

Carbon diffusion in silicon

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Carbon diffusion in silicon has been investigated by using a superlattice structure of carbon spikes (10 nm-wide, carbon concentration $> 10^{19} \text{ cm}^{-3}$, spikes spaced 100 nm apart) grown epitaxially by Si molecular beam epitaxy. Samples were annealed in the range between 680 and 850 °C. The diffusive behavior of carbon was monitored by secondary ion mass spectrometry. Carbon diffusion profiles observed at temperatures above 800 °C show highly nonregular behavior. The diffusion results are interpreted in terms of the kick-out mechanism. © 1998 American Institute of Physics. [S0003-6951(98)01743-4]

In silicon, carbon represents beside oxygen, the main impurity. Carbon is substitutionally dissolved and plays an important role in the interactions between point defects in this material. For example, transient enhanced diffusion (TED) of boron, which occurs during ion implantation into silicon and annealing due to the implantation-generated excess of Si self-interstitials, is reduced in the presence of carbon.¹ It is assumed that substitutional carbon (sC) interacts with Si self-interstitials (I), forming a highly mobile interstitial carbon complex (iC), which some 20 years ago had been qualitatively proposed based on electron paramagnetic resonance (EPR) measurements:²



As a result of this kick-out reaction, I's are consumed, i.e., do no longer take part in the diffusion of boron.^{3,4} On one hand, the undersaturation of self-interstitials I in C supersaturated regions may reach values of 0.01 in comparison to its equilibrium concentration, drastically decreasing diffusion of interstitial diffusers, such as boron, in these regions. On the other hand, iC's are fast diffusing, possibly releasing I's in part of the sample where the I concentration/supersaturation is smaller. Very little is known about the details of these point defect interactions, and in particular their kinetics.

The diffusion of carbon has almost exclusively been studied via indiffusion experiments using radiotracer techniques.^{5,6} Assuming a kick-out mechanism⁷ according to Eq. (1) the transport of carbon during its diffusion can be described by a carbon diffusion coefficient, D_C , given by

$$D_C = (D_{\text{iC}} C_{\text{iC}}^*) / C_{\text{sC}}^*, \quad (2)$$

where D denotes a diffusivity and C a concentration, iC interstitial, and sC substitutional carbon ($C_{\text{sC}} \approx \text{total C concentration}$). The superscript * denotes equilibrium conditions. D_C is independent of space and time, leading in turn to the characteristic complementary error-function profiles for the carbon concentration.

In practice, however, the carbon concentration is rarely at or below solubility, since the solid solubility is very low, e.g., $1.9 \times 10^{14} \text{ cm}^{-3}$ at 850 °C.⁸ Typical Czochralski (Cz) silicon exhibits carbon concentrations in the order of 10^{17} cm^{-3} , and floating zone (FZ) silicon in the order of 10^{15} cm^{-3} . Under these nonequilibrium conditions the assumption of an unique, invariant carbon diffusion coefficient is no longer valid and the kick-out mechanism of carbon diffusion has to be taken into account explicitly.

In this letter we investigate the diffusion behavior of carbon in silicon by utilizing a super lattice structure (SL) of carbon spikes. Similar to extensively used boron doping SL,^{1,9} carbon SLs (6 C spikes, 10 nm wide, carbon concentration $2 \times 10^{19} \text{ cm}^{-3}$, spaced 100 nm apart, capped with 50 nm silicon) were epitaxially grown by molecular beam epitaxy (MBE) on FZ (100) Si substrates. Carbon was evaporated in elemental form from a special high-temperature carbon source. At the growth temperature of 450 °C it is assumed that carbon is fully substitutional incorporated,⁹ no segregation or agglomeration could be observed using transmission electron microscopy (TEM). Samples were annealed in a tube furnace between 680 and 850 °C in Ar (accuracy ± 10 K). The diffusive behavior of C was monitored before and after annealing by secondary ion-mass spectroscopy (SIMS).

Figure 1 shows the carbon concentration as a function of depth before (solid line) and after annealing (dashed lines), at 730 °C/20 h [Fig. 1(a)] and 850 °C/3 h [Fig. 1(b)], respectively. A peak concentration of $2 \times 10^{19} \text{ cm}^{-3}$ within the as-grown spikes was reached, with a background concentration of about 10^{18} cm^{-3} . Six spikes were intentionally grown; the 7th spike at a depth of about 700 nm represents residual carbon at the substrate–film interface. Annealing leads to quite unusual diffusion behavior, which is obvious from a comparison of dashed and dotted lines, where the latter represent a calculated diffusion profile assuming Fickian diffusion with a constant D_C according to Eq. (2).

