Enhanced elimination of implantation damage upon exceeding the solid solubility

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Implantation of silicon wafers with Ga and P, under specific conditions, results in enhanced category-II (end of range) dislocation loop elimination after short thermal cycling. Comparison of these results with transmission electron microscopy studies of Si-, Ge-, As-, Al-, and Sb-implanted samples indicates that the enhanced elimination process occurs only when the peak of the impurity concentration exceeds the solid solubility of the impurity in silicon at the annealing temperature and the resulting precipitates are dissolving. The activation energy for enhanced elimination of these extrinsic category-II dislocation loops is shown to be 5 ± 0.5 eV. It is proposed that vacancy emission by the dissolving precipitates is responsible for the enhanced elimination.

INTRODUCTION

Removal of implant damage is necessary for the production of low leakage current p-n junctions. Most extended defects which arise from implant damage can be avoided by adjusting the implantation parameters. A thorough review of the source of most implant-related defects and a classification scheme for these defects will be presented elsewhere. The optimal "as-implanted" morphology is an amorphous layer continuous to the surface, with a smooth amorphous/crystalline interface (no hairpin dislocation nuclei) on a {100} substrate (avoiding microtwin formation associated with {111} substrates). Production of an amorphous layer leads to category-II (end-of-range) defects which are favored over category-I (subthreshold) damage. One reason category-I defects are not preferred is that the concentration of category-I damage is very dose dependent, leading to dislocation network formation at doses >2 × 10¹⁵/cm². Such networks are stable and difficult to eliminate by annealing. In addition, category-I damage is believed to be associated with reverse annealing and may influence the high diffusivities observed with increasing dose.

Since category-II defects are the one form of damage which cannot be avoided for implants resulting in an amorphous layer, understanding the dissolution kinetics of these defects is imperative for optimizing the production of shallow junction defect-free contacts. The category-II defects are extrinsic dislocation loops which form, upon annealing, beyond the location of the amorphous/crystalline interface. They are thought to be composed primarily of Si atoms, and so their elimination by positive climb is expected to be governed by self-diffusion. For Si and Ge implants as well as low dose (well below solid solubility) implants of other species, the category-II defects were stable (1075 °C, 24 h). However, for some implant species where the solid solubility was exceeded, enhanced elimination of the category-II dislocation loops was observed (P, Ga, and As). For other species implanted above solid solubility, a network of dislocations was observed to form (Al and Sb). Understanding this enhanced elimination phenomena could provide a processing means of rapidly dissolving category-II defects.

EXPERIMENT

The silicon used was typically 5–10 Ω cm Czochralski-grown 4-in. wafers of type opposite that of the dopant to be implanted. A Waycool end station was used for all implants, which stabilized the wafer temperature during implantation to room temperature (or slightly above). The dose rate was 265 μA. An amorphous layer, continuous to the surface (not buried), was produced for all implantations. This was verified by cross-sectional transmission electron microscopy (TEM) examination of the as-implanted morphology. The annealing treatments were done either in a furnace or with a halogen lamp system under an inert ambient. For all samples, the amorphous layer was regrown at 550 °C (16 h) prior to additional annealing. Each additional anneal was done prior to preparation of the TEM samples (i.e., on the bulk wafer).

The defects were studied by transmission electron microscopy using bright field, two-beam conditions. Both plan-view and cross-sectional TEM samples were prepared. All plan-view TEM micrographs were taken at the same magnification with a g₀₀₀ two-beam condition, and all cross-sectional micrographs were taken at the same magnification with a g₂₂₀ two-beam condition. Further experimental details are given in Ref. 2.

RESULTS AND DISCUSSION

Figure 1 is a series of TEM micrographs illustrating the enhanced elimination phenomena. The cross-sectional micrographs show the position of category-II defects relative to the location of the amorphous/crystalline interface prior to annealing. After annealing for 60 min at 900 °C, only category-II dislocation loops are observed for both the 50-keV 1 × 10¹⁶/cm² P implant and the 100-keV 1 × 10¹⁵/cm² Ga implant. After 8 h at 900 °C all of the loops have completely dissolved. The doses investigated ranged from 2 × 10¹⁴/cm². 

[References and further experimental details are included in the full text of the article.]
to $1 \times 10^{16}/\text{cm}^2$. Figure 2 shows the role of dose in enhanced category-II dislocation loop dissolution. For lower phosphorus doses ($1 \times 10^{15}/\text{cm}^2$), the category-II dislocation loops were observed to be relatively stable and still existed after 72 h at 900 °C (the longest time studied). However, at the higher dose ($1 \times 10^{16}/\text{cm}^2$), complete elimination occurred after relatively short thermal cycling.

