefore point to a mechanism that is

electronic rather than vibrational and suggest that the non-thermal carriers may alter the ionization state of point defects, thus changing diffusivity close to the surface.

The spectrum of near-infrared lamps contains some photons that generate electron-hole pairs in silicon, although few compared to the spectrum of an RTP furnace. Some light is definitely visible through the openings at both ends of the IR furnace. The presence of light-generated carriers might possibly help explain the observation that faster diffusion occurs in an IR- than in a resistance-heated furnace. The higher heating rate might also help explain the faster diffusion. It was in fact observed that faster heating rates enhance rapid thermal diffusion of phosphorus from spin-on dopant layers into silicon [30]. The enhancement was ascribed to the stress induced during the heat-up phase.

The type of furnace can also influence the wafer temperature distribution and, hence, the junction uniformity. Since emitter junctions are shallow, diffusion uniformity is necessary in order to assure process reproducibility and a high yield. For screen-printed cells, this becomes critical in order to avoid shunting and contact resistance problems. Infrared belt furnaces used in conjunction with thick SOD layers can give appropriate standard deviations, equal to those obtained with resistance-heated belt furnaces, typically $\pm 1.5 \Omega/\text{sq}$ for a $40 \Omega/\text{sq}$ emitter [3].

3.3 Influence of Baking of SOD Layer

The influence of baking temperature on sheet resistance was observed during proximity diffusion experiments [31]-[33]. (Proximity diffusion is a technique that consists in placing, during high temperature treatment, the processed (bare) wafer a few millimetres away from a source wafer coated with a SOD layer.) The lowest sheet resistance was

found at 150°C for both the processed and source wafer, indicating that phosphorus release from the SOD layer to the ambient and to the source wafer is most efficient at this temperature. Higher baking temperatures lead to larger film densification and, hence, slower diffusion within the oxide. They also lead to larger phosphorus loss, as shown by measurements of the dopant content within the layer after baking [31]. Lower baking temperatures result in weaker polymer cross-linking and in more solvent left in the pores. It was suggested that this might slow down phosphorus diffusion within the oxide [34], retard phosphorus liberation from the polymer chains or cause phosphorus to evaporate, together with volatile solvents, at the beginning of the diffusion cycle [31]-[33]. Finally, sheet resistance was seen to depend more pronouncedly on baking temperature for thinner SOD layers, for both the processed and source wafer. This is because the relative portion of phosphorus that evaporates during baking is larger for thinner layers [31].

Baking time seems to have received less attention than baking temperature. However, early diffusion experiments [35] that included a pre-diffusion baking at 190°C for up to four hours showed that sheet resistance after diffusion was higher for longer time periods.

3.4 Characteristics Specific to SOD Layers

Diffusion from spin-on dopant layers differs from diffusion from other types of oxide. For example, it is well known that phosphorus diffusion in oxide layers strongly depends on the oxide structure. Diffusion is fastest in porous structures such as SOD layers and slowest in thermal oxides; chemical vapor deposited oxides lie in between [31].

Baking and high temperature diffusion densify the SOD structure, making it less porous and reducing phosphorus in- and out-diffusivity.

Other characteristics such as surface diffusion, injection of point defects into the substrate and surface stress may distinguish SOD oxides from thermal and chemical vapor deposited oxides. Slaoui *et al.* [36] compared diffusion from SOD layers and from phosphosilicate glass (PSG) deposited by atmospheric pressure chemical vapor deposition (APCVD). Both types of oxide layers contained comparable phosphorus concentrations. Sheet resistance measured after thermal diffusion was lower for SOD layers, with the difference much reduced at high temperatures. Based on this result, the authors suggested that the energy barrier to be overcome before surface diffusion can happen is lower for SOD layers.

3.5 Qualitative Influence of Diffusion Time and Temperature and of SOD Thickness and Concentration

Diffusion theory can predict, if not always the exact diffusion profile, then at least the qualitative influence of the main process parameters. For instance, the amount of diffused phosphorus increases with phosphorus supply. Thicker or more heavily doped layers result in lower sheet resistances, deeper junctions and higher surface concentrations. Higher temperatures have the same effect, unless the SOD layer is fairly thin. In this case, the greater phosphorus evaporation that occurs at higher temperatures can cause surface concentration to decrease over time.

For wafers coated with thick SOD layers, longer times result in lower sheet resistances, deeper junctions and the same surface concentration. However, when the source layer is thin enough to become sufficiently depleted of phosphorus, surface concentration

decreases over time. Junction depth always progresses over time, although more slowly when surface concentration is decreasing. The combination of lower surface concentration and deeper junction can cause sheet resistance to become either higher or lower. Hence, depending on the level of source depletion, sheet resistance can either increase or decrease over time.

Diffusion theory predicts that the $R_{sh} \cdot X_j$ product goes up when diffusion time is increased and goes down when phosphorus concentration, source thickness or diffusion temperature is increased [35]. This applies to any level of source depletion.

3.6 Influence of SOD Thickness

Flowers and Wu [35] noted, more than twenty years ago, that SOD thickness can be readily varied by changing the spin speed. The higher the speed, the thinner the layer. They controlled diffusion over a small range by varying the thickness of layers about 300 nm thick.

To change layer thickness substantially, the as-received spin-on dopant source must be diluted with a solvent. The higher the dilution level, the thinner the layer for a given spin speed. Ventura *et al.* [37] varied the oxide thickness between 10 nm and 150 nm by diluting their SOD source with methanol. For thin SOD layers, sheet resistance and junction depth strongly depended on SOD thickness, indicating that doping was limited by the supply of phosphorus. Furthermore, surface concentration decreased with decreasing thickness. Sheet resistance became independent of SOD thickness for layers thicker than about 65 nm when SOD concentration was $2 \times 10^{21} \text{ P/cm}^3$.

Phosphorus diffusion limited by the dopant source was also reported in proximity diffusion [31]. Sheet resistance of the processed wafer strongly depended on SOD thickness, indicating that phosphorus is released from the whole SOD volume rather than from a thin layer close to the surface. The source wafer also showed this dependence, although to a lesser extent. For both the processed and source wafer, sheet resistance decreased with increasing SOD thickness even with layers thicker than 350 nm. As expected, the dependence became weaker with increasing thickness.

3.7 Influence of SOD Concentration

It is well known that surface concentration can be controlled through the adjustment of the dopant concentration in the SOD film. Noel *et al.* [11] measured the decrease in emitter surface concentration with decreasing source concentration. The diffusion temperature was fixed at 860°C and the diffusion time was varied in order to obtain a unique sheet resistance. Samples with films of lower concentration obviously required more time and, hence, probably lost more phosphorus by evaporation. However, thick SOD layers covered the wafers, justifying the approximation that surface concentration depended only on SOD concentration and not on time. The difference between source and surface concentration decreased with decreasing source concentration and both became equal at $5 \times 10^{19} \text{ P/cm}^3$.

Doshi *et al.* [22][38] made their first RTP emitters with a heavily doped SOD source of concentration 10^{21} P/cm^3 . The emitters had surface carrier concentrations around $4 \times 10^{20} \text{ e/cm}^3$. They later changed to a SOD source of concentration 10^{20} P/cm^3 in order to reduce surface concentration to about $2 \times 10^{20} \text{ e/cm}^3$. (The fact that surface

concentration is higher than source concentration may be due to the dependence of SOD concentration on the level of oxide densification.)

3.8 Influence of Time

When the SOD source is approximated to an infinite dopant source, the junction depth and the reciprocal of the sheet resistance both increase linearly with the square root of the diffusion time. If the source becomes sufficiently depleted, the plotted lines curve. The higher the diffusion temperature, the sooner the SOD layer becomes depleted and the sooner the lines curve.

Tube furnace diffusion of phosphorus in silicon using the heavily doped SOD source P-8545 (Honeywell) was reported in [34]. The plotted junction depth and reciprocal of sheet resistance followed the behaviour mentioned above. For example, at 900°C, quadrupling the time from 15 minutes to one hour lowered the sheet resistance from 243 to 23 Ω/sq , whereas quadrupling the time from one to four hours only lowered the sheet resistance from 23 Ω/sq to 12 Ω/sq . The slowdown in junction depth progression is also visible, although less obvious. The junction depth goes from 0.6 μm after 15 minutes, to 1.17 μm after one hour and to 2.08 μm after four hours.

Flowers and Wu [35] also observed the square-root law. They diffused samples coated with a heavily doped spin-on phosphorus source in a tube furnace and measured 19, 15 and 12 Ω/sq after 30, 60 and 90 minutes at 900°C.

Sheet resistance of samples diffused in an infrared furnace also showed the same tendency [3]. At 920°C, sheet resistance was 53, 44 and 41 Ω/sq after 1.9, 2.1 minutes and

3.5 minutes respectively. The given measurements do not allow for the verification of the square-root law.

3.9 Influence of Temperature

Phosphorus diffusivity in silicon follows Arrhenius behaviour and, hence, increases exponentially with temperature. Arrhenius plots ($\log y$ versus $1/\text{temp.}$) of sheet resistance and junction depth produce straight lines. This behaviour was verified using SOD layers thicker than 150 nm [39][33] and thin layers of only 18 nm [40].

Surface concentration was seen to slightly rise when temperature increased from 950°C to 1050°C [41] and to markedly go up from 10^{20} P/cm³ to 9×10^{20} P/cm³ when temperature increased from 850°C to 1000°C [36]. Surface concentration can also go down with an increase in temperature, as shown by results in proximity diffusion [31]. Surface concentration of the source wafer was slightly lower at 1150°C than at 1050°C, indicating that the SOD layer becomes more rapidly depleted of phosphorus at higher diffusion temperatures. The junction depth of the source wafer was, however, almost twice as deep at 1150°C than at 1050°C. No example was found in the literature of higher temperatures giving higher sheet resistances or shallower junctions.

3.10 Influence of Ambient

The oxygen content in a nitrogen/oxygen ambient was varied from 0% to 75% and thus shown to influence sheet resistance when phosphorus is diffused into silicon from a spin-on dopant source layer [35]. For 30 minutes of tube diffusion at 900°C, sheet resistance sharply decreased from 19 Ω/sq in pure nitrogen to a minimum of 15 Ω/sq around 7% oxygen and slowly increased to 17.6 Ω/sq at 75% oxygen. The sudden decrease is

probably due to the enhancement of phosphorus diffusion that happens when the silicon surface is oxidized [16]. The slow increase at higher oxygen concentrations is easily explainable since oxygen causes SiO_2 to grow at the SOD-Si interface, thus retarding diffusion from the SOD layer to the wafer. This effect was also seen during rapid thermal diffusion [33]. Finally, no difference was observed between emitters diffused in an IR furnace when either nitrogen or air was used [3].

3.11 Implications of the Research for the Field

Only a few papers [3][20][42] exist regarding IR furnace diffusion of homogeneous emitters, probably because companies lack the motivation to publish their fabrication processes. Despite corporate secretiveness, it appears sensible to claim that the present research makes an original contribution to the field of IR diffusion for solar cells. First of all, all reviewed reports on emitter diffusion for solar cells applied either a best-guess approach or a one-factor-at-a-time approach to conducting experiments. The former strategy consists in changing the value of one, or perhaps two, factors for the next test, based on the results of the current test. The latter strategy consists in selecting a starting point and then successively varying each factor over its range while keeping the other factors constant. Even if some process developers did apply the DOE approach to IR emitter diffusion, they likely chose a simpler technique than the one used in this thesis, i.e. to model mathematically the influence of three process parameters on junction depth, sheet resistance and surface concentration over a wide range. In fact, to find a diffusion process suited to the current need of the fabrication line, process developers would probably start by identifying regions of the process parameter space that meet the requirements for sheet resistance. They would only characterize the complete profile when scanning the identi-

fied regions to find optimum process conditions. This approach could probably require knowing fewer profiles than the method proposed in this thesis. Profile measurement requires expensive techniques such as spreading resistance analysis (SRA) or secondary ion mass spectrometry (SIMS). However, this thesis proposes an alternative method for characterizing the diffusion profile at low cost and with enough precision to select approximate process conditions. The method requires process simulation software and only two precise profile measurements. Subsequent optimization would require profiling only a few junctions, in addition to making solar cells. The proposed approach to emitter profile control also gives additional information on the influence of the process parameters and thus facilitates future changes to the diffusion process.

Another idea this thesis introduces is the use of thin (< 65 nm) and heavily doped ($\sim 3.5 \times 10^{21}$ P/cm³) spin-on dopant layers for infrared emitter diffusion. This option is examined for the first time since the common practice consists in applying a thick (> 100 nm) SOD layer of lower concentration ($< \sim 3 \times 10^{20}$ P/cm³). The thick layer acts like an infinite source of phosphorus, thus providing uniform diffusion regardless of whether the layer was applied uniformly or not. However, as explained in the following chapters, diffusing the emitter from thin layers works well and has advantages that could justify acquiring equipment able to apply thin SOD layers with high uniformity, precise thickness control and a high enough throughput for mass-production of solar cells.

4.1 Introduction

A series of experiments were conducted to achieve the objectives of this project. Nearly a hundred diffusion runs were carried out in a quartz tube furnace and in an IR conveyor belt furnace. One wafer per run was characterized after diffusion. This chapter presents the experiments in detail, including the starting materials, equipment, procedures, measurement techniques, strategy of experimentation and selected factor levels.

4.2 Starting Wafers

The silicon wafers were p-type (boron-doped), <111>-oriented, Czochralski-grown and 5.715 cm in diameter. Thickness, measured with a contact thickness gauge, was about 300 μm . The front side of the wafers was mirror polished and the back side was etched. The manufacturer's specified resistivity was 5-15 $\Omega\text{-cm}$. This resistivity range corresponds to background doping levels from $7 \times 10^{14} \text{ B/cm}^3$ to $2 \times 10^{15} \text{ B/cm}^3$. Spreading resistance analysis of two wafers revealed background concentrations of 10^{15} B/cm^3 .

The cleaning procedure (modified RCA) consisted of immersing the wafers in an $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (0.25:1:5) solution at 80°C for 5 minutes, rinsing for 10 minutes in

deionized water, immersing the wafers in an $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:6) solution at 80°C for 5 minutes and again rinsing for 10 minutes. The wafers were then dipped for 30 seconds in a dilute HF solution (1%), rinsed for 10 minutes and blown dry with a nitrogen gun.

4.3 Spin-On Dopant Source

The SOD source available for experimentation was phosphorus-doped P-854 2:1 (Honeywell). This liquid dopant source is produced using phosphoric acid, deionized water, ethanol and tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$, known as TEOS). The final product is a transparent solution of ethanol containing phosphosilicate polymer molecules. Decomposition of P-854 2:1 produces emissions of metaphosphoric acid (HPO_3) above 300°C . Metaphosphoric acid is corrosive but relatively weak when compared to orthophosphoric acid (H_3PO_4). Decomposition of P-854 2:1 also forms water, oxygen and nitrogen. The solid content (weight percentage that forms the film after solvent evaporation) is 3.96% and the weight percentage of phosphorus in the solid content is 8%.

