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Anomalous diffusion of tin in silicon

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The diffusion of Sn in Si has been studied using molecular-beam epitaxially grown Si layers with Sn and Sb distributions included during growth. The Sn and Sb profiles were measured by secondary-ion mass spectrometry. By comparing the diffusion of Sn and Sb in an inert N_2 ambient to that in a nitridating NH_3 ambient, in which case vacancies are injected, the fractional-vacancy contribution to the diffusion of Sn in Si was found to be equal to that of Sb which is known to be close to one. Thus, it is concluded that Sn diffuses predominantly by a vacancy-mediated mechanism in Si. The activation energy of diffusion, however, is found to be higher than expected for a vacancy-mediated diffusion mechanism; this is discussed considering Sn-vacancy configurations different from the configuration in which a vacancy is trapped next to a Sn atom. [S0163-1829(97)05335-6]

Tin is isovalent to silicon and is electrically neutral as a substitutional impurity in the diamond lattice; it is a large-size impurity in silicon and is, from a strain-relief argument, expected to diffuse predominantly via a vacancy-assisted mechanism, as the similar-sized antimony impurity does.[1,2] Contrary to the case of antimony diffusion in silicon, however, where several experiments have been devoted to the exposure of the diffusion mechanism,[1] to the knowledge of the authors only a single experiment has been carried out to reveal the diffusion mechanism of tin in silicon.[3]

It has been known for some time that oxidation of a bare silicon surface generates silicon self-interstitials, whereas surface nitridation generates vacancies.[4] The relative contribution of self-interstitials and vacancies to the diffusion of a given impurity or to self-diffusion can therefore be estimated from a comparison of the retardation or enhancement of the diffusivitity as a result of an oxidation or nitridation of the surface during the diffusion process. In this way Fahey *et al.*[2] has determined the fractional vacancy component in the diffusion of Sb in Si, f_{SbV}, at 1100 °C to $f_{\mathrm{SbV}} \geqslant 0.78$; this fraction is foreseen to be larger at lower temperatures due to an expected smaller activation energy for vacancy-assisted diffusion than for interstitialcy-assisted diffusion.[5] Thus, in agreement with the strain-relief argument, Sb diffuses predominantly by a vacancy-assisted mechanism in Si.

Marioton and Gösele[3] have reported the results of surface nitridation during the diffusion of Sn in Si at 1100 °C. They observed a diffusivity enhancement during nitridation; however, using a literature value of the vacancy supersaturation expected to prevail under the actual circumstances the fractional-vacancy component was estimated to be $f_{\mathrm{SnV}} = 0.33$. A possible cause of this unexpectedly low value could be a lowering of the vacancy injection due to the presence of tin on the surface, as discussed by Marioton and Gösele.[3] Only a few determinations of the activation energy of Sn diffusion in Si have been published, resulting in values differing by as much as 40%: Yeh, Hu, and Kastl[6] reported a value of 4.25 eV based on in-diffusion of Sn from a surface source and measurements by neutron-activation analysis in the temperature range 1050–1200 °C; Akasaka *et al.*[7] reported a value of 3.5 eV also based on in-diffusion of Sn from a surface source and measurements by Rutherford backscattering spectrometry at the two temperatures of 1100 and 1200 °C, and Kringhøj and Elliman[8] recently reported a value of 4.91 ± 0.09 eV based on redistribution of ion-implanted Sn distributions in the temperature range of 1000–1200 °C measured with secondary-ion mass spectrometry (SIMS).

Diffusion in silicon by the simple vacancy-exchange mechanism, in which the substitutionally dissolved atom A jumps into a vacancy on a nearest-neighbor site, proceeds with an activation energy which is smaller or equal to that of self-diffusion by the vacancy-exchange mechanism. Dunham and Wu[9] have recently demonstrated that the activation energy in this case, Q_{AV} is given by

$$Q_{AV} = Q_{\mathrm{SiV}} - (\Delta E_{AV}^2 - \Delta E_{AV}^3)/2, \qquad (1)$$

where Q_{SiV} is the activation energy of self-diffusion by the vacancy-exchange mechanism, and ΔE_{AV}^2 and ΔE_{AV}^3 are the binding energies between the substitutional atom A and the vacancy in the second- and third-nearest neighbor positions, respectively. If the interaction potential between the atom A and the vacancy does not extend to the second-nearest-neighbor position, the activation energy will be equal to that of self-diffusion. If, on the other hand, it does extend beyond the second-nearest-neighbor position, the activation energy will be smaller than that of self-diffusion; in this case the impurity and the vacancy will diffuse as a pair and the diffusion mechanism is called E-center diffusion.

