Germanium for post Si CMOS … Implantation, doping and defects

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Abstract

The higher carrier mobility of germanium has stimulated an interest in using it as a channel material in extremely scaled CMOS. However there are many scientific and technological problems to be resolved before the economic and practical viability of Ge CMOS can be assessed realistically. Among these is the problem of achieving the necessary high doping levels in the drain and source regions of the transistor, an issue which is particularly problematic in n-type material and implantation doping. Although the principles of ion implantation, dopant activation and defect removal in germanium are very similar to silicon, in practice quantitative differences in behavior have important practical consequences. In this talk these issues are reviewed briefly and recent work on the defect reactions which deactivate donors in germanium are presented.

1. Germanium CMOS

Extreme scaling of MOS devices has stimulated a search for channel materials exhibiting higher mobilities. This is primarily because gains from conventional scaling are yielding less significant returns at the 45nm node and beyond. Many issues contribute to reduce the effective mobility in nano-channels eg surface scattering, high halo doping, coulombic scattering from dielectric charge and remote phonon scattering. Strained silicon using either global or local strain is already used to provide some device advantage [1]. However in the longer term more radical solutions appear to be necessary. The introduction of high-k dielectrics and metal gates has led people to question whether semiconductors other than silicon might be considered as channel materials. The issue of hole mobility has always been a problem in silicon CMOS, the disparity between the hole and electron mobilities has necessitated a larger PMOS transistor than NMOS so as to balance drive currents. This issue has been accentuated with the advent of extreme scaling and it is now evident that the concept of channel mobility is only a partial descriptor of carrier motion in strained nano-materials and many parameters affect the delivered current an MOS transistor can provide [2].

<table>
<thead>
<tr>
<th>TABLE 1. Bulk Semiconductor Properties</th>
<th>Si</th>
<th>Ge</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron mobility (cm²/Vs)</td>
<td>1350</td>
<td>3900</td>
<td>8500</td>
</tr>
<tr>
<td>Hole mobility (cm²/Vs)</td>
<td>450</td>
<td>1900</td>
<td>400</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>1.12</td>
<td>0.67</td>
<td>1.42</td>
</tr>
<tr>
<td>Electron saturation velocity (x10⁷ cm²/s)</td>
<td>1</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>Thermal conductivity at 300K (W/cm²/°C)</td>
<td>1.3</td>
<td>0.58</td>
<td>0.55</td>
</tr>
</tbody>
</table>

However it can be seen from Table 1 that if we consider low field bulk properties germanium offers particular advantages in relation to hole mobility while also benefiting electron mobility and so quite obviously is a serious candidate as an alternative channel material. If we want to make an extremely scaled high performance CMOS chip from an alternative channel material the fundamental device requirements are no different to silicon. We need a high quality interface with the gate dielectric, we need to incorporate dopants with very precise control of concentration and spatial distribution and we need to create a highly conductive source and drain. We must anneal to remove damage while with the same heat treatment put the dopants on a substitutional site and avoid the formation of extended defects in the active region. The issues of the dopants diffusing away from where we want them is just as an acute concern as in silicon so we need to understand (and avoid) enhanced diffusion in these materials. An important fundamental difference between silicon and germanium is the behavior of vacancies. Firstly the energy needed to create a vacancy in germanium is rather low. Reported values are ~1.9eV for the creation of the neutral vacancy compared to 3.3eV in silicon. This results in self-diffusion and the diffusion of
most impurities being controlled by the vacancy population rather than interstitials as in the silicon case. However boron is an exception to this [3]. This is important in relation to transient-enhanced diffusion which for the case of dopants other than boron would then be expected to result from metastable vacancy clusters, unlike the case of silicon where interstitials dominate. The other rather unexpected difference in behavior is the ease which vacancies cluster to form, firstly small clusters, and then voids.

2. Implantation Doping and Activation of Dopants in Ge

The damage produced in Ge is significantly greater than that for comparable implants in Si. This results in greater surface damage and amorphisation at much lower doses. However what is dramatically different is the formation of buried voids in germanium. The vacancies created during implantation cluster and in the case of heavy implants with heavy ions these develop into substantial voids [4-6]. These issues tend to favour doping with elements of smaller mass so the donor of choice is phosphorous and the acceptor boron.

