

Relaxation of vacancy depth profiles in silicon wafers: A low apparent diffusivity of vacancy species

V. V. Voronkov,¹ R. Falster,¹ and P. Pichler²

¹*SunEdison, via Nazionale 59, 39012 Merano, Italy*

²*Fraunhofer Institut, Schottkystrasse 10, D-91058 Erlangen, Germany*

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Vacancy depth profiles in silicon wafers—installed by Rapid Thermal Annealing and monitored by Pt diffusion—show, upon subsequent annealing at 975 or 950 °C, a peculiar evolution: the concentration profile goes down without any trace of vacancy out-diffusion. The estimated apparent diffusivity is less than 10^{-7} cm²/s at 975 °C. The monitored vacancy species is tentatively identified as a “slow vacancy” that was recently concluded to exist along with other (highly mobile) vacancy species. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4863225>]

Lattice vacancies in silicon play a crucial role in many important phenomena such as impurity diffusion,¹ radiation-produced defects,^{2,3} and grown-in microdefects.⁴ The properties of vacancies—diffusivity and equilibrium concentration—have been discussed for decades. A unified treatment of different sources of data leads to a seemingly self-consistent set of vacancy parameters.⁴ In particular, the vacancy diffusivity in a high-temperature range—deduced from the density and size of grown-in voids—is consistent⁴ with a value reported for neutral vacancy at cryogenic temperatures³ and extrapolated to higher T

$$D_V = (0.0012 \text{ cm}^2/\text{s}) \exp(-0.45 \text{ eV} / kT). \quad (1)$$

This “Watkins diffusivity” is remarkably high, about 3×10^{-5} cm²/s at 1100 °C (which is a typical formation temperature of grown-in voids). However, it was later realized that in some cases the apparent vacancy diffusivity is much lower than the value given by Eq. (1). For instance, self-diffusivity enhancement⁵ by hot proton irradiation at around 850 °C shows an apparent diffusivity lower by 3 orders of magnitude. The suggested explanation⁶ is that the vacancy (V) exists not as a single species but rather that there are several independent kinds of V differing in atomic configuration and strongly differing in the value of the diffusivity. In the present paper, we provide further evidence for existence of a “slow vacancy” species.

A simple and most straightforward way to deduce the vacancy properties is to monitor the vacancy depth profiles^{7,8} installed by Rapid Thermal Annealing (RTA) of silicon wafers at around 1240 °C. At first, we will treat these profiles using a conventional notion of a single V species for free vacancies. The vacancy species produced by RTA in Czochralski (oxygen-rich) wafers were thought to be not free vacancies V but rather vacancy complexes with oxygen, VO, and VO₂. Below some characteristic binding temperature T_b (roughly estimated to be around 1050 °C), the dominant vacancy species in the equilibrated V + VO + VO₂ community was expected^{8,9} to be VO₂. The concentration profile $C_V(z)$ of RTA-produced vacancy species (thus believed to be VO₂) was monitored, in dependence of the depth coordinate z , by Pt in-diffusion^{7,8} at around 730 °C. In this process, interstitial platinum atoms Pt_i react with the vacancy species replacing

them with substitutional atoms Pt_s. Particularly, in case of the VO₂ species, this reaction produces Pt_s atoms and oxygen dimers O₂ that diffuse away from the original location of VO₂. The resulting concentration [Pt_s]—identical to that of the frozen-in vacancy species—is measured by DLTS.

The measured depth profiles $C_V(z)$, after RTA in an Ar ambient, have an inverse-U shape: the concentration is reduced in the near-surface regions of wafers due to vacancy out-diffusion in the course of fast cooling that follows the RTA. If an RTA-treated wafer is then annealed again at T below T_b (for example, at around 1000 °C), the vacancy out-diffusion is expected to go on with an apparent diffusivity D_{VA} , which is essentially smaller than the true diffusivity of free vacancies D_V —because the fraction of V in the V + VO + VO₂ community is small. Comparing D_{VA} with the known value of D_V , Eq. (1), it could be possible to find an important property of vacancy-oxygen interaction: the equilibrium binding ratio $([VO_2] + [VO])/[V]$ in dependence of T . In this way, the actual value of the binding temperature T_b could be obtained.

