# Determination of aluminum diffusion parameters in silicon

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Aluminum as the fastest diffusing acceptor dopant in silicon is commonly used for the fabrication of power semiconductors with p-n junction depths ranging from some microns to more than a hundred microns. Although long used, its diffusion behavior was not sufficiently characterized to support computer-aided design of devices. In this work, the intrinsic diffusion of aluminum was investigated in the temperature range from 850 to 1290 °C. Combining nitridation and oxidation experiments, the fractional diffusivity via self-interstitials was determined. By diffusion in high-concentration boron- and phosphorus-doped silicon the behavior of aluminum under extrinsic conditions was investigated. © 2002 American Institute of Physics. [DOI: 10.1063/1.1465501]

# I. INTRODUCTION

Aluminum is traditionally used to fabricate deep p-njunctions with depths of more than 100  $\mu$ m because it is the fastest diffusing acceptor dopant in silicon. Nevertheless, process temperatures of up to 1200 °C and process times of some 40 h and more are usual. These processes stand for a tremendous thermal budget which gives rise to the formation of extended defects and to possible contamination. Deep p-n junctions, on the other hand, are often needed only to separate the space-charge region around the p-n junction from the surface near layer of process-induced defects. Modern concepts for the fabrication of power devices are, therefore, often based on short-time processes at comparatively low temperatures<sup>1,2</sup> to avoid defect formation and contamination. Because of the traditional application of aluminum for deep p-n junctions, most investigations covered temperatures above 1200 °C. The results disagreed by up to a factor of 50.<sup>3,4</sup> Early publications<sup>5–9</sup> were based entirely on open- and closed-tube deposition and junction delineation by lapping and staining. In later publications, ion implantation<sup>10,11</sup> and electrical characterization methods such as spreading resistance profiling have been used. Only a few authors<sup>1,2,12,13</sup> used more reliable characterization methods like secondary ion mass spectroscopy (SIMS). Especially for short diffusion times and low diffusion temperatures, the diffusion of aluminum is characterized insufficiently. Based on the diffusion enhancement of aluminum during oxidation,<sup>14</sup> Gösele and Tan<sup>15</sup> estimated the fractional diffusivity  $f_I$  via self-interstitials as  $f_I > 0.85$  at 1150 °C.

# **II. EXPERIMENTAL PROCEDURE**

All experiments were carried out using float-zone (FZ) silicon. For diffusion experiments under extrinsic conditions,

boron-doped layers with concentrations of  $4.6 \times 10^{19}$  and  $7.0 \times 10^{19}$  cm<sup>-3</sup> were fabricated by epitaxial deposition. Alternatively, phosphorus was diffused from a POCl<sub>3</sub> source and resulted in a homogeneous concentration of  $1.3 \times 10^{20}$  $cm^{-3}$  within 2  $\mu m$ . Experiments for determination of the diffusion coefficient under inert intrinsic and extrinsic conditions were performed with aluminum implanted with 60 keV and a dose of  $3 \times 10^{13}$  cm<sup>-2</sup>. For the estimation of  $f_I$ , Al and P were implanted with 10 keV and a dose of  $2 \times 10^{13}$  cm<sup>-2</sup> each, and Sb with 40 keV and a dose of  $2 \times 10^{13}$  cm<sup>-2</sup>. The Al doses were kept low to minimize Al precipitation and the formation of extended defects. All implantations were performed under a tilt angle of 7°. Immediately before the implantation process, the native oxide was removed by a HF dip to avoid knock on of oxygen into the silicon. After the implantation, all samples were subjected to heat treatment at 1060 °C for 10 s to anneal the implantation damage. The diffusion processes were carried out in a horizontal furnace from 850 to 1100 °C for times from 30 to 10000 min and in a rapid thermal processing (RTP) system from 930 to 1290 °C for times from 3 s to 15 min. For inert diffusion, oxidation, and nitridation processes, nitrogen, dry oxygen, and ammonia ambients were used, respectively. For inert processes with temperatures higher than 1100 °C, samples were covered with a 100-nm-thick low-temperature oxide (LTO) to avoid injection of vacancies into silicon due to nitridation effects.<sup>16</sup> After diffusion, oxide and nitride thicknesses were measured by ellipsometry.

