# Determination of vacancy concentrations in the bulk of silicon wafers by platinum diffusion experiments

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Diffusion of platinum at low temperatures is a convenient way to characterize vacancy profiles in silicon. This article summarizes the experiments performed to find a standard procedure, discusses the pitfalls and limitations, and shows the applicability of the method. The results of experiments with float-zone and Czochralski-grown samples in the temperature range from 680 to 842 °C were found to disagree with the predictions of models published in the literature. Therefore, parameters governing the diffusion of point defects and platinum in silicon were determined for this temperature range. © *1997 American Institute of Physics*. [S0021-8979(97)03613-X]

## I. INTRODUCTION

Since the publication of Seeger and Chik,<sup>1</sup> various experiments gave evidence for the theory established therein that self-diffusion and dopant diffusion are mediated by self-interstitials as well as by vacancies. The concentrations of these intrinsic point defects are so low that they cannot be measured on the one hand by direct methods such as the Simmons–Balluffi experiment.<sup>2</sup> On the other hand, intrinsic point defects are known to have a distinct influence on various process steps in silicon technology.<sup>3</sup>

Probably the most prominent example for the influence of intrinsic point defects on dopant diffusion is the enhanced diffusion of boron and phosphorus and the retarded diffusion of antimony in an oxidizing atmosphere. The current understanding of such phenomena is based on the suggestions of Dobson<sup>4</sup> and Hu.<sup>5</sup> They proposed that, in order to accommodate the volume expansion accompanying oxidation of silicon, a small fraction of self-interstitials is injected into the bulk. Diffusion of boron and phosphorus, postulated to proceed to a sufficient degree via self-interstitials as diffusion vehicles, will then be enhanced. The injected point defects will also reduce the concentration of vacancies so that the diffusion of antimony, postulated to proceed predominantly via vacancies, is retarded. Closely related to oxidation is the precipitation of oxygen in the bulk of Czochralski (CZ)grown silicon wafers. Here, the change in molar volume during precipitation has to be mediated entirely by injection of self-interstitials and consumption of vacancies. Mizuo and Higuchi<sup>6</sup> reported an enhanced diffusion of boron and phosphorus below nitride-covered surfaces and ascribed it to selfinterstitials injected during oxygen-precipitate growth. Increased self-interstitial concentrations reduce the free volume required for oxygen precipitation and Hu<sup>7</sup> consequently reported that oxygen precipitation is retarded significantly in oxidizing atmospheres. Finally, vacancies are assumed to precipitate to D defects which have a negative influence on yield in ultra-large-scale integration (ULSI) fabrication.<sup>8</sup>

In spite of the importance of intrinsic point defects, literature values for the equilibrium concentrations and for the diffusivities of intrinsic point defects differ by several orders of magnitude. This might be caused by traps for intrinsic point defects in the bulk of silicon wafers as suggested by Griffin et al.,9 but it might also indicate an influence of the initial distribution of intrinsic point defects.<sup>10</sup> Although there is no direct way to measure intrinsic point defect concentrations in silicon up to now, a method to determine vacancy concentrations by platinum diffusion was proposed by Zimmermann and Ryssel.<sup>11</sup> This method will be reviewed shortly in the next section. Although the theory is straightforward, its application to real problems is not. The various experiments performed to find a standard procedure are summarized in Sec. III. The results of these experiments are shown and discussed in Sec. IV. In Sec. V, a standard procedure for the evaluation of vacancy concentrations is presented. The point-defect-related parameters extracted from the experiments are listed in Sec. VI and the differences to the work of Zimmermann and Ryssel are discussed.

#### **II. THEORY**

Platinum as well as gold is generally assumed to diffuse predominantly as interstitial atoms. In equilibrium, however, platinum atoms occupy mainly substitutional sites. One possible way for an impurity to change from an interstitial position to a substitutional site has been proposed by Frank and Turnbull.<sup>12</sup> The model assumes the interstitial impurity atom  $Pt_i$  to recombine with a lattice vacancy *V* leading to a substitutional impurity atom  $Pt_s$ . Such a reaction can be written as

$$\operatorname{Pt}_{i} + \bigvee_{\substack{k_{\mathrm{FT}} \\ k_{\mathrm{FT}} \\ k_{\mathrm{FT}}}}^{k_{\mathrm{FT}}} \operatorname{Pt}_{s}.$$

$$\tag{1}$$

The symbols  $k_{\text{FT}\rightarrow}$  and  $k_{\text{FT}\leftarrow}$  denote the forward and backward reaction constants of the Frank–Turnbull reaction. Al-

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ternatively, the so-called kick-out mechanism was proposed by Gösele *et al.*<sup>13</sup> for gold diffusion and later by Mantovani *et al.*<sup>14</sup> to explain platinum diffusion profiles. Within this mechanism, an interstitial platinum atom generates a silicon self-interstitial I when occupying a substitutional site according to the reaction

$$\mathsf{Pt}_{i}^{k_{\mathsf{ko}\rightarrow}} \mathsf{Pt}_{s} + I. \tag{2}$$

As before,  $k_{ko \rightarrow}$  and  $k_{ko \leftarrow}$  stand for the forward and backward reaction constants of the kick-out mechanism. In addition to these reactions, the reaction of self-interstitials and vacancies to undisturbed lattice sites via

$$I + V \underset{k_{b \leftarrow}}{\overset{\kappa_{b \rightarrow}}{\rightleftharpoons}} 0 \tag{3}$$

has to be taken into account with  $k_{b\rightarrow}$ ,  $k_{b\leftarrow}$ , and 0 symbolizing the forward and backward reaction rates of the bulk recombination mechanism, and an undisturbed lattice site, respectively.