A number of groups have estimated the activation energies for self-diffusion in silicon via vacancies Q_{SiV} and interstitials, Q_{SiI}.[1] The results tend to converge towards $Q_{\mathrm{SiV}} \simeq 4.1$ eV and $Q_{\mathrm{SiI}} \simeq 4.9$ eV, which includes a recent experimental result by Bracht, Stolwijk, and Mehrer[10] of $Q_{\mathrm{SiV}} = (3.80 \pm 0.08)$ eV and $Q_{\mathrm{SiI}} = (4.95 \pm 0.03)$ eV. For intrinsic-vacancy assisted diffusion of Sb in Si, the vacancy is expected to be in its neutral charge state and, hence, the binding between the positively charged Sb atom and the neutral vacancy will be due to strain. This type of interaction is normally short range in nature, and $(\Delta E_{\mathrm{SbV}}^2 - \Delta E_{\mathrm{SbV}}^3)/2$ is therefore expected to be small in this case. In agreement with that, the activation energy for intrinsic-antimony diffusion in silicon is found to be $Q_{\mathrm{SbV}} = (4.08 \pm 0.06)$ eV,[11] identical to that of vacancy-assisted self-diffusion. Moreover, Fair,

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Manda, and Wortman[12] have observed a decrease in the activation energy Q_{SbV} as a result of an increase in the doping level. An increase in the doping level results in an increase in the concentration of singly charged negative vacancies and, therefore, also in an increased importance of the Coulomb interaction between the positively charged Sb atoms and the vacancies, which is long range in nature. This will result in a reduced activation energy, in agreement with the observation by Fair, Manda, and Wortman.[12] Thus, the diffusion of Sb in Si is a good example of vacancy-assisted diffusion.

Although Sn as a dilute impurity in Si has only little technological importance, it is considered an interesting impurity due to its assumed high fractional-vacancy component of diffusion and its electrical neutrality that allow for tests of diffusion models without having to consider Fermi-level effects. However, the big scatter in the reported activation energies for diffusion and the uncertainty in the reported fractional-vacancy component of diffusion has limited its applicability. In the present investigation of Sn diffusion in Si we have utilized the exceptional possibilities offered by the molecular-beam epitaxial technique to grow very-well-defined samples, tailor-made to the actual experiments, without limitations from residual defects as in the case of ion implantation or interface problems as in the case of in-diffusion experiments.

All the diffusion experiments reported below were done in epitaxial Si layers grown by molecular beam epitaxy on Sb-doped ⟨100⟩Si wafers. The Sb and Sn distributions were included during growth; the peak concentrations were $\lesssim 5 \times 10^{18}$ cm^{-3} and the full width at half manimum ~250 Å. The peak concentrations were chosen to be below the solubility limits to avoid precipitation effects and, in the case of Sb, below the intrinsic carrier concentration to assure diffusion in the intrinsic regime. The concept we have chosen for the determination of the fractional-vacancy contribution is based on the use of the Sb diffusivity as a reference. For that purpose we grew samples containing both Sn and Sb distributions, allowing us to compare the diffusivity of Sb and Sn under exactly the same experimental conditions. In addition, we grew samples containing only Sb or Sn distributions to check if the presence of both distributions in the same sample somehow influenced the diffusivity. A comparison was made between the diffusivities at ~1000 °C in either an inert N_2 or a nitridating NH_3 ambient; the diffusion time in both cases was ~50 min.[13] In order to determine the activation energy of diffusion, the diffusivity was studied as a function of temperature in an inert N_2 ambient in the temperature range of 900–1075 °C; the annealing times were chosen to result in similar diffusion lengths. The chemical profiles of Sb and Sn were measured by SIMS using an Atomika instrument. Sputtering was performed with a 3.5 keV O_2 beam in an incoming angle of 22 ° relative to the normal. The ^{124}Sn and ^{123}Sb isotopes were detected as positive secondaries.