The SIMS analyses were performed using a CAMECA IMS 4f using 10–15 keV  $O^+$  primary beams for Al (high mass resolution 4000) and a 10 keV Cs<sup>+</sup> primary beam for P and Sb. The diffusion coefficients were extracted using the optimization tool of ICECREM 4.3.<sup>17</sup> In all simulations, the profile measured after the postimplantation anneal was taken as the initial condition and the model parameters adjusted until an optimum description of the profiles measured after diffusion was achieved. Furnace and RTP ramp rates and oxide growth were taken into consideration consistently.

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Due to the exceptional long diffusion times the RTP cooling system was insufficient to avoid a heating up of the cold-wall process chamber. The temperature measurement by a pyrometer on the silicon wafer was affected by radiation of the upheated process chamber, so that temperature measurement became unreliable. An effective temperature during the diffusion processes has been estimated in two ways: First, by fitting the diffusion profiles of P and Sb and comparing the diffusivities to the well-known diffusivities of these elements.<sup>18,19</sup> Second, by comparing the oxide thicknesses after oxidation to established oxidation models. The effective temperature was set as the mean value of those three estimates. The standard deviation of those three estimations is plotted as a temperature error bar in Fig. 2. Diffusion in a horizontal furnace was affected by backdiffusion of oxygen into the process tube. The influence of injection of selfinterstitials due to this oxygen backdiffusion into the bulk material was taken into account. The oxide thicknesses were measured after heat treatments and fitted with ICECREM 4.3 by adjusting the oxygen partial pressure. The interstitial oversaturation was estimated via the model of Dunham.<sup>20,21</sup> For the influence of the self-interstitial injection on the diffusion of aluminum a diffusion mechanism exclusively via self-interstitials was supposed. In an earlier publication<sup>22</sup> those corrections were not taken into account but their effects remained unnoticed because of a numerical problem in the data conversion.

#### **III. RESULTS AND DISCUSSION**

#### A. Intrinsic diffusion

During heat treatment, a non-negligible fraction of aluminum diffuses out of the silicon and reacts with oxygen atoms in the native oxide on the wafer surface. To simulate this effect, the silicon surface is modeled as an infinitely effective sink for aluminum atoms. The resulting surface peak in the SIMS profiles is not shown in the figures for the sake of clarity. For determination of the intrinsic diffusion coefficient, four diffusion processes with gradually increasing process times were carried out at each temperature. Simulations were performed with the same parameter set for all four profiles. Figure 1 shows, as an example, the series processed at 1100 °C. A similarly good agreement was obtained also for the other temperatures and no indications for transient phenomena could be found. From these data, the diffusivity of aluminum was calculated in the form of an Arrhenius law with the prefactor  $D_0 = 4.73 \text{ cm}^2/\text{s}$  and activation energy  $E_A = 3.35$  eV. Figure 2 shows the values of the diffusivities in comparison with the results of various other authors.<sup>2–8,10,12,23,24</sup> In the temperature range above 1000 °C our values are in a very good agreement with the majority of reliable data. In the low-temperature regime, our values agree with those of Ortiz.<sup>13</sup> The data of Kao<sup>7</sup> are presumably influenced by effects associated with the indiffusion of aluminum during the closed-tube-diffusion method.



FIG. 1. Diffusion profiles of aluminum annealed at 1100 C by RTP in  $N_2$ . Comparison of SIMS profiles and ICECREM simulations with one parameter set.

