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TRANSIENT ENHANCED DIFFUSION AND GETTERING OF DOPANTS
IN ION IMPLANTED SILICON*

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ABSTRACT

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We have studied in detail the transient enhanced diffusion observed during furnace or rapid-thermal-annealing of ion-implanted Si. We show that the effect originates in the trapping of Si atoms by dopant atoms during implantation, which are retained during solid-phase-epitaxial (SPE) growth but released by subsequent annealing to cause a transient dopant precipitation or profile broadening. The interstitials condense to form a band of dislocation loops located at the peak of the dopant profile, which may be distinct from the band formed at the original amorphous/crystalline interface. The band can develop into a network and effectively getter the dopant. We discuss the conditions under which the various effects may or may not be observed, and discuss conflicting observations on As⁺ implanted Si.

INTRODUCTION

There have been a number of reports of transient enhanced dopant diffusion during furnace¹ or rapid-thermal-annealing²⁻⁶ (RTA) and occasional reports of no enhancement.⁷ A series of careful furnace annealing experiments has identified the mechanism of the transient, and allowed the prediction of the transient effects (or lack of them) over a wide range of temperature and dopant concentrations, at least for Sb and Bi implantations. We summarize these results below and extend the observations to dopant concentrations below the solubility limit. The trapped interstitials responsible for the transient may condense into a band of dislocation loops. This band is in addition to any band formed at the original amorphous/crystalline interface. Above a critical concentration of interstitials the loop coalesce to form an extended dislocation network and cause gettering of the dopant, and a sharpening of the dopant profile. Finally we discuss the case of As⁺ implanted Si, where it appears at present that interstitials are indeed trapped but for some reason do not cause detectable transient dopant diffusion.

TRANSIENT ENHANCED DIFFUSION FROM TRAPPED INTERSTITIALS

We have observed transient enhanced diffusion in ¹²¹Sb⁺ and ²⁰⁹Pb⁺ implanted Si which was recrystallized by solid-phase-epitaxial (SPE) growth. By furnace annealing at low temperatures, the transient was slowed sufficiently for an accurate determination to be made of the diffusion coefficients during the transient, and the extent of the transient effects.⁸ The same transient effects occur at typical temperatures of rapid-thermal-annealing, although in a much shorter time. The transient enhanced diffusion coefficients D* were measured by precipitating out a small fraction of dopant and measuring the resulting size distribution by

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transmission electron microscopy (TEM). Figure 1 shows an Arrhenius plot for a variety of dopant concentrations and implantation conditions. All points are enhanced many orders of magnitude over the tracer values and show a low activation energy of only 1.8 ± 0.2 eV. Figure 2 shows that the transient diffusion coefficients are proportional to dopant concentration and dependent on implantation conditions. The transient ends when only a small fraction of dopant has been precipitated, 15% for room temperature implants and 7% for liquid nitrogen temperature implants. This fraction is independent of dopant concentration. In high concentration samples, the end of the transient is also marked by the formation of a band of interstitial dislocation loops. All these effects occurred far from the original amorphous/crystalline interface where radiation enhanced diffusion can occur. A new mechanism is needed to explain these effects, which we refer to as an interstitial trapping mechanism. We propose that during implantation, it is possible for an implanted group V ion to saturate its valence bonds by capturing a mobile Si atom thus forming a stable complex. Only a small fraction of the implanted ions need do this to explain the observed effects (2% for room temperature implants and 1% for liquid nitrogen temperature implants). These extra neighbors are retained during SPE growth to become trapped interstitials, but are released by additional annealing to cause the observed transient effects before finally condensing into loops. We note that Sb, which normally prefers a vacancy mechanism of diffusion,¹⁰ can diffuse by an interstitialcy mechanism given a high enough interstitial supersaturation. The activation energy corresponds to the migration enthalpy by this mechanism. We have not observed analogous effects with B⁺ implanted into preamorphized Si.⁸ We presume that there is no analogous mechanism for vacancy trapping by group III atoms since a saturated group III atom can easily be incorporated into the Si lattice by bond rearrangement during SPE growth, whereas incorporation of a saturated group V atom would require a bond to be broken.

