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Sb-precipitation-induced injection of Si self-interstitials in Si

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The issue of point-defect injection during antimony precipitation in silicon is addressed in the present investigation. By studying the effect of Sb precipitation in an Sb-box distribution on the diffusion of B or Sb in deeper-lying spikes it is unambiguously concluded that Si self-interstitials are injected during the precipitation process. Possible causes of the self-interstitial injection are discussed. [S0163-1829(99)09411-4]

The formation of thin layers of high concentrations of electrically active dopants in Si is both a challenging and technologically important task. It involves, among other things, impurity-defect interactions at nonequilibrium point-defect concentrations, impurity diffusion at extreme impurity concentrations, and deactivation processes in the form of precipitation and formation of impurity-defect complexes.[1] Studies of the formation and stability of these layers therefore involve critical tests of models of the kinetics of impurity-defect interactions. Moreover, such layers are frequently of interest in micro-electronic components, e.g., as emitter layers in bipolar transistors or source and drain contacts in field-effect transistors.[2]

The layers are typically produced by ion implantation combined with a suitable anneal treatment[3] or by an epitaxial growth procedure.[4] They are often metastable in as much as their electrically active dopant concentrations exceed a critical temperature-dependent concentration above which the dopants will be electrically inactive in equilibrium. This critical concentration can be, e.g., the solid-solubility limit or the critical concentration for the formation of dopant-vacancy complexes. A subsequent high-temperature treatment, which is usually an unavoidable step in the fabrication process of an integrated circuit, will result in a deactivation of a certain number of electrically active dopants; these inactive dopants will then be contained in precipitates or dopant-defect clusters.

The question is now as to whether the process of precipitate or dopant-defect cluster formation results in supersaturated concentrations of point defects (self-interstitials and vacancies) that might diffuse away from the regions of deactivation. Such an injection of point defects can influence other dopant distributions in the component and thereby be harmful to its structure or, if a diffusion process is under investigation, can affect this process in an unwanted way.

In the case of As in Si, a system in which precipitates are only formed at very high As concentrations ($\geqslant 1\times10^{21}\,\mathrm{cm}^{-3}$),[5] it has been demonstrated that de-activation of metastable electrically active concentrations below $\sim 1\times10^{21}\,\mathrm{cm}^{-3}$ proceeds via the formation of As-vacancy clusters with a resulting injection of high concentrations of self-interstitials.[6,7] Antimony in Si is, on the other hand, a system with a relatively low solid solubility limit[8] and for metastable Sb concentrations exceeding about $6-7\times10^{19}\,\mathrm{cm}^{-3}$ precipitates form during a heat treatment of approximately 800 °C for 30 min. Indications of self-interstitial injection during Sb precipitation in Si have been reported in the literature either in the form of a slightly retarded Sb diffusivity in isoconcentration experiments when the Sb concentration exceeds the solubility limit[9] or as an enhanced B diffusion in a boron-doped base layer of a bipolar transistor with an Sb doped emitter layer exceeding the solubility limit.[10]

To discriminate between self-interstitial and vacancy injection the observation of an enhancement or retardation in the diffusion of B or Sb in Si is most useful since B and Sb are known to diffuse almost entirely via a self-interstitial assisted mechanism and a vacancy assisted mechanism, respectively.[11]

In the present investigation, this last mentioned experimental fact will be applied to study point-defect injections resulting from the precipitation process of Sb in Si. Advantage will be taken of the great possibilities offered by the epitaxial growth procedures, in the present case, molecular-beam epitaxy (MBE), with which very well defined, tailor-made structures for such studies can be produced.