# B. Determination of the dominating diffusion mechanism

To determine the dominating diffusion mechanism of aluminum, diffusion processes under inert, dry oxidizing, and nitriding condition were performed. Figure 3 shows SIMS profiles after processing at 1100 °C. It is obvious that the diffusivity of aluminum is strongly enhanced during oxidation and retarded during nitridation. This leads to the conclusion that aluminum is diffusing predominantly via self-interstitials as diffusion vehicles. Assuming diffusion via self-interstitials *I* and vacancies *V*, the diffusion coefficient *D* of a dopant can be written approximately in the form

$$D = D^{eq} \left( f_I \frac{C_I}{C_I^{eq}} + f_V \frac{C_V}{C_V^{eq}} \right) \tag{1}$$

with  $D^{eq}$  denoting its diffusion coefficient under inert conditions.  $f_I$  and  $f_V$  stand for the fractional diffusivities via self-



FIG. 2. Intrinsic diffusivity of aluminum in silicon. For diffusions in RTP the standard deviations in temperature determination are plotted as error bars.



FIG. 3. Diffusion profiles of aluminum, antimony, and phosphorus annealed at 1044 C for 5 min in inert, oxidizing, and nitriding ambients. Profiles in oxidized samples are given relative to the initial surface.

interstitials and vacancies, and  $C_I$  and  $C_V$  for their concentrations, respectively. The superscript "eq" indicates concentrations under inert conditions. In the derivation of Eq. (1) it was already assumed that other mechanisms are ineffective so that  $f_I$  equals  $1-f_V$ . Following Fahey et al.,<sup>25</sup> an estimation of  $f_I$  and  $f_V$  can be obtained under conditions of nitridation from

$$f_I \ge 1 - \frac{D/D^{eq}}{C_V/C_V^{eq}},\tag{2}$$

where  $C_V/C_V^{eq}$  can be estimated from the diffusion enhancement of antimony showing always the highest diffusivity enhancement during nitridation. Similarly, from oxidation experiments,  $f_V$  can be estimated from

$$f_V \ge 1 - \frac{D/D^{eq}}{C_I/C_I^{eq}},\tag{3}$$

with  $C_I/C_I^{eq}$  to be estimated from the impurity that shows the highest diffusion enhancement during oxidation. In the experiments of Fahey *et al.* the diffusivity enhancement was highest for phosphorus but aluminum was not investigated.



FIG. 4. Diffusion profiles of aluminum in intrinsic and extrinsically borondoped silicon.

In our experiments aluminum was showing stronger diffusion enhancement during oxidation (OED) at temperatures lower than 1100 °C and similar diffusion enhancement than phosphorus at higher temperatures. This means that  $C_I/C_I^{eq}$  has to be estimated from the diffusivity enhancement of aluminum so that the lower limit for  $f_V$  becomes zero. With increasing temperatures OED is decreasing, which is in agreement with the work of Mizuo<sup>14</sup> for aluminum and Ural<sup>26</sup> for phosphorus. A summary of values of OED and the estimates for  $f_I$  of aluminum and phosphorus from Eqs. (2) and (3) can be found in Table I.

#### C. Extrinsic diffusion

Because of the low solubility of aluminum in silicon, which would not allow to investigate the extrinsic diffusion behavior in samples doped with aluminum only, silicon substrates with high homogeneous concentrations of boron and phosphorus were used. Diffusion of Al in the extrinsic boron background is strongly enhanced. Due to the high dopant concentrations, shifts in the Fermi level generate an additional amount of charged point-defect–dopant pairs. Figure 4 shows SIMS profiles of aluminum diffused under intrinsic and extrinsic conditions. For determination of the diffusivity of aluminum under extrinsic conditions  $D_{ex}^{Al}$ , the influence of injection of self-interstitials due to backdiffusion of oxygen must be included. Because of high dopant concentrations, the suppression of oxidation enhancement was presumed.<sup>27</sup> As-

TABLE I. Values of OED and fractional contribution of diffusion via interstitial mechanism of aluminum and phosphorus. Lower limits for  $f_I$  result from nitridation experiments; upper limits from oxidation experiments.

