IRON–BORON PAIR IN SILICON: OLD PROBLEM ANEW*

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For the iron–boron pair in the p-type silicon two different configurations of the defect are observed: stable and metastable. The reported metastable configuration is the first step in a dissociation process of the stable, i.e. of trigonal symmetry, configuration of the pair. Rate equations for the two-step iron–boron pair dissociation allowed us to evaluate the dissociation rates for both configurations of the pair. The driving force for the creation and, then, dissociation of the metastable pair is the minority carrier injection followed by the electron–hole recombination process in the space charge region. A use of the high-resolution Laplace-transform deep level transient spectroscopy allowed us to demonstrate for both of the configurations the influence of the magnetic field on the hole emission.

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1. Introduction

Iron and other transition metal (TM)-related impurities still seem to play a key role as the most common contaminants of silicon. The modern silicon technology allows one to produce devices in an almost atomic scale [1], as a result, a problem of defects limiting the device yield becomes more and more important. Although TM-related defects have attracted the people attention for at least thirty years they still receive a growing interest from a point of view of high-quality Si--crystal production. Besides an initial residual contamination of as-grown crystals, these metals influence the device performance if introduced unintentionally during the silicon crystallization process. TMs in silicon are characterised by very high diffusion coefficients which makes them even more undesired contaminants in this material as most of them are mobile in this material even at room temperature [2].

One of the characteristic features of TM impurities in silicon is that they very effectively form pairs with intentionally introduced shallow acceptor centres. Iron itself forms numerous complexes and multiple energy states associated with different charge states in the silicon band gap. The main feature of the iron–acceptor

complexes is that they are easily formed and dissociated [3–6]. Their formation is driven by an electrostatic attraction between both constituents of the defect [3]. In the boron-doped silicon the iron–boron pair forms the very characteristic 0.1 eV energy level (above the valence band). Electron spin resonance (ESR) measurements revealed that the symmetry of this pair is trigonal with the interstitial position of iron next to the substitutional boron [7]. This pair, and consequently, this energy state, can be easily annihilated by a short period of annealing at approximately 200°C [5]. Alternatively, this pair also dissociates at low temperatures in regions where an intensive electron–hole recombination process occurs [6]. After the dissociation process a much deeper (0.43 eV above the valence band) energy state appears in the band gap. This state is associated with the isolated interstitial iron atom.

For the case of the iron–aluminium pair it was evidenced that there is an intermediate state in the dissociation process. The iron atom before it leaves the immobile aluminium acceptor takes the position of the second-nearest neighbour (along the ⟨100⟩ direction). In this interstitial position it forms another pair with the orthorhombic symmetry [4]. This metastable configuration forms in the band gap an energy level shallower than that for the stable configuration. The observation of the second-nearest neighbour configuration of the iron–boron pair has not been reported in electrical measurements yet, but recently this configuration has been observed in the ESR experiment [8].

In this paper, the observation of the metastable configuration of the iron–boron pair with a use of the deep level transient spectroscopy (DLTS) is reported. The kinetics of the pair association and dissociation processes is analysed in terms of a two-step reconfiguration of the pair. This reconfiguration is invoked by the electron–hole recombination process in the space charge region of a diode. A use of rate equations allowed us to evaluate the dissociation and association rates for both configurations of the pair. The processes are discussed within the framework of the radiative enhanced defect reaction (REDR) theory.

Although the standard DLTS technique gained an unquestioned position as a tool for semiconducting material characterization, it still has limited abilities for the identification of the defect. A price to pay for the very high sensitivity offered by this technique is its rather poor resolution. Local defect environment sensitive methods have to be able to discriminate interactions between a defect and its environment of the order of millielectronvolts or less in the energy scale. The defect energy is modified in this energy range by, e.g., magnetic field, uniaxial stress, or crystal disorder. It has been already demonstrated that the resolution of DLTS can be substantially increased when the so-called Laplace transform DLTS is used [9]. This method allows the observation of the influence of small disturbances on the process of carrier thermal emission. As a result, in some cases, it provides a new insight into defect microscopy or, alternatively, makes possible to distinguish defects with slightly different emission characteristics. In this paper the Laplace transform DLTS has been used to study the magnetic features of the defects related to the presence of iron in the boron-doped silicon.