The samples were grown by MBE on ⟨001⟩-oriented Si n^+ substrates, and the total thickness of each epitaxial layer was 10 000 Å. Samples were grown with and without a high concentration Sb-box distribution. This Sb-box distribution was situated from a depth of ~1000 to ~3000 Å [see Fig. 1(a)], and different maximum concentrations were chosen between 6×10^{19} and $1.6\times10^{20}\,\mathrm{cm}^{-3}$ as determined by Rutherford backscattering spectrometry (RBS) using 2-MeV α particles. At depths of ~7000 Å either a narrow B or Sb distribution was placed having peak concentrations between 1×10^{18} and $5\times10^{18}\,\mathrm{cm}^{-3}$ and full widths at half-maximum of ~300 Å. The peak concentrations were chosen as compromises between values as small as possible relative to the intrinsic carrier concentration n_i [$n_i(800\,^\circ\mathrm{C})\cong 5\times10^{17}\,\mathrm{cm}^{-3}$] in order to minimize the extrinsic-diffusivity component and values large enough to facilitate the secondary-ion mass spectrometry (SIMS) analysis. The dopant spike is followed by a ~3000 Å-thick undoped Si layer. The samples were heat treated in a furnace in a N_2 ambiance at temperatures between 800 and 1000 °C and for times between 5 and 30 min. Care was taken that at least two samples, with and without the Sb-box distribution, were always heat treated together in order to eliminate any possible temperature and time errors when estimating the effect of Sb precipitation on the diffusion of the dopants in the spikes. All samples were characterized by transmission-electron micros-

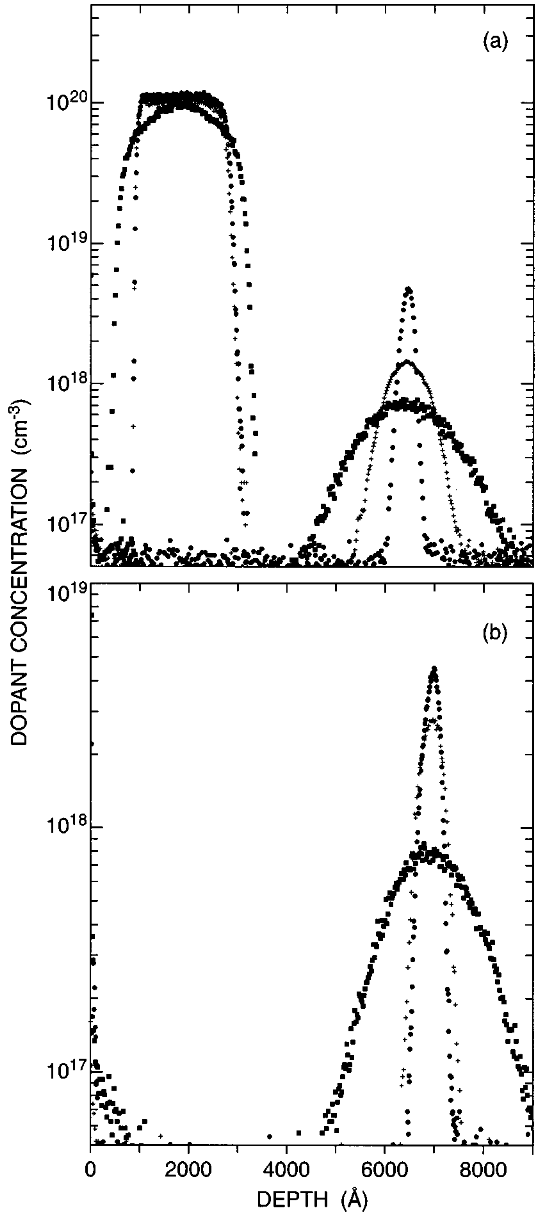

FIG. 1. SIMS profiles of structures with B spikes, with Sb-box profiles (a) and without (b). As grown (●), after heat treatment at 800 °C/30 min (+) and 1000 °C/30 min (■).

copy (TEM), before and after heat treatment, in plane view, and for selected samples in cross-section view. The impurity profiles were measured by SIMS using an Atomika instrument with a 2.5-keV O_2^+ beam. The depth calibration was obtained by measuring the total crater depth and assuming constant sputtering rate.

The effect of the presence of a high-concentration Sb-box distribution on the diffusion of B in the spike at different temperatures is illustrated in Fig. 1. It is immediately appreciated that the presence of the Sb-box distribution enhances the redistribution of the B spike; this is, in particular, evident in the case of the 800 °C heat treatment. When the maximum concentration of the Sb-box profile is reduced to a value near the solubility limit the B redistribution is similar to that obtained without an Sb-box profile (not shown).