The diffusion of carbon was simulated assuming the kick-out mechanism [Eq. (1)], based on the appropriate system of partial differential equations.¹⁰ Concentrations are

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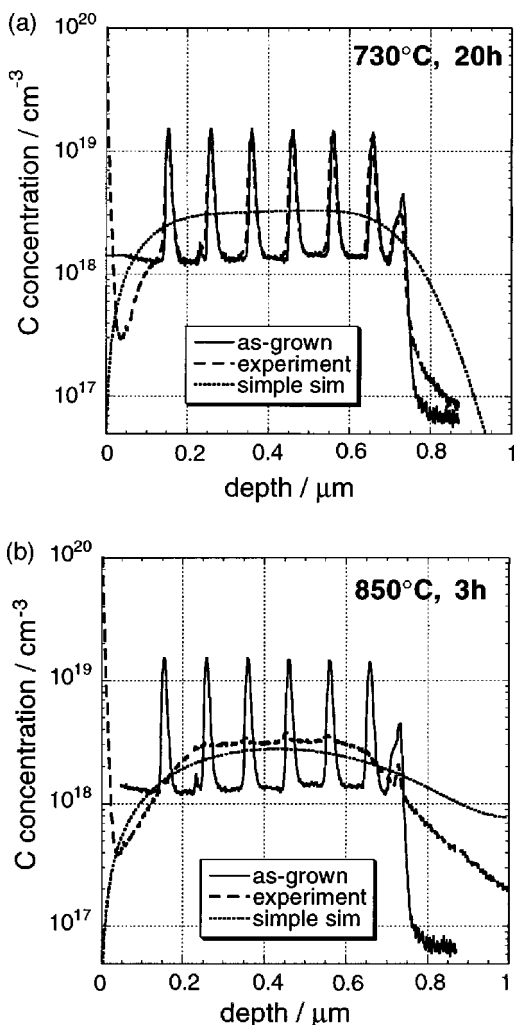


FIG. 1. Carbon concentration as a function of depth: as-grown (solid line) and after annealing (dashed lines) at (a) 730 °C for 20 h, and (b) 850 °C for 3 h. Dotted lines represent Fickian diffusion with constant D_C .

pinned at their equilibrium values at the surface. No clustering of carbon is taken into account, but a Si-C layer is assumed at the surface, i.e., C_{sC} equals the solid solubility of carbon. Diffusivities and concentrations relate to the general form $C = C_0 \exp(-E_C/kT)$ and $D = D_0 \exp(-E_D/kT)$. Prefactors and activation energies of the parameters were taken from the literature and are listed in Table I. Values of C_{iC} and of the reaction constant k_{iC} have been calculated using the other data and the kick-out mechanism. As a consequence, there are no free parameters for the simulation.

The corresponding solutions¹¹ for 730 °C/20 h and

TABLE I. Prefactors and activation energies for entities involved in the diffusion of carbon taken from the literature. C_{iC} and k_{iC} have been calculated from values given in the upper part of the table.

Parameter	D_0, C_0	E (eV)	Ref.
D_I	0.2 cm ² /s	1.2	12
C_I^*	1.0×10^{27} cm ⁻³	3.8	12
D_{sC}	0.95 cm ² /s	3.04	6
C_{sC}^*	4×10^{24} cm ⁻³	2.3	8
D_{iC}	0.44 cm ² /s	0.87	13
C_{iC}	8.6×10^{24} cm ⁻³	4.47	
k_{iC}	9.3×10^4	1.63	

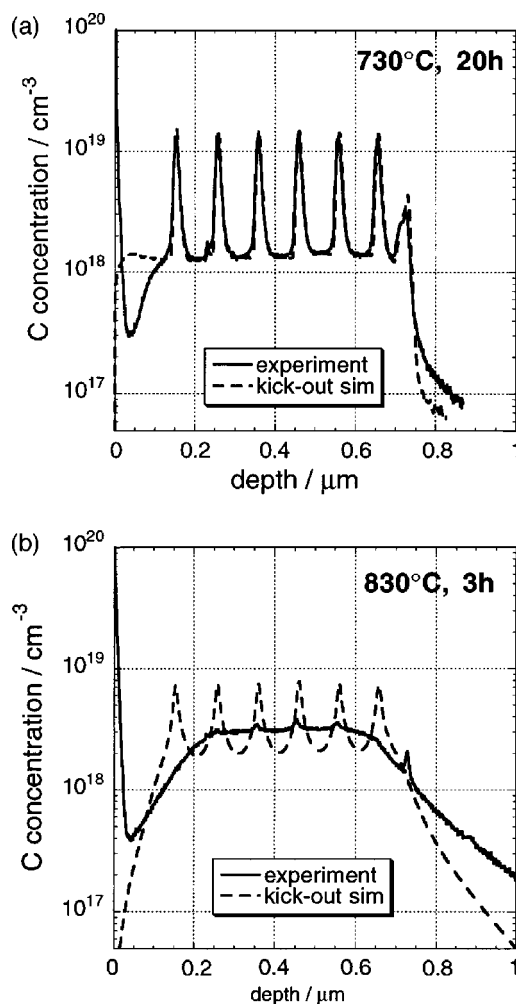


FIG. 2. Experimental and simulated carbon diffusion profiles for annealing at 730 °C/20 h (a) and at 850 °C/3 h (b). Experiment—full line, simulation assuming a kick-out mechanism—dashed line.