Fig. 1. Arrhenius plot of Sb and Bi transient diffusion coefficients D^* for various concentrations and implant conditions. IBA = ion beam annealed⁹

Fig. 2. Plot of D^* at 680°C against dopant concentration.

In Figs. 3 and 4, we extrapolate our results to typical temperatures of RTA and to lower dopant concentrations. Note that at a sufficiently high temperature the tracer diffusion coefficient will exceed the transient diffusion coefficient, and enhanced diffusion will not be observed (the dashed regions of Figs. 3 and 4). However, the dislocation band may still remain as evidence of the trapped interstitials, although this too can be annealed out under suitable conditions, discussed later. To test the extrapolation in temperature, we have compared the effects of furnace annealing with RTA for times just exceeding the respective values of t^* , and see practically identical microstructures (Fig. 5).⁸ To test the extrapolation to low

Fig. 3. Predicted D^* for RT implants as a function of dopant concentration and temperature. D^* for LN_2 implants are half these values.

Fig. 4. Predicted duration of the transient as a function of dopant concentration and temperature.

dopant concentrations, we have used Si implanted with Sb^+ (80 keV, $3 \times 10^{14} \text{ cm}^{-2}$), giving a concentration below the solubility limit, and again annealed for a time just exceeding t^* . In this case, the transient enhanced diffusion caused broadening of the dopant profile as shown in Fig. 6. The observed broadening is approximately 100 Å on each side of the profile considerably enhanced over the 10 Å expected from normal thermally activated diffusion. However, it is less than the predicted broadening due to the transient, which is given by $x \approx \sqrt{2D^*t^*} = 280 \text{ Å}$. A lower supersaturation of interstitials is produced by a lower dopant concentration and at higher annealing temperatures a considerably higher concentration of thermally generated vacancies exists. Thus, vacancy-interstitial recombination may become a significant process, reducing the lifetime of the released interstitials and therefore the amount of dopant diffusion they can cause.

Fig. 5. Comparison of Si-Sb alloy ($9.3 \times 10^{20} \text{ cm}^{-3}$) after (a) furnace annealing at $700^\circ\text{C}/90 \text{ min}$. and (b) RTA at $1050^\circ\text{C}/15 \text{ s}$ nominal time.

Fig. 6. RBS analysis showing broadening of Sb profile below the solubility limit.

DISLOCATION BAND FROM TRAPPED INTERSTITIALS

For dopant concentrations exceeding about $2 \times 10^{20} \text{ cm}^{-3}$ loops are observed following the transient, representing the condensation of the trapped interstitials.⁸ Annealing at higher temperatures or longer times allows these loops to move by conservative climb and glide processes. In particular, isolated loops can be lost to the surface by glide if they lie

Fig. 7. Formation of dislocation network in Sb^+ (200 keV, $5 \times 10^{15} \text{ cm}^{-2}$) implanted Si(100), SPE grown at $550^\circ\text{C}/20 \text{ min.}$ after annealing for (a) $800^\circ\text{C}/10 \text{ min.}$, (b) $800^\circ\text{C}/20 \text{ min.}$, (c) $800^\circ\text{C}/20 \text{ min.}$, (d) $800^\circ\text{C}/45 \text{ min.}$, (e) $800^\circ\text{C}/60 \text{ min.}$, (f) $800^\circ\text{C}/90 \text{ min.}$, and (g) additional $825^\circ\text{C}/10 \text{ min.}$

Fig. 8. (100) Si preamorphized and implanted with Sb^+ (150 keV, (a) $3 \times 10^{15} \text{ cm}^{-2}$, (b) $5 \times 10^{15} \text{ cm}^{-2}$) SPE grown and annealed at $900^\circ\text{C}/30 \text{ min.}$

Fig. 9. RBS profiles showing gettering of dopant by dislocation network.