Phosphorus concentration of the solid film in atoms per unit volume is not available from the manufacturer. However, Nguyen [34] measured the phosphorus concentration of solid films formed by coating wafers with P-8545, a source identical to P-854 2:1 in all respects except for the percentage of ethanol. He found $6.79\text{--}8.9 \times 10^{21} \text{ P/cm}^3$ after 30 minutes of baking at 150°C and $3.5\text{--}9.47 \times 10^{21} \text{ P/cm}^3$ after 30 minutes of diffusing at 800°C . A value of the same order of magnitude is obtained by approximating the SOD film density to the well-known value for dry SiO_2 of 2.27 g/cm^3 . First, the concentration in weight per volume is calculated:

$$8\% \text{ (P solid content) of } 2.27 \text{ g/cm}^3 \text{ (film density)} = 0.1816 \text{ g of P per cm}^3 \text{ of SOD film.}$$

Since the atomic weight of phosphorus is 30.97 g/mole, the number of atoms per volume is: $(0.1816 \text{ g/cm}^3 / 30.97 \text{ g/mole}) \times 6.022 \times 10^{23} \text{ atoms/moles} = 3.5 \times 10^{21} \text{ P/cm}^3$.

By comparison, a liquid phosphorus source available from the company Emulsitone [43], specifically intended for diffusion of industrial solar cells, contains $3 \times 10^{20} \text{ P/cm}^3$.

4.4 Application of Spin-On Dopant Source

Since the source P-854 2:1 is heavily doped, coating wafers with thick layers approximating an infinite source of dopant material would result in surface concentrations near solid solubility. To obtain lower surface concentrations, as desired for solar cell fabrication, one option is to dilute the dopant source with a silicate spin-on glass. The other option is to apply a thin layer that acts like a finite source of phosphorus. The emitter profile then, in the latter case, strongly depends on SOD thickness. The latter option was selected for a few reasons. First, the fabrication laboratory owned an ellipsometer, but had no equipment to measure the phosphorus concentration in the film. Hence, only the option of varying source thickness would allow the experimenter to measure the actual process parameter values. Second, varying source thickness was simpler than varying source concentration. The former was achieved by applying the source with a spin coater (Solitec Wafer Processing, model 5110C-T) and varying the spin speed, whereas the latter would have required acquiring a spin-on glass solution and preparing, as precisely as possible, many mixes with P-854 2:1. Third, there exist no results in the scientific literature of infrared furnace diffusion from a thin SOD layer acting like a finite source. Therefore, a goal of this thesis is to examine this option. The only disadvantage of thin layers is the need for equipment able to apply uniform layers, like a spin coater, but with a high enough

throughput for industrial solar cell production. However, some spray systems already exist that deposit the source with a uniformity of $\pm 15\%$ (Sono-Tek Corporation, MCS*Infinity System). Furthermore, NewSun Technologies, a sponsor of this work, is developing a spray system to provide a uniformity of $\pm 5\%$.

For good coating reproducibility, the SOD solution was taken out of the refrigerator to warm up to room temperature at least 12 hours before spin coating. The last step of the cleaning procedure, the etch in dilute HF, was done just before spin coating. Five drops of solution (approximately 0.15 ml) were applied to the centre of the dry wafer placed on the spin coater chuck. The spin cycle was 30 seconds long. Coated wafers were baked on a digital hot plate (PMC Industries, model 731) in normal atmosphere. After diffusion, the SOD layer was etched in 1% HF until the wafer would become hydrophobic.

Spin speed was varied between 1000 rpm (revolutions per minute), the lowest speed that gives good uniformity, and the upper speed limit of 10000 rpm. Thickness was measured, after a fixed baking, with an ellipsometer (Sagax Instrument AB, model 125). Thickness was read on a scale from 0 to 100 nm with divisions every 2.5 nm. Since the line indicating thickness was about one division wide, precision was on the order of 1.5 nm. Thickness was plotted as a function of spin speed and seen to vary approximately inversely with the square root of spin speed, as expected [43]. To cover the desired thickness range, the SOD source was diluted with a few different ratios of isopropyl alcohol (IPA). Figure 4.1 gives an example of the variation of thickness versus spin speed.

Figure 4.1: Layer thickness vs. spin coater speed, after baking for 30 minutes at $\sim 400^{\circ}\text{C}$, for SOD source made of 7 parts of P-854 2:1 and 3 parts of IPA.

Table 4.1 shows all combinations of solution and spin speed used in this project. Two different preparations of the mix of 7 parts of P-854 2:1 and 3 parts of IPA gave two slightly different curves of thickness vs. spin speed, thus showing the importance of very precise liquid measurements.

TABLE 4.1: Combinations of SOD solution and spin speed and corresponding SOD thicknesses after baking for 30 minutes at $\sim 400^{\circ}\text{C}$.

P-854 2:1 (parts)	IPA (parts)	Spin Speed (rpm)	SOD Thickness (nm)
4	6	8500	20
		1500	40
6	4	8500	25
7 (first mix, used for tube furnace experiments)	3	3400	50
		2000	60
		1300	80
		1000	85
7 (second mix, used for IR furnace experiments)	3	5900	32.5
		2900	45
		2700	47.5
		1500	62.5
		1400	65

4.5 *Baking*

During the first screening (preliminary) experiment, wafers were baked at either 150°C or 400°C for times varying from 5 to 60 minutes. Low temperatures and short times have the advantage of better imitating industrial practices, but high temperatures and long times lead to evaporation of all solvents and further densify the film, thus reducing moisture trapping and the amount of toxic gases that come out of the diffusion furnace. This last point was considered an advantage due to concerns about the exhaust system of the IR furnace. Moisture trapping was also a worry because the wafers had to be carried from the fabrication laboratory equipped with the spin coater at Carleton University to the building with the IR furnace off campus, a trip of at least half an hour. Even though the wafers were carried in a vacuum dessicator with silica gel granules, the vacuum was not perfect and, therefore, the source layers would absorb humidity, thus affecting the diffusion results. Baking the wafers for a long time at high temperatures would alleviate the problem since denser layers absorb less moisture. The first screening experiment showed that baking for either 5 minutes at 150°C or for 60 minutes at 400°C influences the diffusion profile negligibly compared to the major process parameters. It was decided to use an extensive baking of 30 minutes at 400°C for all subsequent experiments.

Baking was carried out on a hot plate. Temperature was indicated on a display window and also measured with a dial thermometer. At 150°C the two readings agreed closely. However, when set to its maximum temperature of 400°C, the hot plate temperature never became perfectly stable. The maximum temperature ever indicated on the display window, 385°C, was obtained rarely and never before one hour of heating. Since temperature was not critical during the experiments, the baking was started when the dis-

play window indicated a temperature above 360°C. The hot plate could hold as many as eight wafers. During the second last experiment, the temperature distribution of the hot plate was measured using a dial thermometer and found to be very non-uniform. When the display window indicated around 370°C, the dial thermometer indicated 350°C at some locations and almost 400°C at others. Hence, the baking procedure was changed for the last experiment to improve uniformity. In this new procedure, at most four wafers, instead of eight, were baked at the same time. The four wafers were placed around the centre of the plate, as close as possible to each other. The first wafer was placed at the top-left corner when the display window indicated exactly 360°C, followed by the next three wafers in the clockwise direction. Every 7.5 minutes (a quarter of the total time), each wafer was moved to the next baking location, in the clockwise direction. Since each wafer was placed on the hot plate immediately after spin coating, the fourth wafer was placed about five minutes later than the first one. In addition, the displayed temperature had risen to between 372°C and 380°C by the end of the baking. Hence, the four wafers were baked at the same location for the same length of time, but were not exactly subjected to the same thermal cycle. In view of the fact that the first screening experiment showed negligible effect of the baking cycle on the diffusion profile, the differences in the baking cycles due to equipment problems should not detract from the validity of the diffusion experiments.

4.6 Diffusion in Quartz Tube Furnace

Like the spin coater, the quartz tube furnace (Bruce, model BDF82DWN7) was located in the fabrication laboratory at Carleton University. The outside/inside tube diameter was 146/140 mm. The 74 in. (188 cm) long heated zone included a 30 in. (76.2 cm) long flat zone with a temperature control of $\pm 0.5^\circ\text{C}$. The wafers were diffused at the centre

of the flat zone. The boat loader speed was 52.5 ipm (52.5 in. per minute or 133.35 cm per minute) or half the maximum value of 105 ipm (266.7 cm per minute). During the loading, the boat moved along a distance of 35 in. (88.9 cm). The time required for wafer loading (or unloading) was therefore: $35 \text{ in.} / 52.5 \text{ ipm}$ ($88.9 \text{ cm} / 133.35 \text{ cm per minute}$) = 40 seconds. Nitrogen flowed at a rate of 4 litres/minute while oxygen flowed at a rate of either 100, 200 or 400 sccm (standard cubic centimetres per minute). Diffusion temperature varied from 850°C to 910°C.

During boat loading, the furnace temperature drops due to the added thermal mass. Temperature profiling for a setpoint of 900°C was performed to estimate the time spent by the wafer at peak temperature. To measure the wafer heat-up and cool-down rates, a thermocouple inside a quartz rod was attached with teflon tape to the extremity of the push rod that stays outside of the furnace. The thermocouple rod was then inserted through the hole of the end cap, along the push rod. The thermocouple rested at approximately the wafer location. An additional boat had to be placed upside down on top of the boat carrying the wafer, so that the thermocouple quartz rod would rest without moving. The thermocouple was pushed during boat loading along with the push rod. The thermal mass of the thermocouple and additional boat certainly affected the temperature ramps. The profiling therefore gave upper limits for the wafer heating and cooling times. The thermocouple temperature was read on a display window, written down and plotted as a function of time elapsed since the beginning of loading or unloading. The plots shown on Figure 4.2 indicate that heating to peak temperature minus 5°C took about 7 minutes. Cooling down to 5°C below peak temperature took almost no time in comparison, less than 10 seconds. Therefore, the diffused wafers stayed at peak temperature for, at least, the total diffusion

time, from beginning of loading to end of unloading, minus 7 minutes. The following text refers to the total diffusion time, unless specified otherwise.

Figure 4.2: Temperature profiling in tube furnace for a setpoint of 900°C.

4.7 Diffusion in Infrared Belt Furnace

The IR furnace (Radiant Technology Corporation, model LA-310) had a total length of 90 in. (228.6 cm). The heated portion was divided in three zones of 7.5, 15 and 7.5 in. (19.05, 38.1 and 19.05 cm) respectively. The temperature setpoint was identical for the three zones and varied from 850°C to 950°C. The conveyor belt was set up to operate in the 0.4-40 ipm (1.016-101.6 cm per minute) speed range. However, the calibration software was modified so as to allow speeds as low as 3 ipm (7.62 cm per minute). Clean dry air flowed in the furnace during all diffusion runs, at the following rates: entrance eductor: 30 cfh (cubic feet per hour¹), entrance baffle: 75 cfh, three heated zones: 150 cfh, exit baffle: 75 cfh, exit eductor: 30 cfh, plenums: 165 cfh, cooling zone: 195 cfh.

1. 1 cubic foot per hour = 28.317 litres per hour

Temperature profiling was performed using the trailing wire profiling method. A wafer was placed on the metal mesh belt and a thermocouple cable was fixed to the belt with some twisted metal wire, right behind the wafer. The thermocouple cable was shaped after the attachment point so that the tip of the thermocouple would rest on the centre of the wafer. The “GO” button of the profiling software was pressed when the tip of the thermocouple would enter the furnace tunnel. The temperature profile was measured at 850°C and 950°C for belt speeds of 3 and 7.5 ipm (7.62 and 19.05 cm per minute) and at 900°C for belt speeds of 3, 4.7 and 11.25 ipm (7.62, 11.94 and 28.58 cm per minute). All curves had the same general appearance. An example is shown on Figure 4.3. The thermocouple temperature rose to attain the furnace setpoint around the middle point of the first zone, stayed stable until about the middle point of the third zone and then decreased to room temperature.

Figure 4.3: Temperature profiling in IR furnace for a setpoint of 900°C and a belt speed of 4.7 ipm.

The time spent above the setpoint was read from the profiling data. As expected by looking at the plots, this time corresponded approximately to the time taken by the wafer to move from the centre of the first zone to the centre of the third zone, a distance of 22.5 in. (57.15 cm). Table 4.2 compares, for three belt speeds and the temperature setpoint of 900°C, the times taken by the wafer to move along 22.5 in. and the times spent at temperatures higher than 895°C or 900°C. Since repeated temperature profiles disagreed by up to 10 seconds, the approximation for the time spent at peak temperature was adopted. The following text always refers to the time spent at peak temperature or, more precisely, to the time required by the wafer to go over 22.5 in.

TABLE 4.2: Comparison between times with temperature > 900°C (setpoint) or > 895°C and times required by the wafer to move over 22.5 in.

belt speed (ipm)	time needed to go over 22.5 in. (s)	time with temp. > 895°C (s)	time with temp. > 900°C (s)
3	450	463	436
4.7	285	283	267
11.2	120	110	102

4.8 Sheet Resistance Measurement

Sheet resistance was measured using a four-point probe (Lucas/Signatone Corporation, model SYS-301), a programmable current source (Keithley Instruments, model 224) and a digital multimeter (Keithley Instruments, model 196). The wafer was positioned under the pins of the probe and covered with an opaque cloth so as to eliminate the influence of the photoconductivity effect. Software automated the measurement by setting the current source to 4.53 mA, zeroing the voltmeter and indicating when the voltage had settled. The reading in mV, equivalent to sheet resistance in Ω/sq , was then manually recorded. Sheet resistance was measured at five locations on the sample, as shown on

Figure 4.4. The small lines indicate the orientation of the probe pins. The peripheral measurements were made about one centimetre away from the edge, therefore more than three times the spacing between probe pins (0.15 cm or 0.06 in.) as required.

Figure 4.4: Locations of sheet resistance measurements on the wafer.

The measurement was made twice at each location, the second time by switching the connections of the current supply so as to reverse current polarity. The two measurements, usually within $0.5 \text{ } \Omega/\text{sq}$ but in some cases $1 \text{ } \Omega/\text{sq}$ apart, were averaged. To obtain the best possible precision, the measurements should have used the dual-configuration procedure [44], but the author only learnt about this method towards the end of the project, after destroying most of the wafers to measure junction depth. In this method, sheet resistance is measured with both current polarities for two different pin configurations. In the second configuration, a current pin is interchanged with a voltage pin. Sheet resistance of a few wafers was measured with the dual-configuration procedure to see the effect of the added precision. Low sheet resistances kept practically the same value whereas high sheet resistances changed by a few Ω/sq , for example from 95.4 to $92.4 \text{ } \Omega/\text{sq}$.

4.9 Junction Depth Measurement

Measuring junction depth is less straightforward than sheet resistance. Several methods to measure the complete doping profile can be accessed from commercial vendors, but they all cost over \$100 per sample. Since the analysis of experiments required knowing the junction depth of many samples, the low-cost method of bevel and stain was used. The precision of this method is, as discussed later, limited for shallow junctions. However, as the measurement was performed many times, the technique was improved during the course of the project. In the end, the technique could give measurements clearly very close to the actual values, within 0.05 μm , but only under favorable conditions. Software simulations and spreading resistance analysis of two samples later permitted precision to improve.

The bevel and stain measurement proceeded as follows. To begin with, a small sample was cut from the wafer with a diamond scribe. The sample was mounted with wax on a metal bevel block previously heated on a hot plate. The sample was then bevelled by manually sliding the metal block on a polished glass plate covered with a liquid mixture made of water and micropolish powder (Buehler, 0.05 micron gamma alumina). The sliding motion followed the shape of an “8” to bevel the sample uniformly. Bevelling was stopped when a slope about 1 mm long was visible along the edge of the sample.