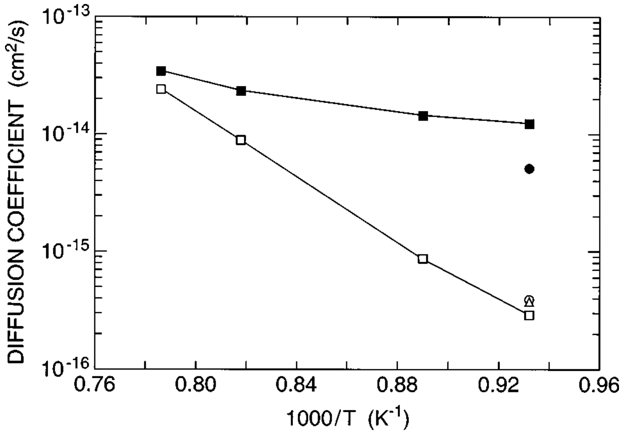

FIG. 2. Time-averaged diffusion coefficients (■,●,△) and equilibrium-diffusion coefficients (□,○) for B, extracted from SIMS profiles after 30 min. diffusion with Sb-box concentrations of 1.6×10^{20} (■), 1.1×10^{20} (●), and 6×10^{19} cm^{-3} (△). For each temperature, samples with and without an Sb box were annealed together.

In order to have a parameter which characterizes the redistribution of the impurity spikes under these nonequilibrium and, as will be apparent in the following, transient conditions we have determined what might be called a ''time-averaged diffusion coefficient.'' It is determined from the experimental SIMS profiles in the same way as equilibrium-diffusion coefficients are normally determined by a minimization procedure, in which the difference between a numerically diffused profile, using the as-grown profile as input, and the diffused profile is minimized, with the time-averaged diffusion coefficient as a free parameter. It should be noted, however, that under these transient and nonequilibrium conditions an effective-diffusion coefficient is not defined.[12] Extracted time-averaged diffusion coefficients for B as a function of diffusion temperature for a constant diffusion time of 30 min. are shown in Fig. 2. It appears, that the diffusion at a temperature of 800 °C is enhanced by approximately a factor of 50 for the highest Sb-box concentration (1.6×10^{20} cm^{-3}); the enhancement is reduced to about a factor of 10 if the Sb-box concentration is reduced to 1.1×10^{20} cm^{-3}, and there is no detectable enhancement if the Sb-box concentration is reduced to 6×10^{19} cm^{-3}. For higher temperatures the enhancement is reduced and it disappears at about 1000 °C. The enhancement is transient in time as demonstrated in Fig. 3 for the case of diffusion at 1000 °C; this was also observed in the case of diffusion at 800 °C.

The diffusion of Sb, in samples in which the B spike has been replaced by an Sb spike, is retarded as demonstrated in Fig. 4. In the case of Sb, the diffusion was only studied for temperatures higher than 950 °C as the slow diffusion at lower temperatures made it difficult to characterize the diffusion in a reliable way. It can be appreciated from Fig. 4, however, that the Sb diffusion at 950 °C is retarded by approximately the same factor as the B diffusion is enhanced (Fig. 2). Also in this case the effect almost disappears at 1000 °C.

Thus, the results strongly support the hypothesis that Si self-interstitials are injected from the Sb-box distributions during high-temperature heat treatments. From a vast number of TEM investigations of samples heat treated differently with respect to temperature and time (some of the results are shown in Fig. 5) we can conclude that the B-diffusion en-

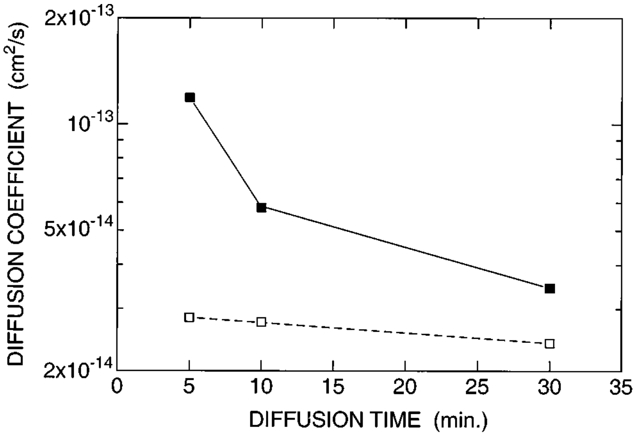

FIG. 3. Time-averaged diffusion coefficients (closed symbols) and equilibrium-diffusion coefficients (open symbols) for B extracted from SIMS profiles after 1000 °C diffusion with an Sb-box concentration of $1.6\times10^{20}\,\mathrm{cm}^{-3}$.

