Stable and metastable configurations of iron atoms in SiGe alloys

Stable and metastable configurations of iron atoms in SiGe alloys

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Abstract
In this study the alloy effect for iron-related defects in p-type unstrained B-doped $Si_{1-x}Ge_x$ ($0 < x < 0.071$) bulk crystals grown by the Czochralski technique have been analysed. This effect has been studied as the defect level splitting observed by the use of high-resolution Laplace DLTS. Two configurations of iron have been compared: isolated interstitial and paired with boron. For the interstitial configuration the alloy pattern suggests that the first- and second-nearest neighbours equally influence the defect energy level. For the iron–boron pair the observed DLTS signal is due to the ionization process of iron, and thus the alloy pattern represents the siting of iron in the more dilute samples ($Si_{0.98}Ge_{0.02}$), while for alloy compositions containing more Ge the signal comes from the ionization of boron, and so the observed pattern represents the siting of boron.

1. Introduction

The deleterious effects of iron atoms on silicon device performance have attracted much interest over a long period of time [1–4], and considerable progress in understanding the properties of iron has been achieved. It is well known that in silicon isolated iron occupies tetrahedral interstitial sites and provides a deep donor level at the $E_v + 0.43$ eV in the band gap, where E_v is the valence band edge. Because of its low migration energy, interstitial iron is mobile even at room temperatures. In p-type silicon positively charged iron atoms are attracted to negative shallow acceptors forming the well-known iron–acceptor pair. This configuration of the pair has the $\langle 111 \rangle$ axial symmetry where a positively charged iron atom is located on the nearest interstitial site to negative boron. If the iron loses its charge this pair is only weakly bound and can easily dissociate just above room temperature. This happens provided that the isolated iron energy level is below the Fermi level, i.e. the iron atom is neutral. During this annealing

process when iron leaves the acceptor it forms a more distant metastable configuration of the pair where Fe_i is located in the next hexagonal site along the $\langle 100 \rangle$ direction [5, 6].

During recent years interest in SiGe alloys has increased, because of the possibilities of improvements in both electron and hole mobilities using existing silicon device fabrication technology. Si and Ge atoms form $Si_{1-x}Ge_x$ alloys with a random distribution of components [7]. The band gap of such structures can be modified over the range between that of the two elemental semiconductors. On the other hand, the electronic properties of defects, their reconfigurations and short-range diffusion processes are governed by short-distance interactions with host atoms. In consequence the spatial local alloy fluctuations may substantially alter the defect properties. Gold and platinum atoms occupy a substitutional position in the crystal lattice, and thus the alloy effect observed for them in SiGe represents the distribution of atoms around the substitutional site [8]. The situation of the isolated iron is somehow different, as in this case the alloy effect should reflect the crystal environment for the interstitial site. Moreover, when iron forms a complex with an acceptor this alloy pattern should be modified, depending on how the pairing process modifies the complex electronic level. In this study we have analysed the alloy effects observed for the energy levels of iron in the metastable isolated configuration with those observed when it forms a stable pair with boron. These observations have been performed using high-resolution Laplace deep level transient spectroscopy (Laplace DLTS [9]).

2. Samples and experimental procedure

Samples for this study were prepared from p-type unstrained B-doped $Si_{1-x}Ge_x$ ($0 < x < 0.071$) crystals which were grown by the Czochralski technique in an argon atmosphere. The alloy compositions were measured by Rutherford backscattering spectrometry. The boron concentration ranged from 1×10^{14} to 3.5×10^{15} cm^{-3}. Highly pure iron was scratched on one side of the wafers and diffused at 950 °C. Schottky barriers were fabricated by thermal evaporation of aluminium. After the above procedure only the energy level at $E_v + 0.1$ eV related to the iron–boron pair has been observed in the DLTS spectra. In order to split this complex and observe the interstitial isolated iron the samples were heated at 360 K for 60 min. During this procedure the samples were biased with -9 V in order to establish the neutral charge state of iron and prevent the Coulombic attraction between iron and negatively charged boron so facilitating the dissociation of the iron–boron pair. This annealing procedure led to the formation of the isolated interstitial iron centres observed in the DLTS spectra as the $E_v + 0.43$ eV donor level and the disappearance of the iron–boron pairs.

3. Results and discussion

Figures 1 and 2 show the Laplace DLTS spectra for the iron donor centre and iron–boron pair in SiGe bulk crystals with 0–7.1% of Ge. Normally the isothermal Laplace DLTS spectra are presented on a frequency scale [10]; however, in these cases the frequency scales have been converted to energy-difference scales according to the formula $\Delta E = -kT \times \ln(e_n/e_{n0})$, where e_{n0} is a reference frequency of the dominant peak observed for Fe_i and Fe_iB for 0% of Ge, respectively. It has to be stressed here that this transformation has been possible only because the capture cross sections for both donor levels do not depend on the Ge content in the crystal [11]. The spectra have been normalized in terms of magnitude to the value of the pure Si peak and are displaced vertically according to the germanium content of the samples.

