Sn-Background-Induced Diffusion Enhancement of Sb in Si

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The diffusion of Sb in Si has been studied as a function of Sn-background concentration, and enhanced Sb diffusion is observed for backgrounds higher than $C'_{\mathrm{Sn}} \approx 5 \times 10^{19}$ cm^{-3}. This concentration for the onset of enhanced diffusion is significantly lower than in other reports of high-concentration vacancy-mediated diffusion in Si. These reports, however, have up to now been concerned with donor impurities, whereas Sn is an electrically neutral impurity. Some Sn precipitation occurred, and the influence upon the diffusion is estimated from experiment to be small. A number of proposed models of high-concentration diffusion are discussed on the basis of the data. [S0031-9007(98)07983-6]

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Atomic diffusion in Si at very high dopant concentrations has been a subject of intensive investigations in recent years [1–8]. The field, besides being of crucial importance in device processing, provides a new way of improving fundamental knowledge of dopant-dopant and dopant-point defect interactions. So far both experiment and theory have focused mostly on vacancy-mediated diffusion in high background concentrations of the donor impurities As and P, and, experimentally, strong diffusion enhancement is observed for concentrations exceeding $\sim 2 \times 10^{20}$ cm^{-3} [3,9].

We present here a study of Sb diffusion in high background concentrations of Sn. Being isovalent to Si and having a large covalent radius, Sn interacts with vacancies by strain relief only, whereas donor atoms have a long range Coulomb-type interaction with negatively charged vacancies. At the same time Sn enables a diffusion study with no change of Fermi level to influence the concentration of charged vacancies. Since Sb is known to diffuse predominantly by a vacancy-assisted mechanism this system is considered a rather simple one, suitable for critical tests of the diffusion theories in Si.

Samples were grown on Si ⟨001⟩ substrates in a VG-80 molecular-beam epitaxy (MBE) system. In the structures thin Sb spikes were placed in pure Si, inside Sn-box profiles in Si, or next to Sn-box profiles in Si. A typical sample with an Sb spike inside a Sn box is shown in Fig. 1 [10]. Sb peak concentrations were low enough to not affect the Fermi level, i.e., $C_{\mathrm{Sb}}^{\mathrm{peak}} < n_i$, where the intrinsic carrier density at 1000 °C is $n_i \approx 5 \times 10^{18}$ cm^{-3}.

Annealings were performed at 995 °C in a flow furnace using an inert Ar ambience, and the diffusion times were corrected for furnace ramping-up and ramping-down times [11].

Depth profiles were measured with secondary-ion mass spectroscopy (SIMS), and two instruments were used: An Atomica 4000 magnetic quadrupole instrument with a primary O_2^+ beam, impact energy 4.5 keV and incidence angle 20° off normal, and a Cameca ims 4f magnetic sector instrument with an O_2^+ beam, impact energy 5.5 keV and a mechanical angle of 30° off normal. The Cameca was used to profile one series of samples that contained Sb spikes inside Sn boxes, with $C_{\mathrm{Sb}}^{\mathrm{peak}} \approx 5 \times 10^{17}$ cm^{-3} and Sn concentrations 1×10^{18} cm$^{-3} \leq C_{\mathrm{Sn}} \leq 9.9 \times 10^{19}$ cm^{-3}. All other samples had $C_{\mathrm{Sb}}^{\mathrm{peak}} \approx 3 \times 10^{18}$ cm^{-3} and were profiled with the Atomica. Depth calibrations were made by measuring the crater depths using a Dektak profilometer with a relative accuracy better than 3%.

Extraction of diffusion coefficients was done by numerically diffusing the SIMS profile of the as-grown sample according to Fick's 2nd law, and minimizing the error between the simulated diffused profile and the measured diffused profile with respect to the diffusion coefficient.

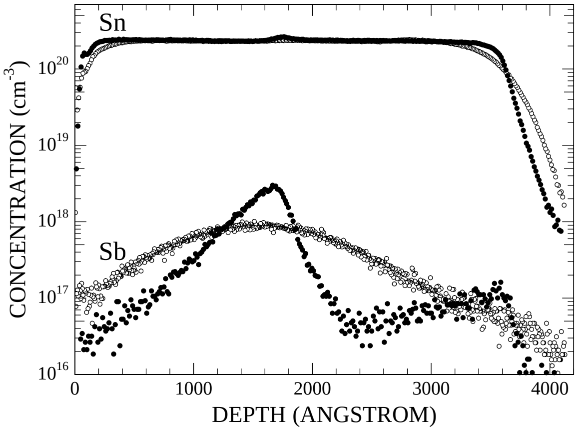

FIG. 1. SIMS profiles of an Sb spike contained within a Sn box, as-grown (filled symbols) and diffused at 995 °C for 2 h (open symbols). The solid curve is a Fick's law fit.