Figures 1 and 2 show examples of SIMS profiles measured before and after heat treatment at 1000 °C in a N_2 and a NH_3 environment, respectively. The full curves in the figures are profiles calculated in a procedure in which the as-grown profile is allowed to broaden with time in accordance with the diffusion equation; the difference between the calculated and the diffused profiles is minimized with the diffusion coefficient as a free parameter.[14] From a visual inspection of Figs. 1 and 2 it can immediately be concluded that the diffusivity of Sb is larger than that of Sn and that the heat treatment in a NH_3 environment results in a strong enhancement in the diffusivity of both Sb and Sn as expected at least for the Sb diffusivity. Extracted diffusion coefficients using the above-mentioned minimalization procedure are collected in Table I. The diffusivity during nitridation is found to be depth independent An analysis of the shallow or the deep Sn/Sb distribution resulted in the same diffusion coefficients; thus, the vacancy supersaturation is constant in

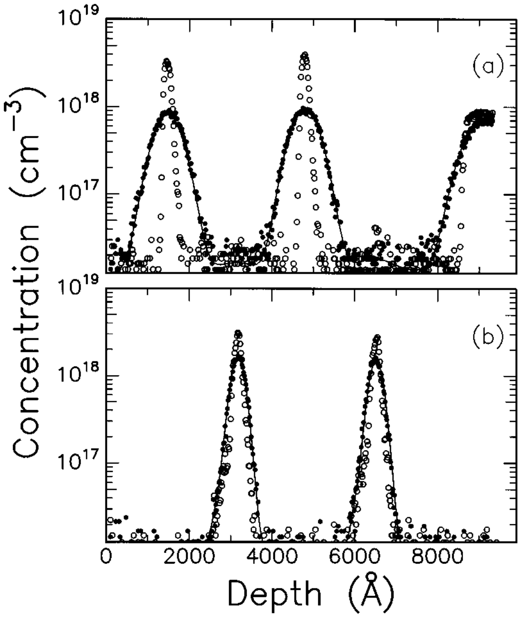

FIG. 1. Chemical profiles measured by SIMS of (a) Sb in Si and (b) Sn in Si. The open symbols refer to as-grown profiles, the closed symbols to profiles after heat treatment at ~1000 °C for ~50 min in an inert (N_2) ambient. The full curves are calculated profiles (see text).

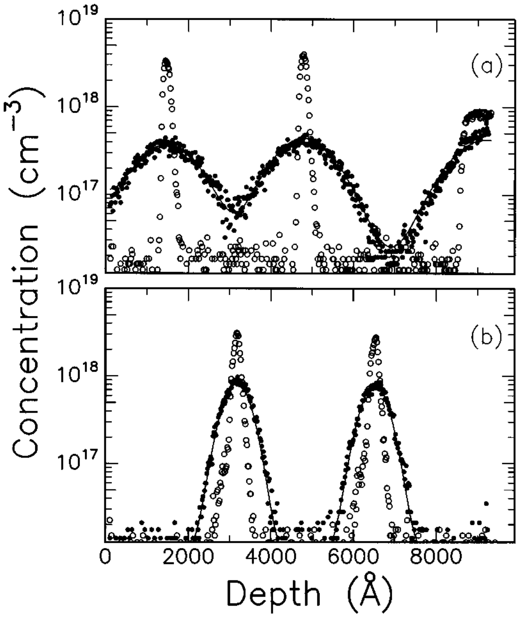

FIG. 2. As in Fig. 1 except for the fact that the heat treatment was done in a surface-nitridating (NH_3) ambient.

TABLE I. Diffusion coefficients of Sn and Sb at 1000 °C measured in an inert (N_2) ambient and in a surface nitridation (NH_3) ambient, and calculated diffusion-enhancement factors $F = D_{Sn/Sb}(NH_3)/D_{Sn/Sb}(N_2)$. A total of four wafers were grown and measured: Sample 1 had both Sn and Sb distributions, sample 2 had only a Sb distribution, and samples 3 and 4 had only Sn distributions. The stated uncertainties include uncertainties of heat-treatment temperature and time, and on the fitting procedure for the determination of the diffusion coefficients.

	$D_{Sn}(N_2)$ (cm^2/s)	$D_{Sn}(NH_3)$ (cm^2/s)	$D_{Sb}(N_2)$ (cm^2/s)	$D_{Sb}(NH_3)$ (cm^2/s)	F(Sn)	F(Sb)
Sample 1: Sn and Sb	$(2.55\pm0.13)\times10^{-16}$	$(1.40\pm0.07)\times10^{-15}$	$(1.57\pm0.08)\times10^{-15}$	$(8.00\pm0.40)\times10^{-15}$	5.5±0.4	5.1±0.4
Sample 2: Sb only			$(1.58\pm0.08)\times10^{-15}$	$(7.45\pm0.37)\times10^{-15}$		4.7±0.3
Sample 3: Sn only	$(3.10\pm0.16)\times10^{-16}$	$(1.52\pm0.08)\times10^{-15}$			4.9±0.3	
Sample 4: Sn only	$(3.15\pm0.16)\times10^{-16}$	$(1.49\pm0.07)\times10^{-15}$			4.7±0.3	