Once bevelled, the sample was covered with a few drops of 1% cupric sulfate (CuSO_4). The solution contained one or two drops of concentrated HF per 10 ml so as to etch the native oxide. The copper ions of the solution react with the electrons of the n-type side of the junction to form an orange-red stain. The bevel block was then rinsed, dried with a nitrogen gun and heated on the hot plate until the wax was sufficiently warm for the

sample to come off the block. Wax was removed from the back of the sample with a cotton swab and acetone. As shown on Figure 4.5, junction depth is deduced from the angle of the slope and from the horizontal distance between the junction line and the line where the slope begins.

Figure 4.5: Bevelled and stained sample.

To begin the measurement of the horizontal distance, the sample was placed on a glass slide and viewed under a microscope. The line of demarcation between n- and p-type was remarkably straight and well defined at some locations, but blurred at others. In addition, the stain prevented the line of demarcation between sloped and flat regions from showing. Therefore, locations selected for measurement had to have, in addition to a clear junction line, surface defects that would stay visible once the stain was removed. Selected areas were photographed at 200 times- and 50 times-magnification with a digital camera attachment.

The stain was then removed with a cotton swab wet with water and the sample was once again examined under the microscope. Each previously selected area was located using its picture at 50 times-magnification and again photographed at 200 times-magnification. The border between sloped and flat regions was only faintly discernible. A pair of polarizing filters was thus added in the light path in order to examine the sample with the

method of differential interference contrast microscopy. The flat and sloped surfaces of the sample then appeared with two very different intensities. The image was much clearer in the microscope objective than on the computer screen. Hence, the computer image without stain, magnified 200 times, was sketched on a piece of paper and the border location relative to the defects was marked. Afterwards, the pictures with and without stain at 200-times magnification were printed. With the help of pencil, ruler, surface defects and simple geometry, the distance between the line where the slope begins and the junction line was measured and converted to the actual distance. The measurement was considered acceptable if at least three sample areas gave horizontal distances within $3\text{ }\mu\text{m}$ of each other.

The slope of the sample was also measured. The bevel block indicated an angle of 0.5° , but measured angles varied from 0.2° to 1° . To start the measurement, the sample was examined at 100-times magnification with a microscope equipped with a sodium light and an interferometer. The mirrors of the interferometer were adjusted so that interference fringes would only appear on the sloped region, as shown on Figure 4.6.

Figure 4.6: Measurement of the slope of the bevelled sample.

Since the light wavelength was $0.6\text{ }\mu\text{m}$, a vertical distance of $0.3\text{ }\mu\text{m}$ separated points corresponding to adjacent fringes. The sample was photographed with a Polaroid camera attachment. The horizontal distance between adjacent fringes was then measured and converted to the actual distance. Finally, the angle was calculated with the Pythagorean theorem.

The error in measuring junction depth was caused by a few factors. First, the border between flat and sloped regions was not perfectly sharp and its location was often difficult to discern. The horizontal distance between the junction line and the line where the slope begins could contain an error up to about 5 mm on the printed pictures, corresponding to $6.88\text{ }\mu\text{m}$. The precision of the distance between fringes on the Polaroid picture was also limited. An error of 0.25 mm translated into an error of about 0.1° . These errors on horizontal distance and angle combine to give an error on junction depth of about $0.12\text{ }\mu\text{m}$. However, if the horizontal distance and angle only contained errors of $2.75\text{ }\mu\text{m}$ (2 mm on the printed pictures) and 0.05° respectively, then the error on junction depth was only around $0.05\text{ }\mu\text{m}$. Considering that the junction depths of the emitters diffused in the IR furnace varied from about 0.15 to $0.50\text{ }\mu\text{m}$, an error on the order of at most $0.07\text{ }\mu\text{m}$, or 20% of the range, seems acceptable. However, the time required to obtain this precision with certainty is hardly acceptable. More sophisticated equipment exists to directly measure junction depth, for example diamond wheels to grind a circular groove of precise diameter and microscopes to obtain from a digital readout the horizontal distance between two points of the sample. These instruments would make it easier to produce acceptable results in reasonable time.

4.10 Design of Experiments

Design of Experiments (DOE) is a statistical technique for planning and conducting experiments and analyzing the data. Designed experiments provide information on the main effects of the process factors (process parameters) and on any possible interaction between factors. A factor's main effect is the variation in response due to a change in the factor. An interaction with another factor exists if the variation in response depends on the value of the other factor. An example of interaction between factors is shown on Figure 4.7.

Figure 4.7: Example of an interaction between two factors.

The modern development of statistical design of experiments was led by the pioneering work of R. A. Fisher in the 1920's and early 1930's. During this time, Fisher was working at an agricultural research station near London, England. He introduced some basic concepts for studying the effects of multiple variables simultaneously, including factorial design and analysis of variance. Industrial applications of statistical design grew substantially in the 1950's with the development of response surface methodology (RSM) by G. E. P. Box and K. P. Wilson. Statistical design then became widespread in the late 1970's with the advent of user-friendly software and with the increasing interest of the

industry in quality improvement. The work of G. Taguchi in the 1980's significantly helped statistical design to become widely used in many industries, including electronics and semiconductors, where previously little use was made of the technique. The methodology proposed by Taguchi generated much discussion and controversy and thus led to the development of new methods of experimental design. Detailed information on experimental design is found in [45].

This thesis used response surface methodology as the strategy for the main experiments. Screening experiments used other techniques more appropriate for a first rough reconnaissance of terrain, namely a Taguchi design and a 2^2 factorial design in the tube and IR furnace respectively.

4.10.1 Factorial Design

The basic concept underlying all experimental designs is the factorial experiment. Taguchi and response surface designs are two special cases of the factorial design. In a complete factorial experiment, all possible combinations of the levels of the factors are investigated. For example, a two-factor factorial experiment with both design factors at two levels requires four runs. If the design factors "A" and "B" are defined on a coded scale from -1 to $+1$ (the low and high levels of the factors), then the four runs are: A, B = $-1, -1$; A, B = $-1, +1$; A, B = $+1, -1$ and A, B = $+1, +1$.

As another example, Figure 4.8 shows a complete factorial design with three factors, each one at two levels.

Figure 4.8: Complete 2^3 factorial experiment (three factors, two levels).

In general, a complete factorial design with k factors, each one at a levels, requires a^k combinations. Fortunately, when the number of factors of interest increases, a fractional factorial experiment is usually sufficient. In this case, only a subset of all combinations needs to be performed.

4.10.2 Taguchi Design

In the early stages of their work, experimenters typically use screening experiments. Two-level fractional factorial designs can, most often, efficiently provide enough information for this purpose. Taguchi designs are an alternative screening technique. This method adds three- and four-level factors to a two-level design, thus producing mixed-level fractional factorial designs. Taguchi designs can provide a lot of information about the main effects in relatively few runs and can show the presence of curvature in the response. On the other hand, they provide limited information about interactions between factors. In comparison, two-level fractional factorial designs with the same number of factors and runs can estimate more interactions independently of the main effects.

4.10.3 Response Surface Methodology

Response surface methodology is a collection of techniques used for modeling a response of interest y with a mathematical function of the independent variables $(x_1, x_2, \dots)$ influencing the response. The surface represented by the function $y = f(x_1, x_2, \dots)$ is called a response surface. The mathematical model is fitted to the experimental data by using the method of least squares. In most cases, a first- or second-order polynomial can provide an adequate approximation of the relationship between y and the independent variables if the range of the independent variables is reasonably small.

The face-centred central composite design was selected for modeling the influence of the variable process factors on the emitter profile. Central composite designs (CCD's) form the most popular class of response surface designs for fitting a second-order model. A CCD contains a 2^k factorial design augmented with $2k$ axial runs and a few (normally three to six) centre runs. The factorial and centre points can only provide a first-order model. The axial points permit the introduction of quadratic terms in the model. The replicated centre runs provide an estimate of experimental error. Figure 4.9 shows a central composite design for $k = 3$.

Figure 4.9: Central composite design for three factors.

The parameter α gives the distance of the axial runs from the design centre when the design factors are defined on a coded scale such that -1 to $+1$ correspond to the low and high levels of the factorial design. For this thesis project, the face-centred CCD, in which α is set to 1, was selected. All factorial and axial points then lie on a cube. Figure 4.10 shows the face-centred CCD for $k = 3$.

Figure 4.10: Face-centred central composite design for three factors.

The face-centred CCD only requires three levels for each factor and thus simplifies the experiments. Furthermore, this value of α can give three round numerical values for the factor levels, thus making the collected data more intuitively accessible. In addition, SOD thickness is more convenient to fine-tune if the required level corresponds to one of the divisions of the ellipsometer.

The choice of α also determines the ability of the design to provide good predictions throughout the experimental region. For the face-centred design, the investigated region is cubical and the quality of the predicted response is constant on a rounded cube. The face-centred CCD fitted the purpose of this project since the collected data were used for plotting the predicted response across the experimental region. The disadvantage of face-centred CCD's is that they are not rotatable. In a rotatable design, the quality of the

prediction is the same at all points equidistant from the design centre, regardless of their direction relative to the centre. Equal precision of estimation in all directions is often desired because the most common purpose of RSM is optimization. For the present project, rotatability was not necessary since the collected data were intended for studying the process rather than for optimizing it.

4.10.4 Model Significance and Adequacy Checking

This thesis models the variation of the three parameters characteristic of the emitter profile (sheet resistance, junction depth and surface concentration) due to changes in three variable design factors. A regression function fitted to the experimental data relates mathematically each response to all three independent variables. Significance of each term of the fitted model is tested by the analysis of variance (ANOVA). The name of this technique comes from the partitioning of total variability into its component parts. The total sum of squares, a measure of overall variability, is decomposed into sums of squares due to model terms and into a residual¹ (or error) sum of squares. A sum of squares divided by its number of degrees of freedom (number of independent elements in the sum) is a mean square. The mean square of an effect (interaction or main effect) gives information on the observed magnitude of the effect whereas the residual mean square estimates the variance of the residuals and thus gives information on model error. Significance of a model term due to an effect is tested by dividing the corresponding mean square by the residual mean square. Large values of this ratio imply that the effect is significant. The ratio of mean squares follows an F distribution (named after R.A. Fisher) whose shape depends on the

1. Residual: difference between the response observed for a combination of the independent variables and the corresponding prediction computed using the regression function.

degrees of freedom of the numerator and denominator. If the probability of observing a greater ratio ($\text{Prob} > F$) when the effect is non-existent is very small (less than 5%), then the effect is considered significant. The complete model is evaluated by using the sums of squares for all terms in the model.

Before the model is accepted, its adequacy must be checked. The primary tool to test if the model fits the data is residual analysis. The lack-of-fit test, a numerical method of residual analysis included in ANOVA, uses F statistics to decide whether the regression equation represents the data well. The residual sum of squares is partitioned into a sum of squares due to lack of fit and a sum of squares due to pure experimental error. Replicated experimental runs provide an estimate of pure experimental or “random” error. The mean square of the lack of fit is divided by the mean square of the pure error. Large ratios imply that the lack of fit is significant relative to pure error and either the selected model does not represent the data well or the estimate of pure error is inaccurate. More precisely, the lack of fit is considered significant if the probability of observing a greater ratio ($\text{Prob} > F$) with an adequate model is very small (less than 5%).

Graphical methods of residual analysis have an advantage over numerical methods for model validation because they encompass several complex aspects, whereas numerical methods tend to focus narrowly on one particular criterion. Graphical residual analysis consists in the evaluation of several plots of residuals in order to verify the assumptions of the analysis of variance. If the plotted residuals behave randomly, it suggests that the model represents the data adequately. For instance, the normal probability plot verifies the assumption that the residuals follow a normal distribution; the plot of residuals versus run number checks for any physical or environmental variable correlated with time; and the

plot of residuals versus factor checks whether the residuals have some structural relationship with any factor accounted for by the model. If the model is adequate and complete, then the residuals should have no structural relationship with any recorded variable. Validating the regression equation thus means checking whether any variables left out of the equation should have rather been included in the model.

4.11 Conducted Experiments

Design of Experiments software (Design-Expert, version 6) was used for planning the experiments and analyzing the results. Given information on design configuration, design factors and factor levels, the software generates a random sequence for the experimental runs. This section presents, in the chronological order of the experiments, the information related to each experiment.

4.11.1 Screening Experiment in Tube Furnace

A Taguchi “L” orthogonal array design with 16 runs was selected as the tube furnace screening experiment. The objective was to examine the relative influence of the controlled factors on the profile and select factor levels for the subsequent response surface design. Each wafer was baked alone on the hot plate just before diffusion. Table 4.3 shows the factor levels.

TABLE 4.3: Factor levels for Taguchi design in tube furnace.

Factors	Level 1	Level 2	Level 3	Level 4
Diffusion time (min.)	15	25	35	45
Diffusion temperature (°C)	850	870	890	910
SOD thickness (nm)	20	40	60	85
Baking time (min.)	5	15	35	60
Baking temperature (°C)	150	400		
O ₂ flow (sccm)	100	400		

No precise instruction on the percentage of oxygen in the nitrogen ambient was available. However, it is known that some oxygen facilitates the removal of the SOD layer after diffusion. Emulsitone recommends 1-2% [43]. The design included two oxygen flow rates so as to confirm that this factor has little influence on the process.

4.11.2 Response Surface Experiment in Tube Furnace

A face-centred CCD with three factors and a total of 20 runs (eight factorial runs, six axial runs and six centre runs) was employed for modeling tube furnace diffusion. The Taguchi experiment had previously shown that controlling SOD thickness, diffusion time and temperature would suffice to control the diffusion profile over the desired range. The oxygen flow rate was fixed to 200 sccm or 5% of the total gas flow rate. The baking was fixed to 30 minutes at $\sim 400^{\circ}\text{C}$. Since the spin coater was shared by several people, wafers were coated up to four in a row and stored in a vacuum dessicator after their baking. Table 4.4 shows the factor levels.

TABLE 4.4: Factor levels for face-centred CCD in tube furnace.

Factors	Low Level	Middle Level	High Level
Diffusion time (min.)	15	30	45
Diffusion temperature ($^{\circ}\text{C}$)	875	900	925
SOD thickness (nm)	20	50	80

4.11.3 Screening Experiment in Infrared Furnace

A 2^2 factorial experiment was carried out in the IR furnace in order to ensure that the subsequent RSM design would cover the desired range of emitter profiles. Table 4.5 shows the factor levels. The upper limit on time corresponds to the lower limit on the belt speed of 3 ipm. SOD thickness was fixed to 45 nm for all runs.

TABLE 4.5: Factor levels for 2^2 factorial design in IR furnace.

Factors	Low Level	High Level
Diffusion time (s)	180	450
Diffusion temperature (°C)	850	950

4.11.4 Response Surface Experiments in Infrared Furnace

Two face-centred CCD's were used for modeling IR furnace diffusion. The first design contained eight factorial runs, six axial runs and six centre runs. Table 4.6 gives the factor levels.

TABLE 4.6: Factor levels for first face-centred CCD in IR furnace.

