Groups III and V impurity solubilities in silicon due to laser, flash, and solid-phase-epitaxial-regrowth anneals

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In this work the authors studied impurity solubilities of groups III and V elements in silicon resulting from laser anneal, flash anneal, and solid-phase-epitaxial regrowth. Rutherford backscattering channeling analysis was used to determine substitutional impurity depth profiles generated from the difference between the random and aligned spectra. Despite the large difference in peak temperatures and times, the anneals produce similar results with maximum solubilities beating the maximum equilibrium values by one to two orders of magnitude depending on the impurity. The correlation between the metastable solubility and the equilibrium distribution coefficient allows a prediction of values for other impurities not extracted experimentally. © 2006 American Institute of Physics. [DOI: 10.1063/1.2337081]

In the 1940s and 1950s many equilibrium impurity solubilities in silicon were determined experimentally. In a review paper by Trumbore this body of work is nicely summarized, and the graph therein of impurity solubility versus temperature is frequently reproduced in textbooks. Above-marshaled, and the graph therein of impurity solubility versus temperature is frequently reproduced in textbooks. Above-

For example, the solubility of arsenic in silicon at 1000 °C is approximately 1022 at./cm−3, while the equilibrium solubility at 1000 °C is approximately 1020 at./cm−3. This indicates that the impurity is in a metastable state at 1000 °C. The equilibrium solubility is the concentration at which the solubility increases to a constant value as the temperature increases. This is due to the fact that impurities tend to segregate to the surface of a crystal as the temperature increases, which reduces their solubility.

Experiments were performed using Czochralski-grown, p-type silicon wafers. Implants were performed to high doses to create impurity profiles with very high concentrations. Implant energies were such that the projected range of the impurity profile was not at the surface, thus reducing the influence of surface effects during processing and analysis.

The SPER anneal was at 700 °C for 180 s, which is longer than the usual SPER anneal, as retarded recrystallization rates were anticipated due to the extremely high impurity concentrations. The peak temperature for both flash and laser anneals was 1300 °C. Flash anneal had an intermediate temperature of 700 °C.

Rutherford backscattering (RBS) channeling analysis was used to determine the substitutional impurity depth profiles and residual amorphous silicon layer thicknesses. The RBS analysis was performed with 2 MeV helium ions. The incident beam was directed in the ⟨100⟩ channeling direction, perpendicular to the silicon surface. The scattering angle for the outgoing helium ions was 100°, an exit angle of 10° with the surface. Glancing exit angle RBS enhances the depth resolution. The stopping cross sections as given by RUMP, the computer simulation program for RBS spectra. Dividing the at./cm2 quantity by the density of silicon (4.98 × 1022 at./cm3) gives the layer thickness per eV. Multiplying the layer thickness per eV with the channel width in eV, we derived the thickness per channel (nm/ch). RUMP showed that the variation in the depth per channel as a function of depth and as a function of element is less than 2%. We used the mean value (0.514 nm/keV) to obtain the depth scale of our impurity concentration plots. Substitutional profiles were generated

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from the difference between the random and aligned spectra. The total number of dopant atoms is determined from the integrated area under the profiles. The internal calibration in the spectra is the silicon random height. The number of counts in one channel leads to the number of dopant atoms per cm$^2$. Thus by dividing this number by nm/ch, the concentration (at./cm$^3$) is calculated. The error in the concentration scale is less than 10%.

Figure 1(a) shows substitutional arsenic versus depth profiles for the $4 \times 10^{16}$ cm$^{-2}$, 30 keV implant after SPER, flash, and laser anneals. The maximum equilibrium solubility of $1.5 \times 10^{21}$ cm$^{-3}$ is marked for comparison. For these samples RBS indicated 4–7 nm of residual amorphous silicon (i.e., not recrystallized) close to the surface after the anneals. All three advanced annealing approaches beat the maximum equilibrium value. In this case SPER generates the highest substitutionality with a peak at $9.6 \times 10^{21}$ cm$^{-3}$. Flash anneal and laser anneal produce peak values of $2.9 \times 10^{21}$ and $3.6 \times 10^{21}$ cm$^{-3}$, respectively. Literature also indicates that SPER (Ref. 2) produces higher arsenic solubilities than full-melt laser anneal.4

Figure 1(b) shows substitutional antimony versus depth profiles for the $1 \times 10^{16}$ cm$^{-2}$, 90 keV implant after SPER, flash, and laser anneals. The maximum equilibrium solubility is $7 \times 10^{19}$ cm$^{-3}$. For these samples RBS indicated residual amorphous silicon depths of 13, 4.5, and 4.5 nm after SPER, flash, and laser anneals, respectively. All three advanced annealing approaches beat the maximum equilibrium value. SPER, flash, and laser anneals produce peak values of $6.4 \times 10^{20}$, $3.1 \times 10^{20}$, and $4.2 \times 10^{20}$ cm$^{-3}$, respectively.

Figure 1(c) shows substitutional bismuth versus depth profiles for the $1 \times 10^{16}$ cm$^{-2}$, 120 keV implant after SPER, flash, and laser anneals. The maximum equilibrium solubility is $8 \times 10^{17}$ cm$^{-3}$. For these samples RBS indicated residual amorphous silicon depths of 67, 44, and 55 nm after SPER, flash, and laser anneals, respectively. All three advanced annealing approaches beat the maximum equilibrium value. SPER, flash, and laser anneals produce peak values of $9.4 \times 10^{19}$, $7.9 \times 10^{19}$, and $1.2 \times 10^{20}$ cm$^{-3}$, respectively.