With this purpose in mind, several Czochralski-grown silicon wafers, 670 μm thick, were subjected to RTA in Ar at 1240 °C for 20 s, with a subsequent fast quench at a rate close to 70 K/s. The material was lightly doped with boron and the oxygen concentration was 7×10^{17} cm⁻³ using an optical calibration factor 2.45×10^{17} cm⁻². The depth profile of vacancy species, along a cleaved surface, was measured right after RTA and also after subsequent annealing at 975 °C and 950 °C for 18 and 58 s. The Pt diffusion was performed at 730 °C for 40 min. The measured vacancy profiles are shown in Fig. 1 (for 975 °C annealing) and Fig. 2 (for 950 °C annealing). The as-frozen profile (curve 1 in Figs. 1 and 2) is of the usual shape with a near-surface depletion due to vacancy out-diffusion in the course of fast cooling. An appreciable width of the depleted zone implies a relatively high vacancy diffusivity. In the course of subsequent annealing, the depleted zone should gradually expand and finally—when this zone spreads over the whole wafer—the bulk vacancy concentration will also be reduced.

Quite surprisingly, however, the measured profiles in the annealed wafers (curves 2 and 3 in Figs. 1 and 2) show no trace of further out-diffusion: the vacancy profile goes down as a whole, without any increase in the width of the

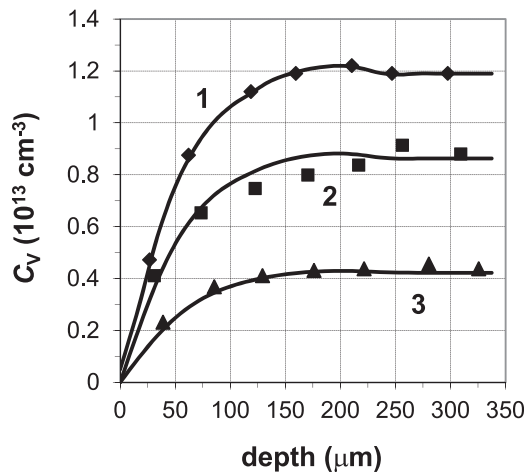


FIG. 1. The concentration C_V of RTA-produced vacancy species monitored by Pt diffusion, in dependence of the wafer depth. The curve 1 is right after RTA, the curves 2 and 3 are after subsequent annealing at 975 °C for 18 and 58 s, respectively. The symbols show the experimental points; the solid curves 2 and 3 are computed by solving the diffusion equation (2) with the best-fit loss time $\tau = 56$ s and a low apparent diffusivity $D^* = 5 \times 10^{-8}$ cm²/s.

near-surface depleted zone. The anneal-induced relaxation in $C_V(z)$ is well described assuming that the vacancy species monitored by Pt are almost immobile at $T \leq 975$ °C, and that the loss of these vacancy species, through the wafer depth, occurs at a rate proportional to the local value of C_V . In a general form—including also some out-diffusion with a low diffusivity D^* —this loss equation reads

$$\partial C_V / \partial t = D^* \partial^2 C_V / \partial z^2 - C_V / \tau, \quad (2)$$

where τ is the characteristic loss time of monitored vacancy species. The solid curves 2 and 3 in Figs. 1 and 2 are computed using the best-fit value of τ : 56 s at 975 °C and 117 s at 950 °C. In both cases the assumed value of the diffusivity D^* should be $\leq 10^{-7}$ cm²/s, otherwise the fit quality is deteriorated.

