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Interaction between Iron and Point Defects in Silicon

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By the EPR method the dose dependence of the interstitial iron concentration (N_{Fe}) in silicon is studied after 4 MeV electron irradiation in the temperature range 80 to 300 K. It is obtained that electron irradiation at temperatures lower than 280 K decreases N_{Fe} and leads to a constant value N_{Fe}^c . This value N_{Fe}^c depends on carbon concentration and does not depend on oxygen contamination in the crystals. Analysis of the possible reactions between Frenkel pair components and impurity atoms shows that iron atoms are effective centers of indirect annihilation of vacancies and interstitials in silicon.

Методом ЭПР изучена дозовая зависимость концентрации междоузельного железа (N_{Fe}) в монокристаллическом кремнии при облучении электронами с энергией 4 МэВ в диапазоне температур 80 до 300 К. Обнаружено, что в результате облучения при $T < 280$ К N_{Fe} уменьшается и стремится к постоянному значению N_{Fe}^c , которое зависит от концентрации углерода в образцах и не зависит от содержания кислорода. Анализ возможных реакций взаимодействия между компонентами пар Френкеля и примесными атомами показывает, что атомы железа являются эффективными центрами не прямой аннигиляции компонентнов пар Френкеля в кремнии.

1. Introduction

Iron is a common impurity in thermally annealed monocrystalline silicon [1]. Since iron in silicon has a high mobility, it is involved in complex formation processes. The properties of iron-impurity complexes has been studied intensively during the past three decades using the EPR method [2 to 4]. But there are only few papers which report on the behavior of iron in silicon with the primary lattice defects (Frenkel pair components, i.e. vacancy (V) and self-interstitial (I)) which are produced by electron irradiation [5 to 7]. After electron irradiation at room temperature the concentration of interstitial iron (N_{Fe}) in silicon decreases very fast [6, 7] and irradiation yields several EPR spectra related with iron [7]. The disappearance of isolated interstitial iron and the formation of iron-related complexes during irradiation at room temperature shows that iron is involved in radiation-induced diffusion [7].

The aim of the present work is an experimental study and a quantitative description of the interaction between interstitial iron and primary point defects in electron-irradiated silicon in a temperature range where radiation-induced diffusion of iron does not occur.

2. Experimental Techniques

Samples were prepared by diffusion of iron in dislocation-free silicon with different concentrations of oxygen (N_O) and carbon (N_C). Concentrations of shallow impurities were

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less than $5 \times 10^{14} \text{ cm}^{-3}$. Heat treatment was performed at 1200°C in an open quartz tube during 1 h. Typical dimensions of samples were $3 \times 3 \times 10 \text{ mm}^3$ with the long side in $[110]$ direction. After fast quenching the samples were etched to remove elastic stresses which were introduced during quenching.

EPR measurements were performed in an X-band spectrometer at 30 K. N_{Fe} was obtained by double integration of the first derivative of the EPR signal and compared with the signal of a reference sample. The error of the relative concentration measurement was less than 5%. Before irradiation the initial concentration of iron was $N_{\text{Fe}}^0 = (7 \pm 1) \times 10^{15} \text{ cm}^{-3}$. Irradiations were performed with 4 MeV electrons at temperatures 80 to 300 K, the dose varied between 1×10^{16} and $6 \times 10^{18} \text{ e}^- \text{ cm}^{-2}$. Samples were cooled with liquid nitrogen. Accuracy of the temperature setting was $\approx 3 \text{ K}$.

The concentration of the paramagnetic A-centers was looked for at 4.2 K on a K-band EPR spectrometer.