Enhanced elimination occurred only for the P (and As) implants at doses $>5 \times 10^{15}/\text{cm}^2$, whereas it occurred for Ga implants at doses as low as $2 \times 10^{14}/\text{cm}^2$. Both of these critical doses represent the amount of dopant necessary for the peak concentration to exceed their respective solid solubilities at 900 °C (Table I). It is possible to determine the activation energy for removal of the category-II defects by producing an Arrhenius plot $[t_D = t_0 \exp(E_a/kT)]$ of the universe of the time necessary to remove all category-II defects versus the annealing temperature. In a recent paper, Seidel et al. reported an activation energy of $\sim 5 \text{ eV}$ for removal of the category-II defects in As-implanted Si (Fig. 3). It is noted here that the energy and dose in their experiment were such that the peak concentration exceeded the solid solubility for the annealing temperatures studied, indicating that category-V (precipitation-related) defects were expected and, in fact, were observed. It has been shown that for high-dose ($>5 \times 10^{15}/\text{cm}^2$) As implants, category-V defects evolve into relatively stable half-loop dislocations upon 900 °C annealing. Therefore, the 5-eV activation energy corresponds to the removal of category-II loops only, not the half-loop dislocations. At higher annealing temperatures (1100 °C), half-loop dislocation formation is suppressed; thus, the Arrhenius curve at this temperature reflects complete removal of the defects.

Similar Arrhenius plots were made for P and Ga implants above solid solubility and are also shown in Fig. 3 along with the As data. The implant conditions were 50 keV, $1 \times 10^{16}/\text{cm}^2$ and 100 keV, $5 \times 10^{14}/\text{cm}^2$ for the P and Ga, respectively. An activation energy of $\sim 5 \pm 0.5 \text{ eV}$ was observed for all of the species. If category-II dislocation loops are composed primarily of Si atoms, then the activation energy of $\sim 5 \text{ eV}$ is explainable in the context of self-diffusion away from the loops or diffusion of vacancies to the loops. The shift in $t_0'$ is uncertain within the error bars of the experiment, but may imply that P accelerates the defect dissolution slightly better than As and Ga. We have noticed a smaller shift in $t_0'$ upon increasing the dose for preliminary As investigations. However, for samples implanted with the same dose of P or As, P accelerated the defect elimination better than the As.

Ga also accelerates the defect elimination, but at a much lower dose. For all Ga-implant doses studied ($2 \times 10^{14}/\text{cm}^2$ to $1 \times 10^{15}/\text{cm}^2$), the peak of the impurity profile exceeded the solid solubility of Ga in Si at the annealing temperatures studied. The amount of data at different temperatures was limited for Ga, and further studies are needed to determine

Table I. Solubility data for impurity species investigated.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Impurity</th>
<th>Solid solubility ($\times 10^{20}/\text{cm}^3$) ± 50%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>900 °C</td>
</tr>
<tr>
<td>17</td>
<td>Al</td>
<td>3.5</td>
</tr>
<tr>
<td>18</td>
<td>P</td>
<td>5.9</td>
</tr>
<tr>
<td>19</td>
<td>Ga</td>
<td>0.2</td>
</tr>
<tr>
<td>20</td>
<td>As</td>
<td>13</td>
</tr>
<tr>
<td>21</td>
<td>Sb</td>
<td>0.3</td>
</tr>
</tbody>
</table>

FIG. 1. Bright-field TEM micrographs of implanted samples with a peak concentration above solid solubility and annealed under conditions such that the precipitates are dissolving. s, surface; a/c, amorphous/crystalline interface prior to annealing.

FIG. 2. Bright-field TEM micrographs of $^{31}\text{P}^+$-implanted samples with peak concentrations below and above the solid solubility of the impurity.
FIG. 3. Arrhenius curve for P, Ga, and As category-II dislocation loop elimination, peak concentration above solid solubility.

accurately the activation energy. The results for Ga and P represent complete defect removal. This is because either no category-V defects were observed (P) or the category-V precipitates dissolved simultaneously with the category-II dislocation loops (Ga). That Ga enhanced the defect elimination at such a low dose is a strong argument in favor of relating this phenomena to exceeding the solid solubility and not to the diffusion of the implanted impurity. The diffusivity of Ga ($4 \times 10^{-16}$ cm$^2$/s) is between that of P ($1 \times 10^{-15}$ cm$^2$/s) and As ($8 \times 10^{-17}$ cm$^2$/s) at 900 °C. However, at lower doses ($1 \times 10^{15}$/cm$^2$) where their peak concentrations are below the solid solubility, both P and As category-II defects were stable after 72 h at 900 °C (the longest time studied). In addition, there is evidence that diffusion of P results in a supersaturation of interstitials$^{12-14}$ which would favor a negative, not a positive, climb of the category-II loops. Also, an impurity diffusion argument suggests that Sb diffusion, believed to have a vacancy flux associated with it,$^{15}$ would favor the elimination of the extrinsic category-II dislocation loops, which was not observed.