Factors	Low Level	Middle Level	High Level
Diffusion time (s)	120	285	450
Diffusion temperature (°C)	875	900	925
SOD thickness (nm)	25	45	65

The thickness range was based on the response surface design conducted in the tube furnace. It was selected so as to exclude layers yielding too high sheet resistances and so as to include layers almost acting like an infinite source. The ranges of time and temperature were based on the 2^2 design, with some modifications explained in Chapter 5 (See "Screening Experiment in Infrared Furnace" on page 56).

Previously, at the end of the RSM experiment in the tube furnace, it had been observed that sheet resistance of the replicated centre point had decreased during the

course of the experiment. SOD thickness of the centre point was then measured and found to have increased from 50 nm to about 60 nm, most probably because the bottle of solution made of 7 parts of P-854 2:1 and 3 parts of IPA was almost empty, and surface evaporation of IPA had significantly affected the solution composition. To reduce the effect of IPA evaporation during subsequent experiments, a larger quantity of solution was prepared, approximately 250 ml. SOD thickness of each sample was also measured after baking to ensure thickness consistency.

The first RSM design in the IR furnace yielded a valid model. However, the centre runs suggested an experimental error close to 10%. Therefore, a second RSM design was performed in the IR furnace in order to verify the first one. The second design improved precision in four ways. First, only four wafers were carried to the IR furnace at a time to reduce the effect of the ageing of the source layer. Second, the baking procedure was improved, as explained earlier (See “Baking” on page 32). Third, each axial and factorial point was replicated in order to improve the estimate of experimental error. This augmented the design to a total of 34 runs. Finally, the range of process factors was narrowed so as to obtain sheet resistances between 30 and 100 Ω/sq . This improved the precision of interpolations and provided experimental data to assess the quality of predictions made by the first design. Table 4.7 shows the factor levels of the second design in the IR furnace.

TABLE 4.7: Factor levels for second face-centred CCD in IR furnace.

Factors	Low Level	Middle Level	High Level
Diffusion time (s)	175	275	375
Diffusion temperature ($^{\circ}\text{C}$)	880	900	920
SOD thickness (nm)	32.5	47.5	62.5

5.1 Introduction

Chapter 4 detailed the procedures followed to obtain the experimental data. For example, it introduced the Design of Experiments approach and described the five experiments conducted. By analyzing and exploiting the experimental data, the present chapter proposes a method to characterize the emitter profile in a simple and low-cost way, explains how to control the diffused profile, and demonstrates that the emitter can be diffused from thin SOD layers rather than from layers thicker than 100 nm as done in common practice. Rather than giving numerous numerical examples of emitter profiles and the process conditions to obtain them, the present chapter focuses on an explanation of the method utilized for controlling the diffused emitter and on a qualitative verification of the resultant response surfaces.

Information drawn from the two screening experiments is given first, followed by a discussion of the response surface experiments conducted in the IR furnace. Response surface fitting in the tube furnace is then compared to the results of the IR furnace.

5.2 Screening Experiment in Tube Furnace

The Taguchi design studied the effects of six factors with only 16 runs and, therefore, gave only the minimum information needed to proceed with the RSM experiment in the tube furnace. The conclusions were drawn from the sheet resistance data since the junction depths, then obtained from bevel and stain measurements only, were considered too unreliable. The range of sheet resistances (21-137 Ω/sq) was judged broad enough to correspond to the desired range of emitter profiles. In fact, the 30-100 Ω/sq range was deemed, based on current industry trends, sufficiently wide to cover the needs of homogeneous screen-printed cells made over the next few years. The measured junction depths varied from 0.12 to 0.75 μm and thus reinforced the idea that the experimental range covered all desired emitter profiles.

The effect of each process factor on sheet resistance was examined. Increasing SOD thickness caused a large decrease in sheet resistance. Sheet resistance decreased less, yet significantly, with increasing temperature. Due to aliased¹ interactions, the Taguchi design failed to demonstrate the influence of diffusion time on sheet resistance. As expected from the literature, the oxygen flow rate influenced sheet resistance only weakly. An intermediate flow rate of 200 sccm (0.2 litres/minute) was selected for the subsequent RSM experiment in the tube furnace. Also as expected, baking time and temperature influenced sheet resistance. Baking for 15 rather than 5 minutes increased sheet resistance by about 7 Ω/sq , but no real influence was seen beyond 15 minutes. Raising baking tempera-

1. Two (or multiple) effects (main effects or interactions between factors) are “aliased” or “confounded” if one estimated value includes both (or all) effects.

ture from 150°C to 400°C increased sheet resistance by, at most, 10 Ω/sq , similarly to observations made in [31].

From these results, it was concluded that the observed profile variation was mostly caused by the variations in SOD thickness, diffusion temperature and diffusion time. It was also decided that the diffusion process would be studied with long baking at high temperature, as desired due to particular circumstances (See “Baking” on page 32), even though the baking would then not imitate industrial practices. However, diffusion is governed by the same logic whether the baking is extensive or non-existent. The conclusions of the study therefore apply to low degrees of baking. Only the numerical values would change, although not greatly.

5.3 Screening Experiment in Infrared Furnace

The 2^2 screening experiment in the IR furnace contained four runs to investigate the influence of time and temperature only, since the thickness range had already been selected based on the previous tube furnace RSM experiment. The 2^2 factorial design was conducted with SOD thickness fixed at 45 nm.

The results, shown in Table 5.1, permitted the selection of time and temperature ranges for the first RSM design in the IR furnace. First, the lowest temperature was increased to 875°C, because thin layers would have otherwise yielded sheet resistances significantly higher than the desired limit of 100 Ω/sq . Second, the highest temperature was decreased to 925°C to narrow the studied range and to prolong the service life of the furnace lamps. It was (correctly) expected that thicker layers would allow the design to still yield sufficiently low sheet resistances. Third, the shortest time was reduced to 120

seconds so as to assess how quickly emitters for screen-printed cells could be diffused. Finally, the longest time, corresponding to the lowest possible belt speed, was retained.

TABLE 5.1: Sheet resistance for 2^2 factorial design in IR furnace.

	Diffusion temperature (°C)	
	850	950
	Sheet resistance (Ω/sq)	
Time (s)		
180	137.6	40.8
450	115	36.9

5.4 Results of Response Surface Experiments in Infrared Furnace

The core of this project, the face-centred CCD's conducted in the IR furnace, permitted the modeling of the influence of source thickness, diffusion time and temperature on the diffused emitter. Sheet resistance was readily characterized with a four-point probe. Junction depth was measured by the method of bevel and stain, but the measurement error was large relative to the junction depth range. As a consequence, the fitted model predicted some illogical behaviour, such as a decrease in junction depth with increasing SOD layer thickness. An alternative method was therefore developed to estimate junction depth with sufficient accuracy and thus obtain a response surface that agrees with diffusion theory. Surface concentration was then estimated in a similar manner. This section explains the procedure followed to characterize the diffused profiles and section 5.5 will analyze the data.

5.4.1 Results of Bevel and Stain Measurements

The efforts invested to improve the accuracy of the bevel and stain technique resulted in fairly accurate measurements, with an estimated error of $0.05\ \mu\text{m}$ in the best cases. The largest effort was put into measuring the junction depth of one sample for each design point of the second RSM design in the IR furnace. Column “ X_j bevel and stain $1\text{e}15$ ” of Table 5.3 on page 70 gives the measured junction depths. The number “ $1\text{e}15$ ” refers to the background concentration in boron atoms per cm^3 of silicon substrate.

The Design-Expert software can fit a response surface to the measured junction depths when the experimental error is approximated to $0.05\ \mu\text{m}$. Most, but not all, variations in junction depth follow the expected behaviour, as illustrated by Figure 5.1: junction depth actually increases with increasing temperature (*a*), but is very unlikely to decrease with increasing SOD thickness (*b*). All the seemingly erroneous variations can be attributed to the estimated error in the measured junction depths.

Figure 5.1: Example of (a) explainable and (b) illogical behaviour of the response surface fitted to the junction depth data obtained from bevel and stain measurements.

5.4.2 Estimation of Junction Depth and Surface Concentration

The bevel and stain measurement technique presented a few disadvantages. First, a precise measurement required at least one hour, not to mention sheer luck. In addition, some measurements had to be repeated several times in order to give a trustworthy result. Finally, the method is subject to individual judgement. The overall lack of precision of the measured junction depths led to the search for an alternative to the bevel and stain method. The process simulation software TSUPREM-4 was exploited to estimate junction depth and, at the same time, surface concentration. The measurements made by bevel and stain agreed reasonably well with the simulated junction depths and thus gave reasons to conclude that the simulated doping profiles were close to the actual profiles. Moreover, the response surfaces fitted to the simulated data only followed behaviours that simple physical rules can explain. Once the simulations were judged useful in estimating the diffusion profile, their validity was assessed by spreading resistance analysis of two samples.

5.4.2.1 Software Simulations

The TSUPREM-4 software was exploited to deduce junction depth and surface concentration from sheet resistance and process conditions only. Figure 5.2 shows an example of an input file.

```
$ 275 sec, 475 A, 900C
INITIALIZE <111> BORON=1E15
METHOD PD.TRANS
AMBIENT AMB.1 F.O2=0.21 F.N2=0.79
$ Measured thickness = 47.5 nm = 0.0475 microns.
$ Vary SOD thickness (in microns) until Rsh = 53 ohms/sq.
DEPOSITION OXIDE PHOS=3.5*10^21 THICKNESS=0.0475
$ Diffuse for 4.6 minutes at peak temperature.
DIFFUSION TIME=4.6 TEMPERATURE=900 AMB.1
$ Plot profile.
SELECT Z=LOG10(PHOSPHORUS) TITLE="Emitter profile"
PLOT.1D RIGHT=0.5 BOTTOM=15
$ Display concentration versus depth and diffused dose.
SELECT Z=PHOSPHORUS
PRINT.1D
PRINT LAYERS
$ Display sheet resistance and junction depth.
ELECTRIC X = 1.0
```

Figure 5.2: Typical TSUPREM-4 input file used for estimating junction depth and surface concentration.

The time and temperature of the diffusion, as well as the percentage of oxygen in the ambient (dry air), corresponded to the experimental conditions. The phosphorus concentration in the oxide was approximated based on the phosphorus solid content and SiO_2 density (See “Spin-On Dopant Source” on page 28). Regardless of whether SOD concentration was exact or not, the input file cannot represent the process conditions perfectly since the software deposits the oxide by chemical vapor deposition instead of by spin coating. An oxide formed by the latter method is more porous and hence loses more phosphorus by evaporation during diffusion. Nevertheless, the simulation can give the same sheet resistance as the one measured with the four-point probe if the amount of phosphorus

specified in the input file is adjusted. For all diffusion runs, the phosphorus supply provided by the oxide layer had to be decreased for the simulation to give the measured sheet resistance. The available amount of phosphorus was decreased by decreasing either the source thickness or the source concentration. Both options gave practically the same junction depth and surface concentration. This method therefore assumes that given the starting wafer orientation and doping, oxygen content in the ambient, diffusion time, diffusion temperature and sheet resistance, the doping profile is uniquely determined. In fact, the only way to obtain a different profile from the simulation, while keeping the same process conditions, is to change the parameters describing phosphorus diffusion in silicon and at the interface.

Column “ $X_{j \text{ suprem } 1e15}$ ” of Table 5.3 on page 70 shows the simulated junction depths for all points of the second RSM design in the IR furnace. Junction depths of factorial and axial points correspond to the average of the two replicates. Junction depths differed by at most $0.01 \mu\text{m}$ between the two runs.

Comparing column “ $X_{j \text{ suprem } 1e15}$ ” of Table 5.3 with measurements made by the bevel and stain method (column “ $X_{j \text{ bevel and stain } 1e15}$ ” of the same table) shows that simulated and measured junction depths agreed reasonably well, within $0.09 \mu\text{m}$. This relatively good concordance suggested that the simulated junction depths probably represented the actual values at least as well as the measurements made by bevel and stain.

5.4.2.2 Spreading Resistance Analysis

To assess the quality of the estimates made by TSUPREM-4 and by the method of bevel and stain, spreading resistance analysis of two samples, the ones with the smallest

and largest amounts of diffused phosphorus, was requested. The SRA was performed by Solecon Laboratories. Figure 5.3 shows the SRA profiles superimposed with the TSUPREM-4 profiles and compares the junction depths found by SRA, by TSUPREM-4 and by the method of bevel and stain. In addition, Figure 5.3 compares sheet resistance measurements made by Solecon Laboratories with those made by using the four-point probe available for this project.

Only these two doping profiles were measured during the project. Hence, they constituted the most objective information on the emitter profiles and were considered as a reference with which the simulations should agree. Measured profiles, however, always contain some error. In fact, Solecon specifies a typical limit of $\pm 20\%$ on the accuracy of carrier concentration. Fortunately, the sheet resistances measured by Solecon's four-point probe and calculated from the SRA profiles agreed well. Nearly always, the sheet resistance obtained by the four-point probe is more reliable [46]. The good concordance between the two sheet resistances therefore gives credibility to the SRA. To further investigate the reliability of the profile measurements, some samples could be profiled by more than one organization and by another method, for instance by four-point probe and anodic oxidation. This last technique was found to give different results than SRA, especially in regions of concentration higher than 10^{20} P/cm^3 [15].

(a) 175 s, 880°C, 32.5 nm

Junction depth:

- SRA: $X_j = 0.17 \mu\text{m}$
- TSUPREM-4: $X_j = 0.20 \mu\text{m}$
- Bevel and stain: $X_j = 0.18 \mu\text{m}$

Sheet resistance:

- Four-point probe, Solecon: $115.2 \Omega/\text{sq}$
- SRA: $R_{sh} = 117.4 \Omega/\text{sq}$
- Four-point probe, this project: $104.6 \Omega/\text{sq}$

(b) 375 s, 920°C, 62.5 nm

Junction depth:

- SRA: $X_j = 0.43 \mu\text{m}$
- TSUPREM-4: $X_j = 0.38 \mu\text{m}$
- Bevel and stain: $X_j = 0.32 \mu\text{m}$

Sheet resistance:

- Four-point probe, Solecon: $30.8 \Omega/\text{sq}$
- SRA: $R_{sh} = 30.5 \Omega/\text{sq}$
- Four-point probe, this project: $31.3 \Omega/\text{sq}$

Figure 5.3: Spreading resistance analysis of the samples with (a) the lowest and (b) the largest amounts of diffused phosphorus, and corresponding profiles calculated by TSUPREM-4.

The junction depths found by SRA and by TSUPREM-4 agreed within $0.05 \mu\text{m}$.

To try to improve the precision of all estimated junction depths, the TSUPREM-4 values were modified by a linear transformation so that the two points measured by SRA would

be reflected by the corresponding TSUPREM-4 values. The parameters of the linear transformation ($a X_{j \text{ suprem}} + b = X_{j \text{ suprem adjusted}}$) were obtained from the following two equations:

$$a X_{j \text{ TSUPREM-4}} + b = X_{j \text{ SRA}}$$

$$0.20 a + b = 0.17 \text{ (1}^{\text{st}} \text{ equation)}$$

$$0.38 a + b = 0.43 \text{ (2}^{\text{nd}} \text{ equation)}$$

$$\Rightarrow a = 1.44 \text{ and } b = -0.12$$

Comparing column “ $X_{j \text{ suprem } 1e15, \text{ adjusted}}$ ” of Table 5.3 on page 70 with column “ $X_{j \text{ bevel and stain } 1e15}$ ” of the same table shows that the TSUPREM-4 junction depths, once adjusted to reflect the SRA results, still agree reasonably well with the bevel and stain measurements, within $0.11 \mu\text{m}$.

