PHYSICAL REVIEW B, VOLUME 64, 073202

# Nonequilibrium point defects and dopant diffusion in carbon-rich silicon

H. Rücker, B. Heinemann, and R. Kurps
*IHP, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany*

(Received 19 February 2001; published 30 July 2001)

We show that B and P exhibit suppressed and As and Sb enhanced diffusion in Si with C atom concentrations of about $10^{20}$ cm$^{-3}$. Since B and P diffuse via an interstitial mechanism and Sb and As diffuse via a vacancy mechanism, this indicates a suppressed density of self-interstitials and an enhanced density of vacancies in C-doped Si. Simultaneous measurements of vacancy supersaturation by means of Sb diffusion and of the clustering kinetics of C are used to study the annihilation of excess vacancies at the Si surface. The surface acts as an effective sink for vacancies with a recombination length $\lambda \leqslant 70$ nm.

DOI: 10.1103/PhysRevB.64.073202 PACS number(s): 66.30.Jt, 61.72.Ji

Diffusion coefficients of dopant atoms in Si can be changed by more than one order of magnitude due to incorporation of other group IV elements in the Si lattice.[1–5] While isoelectronic substitutional impurities in a concentration range of less than 1 at. % do not significantly change the electronic structure of Si they strongly interact with point defects and other dopants. This opens a way to study fundamental interaction processes of dopant atoms and point defects. Moreover, the possibility of controlling diffusion of donor and acceptor atoms in Si by doping with electronically inactive group IV elements provides fascinating options for the fabrication of very-large-scale integrated circuits. In fact, it has already been demonstrated that supersaturated C can be used to stabilize ultrasteep B profiles in integrated high-speed SiGe:C heterojunction bipolar transistors.[6]

We present here a study of the impact of substitutional C on the diffusion of common acceptor and donor impurities in Si. Our primary results are as follows. (1) As and Sb exhibit enhanced, and B and P suppressed diffusion in Si with C concentrations of about $10^{20}\,\mathrm{cm}^{-3}$. (2) The diffusion enhancement/suppression is almost constant over finite period of time and ends when all supersaturated C is precipitated. (3) The Si surface acts as an effective sink for excess vacancies with a recombination length $\lambda \leqslant 70$ nm.

The experimental procedure was as follows. Si wafers with uniform dopant concentration in the surface region were prepared by implantation of P, As, or Sb ions and subsequent annealing to remove all implantation damage. *In situ* B-doped Czochralski-grown Si wafers were used for B diffusion experiments. Next, epitaxial layers with and without *in situ* carbon doping at a concentration of $C_{\mathrm{C}} \approx 10^{20}$ cm$^{-3}$ were grown by low-temperature chemical vapor deposition. The epitaxial C-doped layers were 160-nm thick caped with 160-nm pure Si. Additional annealing steps in inert $N_2$ atmosphere were performed to diffuse dopant atoms from the doped substrates into the C-rich epitaxial layers and into the C-free reference layers. Depth profiles of dopants were measured by secondary ion mass spectroscopy (SIMS).

Measured outdiffusion profiles of B, P, As, and Sb from highly doped substrates into Si and Si:C layers are shown in Fig. 1. Diffusion of B and P is strongly suppressed in the C-rich layer, while diffusion of As and Sb is enhanced in the samples with the elevated C concentration of $10^{20}$ cm$^{-3}$. To our knowledge, this is the first observation of enhanced diffusion of As and Sb in the presence of C.[7] Suppressed diffusion of B was investigated previously using B marker layers in Si:C.[2]

For quantitative assessment of the effect of C on dopant diffusion we have fitted diffusion coefficients to the measured profiles. The Fermi-level dependence of the diffusion coefficient was included in the fit.[8] The diffusion profiles of As and Sb in Si:C can be described by scaling the corresponding diffusion coefficients of C-free Si by constant factors given in Table I. The measured diffusion profiles of B and P in Si:C decay significantly steeper than the calculated profiles with diffusion coefficients scaled to one tenth of their value in C-free Si [Figs. 1(a),(b)]. This indicates that the suppression of B and P diffusion in the C-doped layer is even stronger than a factor of ten.

