Shallow-Level Centers in Semiconductors (Amsterdam, 17–19 July 1996) pp. 345–350 Eds. C. A. J. Ammerlaan & B. Pajot © 1997 World Scientific Publishing Company

REACTIONS OF INTERSTITIAL IRON WITH SHALLOW ACCEPTORS IN SILICON

A.A. EZHEVSKII

Lobachevsky State University, 603600 Nizhny Novgorod, Russia

C.A.J. AMMERLAAN

Van der Waals - Zeeman Institute, University of Amsterdam, Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands

Reactions of interstitial iron with substitutional acceptors in silicon in the temperature range 0 - 100°C have been studied by EPR. The association of the interstitial iron with acceptors (B, Al) and the formation of FeFe-acceptor complexes of different modifications were considered on the basis of the diffusion model of iron motion to the reaction sites. The system of kinetic differential equations has been solved by numerical methods for different temperature ranges of the associative and dissociative iron-acceptor reactions. The parameters of the reactions are discussed on the basis of the applied model and agree reasonably well with well-known values for iron-boron pair reactions.

1 Introduction

After the work of Reiss *et al.*¹ reactions in silicon became well-known phenomena. Iron is a very common impurity in silicon, which often takes part in reactions with defects and forms pairs and complexes. The iron-boron pair reaction was studied by Shepherd and Turner² and later by Kimerling and Benton.³ As was shown recently ^{4,5} iron forms complexes with acceptors, in which two iron atoms are included. The monoclinic-I and orthorhombic symmetry of the Fe⁺Fe⁰B⁻ complexes and two different monoclinic-I Fe⁺Fe⁰Al⁻ complexes were observed and studied by EPR.^{4,5}

Owing to the fact that by EPR one can observe many of the components of the defect reactions this method may be used for study of the reaction kinetics. In this work the data of the interaction between iron and acceptors (B^- , AI^-) obtained by the EPR experiment, in which the paramagnetic centres Fe⁺, Fe⁰ [Ref.6], FeFe [Ref.7], FeB [Ref.6] or FeAl [Ref.8] and complexes FeFeB [Ref.4] or FeFeAl [Ref.5] with different symmetries were observed simultaneously, are presented.

2 Experimental Details

For the present studies Czochralski dislocation-free p-type silicon samples doped with boron or aluminium with concentrations about 1.3×10^{16} cm⁻³ and 5×10^{15} cm⁻³, respectively, were used. Dimensions of the samples were 1.5mm×1.5mm×1.5mm with the length along the [011] crystal orientation. Iron was diffused into the samples at 1300 °C

in a closed quartz ampoule under argon atmosphere. After diffusion the ampoule with samples was quenched in water. A surface layer was removed mechanically and after a short heating again to 1300 $^{\circ}$ C the second quenching of samples in an open ampoule followed. A thin layer from the surface was removed again. After that the samples were stored at liquid nitrogen temperature or at a higher temperature for carrying out the reactions.

The EPR spectra were measured on a K-band (microwave frequency $v \approx 23$ GHz) superheterodyne spectrometer, which was tuned to observe the dispersion of the susceptibility. The sample temperature for EPR measurements was fixed at 1.5 or 4.2 K.

3 Results and Analysis

After diffusion and quenching of the silicon samples which were stored at liquid nitrogen temperature spectra of the two single iron centres Fe^o and Fe⁺ and the monoclinic-I FeFe-complex centre were observed with weak intensity. Keeping the samples at ice-melting temperature gives rise to an increase of the FeFe-complex intensity and arising of the trigonal FeB pair and the monoclinic-I FeFeB complex. The increase of temperature up to room temperature leads to a disappearance of the FeFe complex and more intensive increase of the FeB-pair concentration and especially the monoclinic-I FeFeB complex. Besides that one could observe the appearance of a weak signal of the orthorhombic FeFeB complex and monotonic decreasing of the Fe^o and Fe⁺ concentrations. Formation of the orthorhombic Fe^oFe⁺B⁻ complex is substantially less intensive compared to the monoclinic-I Fe^oFe⁺B⁻ complex. Details of the reaction kinetics are shown in figure 1. Further annealing was carried out at fixed temperatures 40, 60, 80 and 100 °C. The results are shown in figure 2. At 40 °C the annealing gives rise to a monotonic decrease of the $Fe^{0}Fe^{+}B^{-}$ complex and the Fe^{+} centre. At the next fixed temperature (60 °C), during four hours the dissociation rate of the complexes became higher and the concentration of the Fe⁺ centres began to increase.