Process parameters	OED(Al)	OED(P)	$f_I^{ m Al}$	$f_I^{\mathrm{P}}$
930 C, 45 min	4.73	4.54	0.92 - 1.00	0.94 - 0.96
1044 C, 5 min	4.68	4.51	0.89 - 1.00	0.81 - 0.96
1100 C, 3 min	2.44	2.50	0.84-0.98	0.83–1.00
1290 C, 1.5 min	1.78	1.78	0.75-1.00	0.77–1.00



FIG. 5. Diffusion enhancement of aluminum vs normalized hole concentration.

suming also total electrical activation of boron in Fig. 5, the diffusivity enhancement  $D_{\rm ex}^{\rm Al}/D_i^{\rm Al}$  of aluminum is plotted versus the normalized hole concentration. A linear dependence is obvious. But, following the description of extrinsic diffusion behavior by Shaw<sup>28</sup>

$$D_{\rm ex} = D_i \frac{1 + \beta (p/n_i) + \gamma (p/n_i)^2}{1 + \beta + \gamma}, \qquad (4)$$

diffusion enhancement cannot be higher than the charge carrier supersaturation supposing a strictly linear diffusion enhancement. From this it follows that  $\gamma$  must have a positive value. Because of uncertainties in the suppression of OED of high dopant concentration and the limited amount of values of normalized hole concentrations, no exact value for  $\beta$  and  $\gamma$  can be given.

In extrinsically phosphorus-doped silicon, the diffusion of aluminum is retarded drastically. Figure 6 shows a SIMS profile and simulations of Al diffused at a temperature of 900 °C in intrinsically and extrinsically phosphorus-doped silicon. Beside a



FIG. 6. Diffusion profile of aluminum and simulation at a temperature of 900 C in extrinsically phosphorus-doped silicon and the expected aluminum profile under identical conditions in intrinsically doped silicon.

TABLE II. Intrinsic  $D_i^{\text{Al}}$  and effective diffusivity of aluminum  $D_{\text{eff}}^{\text{al}}$  in silicon. The effective value includes Fermi-level effects and ion pairing.

Temperature	$D_i^{\rm Al}$ (cm <sup>2</sup> /s)	$D_{\rm ex}^{\rm Al}~({\rm cm}^2/{\rm s})$	Reduction of diffusivity $D_{ex}^{Al}/D_i^{Al}$
900 C 1000 C 1100 C	$1.9 \times 10^{-14} \\ 2.5 \times 10^{-13} \\ 2.3 \times 10^{-12}$	$\begin{array}{c} 1.2 \times 10^{-16} \\ 1.4 \times 10^{-15} \\ 1.0 \times 10^{-13} \end{array}$	$6.67 \times 10^{-03} \\ 5.99 \times 10^{-03} \\ 4.35 \times 10^{-02}$

reduction of charged-point-defects-dopant pairs due to Fermi-level effects, formation of aluminum phosphorus ion pairs can be expected. Compared to the intrinsic case diffusivity of aluminum is reduced by up to two orders of magnitude. Table II lists the values of the diffusivity under intrinsic and extrinsic conditions. A separation of the influences is not possible from the current experiments.

## **IV. CONCLUSIONS**

The diffusivity of aluminum was determined in a temperature range from 850 to 1290 °C. The values found agree very well with previous reports and reduce the uncertainties in the low-temperature regime. A combination of diffusion experiments in inert, oxidizing, and nitriding ambients allowed the determination of the dominating diffusion mechanism of aluminum. It was found that aluminum diffuses predominantly via self-interstitials as diffusion vehicles and shows, at temperatures lower then 1100 °C, an even higher diffusion enhancement under oxidizing conditions than phosphorus. In extrinsically boron-doped silicon, diffusion of aluminum is enhanced due to Fermi-level effects with aluminum diffusing primarily via charged-point defects. In a highly phosphorus-doped background, diffusion of aluminum is strongly retarded.

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