In Eqs. (1)–(3), reactions between electrically neutral particles are assumed implicitly. In general, the particles involved may be in an ionized state, e.g., for the vacancy, besides the electrically neutral state, singly and doubly positive and negative charge states were proposed.<sup>15</sup> These charge states would have to be included and conservation of charge has to be fulfilled. Also the reaction rates in Eqs. (1)-(3) vary with the charge state of the involved particles.<sup>16</sup> Therefore, individual recombination reactions have to be taken into consideration for all combinations of charged particles. However, the relation between the concentration of charged particles and the respective total concentration is determined by the Fermi level and will be established by emission or capturing of charge carriers on a much shorter time scale than the time constants involved in the recombination reaction, Eqs. (1)–(3).

This allows to lump all reactions which differ only by the charge states of the involved particles to single reaction equations. These reaction equations can also be written in the form of the reaction Eqs. (1)–(3). But the symbols refer to the total concentrations and the effective reaction constants will depend on the Fermi level. Likewise, migration of the mobile particles in the various charge states will be linked by the rapid exchange of charge carriers. Adding all contributions of the various charge states to the diffusion current results in a diffusion equation for the total concentration with Fermi-level dependent effective diffusion coefficient and Fermi-level dependent effective mobility.<sup>17</sup>

Our experiments as well as nearly all other experiments on the diffusion of platinum or gold in silicon were carried out in samples in which the dopant concentrations were always significantly below the respective intrinsic charge carrier concentration. Under such intrinsic conditions, the Fermi level is always fixed at the intrinsic level so that the electrostatic potential vanishes. Also, the reaction constants of the reaction equations as well as the diffusion coefficients will be functions of temperature only. Based on these considerations, a system of partial differential equations for the substitutional platinum atoms, the interstitial platinum atoms, the silicon self-interstitals, and the vacancies can be derived from the reaction Eqs.  $(1)-(3)^{18}$ describing the redistribution of the metal atoms during diffusion steps

$$\frac{\partial C_s}{\partial t} = k_{\text{FT}} - C_i C_V - k_{\text{FT}} - C_s + k_{\text{ko}} - C_i - k_{\text{ko}} - C_s C_I, \quad (4)$$

$$\frac{\partial C_i}{\partial t} = \operatorname{div}(D_i \text{ grad } C_i) - k_{\text{FT}} - C_i C_V + k_{\text{FT}} - C_s$$

$$-k_{\text{ko}} - C_i + k_{\text{ko}} - C_s C_I, \quad (5)$$

$$\frac{\partial C_I}{\partial t} = \operatorname{div}(D_I \operatorname{grad} C_I) + k_{\mathrm{ko} \to} C_i - k_{\mathrm{ko} \leftarrow} C_s C_I$$
$$-k_{b \to} C_I C_V + k_{b \leftarrow}, \qquad (6)$$

$$\frac{\partial C_V}{\partial t} = \operatorname{div}(D_V \operatorname{grad} C_V) - k_{\mathrm{FT} \to} C_i C_V + k_{\mathrm{FT} \leftarrow} C_s$$
$$-k_{b \to} C_I C_V + k_{b \leftarrow} . \tag{7}$$

The symbols *C* and *D* stand for concentrations and diffusion coefficients and the indices *s*, *i*, *I*, and *V* refer to substitutional platinum, interstitial platinum, self-interstitials, and vacancies, respectively. These equations are the same as if we would have assumed that only the electrically neutral charge states exist for the respective species and the difference will no longer be mentioned in the following. However, it should be kept in mind that all concentrations *C* refer to total concentrations, and all diffusion coefficients *D* and reaction constants *k* to effective quantities under intrinsic conditions. In (4)–(7) the absence of dislocations and swirls which may act as sources or sinks for intrinsic point defects is assumed.

As boundary conditions for self-interstitials and vacancies at the wafer surfaces, Dirichlet boundary conditions with the respective equilibrium concentrations were assumed in our calculations. For platinum interstitials below surfaces where platinum was deposited, it was assumed that their concentration can also be described by a Dirichlet boundary condition. The respective concentration results from segregation to the covering platinum-containing phase. At other surfaces, Neumann boundary conditions were assumed. The initial concentrations of the platinum interstitials and platinum substitutional atoms in the bulk were assumed to be zero. Initial concentrations for the intrinsic point defects will be discussed in detail below.