For a description of the experimental results the model of the diffusion motion of the Fe-atoms to their reaction sites was considered on the basis of the model of Pell and Ham.⁹ This model supposed that the number of the reaction sites cannot be constant during the reaction and is determined by the concentration of the unpaired acceptors. In this case one can write

$$dN(t)/dt = 4\pi R D N(t) B(t), \qquad (1)$$

where N(t) is the concentration of the unpaired donors, B(t) the concentration of the unpaired acceptors, D the diffusion coefficient for the donor and R the capture radius for the reaction. For pure electrostatic interaction between ionised donors and acceptors the capture radius can be written as $R=q^2/4\pi \epsilon kT$ and it gives an estimation for the radius as $R\approx 40$ Å for the reaction temperature range. In case of the unionised atoms the inter-



Figure 1: Observed concentrations of the components of the iron-boron reaction versus time of the reaction carried out at 0 $^{\circ}$ C (a) and 25 $^{\circ}$ C (b).



Figure 2: Annealing curves for different components of the iron-boron reaction in the temperature range 40-100 °C; 40 °C for the first 5 hours, 60 °C after 5 hours, 80 °C after 9 hours, 100 °C after 11 hours.

action has chemical character and the capture radius R must have the order of the lattice period ≈ 5 Å. The diffusivity of the donor atoms is determined by the diffusion coefficient $D=D_0 \exp(E_d/kT)$, where E_d is the activation energy, which for iron in silicon has a value of 20 kcal (0.87 eV) for temperature T=1000 °C and 18 kcal (0.78 eV) obtained from the dissociation data for the FeB pair. The extrapolation of the diffusion coefficient D from the high temperature to the temperature range of the pairing reaction leads to a lower value of D ($D\approx 2\times 10^{-17}$ cm²/s at 30 °C, instead of the 5×10^{-15} cm²/s, obtained from the pairing experiment).

Formation of different complexes with two iron atoms, monoclinic-I and orthorhombic FeFeB centres (or two monoclinic-I FeFeAI), has not been considered in Refs 2 and 3. But as can be seen from the presented experimental data, formation of the monoclinic-I FeFeB centre predominates over pairs and other complexes in the whole range of the iron-boron reaction and must be taken into consideration for interpretation of the experimental data and theoretical models. Solution of the system of the kinetic differential equations has been obtained by a numerical method. This system can be written as

$$d [Fe^{+}]/dt = -4\pi RD [Fe^{+}] [B^{-}] + Z \exp(-E_{b}/kT) [FeB] -4\pi R_{1} D [Fe^{+}] [FeB] + Z_{1} \exp(-E_{b1}/kT) [FeFeB]_{1} -4\pi R_{2} D [Fe^{+}] [FeB] + Z_{2} \exp(-E_{b2}/kT) [FeFeB]_{2},$$
(2a)

$$d[FeB]/dt = +4\pi RD[Fe^+][B^-] - Zexp(-E_b/kT)[FeB] -4\pi R_1 D[Fe^+][FeB] + Z_1 exp(-E_{b1}/kT)[FeFeB]_1 -4\pi R_2 D[Fe^+][FeB] + Z_2 exp(-E_{b2}/kT)[FeFeB]_2,$$
(2b)

$$d[B^{-}]/dt = -4\pi RD[Fe^{+}]/B^{-}] + Zexp(-E_{b}/kT)[FeB], \qquad (2c)$$

$$d[FeFeB]_{1}/dt = +4\pi R_{1}D[Fe^{0}][FeB] - Z_{1}\exp(-E_{b1}/kT)[FeFeB]_{1},$$
(2d)

$$d[FeFeB]_{2}/dt = +4\pi R_{2}D[Fe^{0}][FeB] - Z_{2}\exp(-E_{b2}/kT)[FeFeB]_{2}.$$
 (2e)

In these equations R, R_1 and R_2 are the capture radii for the FeB-pair, [FeFeB]₁-monoclinic-I and [FeFeB]₂-orthorhombic defect reactions and E_b , E_{b1} and E_{b2} the binding energies, correspondingly. Kinetic curves calculated for temperatures 0, 25 and 80 °C are shown in figures 3 and 4. They are in satisfactory concordance with the experimental data (figures 1 and 2) for the following parameters:

T=0 °C:
$$R=1\times10^{-7}$$
 cm, $R_1=20\times R$, $R_2=R$, $E_d=0.71$ eV,
 $E_b=0.65$ eV, $E_{b1}=0.56$ eV, $E_{b2}=0.45$ eV, $Z=Z_1=Z_2=2\times10^3$ s⁻¹;

T=25 °C:
$$R=2\times10^{-7}$$
 cm, $R_1=10\times R$, $R_2=0.1\times R$, $E_d=0.73$ eV,
 $E_b=0.65$ eV, $E_{b1}=0.56$ eV, $E_{b2}=0.45$ ev, $Z=Z_1=Z_2=2\times10^3$ s⁻¹;

T=80 °C:
$$R=2\times10^{-7}$$
 cm, $R_1=R$, $R_2=0.1\times R$, $E_d=0.78$ eV,
 $E_b=0.65$ eV, $E_{b1}=0.55$ eV, $E_{b2}=0.45$ eV, $Z=Z_2=2\times10^3$ s⁻¹, $Z_1=5\times10^3$ s⁻¹.