In Figs. 1(b) and 1(c) we observe that the metastable solubilities produced by the different anneals are largely similar relative to the maximum equilibrium values. This is a remarkable result as there is a $600 \, ^\circ$C difference between the SPER anneal and the other two anneals. The anneal time for SPER is at least $10^6$ times longer than the laser anneal. This temperature independence of metastable solubility is in contrast to the well-established temperature dependence of equilibrium solubility.

Consider an alloy binary phase diagram of host material $\alpha$ (silicon) with impurity element $\beta$ (dopant) dissolved therein. Under equilibrium conditions the solid solubility limit is temperature dependent. After recrystallization, under metastable conditions, we have solid material $\alpha$ with higher concentrations of dissolved impurity $\beta$. Thus in phase diagram terms, the solid solubility limit is shifted along the composition axis towards higher $\beta$ content. Furthermore, based on our experimental data it is temperature independent across the range of 700–1300 $^\circ$C for antimony and bismuth, and retrograde dependent for arsenic.

In our previous work we highlighted the correlation between metastable solubility and the equilibrium distribution coefficient $k$, which is defined as the relative tendency of various impurities to dissolve in solid silicon. Trumbore reports $k$ values for many impurities in silicon.1 In terms of concentrations, $k=C_{\text{solid}}/C_{\text{liquid}}$ at the melting point of silicon.
This work was performed under equilibrium conditions and after SPER, flash, and laser anneals. The full-melt laser data of White and advanced anneals is greater for larger sized impurities such as indium and bismuth. The full-melt laser data of White et al. appear to beat the other techniques, at least for impurities other than arsenic. This difference is currently not understood as flash, submelt laser, and full-melt laser anneals all melt and recrystallize the amorphous silicon within a submicrosecond time frame, leading to largely similar regrowth conditions. However, it is difficult to make a fair comparison without processing the same impurity profile.

Returning again to the correlation between metastable solubility and \( k \), we fitted a trendline to each set of experimental data. For clarity these trendlines are not included in Fig. 2 (see Fig. 15 in Ref. 9 for an example). Using these we extracted the metastable solubilities for impurities not investigated experimentally. The extracted values are shown in Table I. With respect to metal-oxide-semiconductor device applications, advanced anneals can facilitate the potential of impurities not useful under equilibrium conditions. For example, with source and drain regions typically requiring concentrations \( >10^{20} \text{cm}^{-3} \), antimony and gallium could be candidates under metastable conditions. Channel and pocket doping concentrations can reach \( \sim5 \times 10^{19} \text{cm}^{-3} \), thus bismuth and indium could be useful with SPER, flash, and laser anneals. Note that solubility does not guarantee electrical activity, but it is generally understood that nonsubstitutional impurities will not contribute to the electrical behavior of the device.

The arsenic data of Fig. 1(a) deserve further comment in relation to the work of Pawlak et al., where increased ramp rates for 700 °C anneals produced higher substitutability. As stated previously, with prolonged annealing metastable solubility returns to the equilibrium value. In other words metastable solubility is created during recrystallization and destroyed with additional energy added to the system after recrystallization. Thus with faster ramp rates, with fixed peak temperature and hold time, the overall energy input is reduced, and thus the destructive postrecrystallization energy input is lower.

In summary, we studied impurity solubilities of groups III and V elements in silicon resulting from SPER, flash, and laser anneals. By applying these advanced anneals to the same impurity profiles, we were able to make a direct comparison between the different approaches. Despite the large difference in anneal temperatures and times they produce similar results, with maximum solubilities beating the maximum equilibrium values by approximately one to two orders of magnitude.

The authors would like to acknowledge Applied Materials for laser anneal support, and Matsson for flash anneal support.

![Figure 2](image_url)

**TABLE I. Maximum solubilities of groups III and V impurities in silicon under equilibrium conditions and after SPER, flash, and laser anneals.**

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Type</th>
<th>Equilibrium</th>
<th>SPER</th>
<th>Flash</th>
<th>Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>n</td>
<td>1.3 × 10^{22}</td>
<td>( \geq 10^{21} )</td>
<td>( \geq 10^{21} )</td>
<td>( \geq 10^{21} )</td>
</tr>
<tr>
<td>As</td>
<td>n</td>
<td>9.6 × 10^{21}</td>
<td>9.0 × 10^{21}</td>
<td>2.9 × 10^{21}</td>
<td>6.0 × 10^{21}</td>
</tr>
<tr>
<td>Sb</td>
<td>n</td>
<td>7.0 × 10^{21}</td>
<td>6.4 × 10^{21}</td>
<td>1.3 × 10^{21}</td>
<td>3.1 × 10^{21}</td>
</tr>
<tr>
<td>Bi</td>
<td>n</td>
<td>9.4 × 10^{21}</td>
<td>9.0 × 10^{21}</td>
<td>7.9 × 10^{21}</td>
<td>1.2 × 10^{21}</td>
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<tr>
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<td>2.0 × 10^{21}</td>
<td>1.0 × 10^{21}</td>
<td>2.0 × 10^{21}</td>
</tr>
<tr>
<td>Ga</td>
<td>p</td>
<td>5.5 × 10^{21}</td>
<td>2.5 × 10^{21}</td>
<td>3.0 × 10^{21}</td>
<td>4.5 × 10^{21}</td>
</tr>
<tr>
<td>In</td>
<td>p</td>
<td>6.0 × 10^{21}</td>
<td>5.0 × 10^{21}</td>
<td>5.0 × 10^{21}</td>
<td>7.0 × 10^{21}</td>
</tr>
</tbody>
</table>

*References 1.
*Reference (estimated from trendline).
*This work (experiment).
*Reference 2.
*Reference 4.
*Reference 3.
*Reference 10.