Point Defect Properties from Metal Diffusion Experiments — What Does the Data Really Tell Us?

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Point defect properties, including diffusivities and equilibrium concentrations for both interstitials and vacancies, are commonly extracted from metal diffusion experiments, and these values are widely used in process simulation software. However, in many cases, these parameter values were extracted using oversimplified models which ignore interactions between interstitial and vacancy diffusion mechanisms. Questions about the accuracy of these parameters have come from *ab-initio* defect calculations which conclude that vacancies diffuse faster than interstitials, in contrast with published reports on metal diffusion which find vacancies diffuse much more slowly than interstitials. We have reanalyzed published data for zinc and platinum diffusion and find that it is possible to match all of the data using fast vacancy diffusivity. The most direct evidence for slow vacancy diffusion (and a high equilibrium concentration) comes from platinum diffusion experiments. However, we are able to reproduce these results with fast V diffusion and carbon/interstitial clustering, using carbon concentrations typical of Czochralski and float zone silicon ($10^{16}\mathrm{cm}^{-3}$). We evaluate the effectiveness of metal diffusion experiments in determining point defect parameters, and find that it is not possible to reliably determine both diffusivities and equilibrium concentrations for both interstitials and vacancies from metal diffusion results.

1. INTRODUCTION

Modeling of diffusion processes in Si has come a long way over the last 30 years. Despite this, the relative influence of interstitials and vacancies to diffusion remains a subject of controversy. Reported values for the equilibrium concentrations of interstitials vary over many orders of magnitude and only a few estimates exist for vacancies. This is primarily due to the fact that native point defects are present in such small concentrations that direct observation of vacancy or interstitial properties is difficult. It is generally accepted that in Si both self-interstitials and vacancies have to be taken in to account in order, to effectively model dopant diffusion.[1] Mainly two types of experiments give us information about point defects. Analysis of diffusion profiles for metals such as Au, Pt and Zn, and study of dopant diffusion under point defect injection conditions such as oxidation and nitridation. However, the latter method has provided a wealth of data about dopant diffusion mechanisms and much less on the intrinsic point defects involved. The most widely used estimates of vacancy parameters come from metal diffusion experiments, but even here the issue of vacancy diffusivity is not clear. Most of the metal diffusion experiments predict a relatively low vacancy diffusivity[2,3] whereas molecular dynamics based defect calculations predict a much higher vacancy diffusivity.[4] This issue has been recently been complicated further as carbon has been shown to act as an interstitial trap and hence reduces the effective interstitial diffusivity if present in large amounts.[5]

In this paper we reanalyse the experimental data from metal diffusion experiments within a consistent framework, taking into account the couplings between impurities and point defects. We also include carbon clustering and evaluate its influence on the extracted metal diffusion parameters.

2. THEORY OF METAL DIFFUSION

The metals Au, Pt and Zn diffuse mainly via the kick-out and Frank-Turnbull (or dissociative mechanism).[2,3,6] This leads to the reactions,

$$M_s + I \Leftrightarrow M_i, \tag{1}$$

$$M_s \Leftrightarrow M_i + V, \tag{2}$$

where M_i and M_s represent interstitial and substitutional metal as well as their concentrations. A third reaction that needs to be considered is the bimolecular recombination between interstitials and vacancies,

$$I + V \Leftrightarrow \phi. \tag{3}$$

Assuming that substitutional metal is immobile we can now write the full set of equations that need to be solved.

$$\frac{\partial M_s}{\partial t} = -k_{ko}(M_s I - K_{ko}^{eq} M_i) - k_{ft}(M_s - K_{ft}^{eq} M_i V), \tag{4}$$

$$\frac{\partial M_i}{\partial t} = \vec{\nabla} \cdot D_{M_i} \vec{\nabla} C_{M_i} + k_{ko}(M_s I - K_{ko}^{eq} M_i) + k_{ft}(M_s - K_{ft}^{eq} M_i V), \tag{5}$$

$$\frac{\partial I}{\partial t} = \vec{\nabla} \cdot D_I \vec{\nabla} I - k_{ko}(M_s I - K_{ko}^{eq} M_i) - k_{bi}(IV - I^* V^*), \tag{6}$$

$$\frac{\partial V}{\partial t} = \vec{\nabla} \cdot D_V \vec{\nabla} V + k_{ft}(M_s - K_{ft}^{eq} M_i V) - k_{bi}(IV - I^* V^*), \tag{7}$$

