

DEFECT COMPLEXING IN IRON-DOPED SILICON

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1. Introduction

Many impurities are solvable in silicon. In the crystal lattice they can occupy substitutional sites, interstitial sites, or new bond structures are locally formed involving the impurity and some silicon atoms. Impurities which are normally substitutional, such as Ge, B, P, and S are characterized by low diffusion coefficients. Interstitial impurities, examples are Li and Fe, have high mobilities. Oxygen, which occupies a bond-centered position, is an intermediately fast diffuser. With a mobile impurity species present, interactions between impurities become possible. Reaction rates are often diffusion-limited. Reaction products can vary in size from point-like defects via small complexes to macroscopic clusters. Impurity chemistry in silicon is rich in appearance. The possibilities are too numerous to be treated in any detail in limited space. Therefore, this review deals only with iron-doped silicon. First, the properties of isolated iron will be summarized. Subsequently, a discussion will be given on iron-impurity pairs, small iron complexes, and iron precipitation. Other 3d-transition metal impurities, for example chromium and manganese, show very similar behaviour in silicon. However, the most data are available for iron as it is the more common impurity.

2. Isolated Iron Impurity Atoms

Iron is a fast-diffusing element in silicon. The diffusion constant, measured over the range 1100-1300 °C is expressed by $D_{\text{Fe}} = 8.9 \cdot 10^{-3} \cdot \exp(-0.90 \text{ eV}/kT) \text{ cm}^2/\text{s}$ [1]. The solubility at 1200 °C is about $1.5 \cdot 10^{16} \text{ atoms/cm}^3$ [1-3]. Because of the high mobility, it is difficult to prevent iron contamination of crystals during treatments at high temperatures. Iron is easily introduced unintentionally [4-7] and has been identified as a thermal defect [8-14]. Iron diffuses intersti-

tially [3]. After quenching to room temperature iron is found to occupy the tetrahedral interstitial lattice sites. A deep donor level in the silicon bandgap is associated with this impurity [15-17]. The level position at $E_{vb} + (0.39 \pm 0.02)$ eV was determined by Hall effect [2,18,19] and deep level transient spectroscopy (DLTS) [19-26]. Carrier capture cross-section, reported to be $\sigma_p^0 \approx 3 \cdot 10^{-16}$ cm² and $\sigma_n^+ \approx 15 \cdot 10^{-16}$ cm² [27] are temperature dependent with an activation energy of 43 meV [19]. Both neutral Fe_i^0 and positively charged Fe_i^+ are paramagnetic due to the partial filling of the 3d electron shell. The model of Ludwig and Woodbury accounts for the electronic structure [28]. Neutral iron has (3d)⁸ configuration, spin $S = 1$, and isotropic Zeeman splitting factor $g = 2.070$ [29,30]. The coincidence of the two electron paramagnetic resonance (EPR) transitions is lifted when the symmetry of the centre is lifted by applying uniaxial stress [31-34]. Positively charged Fe_i^+ has a configuration (3d)⁷. The ground state is an orbital triplet T_1 with effective momentum $L' = 1$, which couples to the spin $S = 3/2$ to give a total momentum $J = 1/2$. The isotropic g value is $g = 3.524$ [30,31]. The centre exhibits dynamical Jahn-Teller effects [38]. Spin-lattice relaxation rates were determined [35-37]. Photoluminescence from deep states associated with iron was observed [38]. Theoretically, the electronic structure has been described using the spin-restricted scattered-wave X α method for a small cluster containing a central iron atom [39-41]. A deep bandgap donor level was found indeed. An electronic level at $E_{cb} - 0.55$ eV, frequently reported [2,16,42-44] is probably not associated with a single iron impurity.

After 1.8 MeV electron irradiation of iron-doped silicon an EPR spectrum arising from a centre with one iron atom was observed [45,46]. The spectrum was ascribed to substitutional iron. Vacancies created by the irradiation may have enabled the interstitial to substitutional conversion. The centre has $\langle 111 \rangle$ axial symmetry.

3. Iron-Impurity Pairs

3.1. Iron-Acceptor Pairs

Keeping silicon crystals at room temperature interstitial iron is lost from solid solution. This process proceeds faster in p-type silicon; n-type material is more stable [47]. In p-type silicon iron atoms will release their donor electron to the acceptors, thereby becoming positively charged. The attraction between mobile positive iron ions Fe_i^+ and negative acceptor ions A^- , is sufficiently strong to