hancement is correlated with the appearance of Sb precipitates in the Sb-box distributions. The observation of no enhancement or retardation at 1000 °C for B and Sb, respectively, indicates that the supersaturation of self interstitials is similar in concentration to the equilibrium concentration of self interstitials at 1000 °C [$\sim1\times10^{12}\,\mathrm{cm}^{-3}$ (Ref. 1)].

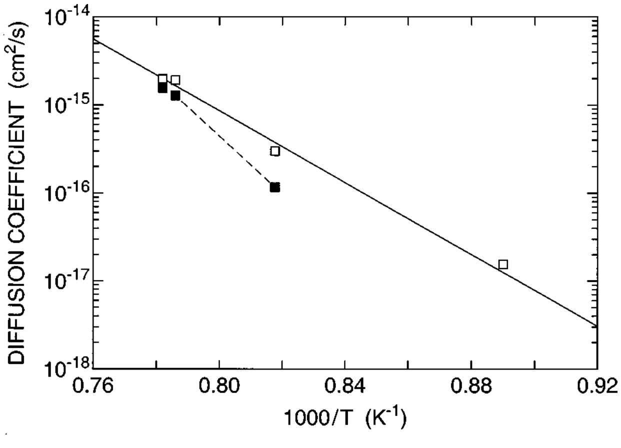

FIG. 4. Time-averaged diffusion coefficients (closed symbols) and equilibrium-diffusion coefficients (open symbols) for Sb extracted from SIMS profiles after 30 min. diffusion with an Sb-box concentrations of $1.6\times10^{20}\,\mathrm{cm}^{-3}$.

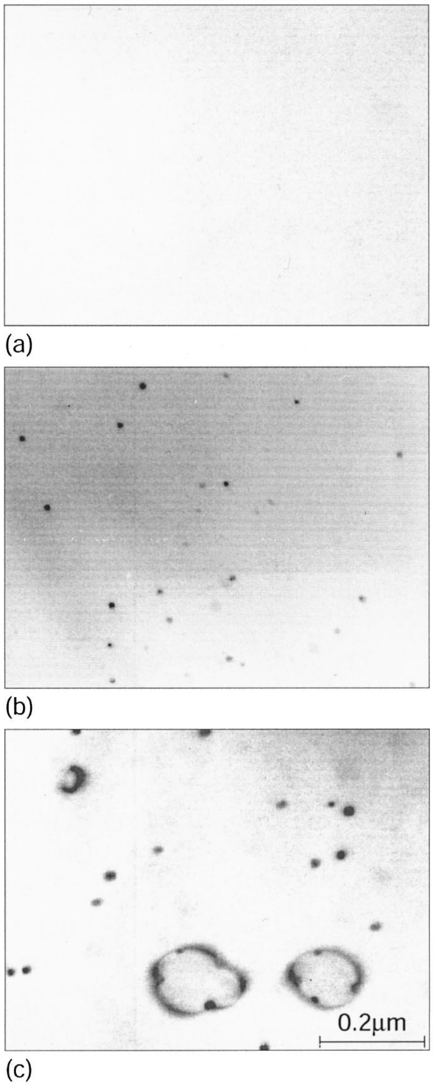

FIG. 5. TEM images in plane view after diffusion at 900 °C for 30 min of structures containing B spikes and Sb-box concentrations of 6×10^{19} (a), 1.1×10^{20} (b), and $1.6\times10^{20}\,\mathrm{cm}^{-3}$ (c). Sb precipitates (dark dots) are observed in (b) and (c) and interstitial loops only in (c).