In thermal equilibrium, all reactions are in equilibrium individually and the backward reaction constants can be expressed by the forward reaction constants and the equilibrium concentrations (indicated by a superscript eq) as

$$k_{\rm FT\leftarrow} = k_{\rm FT\rightarrow} \frac{C_i^{\rm eq} C_v^{\rm eq}}{C_s^{\rm eq}},\tag{8}$$

$$k_{\mathrm{ko}\leftarrow} = k_{\mathrm{ko}\rightarrow} \frac{C_i^{\mathrm{eq}}}{C_s^{\mathrm{eq}} C_i^{\mathrm{eq}}},\tag{9}$$

$$k_{b\leftarrow} = k_{b\rightarrow} C_I^{\text{eq}} C_V^{\text{eq}}. \tag{10}$$

At sufficiently low temperatures, diffusion of intrinsic point defects is negligible. Changes in the point-defect concentrations result only from the reactions (1) and (2) with the platinum atoms. When the Frank–Turnbull mechanism dominates the transition of platinum atoms from interstitial positions to substitutional sites, the initial concentration of vacancies, i.e., the concentration before the diffusion process,  $C_V^0$ , will be reduced by the substitutional platinum atoms to

$$C_{V} = C_{V}^{0} - C_{s}. \tag{11}$$

When local equilibrium is established for the Frank– Turnbull mechanism (1), and when the diffusion of platinum interstitials is fast enough to maintain their equilibrium concentration, the initial vacancy concentration and the concentration of substitutional platinum atoms are related by<sup>19</sup>

$$C_V^0 = C_s \left( 1 + \frac{C_V^{\text{eq}}}{C_s^{\text{eq}}} \right). \tag{12}$$

On the other hand, when the kick-out mechanism dominates, platinum diffusion results in the typical U-shaped profiles. For the concentration in the middle of a dislocation-free silicon wafer of thickness d, Gösele *et al.*<sup>13</sup> derived an analytical approximation which predicts an increase which is proportional to the square root of time according to

$$C_s\left(\frac{d}{2},t\right) = \frac{2}{d} \sqrt{\pi C_s^{\rm eq} D_I C_I^{\rm eq} t}$$
(13)

for the case of a low density of self-interstitial sink in the bulk, low initial metal concentration, and for times not sufficient to reach steady state.

#### **III. GENERAL EXPERIMENTAL PROCEDURE**

The main goal of the investigations presented here was to find a standard procedure for platinum diffusion to evaluate the distribution of vacancies in silicon samples, especially in Czochralski (CZ)-grown wafers, via measured platinum profiles. In general, platinum was deposited at the samples and diffused in a horizontal furnace. Some of the process steps like platinum deposition or the furnace parameters were varied in the search for an optimal process. The details of the experimental procedures are included in the discussion of the results.

Our experiments were performed on as-grown dislocation-free (100)-oriented *p*-type silicon substrates with one surface polished. The CZ wafers used in this study were from MEMC and had diameters of 150 mm, thicknesses of 615  $\mu$ m, and resistivities of 5  $\Omega$  cm and 60  $\Omega$  cm. In addition, commercial float zone (FZ) wafers with diameters of 100 mm, thicknesses of 535  $\mu$ m, and resistivities of 4–6  $\Omega$  cm were investigated.

Immediately before the platinum deposition, the wafers were cleaned in a standard cleaning procedure using Caro's acid followed by a dip in 5% fluoric acid. In the first experiments, platinum layers of about 50 nm thickness were deposited by e-gun evaporation. Later, the e-gun evaporation was For investigation of backside contamination with platinum after one-sided deposition, the backsides of some samples were covered by low temperature oxide (LTO) layers of 200 nm thickness prior to the platinum deposition by the following procedure: at first, LTO layers were deposited at 430 °C on both surfaces of the samples. A special sample holder enabled the removal of the oxide film only from the front side by a second dip in fluoric acid. The remaining LTO on the backside acted as diffusion barrier against undesired contamination with platinum from the ambient.

Drive-in diffusions were performed in a horizontal furnace at temperatures from 680 to 842 °C for times between 8 min and 4 h in a nitrogen ambient flowing with 10  $\ell/min$ . The samples were loaded into the furnace by unloading the warm wafer holder, inserting the samples into the wafer holder, and loading the wafer holder into the furnace, all within 2 min. During one diffusion step at 730 °C for 20 min, the temperature was recorded by a Pt/PtRh thermocouple which was held in thermal contact to the middle of a wafer of 100 mm diameter. This wafer was annealed in the same way as the wafers which had to be diffused. Already 2 min after loading, the deviation of the wafer temperature from the furnace temperature was smaller than 12 °C, 4 min after loading it was smaller than 5 °C, and after 6 min it was smaller than 2 °C. During the first 20 s of unloading, the wafer temperature was lowered about 5 °C. Then it dropped to 600 °C within 20 s.