The main result is presented in Fig. 2: At low Sn concentrations a constant Sb diffusivity $D_{\mathrm{Sb}}(995\,^\circ\mathrm{C}) = 1.18 \times 10^{-15}\ \mathrm{cm}^2/\mathrm{s}$ is observed, in perfect agreement with the intrinsic value [12]. Enhanced Sb diffusion occurs at Sn concentrations higher than $C'_{\mathrm{Sn}} \approx 5 \times 10^{19}\ \mathrm{cm}^{-3}$, and at $C_{\mathrm{Sn}} = 4.7 \times 10^{20}\ \mathrm{cm}^{-3}$ the enhancement is a factor of 3 relative to the intrinsic value.

We may note, from analyzing the box profiles, that also Sn diffusivity increased with concentration. No systematic investigation was made, however, since this diffusion was not under isoconcentration conditions.

We first demonstrate that the observed enhancement cannot be explained by lattice strain, nor by point defect injection related to Sn precipitation. The latter topic received special attention, the solid solubility limit of Sn being $\sim 5 \times 10^{19}\ \mathrm{cm}^{-3}$ at 1000 °C [13].

Biaxial, compressive *lattice strain* may in general exist in $\mathrm{Si}_{1-x}\mathrm{Sn}_x$ layers that are grown epitaxially upon Si substrates. Kringhøj *et al.* [14] recently showed, from a $\mathrm{Si}_{0.91}\mathrm{Ge}_{0.09}$ system, that a compressive strain s causes an Sb diffusivity enhancement $F_{\mathrm{strain}} = \exp(-Q's/kT)$ with $Q' = 13 \pm 3$ eV. This value does not include chemical effects related to Ge. The strain in epitaxial $\mathrm{Si}_{1-x}\mathrm{Sn}_x$ layers on Si is determined with great precision [15] from Vegard's linear interpolation between the lattice parameters of Si ($a_{\mathrm{Si}} = 5.4311$ Å) and α-Sn ($a_{\mathrm{Sn}} = 6.4890$ Å), so that $s = (1 - a_{\mathrm{Sn}}/a_{\mathrm{Si}})x = -0.1948x$. Supposing that the Sn layers were fully strained under diffusion and inserting $x = 0.01$, corresponding to the highest Sn concentration, we find an upper limit $F_{\mathrm{strain}}^{\max} = 1.26$. Thus lattice strain can at most account for a small contribution to the diffusivity enhancement, the major effect still being specifically related to the chemical nature of Sn.

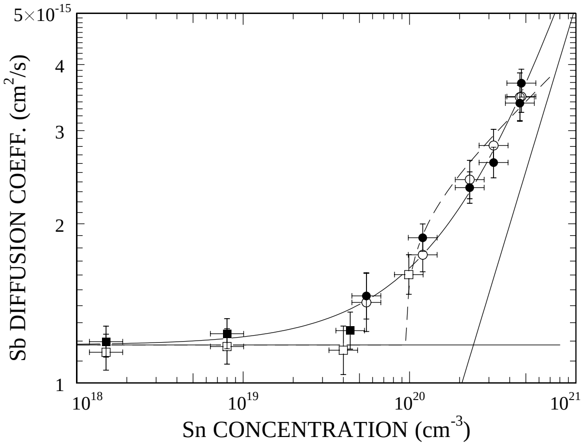

FIG. 2. Sb diffusivity at 995 °C vs Sn-background concentration in samples of the type shown in Fig. 1. The solid curve is Eq. (3) of which the two straight lines are the individual terms. The dashed curve is Eq. (1). Samples were diffused for 2 h (filled symbols) or 3 h (open) and profiled with an Atomika (circles) or a Cameca (squares). Identical symbols also correspond to samples that were annealed simultaneously, under exact identical conditions. Vertical errors here and in Fig. 3 are from fitting and depth calibration. Horizontal errors stem from scaling of SIMS signals relative to calibration samples that were measured with Rutherford backscattering.