where I and V are the interstitials and vacancy concentrations, D_A is the diffusivity of A ($A \in M_i$, M_s, I, V), and the asterisks indicate the thermal equilibrium concentrations. The last term in the I and V equations accounts for the bimolecular recombination given by Eq (3). In Eqs. (4) – (7), k_{ft} and k_{ko} represent the forward rates for the Frank-Turnbull (FT) and kickout (KO) mechanism, with K_{ko}^{eq} and K_{ft}^{eq} the associated equilibrium constants. Assuming diffusion limited reactions, these rates can be written as

$$k_{ko} = 4\pi r_{ko} D_{M_i}, \tag{8}$$

$$k_{ft} = 4\pi r_{ft}(D_I + D_{M_i}), \tag{9}$$

$$k_{bi} = 4\pi r_{bi}(D_I + D_V). \tag{10}$$

where r_A is the radius of capture for that reaction.

The system of Eqs. (4) – (10) contains a number of parameters which need to be determined. To reduce the number of fitting parameters, we can approximate the capture radii $r_{ft} = r_{ko} = r_{bi}$ by the nearest neighbor distance 2.35Å. Also in many cases metal diffusivity and solubility are known from other types of experiments.

It is also necessary to specify the initial boundary conditions. For point defects, we assume that the Si/metal surface is an infinite source and sink for point defects. Hence, the concentrations of interstitials and vacancies are fixed at their equilibrium values (I^* and V^*) at all times during the diffusion process. The initial interstitial concentration is taken to be equal to I^*. However, there is some debate over the initial vacancy concentration since previous work on metal diffusion has used different initial concentrations of vacancies.[2,3] We discuss this issue further in the subsequent sections. For the metals, the initial concentration in the silicon is considered negligible ($< 10^8 \text{cm}^{-3}$). The surface concentration of interstitial metal is set to its solubility ($M_i(x = 0) = M_i^*$).

3. ZINC DIFFUSION

Since extensive zinc diffusion data is available for both heavily dislocated and defect-free material[2,7] we focus on this metal for much of our analysis. In the experiments, Bracht *et al.*[2] first equilibrated the samples at diffusion temperatures ranging from 870°C to 1208°C and then introduced zinc, which diffused in from both surfaces. Dislocations act as sources and sinks for point defects. Hence, in heavily dislocated material, point defect concentrations remain near equilibrium ($I = I^*$, $V = V^*$) and diffusion is independent of the intrinsic point defect properties. We use the metal properties found by Bracht *et al.*[7] for diffusion in dislocated silicon in our modeling of the defect-free material. For consistency, instead of fitting single temperatures, all the curves were simultaneously fit using temperature activated parameters. Bracht *et al.*[2] extracted a high value for V^* from this data, but required an initial vacancy concentration much less than equilibrium ($V(t = 0) \leq 10^{-4}V^*$). The simulated and measured profiles using the parameters extracted by Bracht *et al.*[2] are shown in Fig. 1. Using $V(t = 0) = V^*$ we are also unable to fit the data. However, we were able to obtain a similar fit to the observed data using a much lower value of V^* (Fig. 2). The extracted V^* has the advantage of being much closer to theoretical predictions.[4] The point defect parameter values we obtained are tabulated in Table 1 and compared to literature values in Figs. 6 and 7.

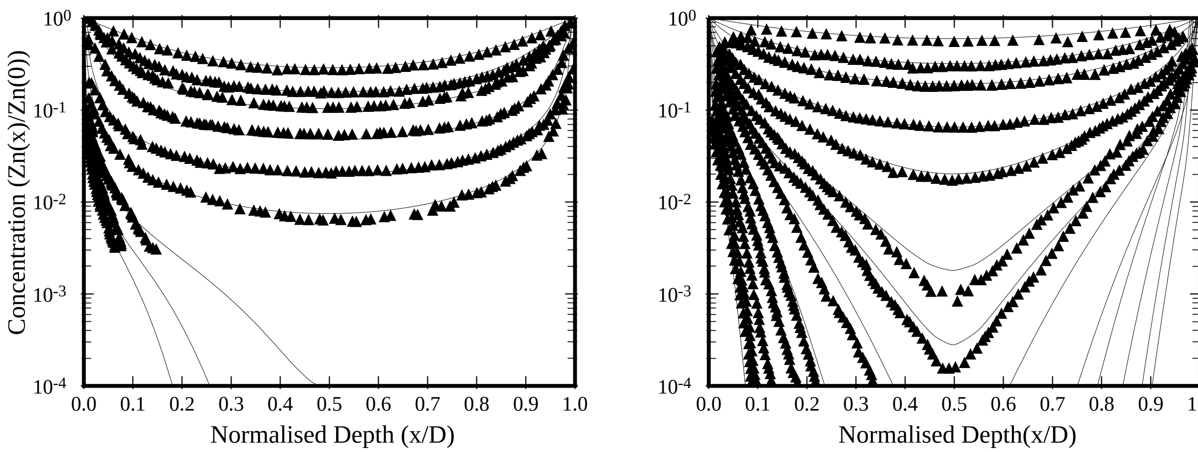

Fig. 1: Normalized zinc diffusion profiles at (a) 870°C and (b) 1208°C into defect-free silicon and comparison to simulations using point defect parameters from Bracht *et al.*[2]