the investigated depth range. The diffusion coefficients in Table I are determined using the entire profile. The enhancement factors f calculated as $D(NH_3)/D(N_2)$, and neglecting the small temperature difference,[13] are also included in Table I. There are two conclusions that can be drawn from these enhancement factors. First, for each of the two impurities the enhancement factors are identical within the uncertainties for the different samples, and second, the enhancement factors for Sb and Sn are identical within the uncertainties. Thus, it is concluded that at 1000 °C the fractional vacancy contribution to the diffusion of Sn in Si is equal to that for Sb in Si, $f_{SnV} \approx f_{SbV}$.

Diffusion coefficients of Sn in Si measured at different temperatures are shown in Fig. 3 as a function of the reciprocal temperature. Also shown in Fig. 3 are results reported by Kringhøj and Elliman[8] obtained from ion implanted Sn distributions in Si. It appears that the data are very similar: the activation energy of diffusion extracted from the present investigation is $Q_{SnV} = (4.8\pm0.3)$ eV which is identical, within the uncertainties, to the value reported by Kringhøj and Elliman[8] of (4.91±0.09) eV but higher than the value of Yeh, Hu, and Kastl[6] of 4.25 eV and significantly higher than the value reported by Akasaka *et al.*[7] of 3.5 eV. The preexponential factor from the present investigation is $D^0_{SnV} = (1.4\pm3.6)\times10^3$ cm^2/s, the large uncertainty renders meaningless a comparison to the values measured by Kringhøj and Elliman[8] of $D^0_{SnV} = (5\pm4)\times10^3$ cm^2/s and by Yeh, Hu, and Kastl[6] of $D^0_{SnV} = 32$ cm^2/s It should be noted, however, that the preexponential value for Sb diffusion in Si is reported by Fair, Manda, and Wortman[12] to be 17.5 cm^2/s and by Nylandsted Larsen and Kringhøj[11] to be 20±12 and thus similar to the value for Sn reported by Yeh, Hu, and Kastl;[6] the value for self-diffusion via interstitialcies is reported by Bracht, Stolwijk and Mehrer[10] to be $(3\pm1)\times10^3$ cm^2/s, a value similar to the one for Sn reported by Kringhøj and Elliman.[8] It is not clear to us why the activation energies based on in-diffusion experiments measured by Yeh, Hu, and Kastl[6] and Akasaka *et al.*[7] are smaller than those measured in the present investigation and by Kringhøj and Elliman.[8] Both in-diffusion values are determined at high temperatures in the ranges of 1050–1200 (Ref. 6) and 1100–1200 °C (Ref. 7) which would normally favor an interstitialcy-mediated fraction and therefore a high activation energy.

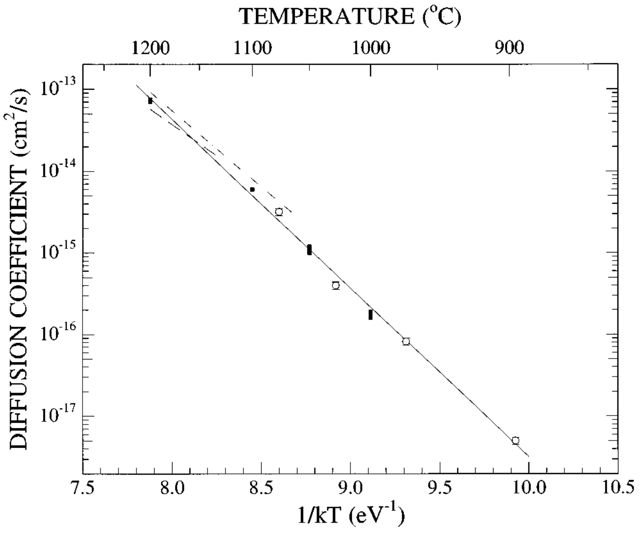

FIG. 3. Diffusion coefficients versus reciprocal temperature. The results from the present investigation are indicated with (○) and the fit to these results is shown as the full line. The diffusion coefficient from Table I measured at 1000 °C has not been included in this figure as this value is based on a heat treatment in a modified furnace. The indicated uncertainties include statistical uncertainties as well as uncertainties from anneal time and temperature, and from the fitting procedure used to extract the diffusion coefficients. Also shown are results by Kringhøj and Elliman (Ref. 8) (■, the size of the symbol indicate their quoted uncertainties), Akasaka *et al.* (Ref. 7) (dot-dashed line), and Yeh, Hu, and Kastl (Ref. 6) (dashed line).