To reveal whether *Sn precipitation* would create an injection of point defects and thereby affect Sb diffusion, two MBE structures were grown that contain, respectively, two Sb spikes in pure Si and one Sb spike positioned next to a high concentration ($3.3 \times 10^{20}\ \mathrm{cm}^{-3}$) Sn box in Si; see Fig. 3. As shown in Fig. 4, Sb diffusivities were then measured in these two samples at 995 °C after different annealing times. We see that at short times ($\frac{1}{2}$ h, 1 h) Sn precipitation leads to a slight retardation of Sb diffusion. Sb being a vacancy-assisted diffuser, this suggests that Si self-interstitials are injected. At long diffusion times (2 h, 3 h), however, the retardation is no longer significant, indicating that the injection is only transient.

This is in accordance with plan-view transmission-electron microscopy (TEM) investigations of Sn precipitates in samples of the type shown in Fig. 1, after, respectively, 1 and 3 h annealing at 995 °C. After 1 h precipitates had formed in samples with $C_{\mathrm{Sn}} \geq 1.2 \times 10^{20}\ \mathrm{cm}^{-3}$, all of a distinct size of approximately 10 nm. After 3 h, sizes ranged from ~ 5 to ~ 18 nm, the size evolution probably taken place by Ostwald ripening. A rough estimate of precipitate volumes gives the important result that the fraction of Sn atoms that have gone into precipitates is very small, less than 1% in any sample (assuming that all precipitates are seen by TEM and that precipitates are pure Sn). Moreover, this fraction did not increase from 1 to 3 h of annealing.

One should be cautious when generalizing the results of Fig. 4 to Sb diffusion *inside* a Sn box, but we still estimate that diffusivities extracted from long diffusion times (2 h, 3 h) are only slightly influenced by point defect injection from Sn precipitation. In any case, such an injection can at most have a retarding—not enhancing—effect.

Important also, *dislocation* densities were low enough to not affect the diffusion. At $C_{\mathrm{Sn}} = 4.7 \times 10^{20}\ \mathrm{cm}^{-3}$ the density of misfit dislocations, estimated from TEM on plan-view and cross-sectional samples, both before and after annealing, was $\sim 10^6\ \mathrm{cm}^{-2}$ or less. The far

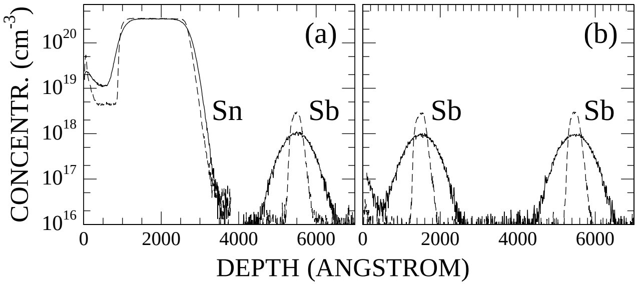

FIG. 3. MBE structures for testing Sb diffusion (a) with and (b) without a Sn box, as-grown (dashed) and annealed at 995 °C for 1 h (solid). The two spikes in (b) have the same diffusivities, showing that surface effects are unimportant.

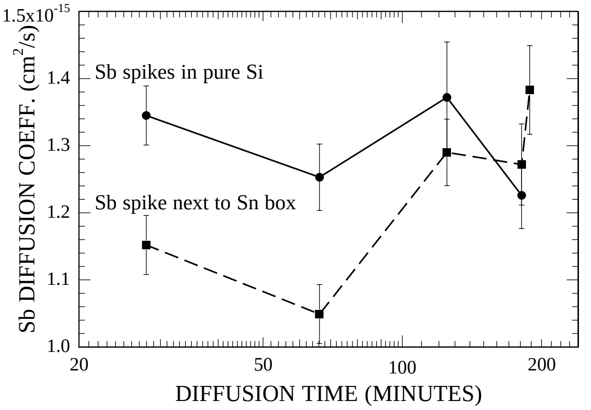

FIG. 4. Diffusion coefficients at 995 °C of the Sb profiles in Fig. 3 vs annealing time. Points that are vertically above each other represent samples that have been annealed simultaneously, under exact same temperature and time conditions.

majority was located at the SiSn/Si interface. Threading dislocations were seen at a density at least 10 times lower. Hardly any dislocations were found at $C_{\mathrm{Sn}} = 3.2 \times 10^{20}$ cm^{-3}, and none below this concentration.