Depth profiles of substitutional platinum were obtained from deep level transient spectroscopy (DLTS) measurements. Platinum concentrations were determined from the height of the peak in temperature scans associated with the donor level of substitutional platinum.<sup>20</sup> For a frequency of 475 Hz the peak appears at 185 K. For DLTS measurements, the wafers were cut into pieces of approximately 1 cm<sup>2</sup>, bevelled with angles of 1.17° or 2.86°, and polished. Then, layers of approximately 15  $\mu$ m of silicon were etched off with  $HF(50\%) - HNO_3(100\%) - CH_3COOH(100\%)$  mixture an (composition 2:1:2) and Schottky contacts were deposited by evaporation of hafnium. For ohmic contacts at the backside, gallium was used. The detection range of substitutional platinum concentration  $C_s$  depends on the dopant concentration  $C_d$  as  $C_d \times 10^{-4} < C_s < C_d \times 10^{-1}$ . The relative accuracy of the results is better than 30%.

#### **IV. RESULTS AND DISCUSSION**

The first diffusion experiments within this work were designed to merely confirm the model parameters published by Zimmermann and Ryssel<sup>21</sup> and to demonstrate the applicability of their method to evaluate vacancy distributions in silicon. However, the results were quite unexpected and could not be explained straightforwardly within the models



0 100 200 300 400 Depth (µm) FIG. 2. Platinum profiles in FZ wafers after diffusion at three different

С m

 $14\\10$ 

Platinum Concentration (cm<sup>-3</sup>)

 $\begin{smallmatrix}&13\\10\end{smallmatrix}$ 

12

temperatures for 20 min.

10

FIG. 1. Platinum profiles in FZ wafers after diffusion at 780 C for three different times.

published for platinum diffusion. One reason might be that most of the previous experiments published were performed at considerably higher temperatures. In addition, unexpected experimental problems had to be identified and solved. In this section, the experiments performed are described and their results are discussed.

In a first series of experiments, FZ and CZ wafers were processed at temperatures from 680 to 842 °C for times from 8 min to 4 h. While the main goal was always to measure vacancy distributions in CZ wafers, the bulk of previously published experiments was performed on FZ wafers which were included for the sake of comparability.

# A. FZ silicon

On the front side of one single FZ wafer with a resistivity of 5  $\Omega$  cm a platinum layer of 50 nm thickness was evaporated. Three pieces of this wafer were annealed at 780 °C for 8 min, 20 min, and 4 h, respectively. Figure 1 gives the depth profiles of substitutional platinum. The accuracy of the DLTS measurements is indicated in the lower right part of the figure. As in the following representations of platinum depth profiles, the depth of 0  $\mu$ m refers to the polished front side of the wafer.

A first characteristic of the curves is that the distribution of platinum remained nearly unchanged for diffusion times from 8 min up to 4 h. This behavior indicates the dominance of the Frank-Turnbull mechanism. However, it is conspicuous that the spatial distributions are rather inhomogeneous with minima in a depth of about 170  $\mu$ m.

This asymmetry can also be seen in Fig. 2 which shows profiles in samples diffused for 20 min at temperatures from 680 to 780 °C and processed otherwise like the samples mentioned above. Especially at the lower temperatures, the concentrations near the backside were found to be higher than near the front side. In comparison, double-sided depo-

sition of platinum layers of 50 nm thickness as shown in Fig. 3 leads to symmetrical platinum profiles. The concentration of platinum near the backside was found to be significantly lower after double-sided platinum deposition than after single-sided deposition.

Such inhomogeneous distributions were not expected in the as-grown wafers used. In as-grown wafers, the initial distribution of point defects with respect to depth (not with respect to the position at the wafer surface) should be homogeneous since point-defect concentrations in grown ingots



FIG. 3. Platinum profiles after diffusion at 730 C for 20 min in three similar FZ wafers, but after platinum evaporation onto different surfaces.

°C

°C

°C

500

° 680

o 730

x 780

vary on much larger length scales and wafer preparation is hardly able to result in significant changes of point-defect distributions in the bulk of the wafers. Therefore, except near the surface, we also expect a homogeneous platinum distribution for sufficiently long and high temperature steps. We will show later that the double-sided profiles in Figs. 1-3measured after single-sided deposition of platinum are the results of an unintentional contamination of the backside via the gas flux in the diffusion furnace. Still, this would not completely explain the shape of the profiles. An additional aspect can result from the silicidation reaction of the platinum layer deposited at the front side taking place at temperatures above 200 °C.<sup>22</sup> The resulting platinum silicide at the front side and the platinum contamination at the backside result in different boundary conditions for the interstitial platinum atoms. In addition, point defects may be injected during silicidation<sup>23</sup> and also mechanical strain originating from the silicide layer might have a non-negligible influence on platinum diffusion.