Figure 5.3 showed that the software simulations did not produce doping profiles with a similar shape as the SRA profiles. However, the ranking of the diffusion runs in ascending order of their actual junction depth or surface concentration probably matches quite well, if not perfectly, the ranking obtained from TSUPREM-4. To try to obtain a different ranking, the input parameter files were modified to replace the PD.TRANS point defect model by PD.FULL. The PD.FULL model created the kink and tail of the profile, but yielded junction depths deeper than the measured values by a factor of at least two. After linear transformation of these newly simulated junction depths to make them reflect the two points measured by SRA, the new set of junction depth data matched the previous one (“ $X_{j \text{ suprem } 1e15, \text{ adjusted}}$ ”) within $0.04 \mu\text{m}$. Taking this difference into account, the ranking of the diffusion runs was unchanged. The simulations might possibly produce a signifi-

cantly different ranking if they would use the PD.FULL model and still yield junction depths close to the measured ones. In order to accomplish this, it appears necessary to modify the parameters modeling the physical processes of diffusion. The number of SRA measurements, however, was insufficient for this task.

The starting wafers available for the experiments had a resistivity around 10 $\Omega\text{-cm}$, corresponding to a doping concentration of 10^{15} B/cm^3 . However, the resistivity of wafers used for making solar cells normally varies from 0.1 to 1 $\Omega\text{-cm}$. This range corresponds to background doping levels from $7 \times 10^{16} \text{ B/cm}^3$ to $2 \times 10^{17} \text{ B/cm}^3$. Diffused wafers with background concentrations of either 10^{15} B/cm^3 or 10^{17} B/cm^3 have almost exactly the same sheet resistance and surface concentration, but their junction depths significantly differ. To get the TSUPREM-4 junction depths for a background doping of 10^{17} B/cm^3 , the boron concentration was accordingly modified in the input file. Column “ $X_{j \text{ suprem } 1e17}$ ” of Table 5.3 on page 70 gives the resultant junction depths. A linear transformation was applied to all values of this column so that the depths of the two SRA profiles where carrier concentration equals 10^{17} e/cm^3 would coincide with the corresponding TSUPREM-4 values. The following two equations gave the parameters a and b of the transformation. Column “ $X_{j \text{ suprem } 1e17, \text{ adjusted}}$ ” of Table 5.3 on page 70 gives the resultant junction depths.

$$a X_{j \text{ TSUPREM-4 } 1e17} + b = X_{j \text{ SRA } 1e17}$$

$$0.155 a + b = 0.16 \text{ (1}^{\text{st}} \text{ equation)}$$

$$0.315 a + b = 0.40 \text{ (2}^{\text{nd}} \text{ equation)}$$

$$\Rightarrow a = 1.5 \text{ and } b = -0.07$$

Junction depths simulated with background doping levels of 10^{15} B/cm³ or 10^{17} B/cm³ (columns “ $X_{j \text{ suprem } 1e15}$ ” and “ $X_{j \text{ suprem } 1e17}$ ” of Table 5.3) differ by 0.04 to 0.06 μm , but adjusted junction depths (columns “ $X_{j \text{ suprem } 1e15, \text{ adjusted}}$ ” and “ $X_{j \text{ suprem } 1e17, \text{ adjusted}}$ ” of Table 5.3) differ by at most 0.03 μm , because doping concentration decreased more steeply from 10^{17} e/cm³ to 10^{15} e/cm³ on the profiles measured by SRA than on the profiles plotted by TSUPREM-4. From this point on, unless specified otherwise, the text refers to the junction depths found in columns “ $X_{j \text{ suprem } 1e17, \text{ adjusted}}$ ” of Table 5.3 and Table 5.4. Junction depths of the first RSM design in the IR furnace were calculated using the same a and b parameters as for the second design.

The third parameter characteristic of the profile, surface concentration, was estimated in a similar way to junction depth. TSUPREM-4 simulations report chemical concentrations by default and electrically active concentrations if the ACTIVE function is specified. However, within the concentration range covered by this study, the software calculated equal values for both the active and inactive populations. Column “ $n_s \text{ suprem}$ ” of Table 5.5 gives the average surface concentration of the replicates for each design point.

Phosphorus concentrations measured by SRA increased with increasing depth close to the surface whereas, for all TSUPREM-4 profiles, phosphorus concentration only decreased. The profiles of emitters diffused from spin-on dopant sources and measured by SRA or SIMS often indicate an initial increase in concentration, for example in [47] or [22], but surface concentration is always defined as the peak concentration near the surface. Doping profiles measured by SIMS indicate an increase in phosphorus concentration over a depth of at most 15 nm [47]–[49], even when surface concentration approaches 10^{21} P/cm³, but SRA profiles can indicate an increase over as much as 100 nm [22]. If SIMS

analysis is performed on samples coated with PECVD silicon nitride, then phosphorus diffusion into the nitride layer is seen to cause the increase in concentration over depth near the surface of the silicon substrate [49]. SIMS analysis performed following the removal of the SOD layer can also show the initial increase [48], possibly due to phosphorus diffusion into the oxide grown during the etching of the SOD layer. The more noticeable increase on some SRA profiles is probably due to lower carrier lifetimes close to the surface, especially since the increase seems more important for higher surface concentrations (e.g. [22] and Figure 5.3), contrarily to the case of SIMS profiles [48].

Spreading resistance analysis measured carrier concentrations ($3.4 \times 10^{20} \text{ e/cm}^3$ and $2.4 \times 10^{20} \text{ e/cm}^3$) higher than the corresponding TSUPREM-4 concentrations ($2.5 \times 10^{20} \text{ e/cm}^3$ and $1.5 \times 10^{20} \text{ e/cm}^3$) by more than the 20% error range specified by Solecon Laboratories. A linear transformation was thus applied to TSUPREM-4 surface concentrations in order to reflect the magnitude of the SRA measurements. The following equations gave the parameters of the linear transformation.

$$a n_s \text{ TSUPREM-4} + b = n_s \text{ SRA}$$

$$1.5 \times 10^{20} a + b = 2.4 \times 10^{20} \text{ (1}^{\text{st}} \text{ equation)}$$

$$2.0 \times 10^{20} a + b = 3.4 \times 10^{20} \text{ (2}^{\text{nd}} \text{ equation)}$$

$$\Rightarrow a = 2 \text{ and } b = -0.6 \times 10^{20}$$

Column “ $n_s \text{ suprem adjusted}$ ” of Table 5.5 gives the average of the adjusted TSUPREM-4 surface carrier concentrations for each design point.

5.4.2.3 Estimation of Surface Concentration Using Fair's Model

According to Fair [13], surface concentration is fixed, given the diffusion temperature, substrate background doping, sheet resistance and junction depth. The curves reproduced earlier (Figure 2.2 on page 11) relate surface concentration to diffusion temperature and to the product of sheet resistance and junction depth, for a background doping of 10^{17} B/cm³. These curves come from equations modeling the POCl₃ diffusion process. Some profiles found in the literature and the ones presented earlier (Figure 5.3) were used for assessing the usefulness of Fair's curves in predicting the surface concentration of emitters diffused from spin-on dopant layers. The examples in Table 5.2 indicate that concentrations read from the curves agree to some extent with measurements. Hence, if an adequate method for measuring the junction depth is available, then Fair's curves, in conjunction with measurements of sheet resistance, can provide an approximation of surface concentration.

TABLE 5.2: Comparison between measurements and Fair's predictions.

Source	X_j 1e17 (μ m)	R_{sh} (Ω /sq)	$X_j R_{sh}$ (cm $\times 10^{-3}$ $\times \Omega$ /sq)	Temp. ($^{\circ}$ C)	C_s measured (SIMS) ($\times 10^{20}$ P/cm ³)	n_s measured (SRA) ($\times 10^{20}$ e/cm ³)	C_s Fair ($\times 10^{20}$ P/cm ³)	n_s Fair ($\times 10^{20}$ e/cm ³)
Ref. [47]	0.41	33	1.35	900-950	3		3-3.3	1.6-2
Ref. [21]	0.26	45	1.2	925		2.4	4	2
Figure 5.3 a)	0.16	115	1.8	880		2.4	2.6	1.6
Figure 5.3 b)	0.4	31	1.2	920		3.4	4	2

Columns " $C_{s \text{ Fair}}$ " and " $n_{s \text{ Fair}}$ " of Table 5.5 give respectively the chemical and electrically active surface concentrations predicted by Fair's curves for all points of the second RSM design in the IR furnace. Carrier concentrations " $n_{s \text{ suprem adjusted}}$ " calculated by TSUPREM-4 and adjusted to reflect the SRA measurements always fall in the range defined by " $C_{s \text{ Fair}}$ " and " $n_{s \text{ Fair}}$ ". Carrier concentrations " $n_{s \text{ suprem adjusted}}$ " also tend to be

closer to Fair's chemical concentrations " $C_{s \text{ Fair}}$ ". Therefore, Fair's curves predicted carrier concentrations " $n_{s \text{ Fair}}$ " lower than the carrier concentrations " $n_{s \text{ suprem adjusted}}$ ". Despite this difference, the ranking in ascending order of TSUPREM-4 and Fair's concentrations (columns "Rank" of Table 5.5) is almost the same. This reasonable concordance provides an additional reason to believe that the ranking found by TSUPREM-4 corresponds well to the ranking of the diffusion runs in order of their actual surface concentration.

5.4.3 Numerical Results

Table 5.3 to Table 5.5 present the data utilized for characterizing the emitter profiles. The first eight rows of a table correspond to factorial points, followed by six rows of axial points and by one or six rows of centre points.

Columns " R_{sh} " give average sheet resistances calculated using five locations on the sample. Standard deviation across the wafer varied from 0.4 to 4.1 Ω/sq and uniformity (defined as twice the standard deviation divided by the average) varied from 1.1 to 7.2%. For example, for the centre point of the second design, the greatest difference among locations on a wafer was 3 Ω/sq . This corresponded to a standard deviation of 1.15 Ω/sq and a uniformity of 4%. In general, wafers with lower sheet resistances tended to have better uniformities.

TABLE 5.3: Second response surface design in IR Furnace: R_{sh} and X_j .

Time (s)	Temp. (°C)	Thick-ness (nm)	R_{sh} (Ω/sq)	R_{sh} replicate (Ω/sq)	X_j bevel and stain 1e15 (μm)	X_j suprem 1e15 (μm)	X_j suprem 1e15, adjusted (μm)	X_j suprem 1e17 (μm)	X_j suprem 1e17, adjusted (μm)
175	880	32.5	94.70	104.56	0.18	0.20	0.17	0.16	0.16
375	880	32.5	98.44	88.40	0.23	0.24	0.23	0.19	0.21
175	920	32.5	72.96	69.28	0.19	0.26	0.25	0.21	0.24
375	920	32.5	68.04	68.14	0.32	0.32	0.34	0.25	0.31
175	880	62.5	71.90	67.52	0.14	0.22	0.20	0.17	0.19
375	880	62.5	51.68	51.82	0.22	0.28	0.28	0.22	0.26
175	920	62.5	40.56	39.48	0.21	0.30	0.31	0.25	0.30
375	920	62.5	31.64	31.32	0.32	0.38	0.43	0.32	0.40
175	900	47.5	61.92	62.54	0.19	0.25	0.23	0.20	0.22
375	900	47.5	48.90	50.08	0.26	0.31	0.33	0.25	0.31
275	880	47.5	65.48	70.62	0.20	0.24	0.23	0.19	0.22
275	920	47.5	41.90	43.56	0.34	0.33	0.36	0.27	0.33
275	900	32.5	87.02	76.20	0.21	0.26	0.25	0.20	0.23
275	900	62.5	44.14	42.90	0.29	0.30	0.30	0.24	0.29
275	900	47.5	52.64		0.27	0.28	0.28	0.28	0.28
275	900	47.5	53.40			0.28	0.28	0.28	0.28
275	900	47.5	53.18			0.28	0.28	0.28	0.28
275	900	47.5	52.72			0.28	0.28	0.28	0.28
275	900	47.5	52.98			0.28	0.28	0.28	0.28
275	900	47.5	52.54			0.28	0.28	0.28	0.28

TABLE 5.4: First response surface design in IR Furnace: R_{sh} , X_j and n_s .

Time (s)	Temp. (°C)	Thickness (nm)	R_{sh} (Ω/sq)	X_j suprem 1e17, adjusted (μm)	n_s suprem, adjusted ($\times 10^{20} e/cm^3$)
120	875	25	142.82	0.13	2.14
450	875	25	130.84	0.19	1.13
120	925	25	94.22	0.20	1.88
450	925	25	108.84	0.29	0.744
120	875	65	89.1	0.16	3.26
450	875	65	49.94	0.28	3.02
120	925	65	43.36	0.28	4.20
450	925	65	26.68	0.50	3.62
120	900	45	73.26	0.19	3.02
450	900	45	52.1	0.31	2.26
285	875	45	75.92	0.20	2.42
285	925	45	39.72	0.35	2.96
285	900	25	106.36	0.22	1.36
285	900	65	44.4	0.29	3.32
285	900	45	57.84	0.26	2.52
285	900	45	58.2	0.26	2.52
285	900	45	59.46	0.26	2.48
285	900	45	55.06	0.27	2.66
285	900	45	60.14	0.26	2.46
285	900	45	59.6	0.26	2.46

TABLE 5.5: Second response surface design in IR Furnace: n_s .

Time (s)	Temp. (°C)	Thick-ness (nm)	n_s suprem ($\times 10^{20}$ e/cm ³)	n_s suprem adjusted ($\times 10^{20}$ e/cm ³)	Rank	$X_j \cdot R_{sh}$ (cm $\times 10^{-3}$ $\times \Omega$ /sq)	C_s Fair ($\times 10^{20}$ P/cm ³)	n_s Fair ($\times 10^{20}$ e/cm ³)	Rank
175	880	32.5	1.46	2.32	5	1.6	2.60	1.55	5
375	880	32.5	1.14	1.67	2	2.0	2.40	1.50	4
175	920	32.5	1.40	2.20	4	1.7	2.40	1.50	3
375	920	32.5	1.08	1.56	1	2.1	2.00	1.20	1
175	880	62.5	1.85	3.10	12	1.3	3.60	1.90	13
375	880	62.5	1.79	2.98	11	1.35	3.50	1.80	12
175	920	62.5	2.24	3.87	14	1.2	4.00	2.00	15
375	920	62.5	2.07	3.53	13	1.3	3.90	1.90	14
175	900	47.5	1.79	2.97	10	1.4	3.00	1.60	9
375	900	47.5	1.58	2.56	6	1.5	2.90	1.60	6
275	880	47.5	1.62	2.63	7	1.5	3.20	1.65	10
275	920	47.5	1.77	2.93	9	1.4	3.00	1.60	8
275	900	32.5	1.22	1.84	3	1.9	2.20	1.40	2
275	900	62.5	2.00	3.40	12	1.3	3.40	1.75	11
275	900	47.5	1.71	2.82	8	1.5	2.90	1.60	7

5.5 Analysis of Response Surface Experiments in Infrared Furnace

Once the profile is known for all experimental runs of the RSM designs in the IR furnace, an analysis with the Design-Expert software can begin. The first goal of the project was to predict the process conditions that yield a given profile. The prediction tools of the software can perform this operation quickly and simply, once the software has fitted response surfaces to the experimental data. Before looking at predictions for screen-printed cells, the fitted response surfaces are examined qualitatively. Viewing the graphs helps understand the influence of the three design factors on the three responses. Furthermore, verifying the logic behind the curves for junction depth and surface concentration increases confidence that the method utilized for their estimation is workable. The analysis

of the response surfaces for IR diffusion ends with a comparison between diffusion from thin and heavily doped source layers and from thicker layers of lower phosphorus concentration.