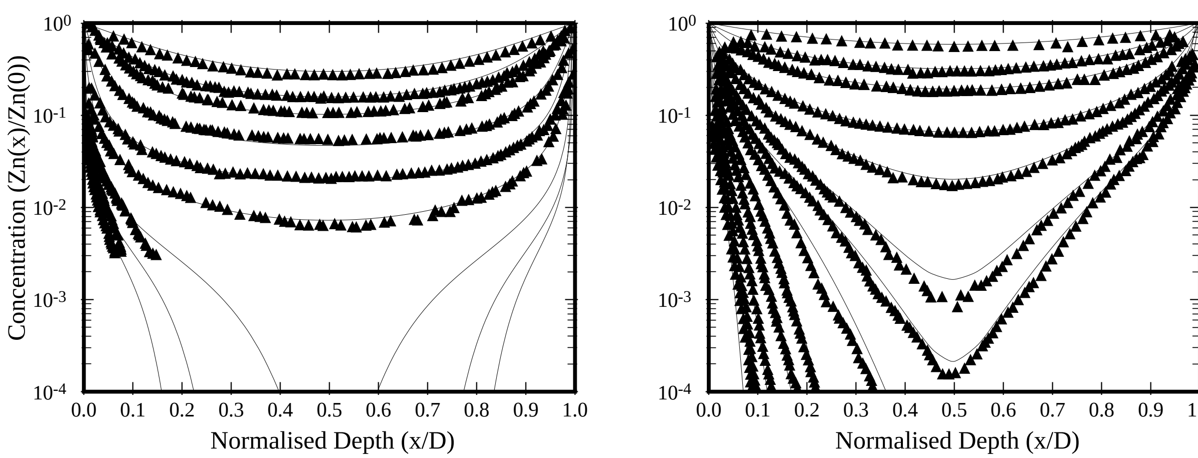

Fig. 2: Normalized zinc diffusion profiles at (a) 870°C and (b) 1208°C into defect-free silicon and comparison to simulations using point defect parameters obtained in this work.

Table 1: Point defect parameters extracted from comparison to zinc diffusion experiments of Bracht *et al.*[2]

Parameter	Pre-exponent	Energy
$V^*(\mathrm{cm}^{-3})$	1.2×10^{19}	2.0
$D_V V^*(\mathrm{cm}^2/s)$	6.95×10^{21}	3.88
$I^*(\mathrm{cm}^{-3})$	1.6×10^{19}	2.0
$D_I I^*(\mathrm{cm}^2/s)$	5.1×10^{26}	5.1

4. PLATINUM DIFFUSION

Low temperature diffusion data exist for Pt as it diffuses faster than Zn or Au.[8] Platinum profiles are characterised by uniform bulk concentrations of the substitutional Pt which do not change with time, and at the lowest temperature an inverse U profile is seen in non-equilibrated samples.[9] The flat profiles have been attributed to the initial concentration of point defects, and assuming the dominance of the dissociative reaction, Zimmermann *et al.* calculated V^* similar to that of Bracht *et al.*[2] The inverse U profiles were explained by an initial super-saturation of vacancies, leading to a metal concentration in the bulk greater than its solid solubility. However, we find this behavior can also be explained by a carbon clustering model as discussed in the next section and shown in Fig. 3.