In both figures the Laplace DLTS spectra for the germanium-free (pure silicon) samples consist of one sharp dominant line. This indicates that the transients are mono-exponential
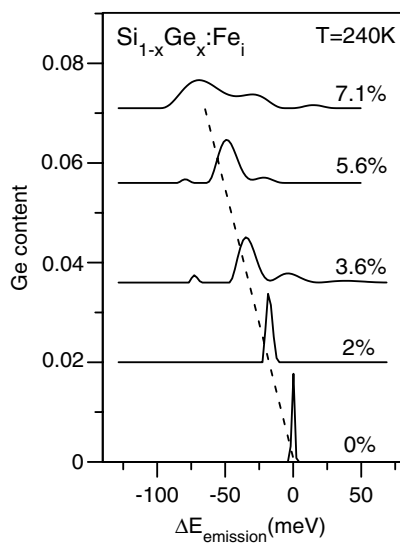
Figure 1. Laplace DLTS spectra observed for interstitial isolated iron in $Si_{1-x}Ge_x$ ($0 < x < 0.071$). The usual frequency scale has been converted to an energy scale according to the procedure described in the text. The baselines of the spectra are displaced vertically according to the germanium content of the crystal as indicated on the vertical scale. The peak magnitudes are plotted to an unmarked arbitrary scale. The dashed line connects the centres of gravity of the main peak in each of the spectra, demonstrating the linear alloy shift of this peak.
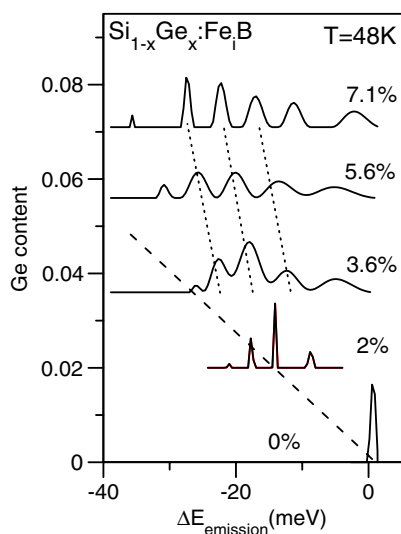

Figure 2. Laplace DLTS spectra observed for the iron–boron pair in $Si_{1-x}Ge_x$ ($0 < x < 0.071$). This figure has been prepared in a similar way to figure 1. The dashed line represents the same alloy shift as the one shown in figure 1. The dotted line connect the centres of gravity of the main peaks observed for the 3.6%, 5.6%, and 7.1% of Ge samples. See the text for more details.

and that these defects form well-defined single energy levels. For isolated interstitial iron (figure 1), when the germanium content increases, the dominant line broadens and some additional satellite features on both sides of the main peak appear. At the same time the

emission energies of the dominant and satellite lines decrease, which is seen as a shift of the peaks to the left-hand side. This means that these levels move closer to the valence band edge. The dashed line in figure 1 joins the centres of gravity of the main peaks on each of the spectra, indicating a linear energy shift of the dominant peak with the alloy composition.

The dashed line in figure 2 starts at the centre of gravity of the peak for pure silicon and has the same slope as the dashed line in figure 1. It is clearly seen that the dashed line in figure 2 joins the centres of gravity for the samples of 0% and 2% of Ge but misses the dominant peaks in the remaining three spectra. An extrapolation of the alloy slope for Fe_iB for more than 2% of Ge shows that for the three samples having more germanium the Fe_iB level should be resonant with the valence band. Similar alloy slopes have been observed by Mesli *et al* [11] for both these cases using conventional DLTS.

In general, it is expected that both Fe_i and Fe_iB levels in SiGe alloys should have the same or very similar alloy shifts over the range studied for two main reasons. First, comparing with the transition metal behaviour in $Ga_{1-x}Al_xAs$ alloys where the carrier emission to the conduction and valence band has been observed as a function of the alloy composition it has been concluded that the iron-related energy levels on an absolute energy scale (indexed to the average dangling bond energy) do not change with the alloy composition [12]. Second, the ionic model of the iron–acceptor pair formation implies that the Coulombic interaction between iron and acceptors modifies the energy levels for the isolated iron. As a result, for both configurations of iron, i.e. when it is isolated or paired, the iron atom binds a carrier which is observed in the emission process. The difference between these cases is a shift of the iron-related levels due to the Coulombic interaction when iron is accompanied by a charged acceptor.