2. Experimental details, results and discussion

The samples used in our study were grown by the vapour phase epitaxy on p^+- or p-type (boron doped) substrates. The active layer was lightly doped with boron and covered by the n^+-type layer to form the p–n junction. Prior to the growth process the back surface of the substrate was intentionally covered by the 4N purity Fe-foil. After the growth iron was diffused from the substrate to the space charge region by the sample annealing at 1200°C during 30 min. In each of the growth processes always one uncontaminated layer was grown in order to produce the reference sample.

It has been observed on the DLTS spectra that at temperatures lower than 55 K after a moderate electron injection an additional signal could be detected. This new centre was not observed prior to the injection (even in a residual concentration) and it could be completely annihilated by a prolonged electron injection. The hole emission activation energy for this new centre was found to be equal to 0.074 eV. The electron injection caused that the DLTS signal related to the stable configuration of the pair decreased and the signal attributed to the isolated interstitial iron increased. Room temperature annealing of the sample for a few hours restored the initial amplitudes for all three signals. The metastable appearance of the 0.074 eV level and its obvious correlation with the presence of iron in the crystal can be, by an analogy to the case of the iron–aluminium pair, considered as a creation of the second-nearest neighbour configuration of the iron–boron pair (presumably with the orthorhombic local symmetry).

A simple model of the pair binding process based on the electrostatic interaction between iron and the acceptor [4] reproduced the difference in the energy levels for two configurations of the iron–aluminium pair (equal to 0.07 eV). However, this difference becomes larger and larger when the acceptor becomes a heavier group III element, i.e., gallium (0.09 eV) and indium (0.12 eV, see e.g. Ref. [10]). As a result, if one considers the lighter group III element, i.e., boron, this difference in the energy levels formed by the first- and second-nearest neighbour configurations of the iron–acceptor pair should be smaller than 0.07 eV. According to our results this difference for the iron–boron pair equals 0.026 eV.

The following experimental procedure has been employed to obtain the complete formation and annihilation kinetics of both pair configurations at a given temperature. (i) The initial conditions have been usually established after a room-temperature sample annealing for a few hours. It turns out that the iron diffusivity is sufficient to assure the initial conditions reproducibility prior to the kinetics measurement at each temperature. (ii) The concentrations of the stable and metastable pairs and the interstitial iron have been measured via the DLTS signal monitoring at around 65, 45, and 265 K, respectively. For the measurements at higher temperatures it was necessary to keep the sample reverse biased during heating up and the temperature stabilization in order to quench the pair association process. It has been already well established that in this condition the isolated iron centre is neutral and is not attracted by the long-range Coulomb potential of the acceptor [3]. (iii) The sample temperature has been stabilised at the temperature for which the association–dissociation kinetics is analysed, and then the
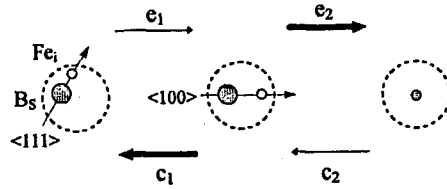
Fig. 1. Association and dissociation processes considered in the rate equations.
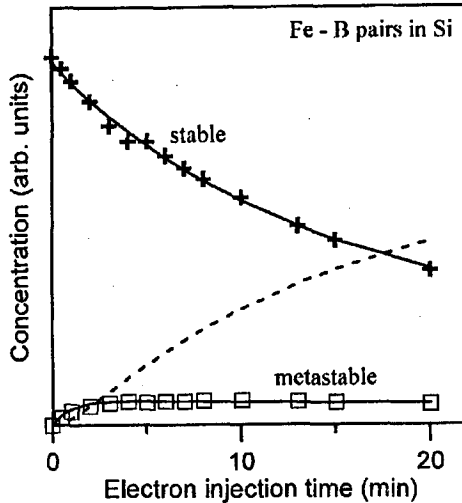

Fig. 2. The kinetics of the association and dissociation driven by the minority carrier injection for both configurations of the iron–boron pair in silicon. The dashed line shows an expected concentration of the interstitial iron which formed with boron neither stable nor metastable pair.

well-defined electron injection current has been applied to the sample. (iv) The steps (ii)–(iii) have been repeated.