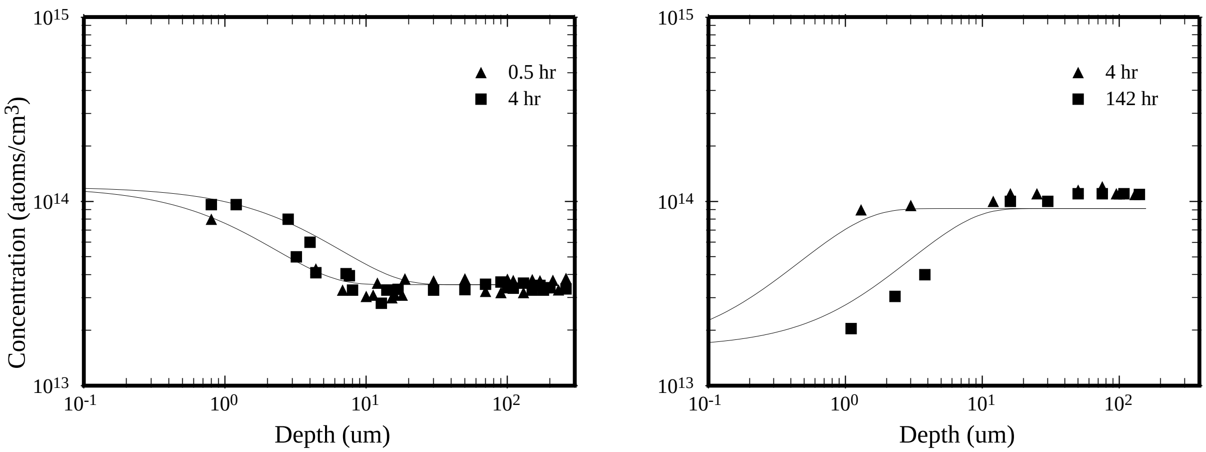

Fig. 3: Measured and simulated platinum profiles at (a) 770°C[10] and (b) 700°C.[9] Note the uniform Pt concentration in bulk which is unchanged with time, and the inverse U profile at 700°C.

5. CARBON CLUSTERING MODEL

It has been reported based on MBE grown samples with elevated carbon concentrations that carbon acts as an interstitial trap.[5] Carbon in silicon can be modeled[4] based on diffusion as an interstitial,

$$C_s + I \Leftrightarrow C_i, \tag{11}$$

plus reaction of interstitial carbon with substitutional carbon to form an immobile complex,

$$C_i + C_s \Leftrightarrow C_{is}. \tag{12}$$

Since carbon clusters with an interstitial, each cluster formation annihilates an interstitial or generates a vacancy. If the initial carbon cluster concentration is less than its equilibrium value, the formation of carbon clusters leads to an under-saturation of interstitials (or a corresponding super-saturation of vacancies) which leads to the inverse U profile. This is possible during FZ crystal growth, if we assume that the material is quenched from a high temperature at which the clusters are unstable. It should be noted that the flat profile of platinum in the bulk is expected even if the samples were equilibrated before the in-diffusion,[11] although the bulk Pt concentration is lower in this case. We assume a total carbon concentration of $10^{16}\mathrm{cm}^{-3}$, typical of Cz or FZ Si and find an equilibrium value for the relative concentration of C_s and C_{is} of

$$\frac{C_s^2}{C_{is}} = 1.2 \times 10^{43} \exp(-5.0/kT). \tag{13}$$

To check our analysis, the same carbon model and parameters were used for simulations of zinc diffusion. As seen in Fig. 4, we find that at the higher temperatures used for zinc, moderate carbon levels carbon do not produce a significant change in the profiles.

It has also been observed that a carbon concentration of $2 \times 10^{19}\mathrm{cm}^{-3}$ suppresses TED completely,[5] while there is considerable TED even with $10^{18}\mathrm{cm}^{-3}$. We simulated boron TED with 2×10^{19} and $10^{18}\mathrm{cm}^{-3}$ of total carbon, using the RPM model for TED.[12] The simulations qualitatively predict the suppression of TED for $2 \times 10^{19}\mathrm{cm}^{-3}$ carbon in Si (Fig. 5).

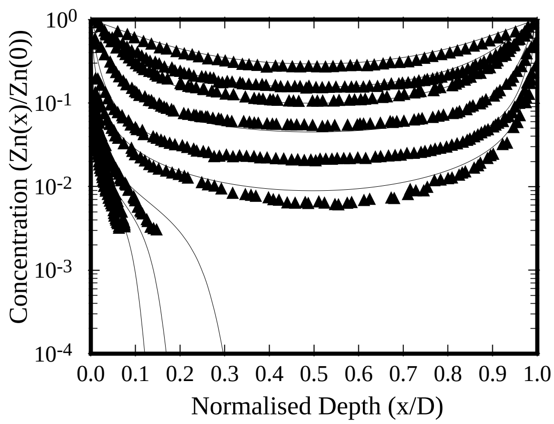

Fig. 4: Effect of carbon on zinc diffusion at 870°C. Carbon has only a minor effect even at the lowest available diffusion temperature.