5.5.1 Response Surface Fitting

The quadratic models fitted to IR diffusion data are given in Appendix A. Both RSM designs yielded three models: one for sheet resistance, one for junction depth and one for surface concentration. Each one of the six models is composed of ten terms: a constant term, three terms due to linear main effects, three terms due to quadratic main effects and three terms due to the linear component of two-factor interactions.

Figure 5.4 shows excerpts of the analysis of variance for sheet resistance. The model sum of squares, a measure of the variability accounted for by the model, is calculated using nine sums of squares, one for each variable model term. The number of model degrees of freedom is equal to the number of variable model terms, nine in this case. The number of residual degrees of freedom is equal to the number of samples, 20 and 34 for the first and second design respectively, minus the number of fitted coefficients in the model, 10 in this case.

For each one of the six models obtained with the IR diffusion data, the probability that an F value this large would occur due to noise is smaller than 0.01%. This means that at least one process factor has a significant effect on the response.

Response: Rsh, first RSM design

Source	Sum of Squares	Degrees of Freedom	Mean Square	F Value	Prob > F	
Model	18427.80	9	2047.53	278.63	< 0.0001	significant
Residual	73.48	10	7.35			
Lack of Fit	56.39	5	11.28	3.30	0.1082	not significant
Pure Error	17.10	5	3.42			

Response: Rsh, second RSM design

Source	Sum of Squares	Degrees of Freedom	Mean Square	F Value	Prob > F	
Model	11189.05	9	1243.23	132.47	< 0.0001	significant
Residual	225.24	24	9.39			
Lack of Fit	33.87	5	6.77	0.67	0.6492	not significant
Pure Error	191.37	19	10.07			

Figure 5.4: Excerpts of ANOVA output for sheet resistance surface fitting in IR furnace.

ANOVA checks model adequacy with the lack-of-fit test. For all fitted response surfaces, “Prob > F” is greater than 10%, meaning that the lack of fit is not significant relative to pure (experimental) error and the quadratic model fits the data well.

The number of pure error degrees of freedom is equal to the number of samples that have an independent copy. The first design only replicated the centre point, whereas the second design also replicated the axial and factorial points. The number of pure error degrees of freedom is thus 5 and 19 for the first and second design respectively. The centre point is normally replicated so as to estimate the average pure error over the whole design space. If the centre point does not represent the average error well, then adding replicated axial and factorial points can help improve the estimate.

Comparing the two lack-of-fit tests of Figure 5.4 shows the usefulness of the replicates of factorial and axial points in improving the estimate of pure error. The software computed a larger pure error mean square for the second design (10.07 compared to 3.42), thus indicating larger variations in replicates of design points. However, the second design most likely reduced experimental error, as suggested by the sheet resistances of the centre point runs in Table 5.4 and Table 5.3; the sheet resistances varied by almost 10% in the first design whereas they rounded up or down to 53 Ω/sq in the second design. In fact, the software computed a larger pure error mean square for the second design because replicates of factorial and axial points differed more, on average, than replicates of the centre point; replicates of design points away from the centre could differ by as much as 10 Ω/sq . Hence, the first design underestimated pure error and most of the residual error was attributed to lack of fit. The quadratic model was then considered an acceptable fit for the data, but not with high confidence (“Prob > F” = 0.1082 compared to the threshold of 0.05). For the second design, ANOVA attributed most of the residual error to pure error. The quadratic model was then considered, without doubt, a good fit for the data (“Prob > F” = 0.6492). In fact, the design could have only replicated the centre and axial points (“Prob > F” = 0.6234) or the centre and factorial points (“Prob > F” = 0.3688). If only one experimental run is retained for all factorial and axial points of the second design, then the estimate of pure error becomes much smaller and the lack of fit becomes significant (“Prob > F” = 0.0001). The same conclusions are drawn when comparing the lack-of-fit tests for junction depth and surface concentration.

Model adequacy must also be checked using graphical residual analysis. Specific structural patterns in the residual plots would indicate the need for a different model or for

the inclusion of additional variables. For both designs, the residual plots did not reveal anything particularly troublesome. The points of the normal probability plot followed approximately a straight line and other plots of residuals exhibited a random scatter. The residuals of the sheet resistance models varied from -4.6 to $2.7 \text{ } \Omega/\text{sq}$ for the first RSM design and from -6.5 to $7.1 \text{ } \Omega/\text{sq}$ for the second RSM design. In this last case, three residuals corresponding to three of the highest sheet resistances somewhat stood out from the others. Ignoring these three values, the residuals varied from -4.2 to $3.4 \text{ } \Omega/\text{sq}$.

Finally, model adequacy can be assessed by checking the quality of predictions. For instance, Table 5.6 shows that the first design is successful in predicting sheet resistances of the second design. The 95% prediction interval is the range into which any individual sample is expected to fall 95% of the time. Table 5.7 shows that both designs accurately predict the sheet resistance of two additional runs performed with random process factor settings.

TABLE 5.6: Sheet resistances from second RSM design in IR furnace predicted using the first design.

Time (s)	Temp. (°C)	Thickness (nm)	Result from 2 nd design (Ω/sq)	Type of result	Prediction from 1 st design and 95% prediction interval (Ω/sq)
175	880	62.5	99.63	average of two runs	98.69 (91.85-105.54)
275	900	47.5	52.91	average of six runs	54.14 (47.75-60.52)
200	900	40	68.46	prediction	71.54 (65.08-78.01)
310	910	61	36.84	prediction	35.31 (28.51-42.11)

TABLE 5.7: Sheet resistances from additional diffusion runs in IR furnace predicted using both RSM designs.

Time (s)	Temp. (°C)	Thickness (nm)	R_{sh} (Ω/sq)	Prediction from 1 st design and 95% prediction interval (Ω/sq)	Prediction from 2 nd design and 95% prediction interval (Ω/sq)
200	905	41.5	66.22	64.65 (58.19-71.11)	62.58 (55.86-69.31)
325	910	39	59.07	62.01 (55.59-68.43)	59.18 (52.54-65.82)

5.5.2 Qualitative Influence of Time, Temperature and SOD Thickness

The Design-Expert software displays response surfaces in several ways. The most appropriate type of graph for observing interactions between factors, the “Interaction View”, contains two curves; these curves plot the response against one factor for the highest and lowest levels of a second factor. The third factor can be set anywhere between its lowest and highest levels.

A survey of the graphs plotted by the Design-Expert software showed that the first RSM design informs more intuitively than the second one about the influence of the process factors, due to the greater range of the factors and, hence, greater visibility of response surface curvatures. Therefore, the qualitative influence of time, temperature and SOD thickness is explained by referring to the graphs of the first design. The graphs of the more precise second design confirmed all of the main effects and interactions between factors. Figure 5.6 to Figure 5.8 (page 83 to page 85) contain graphs from the first design referred to by this section.

5.5.2.1 Main Effects

The main effect of a factor indicates the change in response due to a change in the level of the factor. With three factors and three responses, nine main effects exist.

First, an increase in SOD thickness causes sheet resistance to decrease (Figure 5.6a,b), junction depth to increase (Figure 5.7a) and surface concentration to also increase (Figure 5.8a). The small increase in sheet resistance on Figure 5.6a for layers thicker than about 60 nm is absent from the second design, becomes insignificant in the first design if the 95% prediction interval is plotted and can thus be attributed to imprecise

surface fitting. Second, an increase in temperature causes sheet resistance to decrease (Figure 5.6c), the junction to become deeper (Figure 5.7b) and surface concentration to either increase or decrease (Figure 5.8c,d). Third, an increase in time causes the junction to become deeper (Figure 5.7c), surface concentration to decrease (Figure 5.8b) and sheet resistance to either increase or decrease (Figure 5.6d). Junction progression slows down over time, as predicted by the square-root law (See “Influence of Time” on page 23).

Factor variations that cause the response to either increase or decrease point to an interaction with other factors. In fact, the majority of main effects involve at least one interaction, as explained in the next three sections.

5.5.2.2 Interaction Between SOD Thickness and Time

For all three responses (R_{sh} , X_j and n_s), a variation in SOD thickness fails to produce the same variation in response for different time lengths. Therefore, an interaction exists between diffusion time and source thickness for all three responses, as confirmed by the ANOVA output. (The model term due to the interaction is considered significant if “Prob > F” < 0.05. For the first and second design respectively, for R_{sh} : “Prob > F” < 0.0001 and = 0.0095, for X_j : “Prob > F” = 0.0002 and < 0.0001, and for n_s : “Prob > F” = 0.0005 and = 0.0005.)

This interaction exists because the percentage of phosphorus lost by the source layer during diffusion depends on both diffusion time and source thickness. For large enough percentages of source depletion, the SOD layer behaves as a finite source and surface concentration decreases over time. Longer times cause more source depletion and thus lead to a lower surface concentration. Similarly, thinner layers lose a larger percent-

age of their phosphorus and yield lower surface concentrations. Combining these two effects gives the interaction: an increase in diffusion time leads to a greater decrease in surface concentration for thinner layers (Figure 5.8a,b). The longer the time, the stronger the influence of source thickness on final surface concentration. Since the junction becomes deeper more slowly for lower surface concentrations, an increase in diffusion time produces a smaller increase in junction depth for thinner layers (Figure 5.7c).

This interaction is also observed by looking at the thickness threshold above which surface concentration stays constant during diffusion and, consequently, above which the profile is independent of thickness. The threshold depends on diffusion time. For shorter times, the threshold occurs at thinner layers (Figure 5.6e, Figure 5.7e, Figure 5.8a). Shorter times cause less source depletion; hence, thinner layers can provide a sufficient supply of phosphorus to act like an infinite source.

Finally, sheet resistance can either increase or decrease over time, depending on source thickness (Figure 5.6d). For thick layers, the effect of a deeper junction prevails over the effect of a lower surface concentration, hence sheet resistance decreases over time. For thin layers sufficiently depleted during diffusion, the opposite happens and sheet resistance increases. The prospect of sheet resistance increasing over time is not interesting for solar cell fabrication. To avoid wasting time, the emitter formation process should avoid such factor regions.

5.5.2.3 Interaction Between SOD Thickness and Temperature

Higher temperatures increase phosphorus diffusivity in silicon dioxide [50][51] and volatility of phosphorus compounds, among other effects. It is therefore expected that

temperature helps determine, along with time, whether the SOD layer is thin enough for source depletion to significantly affect the diffusion profile. In fact, the ANOVA output signals an interaction between source thickness and temperature, although only for junction depth and surface concentration. (For the first and second design respectively, for R_{sh} : “Prob > F” = 0.8389 and = 0.5326, for X_j : “Prob > F” = 0.0008 and < 0.0001, and for n_s : “Prob > F” < 0.0001 and < 0.0001.)

This interaction comes about because higher temperatures modify surface concentration differently for different source thicknesses (Figure 5.8*c,d*). For thick SOD layers, an increase in temperature makes surface concentration increase. This appears logical since higher temperatures increase the ratio of wafer surface concentration to source interface concentration. However, for thin layers, an increase in temperature can make surface concentration decrease, especially for long diffusion times (Figure 5.8*e*). This suggests that higher temperatures enhance source depletion. It is thus observed that higher temperatures can affect surface concentration in two opposite ways and the predominant effect depends on source thickness. The junction can only become deeper with increasing temperature, but less noticeably for thinner layers (Figure 5.7*a,b*) due to lower surface concentrations.

Since both surface concentration and junction depth increase more, with increasing temperature, for thicker layers, it is presumable that sheet resistance would decrease more, with increasing temperature, for thicker layers. However, sheet resistance always decreases by the same amount for a given increase in temperature, regardless of source thickness (Figure 5.6*a,b*). The interaction deduced from the junction depth and surface concentration data can still exist even though sheet resistance was reliably measured, con-

trarily to junction depth and surface concentration. In fact, an increase in temperature may cause greater increases in surface concentration and junction depth for thick rather than thin source layers, but the difference between the resultant sheet resistances may be too small for the interaction to show on the response surface fitted to the sheet resistance data.

5.5.2.4 Interaction Between Time and Temperature

The variation in emitter profile over time involves an interaction with temperature. The ANOVA output indicates this interaction, although only for sheet resistance and junction depth. (For the first and second design respectively, for R_{sh} : “Prob > F” < 0.0001 and 0.0508, for X_j : “Prob > F” = 0.0004 and < 0.0001, and for n_s : “Prob > F” = 0.1076 and = 0.3193.)

This interaction stems from the temperature dependence of the square-root law governing the variation in junction depth over time. Figure 5.5 illustrates conceptually the progression of junction depth for two temperatures, from the start of the diffusion to the time when both “junctions” are equal to the sample thickness, for the case of an infinite phosphorus supply. The curves illustrate the relatively rapid progression of junction depth at the beginning of the diffusion and the subsequent slowdown. The junction becomes deeper faster in the beginning because the phosphorus concentration gradient in silicon is then steeper. As phosphorus diffuses, the concentration gradient flattens and diffusion slows down. For the higher temperature, the relative importance of early diffusion is greater; the junction becomes deeper faster at the beginning and slows down more quickly because the concentration gradient disappears more quickly. The time period covered by the experiments corresponds to the left side of the figure: the higher the temperature, the larger the increase in junction depth for a given increase in time (Figure 5.7d).

Figure 5.5: Junction depth vs. time for two temperatures.

The interaction between time and temperature also shows on the response surface fitted to the sheet resistance data. An increase in diffusion time causes a smaller decrease in sheet resistance for higher temperatures (Figure 5.6f). This happens because sheet conductance, the inverse of sheet resistance, also follows a square-root curve whose shape depends on temperature. Similarly to junction depth, sheet conductance increases quickly at the beginning of the diffusion and more slowly afterwards.

According to the ANOVA output, an increase in time produces a constant decrease in surface concentration, regardless of temperature. However, the interaction between time and temperature may actually affect surface concentration since the “Prob > F” fractions are relatively close to the threshold (0.1076 and 0.3193 compared to 0.05). Moreover, a visual inspection of the graphs indicates that surface concentration decreases more quickly for higher temperatures (Figure 5.8f). Equivalently, an increase in time results in a greater decrease in surface concentration for higher temperatures. Therefore, this interaction agrees with the idea that a given diffusion time causes more source depletion at higher temperatures. This was observed earlier for sufficiently thin layers (See “Interaction Between SOD Thickness and Temperature” on page 79, second paragraph).

Figure 5.6: Views of the response surface fitted to the sheet resistance data of the first RSM design in the IR furnace.

Figure 5.7: Views of the response surface fitted to the junction depth data of the first RSM design in the IR furnace.

Figure 5.8: Views of the response surface fitted to the surface concentration data of the first RSM design in the IR furnace.