In extremely scaled devices the series resistance of the transistor in the on state is a crucial factor affecting the delivered current and hence the overall performance. In general, the requirement in extremely scaled devices means that an electrically active dopant concentration \( >10^{20} \text{ cm}^{-3} \) is required. This has to be done while still maintaining extremely shallow drain source extensions (ie it is necessary to minimize diffusion during annealing). Taking equilibrium solid solubility data [7] and bulk values of mobility the resistance of a 10nm boron implant would be 30k\( \Omega \)-square. The ITRS requirement for silicon at the 30nm node is 300\( \Omega \)-square for a 12nm implant. This means that boron would have to activate at a concentration very much more than the 600°C solid solubility to be usable as a dopant in pMOS at the 30nm node. In general implantation and anneal can be a very non-equilibrium process so it is not unusual to achieve an order of magnitude higher concentrations on substitutional sites (ie electrically active) than the equilibrium values. In the case of Ge:B significant activation is present after implantation into crystalline Ge without annealing. After implantation into amorphous Ge carrier concentrations two orders above the solubility limit of the acceptor appears to be achievable with annealing schedules that produce shallow junctions [8]. This surprising result makes Ge pMOS a possibility. Discrete long and short channel pMOS Ge devices have been made with performance as good as strained silicon so it seems that enhanced pMOS performance from Ge may be achievable in the near future.

The situation is dramatically worse for the n-type dopants although at 600°C in equilibrium they have a higher equilibrium solid solubility. This is because solid solubility is only one issue in achieving adequate carrier concentrations. Defect reactions come into play and reduce the electrical activity of the dopant population. Fig 1 shows some of the effects observed after a phosphorous implant.

![Figure 1 SIMS profiles of a shallow P implant (5x10^{15} \text{ cm}^{-2}, 15keV) for the as implanted case and after 500°C anneals. The cross section view TEM micrograph shows precipitates near the peak of the implant after the 500°C 60s anneal.](image)
In Fig 1 the peak chemical concentration is $\sim 2 \times 10^{21} \text{ cm}^{-3}$ with almost no electrical activity. This contrasts with low implantation doses ($< 10^{18} \text{ cm}^{-3}$) where almost 100% activation can be achieved after RTA. On annealing the chemical profile changes radically and a number of features are evident. Firstly there is a marked segregation to the surface; secondly substantial diffusion has occurred with a tendency towards a box shaped profile … a feature very characteristic of concentration enhanced diffusion. However, in addition, a very pronounced peak is apparent near the original implant maximum. Cross section TEM reveals that this represents precipitates. These are relatively immobile at the anneal temperature, rich in phosphorous and electrically inactive. Calculations based on the resistance/square and an implant/anneal depth of 100nm give an active P concentration of 5–6$\times 10^{19} \text{ cm}^{-3}$ for RTA conditions up to 600°C. If we look at a deeper lower concentration implant we can use spreading resistance techniques to determine the carrier concentration and hence the active phosphorous concentration. This is shown in Fig 2

![Graph showing SIMS and spreading resistance profiles of a 150keV 10^{16} \text{ cm}^{-2} phosphorous implant annealed at 600°C for 60s](image)

Figure 2. SIMS and spreading resistance profiles of a 150keV 10^{16} \text{ cm}^{-2} phosphorous implant annealed at 600°C for 60s

It is evident that although the implanted concentration is an order of magnitude lower than the Fig 1 case there is almost no difference in the maximum concentration of electrically active phosphorous. If we take the two profiles in the figure it is evident that the carrier concentration near the surface where the phosphorous concentration is greatest is actually less than in the region where the phosphorous concentration is lower.

Vacancies play an important role in the precipitation of donors in silicon by the formation of vacancy donor complexes that capture additional donors and evolve into electrically inactive cluster so removing electrons from the material. Experimental evidence and ab-initio calculations provide very strong support for such a mechanism in silicon [9, 10] and fundamental evidence that these effects will be more pronounced in germanium support the extrapolation to germanium [11]. Because of the ease of formation of vacancies in Ge that the doping limitation mechanisms in n-type Ge will be more dramatic than in silicon. However there seem to be several mechanisms combining to reduce the activity of phosphorous but a sequence of reactions in which the unstable but mobile acceptor like phosphorous-vacancy pair reacts with another phosphorous ion to initiate a reaction leading to an inactive phosphorous rich cluster is likely to be the dominant path for precipitation.

