Modeling platinum diffusion in silicon

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(Received 8 August 2014; accepted 20 September 2014; published online 1 October 2014)

Simulations based on diffusion-limited reaction rates were able for the first time to reproduce platinum profiles in silicon for in-diffusion in a wide temperature range from 730 to 950 °C and out-diffusion associated with the ramping-down of the temperature at the end of an industrial diffusion process at 830 °C. A rigorous analysis of the out-diffusion and short-time in-diffusion profiles allowed narrowing down the parameter range for the intrinsic point defects in silicon. © 2014 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4896909]

I. INTRODUCTION

Since the mid-1970s, platinum diffusion into silicon has been utilized for life-time control in silicon power devices. The platinum deep energy level at Ec–0.243 eV acts as an effective recombination and low generation center. Therefore, devices doped with platinum feature low leakage currents and high thermal stability.1 In order to engineer the trade-off between on-state and switching losses of devices, a thorough understanding of platinum diffusion is required. Quantitative models for the diffusion of platinum in silicon like those of Zimmermann and Ryssel2 and Jacob et al.3 were already established about two decades ago. However, when using them to simulate our own experiments involving out-diffusion of platinum from the silicon during the ramping-down phase of the furnace anneals,4 we found striking differences between simulations and experiments close to the surfaces. Although the model presented previously by Badr et al.5 was able to describe the out-diffusion experiments and in-diffusion experiments at low temperatures, it turned out that it could not describe the experimental data of Zimmermann and Ryssel2 at high temperatures as well. In this work, we present a model capable of consistently reproducing for the first time all the experimental data reported in the temperature range from 730 to 950 °C for platinum diffusion in dislocation-free silicon. Moreover, a rigorous investigation of the parameter space revealed that platinum out-diffusion allows narrowing down the parameter range for vacancies, while complementary conclusions could be derived for the self-interstitial parameters from in-diffusion profiles.

II. THEORY

Platinum is a hybrid element in silicon. It diffuses as interstitial platinum PtI and resides predominantly as substitutional platinum Pts. The diffusion behavior of platinum results from its interaction with silicon point defects (vacancies V and self-interstitials I) according to the Frank-Turnbull5 and kick-out6 mechanisms, respectively. In addition, bulk recombination between self-interstitials and vacancies has to be taken into account. The Frank-Turnbull, kick-out and bulk recombination mechanisms are represented by the following quasi-chemical reactions:

\[
\begin{align*}
Pt_I + V \rightleftharpoons & \text{ Pt}_{\text{s}}, \\
& k_{\text{FT}} \\
Pt_I \rightleftharpoons & \text{ I} + \text{ Pt}_{\text{s}}, \\
& k_{\text{KO}} \\
I + V \rightleftharpoons & \text{ O}, \\
& k_{\text{IV}}
\end{align*}
\]

where O stands for an undisturbed lattice and \( k_{\text{FT}}, k_{\text{FT}} \), \( k_{\text{KO}}, k_{\text{KO}} \), \( k_{\text{IV}}, k_{\text{IV}} \) are the reaction constants in forward and backward direction, respectively. A system of partial differential equations for the substitutional platinum, interstitial platinum, self-interstitials and vacancies presented elsewhere4 has been used. Assuming diffusion-limited reactions without energy barriers, a part of the reaction constants can be expressed as:

\[
\begin{align*}
k_{\text{FT}} &= 4\pi a_{\text{FT}} (D_P + D_V), \\
k_{\text{KO}} &= 4\pi a_{\text{KO}} D_I,
\end{align*}
\]

\[(\text{k}_{\text{KO}} \text{ and } k_{\text{KO}} \text{ were used in this form already in Ref. 4 but reported incorrectly})
\]

\[
k_{\text{IV}} = 4\pi a_{\text{IV}} (D_I + D_V),
\]

with the Ds denoting the respective diffusion coefficients. As a starting point, the capture radii \( a_{\text{FT}}, a_{\text{KO}} \) and \( a_{\text{IV}} \) were assumed to be 5 Å. The remaining reaction rates follow from thermal equilibrium in the form:

\[
k_{\text{FT}} = k_{\text{FT}} \frac{C_{\text{PtI}}^{eq} C_{\text{V}}^{eq}}{C_{\text{PtI}}^{eq}},
\]

\[(\text{7})
\]