5.5.3 Cause of Source Depletion

When surface concentration decreases over time, the phosphorus content of the SOD layer does not suffice to replenish the SOD concentration at the interface. In this case, the SOD layer acts like a finite source and phosphorus concentration decreases over time everywhere within the layer. Some phosphorus evaporates and some diffuses into the wafer. Phosphorus loss by evaporation, rather than by diffusion, is mainly responsible for source depletion and for dependence of doping on SOD thickness, as W. Zagodzón-Wosik *et al.* suggested [31]. This can be verified by comparing the diffused phosphorus doses, calculated by Solecon Laboratories, for the two spreading resistance profiles shown earlier (See Figure 5.3). For (a) 175 seconds of diffusion at 880°C from a 32.5 nm thick layer, a dose of 6.4×10^{14} P/cm² diffused into the silicon, whereas for (b) 375 seconds of diffusion at 920°C from a 62.5 nm thick layer, the diffused dose was 2.75×10^{15} P/cm². These doses correspond to (a) 2×10^{13} and (b) 4.4×10^{13} P/cm² per nm of source layer. Less phosphorus diffused per unit source thickness in the former case, but the layer acted more like a finite source, as shown on Figure 5.9: thickness influenced sheet resistance more strongly. This means that the ratio of diffused dose to original supply does not determine the level of source depletion. Instead, the ratio of evaporated phosphorus to original supply determines whether the layer acts like a finite source. The thinner the layer, the greater the percentage of phosphorus exposed to the ambient at the surface and, therefore, the greater the importance of source depletion by evaporation.

Figure 5.9: Influence of thickness on sheet resistance for the cases with (a) the lowest and (b) the largest amounts of diffused phosphorus.

All three design factors differed between the two profiles measured by SRA. Hence, a judgement cannot be made from this example about whether a source layer that becomes more depleted due to either a longer time or a higher temperature becomes more depleted mainly because of additional evaporation or diffusion into silicon. However, diffused phosphorus doses calculated by TSUPREM-4 suggest that a longer time causes more source depletion because of additional evaporation, whereas the cause of greater source depletion due to a higher temperature is not as clearly defined. For instance, TSUPREM-4 calculated practically the same diffused dose for diffusions at 920°C from a 32.5 nm thick layer for 175 or 375 seconds. Hence, the increase in source depletion after a longer time necessarily arises from additional evaporation. On the other hand, TSUPREM-4 calculated a diffused dose larger by a factor of 1.4 at 920°C rather than 880°C, when phosphorus is diffused from a 32.5 nm thick layer for 375 seconds. Hence, the cause

of increased source depletion at higher temperatures is more ambiguous and probably arises from a mix of increased evaporation and increased diffusion into silicon.

5.5.4 Arrhenius and Square-Law Behaviours

Model validity was previously verified by residual analysis and by examining the qualitative behaviour of the fitted response surfaces. An additional way of verifying the model is to check whether the data follow the square-root and Arrhenius behaviours. As expected, Arrhenius plots ($\log y$ versus $1/\text{temp.}$) of sheet resistance and junction depth produced straight lines for any time and SOD thickness. The square-root law was also checked for junction depth and sheet resistance. The plots of junction depth followed approximately straight lines for any level of temperature and source thickness. The plots of sheet conductance, however, clearly showed the effect of source depletion as they curved more pronouncedly for higher temperatures and thinner source layers. Figure 5.10 shows the plots for the two extreme temperatures and source thicknesses of the second response surface design.

Figure 5.10: Sheet conductance vs. square root of time for the two extreme temperatures and SOD thicknesses.

5.5.5 Infrared Emitter Diffusion for Screen-Printed Cells

Once the fitted response surfaces are checked and judged valid, the Design-Expert software can be utilized as a prediction tool for selecting process conditions. In the following example, the emitter is assumed to require a sheet resistance between 50 and 52 Ω/sq , a junction depth between 0.25 and 0.27 μm and a carrier surface concentration in the $2\text{--}3 \times 10^{20} \text{ e/cm}^3$ range, somewhat like emitters of screen-printed cells found in the literature.

The Design-Expert software provides numerical and graphical prediction capabilities. Two numerical tools find exact points of the design space that satisfy criteria related

to profile and process factors while a graphical tool gives an overview of the regions of the design space that satisfy multiple constraints imposed on the profile. The graphical tool overlays contour plots for all three responses and highlights the “windows” that simultaneously meet the requirements for sheet resistance, junction depth and surface concentration. Figure 5.11 shows overlay plots displayed with time and temperature on the x and y axis respectively. Areas that meet the requirements are highlighted in grey.

Figure 5.11: Overlay plots showing regions of the factor space that meet the specified requirements for the emitter profile.

The highlighted area (*a*) appears in the top-left corner for a 45 nm thick layer, (*b*) lies close to the middle of the overlay plot at 50 nm, (*c*) prepares to leave the graph at 55 nm and (*d*) has almost disappeared at 62.5 nm. (The contour for $n_s = 2 \times 10^{20} \text{ e/cm}^3$ crosses the right side of the graph around 39 nm.) The path followed by the highlighted region through the time-temperature graph shows that the specified profile is obtained either with high temperatures, short times and thin layers or with lower temperatures, longer times and thicker layers. On the one hand, a junction diffused from a thin source layer must reach the specified depth quickly because otherwise too much phosphorus evaporates during the diffusion process, surface concentration ends up too low and sheet resistance ends up too high. On the other hand, diffusion from thick layers must take a long time, or else not enough phosphorus evaporates and surface concentration remains too high. Different source thicknesses therefore require different sets of process conditions. If SOD thickness can be controlled, then time and temperature can be set in many different ways. For instance, the process could occupy the whole time slot available in a production line and thus use the lowest possible furnace temperature.

Process development aims at setting the process factors so that the response is almost always near the desired nominal value. To determine whether response variability should help select process conditions, the change in sheet resistance in response to small variations of the design factors was examined for several points of the feasible regions. For instance, Table 5.8 compares two points belonging to the highlighted areas of Figure 5.11 (*a*) and (*d*) respectively.

TABLE 5.8: Sheet resistance variation due to small changes in the process factors.

Time (s)	Temp. (°C)	Thick-ness (nm)	ΔR_{sh} for time – 5 seconds (Ω/sq)	ΔR_{sh} for temp. + 2°C (Ω/sq)	ΔR_{sh} for thickness – 10 Å (Ω/sq)
190	915	45	0.35	–1.18	1.27
375	880	62.5	0.23	–1.38	0.23

For all examined points, variations in time and temperature affected sheet resistance almost equally. In addition, furnaces can control these two process factors precisely. Time and temperature selection, therefore, does not need to consider response sensitivity to small changes in process factors. On the other hand, variations in source thickness affected sheet resistance more strongly for thinner layers. Hence, process developers must ensure that the equipment utilized for depositing the source layer satisfies the uniformity requirements. In this project, the spin coater achieved satisfying uniformity across the wafer and from run to run, as demonstrated by the centre runs of the second RSM design in the IR furnace.

5.5.6 Advantages of Thin and Heavily Doped SOD Layers

The preceding section showed that diffusion from thin and heavily doped SOD layers can produce adequate emitters for screen-printed cells. This option not only works but also has several advantages compared to using thick (> 100 nm) and moderately doped ($< 3 \times 10^{20}$ P/cm³) layers.

First, thin layers lower the emissions of organic solvents and phosphorus compounds, reduce chemical wastes, as well as the time required to strip off the layer in HF after diffusion. Thin layers also decrease material cost, although the need for well-controlled source deposition may increase equipment cost. Next, diffusion of a given profile

from thin and heavily doped layers probably takes less time. This point cannot be proven due to lack of data, but the following reasoning seems correct and leads to this conclusion. As illustrated on Figure 5.12, if a given profile is diffused from both types of source layers, then surface concentration remains constant during diffusion in the case of the thick layer, but decreases in the case of the thin layer. Surface concentration of the wafer coated with the thin layer is higher, not only at the beginning of the diffusion, but during the whole process, until the final moment where surface concentration reaches the required value. Since surface concentration is always higher, the concentration gradient is steeper for any junction depth. And the rate of junction depth progression increases with the concentration gradient. Therefore, if both diffusions happen at the same temperature, then diffusion from the thin layer should take less time to achieve the same junction depth and surface concentration.

Figure 5.12: Diffusion from (a) thick and moderately doped SOD layer and (b) thin and heavily doped SOD layer.

The next advantage of thin and heavily doped source layers concerns the reliability of interpolation within the factor space. With the thin-layer option, the diffusion process is controlled by varying SOD thickness, in addition to diffusion time and temperature, whereas diffusion from thick layers is controlled by varying source concentration as the third process factor. Varying a third factor gives more flexibility to the process since an infinite number of combinations of time and temperature can then yield the required profile (See Figure 5.9 on page 87). In theory, varying SOD concentration can provide as much flexibility as varying SOD thickness. However, varying source concentration is likely to engender greater experimental errors because measured concentrations contain an error on the order of at least 10% [34], whereas ellipsometry can measure source thickness with sub-Angstrom precision. In addition, measuring thickness takes less time and the equipment is more common. Therefore, varying source thickness rather than concentration as the third design factor facilitates the monitoring of the actual experimental values.

Finally, an additional advantage of the thin-layer option results from the ease with which source thickness can be varied, once the relationship between deposition settings and source thickness is known. In comparison, setting source concentration to a new level requires preparing a new solution as precisely as possible and, if the source is applied with a sprayer, replacing the solution in a dispenser. If many mixes are prepared during the experiments, a large volume of remaining solution is likely to be wasted. Since varying source thickness rather than source concentration takes less time and creates no waste, the thin-layer option gives access to the whole design space more conveniently.

5.6 Response Surface Experiment in Tube Furnace

Prior to the experiments on IR diffusion, a face-centred central composite design was used for studying the influence of the three design factors on the profile of an emitter diffused in the quartz tube furnace. Emitter diffusion from a SOD source is almost never performed in a tube furnace in the photovoltaics industry, but a response surface experiment was conducted in the tube furnace in order to compare resistance- and lamp-heating. Despite some imprecision in source thickness (explained on page 52), the analysis of variance considered the lack of fit between modeled and measured sheet resistance insignificant (“Prob > F” = 0.1051). Sheet resistance varied from 21 to 138 Ω/sq . Due to this broad range, a “reciprocal square root” transformation, recommended by the Design-Expert software, was applied to the sheet resistance data in order to obtain an insignificant lack of fit.

The response surface fitted to the sheet resistance data showed that the selected range of SOD thickness was broader than necessary. The range was narrowed for the subsequent response surface design in the IR furnace so as to exclude thin layers yielding sheet resistances above 100 Ω/sq and thick layers in the range where varying thickness hardly affects the profile. Figure 5.13 shows that the correct range is approximately 25-65 nm. (The increase in sheet resistance with increasing thickness can be attributed to imprecise surface fitting.)

Figure 5.13: Sheet resistance vs. source thickness for 15 minutes of quartz tube furnace diffusion at 900°C.

The comparison between models of tube and IR diffusion looked for differences in the influence of the three design factors. The qualitative comparison of the response surfaces showed no significant differences. To make possible quantitative comparisons, the response surfaces would need to contain either identical process conditions or identical profiles diffused with two of the three factors set at the same level. Unfortunately, the response surfaces satisfied neither of these requirements. For example, the results cannot tell which process can diffuse a given emitter faster, because neither the process conditions nor the ranges of profiles obtained from identical sets of temperature and source thickness overlapped. The process conditions did not overlap because the response surfaces covered different time ranges: the minimum time of 15 minutes selected for tube diffusion corresponded to at least 8 minutes at peak temperature while the maximum time at peak temperature in the IR furnace was 7.5 minutes. Further, the ranges of profiles obtained from same temperature and source thickness did not overlap because, for any combination of temperature and SOD thickness, the maximum sheet resistance obtained from tube diffusion was lower than the minimum sheet resistance obtained from IR diffusion. For exam-

ple, for 900°C and 50 nm, tube diffusion resulted in sheet resistances of at most 32 Ω/sq (after 15 minutes) while IR diffusion yielded at least 48 Ω/sq (after 7.5 minutes). The comparison between response surfaces can therefore not determine whether tube diffusion would give lower or higher sheet resistances than IR diffusion for the same short times.

The comparison between response surfaces revealed, however, a significant difference in the effect of source depletion on sheet resistance. For any combination of temperature and source thickness, the increase in sheet resistance over time started a lot earlier during IR diffusion than during tube diffusion. As a consequence, sheet resistance could never possibly become as low during IR diffusion as during tube diffusion. For example, for 900°C and 45 nm, sheet resistance obtained from tube diffusion kept decreasing from 15 to 45 minutes, whereas sheet resistance in the IR furnace started to increase after 6.3 minutes (380 seconds). In fact, in the case of tube diffusion, the increase over time in sheet resistance only becomes clearly visible with very thin layers and after a long time, for example after 37 minutes if the source layer is 22.5 nm thick, as shown on Figure 5.14.

Figure 5.14: Sheet resistance vs. time for tube diffusion at 900°C from a 22.5 nm thick source layer.

These results indicate that after sufficiently long diffusion times, sheet resistance of wafers diffused in the IR furnace increases over time while sheet resistance of wafers coated with the same source layer and diffused in the tube furnace still decreases over time. This suggests that phosphorus evaporates from the source layer at a higher rate during IR diffusion. A possible explanation is that the slow heating rate in the tube furnace allows the SOD layer to densify for several minutes prior to the segment of the thermal cycle responsible for most of the phosphorus evaporation. The faster heating rate in the IR furnace would thus leave the source layer more porous than in the tube furnace when the wafer reaches peak temperature, hence the higher phosphorus evaporation rate.

TSUPREM-4 simulations performed to estimate the depth of junctions diffused in the tube furnace supported the idea that less phosphorus evaporated during the tube diffusion runs. The simulations read the input parameters from files similar to the one shown earlier (See Figure 5.2 on page 60), except that the ambient contained 5% oxygen instead of 21% and that the time was specified as the total diffusion time, from beginning of loading to end of unloading, rather than the time spent at peak temperature. Source thickness was adjusted so that the simulation would give the same sheet resistance as the one measured by the four-point probe. In the case of IR diffusion, the ratio of final thickness in the input file to measured thickness was between 0.13 and 0.32, whereas in the case of tube diffusion, the ratio was between 0.2 and 1. For this last case, increasing thickness in the input file beyond the measured thickness did not yield the measured sheet resistance. Instead, source concentration had to be increased from $3.5 \times 10^{21} \text{ P/cm}^3$ to $7 \times 10^{21} \text{ P/cm}^3$. If the input files specify shorter diffusion times to take into account the delay before

the wafer reaches peak temperature, then a few simulation runs require a concentration greater than 3.5×10^{21} P/cm³.

Even if phosphorus evaporates at a faster rate during IR diffusion, emitter formation does not necessarily need more time at peak temperature since the source layer thickness can be adjusted to provide the right amount of phosphorus despite evaporation. In fact, the most important factors in determining the time required from start to end of the process are the heating and cooling rates. Emitter diffusion takes less time in an IR furnace because radiation can heat wafers faster than convection. Cooling is also faster since the thermal mass to cool down is smaller. In examples of temperature profiles at 900°C shown earlier (See Figure 4.2 and Figure 4.3), peak temperature was reached within four minutes in the IR furnace compared to seven minutes in the tube furnace. The cooling was also quite faster in the IR furnace, taking only about one minute to reach 760°C, compared to 3.5 minutes in the tube furnace. Since emitter diffusion for screen-printed cells from a SOD layer only requires around three to six minutes at peak temperature, the temperature ramps greatly affect the total diffusion time.