Depth profiles of C were measured after various annealing times at 900 °C (Fig. 2). After annealing for 1 h, we observed diffusion of C in the tail region of the C profile. However, there is almost no diffusion in the region of high C concentration. The most striking observation of the measurement is

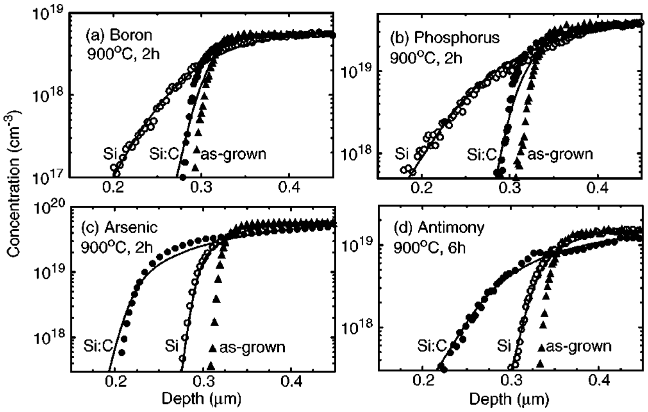

FIG. 1. Diffusion of B, P, As, and Sb from highly doped substrates into Si (open circles) and Si:C layers (filled circles). Symbols are SIMS data. Lines are calculated diffusion profiles using scaled diffusion coefficients for the Si:C samples. The plotted curves correspond to $D(\mathrm{Si{:}C})/D(\mathrm{Si}) = 0.1$ for B and P, $D(\mathrm{Si{:}C})/D(\mathrm{Si}) = 7$ for As, and $D(\mathrm{Si{:}C})/D(\mathrm{Si}) = 8$ for Sb. Carbon profiles of the Si:C layer are shown in Fig. 2 below.

©2001 The American Physical Society

TABLE I. Measured ratio of the diffusion coefficients of common dopant atoms in the Si:C layer and in Si reference samples without intentional C doping.

| Dopant atom | Diffusion coefficient $D(\mathrm{Si{:}C})/D(\mathrm{Si})$ |
|---|---|
| Boron | $<0.1$ |
| Phosphorus | $<0.1$ |
| Arsenic | $7\pm2$ |
| Antimony | $8\pm2$ |

that this C profile stays stationary over several hours at 900 °C. The C concentration in the bulk region increases only slightly between 1 and 12 h annealing. After even longer annealing times the low-concentration tails of the C profile disappear and a phase of immobile C was formed in the originally C-doped region. The C profile after 24 h at 900 °C is steeper than the as-grown C profile and does not change during further annealing. According to the SIMS measurement the total dose of the C peak after 24 h annealing is about 80% of the initial C dose. This difference is of the order of the uncertainty of the SIMS measurement of the C concentration.

Moreover, we found that nonequilibrium diffusion of donor and acceptor atoms in the Si:C samples was also restricted to about 12 h at 900 °C. In order to determine the time dependence of nonequilibrium diffusion in the Si:C sample we have measured the diffusion profiles of Sb after various annealing times. Average diffusion coefficients were fitted to the Sb profiles in the Si and Si:C samples for all annealing times. This allows us to extract the time-integrated diffusion enhancement of Sb in the Si:C sample (Fig. 3):

$$T_{\mathrm{enh}}(t)=\frac{1}{D_{\mathrm{Si}}}\int_0^t (D_{\mathrm{Si:C}}(t')-D_{\mathrm{Si}})dt'. \tag{1}$$

where $D_{\mathrm{Si:C}}$ and $D_{\mathrm{Si}}$ are the diffusion coefficients in the C-doped and C-free samples, respectively. The quantity $T_{\mathrm{enh}}$ has the dimension of time and represents an effective prolongation of the diffusion time of Sb due to the enhanced diffusion coefficient. During the first 12 h $T_{\mathrm{enh}}(t)$ increases almost linearly with a slope of about 8. This corresponds to a constant diffusion enhancement by a factor of 8. Between 12 and 24 h annealing we found only a marginal enhancement of the Sb diffusion in the Si:C sample resulting in a saturation of $T_{\mathrm{enh}}$. Further, suppressed diffusion of B in the Si:C sample was also restricted to about 12 h at 900 °C.

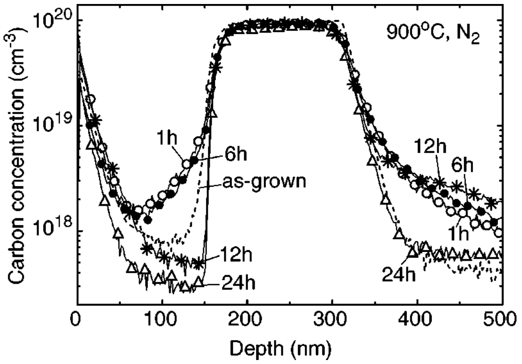

FIG. 2. SIMS depth profiles of the C-rich layer corresponding to the sample of Fig. 1(a). The dashed line is the as-grown C profile. Symbols correspond to different diffusion times at 900 °C in inert $N_2$ atmosphere.