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In all the experiments, the platinum was driven-in from a platinum silicide layer (infinite source) formed at one side of the wafer. Below, a Dirichlet boundary condition was used for Pt$_i$ since it is assumed that platinum does not leave the wafer. The formation of a platinum silicide, e.g., during cooling-down, is considered unlikely since the rapid diffusion to the already existing silicide layer at the other side prevents the concentration of interstitial platinum from exceeding significantly the solid solubility. However, even a second silicide layer would have only a minor influence on the simulation results because of the rapid redistribution of the interstitial platinum atoms. As boundary conditions for vacancies and self-interstitials at the wafer surfaces, Dirichlet boundary conditions with the respective equilibrium concentrations were assumed. We verified that such initial conditions had no noticeable effect on the simulation results. The platinum is driven in from a platinum silicide layer (infinite source) formed at one side of the wafer. The depth profiles of substitutional platinum were obtained from deep level transient spectroscopy (DLTS) measurements.

### III. EXPERIMENTAL DATABASE

In our own experiments, we used dislocation-free (100)-oriented $p$-type boron-doped CZ-grown silicon and $n$-type phosphorus-doped FZ-grown silicon. The $p$-doped wafers had a resistivity of 21 $\Omega$ cm and the $n$-doped wafers had resistivities of 2.1 and 5 $\Omega$ cm. An oxidation step to eliminate grown-in vacancies was performed before introducing platinum into the wafers. Details of the experimental procedure can be found in the original publication. Zimmerman and Ryssel used $p$-type boron-doped FZ-grown silicon. The resistivity of the wafers was 4 to 6 $\Omega$ cm. Jacob et al. used $p$-type boron-doped CZ-grown silicon. The resistivity of the wafers was 60 $\Omega$ cm. In all the experiments, the platinum was driven-in from a platinum silicide layer formed at one side of the wafer. The depth profiles of substitutional platinum were obtained from deep level transient spectroscopy (DLTS) measurements.

### IV. SIMULATION PARAMETERS

An initial concentration of $1 \times 10^8$ cm$^{-3}$ was assumed for Pt$_S$ and Pt$_i$ across the wafer. The simulation results did not depend on this value because it is orders of magnitudes lower than the concentrations of Pt$_S$ and Pt$_i$ after diffusion. As a starting value for the concentrations of vacancies and self-interstitials, unless otherwise noted, the respective equilibrium concentrations at the starting temperatures of the annealing processes were assumed. We verified that such initial conditions had no noticeable effect on the simulation results. The platinum is driven in from a platinum silicide layer (infinite source) formed at one side of the wafer. Below, a Dirichlet boundary condition was used for Pt$_i$. At the other side, a Neumann boundary condition was used for Pt$_i$ since it is assumed that platinum does not leave the wafer. The formation of a platinum silicide, e.g., during cooling-down, is considered unlikely since the rapid diffusion to the already existing silicide layer at the other side prevents the concentration of interstitial platinum from exceeding significantly the solid solubility. However, even a second silicide layer would have only a minor influence on the simulation results because of the rapid redistribution of the interstitial platinum atoms. As boundary conditions for vacancies and self-interstitials at the wafer surfaces, Dirichlet boundary conditions with the respective equilibrium concentrations were assumed.

The parameters $C_{pt}^{eq}$ and $D_{pt}$ were chosen to satisfy the product

$$C_{pt}^{eq}D_{pt} = 7.25 \times 10^{21} \exp\left(\frac{-3.1 \text{ eV}}{kT}\right) \text{cm}^{-1}\text{s}^{-1}$$

deduced from platinum diffusion into dislocated silicon by Lerch et al. Initially, the parameter $C_{pt}^{eq}$ was taken from level transient spectroscopy (DLTS) measurements.

$$k_{KO} = k_{KO} C_{pt}^{eq} C_{pv}^{eq}$$

$$k_{IV} = k_{IV} C_{pv}^{eq} C_{pv}^{eq}$$

where the $C^{eq}$ stand for the respective equilibrium concentrations.

### V. RESULTS

In Figures 2–5, substitutional platinum depth profiles obtained from processing at 730, 780, 900, and 950°C are compared to simulations. In all these processes, the wafers were pulled rapidly out of the furnace at the end of the process. Considering the experimental uncertainty in temperature measurements, the temperature in the simulations was assumed to deviate by up to ±2 K from the nominal annealing temperatures to improve the agreement between the simulations and the experimental data.