favour associations at room temperature. The existence of the iron-acceptor pairs FeB, FeGa and FeIn, is confirmed by their EPR spectra [30,48]. The two chemical components in a pair are unambiguously identified by a characteristic hyperfine structure. The FeB and FeGa pairs have $\langle 111 \rangle$ axial symmetry [30,49], consistently with the simplest pair model of a substitutional acceptor impurity with an iron ion on a nearest interstitial site. The angular dependence of the resonance of FeIn indicates rhombic symmetry [30,49]. Energy levels for the pairs have been measured by Hall effect and DLTS [24]. Donor levels are reported at $E_{vb} + 0.10$ eV for FeB [19,23,25,26,50], at $E_{vb} + 0.19$ eV for FeAl [19,50] and at $E_{vb} + 0.24$ eV for FeGa [19]. An additional level for FeB at $E_{cb} - 0.55$ eV is probably an acceptor level of the same pair [50]. Also for FeAl a second level, at $E_{vb} + 0.13$ eV, is found [50]. It is possibly related to a different pair structure. The formation of pairs proceeds faster at increased temperatures and at higher levels of acceptor doping [22]. This is consistent with a diffusion-limited reaction process and a time constant $\tau = (4\pi n_A D_{Fe} R)^{-1}$, with a Coulomb capture radius R [42]. The activation energy for the pairing process near room temperature, reported ≈ 0.83 eV, is slightly less than for interstitial diffusion at high temperatures [22,42]. Complicated kinetics have been observed [19]. To account for this a separation of the pair process into two phases has been proposed [50]. The pair interaction is an equilibrium process: pairs may associate and dissociate. The equilibrium constant $K = n_{Fe+A-}/n_{Fe+} \cdot n_{A-}$ will have a form $K(T) = K(\infty) \exp(-H/kT)$. Expressing concentrations as site fraction, the pre-exponential constant $K(\infty)$ must be close to the coordination number $Z = 4$ according to theory. The formation enthalpy ΔH may be approximated by $\Delta H = e^2/4\pi\epsilon_0\epsilon_r r_1$. Taking $\epsilon_r = 11.8$ for the dielectric constant and $r_1 = 0.235$ nm, which is the distance between a lattice site and an interstitial T-site, one calculated $\Delta H = 0.52$ eV. Accurate determinations of $K(T)$ have not been performed. Published values for the binding energy of the FeB pair vary from 0.50 to 0.65 eV [22]. Illumination by intense white light causes dissociation of the FeB pair [50]. At temperatures above 150 °C pairs dissociate irreversibly as then iron is lost from the solution by precipitation. Information available for the iron-acceptor pairs is not yet complete.

3.2. Iron-Donor Pairs

Single interstitial iron is not a stable impurity in n-type silicon either. Also in this material the interstitial iron concentration de-

creases when kept at room temperature by a thermally activated process, with longer time constants than in p-type silicon. Interactions of neutral iron atoms with the group V donors, P, As, and Sb, either in the neutral or positive charge state have not been reported [11]. However, with sulphur, which can act as a double donor, iron forms an impurity pair. Four different such pairs were identified by means of EPR [51,52]. They exhibit the expected twofold splitting when the magnetic isotope ^{57}Fe ($I=1/2$) is used for diffusion. For one centre also the ^{33}S ($I=3/2$) hyperfine structure was observed. The g tensor of the spectra indicates orthorhombic symmetry for all centers. One of the pairs is nearly $\langle 111 \rangle$ axial with only a slight orthorhombic distortion. The geometric structure of these defects is therefore rather different from the iron-acceptor pairs. They may consist of an iron and a sulphur atom on a (110) plane. The electrical properties of these pairs were not studied. Information on iron-donor pairing is still incomplete.

3.3. Iron-Gold Pairs

Gold is an amphoteric impurity frequently used to control carrier lifetimes in silicon. After quenching of silicon doped with both gold and iron, the latter impurity sometimes unconsciously, an anisotropic EPR spectrum can be observed [11,53-57]. A fourfold splitting in the spectra indicates the presence of one gold atom (^{197}Au : abundance 100 %, $I = 3/2$). Additional twofold splitting is present due to hyperfine interactions with one ^{57}Fe atom, when this isotope is deliberately diffused [56]. The spectrum arises from a centre with trigonal symmetry. Its angular dependence is usually due to the large electric quadrupole moment of the ^{197}Au nuclei. The hyperfine structure, the anisotropy of the spectrum, and the known properties of gold and iron in silicon allow a reliable interpretation of the spectrum. The model for the centre is a neutral complex consisting of a substitutional gold atom with an iron atom on a nearest neighbour interstitial position.

The electronic structure of the $\text{Au}_\text{s}\text{Fe}_\text{i}$ complex was analysed using LCAO techniques [58]. The most satisfactory description was obtained by assuming the transfer of one electron from the iron to the gold impurity. The electronic configurations then are $(5d)^8 6sp^3$ and spin $S_{\text{Au}} = 1$ for the negative Au_s^- ion, and $(3d)^7$ with spin $S_{\text{Fe}} = 3/2$ for the positive Fe_i^+ ion. Antiferromagnetic coupling between the two localized spins is required to explain the experimentally observed spin $S = 1/2$. Due to covalency the quantities $\langle 1/r^3 \rangle$ for the d-orbitals

on the gold and iron atoms are reduced considerably with respect to the free atoms. Also, the s-core polarizations of these impurities solved in silicon are smaller than in most other materials.