However, as is clearly seen, the dotted lines in figure 2 joining the corresponding peaks on the spectra for samples containing more Ge have distinctly different alloy slopes than is the case for the ones observed for Fe_i and Fe_iB with less germanium. On the other hand, it should be emphasized here that the low-temperature signals observed in the samples with large Ge content clearly originate from iron–boron pairs because they have very similar stabilities and are affected by annealing in the exactly the same way as observed for the 0% and 2% samples. These facts clearly suggest that in the crystals with more germanium the iron atom is not able to bind the hole because this state becomes resonant with the valence band. The isolated boron is a shallow acceptor; however, when it is accompanied by iron its energy deepens enough to be ∼50 meV larger than for isolated boron. The thermal stability of such a complex is not altered, and electronically it can act as a deep defect and is seen in DLTS.

The pattern of peaks observed for the isolated interstitial iron in SiGe allows us to assign particular peaks to specific alloy configuration around the defects with a little less precision than has been done for substitutional gold and platinum in SiGe [8]. The interstitial tetrahedral site in the diamond structure has four nearest neighbours, then six a little more distant and then eight neighbours at twice the distance of the nearest ones. In the case of interstitial iron the amplitudes of peaks in the Laplace DLTS spectra could not be revealed with sufficient accuracy to make a comparison possible with simulated peak patterns. The first- and the second-nearest neighbours have similar distances to iron, thus it could be that the influence of these ten atoms on the iron energy level is comparable. The peak pattern obtained from the simulation procedure showed that this is a very plausible case. However, no definite conclusion concerning a possible siting preference of iron in some particular local environment of the SiGe lattice could be obtained. On the other hand, when one compares the energy distances separating peaks in the spectra in figures 1 and 2 (around 50 and 10 meV for Fe_i and Fe_iB pair, respectively) one possible conclusion can be drawn. Specifically, in the first case the alloy splitting effect is caused by host atoms closer to the iron while in the latter case atoms more distant from the

defect are responsible for the alloy effect. This difference in interpretation of peak distances observed for these two figures comes directly from the fact that the energy resolution of the Laplace DLTS method is inversely proportional to the measurement temperature. The isolated iron signal is observed at temperatures five times larger than the iron–boron pair, thus in the first case only stronger alloy effects can be observed. This is a very similar effect to the one observed for gold and platinum in SiGe alloys [8].

It has been concluded above that for alloy compositions larger than 2% in the Fe_iB pair the hole is bound to boron rather then to iron. Hattendorf *et al* [13] demonstrated using a nuclear magnetic resonance technique that for samples originating from the same source the boron atom is randomly distributed in the alloy, i.e. no siting preference for boron in SiGe alloys is observed. As a result, the alloy effect seen in figure 2 for the 3.6%, 5.6%, and 7.1% Ge samples must be related to the boron atom, and this alloy effect is revealed by the presence of iron in the closest lattice position. Knowing that boron in SiGe is substitutional, and assuming no siting preference, one can simulate the alloy pattern either for four nearest neighbours or 12 second-nearest neighbours as the origin of this alloy effect. These two cases produce very much different peak patterns and the latter case fits much better to the observed spectra. In general, for dilute alloys, more atoms are needed in order to obtain an alloy pattern with nearly equal peaks, as seen in the spectra. This change in the peak pattern between the samples with 2% of Ge and those with higher germanium contents is consistent with the change of the energy shift between the main peaks of the 0% and 2% Ge samples and the shift observed between the 3.6%, 5.6%, and 7.1% Ge samples. Below 2% of Ge the hole bound by the complex is closer to iron, while for 3.6% of Ge and more the hole is closer to boron, which results in such a dramatic change in the peak patterns and the peak energy slopes.

4. Summary

We have applied a Laplace DLTS technique to study the origin and strength of the alloy effect for iron when it is isolated or paired with boron in SiGe alloys. We have concluded that for isolated interstitial iron the first- and the second-nearest neighbours have a similar contribution to the alloy pattern in the SiGe alloy. We have proposed that for FeB in $Si_{1-x}Ge_x$ ($x = 0.02$) the iron atom binds the hole, while for $x > 0.02$ the occupied state is formed when the hole is closer to the boron atom. In this latter case it is expected that the boron energy level moves into the band gap under the influence of the closest iron neighbours, and boron in this case becomes a deep trap in silicon. Finally, from simulation results it has been concluded that only the second-nearest neighbours influence the alloy pattern of boron levels modified in this way.

Acknowledgments

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