In any case, silicidation has an undesirable influence on our measurement technique. A simple way to prevent silicidation during the diffusion process is to deposit platinum with a surface area concentration as low as possible. For example, a homogeneous platinum concentration of  $10^{15}$  cm<sup>-3</sup> in the bulk of a wafer of 1000 µm thickness requires at least  $10^{14}$  cm<sup>-2</sup> atoms on one of the two surfaces prior to the diffusion process. On the other hand, a platinum monolayer corresponds to a surface area concentration of 2  $\times 10^{15}$  cm<sup>-2</sup>. Assuming that at least a few monolayers are necessary to form a silicide phase and to cause a significant injection of point defects by silicidation, we decided to use surface coverings with area concentrations on the order of  $10^{15}$  cm<sup>-2</sup>. A special geometrical arrangement during the evaporation by e-gun rendered surface area concentrations as small as  $5 \times 10^{14}$  cm<sup>-2</sup> possible. Usage of the acidified platinum standard solution resulted in surface area concentrations in the range from  $4 \times 10^{14}$  to  $10^{15}$  cm<sup>-2</sup>, measured by Rutherford backscattering. In the experiments below, e-gun evaporation was usually used. Within the experimental accuracy, both deposition methods lead to the same results and DLTS measurements after single-sided deposition of a thin film of platinum and diffusion at 780 °C for 20 min showed reproducibly a homogeneous distribution of platinum atoms. But the low surface concentration required for reproducibility results in a thermodynamically ill-defined boundary condition for the platinum atoms. The binary solubility of platinum in silicon in the temperature range investigated is defined by the segregation of platinum atoms between a silicide phase (PtSi) in contact with the silicon phase. In absence of a silicide phase, as is desired here, the "equilibrium" concentration of interstitial platinum atoms, which determines the boundary condition for the respective continuity Eq. (5), and with it the equilibrium concentration of substitutional platinum atoms can be expected to deviate from the values measured in the presence of a silicide. Since equilibrium is virtually never reached in our investigations, the equilibrium concentration can be measured only near the surface. Schottky contacts at the surface are of poor quality and potentially unreliable. In addition, because of the pecu-



FIG. 4. Platinum profiles in two FZ wafers processed together at 730 C for 20 min. Platinum was deposited only on one of the wafers prior to the diffusion step.

liarities of the DLTS method, the platinum concentration measured represents a weighted mean value within a region extending for 5  $\Omega$  cm material from 0.7 to 1.2  $\mu$ m. Our estimate for 730 °C is about  $3 \times 10^{12}$  cm<sup>-3</sup>. This value is about one order of magnitude smaller than the respective values of Mantovani *et al.*<sup>14</sup> and Zimmermann *et al.*<sup>21</sup> The homogeneous distribution of platinum atoms is what was expected for dominating Frank–Turnbull mechanism and sufficient diffusion time to reach steady state and could be explained quantitatively with the platinum diffusion model of Zimmermann and Ryssel<sup>21</sup> by initial vacancy concentrations on the order of  $10^{14}$  cm<sup>-3</sup>.

To investigate the origin of the double-sided profiles shown in the Figs. 1-3, a possible contamination with platinum of the backsides during diffusion has been considered. As a test, three wafers were processed together separated by a distance of about 1 cm. Onto the front surfaces of the two outer wafers, platinum was deposited prior to the drive in, whereas on the wafer in the middle no platinum was deposited. The platinum-covered surfaces of the two outer wafers were turned inwards. Then, the wafers were diffused at 730 °C for 20 min. In Fig. 4, it can be seen that the platinum profile in the middle wafer resembles that in one of the outer wafers. This is a direct evidence for the contamination of initially uncontaminated surfaces with platinum during furnace processing. In addition, a single-sided profile was obtained when only one wafer was processed on which platinum was deposited single-sidedly.

Another method to prevent contamination of the backside is to cover it by oxide layers acting as diffusion barriers. Figure 5 shows platinum depth profiles in three different FZ wafers with LTO-covered backside after diffusion at 730 °C for 20 min. Because the wafers were processed in the same way, the different profiles indicate different initial vacancy



FIG. 5. Measured platinum profiles in three different wafers after diffusion at 730 C for 20 min, compared with simulations (parameter: vacancy concentration).

concentrations. Also shown in this figure are simulations with the parameters published by Zimmermann and Ryssel.<sup>21</sup> The simulations which have been done for three different initial vacancy concentrations (as given in the figure) predict nearly flat profiles. This is in disagreement with the measurements. To be able to reproduce the measured curves obtained in various experiments, some of the parameters governing platinum diffusion had to be modified. These modifications are discussed in detail in Sec. VI. Simulations based on this modified set of parameters are also depicted in Fig. 5 with the initial concentration of vacancies as free parameter. Optimization of this parameter to obtain the best description of the measured profiles allowed an estimation of the initial vacancy concentrations as  $10^{14}$  cm<sup>-3</sup>,  $8 \times 10^{13}$  cm<sup>-3</sup>, and  $4 \times 10^{13}$  cm<sup>-3</sup>.

In Fig. 6, platinum profiles resulting from diffusions at 692, 742, 792, and 842 °C for 1 h of samples with LTOcovered backsides are shown. All samples were quarters from the same wafer so that the initial concentration of vacancies should be the same in all samples. Therefore, the nearly equal platinum concentrations observed at the front side were expected since the proportionality constant 1 + $C_V^{eq}/C_s^{eq}$  in (12) is nearly equal to unity (it decreases from 1.10 at 692 °C to 1.01 at 842 °C). The initial concentration of vacancies was estimated to be  $1.2 \times 10^{14}$  cm<sup>-3</sup> in this example.