Fig 3 shows results from the second type of experiment. Here 0.2 $\Omega$-cm Ge (Sb doped) has been implanted with a) $10^{15} \text{ cm}^{-2}$ 2MeV Ge ions and b) $4 \times 10^{15} \text{ cm}^{-3}$ 950keV Si ions. These values have been chosen because the depth of the implanted profile is almost identical for the Si and Ge and also the total number of vacancy-interstitial pairs created by the implantation is the same in both cases. The samples have then been subjected to different anneals. The case for 30min at 500°C is shown. This was chosen because previous work had demonstrated that these conditions removed all simple radiation induced defects [11]. It can be seen that there is considerable carrier removal in the region 0.4 to 1.2μm. The carrier concentration prior to implantation is shown as the horizontal line. At lower measurement temperatures (not shown) a peak due to carrier accumulation is seen at 1.25μm that is ascribed to condensed interstitials forming extended defects. In silicon such defects are well known at the end of the implant range in the form of extrinsic stacking faults surrounded by Frank partial dislocations. They form during annealing when the surface condition of the silicon is such that interstitials are contained or injected by an oxidized surface. Also shown in this figure is the carrier concentration after the Si implant and anneal. Here the carrier removal extends deeper into the Ge layer and its shape is very different to the Ge implant case.
The key issue is what is the mechanism of carrier removal and can we understand the process in enough depth to extrapolate it to the technologically important cases such as those shown in the first two figures. The well established mechanism of carrier removal in radiation damaged Ge is the formation of acceptors which compensate the donors. The largest concentration acceptor in electron irradiated Ge is the donor-vacancy pair which on formation results in the removal of three carriers [12]. It is easily detectable in DLTS and is removed on annealing at low temperatures (~160ºC for the V-Sb pair). Quite obviously compensation from this acceptor is not the mechanism we are experiencing here because the carrier loss is still present after a 500ºC anneal.

3. Deactivation Mechanisms

Careful analysis of the carrier profile suggests another mechanism. It is evident that the carrier removal is far from uniform throughout the depth of the implant. During implantation interstitial-vacancy pairs are created but the interstitials tend to be migrated to the region beyond the peak of the implant leaving a vacancy rich region around the peak and in the region between the peak and the surface. It is evident that carrier removal is most pronounced in this region so it seems certain that vacancies play the key role in carrier removal. However the mechanism is far from simple because comparison of the Ge implant and the Si implant indicates that the two are very different. Implant conditions were chosen to locate the damage at a similar depth and to produce comparable numbers of Frenkel pairs. There are two fundamental differences in these implants resulting from the mass difference. The Ge damage distribution is more confined than that of Si and produces a very high concentrations of Frenkel pairs in a small volume. Although these clusters of defects are produced during Si implantation the local volume concentration of defects is lower and so the probability of vacancy complex formation is lower.

Previous work on Si based on positron studies [13] suggest that vacancy reactions with donors are the dominant deactivation mechanism. It is proposed that this proceeds through the formation of mobile V-D₁ which reacts with another donor at ~450K to produce V-D₂ with a further reaction to give V-D₃ at ~700K. Previous theoretical calculations on Si [14] indicated that AsₕV and AsₙV₂ were likely candidates for the deactivation of Si:As and were acceptors. Recently Coutinho et al [15] have calculated that a similar mechanism is likely in Ge and studied the properties of small donor vacancy clusters (SbₙVₘ with m,n ≤ 2). They find that these complexes are double acceptors. They consider that Sb₃V is the most likely candidate for deactivation of Ge. This hypothesis is totally consistent with our observations although considerably more work is needed before the case can be proved for spontaneous deactivation of highly doped n-type Ge.

Recently we have conducted an experimental study of n-type Ge implanted with Si or Ge under conditions similar to those used for the samples shown in Fig 3. In this work we have compared the donor activation, positron
studies and DLTS spectra during various annealing stages. The defect levels we studied in these deep self implants resulted in a vacancy population below the detection limit of the positron technique. If Sb$_3$V was responsible (or Sb$_2$V) and this complex was acceptor like, although we would see the vacancies during the anneal process (which we do) they would be too few in the equilibrium state to be detected. A preliminary report of work has been published recently [16] and we are now repeating this study using conditions in which we will be able to undertake the positron measurements and electrical studies in the same samples.

The D$_n$V hypothesis (where D is a generalized donor) also explains why spontaneous deactivation is much more significant in Ge than in Si. Based on these ideas it is evident that if the early stages of phosphorous vacancy complex formation can be avoided the mechanism will be inoperative. This might be done by heating the germanium very rapidly after implantation so as not to give the donor-vacancy reactions time to be effective. Satta et al have done this using flash annealing (900°C 20ms) and achieved higher levels of activation ($\sim 10^{20}$ cm$^{-3}$) but these are not stable and the present situation is that high active concentrations of donors cannot be maintained during subsequent processing [17]. The way ahead now is to engineer the defect reaction path, possibly by the addition of vacancy complexing dopants, to disrupt the deactivation reaction sequence.

4. Conclusion

It is proposed that the de-activation mechanism of high concentrations of donors in Ge is due to the formation of acceptor like complexes of the form V-D$_n$ or possibly V$_2$-D$_n$. These complexes are particularly effective as deactivators because they not only trap one or two electrons but also consume donors during their formation. Positron, CV and DLTS studies suggest that these complexes form with V-D as the precursor which is believed to be mobile at low anneal temperatures.

5. Acknowledgments

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6. References