3. Experimental Results

After electron irradiation at temperatures lower than 280 K the concentration of the interstitial iron decreases and with increasing dose Φ approaches a constant value (N_{Fe}^c). This value N_{Fe}^c is dependent on the carbon concentration. If $N_{\text{C}} < 5 \times 10^{16} \text{ cm}^{-3}$, $(N_{\text{Fe}}^c)_1 \approx \frac{1}{3} N_{\text{Fe}}^0$ and if $N_{\text{C}} > 4 \times 10^{17} \text{ cm}^{-3}$, $(N_{\text{Fe}}^c)_2 \approx \frac{2}{3} N_{\text{Fe}}^0$. The dose dependence of the iron concentration is shown in Fig. 1. The value of N_{Fe}^c does not depend on the oxygen content in silicon, in the limits of the experimental accuracy, if $N_{\text{O}} = (1 \text{ to } 100) \times 10^{16} \text{ cm}^{-3}$.

If the irradiation temperature is less than 280 K there is no temperature dependence of N_{Fe}^c . When temperature was above 285 K we observed a fast decreasing of N_{Fe} to a value lower than the sensitivity of the EPR spectrometer. This result agrees with the results of a previous investigation [7]. But in this case the presence of a high carbon content slowed the fast decreasing of N_{Fe} .

By monitoring the intensity of the EPR spectrum [8] we have observed that doping of iron reduces the concentration of A-centers (oxygen vacancy) in irradiated samples with high oxygen content.

After irradiation there are significant changes in the shape and width of Fe^0 EPR line which are connected with the presence of internal electric and elastic fields in silicon samples.

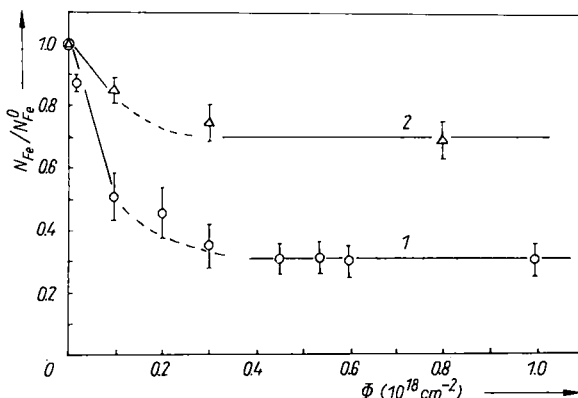


Fig. 1. Dose dependence of the relative Fe^0 concentration in silicon with different carbon contents: (1) $N_{\text{C}} \leq 5 \times 10^{16}$, (2) $\geq 4 \times 10^{17} \text{ cm}^{-3}$

4. Discussion

The fact that the concentration of the interstitial iron after electron irradiation decreases and, in samples with small contents of carbon, approaches a constant value $(N_{\text{Fe}}^{\text{e}})_1 \approx \frac{1}{3} N_{\text{Fe}}^0$ demonstrates that there are interactions of iron with primary point defects (V and I). This corresponds to the annihilation of V and I on impurity atoms in accordance with [9]. It appears that in our case the following reactions are taking place:



Introduction of other impurities produces additional sinks for I and V. Here our main task is to understand under which condition the presence of carbon raises the value of N_{Fe}^{e} and why the presence of oxygen cannot change N_{Fe}^{e} in irradiated silicon.

It is well known that carbon atoms are an effective sink for I [10]; the reaction



takes place with high probability. But in the range of high irradiation doses the inverse process, solution of C_I in a vacancy,



is essential, too [11].

Thus it is simple to show that reactions (1) and (2) and (3) give the possibility to explain the experimentally observed behavior of iron in silicon after electron irradiation. These reactions correspond to the following kinetic equations:

$$\begin{aligned} \frac{dN_{\text{Fe}}}{dt} &= \gamma_{\text{AI}}N_{\text{A}}N_{\text{I}} + \gamma_{\text{BV}}N_{\text{B}}N_{\text{V}} - \gamma_{\text{FeV}}N_{\text{Fe}}N_{\text{V}} - \gamma_{\text{FeI}}N_{\text{Fe}}N_{\text{I}}, \\ \frac{dN_{\text{I}}}{dt} &= \lambda - \gamma_{\text{FeI}}N_{\text{Fe}}N_{\text{I}} - \gamma_{\text{BI}}N_{\text{B}}N_{\text{I}} - \gamma_{\text{CSI}}N_{\text{CS}}N_{\text{I}}, \\ \frac{dN_{\text{V}}}{dt} &= \lambda - \gamma_{\text{FeV}}N_{\text{Fe}}N_{\text{V}} - \gamma_{\text{BV}}N_{\text{B}}N_{\text{V}} - \gamma_{\text{CIV}}N_{\text{CI}}N_{\text{V}}, \end{aligned} \quad (4)$$