Next, we discuss the correlation between the measured diffusion properties of different dopant species and point defect densities in the Si:C sample. It is well established that B and P diffuse in Si almost exclusively by an interstitial mechanism while Sb diffuses almost exclusively by a vacancy mechanism.[9,10] Consequently, the diffusion coefficients of B and P are proportional to the concentration of Si self-interstitials and the diffusion coefficient of Sb is proportional to the concentration of vacancies. The measured diffusion enhancement of Sb in the Si:C sample reveals a vacancy concentration eight times higher than its equilibrium value $C_{\mathrm{V}}^{\mathrm{eq}}$ for a period of twelve hours. The measured suppression of B and P diffusion in Si:C indicates that the density of Si self-interstitials in the Si:C layer is at least ten times lower than its equilibrium value $C_{\mathrm{I}}^{\mathrm{eq}}$. For As diffusion, contributions from both, vacancies and interstitials have been reported.[9] We found similar enhancement factors of As and Sb diffusion in Si:C indicating that at 900 °C a major contribution to As diffusion is due to vacancies. However, the present experiment is not suited for an accurate assessment of the interstitial contribution to the diffusion of As in Si, since this contribution would be suppressed in the Si:C sample due to the extremely low density of self-interstitials.

Further insight into the origin of the observed nonequilibrium point defect densities can be obtained from analyzing the depth profiles of C as a function of annealing time. We discuss the impact of C diffusion first. It is well established that a large diffusive flux of a substitutional impurity $A$ can drive the densities of vacancies and self-interstitials out of equilibrium if the product of its diffusion coefficient $D_{\mathrm{A}}$ and concentration $C_{\mathrm{A}}$ exceeds the corresponding transport capacities for Si self-interstitials ($D_{\mathrm{I}}C_{\mathrm{I}}^{\mathrm{eq}}$) and vacancies

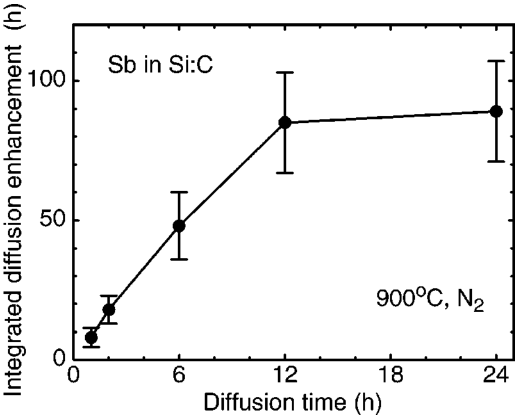

FIG. 3. Integrated diffusion enhancement $T_{\mathrm{enh}}$ of Sb in the Si:C sample as a function of diffusion time. The integrated diffusion enhancement $T_{\mathrm{enh}}$ was determined from measured diffusion coefficients according to Eq. (1) in the main text. Diffusion coefficients were fitted to SIMS profiles of Sb in Si and in Si:C after various diffusion times at 900 °C.

$(D_V C_V^{eq})$.[11] Scholz *et al.*[12,13] have shown that this effect can account for suppressed diffusion of B in Si:C and for the observed concentration dependent C diffusion at short diffusion times.[2,3] The depth profiles of C after annealing for several hours at 900 °C (Fig. 2) clearly demonstrate that in addition to C outdiffusion the formation of an immobile phase of C plays an essential role.

We now discuss the precipitation process of C in more detail. In the as-grown Si:C layer the majority of C atoms are incorporated on Si lattice sites as confirmed by a comparison of the SIMS measurement of the total C concentration and the lattice distortion measured by x-ray diffraction.[14] This concentration is far beyond the solid solubility of substitutional C in Si, which is only about $5\times10^{14}$ cm$^{-3}$ at 900 °C.[15] The only thermodynamically stable phase of Si and C is stoichiometric SiC. In fact, it has been shown previously that SiC precipitates can form during annealing of metastable Si:C alloys.[16] That is why we assume here that the immobile fraction of C observed in the annealed Si:C samples (Fig. 2) corresponds to clusters or precipitates with stoichiometry and atomic density close to those of silicon carbide. We note that the measured preciptation kinetics of C was independent of dopant species in the substrate (B, P, As, or Sb), indicating that these dopants play a minor role for the observed precipitation of C. The oxygen concentration in the region of precipitated C was $1\times10^{18}$ cm$^{-3}$ according to SIMS measurement. Consequently, coprecipitation of C and O is not important in the present experiment.