Although a diffusion barrier like LTO is a convenient way to prevent contamination from the backside, one has to keep in mind that an LTO covering represents a different thermodynamical boundary condition for the migrating point defects than a free surface. Therefore, double-sided deposition of platinum was used to estimate possible side effects of the LTO covering. As an example, in Fig. 7, two profiles measured after double-sided deposition and diffusion at



FIG. 6. Measured and simulated platinum profiles after one-sided diffusion at four different temperatures for 1 h.

730 °C for 20 min and for 1 h are shown. Again, simulation with the optimized set of parameters with an estimated initial concentration of vacancies of  $8 \times 10^{13}$  cm<sup>-3</sup> resulted in a good description of the profiles.

#### **B. CZ silicon**

Depth profiles of substitutional platinum concentration measured in CZ silicon were found to be completely different from those in CZ silicon. Figure 8 shows platinum profiles in CZ samples cut from the same wafer ( $\rho$ 



FIG. 7. Measured and simulated platinum profiles after diffusion from both surfaces at 730 C for 20 min and 1 h.





FIG. 8. Platinum profiles in a CZ wafer after diffusion at 780 C for four different times.

=60  $\Omega$  cm). On the polished front side, platinum was deposited. The drive-in was performed at 780 °C for four different times from 8 min to 4 h. The first evident difference to the depth profiles in FZ silicon is that much lower platinum concentrations were observed in the CZ samples. Furthermore, the evolution of the profiles with increasing diffusion time is different. It was found that the platinum concentration in the middle of the wafer increased proportionally to the square root of diffusion time (see Fig. 9). This observation as well as the *U*-shape of the depth profiles indicates the



FIG. 9. Evolution of the platinum concentration in the middle of the CZ wafer with diffusion time at 780 C. The respective platinum profiles are shown in Fig. 8.

FIG. 10. Platinum profiles in CZ wafers after diffusion at 730 C for four different times.

dominance of the kick-out mechanism. *U*-shaped profiles were already reported by Mantovani *et al.*<sup>14</sup> in the same temperature range and explained by the dominance of the kickout mechanism. In contrast, Zimmermann and Ryssel<sup>19,21</sup> reported a dominance of the Frank–Turnbull mechanism below 850 °C. This discrepancy can be explained by different initial vacancy concentrations. Our experiments indicate a value below  $2 \times 10^{11}$  cm<sup>-3</sup> while Zimmermann *et al.* used FZ silicon which, as shown above, has a much higher initial concentration of vacancies. From Fig. 9, the product  $C_s^{eq}D_IC_I^{eq}$  at 780 °C can be estimated via (13) to be  $C_s^{eg}D_IC_I^{eq} = 5.6 \times 10^{16}$  cm<sup>-4</sup> s<sup>-1</sup>.

As mentioned in the previous section, a characterization of vacancy distributions is possible only when the Frank-Turnbull mechanism dominates the transition of platinum atoms from an interstitial position to a substitutional position. Therefore, to suppress the dislocation of regular silicon atoms via the kick-out mechanism, the same platinum diffusion experiment has been performed with a similar wafer, but now at the lower diffusion temperature of 730 °C (Fig. 10). The lower temperature results in a retardation of the kick-out mechanism in comparison to the higher temperature. The resulting platinum concentrations are about a factor of 10 lower than those given in Fig. 8. The simulations also shown in Fig. 10 used the product  $C_s^{eq} D_I C_I^{eq} = 5.9$  $\times 10^{14}$  cm<sup>-4</sup> s<sup>-1</sup>. The dominance of the kick-out mechanism at 730 °C indicates that the initial concentration of vacancies did not influence the platinum diffusion in the investigated CZ wafers. A value of  $C_V(t=0)=5\times 10^{10}$  cm<sup>-3</sup> was used for the presented simulations.

In various additional experiments, the vacancy concentrations in commercial as-grown CZ wafers were always found to be much lower than in as-grown FZ wafers. Values up to  $3 \times 10^{12}$  cm<sup>-3</sup> could be detected, but in most cases, the



 $\begin{smallmatrix}&&3\\10\end{smallmatrix}$ 3.1014 cm-3 2 10 Diffusion Time (min) mit cm-3  $\begin{smallmatrix}&&1\\10\end{smallmatrix}$ ст-3  $10^{0}$ 730 °C 10 700 720 760 780 800 740Temperature (°C)

FIG. 11. Simulations of platinum diffusion at 730 C for 20 min with different initial concentrations of vacancies in the range between 3  $\times 10^{10} \ {\rm cm^{-3}}$  and  $3 \times 10^{14} \ {\rm cm^{-3}}$ .

concentration was found to be near or below the detection limit.