where λ is the rate of V and I generation and γ_{ij} are the probabilities of the reactions between defects of types i and j. At high irradiation dose the condition

$$\frac{dN_{\text{Fe}}}{dt} = \frac{dN_{\text{I}}}{dt} = \frac{dN_{\text{V}}}{dt} = 0 \quad (5)$$

will be satisfied. Therefore, we can write the following equations:

$$\frac{N_{\text{I}}}{N_{\text{V}}} = \frac{\gamma_{\text{FeV}}N_{\text{Fe}} + \gamma_{\text{BV}}N_{\text{B}} + \gamma_{\text{CIV}}N_{\text{CI}}}{\gamma_{\text{FeI}}N_{\text{Fe}} + \gamma_{\text{AI}}N_{\text{A}} + \gamma_{\text{CSI}}N_{\text{CS}}} = \frac{\gamma_{\text{FeV}}N_{\text{Fe}} - \gamma_{\text{BV}}N_{\text{B}}}{\gamma_{\text{AI}}N_{\text{A}} - \gamma_{\text{FeI}}N_{\text{Fe}}}. \quad (6)$$

The condition of the iron atom conservation in reactions (1) can be written as

$$N_{\text{Fe}} + N_{\text{A}} + N_{\text{B}} = N_{\text{Fe}}^0. \quad (7)$$

Conservation of the Frenkel pair components requires the following equation:

$$N_{\text{A}} = N_{\text{B}}. \quad (8)$$

Let us assume that iron atoms are the centers of indirect annihilation of V and I. First we discuss the situation when there is a small number of carbon atoms: $N_{\text{Cs}}, N_{\text{Ci}} = 0$. The solution of the system (4) with conditions (7) and (8) is given by

$$(N_{\text{Fe}}^{\text{c}})_1 = N_{\text{Fe}}^0 \left[1 + 2 \left(\frac{\gamma_{\text{FeV}} \gamma_{\text{FeI}}}{\gamma_{\text{AI}} \gamma_{\text{BV}}} \right)^{1/2} \right]^{-1}. \quad (9)$$

If the efficiencies of both channels of indirect annihilation of V and I are approximately equal, we must conclude that

$$\frac{\gamma_{\text{FeV}}}{\gamma_{\text{AI}}} \approx \frac{\gamma_{\text{FeI}}}{\gamma_{\text{BV}}} \approx 1. \quad (10)$$

In this case one can obtain $(N_{\text{Fe}}^{\text{c}})_1 = \frac{1}{3} N_{\text{Fe}}^0$.

When the concentration of carbon atoms is not so small, the solution of the system (4) with conditions (7) and (8) can be written as follows:

$$(N_{\text{Fe}}^{\text{c}})_2 = \left[N_{\text{Fe}}^0 - \frac{\gamma_{\text{BV}} - \gamma_{\text{AI}}}{2\gamma_{\text{BV}}\gamma_{\text{AI}}} (\gamma_{\text{CiV}}N_{\text{Ci}} - \gamma_{\text{CsI}}N_{\text{Cs}}) \right] \left(1 + \frac{\gamma_{\text{FeV}}}{\gamma_{\text{AI}}} + \frac{\gamma_{\text{FeI}}}{\gamma_{\text{BV}}} \right)^{-1}. \quad (11)$$

In this situation (10) remains valid and in the limit of small concentrations of C_1 and C_s one obtains the solution $(N_{\text{Fe}}^{\text{c}})_1 = \frac{1}{3} N_{\text{Fe}}^0$.