The observed phase transformation of C was confirmed by x-ray diffraction measurements. Due to the smaller covalent radius of C, the lattice constant of Si:C decreases with increasing concentration of substitutional C. In the present study, we have measured the lattice constant of the Si:C layer in the as-grown state and after anneal at 900 °C for 6 and 24 h. After annealing for 24 h the strain was relaxed completely, indicating that precipitated C does not introduce macroscopic strain. After annealing for 6 h, the strain in the Si:C layer was reduced to 45% of its value in the as-grown sample. This corresponds to a reduction of the concentration of substitutional C after 6 h annealing to about 45% of the initial concentration.

We turn now to the discussion of implications of the present experiment for transport of point defects. In particular, it will be shown that the vacancy concentration at the surface is close to its equilibrium value and an upper limit for the surface recombination length of vacancies is estimated. The density of atoms in SiC precipitates is twice as high as in Si. Consequently, for each C atom that is transformed from a substitutional lattice site into a SiC precipitate one interstitial atom has to move into the C-rich layer or one vacancy has to move out of it.[17] The total dose $N_C$ of precipitated C has to be balanced by the sum of the dose of indiffused interstitials $N_I$ and the dose of outdiffused vacancies $N_V$. The only available source for Si atoms that can provide self-interstitials and absorb vacancies in the surface.

Normalized concentrations of vacancies $\tilde{V}=C_V/C_V^{eq}$ and self-interstitials $\tilde{I}=C_I/C_I^{eq}$ during conditions of nonequilibrium diffusion are shown schematically in Fig. 4. The observed supersaturation of vacancies and undersaturation of interstitials in the C-doped region result in a flux of vacancies towards the surface

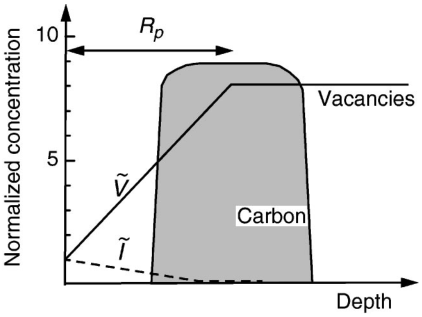

FIG. 4. Schematic of point defect concentrations during C precipitation. Vacancies are generated and interstitials are annihilated in the C-rich layer at an average depth $R_p$. At the surface, the concentrations of self-interstitials and vacancies are pinned near equilibrium $(\tilde{I}=\tilde{V}=1)$.

$$J_V = D_V C_V^{eq} \frac{\tilde{V}_C - \tilde{V}_s}{R_p} \tag{2}$$

and a flux of self-interstitials from the surface into the C-doped layer

$$J_I = D_I C_I^{eq} \frac{\tilde{I}_s - \tilde{I}_C}{R_p}\,. \tag{3}$$

Here, $R_p$ is the average depth of the C profile and $\tilde{V}_{C/s}$ and $\tilde{I}_{C/s}$ are the normalized point defect concentrations in the C-rich layer and at the surface, respectively. In Fig. 4, the point defect concentrations at the surface were set to their equilibrium values. The vacancy and interstitial components of Si self-diffusion $D_V C_V^{eq}$ and $D_I C_I^{eq}$ are well known for 900 °C.[18,19] There is general consensus that both components are approximately equal at 900 °C. In the analysis below we use the values given in Ref. 19.

The acutal fluxes of point defects during C precipitation can be estimated from the total dose of clustered C and the measured duration of vacancy supersaturation and interstitial undersaturation. According to the SIMS measurement, the total dose of precipitated carbon is $N_C=1.2\times10^{15}$ cm$^{-2}$ at an average depth $R_p=240$ nm. For the total dose of indiffused interstititals, we obtain an upper limit of $1.5\times10^{14}$ cm$^{-2}$ using Eq. (3) with $\tilde{I}_s-\tilde{I}_C<1$ and the measured duration of interstitial undersaturation. According to the balance equation $N_C=N_V+N_I$, this imposes the limits

$$1.05\times10^{15}\ \mathrm{cm}^{-2} \leqslant N_V \leqslant 1.2\times10^{15}\ \mathrm{cm}^{-2}. \tag{4}$$

Using on Eqs. (2) and (4), the normalized vacancy concentration $\tilde{V}_s$ at the surface can be estimated from the measured supersaturation of vacancies (Fig. 4). We find $\tilde{V}_s=1\pm2$, i.e., the vacancy concentration at the surface is close to its equilibrium value.