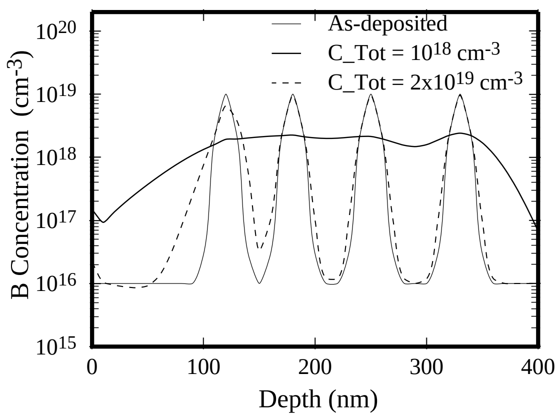

Fig. 5: Simulations of boron diffusion profiles in implanted and 790°C annealed MBE-grown superlattices using carbon clustering model.

6. CONCLUSIONS

We have reanalysed the published data for zinc and platinum experiments and find that the resulting profiles can be explained well by considering a fast vacancy diffusivity closer to *ab-initio* calculations. A carbon clustering model was used to account for the features of low temperature platinum diffusion. In order to evaluate the relative accuracy of the extracted point defect parameters (Figs. 6 and 7), we reoptimised our profiles while fixing each of our extracted parameter in turn. Fig. 8 shows the change in mean squared error as each of the parameter is changed from its optimum value. It can be noted that $D_I I^*$ can be reliably calculated, and $D_V V^*$ and I^* (or D_I) can be estimated reasonably, while the experiments are relatively insensitive to V^* (or D_V).

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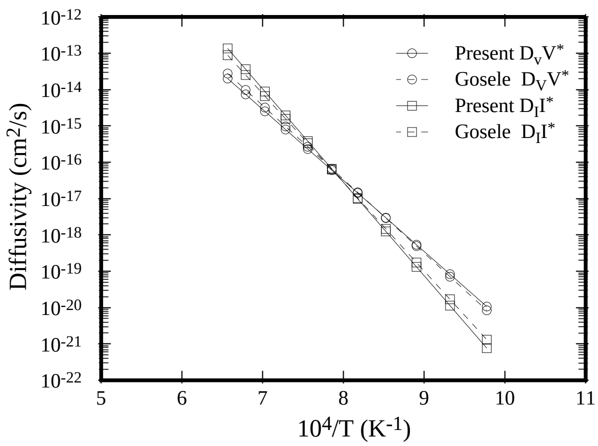

Fig. 6: Temperature dependence of extracted $D_V V^*$ and $D_I I^*$ compared to literature data.[4]

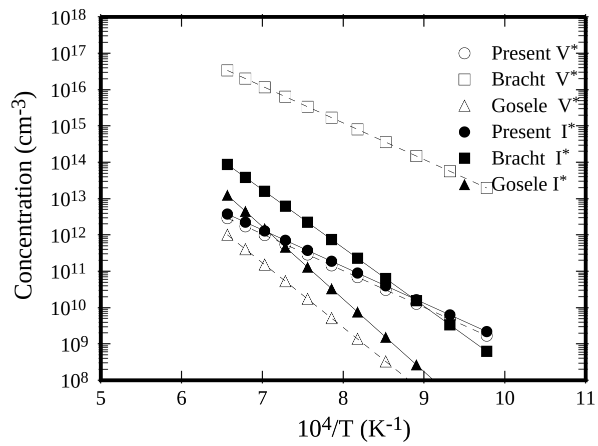

Fig. 7: Temperature dependence of extracted I^* and V^* compared to data from theoretical predictions as cited by Gösele[4] and from previous zinc diffusion analysis.[2]

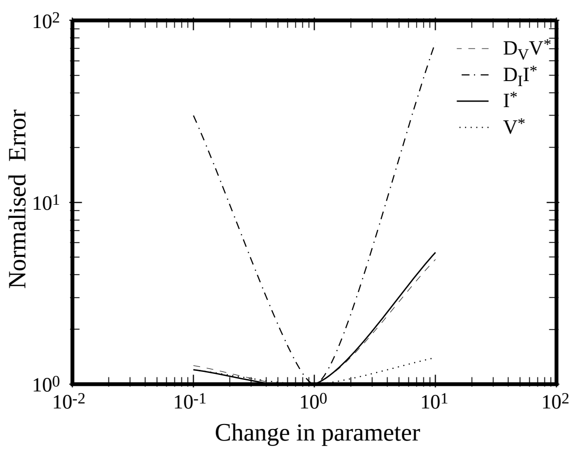

Fig. 8: Effect of variation in a single point defect parameter and reoptimising all the profiles.