For the system at hand a comparison is relevant with Sb diffusion in relaxed $\mathrm{Si}_{1-x}\mathrm{Ge}_x$. Here an enhancement also occurs [12,14], but the mechanism seems to be fundamentally different, since it sets in only in alloys that are increasingly Ge-like; e.g., a factor of 2 enhancement requires $x \geq 0.10$ [12]. The small-size group-IV impurity C is known to retard B diffusion by inducing an undersaturation of Si self-interstitials [16], but effects of high C concentrations upon vacancy diffusers have, to our knowledge, not been studied.

In the following we will discuss a number of proposed models for high-concentration diffusion in Si.

Mathiot and Pfister [1,17,18] put forward a *vacancy-percolation model,* in which the dopants set up a vacancy-percolation network when their concentration exceeds a critical value C^*. In this limit vacancies will, namely, feel a simultaneous attraction to two or more dopants, which results in lowered vacancy migration barriers and formation energies. For any atoms that diffuse via vacancy exchange the effective diffusivity then has two contributions, D^{perc} and D^{norm} ($= 1.18 \times 10^{-15}$ cm^2/s for Sb), from diffusion inside and outside percolation regions,

$$D^{\mathrm{eff}} = P_\infty D^{\mathrm{perc}} + (1 - P_\infty) D^{\mathrm{norm}}. \tag{1}$$

Here P_∞ is the probability that an atom belongs to an "infinite" percolation cluster,

$$P_\infty = \begin{cases} 0 & \text{for } C < C^*, \\ \min[1, K(\frac{C}{C^*} - 1)^\beta] & \text{for } C > C^*, \end{cases} \tag{2}$$

$\beta = 0.4$ and K is a constant. Diffusion in Sn backgrounds is particularly simple, since Sn induces no Fermi-level shift, so D^{norm} and D^{perc} have no doping dependence.

In Fig. 2 the data were fitted according to Eq. (1) (dashed curve). From the fit $K = 0.44 \pm 0.02$. A fixed value $D^{\mathrm{perc}} = 4 \times 10^{-15}$ cm^2/s was used, since this value is slightly above the highest measured value of D_{Sb}. The experiment, however, does not indicate that D_{Sb} reaches a plateau (equal to D^{perc}) at high Sn concentrations, and the diffusivity increase is not as sudden as predicted.

The fitted percolation threshold is $C^*_{\mathrm{Sn}} = 9.6 \pm 0.5 \times 10^{19}$ cm^{-3}, considerably lower than thresholds observed for diffusion in group-V backgrounds. Theory gives $C^* \approx 2 \times 10^{20}$ cm^{-3} [19], corresponding to the limit above which a vacancy that escapes to a 3rd neighbor position from one dopant will be a 2nd neighbor to another dopant, and this value has been in good agreement with group-V diffusion experiments [1,3,9,17,18].

In the above framework the fact that C^* is lower for Sn than for a group-V background would suggest that the Sn-V potential (V denotes vacancy) has a longer range than donor atom-vacancy potentials. But in conflict one will expect *a priori* that the purely elastic Sn-V potential falls off more rapidly than a Coulomb-like donor atom-vacancy potential. (Such a potential was calculated by Pankratov *et al.* [20] for As.) If the Sn-V potential had indeed been long range it would have a strong binding energy ΔE_2 at the 2nd neighbor separation, and this would have caused a much stronger diffusivity enhancement $F = D^{\mathrm{perc}}/D^{\mathrm{norm}} = \exp(\Delta E_2/kT)$ [17] than seen.

Thus it is likely that a different scenario is needed to explain enhanced diffusion of Sb in a Sn background. But vacancy percolation (despite the crudity of the model—see, e.g., [21]) may still provide a good starting point for discussion of high concentration group-V diffusion, and it might also be important at higher Sn concentrations.

Ramamoorthy and Pantelides [5] recently did *first-principles* calculations on As in Si. They found both that As impurities are bound strongly (~1.5 eV per As atom) in $\mathrm{As}_n V$ complexes, $1 \leq n \leq 4$, and that $\mathrm{As}_2 V$ is highly mobile, with a diffusion activation energy of only 2.7 eV. They suggest therefore that $\mathrm{As}_2 V$ complexes play a significant role in enhanced As diffusion at high concentrations, possibly dominating diffusion at concentrations below the percolation threshold. In possible support hereof Sb diffusion in isoconcentration studies [8] in the concentration range 2.3×10^{18}–2.5×10^{19} cm^{-3} was enhanced more strongly than was expected from Fermi-level effects. (At higher concentrations diffusion was retarded due to precipitation.) Here $\mathrm{Sb}_2 V$, due to the similarity of Sb and As, could be the dominating diffusing species.