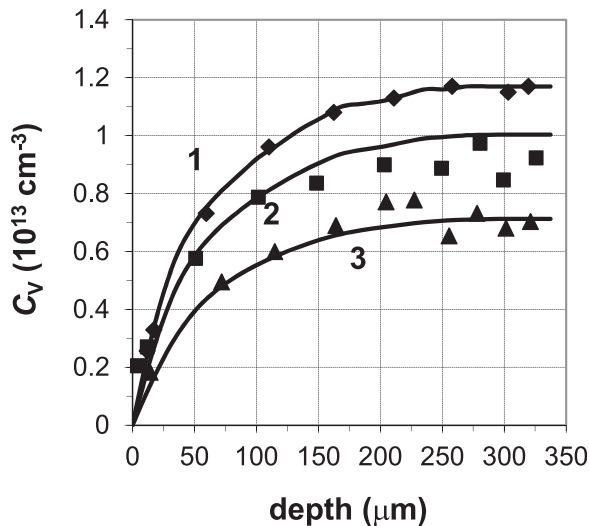


FIG. 2. Vacancy concentration C_V right after RTA (curve 1) and after subsequent annealing at 950 °C for 18 and 58 s (curves 2 and 3, respectively). The solid curves 2 and 3 are computed by solving the diffusion equation (2) with the best-fit loss time $\tau = 117$ s and a low apparent diffusivity, $D^* = 5 \times 10^{-8}$ cm²/s.

The values of τ are available only for two temperatures that are not well separated (975 and 950 °C) and yet—assuming an Arrhenius-type temperature dependence—the loss time τ can be approximately specified in dependence of T

$$1/\tau = (8 \times 10^{13} \text{ s}^{-1}) \exp(-3.88 \text{ eV}/kT). \quad (3)$$

To treat the obtained results, we first note that the vacancy community $V + VO + VO_2$ is definitely equilibrated in the temperature range of annealing. The trapping time of V by O to produce VO is quite short even at cryogenic temperature^{2,3}—about 1000 s at 165 K. Extrapolated to 950 °C, this trapping time is on the order of $2 \mu\text{s}$ which means that V is instantaneously equilibrated with VO . Next, VO is known^{10,11} to become mobile already at $T > 300$ °C and to be trapped by O producing VO_2 . A refined analysis of the reported VO loss should take into account¹² that VO disappears by two competing reactions: one is $VO + O$ and the other is VO dissociation with subsequent annihilation of released V by radiation-produced interstitial clusters. The trapping time of VO by O is then deduced in dependence of T ; a representative value is 1 h at 350 °C, and the activation energy is 1.79 eV. Extrapolated to 950 °C, this trapping time is on the order of 0.3 ms. Again, it is a very short time and VO is instantaneously equilibrated with VO_2 at this T .

With a strictly maintained equilibrium ratio between the individual concentrations, the vacancy community $V + VO + VO_2$ behaves as one species of an apparent diffusivity controlled by a fraction of free vacancies V

$$D_{VA} = D_V [V] / ([V] + [VO] + [VO_2]) = D_V / (1 + R_b), \quad (4)$$

where R_b is the equilibrium binding ratio, $([VO] + [VO_2])/[V]$, with a dominant contribution of VO_2 . The apparent diffusivity D_{VA} is identical to the diffusivity D^* of the monitored vacancy species and has a value as low as $\leq 10^{-7}$ cm²/s—much smaller than D_V (which is 1.8×10^{-5} cm²/s at 975 °C). It corresponds to a very strong vacancy binding: $R_b \geq 180$.