We may note that the equilibrium-diffusion coefficients of B at low temperatures are slightly higher than reported literature values[13] (approximately a factor of 4 at 800 °C). We speculate that this can be a result of self-interstitial injection during precipitation of the relatively high C concentration in MBE-grown Si ($[C]\leq1\times10^{18}\,\mathrm{cm}^{-3}$, determined by SIMS in similar samples grown in our MBE system) as discussed by Cowern.[14] However, the Sb equilibrium diffusion coefficients displayed in Fig. 4 do not differ measurably from literature values.[13] The fact that such self-interstitial injection then affects B diffusion more strongly than Sb diffusion, indicates, as suggested by Tan and Gösele,[15] that the interstitial/vacancy recombination times in the investigated temperature range are much longer than the employed diffusion times (5–30 min). On the other hand, the much stronger interstitial injection related to Sb precipitation does cause a decrease in the vacancy-assisted Sb diffusion at 950 °C. Therefore, under this injection condition, a significant number of vacancies have recombined with interstitials, on a time scale that is less than 30 min.

The question should be addressed as to whether the injection of self-interstitials happens when the Sb precipitates form or when the vacancies, necessary for the transportation of Sb atoms to the precipitates, are produced. The observation that no detectable injection takes place from an Sb-box distribution of maximum concentration $6\times10^{19}\,\mathrm{cm}^{-3}$ but does take place from one of $1.1\times10^{20}\,\mathrm{cm}^{-3}$ demonstrates that it is not a result of the diffusion process as the vacancy-assisted diffusion of Sb at the two concentrations is expected to be very similar.[16] Thus, the self-interstitial injection seems to be correlated to the formation or growth of the precipitates.

A well-studied precipitation process in Si in which a supersaturated concentration of Si self-interstitials is also formed, is the formation of SiO_2 precipitates in Czochralski grown Si. For this system, it has been demonstrated by Hu (Ref. 12) that the SiO_2 precipitates produce local strain and, to reduce this local strain, oxygen precipitation is accompanied by emission of self-interstitials. In the case of Sb precipitation, however, it should be borne in mind that numerous experiments indicate that Sb diffuses via vacancies at the temperatures and concentrations of the present investigation.[1] This is also in agreement with our observation of a retardation of the Sb diffusion in the Sb spikes (Fig. 4), although this diffusion takes place under intrinsic conditions. Thus, every Sb atom brings, so to speak, its own vacancy to the precipitate and local strain is therefore not expected; a supersaturation of released vacancies should rather be expected. Moreover, indications of self-interstitial injection has also been observed from Sn-box profiles in Si during Sn precipitation;[17] Sn is also known to diffuse via vacancies which makes the system somewhat similar to the Sb system. Tin, however, is electrically neutral in Si which excludes electric-field effects affecting the diffusion of the charged defects.

It is quite possible that the self-interstitial injection takes place at the very early stage of the precipitate formation in which an Sb-vacancy cluster might be formed. It has been demonstrated that Sb-vacancy clusters are formed in layers doped to high concentrations of Sb (Ref. 18) prior to Sb precipitation. These clusters could be formed in a kick-out process similar to the one postulated by Rousseau *et al.*[7] as being active in the case of As deactivation followed by self-interstitial injection: $As_nSi \rightarrow As_nV + I$, where As_nSi represents n (integer 1–4) arsenic atoms around a silicon lattice site, As_nV represents a deactivated cluster with a vacancy, and I represents an interstitial.[7] The As_nSi clusters are assumed to be formed statistically at high As concentration. In addition, a process such as $As_nV \rightarrow As_nV_2 + I$ could be envisaged for some values of n.[19] Similar reactions could be expected to take place also in the case of Sb in Si. Such reactions would explain the self-interstitial injection; however, it is still left to be demonstrated why the ripening of the precipitates does not result in a supersaturated concentration of vacancies.

In summary, we have demonstrated that the Sb-precipitation process in Si creates a supersaturated concentration of self-interstitials. This has been done by monitoring the redistribution enhancement and retardation of deeper lying spikes of B and Sb, respectively, during the precipitation of near-surface, high-concentration Sb-box distributions. The supersaturated self-interstitial concentration is especially high at low temperatures. The formation of Sb-vacancy complexes in the early stage of precipitation is pointed out as a possible source of the self-interstitials.

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