Thus, the results of the present investigation show that the activation energy for Sn diffusion in Si is larger than expected for vacancy-mediated diffusion, and are similar to what is expected for interstitialcy-mediated diffusion, in agreement with the observation reported in Ref. 8; however, the vacancy-injection experiment points unambiguously to a vacancy-mediated diffusion mechanism. There are indications that the preexponential factor is of the same order of magnitude as that for interstitialcy-mediated self-diffusion.

A comparison to Ge diffusion in Si might seem relevant as Ge is a group-IV impurity as is Sn although smaller; however, a number of investigations have demonstrated that Ge has a mixed diffusivity making such a comparison doubtful: Fahey, Iyer, and Scilla[15,16] reported interstitial-mediated fractions, f_{GeI}, equal to 0.35±0.05 at 950 °C and 1050 °C and Cowern *et al.*[17] reported a value of $f_{GeI} = 0.22\pm0.04$ at 875 °C. Nevertheless, very large activation energies have been reported: Dorner *et al.*[18] found a value of 5.25 eV in the temperature range of 875–1300 °C and Fahey, Iyer, and Scilla[15] found a value of 4.92 eV in the temperature range of 850–1100 °C. In both cases perfect Arrhenius behavior was observed in the whole investigated temperature ranges. These values are also larger than expected from a comparison to Si self-diffusion values.

Most probably, an explanation of the very large activation energy observed for Sn diffusion in Si, which is ~0.7 eV larger than that for vacancy-mediated self-diffusion in Si, should be found in either a vacancy-based diffusion mechanism different from that of the E-center mechanism, or if the E-center mechanism prevails, in the presence of an energy barrier and/or an energy difference in the equilibrium configuration of the Sn-vacancy pair and the E-center diffusion configuration. There are strong indications in the literature that the equilibrium configuration of Sn-vacancy pair in silicon is different from that of the Sb-vacancy pair. Watkins[19,20] has studied the Sn-vacancy pair in Si using electron-paramagnetic resonance; his results point to an equilibrium Sn-vacancy pair configuration consisting of the Sn atom residing in a position halfway between two normal silicon atom sites. If it is assumed that the vacancy-mediated Sn diffusion proceeds via the E-center mechanism, then the Watkins configuration must transform into the E-center configuration as the first step in the diffusion process; from then on the diffusion could proceed with an activation energy similar to that of vacancy-assisted self-diffusion or intrinsic Sb diffusion. As the E-center configuration in this scenario has a higher total energy than the Watkins configuration has and as, in addition, there might be an energy barrier between the two configurations, the total activation energy will be higher than that of vacancy-assisted self-diffusion. A determination of the degree to which it is higher has to await, e.g., total energy calculations. In this scenario based on the Watkins configuration, the configurational entropy of diffusion is expected to increase relative to that of the normal vacancy-replacement mechanism as the number of equivalent paths are increased by a factor of 2; this will result in an increase in the preexponential factor. Thus, the Watkins configuration combined with the normal vacancy-replacement mechanism will give rise to an increased diffusional-activation energy and entropy; however, it is still questionable whether these increases are sufficient to explain the experimentally observed values.

A different scenario could be the trapping of a vacancy in the second-nearest-neighbor position to the Sn atom in a stable or metastable configuration. Such a configuration will relax the strain around the big Sn atom and, at the same time, maintain the fourfold coordination of the Sn atom. This configuration can also explain the complete lack of any defect lines in Mössbauer spectra of as-implanted, low dose Sn in Si crystals, as Mössbauer spectroscopy is predominantly sensitive to changes only in the first-nearest-neighbor positions to the Sn atom.[21] In similar implants of radioactive Sb a significant contribution from a defect line correlated to Sb-vacancy pairs is observed.[22] The diffusion could then proceed by the E-center mechanism where the vacancy must move to the first-nearest-neighbor position of the Sn atom in order to exchange sites or the Sn atom could make a second-neighbor jump as discussed by Mitha *et al.*.[23] The feasibility of this mechanism also has to await total energy calculations of the energies of the different configurations and the energy barriers between them.

In summary, the diffusion of Sn in Si is found to proceed predominantly by a vacancy-mediated mechanism. However, the activation energy is higher than expected for diffusion via a normal vacancy-replacement mechanism. A high value is shown to be consistent with the Watkins equilibrium configuration for the Sn-vacancy pair combined with the E-center diffusion mechanism. However, a vacancy-assisted diffusion mechanism not based on the E-center mechanism cannot be excluded.

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