The association and dissociation kinetics of the metastable pair configuration can be easily derived from the rate equations assuming that the iron–boron pair dissociates via the two-step process. The processes, which are considered in the rate equations, are schematically depicted in Fig. 1. The measured concentrations of both configurations of the pair as a function of the electron injection allowed us to evaluate the dissociation rates e_1 and e_2 (see Fig. 2). A simple inspection of the measured kinetics for the metastable configuration of the pair shows that for the given dissociation rates the reverse process cannot be ignored (c_1, $c_2 \neq 0$): the concentration of the metastable pair configuration saturates, although one could expect that for a very long injection time this configuration of the pair should disappear. These measurements performed at different temperatures and with different injection current densities revealed that both dissociation processes are proportional to the current and do not depend systematically on temperature.

On the other hand, the association rates c_1 and c_2 substantially increase with the temperature. Usually, the rate e_2 was found approximately ten times larger than e_1, and the association rate c_1 was four to six times larger than c_2 within the investigated temperature range (100–200 K).

This electron injection driven pair dissociation process can be qualitatively analysed within the framework of the standard radiative enhanced defect reaction theory [11]. This model of the defect reaction says that if there is a carrier recombination occurring via the defect then the energy gained from this process can be transferred to the defect invoking the defect reaction process. It has been observed for a number of different defects that the energy, which is necessary to initiate the defect reaction, can be reduced by the recombination energy when REDR occurs. However, in the case when the energy gained from the recombination is larger than the energy necessary to initiate the given defect reaction the whole process becomes athermal with the reaction rate proportional only to the recombination rate. This latter case of REDR has been observed in our experiments, namely, both dissociation rates e_1 and e_2 are proportional to the injection current density, and do not depend on temperature.

This lack of the temperature dependence for both dissociation rates is in agreement with the rather low activation energy for the interstitial iron diffusion (approximately equal to 0.7 eV). One can expect that this, or similar, energy is necessary for the iron atom to move from one interstitial position to another. In the case of the iron–boron pair this energy can be somehow modified by the presence of the charged acceptor in a close vicinity, however, still should be smaller than the energy of the electron–hole recombination. In other well-documented cases of REDR it has been observed that this reaction enhancement can be more efficient in the following cases: for indirect band-gap semiconductors and for defects with a large lattice relaxation effect. In the first case the electron–hole recombination process needs a centre to take some momentum of the carriers and the defect efficiently plays this role. In the latter case, the process of the energy transfer from the recombining pair to the defect is much more efficient when local phonons help to transfer the energy to the defect. The recent theoretical analysis of the iron–boron pair showed that the pair, at least in the first-nearest neighbour configuration, does not form direct bonds and the pair constituents are bound through the lattice distortion [10]. As a result, it seems that for the iron–boron pair there are indeed very advantageous conditions for REDR to occur.

Our observations that the dissociation rate of the stable configuration of the pair is larger than that for the metastable can be interpreted as a weakening of the pair binding when the pair constituents become more and more separated. On the other hand, both dissociation processes are enhanced by the recombination process. This suggests that, despite the different distances between iron and boron for both configurations, the pair, from a point of view of the electron–hole recombination process, is still local. The association rates found by us for both configurations of the pair show a reversed sequence: the stable configuration is formed much faster than the metastable one. This result seems to be obvious and easy to understand: the configuration whose concentration in the thermal equilibrium dominates always should have the fastest formation rate.

The dashed line in Fig. 2 shows an expected concentration of the interstitial iron which formed with boron neither stable nor metastable pair. This predicted concentration is much larger than the observed concentration of the isolated interstitial iron. One should apply much longer electron injection times in order to observe measurable concentration of the isolated interstitial iron. This result clearly shows that the iron atom, before it becomes the isolated point defect, forms a number of other (presumably more distant) pairs with boron. According to a prediction by Watkins [12], these configurations should form in the band gap energy states more shallow when the boron and iron become more separated. If this is true and following the observed by us tendency, the third-nearest neighbour pair should form the energy level coinciding with the level of the isolated substitutional boron, and practically should not be seen in any experiment as its concentration would be by at least three orders of magnitude smaller than the doping level with boron. On the other hand, although the other iron–boron pairs are not able to bind the hole, the interaction between the pair constituents must be effective even from long distances, as one needs to prolong the pair dissociation process to see a noticeable concentration of the isolated iron atoms.