**TABLE I. Set of parameters for the simulation of platinum diffusion.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{eq}$</td>
<td>$8.7 \times 10^{19} \exp(-1.87 \text{ eV} / kT) \text{cm}^{-3}$</td>
</tr>
<tr>
<td>$D_{pt}$</td>
<td>$8.33 \times 10^{7} \exp(-1.23 \text{ eV} / kT) \text{cm}^{2}\text{s}^{-1}$</td>
</tr>
<tr>
<td>$C_{eq}$</td>
<td>$5.7 \times 10^{22} \exp(-2.212 \text{ eV} / kT) \text{cm}^{-3}$</td>
</tr>
<tr>
<td>$C_{eq}$</td>
<td>$1.0 \times 10^{21} \exp(-3.18 \text{ eV} / kT) \text{cm}^{-3}$</td>
</tr>
<tr>
<td>$D_{V}$</td>
<td>$1.48 \times 10^{9} \exp(-1.77 \text{ eV} / kT) \text{cm}^{2}\text{s}^{-1}$</td>
</tr>
<tr>
<td>$C_{eq}$</td>
<td>$7.5 \times 10^{19} \exp(-2.556 \text{ eV} / kT) \text{cm}^{-3}$</td>
</tr>
<tr>
<td>$D_{V}$</td>
<td>$4.06 \times 10^{-3} \exp(-1.474 \text{ eV} / kT) \text{cm}^{2}\text{s}^{-1}$</td>
</tr>
</tbody>
</table>
simulated and measured platinum profiles. Figures 6 and 7 show a similarly good agreement between simulation and experimental data for processes at 832°C and 830°C which were ramped down at the end of the process. Figure 6 shows also that the concentrations of platinum in CZ and FZ silicon samples are identical within the experimental limits. From this, we exclude a major influence of material dependent phenomena like oxygen precipitates in our experiments.

VI. DISCUSSION OF VACANCY-RELATED PARAMETERS

The simulations of platinum out-diffusion in Figure 7 were found to be sensitive to the individual vacancy parameters $D_V$ and $C_V^{eq}$. When $D_V$ is increased and $C_V^{eq}$ decreased inversely proportional (and vice versa) within one order of magnitude, $a_{FT}$ has to be varied in the range from 0.5 to 50 Å in order to describe the experimental data equally well as in Figure 7. Since 0.5 Å is considerably lower than typical values assumed in the literature, an energy barrier for the Frank-Turbull reaction cannot be excluded. Figures 8 and 9 show the effect of a variation of the parameters $D_V$, $C_V^{eq}$ and $a_{FT}$ on the simulation results.

An explanation for the interdependence of the parameters can be found when taking the conditions during ramp-down into considerations. Due to the vicinity of the surface, the concentrations of interstitial platinum and the intrinsic point defects will decrease rapidly. In consequence, the
exchange between interstitial and substitutional platinum is governed by the Frank-Turnbull reaction in the backward direction. The rate of substitutional platinum atoms going to interstitial sites will then be equal to

\[ k_{FT} C_{Pt} \]

which, using Eqs. (7) and (4), can be expressed as:

\[
4\pi a_{FT}(D_{Pt} + D_V) \frac{C_{Pt}^{eq} C_V^{eq}}{C_{Pt}^{eq}} C_{Pt}.
\] (12)

This explains the inverse proportionality of \( a_{FT} \) to \( C_V^{eq} \) in Figures 8 and 9 since then, taking into account that \( D_{Pt} \gg D_V \), the rate (12) and with it the change of the substitutional platinum concentration with time become independent of \( D_V \) and \( C_V^{eq} \).

Varying the activation energy of the vacancy equilibrium concentration between 2.0 and 3.5 eV, we found that we obtained nearly identical solutions for the ramping rate of 0.6 K/min and similar well fits for the higher ramping rates as long as we left the vacancy equilibrium concentration and the vacancy diffusion coefficient at 730°C the same (approximately \( 1.1 \times 10^{10} \text{cm}^{-3} \) and \( 1.6 \times 10^{-8} \text{cm}^2/\text{s} \), respectively, for \( a_{FT} = 5 \text{Å} \)).