within their diameter of the surface. Alternatively, if the loop concentration is high enough, they may coalesce before being lost to the surface. An extended dislocation network can then be formed, which is much more difficult to anneal out. Figure 7 shows this process in detail. Figure 7b corresponds to a time just greater than t^* for this system, and significant loop growth has occurred between (a) and (b) and some additional loops have nucleated (arrowed). Loop coalescence is beginning, and continues with further annealing (see loop marked x) until an extended network is formed. During this process, large precipitates form on many segments of dislocations from fast pipe diffusion of Sb along dislocation cones and/or from the coalescence of highly mobile liquid droplets of Sb along the dislocation lines. This constitutes a gettering action and the dopant distribution tends to follow the dislocation distribution. Figure 8 shows cross-section TEM micrographs after annealing samples below and above the critical dopant concentration C_0^* for loop coalescence. In Fig. 8a, the loops have been lost to the surface, but in Fig. 8b they have coalesced to form a planar dislocation network. These samples were preamorphized by implanting with $^{30}\text{Si}^+$ (175 keV, $1.5 \times 10^{16} \text{ cm}^{-2}$) to move the damage band deep into the crystal. RBS profiles from the sample of Fig. 8b show clearly a sharpening of the dopant profile due to the gettering action (Fig. 9). We deduce that C_0^* lies close to $5 \times 10^{20} \text{ cm}^{-3}$ for room temperature implantations.

TRAPPED INTERSTITIALS IN As⁺ IMPLANTED Si

There have been a number of reports of transient and/or enhanced diffusion observed during rapid-thermal-annealing of As⁺ implanted Si.^{2,3} Some of these observations may be due to radiation-enhanced diffusion below the original amorphous/crystalline interface, which is much closer to the peak of the As profile than for a corresponding Sb⁺ implantation. On further annealing the high density of dislocations in this region may also give enhanced profile broadening due to pipe diffusion. We have excluded these possibilities by implanting As⁺ into Si preamorphized with ³⁰Si⁺ (175 keV, $1 \times 10^{16} \text{ cm}^{-2}$) to search for any effects due to interstitial trapping. However, no broadening of the profile was observed in samples either above or below the solubility limit, which was not consistent with normal concentration enhanced diffusion¹¹ (Figs. 10 and 11). A broadening of 200 Å was observed in the high concentration sample for a 900°C/30 min. anneal, consistent with a concentration enhancement of 20 times.¹¹

Fig. 10. Preamorphized Si(100) implanted with As⁺ (100 keV, $2 \times 10^{16} \text{ cm}^{-2}$) showing no significant change in the profile until 900°C/30 min. anneal.

Fig. 11. Preamorphized Si(100) implanted with As⁺ (100 keV $5 \times 10^{15} \text{ cm}^{-2}$) showing no profile broadening after 800°C/30 min. anneal.

It is possible that no trapping occurs at As atoms during implantation, but this seems unlikely if the mechanism is electronic in nature¹² as suggested by the Sb results. It may be that the Si-As binding energy is lower, allowing the complex to split up as the interface passes. This could be the origin of the clustering phenomena seen during SPE growth, and would explain why clustering occurs even with As concentrations below the solubility limit. However, TEM observations show that dislocation loops are formed in a very similar way to the Sb case. Following SPE growth at 700°C/15 min. a very low density of loops is observed but after annealing at 800°C/30 min. a high density of loops is observed (Fig. 12). These are formed at the peak of the As profile exactly as is the case with Sb. They form even when the As concentration is below the solubility limit, so it seems unlikely that they represent precipitating As. At the present time, these observations present a dilemma: if the loops are formed from the trapped interstitials, as we believe, then we need to explain the lack of As profile broadening. The loops in Fig. 12 would indicate that more interstitials are trapped with As than with Sb, and should result in easily observable broadening. Alternatively, if the loops do not represent trapped interstitials, we need to explain their origin.

Fig. 12. TEM micrograph of sample shown in Fig. 11 showing loops formed by the anneal.

CONCLUSIONS

We believe that ion implantation of group V ions into Si results in stable, five-fold coordinated dopant-Si complexes. These survive SPE growth, to become dopant-interstitial Si complexes, but can be split up by additional annealing, releasing high concentrations of interstitials into the material. These cause transient enhanced dopant diffusion and may condense into a band of dislocation loops, or even form an extended dislocation network which can getter the dopant.

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