5.7 Summary of Results and Discussion

This chapter explained the reasoning followed to obtain a procedure for controlling the phosphorus distribution of an emitter diffused in an IR furnace. The chapter started by giving the conclusions drawn from the screening experiments conducted prior to the RSM experiments. The next part of the chapter explained the approach taken to determine the doping profile of all wafers diffused in the IR furnace. This part discussed the concerns about the method of bevel and stain and presented a substitute approach based on four-

point probe measurements, TSUPREM-4 simulations and spreading resistance analysis. This approach gave surface concentration as well as junction depth, and yet Fair's model was investigated as a way to deduce surface concentration from junction depth and sheet resistance. The model was found to give a useful, though approximate, idea of surface concentration. The chapter then proceeded with a verification of the response surface fitting performed by the Design-Expert software. This verification showed that the studied region of the process parameter space was, on one hand, narrow enough for a quadratic model to fit the data well and, on the other hand, wide enough to allow the distinction of significant factor effects from experimental error. The subsequent qualitative analysis of the response surfaces fitted to the data showed that their behaviour seems correct and thus supported the idea that the suggested method for estimating the doping profile is workable. Next, the chapter presented arguments based on calculated diffused doses in order to show that the phosphorus-doped source layer is depleted mainly by evaporation. Then, Arrhenius and square-law behaviours were briefly mentioned as an additional way of verifying the validity of the response surfaces. Afterwards, the chapter presented an example, tailored to screen-printed cells, of graphical prediction from the response surfaces. This example confirmed that varying SOD thickness, diffusion time and temperature can provide good control over the profile of emitters designed for screen-printed cells. A discussion followed on the advantages of using thin source layers of concentration higher than the solid solubility of phosphorus in silicon, as opposed to thicker layers of concentration close to the desired wafer surface concentration. The chapter ended by giving the conclusions drawn from the tube furnace RSM experiment. This design helped plan the subsequent RSM experiments in the IR furnace, for example by underlining the importance of

monitoring the process parameters and of selecting their ranges appropriately. The data did not permit much comparison between IR- and resistance-heating, but it appears that the source layer became depleted of phosphorus at a lower rate in the tube furnace.

6.1 Introduction

This thesis only studied the formation of the p-n junction, but it seemed worthwhile to fabricate a solar cell and thus demonstrate the validity of the diffusion process. This chapter presents the fabrication steps and the measured characteristics.

6.2 Fabrication

The starting wafer was identical to the ones diffused during the course of the project. After cleaning the bare p-type wafer, a mask oxide approximately 100 nm thick was thermally grown on the surface and then etched to open diffusion windows. The wafer was diffused in the IR furnace using the process parameters corresponding to the centre of the second face-centred central composite design. The wafer was therefore coated with a 47.5 nm thick phosphorus source layer and diffused at 900°C for 275 seconds. This combination had previously yielded 53 Ω/sq , but the presence of a pattern on the wafer modified the thickness of the SOD layer and resulted in a sheet resistance of 61 Ω/sq . After diffusion, the wafer was etched in dilute HF for a time sufficient to remove the SOD layer and short enough to leave the mask oxide on the silicon surface. The wafer was then met-

alized by depositing three layers. First, a 30 nm thick titanium layer was sputtered to provide good adhesion and low-resistance contact with the silicon surface. Second, a 200 nm thick titanium-tungsten alloy was sputtered to form a diffusion barrier preventing the metal atoms from the top layer to reach the silicon wafer. Third, aluminium was deposited by e-beam evaporation to create a 1 μm thick conductive layer. The metallization mask, developed by a former graduate student at Carleton University [52], is shown on Figure 6.1. The larger cell measures 2 cm $\times$ 2 cm and the two smaller cells measure 0.5 cm $\times$ 0.5 cm.

Figure 6.1: Front contact grid and surrounding test devices.

6.3 Characterization

The solar cell characteristics were measured on one of the two smaller cells in order to illuminate the area as uniformly as possible. The dark I-V characteristic was first measured. The curve shown on Figure 6.2 reveals a rather high reverse leakage current

density of 0.4 mA/cm^2 . By comparison, currents on the order of $1 \text{ } \mu\text{A/cm}^2$ are expected from electronic devices. The high leakage current might have been caused by contamination from the furnace metal belt, by the fact that the silicon wafer dated from 25 years ago or by many other factors.

Figure 6.2: Dark characteristic.

The cell was illuminated from a distance of about 10 cm by a 50 W halogen lamp. The light current-voltage curve is plotted on Figure 6.3, along with the curve of power versus voltage.

The short-circuit current density of 35 mA/cm^2 is close to the values expected from industrial cells measured under standard conditions. The open-circuit voltage of 560 mV is slightly lower than desired, as industrial cells commonly reach 600 mV. The fill factor, which is the ratio of the maximum power to the product of the open-circuit voltage and short-circuit current, is 0.7. This is also a little lower than industrial standards, since around 0.77 is expected from screen-printed cells.

Figure 6.3: Illuminated characteristic.

6.4 Conclusion

The simple cell analysis showed the potential of the diffusion process studied in this thesis for fabricating useful energy conversion devices. The illuminated cell characteristic was encouraging for a first trial and it is believed that the diffusion process can yield competitive efficiencies if used in conjunction with current industrial fabrication techniques.

Conclusions and Recommendations

7.1 Conclusions

This thesis focused on one of the many processes involved in fabricating low-cost solar cells, namely, emitter diffusion from a spin-on/spray-on phosphorus source in an IR conveyor belt furnace. The main objective of the study was to develop a method for controlling the emitter profile over a suitable range to accommodate screen-printed cells with homogeneous emitters made within the next few years. The desired profile variation was obtained by varying three process factors: thickness of the phosphorus-doped source layer, diffusion time and diffusion temperature. Design of Experiments, more particularly response surface methodology, was used for mathematically modeling the relationship between design factors and emitter profile. The response surface experiments followed the face-centred central composite design. In this study, most of the experimental error arose from the need to subject the wafers to a long baking at high temperature and to carry them to the building with the IR furnace off campus. In particular, baking temperature and the delay between baking and diffusion inevitably varied. Run-to-run variation would be greatly reduced if the source layer could be applied beside the furnace.

The number of replicated runs needed to estimate pure (experimental) error depends on the experimental conditions and on the risk the process developer is willing to take. At the least, the design needs to estimate pure error sufficiently well for the lack of fit between model and data to be considered insignificant. To estimate pure error, the response surface design always replicates the experimental trial in which all factors are set at the midpoint of the study range. To get a sufficiently precise estimate, the design may also need to replicate trials at the extreme level settings of the variables.

The profile of all diffused samples was characterized by three parameters: sheet resistance, junction depth and surface concentration. While sheet resistance was readily measured using a four-point probe, the two other parameters posed some problems. Junction depth was first measured using the method of bevel and stain available in-house at practically no cost. However, due to the lack of precision, the behaviour of the response surface fitted by the Design-Expert software did not always agree with diffusion theory. Another available method, TSUPREM-4 software simulations of the diffusion process, was tried out. The simulations received, as input parameters, the process conditions and the measured sheet resistances. The software provided estimates of acceptable accuracy, as confirmed by spreading resistance analysis of two wafers. Furthermore, the variations in junction depth and surface concentration can be explained by using simple physical arguments. To improve precision of the simulated results, a linear transformation was applied to all simulated junction depths and surface concentrations so that SRA measurements would perfectly coincide with the corresponding simulations. The need to make response surface fitting affordable therefore led to a low-cost method of estimating junction depth and surface concentration quickly for many samples.

Another positive outcome of this research is that it demonstrates the possibility of diffusing the emitter from a thin and heavily doped SOD layer acting like a finite source of phosphorus rather than from a thick layer of lower concentration. Profiles diffused from thin source layers strongly depend on source thickness because of the dependence on thickness of the percentage of phosphorus lost by evaporation. Predictions made by the fitted response surfaces indicated that infrared furnace diffusion of emitters for screen-printed cells at usual temperatures (880°C-920°C) and from thin source layers (45-62.5 nm) only takes a few minutes. Emitter formation using thin SOD layers therefore proved to work well and, in addition, has several advantages, such as lower chemical emissions and shorter etch after diffusion. The only apparent inconvenience is the need for equipment able to apply the source layer uniformly, with well-controlled thickness and a high enough throughput for mass production.

7.2 Recommendations for Future Work

If future research can verify the procedure suggested for developing the emitter formation process, then the procedure could be used in making complete solar cells. First, the method for estimating junction depth and surface concentration based on software simulations and two precise profile measurements could be verified. Second, the options of diffusing the emitter from thin or thick layers acting respectively like finite or infinite sources of phosphorus could be further compared in experiments in which source concentration as well as source thickness would be varied. If the thin-layer option proves just as good or better, then a comparison could be made between the cost of acquiring or developing proper equipment to apply thin layers in the context of mass production and the cost of

current industrial techniques for applying the phosphorus source. Finally, if the cost of the former is judged reasonable, then complete industrial cells could be developed using thin SOD layers and the DOE approach. The use of response surface methodology would make it easier to control the emitter while optimizing all cell parameters together.

To pursue further research, selective emitters for screen-printed cells could be formed by extending the emitter control procedure and refining the application of the phosphorus-doped source layer. (Selective emitters have a deeply diffused junction of high surface concentration under the metal grid, to assure low contact resistance, and a shallow junction with a relatively low surface concentration in the photon-collecting area, to permit high short-wavelength collection efficiency.) Some ideas for selective emitter formation include adding phosphorus to the metal paste [53], etching back the surface after metallization [54] and applying two different dopant sources to the two different regions [55]. This last option seems complicated because the metallization must be aligned with the previously diffused pattern. However, if this problem is surmounted, then the diffused profiles of the two regions could be controlled nearly independently. Some dependence would remain because the region under the metal grid will affect the light-exposed region to some extent. To realize this option with only one thermal step, the two phosphorus-doped materials must cohabit on the wafer without interfering with each other. To begin with, a phosphorus paste of relatively high viscosity could be applied to the grid region through a patterned screen. Then, the whole wafer could be covered with a layer of liquid phosphorus source. Since the photon-collecting area is relatively lightly diffused and needs a sheet resistance on the order of $100\ \Omega/\text{sq}$, the source layer applied to the whole wafer could be very thin, on the order of 25 nm, and thus exert only little stress on the grid

pattern. The simultaneous diffusion of the two phosphorus-doped regions could well work, but aligning the metal contact grid with the diffused pattern in a simple way suitable for mass production is crucial. The wafer must be uniquely positioned relative to the screen prior to screen printing both the diffusion source and the metal paste. Many mechanical and optical positioning systems exist to align the screen with the wafer, hence a precise alignment of the diffused and metal patterns is probably feasible without significantly increasing the cost of the screen printer. However, an additional screen-printing step is required prior to diffusion. If the cost of selective emitters is considered acceptable and their formation becomes well controlled, then solar cells could be fabricated and optimized so as to fully realize the improved fill factor and blue response.

In conclusion, this thesis gives a small example of all the experimental work that is needed to make the cost of photovoltaic power become comparable to non-renewable sources of energy. Since the size and resources of the photovoltaics community are limited, research efforts must be allocated efficiently. Current technology must be improved, as was the impetus for this thesis, and more drastic changes must be studied and debated. It is hoped that choices made today will allow photovoltaics as well as renewable energies of all kinds to flourish everywhere in the future.

A.1 Equations Obtained from First RSM Design

$$R_{sh} = +3650.60903 - 1.42422 \times \text{time} - 6.44689 \times \text{temperature} - 5.74189 \times \text{thickness} \\ + 2.46131\text{E-}004 \times \text{time}^2 + 2.94545\text{E-}003 \times \text{temperature}^2 + 0.048502 \times \text{thickness}^2 \\ + 1.48727\text{E-}003 \times \text{time} \times \text{temperature} - 2.21515\text{E-}003 \times \text{time} \times \text{thickness} + 4.00000\text{E-}004 \\ \times \text{temperature} \times \text{thickness}$$

$$X_j = +17.67173 - 3.23309\text{E-}003 \times \text{time} - 0.038829 \times \text{temperature} - 0.034141 \times \text{thickness} \\ - 5.88697\text{E-}007 \times \text{time}^2 + 2.13964\text{E-}005 \times \text{temperature}^2 - 2.16932\text{E-}005 \times \text{thickness}^2 \\ + 7.23864\text{E-}006 \times \text{time} \times \text{temperature} + 7.23864\text{E-}007 \times \text{time} \times \text{thickness} + 4.04250\text{E-}005 \\ \times \text{temperature} \times \text{thickness}$$

$$n_s = +1.90222\text{E+}022 + 7.26555\text{E+}017 \times \text{time} - 4.05677\text{E+}019 \times \text{temperature} - \\ 4.44440\text{E+}019 \times \text{thickness} + 2.94582\text{E+}014 \times \text{time}^2 + 2.16320\text{E+}016 \times \text{temperature}^2 - \\ 6.21750\text{E+}016 \times \text{thickness}^2 - 1.54667\text{E+}015 \times \text{time} \times \text{temperature} + 5.53333\text{E+}015 \times \text{time} \\ \times \text{thickness} + 6.00600\text{E+}016 \times \text{temperature} \times \text{thickness}$$

A.2 Equations Obtained from Second RSM Design

$$R_{sh} = +4203.39083 - 0.80035 \times \text{time} - 7.94184 \times \text{temperature} - 5.92856 \times \text{thickness} \\ + 2.02620\text{E-}004 \times \text{time}^2 + 3.89049\text{E-}003 \times \text{temperature}^2 + 0.038805 \times \text{thickness}^2 \\ + 7.87500\text{E-}004 \times \text{time} \times \text{temperature} - 1.43833\text{E-}003 \times \text{time} \times \text{thickness} + 1.61667\text{E-}003 \\ \times \text{temperature} \times \text{thickness}$$

$$X_j = +1.98976 - 2.49091\text{E-}003 \times \text{time} - 4.58868\text{E-}003 \times \text{temperature} - 0.026230 \times \text{thick-} \\ \text{ness} - 6.44366\text{E-}007 \times \text{time}^2 + 2.64085\text{E-}006 \times \text{temperature}^2 - 4.53052\text{E-}005 \times \\ \text{thickness}^2 + 3.28125\text{E-}006 \times \text{time} \times \text{temperature} + 5.62500\text{E-}006 \times \text{time} \times \text{thickness} \\ + 3.43750\text{E-}005 \times \text{temperature} \times \text{thickness}$$

$$n_s = +4.03762\text{E+}021 + 6.59948\text{E+}017 \times \text{time} - 6.86036\text{E+}018 \times \text{temperature} - \\ 4.88665\text{E+}019 \times \text{thickness} - 4.22535\text{E+}013 \times \text{time}^2 + 2.69366\text{E+}015 \times \text{temperature}^2 - \\ 6.63224\text{E+}016 \times \text{thickness}^2 - 1.31250\text{E+}015 \times \text{time} \times \text{temperature} + 6.91667\text{E+}015 \times \text{time} \\ \times \text{thickness} + 6.45833\text{E+}016 \times \text{temperature} \times \text{thickness}$$

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