The observed vacancy loss by annealing at $T \leq 975$ °C implies that there is vacancy sinking to some bulk microdefects. The loss time, for diffusion-limited consumption by spherical sinks of a radius r and a density N is given by a conventional expression

$$1/\tau = 4\pi r N D_{VA}. \quad (5)$$

With $D_{VA} \leq 10^{-7}$ cm²/s, the observed loss time τ at 975 °C corresponds to the rN product of $\geq 10^4$ cm⁻². For comparison, this product for grown-in voids¹³ is only ≈ 10 cm⁻², implying that the presumed sinks are of a different nature—and of a much higher density. Very roughly, assuming that the radius r is several nm, the required density N is estimated as 2×10^{10} cm⁻³. The nature of these presumed vacancy-sinking defects is unclear. One possibility is small vacancy agglomerates produced during post-RTA cooling. Another possibility is grown-in oxygen precipitates that survived the RTA step. Anyway, this is not an important issue since the present model of single V species is dismissed by the arguments discussed below.

The activation energy for $1/\tau$ is equal to the activation energy for the apparent diffusivity D_{VA} given by Eq. (4). For strong binding, D_{VA} is equal to D_V/R_b and has an Arrhenius-type temperature dependence; the activation energy, 3.88 eV, is a sum of the activation energy for D_V (0.45 eV) and the binding energy E_b of the VO_2 complex (thus concluded to be 3.43 eV).

When extrapolated to a typical formation temperature of grown-in voids, 1100 °C, D_{VA} is smaller than 2.7×10^{-6} cm²/s—still much lower than D_V —implying a strong binding of vacancies even at this T . However, as was mentioned above, the apparent vacancy diffusivity at 1100 °C deduced from void properties is high and consistent with the value of D_V . This discrepancy shows that the conventional concept of a single V species is not adequate for the real situation.

Accordingly, we now treat the vacancy profile evolution within an advanced “multi-species” concept⁶ that assumes co-existence of several independent kinds of V:

- One kind is the “Watkins vacancy” of a high diffusivity, Eq. (1). This vacancy species is denoted V_w and this symbol should now replace the general symbol V used above while considering the $V + VO + VO_2$ community.
- The other kind is a “slow vacancy”—denoted by a symbol V_s —of a very low diffusivity.
- There is also the third kind of V responsible for a high- T vacancy contribution into the self-diffusivity. This species—called a “fast vacancy” and denoted V_f —is likely to be even a faster diffuser than V_w .

The diffusivities D_w of V_w and D_s of V_s are shown in Fig. 3 by the solid curves. For V_f , the diffusivity D_f is not yet specified; a tentative value is shown by the broken curve.

During crystal growth, all the three vacancy species are likely to be equilibrated, which results in a relatively high apparent diffusivity (mostly, due to V_f) at the void formation temperature, 1100 °C. However, at T_{RTA} the apparent vacancy diffusivity was found,⁶ by analyzing the reported oxygen precipitation profiles,¹⁴ to be essentially smaller—about 5×10^{-6} cm²/s, intermediate between D_s and D_w . The conclusion is that in case of RTA—when the cooling rate is faster by a factor of 2000 in comparison to crystal growth—the V_f species do not exchange with V_w and V_s ,

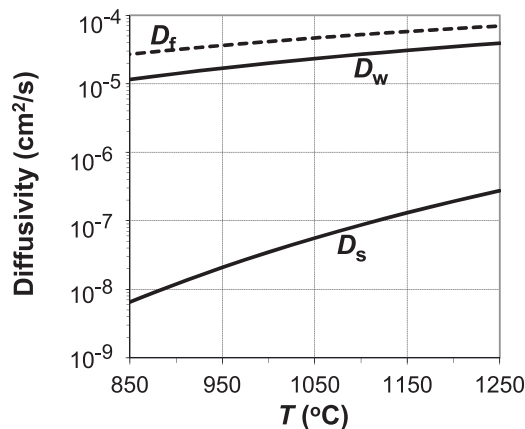


FIG. 3. Temperature dependence of the diffusivity D_w of a highly mobile Watkins vacancy V_w by Eq. (1), and of the diffusivity D_s of a slow vacancy V_s , after Ref. 6. The broken curve is a tentative diffusivity of a fast vacancy V_f .

and out-diffuse almost completely. Hence, in RTA case, we deal with the $V_w + V_s$ sub-community which is still equilibrated; an average diffusivity at T_{RTA} is well below D_w due to the dominance of V_s .