When it was not possible to exceed the solid solubility, as with Si and Ge implants, the category-II defects were very stable. For these implants, determination of the activation energy for elimination of the category-II loops could not be done. A complication which prevented this determination was that after 24 h at 1075 °C in dry N$_2$ (the most extreme thermal cycling), the effect of oxidation overwhelmed any elimination process, and growth of faulted category-II dislocation loops occurred. The lack of defect dissolution for the Ge implants implies that a large biaxial compressive stress field in the implanted layer is not the reason for the enhanced category-II loop elimination. The stability of the category-II defects for the Si implants suggests that elimination, because of the thermodynamic instability of the dislocation loops, is kinetically limited at these annealing temperatures.

Exceeding the solid solubility of the implanted species does not mean that enhanced elimination of the category-II defects will be observed. Annealing of Sb implants above solid solubility resulted in formation of a network of dislocations rather than elimination of the defects. In order to understand why, upon annealing at 900 °C, enhanced category-II loop elimination was observed for Ga and P implants, but not for Sb implants; the sheet resistivity was measured as a function of annealing time for samples implanted above the solid solubility. For P, Ga, and As, the precipitates (category-V defects) were dissolving (sheet resistivity decreasing) during the process of enhanced elimination of the category-II loops. Precipitation was still occurring (sheet resistivity increasing) for the Sb implants. This conclusion from the sheet resistivities is supported by limited Hall-effect measurements, indicating that the sheet resistivity increase is dominated by an increase in the free-carrier concentration and not the mobility. The TEM results supported the electrical measurements. For Ga samples, the metallic precipitates were physically observed to be dissolving; however, no dissolution of the Sb precipitates was observed. These results imply that in addition to exceeding the solid solubility, the enhanced elimination mechanism for category-II defects requires the precipitates to be dissolving during the annealing process.

The question arises: could the flux of dopant atoms from the dissolving precipitates somehow accelerate the category-II elimination? In order to investigate this hypothesis, the surface of a low-dose ($1 \times 10^{15}$/cm$^2$) Si$^+$-implanted sample, which had previously been annealed at 900 °C for 30 min to form the category-II loops, was lightly oxidized ($t_{\text{ox}} < 400$ Å). The category-II dislocation loops grew from injection of interstitials, as expected. Thus, the enhanced elimination observed for the other implanted species does not appear to be related to a supersaturation of self-interstitials, but it does not prove that a flux of phosphorus interstitials is not responsible. However, the activation energy for P diffusion ($\sim 3.5$ eV) is much less than the 5-eV activation energy for enhanced defect elimination.

We propose, from the above-mentioned evidence, that the enhanced elimination observed for the extrinsic category-II dislocation loops is a result of the release of vacancies or generation of an interstitial sink during precipitation dissolution. Precipitation of Si$^+$ has been studied extensively by Bouret and Schroter$^{16}$ for high-concentration (exceeding the solid solubility) P predeposition into Si. Their results indicate that precipitation is an excellent source of interstitials. This would support our model that the dissolution of precipitates is a source of vacancies. It is also possible that the dissolving precipitates act as an interstitial sink. However, this is difficult to accept, since the surface would also behave as an excellent interstitial sink, but no enhanced dissolution was observed as the category-II defect layer varied in depth with respect to the surface. The 5-eV activation energy for enhanced defect elimination correlates well with the activation energy for self-diffusion.

For Ga implants, the volume occupied by the precipitates, which were resolved by TEM, could be filled by $\sim 7 \times 10^{13}$/cm$^2$ atoms if they occupied lattice sites, and the concentration of atoms bound by the extrinsic dislocation
loops was $\sim 6 \times 10^{13}$/cm$^2$. The precipitates and category-II dislocation loops dissolved simultaneously, supporting the proposed enhanced elimination model.

The correlation between the activation energy for impurity diffusion and the activation energy for defect elimination has been investigated for only one species, As. The question of transient enhanced diffusivities is currently being addressed. It appears that a full understanding of the diffusivities observed cannot be made without correlating them with the defect annealing kinetics, since the point defects generated by the process of precipitate dissolution may affect the dopant redistribution. Extensive secondary ion mass spectroscopy investigations of the dopant (i.e., P, Ga) redistribution which occurs during the enhanced elimination of category-II defects are being performed in order to understand the amount of diffusion which accompanies the dissolution process. If the correlation between the activation energy for diffusion and the elimination of category-II defects determined by Seidel et al. for As is also found for the production of defect-free P and Ga implants, then when combined with rapid thermal annealing, adjusting the implant conditions such that enhanced defect elimination occurs may provide a "window" for the production of defect-free submicrometer $p$-$n$ junctions.

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1Category-I (subthreshold) defects arise prior to amorphous layer formation; category-II (end-of-range) defects form beyond the amorphous/crystalline interface; category-III (microtwins, hairpin) dislocations arise during amorphous layer regrowth; category-IV (clamshell or zipper) defects arise from regrowth of a burned amorphous layer; and category-V (projected range) defects (precipitates) arise from exceeding the solid solubility.


10T. E. Seidel (private communication).