In [11] it was obtained that at high irradiation dose

$$\gamma_{\text{CsI}}N_{\text{Cs}} \gg \gamma_{\text{CiV}}N_{\text{Ci}}. \quad (12)$$

It can be shown that agreement with experimental observation requires the following condition:

$$(\gamma_{\text{CiV}}N_{\text{Ci}} - \gamma_{\text{CsI}}N_{\text{Cs}})(\gamma_{\text{BV}} - \gamma_{\text{AI}}) < 0. \quad (13)$$

Thus, (13) means that $\gamma_{\text{BV}} > \gamma_{\text{AI}}$. The obtained results allow to make an estimation of the effectiveness of indirect V and I annihilation on iron atoms. Taking into account conditions (10), (12), and (13) it is simple to show that

$$(N_{\text{Fe}}^{\text{c}})_2 - (N_{\text{Fe}}^{\text{c}})_1 \approx \frac{1}{6} N_{\text{Ci}}^0 \frac{\gamma_{\text{CsI}}}{\gamma_{\text{AI}}}. \quad (14)$$

It is possible to make the estimation that $\gamma_{\text{AI}}/\gamma_{\text{CsI}} \approx 30$.

It should be noted that the probability of the reaction between interstitial oxygen and vacancy (γ_{OV}) is close to the value γ_{CsI} [11]. It means that $\gamma_{\text{BV}} > \gamma_{\text{AI}} \gg \gamma_{\text{OV}}$. Therefore, in irradiated silicon doped with iron it should be expected that the concentration of A centers is smaller than in undoped samples. This prediction agrees with experimental data.

In the range of small irradiation dose the main reactions are A and B in system (1). In this case the first equation from system (4) can be written as

$$\frac{dN_{\text{Fe}}}{dt} \approx -\gamma_{\text{FeV}}N_{\text{Fe}}N_{\text{V}} - \gamma_{\text{FeI}}N_{\text{Fe}}N_{\text{I}}. \quad (15)$$

In quasi-stationary approach

$$\begin{aligned} N_{\text{I}} &\approx \frac{\lambda}{\gamma_{\text{FeI}}N_{\text{Fe}}}, \\ N_{\text{V}} &\approx \frac{\lambda}{\gamma_{\text{FeV}}N_{\text{Fe}}}. \end{aligned} \quad (16)$$

Thus, the initial speed of the interstitial iron recession can be written as follows:

$$-\frac{dN_{\text{Fe}}}{dt} \approx 2\lambda. \quad (17)$$

In samples with high carbon content

$$N_{\text{I}} \approx \frac{\lambda}{\gamma_{\text{FeI}}N_{\text{Fe}}^0 + \gamma_{\text{Csl}}N_{\text{Cs}}^0}. \quad (18)$$

In this case the speed of iron recession is

$$-\frac{dN_{\text{Fe}}}{dt} \approx \lambda \left[1 + \frac{\gamma_{\text{FeI}}N_{\text{Fe}}^0}{\gamma_{\text{FeI}}N_{\text{Fe}}^0 + \gamma_{\text{Csl}}N_{\text{Cs}}^0} \right]. \quad (19)$$

For $N_{\text{Cs}}^0 \rightarrow \infty$ the speed of iron recession is smaller than for $N_{\text{Cs}}^0 \rightarrow 0$. This result also agrees with experiment, as is shown in Fig. 1.

5. Conclusion

Electron irradiation at temperatures lower than 280 K decreases the concentration of interstitial iron and finally a constant value is reached. This value depends on carbon concentration but does not depend on the oxygen content in silicon. Radiation induced diffusion and fast dissolving of the solid solution of iron was observed when the irradiation temperature was higher than 285 K. The results of experiments and calculations have shown that interstitial iron is an effective center for the indirect annihilation of vacancies and interstitials in silicon.

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