Upon lowering T , important changes occur:

- The equilibrium concentration ratio $[V_s]/[V_w]$ decreases⁶ and becomes about 1 at 975 °C.
- In the equilibrated community $V_w + VO + VO_2$ —which will be denoted V_w^* —the contribution of VO_2 becomes dominant, which means $[V_w^*] \gg [V_w]$. Accordingly, the equilibrium concentration ratio $[V_s]/[V_w^*]$ becomes well below 1.
- The conversion time from V_s into V_w increases and it may become quite long at $T \leq 975$ °C.

In this scenario, the vacancy species V_s —that have been dominant at T_{RTA} —are frozen-in, and it is these species (and not VO_2) that are monitored by Pt diffusion. The value of D_s by Fig. 3 satisfies the above limitation on the diffusivity of monitored vacancy species, $\leq 10^{-7}$ cm²/s at 975 °C. During annealing, a slow conversion $V_s \rightarrow V_w$ occurs. The produced V_w species are instantaneously equilibrated with VO and VO_2 , and the effective transition is from V_s into V_w^* . The latter species (represented mostly by VO_2) is now dominant under equilibrium, and the conversion of V_s into V_w^* is almost complete: almost all frozen-in V_s species will be lost. The observed loss time τ is equal to the $V_s \rightarrow V_w$ conversion time. The value of the prefactor in Eq. (3)—roughly on the order of 10^{13} s⁻¹—is consistent with this interpretation.

The produced V_w^* species partially out-diffuse; this process is controlled by the apparent diffusivity expressed by Eq. (4), where V is replaced with V_w and D_V with D_w . The binding ratio R_b for V_w cannot be deduced from the present data, and the amount of out-diffusion is uncertain.

The problem of vacancy loss by annealing was treated above considering only mono-vacancy species, either free or bound to oxygen. Could it be possible that a low apparent diffusivity results from formation of di-vacancies—so that a fraction of monovacancies is strongly reduced? The equilibrium relation between the concentrations of V and V_2 can be specified assuming that the formation free energy of each species is proportional to the number of dangling bonds (4 for V, 6 for V_2). Then the equilibrium concentrations are $[V]_{eq} = \rho \exp(-4f/kT)$ and $[V_2]_{eq} = 2 \rho \exp(-6f/kT)$, where f is the free energy per one dangling bond and ρ is the lattice site density. The factor 2 for V_2 is due to different orientations of V_2 defect. The actual concentrations of V and V_2 are related by the mass-action law

$$[V]^2/[V_2] = K_2 = ([V]_{eq})^2/[V_2]_{eq} = 0.5 (\rho [V]_{eq})^{1/2}. \quad (6)$$

The temperature dependence of $[V]_{eq}$ was estimated in Ref. 4. At 950 °C, $[V]_{eq}$ is about 10^{10} cm⁻³ and then the dissociation constant K_2 is about 10^{16} cm⁻³. The actual vacancy concentration [V] produced by RTA is less than 1.2×10^{13} cm⁻³, by the curve 1 in Figs. 1 and 2. In reality, [V] can be still lower due to binding into VO and VO_2 . Since $[V] \ll K_2$, the concentration ratio $[V]/[V_2]$, by Eq. (6), is very large, more than 1000. It means that the di-vacancies are present in a negligible fraction and cannot affect the behaviour of the

vacancy community. A substantial pairing of V into V_2 would occur only at much lower T , below 650 °C.

In conclusion, the present work shows that the RTA-produced vacancy species are extremely slow diffusers at annealing temperatures ≤ 975 °C. This result—not consistent with a conventional concept of only one V species—strongly supports a notion of a slow vacancy species existing along with the highly mobile vacancy species, including the long-known Watkins vacancy.

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