The Au_sFe_i pairs are formed to highest concentrations by heating the samples as quenched to temperatures of 200-250 °C for 10 minutes [56]. Their formation is accompanied by the disappearance of the interstitial iron component. By heating above 250 °C the pairs are irreversibly lost.

3.4. Iron-Iron Pairs

Also interactions between iron atoms themselves were observed in EPR [46]. To avoid competing processes dislocation-free silicon of high purity was used for these experiments. Pairs of iron atoms at small separation were produced by high-energy electron irradiation followed by modest annealing. Four EPR spectra related to iron pairs were reported. The participation of two iron atoms to form one centre is directly concluded from the characteristic hyperfine structure when using the magnetic isotope ^{57}Fe . The symmetry of the atomic arrangement is trigonal for one centre, monoclinic for one other, and orthorhombic, with slight distortion to lower symmetry, for the two remaining pairs. In all four centres the two iron atoms occupy sites which are equivalent by symmetry. Tentative atomic models for the iron-pair defects were proposed. These models also involve vacancies created by the irradiation. All iron pairs have spin $S = 5/2$. This could be explained in the Ludwig-Woodbury model by assuming the occupation of interstitial sites by the iron atoms and parallel alignment of the spins on the two atoms. Consisting of two iron atoms only, the complexes already act as ferromagnetic inclusions. Every pair is observed in a charged state. Deep bandgap levels are presumably associated with the pairs. Some of the iron-pairs are directly formed during the room temperature irradiation. This shows that the interstitial iron impurity is the subject to radiation-induced diffusion.

4. Iron Complexes

Upon anneal at temperatures above 120 °C the EPR signal of Fe_i^0 decreases and is lost completely ultimately, even in pure silicon crystals. This is not due to a mere shift of the Fermi level as no reso-

nance from Fe_i^+ becomes observable. Anneal in the temperature range 120-150 °C produces a new EPR spectrum [46]. Though this has much smaller intensity, its growth appears to be correlated with the decrease of the Fe_i^0 concentration. The EPR line width is too large for hyperfine interactions with ^{57}Fe , which are expected to be small, to be resolvable. Nevertheless, the formation kinetics and the g value of the spectrum strongly suggest an iron-related defect. Based on the observed spin $S = 4$ of the spectrum, a complex consisting of four interstitial iron atoms in the neutral state is proposed. Ferromagnetic coupling of the four $S = 1$ spins on the Fe_i^0 constituents explains the spin of the complex. The iron atoms are arranged in trigonal symmetry. The $(\text{Fe}_i^0)_4$ centre is reminiscent of $(\text{Mn}_i^0)_4$, though the latter centre has cubic symmetry and its structure is well established by resolved ^{55}Mn hyperfine interactions [59]. The spectrum of $(\text{Fe}_i^0)_4$ is lost by anneal at 250 °C. The identification of this four-iron-atom complex needs further confirmation.

5. Iron Precipitation

5.1. Formation of Clusters

After slow cooling of silicon following iron diffusion at high temperature, no interstitial component is present. Also, dissolved interstitial iron is lost by heating above 250 °C. After such treatments metallic precipitates are observable by transmission electron microscopy and by X-ray topography. The dimensions reported for these segregations vary from 10 nm to several μm 's. The precipitates are not pure iron inclusions, but compounds of silicon and iron, possibly Fe_3Si [60]. They cause the so-called hazy appearance after preferential etching. A large density of minute etch pits, typically with a diameter of 1 μm , is visible on the surface. The density of these bulk clusters is larger in the middle of the crystals than close to the surfaces. The nature of the nucleation sites is not well defined yet. Oxygen can play a role as Czochralski silicon behaves differently from float-zone silicon.

5.2. Precipitation on Dislocations

In strongly dislocated silicon no interstitial iron impurity can be detected after doping and quenching. Though iron is introduced, as evidenced by nuclear activation analysis, the fraction present on

interstitial sites, measured specifically by EPR, is much lower or entirely absent. In the range of 10^5 to 10^7 dislocations per cm^2 , the interstitial iron component falls from normal to zero [61]. Around the dislocations there appear to exist depleted zones with the radius of about $2\text{ }\mu\text{m}$ [61]. Iron atoms within this radius are trapped by the dislocation strain field and are concentrated near the dislocation core already during the initial quenching. Iron atoms originally located outside the dislocation zones can diffuse to and be trapped in these zones in thermally activated anneal. The deposition of iron at the dislocations changes the shape of the etch pits [62].

5.3. Precipitation on Surfaces

When conditions of time and temperature are suitable for iron to migrate over macroscopic distances it can precipitate on surfaces. This has been demonstrated in cases where surfaces were carefully cleaned from iron before the heat treatment. Iron contamination of silicon crystals can thus be remedied by a proper gettering technique. Heating of the samples in a gas stream containing HCl will remove iron impurities, probably because metallic chlorides with high volatility are formed at the surface [12,63].

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