A corresponding complex for mediating Sb diffusion in a Sn background would be Sb-Sn-V, where one group-V atom has been swapped with Sn. The formation of such a complex will benefit from the lack of Coulomb repulsion between Sb and Sn. At the same time one can expect that the vacancy is bound to the two dopants during diffusion because of the positively charged Sb^+ and because of strain, considering the large sizes of Sn and Sb atoms. In first order reaction kinetics the number of such complexes will increase linearly with C_{Sn}, giving a contribution with slope $a = 1$ in a log-log plot of diffusivity vs Sn concentration. Indeed, this is supported by the solid curve fit of Fig. 2, where we used the expression

$$D = D_0 + D_1(C_{\mathrm{Sn}}/C_S)^a. \tag{3}$$

From the fit $a = 1.04 \pm 0.05$, $D_1 = 3.1 \pm 0.8 \times 10^{-13}$ cm^2/s. $D_0 = 1.18 \times 10^{-15}$ cm^2/s was used for intrinsic diffusion via Sb-V pairs, and C_S is the Si atomic density.

For Eq. (3) to hold the vacancy concentration must not increase abruptly, since this itself would cause a diffusivity enhancement. Also, in Eq. (3), in thermodynamical equilibrium the fraction of Sb atoms that are in Sb-V pairs is not affected by formation of Sb-Sn-V complexes. This can be expected to be fulfilled, requiring only that the number of Sb-V pairs and Sb-Sn-V complexes is low relative to the number of Sb atoms.

A number of authors [6,7,22] have used Monte Carlo methods to model high-concentration group-V diffusion. Dunham and Wu [6] obtained good agreement with data from [3] by assuming a linear dopant-vacancy potential with a range to the 3rd coordination order and no dopant-dopant interactions. List and Ryssel [7] performed similar simulations, but with a much larger number of diffusion hops. They found that diffusion would retard at high concentrations due to clustering of dopants as a by-product of the dopant-vacancy attraction. Good results were obtained only with a *nonattractive* potential with low vacancy migration barriers near the dopant atom. It appears that Monte Carlo simulations are still to be improved, incorporating *ab initio* potentials, where possible, and allowing for mobile two-atom complexes.

An alternative model was proposed by Antoncik [4]. In this model diffusion is enhanced when dopant concentrations approach the solubility limit, the argument being that decay of diffusing dopant-vacancy pairs should slow down. But the model cannot explain the enhancement in the Sn system, since even at $C_{\mathrm{Sn}} = 4.7 \times 10^{20}$ cm^{-3} we have effectively not reached a limit on the number of Sn atoms that can be incorporated substitutionally.

Summarizing, we have presented data that show diffusion enhancement at 995 °C of Sb in Si when Sn-background concentrations exceed $\sim 5 \times 10^{19}$ cm^{-3}. It was made probable that Sn precipitation causes injection of self-interstitials, but that the effect upon the Sb diffusion at diffusion times of ~2–3 hours is small and possibly retarding. We argued from the diffusion data that the vacancy percolation model cannot be applied to explain the diffusivity enhancement in the present system, but that a likely diffusion mechanism to prevail at high concentrations is diffusion via Sb-Sn-V complexes.

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[10] Very abrupt Sb profiles cannot be obtained within Sn backgrounds in Si, the presence of Sn causing Sb to float at the growing surface.

[11] In each annealing the temperature T_i is recorded as a function of time t_i. An effective diffusion time t_{eff} is then calculated by summing all time steps $\Delta t_i = t_{i+1} - t_i$ with weights, according to $t_{\mathrm{eff}} = \sum_i \Delta t_i \exp(-[\frac{Q}{kT_i} - \frac{Q}{kT}])$. Here T is the temperature at the plateau (995 °C), and the activation energy of intrinsic Sb diffusion, $Q = 4.08$ eV [12], was used in all cases. Typically t_{eff} is less than 10 min longer than the nominal, preset heating time, so that corrections are insignificant at all but the shortest annealing times.

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