## V. A STANDARD PROCEDURE FOR THE EVALUATION OF VACANCY CONCENTRATIONS

To measure low initial vacancy concentrations, it is necessary to find a set of diffusion temperature and time for which the Frank–Turnbull mechanism dominates the platinum diffusion, but which, on the other hand, is sufficient to reach the steady state of vacancy decoration by platinum atoms. Furthermore, the thermal budget of the diffusion process should be low to prevent a change of the vacancy distribution due to other effects than trapping of platinum like, e.g., diffusion of point defects from the surfaces or injection of self-interstitials by oxygen precipitation. To minimize a possible influence by silicidation processes, only platinum deposition methods were used which result in a surface area concentration below 1 ML.

In CZ silicon, vacancy concentrations are usually low. For such low concentrations, to prevent a significant influence from the kick-out mechanism, the process time has to be kept short. From the experiments with CZ samples presented in Sec. IV one can see that a process time of 1 h at 730 °C leads to concentrations below  $10^{11}$  cm<sup>-3</sup> in the middle of the wafer while less than 1 min would be sufficient to reach steady state for a vacancy concentration of  $10^{12}$  cm<sup>-3</sup>. For our purposes, however, temperature measurement in our rapid-thermal-annealing furnaces was not accurate enough and a minimum process time of 20 min was chosen to make sure that the nominal temperature was reached for a sufficiently long time in the horizontal furnace used.

On the other hand, vacancy concentrations in preprocessed CZ wafers can be significantly higher. Figure 11

FIG. 12. Diffusion times required to reach at least 70% (dashed lines) and 90% (solid lines) of the platinum concentration in steady state vs temperature in dependence on the initial vacancy concentration.

shows simulations of the influence of the initial vacancy concentration on platinum diffusion profiles in wafers with a thickness of 675  $\mu$ m after double-sided platinum deposition and diffusion at 730 °C for 20 min. At the upper vacancy concentration limit, up to a maximum concentration of 3  $\times 10^{13}$  cm<sup>-3</sup>, influences of the platinum diffusion process on the determination of vacancy profiles are negligible. Since this concentration decreases with decreasing temperature, a diffusion process at 730 °C for 20 min was used usually as a compromise between low thermal budget and highest characterizable vacancy concentration. The influence of the kickout mechanism is within the experimental error negligible for vacancy concentrations of  $10^{11}$  cm<sup>-3</sup> except for the first 70  $\mu$ m from the surfaces.

With the same process conditions, higher vacancy concentrations than  $3 \times 10^{13}$  cm<sup>-3</sup> can be characterized only near the surface. In general, it will be necessary to increase diffusion temperature, diffusion time, or both. Figure 12 shows the minimum time needed to reach 70% and 90% of the platinum concentration in steady state in the middle of the wafers for various homogeneous initial concentrations of vacancies between  $10^{12}$  cm<sup>-3</sup> and  $3 \times 10^{14}$  cm<sup>-3</sup>. The higher the initial vacancy concentration and the lower the diffusion temperature, the longer the diffusion time needed to decorate 70% and 90% of the vacancies by platinum atoms.

# **VI. DETERMINATION OF DIFFUSION PARAMETERS**

As outlined in Sec. II, the redistribution of platinum can be simulated solving the system of coupled partial differential Eqs. (4)-(7). Unfortunately, quite a few of the parameters are still under discussion. Values published, e.g., for the diffusion coefficients and equilibrium concentrations of intrinsic point defects, differ by several orders of magnitude, especially at the low temperatures used in this work. The starting point for our simulations was the parameters given by Zimmermann and Ryssel.<sup>21</sup> But, as shown in Sec. IV, they predict nearly flat profiles in disagreement with the measurements. Therefore, several parameters related to the diffusion of the intrinsic point defects and to the diffusion of platinum were modified. Since the standard procedure for vacancy measurement was developed, various profiles in asgrown and preprocessed CZ wafers were measured. In each diffusion process, one FZ wafer was included as a sanity check for possible processing errors. These FZ wafers are the experimental basis of the modifications in the diffusion parameters. Most experiments were used to cover the temperature range from 680 to 842 °C.

For the standard diffusion process, the actual temperature profile during processing as given in Sec. III was used in the simulations. However, the comparison with simulations based on an idealized rectangular temperature profile with a temperature of 730 °C for 20 min showed no significant differences in the simulated platinum profiles.

Simulation of platinum diffusion at low temperatures and high initial vacancy concentrations, i.e., for dominating Frank–Turnbull mechanism, was found to be sensitive predominantly to the quotient  $C_V^{eq}/C_s^{eq}$ , to the product  $C_i^{eq}D_i$ , and to the Frank–Turnbull forward reaction constant  $k_{FT-}$ . Splitting of these composite parameters into individual parameters was attempted but has to be taken *cum grano salis*. Because of the small temperature range which was investigated in this work, the temperature dependences of the single parameters may deviate for experiments at much higher or lower temperatures. The activation energy of the product  $C_V^{eq}D_V$  has been taken from Gösele and Tan.<sup>24</sup>