The Laplace DLTS spectra for both configurations of the pair show no structure producing in the spectra sharp lines and showing that they can be considered as ideal point defects (see Ref. [13]). The fact that these lines are so narrow and that they are observed at relatively low temperatures provide very advantageous experimental conditions for investigations of the influence of the magnetic field on the emission process. From the ESR measurements performed on the stable configuration of the pair it is known that the spin of the defect ground state is 3/2. This should make the Zeeman effect relatively large and easily observed. For both cases of the configuration of the pair the magnetic field slows down the hole thermal emission rate and this effect is seen as a shift of the Laplace DLTS line (see Fig. 2 in Ref. [14]). Figure 3 shows the effect of the magnetic field on the emission where, according to the simple formula $\Delta E = kT^* \ln[e_h(0)/e_h(B)]$, the decrease in the thermal emission rate (e_h) is recalculated on the corresponding increase in the activation energy of the process. Due to the fact that the magnetic field affects both, the initial and the final states of the emission, the total changes in the activation energy of the process is a sum of contributions from the changes in the ground state of the defect and in the final state of the process.

In the magnetic field the initial state of the emission can split into sublevels according to the Zeeman effect. The occupancy between the sublevels is governed by the Boltzmann distribution. As the temperatures, at which the DLTS experiments are carried out, are still relatively high, in the Laplace DLTS spectra one can see only some average energy level which shifts with the increasing field. In general, one can expect that this average energy will increase proportionally to B^2 (see dashed lines in Fig. 3). The pre-factor will be proportional to the total effective magnetic susceptibility of the initial and final states of the process.

The final state for the ionization process of both configurations is a free hole in the valence band. The band density of states forms the Landau subbands with the increasing field. This process is very difficult for a quantitative description. The free hole mobility (μ_h) in silicon is very low, so even for the highest magnetic fields,
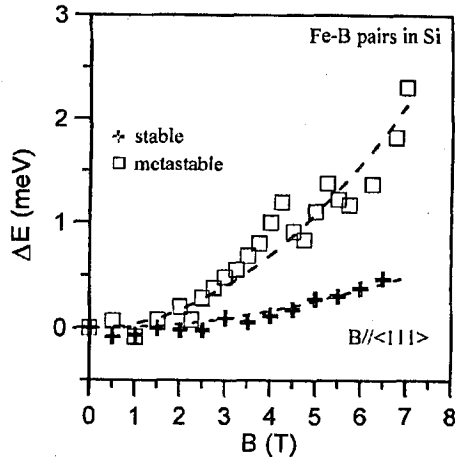
Fig. 3. Changes invoked by the magnetic field in the activation energies of the hole thermal emission for two configurations of the iron–boron pair in silicon. Dashed lines show dependences proportional to B^2.

which can be achieved in our system (7 T), a product $\mu_h B$ is smaller than 0.1. This would mean that the Landau subbands formation is very ineffective. A simple evaluation shows that if the shift of an average density of states in the valence band followed the first Landau subband (this would demand a very high mobility of holes) then the Zeeman splitting effect for the initial state would contribute to the overall changes in the process in a similar magnitude as the modification of the valence band density of states.

Figure 3 shows that the hole emission process is much more affected by the field for the case of the metastable configuration of the pair than it is observed for the stable one. However, one has to keep in mind that these two measurements were carried out at different temperatures, thus the contribution of the Boltzmann factor can be more severe for the measurements at higher temperatures (stable configuration) and result in a larger suppression of the Zeeman effect in this case. In a low-field regime, i.e. where $k_B T$ is much larger than the Zeeman splitting, in order to compensate the effect of the temperature on the pre-factors one has to multiply them by $k_B T$ (see, e.g., Ref. [15]). If the final state for the thermal emission for both configurations of the pair is the same one can assume that it contributes similarly to the effective susceptibilities deduced from Fig. 3. Consequently, an obvious conclusion is that the effective susceptibility of the ground state of the metastable configuration of the pair is a few times larger than the one for the stable configuration.