VII. DISCUSSION OF SELF-INTERSTITIAL-RELATED PARAMETERS

In the initial stage of the annealing process, the interstitial platinum atoms will distribute rapidly in the wafer so that \( C_{Pt} = C_{Pt}^{eq} \) can be assumed even for short times. In the bulk, some of them will interact via the Frank-Turnbull and kick-out mechanisms with intrinsic point defects and become substitutional. The transport capacities (the products of diffusion coefficients and concentrations) of the intrinsic point defects, on the other hand, are orders of magnitude smaller than the one of the platinum interstitials. Thus, in the initial stage, the vacancies consumed cannot be replaced by diffusion from the surface and the self-interstitials generated cannot diffuse to the surfaces. Conservation of the species involved leads then to a relationship between the concentrations of substitutional platinum, vacancies and self-interstitials, as well as the respective initial concentrations \( C_0^V \) and \( C_0^I \) in the form:

\[
C_{Pt} = C_1 - C_1^0 + C_V^0 - C_V.
\] (13)

The reactions (1) to (3) proceed until all of them are in local dynamic equilibrium. Assuming \( C_{Pt} = C_{Pt}^{eq} \) holds across the wafer, the relations for local dynamical equilibrium reduce to:

\[
\frac{C_{Pt}}{C_{Pt}^{eq}} = \frac{C_V}{C_V^{eq}} = \frac{C_I^{eq}}{C_I}.
\] (14)

Inserting Eq. (14) into Eq. (13) results in the following expression for the concentration of substitutional platinum establishing during the initial phase of the annealing process:

\[
C_{Pt}^{ini} = \frac{C_{Pt}^{eq}}{2(C_V^{eq} + C_{Pt}^{eq})} \times (C_V^0 - C_1^0 + \sqrt{(C_V^0 - C_1^0)^2 + 4C_I^{eq} (C_V^{eq} + C_{Pt}^{eq})}).
\] (15)

Under the reasonable assumption that \( C_V^{eq} \ll C_{Pt}^{eq}, C_{Pt}^{ini} \) in the wafer bulk will only depend on the equilibrium...
concentration of self-interstitials and on the initial concentrations $C_V^0$ and $C_I^0$ of vacancies and self-interstitials.

After the initial phase, a further increase of the substitutional platinum concentration is made possible by the diffusion of self-interstitials from the bulk to the surfaces where they recombine and by the diffusion of vacancies generated at the surfaces into the bulk. The increased self-interstitial concentration and decreased vacancy concentration, see Eq. (14), shifts the ratio of the transport capacities of self-interstitials and on the initial concentration of self-interstitials.

As shown in Figures 10–13, the concentration in the middle of the wafer was sensitive to the individual self-interstitial parameters $D_I$ and $C_I^{eq}$. The product $D_IC_I^{eq}$ was kept constant in all cases. $C_V^0 - C_I^0$ was adjusted to reproduce the experimental data for the shortest annealing depth profile while $C_I^{eq}$ was increased until the simulations did no longer result in an acceptable reproduction of the experimental data as a function of annealing time. From the simulations #2 in Figures 10–13, the expression

$$C_I^{eq} < 4 \times 10^{37} \exp \left( \frac{-5.7 \text{eV}}{kT} \right) \text{cm}^{-3} \quad (16)$$

was deduced as an upper limit for the equilibrium concentration of self-interstitials in the temperature range of 730 to 950 °C. A comparison between expression (16) and values published for the equilibrium concentration of self-interstitials is shown in Figure 14. Several of the literature values such as those in the work of Bronner and Plummer,\textsuperscript{15} Chao et al.,\textsuperscript{16} Okino and Shimozaki,\textsuperscript{20} and Wijaranakula\textsuperscript{21} to the temperature range of 730 to 950 °C exceed the upper limit deduced for the equilibrium concentration of self-interstitials.
VIII. SUMMARY

Based on own experiments and experiments reported in the literature, a model was developed for the diffusion of platinum from a silicide source. For the first time, this model is able to reproduce in-diffusion in the temperature range from 730 to 950 °C and out-diffusion associated with the ramping-down of the temperature at the end of an annealing process at 830 °C. Particularly, the experiments involving ramping-down allowed narrowing down the parameter range for vacancies. From the evolution of the platinum concentration in the bulk of the wafers for short annealing times, it was possible to deduce an upper limit for the equilibrium concentration of self-interstitials.