Thus the diffusion model for the iron-acceptor reactions is in good agreement with the experimental data. The difference in the reaction rates for monoclinic and orthorhombic FeFeB complexes, as it follows from the calculated parameters, is described by a difference in the capture radii. It means that the difference in the structure of the centres is responsible for the formation rates of the complexes. As can be seen from the calculations, the capture radii are different for one centre in different temperature ranges. This is due to a shifting of the Fermi level during the reaction and changing of the charge state of the FeB centre: $(Fe^{0}B^{-})^{-} \rightarrow (Fe^{+}B^{-})^{0}$. At the beginning of the reaction,



Figure 3: Calculated kinetic curves of the iron-boron reaction for 0 °C (a) and 25 °C (b).



Figure 4: Calculated kinetic curves of the iron-boron reaction for 80 °C.

in the case when $N_{\rm Fe} > N_{\rm B}$ ($N_{\rm Fe} = 3 \times 10^{16} \, {\rm cm}^{-3}$ at 1300 °C), the Fermi level is positioned in the middle of the silicon gap and then it goes down during the reaction. It crosses levels: $(E_v+0.55 \,{\rm eV})$ - the level of the FeB pair, $(E_v+0.4 \,{\rm eV})$ - the level which corresponds to Fe^o-Fe⁺ transition and $(E_v+0.1 \,{\rm eV})$ - for the (Fe⁺B⁻)⁰-(Fe⁺⁺B⁻)⁺ transition, and then it goes to the acceptor level of boron, because of the iron precipitation processes taking place. In the calculations the precipitation was not taken into account, but as follows from the comparison of the calculated concentrations of Fe^o and Fe⁺ with experimental ones, the decreasing of those concentrations cannot be explained only by the reaction with boron.

To reduce the number of parameters, the same diffusion coefficient for both Fe^o and Fe⁺ centers has been taken. However, as can be seen from the calculations, the activation energy for diffusion is not constant in different temperature ranges. This fact shows that iron, which can exist in different charge states (Fe^o, Fe⁺, Fe⁺⁺), has a different diffusion mobility in silicon. The binding energies for atoms in complexes have reasonable values in comparison with an electrostatic model, for which the Fe⁺B⁻ -pair binding energy has been estimated as $E_b \approx 0.5$ eV [Ref. 3]. This model and the system of equations can be applied for the iron-aluminium reaction, when two pairs with different symmetry - trigonal and orthorhombic - and two similar, but different monoclinic-I FeFeAl complexes could be observed. Some dissimilar behaviour of the FeFeAl complexes has been observed at a long (5 years) room-temperature storage of the samples in comparison with the samples doped with boron. All complexes and FeB pairs have disappeared during 5 years storage at room temperature for samples doped with boron and iron. For silicon doped with aluminium in contrast to the boron reaction, strong EPR lines of the FeAl pairs and FeFeAl complexes were observed. Such a different behaviour of the iron-acceptor reaction system cannot be explained only by the electrostatic model. The different sign of stress field around the defect centres can lead to a different behaviour. In case of the iron-boron centres the lattice is strained around the iron-boron complexes, because the boron atom has a smaller radius than the lattice atom and such a defect can attract other defects (e.g. interstitial iron). So the centres which include boron atoms can yield the precipitations. For the iron-aluminium centres, in contrast, the lattice is compressed around the defect and such strains in the lattice cannot trap other defects to form precipitations.

References

- 1. H. Reiss, C.S. Fuller and F.J. Morin, Bell System Tech. J. 35, 535 (1956).
- 2. W.H. Shepherd and J.A. Turner, J. Phys. Chem. Solids 23, 1697 (1962).
- 3. L.C. Kimerling and J.L. Benton, Physica 116B, 297 (1983).
- 4. A.A. Ezhevskii and C.A.J. Ammerlaan, Sov. Phys. Semicond. 24, 851 (1990) [translated from Fiz. Tekh. Poluprovodn. 24, 1354 (1990)].
- 5. A.A. Ezhevskii, N.T. Son and C.A.J. Ammerlaan, Solid State Commun. 81, 955 (1992).
- 6. G.W. Ludwig and H.H. Woodbury, Solid State Physics 13, 223 (1962).
- 7. J.J. van Kooten, E.G. Sieverts and C.A.J. Ammerlaan, Solid State Commun. 64, 1489 (1987).
- 8. J.J. van Kooten, G.A. Weller and C.A.J. Ammerlaan, *Phys. Rev. B* 30, 4564 (1984).
- 9. E.M. Pell and F.S. Ham, J. Appl. Phys. 32, 1052 (1961).