Values for the Frank–Turnbull forward reaction constant were obtained at first in the fitting process. From the theory of a diffusion-limited reaction,<sup>25</sup> the Frank–Turnbull forward reaction constant would be given by

$$k_{\rm FT} = 4 \pi a_{\rm FT} (D_V + D_i) \tag{14}$$

with  $a_{\rm FT}$  denoting the respective reaction radius. A comparison to the fitted values gave a reaction radius of  $a_{\rm FT} \approx 2$  nm. This is a perfectly plausible value and indicates strongly that the Frank–Turnbull reaction between interstitial platinum atoms and vacancies is indeed diffusion limited. Accordingly, the activation energy of the Frank–Turnbull forward reaction constant was assumed to correspond to that of the interstitial platinum diffusion coefficient since this diffusion coefficient is much larger than the vacancy diffusion coefficient in the given temperature range and dominates the sum in (14).

Simulation of platinum diffusion in silicon with low initial vacancy concentrations, i.e., for dominating kick-out mechanism, was found to be sensitive predominantly to the product  $C_s^{eq}D_IC_I^{eq}$ . It should be noted that the attempted splitting of this product into individual parameters is fragile again. The activation energy 4.84 eV of the product  $C_I^{eq}D_I$ has been taken from Stolwijk,<sup>26</sup> the activation energy of  $C_s$ follows from the temperature dependence of  $C_s^{eq}D_IC_I^{eq}$ . The parameter  $k_{ko\rightarrow}$  was taken directly from Zimmermann and Ryssel.<sup>21</sup> An estimate for the bulk recombination rate of va-

TABLE I. Parameters for simulation of platinum diffusion between 680 and842C.

Parameter	Arrhenius expression
$C_i^{ m eq} \ D_i \ C_s^{ m eq} \ C_v^{ m eq} \ D_V \ C_1^{ m eq}$	$4.8 \times 10^{19} \times \exp(-1.7 \text{ eV}/kT) \text{ cm}^{-3}$ $1.0 \times 10^{1} \times \exp(-1 \text{ eV}/kT) \text{ cm}^{2} \text{ s}^{-1}$ $6.4 \times 10^{29} \times \exp(-3.45 \text{ eV}/kT) \text{ cm}^{-3}$ $1.7 \times 10^{21} \times \exp(-2 \text{ eV}/kT) \text{ cm}^{-3}$ $1.8 \times 10^{1} \times \exp(-2.03 \text{ eV}/kT) \text{ cm}^{2} \text{ s}^{-1}$ $4.2 \times 10^{30} \times \exp(-4.4 \text{ eV}/kT) \text{ cm}^{-3}$
$D_{I}$ $k_{\mathrm{FT} ightarrow}$ $k_{\mathrm{ko} ightarrow}$ $k_{b ightarrow}$	$9.8 \times 10^{-5} \times \exp(-0.44 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$ 1.1×10 <sup>-6</sup> ×exp(-1 eV/kT) cm <sup>3</sup> s <sup>-1</sup> 1.5×10 <sup>23</sup> ×exp(-5.2 eV/kT) s <sup>-1</sup> 1.1×10 <sup>-10</sup> ×exp(-0.44 eV/kT) cm <sup>3</sup> s <sup>-1</sup>

cancies and self-interstitials was also estimated from the theory of diffusion-limited reaction assuming a reaction radius of 2 nm.

The parameters used in the simulations are summarized in Table I. With the set of parameters all profiles measured in FZ samples after platinum deposition with a low surface area concentration and diffusion at temperatures from 680 to 842 °C could be reproduced and the initial vacancy concentrations in the FZ samples could be determined. Also, all of the platinum profiles measured in as-grown CZ silicon could be described. We would like to add that the agreement between measurements and simulations in Figs. 6–11 is really typical and not *typical* in the sense of *the best agreement ever seen*.

## **VII. CONCLUSIONS**

Platinum diffusion was investigated in the low temperature range from 680 to 842 °C to find a standard method to characterize vacancy profiles in silicon. In as-grown CZ silicon wafers, the vacancy concentrations were so low that the kick-out mechanism was found to dominate platinum diffusion at 780 °C. In contrast, in as-grown FZ silicon, vacancy concentrations were found in the range from  $4 \times 10^{13}$  to  $2 \times 10^{14}$  cm<sup>-3</sup>. The applicability of the standard method to the measurement of vacancy profiles, especially in preprocessed CZ wafers, was demonstrated.

From a comparison between experimental results and numerical simulations of platinum diffusion, several parameters related to point-defect diffusion and platinum diffusion could be determined. From the experiments with CZ wafers, the product of self-interstitial diffusion coefficient and the equilibrium concentrations of self-interstitials and substitutional platinum could be determined for 780 °C. From the experiments with FZ wafers, the product of interstitial platinum diffusion coefficient and interstitial platinum equilibrium concentration as well as the quotient of equilibrium vacancy concentration and substitutional platinum equilibrium concentration could be determined in the temperature range from 680 to 842 °C. The Frank–Turnbull forward reaction was found to be diffusion limited with a reaction radius of 2 nm.

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