The effectiveness of the surface as a recombination sink for vacancies can be quantified by a surface recombination length $\lambda = D_V / k_V$, where $k_V$ is the recombination velocity. An upper limit of $\lambda$ can be determined from the total number of annihilated vacancies $N_V$ and the duration of vacancy supersaturation. Using Eq. (2) and $\tilde{V}_s < 3$, we get a surface recombination length $\lambda \leqslant 70$ nm. This indicates that the surface is an effective sink for excess vacancies. Previously, a surface recombination length of the same order was reported for Si self-interstitials.[20]

In summary, we have shown that supersaturated C in Si can enhance the diffusion of As and Sb and suppress the diffusion of B and P. The presented simultaneous measurement of nonequilibrium point defects by means of dopant diffusion and of the clustering kinetics of supersaturated C provides a new way to study the transport of point defect in Si. The surface was found to act as an effective recombination sink for vacancies with a recombination length $\lambda \leqslant 70$ nm.

The authors would like to thank B. Tillak and D. Wolansky for sample growth and P. Zaumseil for x-ray diffraction measurements. The work was financially supported by Deutsche Forschungsgemeinschaft.

---

[1] P.A. Stolk, D.J. Eaglesham, H.-J. Gossmann, and J.M. Poate, Appl. Phys. Lett. **66**, 1370 (1995).

[2] H. Rücker, B. Heinemann, W. Röpke, R. Kurps, D. Krüger, G. Lippert, and H.J. Osten, Appl. Phys. Lett. **73**, 1682 (1998).

[3] P. Werner, H.-J. Gossmann, D.C. Jacobson, and U. Gösele, Appl. Phys. Lett. **73**, 2465 (1998).

[4] J. Fage-Pedersen, A. Nylandsted Larsen, P. Gaiduk, J. Lundsgaard Hansen, and M. Linnarsson, Phys. Rev. Lett. **81**, 5856 (1998).

[5] N.E.B. Cowern, P.C. Zalm, P. van der Sluis, D.J. Gravensteijn, and W.B. de Boer, Phys. Rev. Lett. **72**, 2585 (1994).

[6] K.E. Ehwald *et al.*, *Technical Digest, International Electron Device Meeting*, (IEEE, Piscataway, NJ, 1999), p. 561.

[7] Preliminary results were published in H. Rücker *et al.*, *Technical Digest, International Electron Device Meeting* (Ref. 6), p. 109.

[8] R.B. Fair, in *Impurity Doping Processes in Silicon*, edited by F.F.Y. Wang (North-Holland, Amsterdam, 1981), p. 315.

[9] A. Ural, P.B. Griffin, and J.D. Plummer, J. Appl. Phys. **85**, 6440 (1999).

[10] H.-J. Gossmann, T.E. Haynes, P.A. Stolk, D.C. Jacobson, G.H. Gilmer, J.M. Poate, H.S. Luftman, T.K. Mogi, and M.O. Thompson, Appl. Phys. Lett. **71**, 3862 (1997).

[11] W. Frank, U. Gösele, H. Mehrer, and A. Seeger, in *Diffusion in Crystalline Solids*, edited by G.E. Murch and A.S. Nowick (Academic Press, Orlando, 1984), p. 63.

[12] R. Scholz, U. Gösele, J.-Y. Huh, and T.Y. Tan, Appl. Phys. Lett. **72**, 200 (1998).

[13] R.F. Scholz, P. Werner, U. Gösele, and T.Y. Tan, Appl. Phys. Lett. **74**, 392 (1999).

[14] H.J. Osten, J. Griesche, and S. Scalese, Appl. Phys. Lett. **74**, 836 (1999).

[15] A.R. Bean and R.C. Newman, J. Phys. Chem. Solids **32**, 1211 (1971).

[16] A.R. Powell, F.K. LeGoues, and S.S. Iyer, Appl. Phys. Lett. **64**, 324 (1994).

[17] U. Gösele, in *Oxygen, Carbon, Hydrogen, and Nitrogen in Crystalline Silicon*, edited by J.C. Mikkelsen, Jr. *et al.*, Mater. Res. Soc. Symp. Proc. No. 59 (Materials Research Society, Pittsburgh, 1986), p. 419.

[18] A. Ural, P.B. Griffin, and J.D. Plummer, Phys. Rev. Lett. **83**, 3454 (1999).

[19] H. Bracht, E. E. Haller, and R. Clark-Phelps, Phys. Rev. Lett. **81**, 393 (1998).

[20] D. R. Lim, C. S. Rafferty, and F. P. Klemens, Appl. Phys. Lett. **67**, 2302 (1995).