850 °C/3 h are shown in Figs. 2(a) and 2(b), respectively (dashed lines). The measured as-grown profile was used as the initial concentration for C_{sC} ; all other concentrations' initial values were set to zero. The full line in both figures represents the corresponding experimental result already shown in Fig. 1. The simulation reproduces the main features of the experiment, quite in contrast to the results from a constant D_C . Nevertheless, quantitatively, the calculated surface depletion is not deep enough, and at 850 °C there is insufficient diffusion in the spikes.

The discrepancies between simulation and experiment may be caused by the following effects:

- (i) Precipitation: Concentrations are far beyond solid solubility and one would expect significant cluster formation. Nevertheless, no clusters were observed experimentally by TEM, with a resolution of 1.5 nm. A very simple form of precipitation, consisting of sC-iC was in fact assumed to exist.² However, the binding of the carbon doublet¹⁴ is too small to have a significant impact. In the case of more stable clusters the diffusion would be decreased too much.
- (ii) Accuracy of the parameters listed in Table I: A change in D_{iC} leads to an equal and opposite change in C_{iC} [Eq. (2)] and has no influence on the diffusion

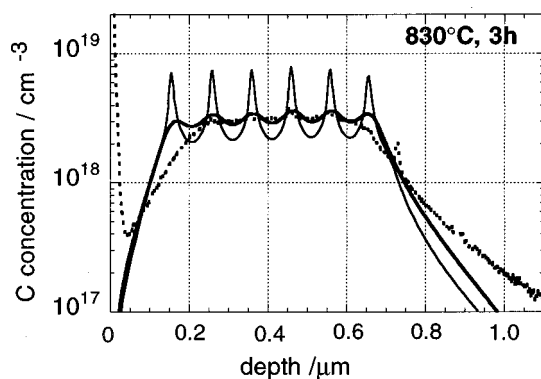


FIG. 3. Comparison between experimental (dashed line) and simulated concentration profile (bold lines) for 850 °C/3 h. The weak full line correlates to a simulated kick-out profile using data from Table I. The bold full line represents the simulation, where the prefactor for D_I has been increased by a factor of 2.

profile. However, increasing the mass flow of interstitials by increasing either D_I or C_I^* in the self-diffusion coefficient $D_I C_I^*$ via I's leads to a higher concentration C_{iC} throughout the film and hence more diffusion in the spikes. At 850 °C it takes an increase in $D_I C_I^*$ of about a factor of 2 beyond the value in Ref. 15, well within the error bar of the available data on $D_I C_I^*$. Figure 3 demonstrates the good fit between experiment (dashed line) and a simulated profile (bold full line) within the spike region, where the value of the prefactor for D_I was increased by a factor of two in comparison to Table I. The result at 730 °C cannot be analyzed quantitatively since no diffusion in the spikes is observed. Hence, if one ignores the discrepancy close to the surface, the regular kick-out mechanism describes the experiments reasonably well.

(iii) Vacancies: C can also diffuse via the dissociative mechanism [Frank–Turnbull mechanism, (FT)]. We have simulated this situation by corresponding extension of the system of partial differential equations (see, e.g., Ref. 15). Based on data from Ref. 15 for diffusivity D_V and thermal equilibrium concentration of vacancies C_V^* no noticeable influence on the diffusion profiles are obtained in the simulations. How-

ever, a better correlation between experimental and simulated diffusion behavior is achieved by increasing the vacancy diffusivity D_V , while keeping the product $D_V C_V^*$. The possibility of high D_V values has been reported in the recent literature.^{16,17} A more detailed discussion of the diffusion behavior of carbon based on the contribution from the kick-out and the Frank–Turnbull mechanism will be given elsewhere.¹⁸

In conclusion, carbon diffusion in the investigated temperature range can be reasonably well described based on the kick-out mechanism. The inclusion of vacancies via the Frank–Turnbull mechanism does not significantly improve the agreement between simulation and experiment. Both approaches cannot explain the experimentally observed fast diffusion close to the surface.

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