The resolution of the method allowed us to attempt to investigate an isotropy of the g-factor in a similar manner as it is done in the ESR measurements. Figure 4 shows an angular dependence of the emission rate observed for the metastable configuration of the pair. As explained above, the Laplace DLTS measurements does not recognise particular Zeeman sublevels, and consequently, only the angular dependence of the average level can be observed. For our samples not all of the
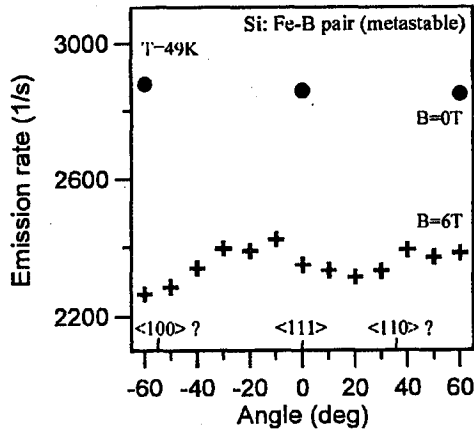
Fig. 4. Angular dependence of the thermal emission rate for the metastable configuration of the iron–boron pair.

crystallographic directions were recognised, thus assignments of the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions in Fig. 4 are only tentative. The angular dependence shows a typical oscillatory behaviour with the angular distance between minima equal to 90°. This indicates that the system spin Hamiltonian is of the fourth order. It is obvious that the accuracy of this result is rather low and cannot be compared to the direct ESR measurements. However, one has to keep in mind that this particular experiment attempts for the first time to link the DLTS with magnetic measurements and to identify the defects successfully measured by the standard DLTS with those observed in the ESR experiments.

Similar studies of the magnetic field influence on the thermal emission process have been already performed in the case of defects in the n-type silicon. Two charge states of the thermal donors (TD) have been observed. The Laplace DLTS spectra for both of them show two or three peaks which are related to different configurations of TD: it has been already well-established that these defects always form a family of centres [16]. In our analysis only the dominant peaks in the spectra for both charge states have been considered. It has been found that despite the fact that both energy levels differ in the number of electrons bound by the centre, and consequently, in their spins, they move in a similar manner with the magnetic field. Moreover, the shift of both activation energies could be explained as being solely due to the shift of the first Landau subband in the conduction band [14]. Consequently, if there is any participation of the Zeeman effect in the overall shift of the levels it must be hidden in the experimental error. It seems that the conduction band of silicon contributes too strongly to the total changes in the emission rate making the observations of the magnetic field effect on the defect ground state much more difficult than it is in the p-type crystals of silicon. However, an important conclusion from this particular study is that in this case the final state for the thermal emission process is for sure the electron in the conduction band. No intermediate states in the process can be involved.

3. Summary

For the iron–boron pair in p-type silicon two different configurations of the defect have been observed: stable and metastable, and for both of them the influence of the magnetic field on the hole emission has been demonstrated. This metastable defect appears only when the stable configuration of the iron–boron pair dissociates and before the isolated interstitial iron centres are formed. This fact and a very close resemblance to the case of the metastable configuration of the iron–aluminium pair allows us to conclude that the metastable defect observed in this paper can be identified with the iron–boron pair with the orthorhombic symmetry. For the measurements of the carrier emission process in the magnetic field a crucial factor is how the modification of the band density of states participates in this process. It was found that for n-type silicon the Landau subbands formation is very effective and it obscures the effect of the field on the defect ground state. However, in p-type silicon the influence of the field on the defects ground state can be observed by Laplace DLTS. For the iron–boron pair our studies showed that the magnetic susceptibility of the ground state of the metastable configuration of the pair is much larger than the one for the stable configuration. For the first time these experiments attempt to link DLTS with magnetic measurements and to identify the defects successfully measured by the standard DLTS with those observed in the ESR experiments.

Acknowledgments

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