

IRON IN SILICON AND ITS RELATION TO THERMAL DEFECTS*

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Received 28 April 1983

UDC 538.953

Original scientific paper

The behaviour of iron in quenched silicon single-crystals and its relation to thermal defects have been studied by radioactive tracer method and *ESR*-spectroscopy. It was established that diffusion of iron in silicon occurs via an interstitial mechanism. During the quenching the dissolved iron interstitials easily precipitate on specimens surfaces and more effectively on dislocations, the process which strongly influences the diffusion profile of iron. As experimental results showed a certain quantity of iron interstitials is associated with thermal defects i. e. with self-interstitials making the $(Fe^i - I_{Si})$ pairs regarded as the origin of further growing of micro-defects earlier observed in quenched silicon by *TEM*.

1. Introduction

The former results^{1,2)} have indicated the dissociative mechanism of iron diffusion in silicon expressed as $Fe^i + V \rightleftharpoons Fe^s$, where Fe^s designates the concentration of substitutional iron, Fe^i -concentration of iron interstitials and V -concentration of single-vacancies which were presumed to be the predominant lattice defects in thermal equilibrium at high temperatures^{3,4)}. The concentration of iron interstitials- Fe^i is considered to be temperature dependent as $Fe^i \sim \exp(-G_{eff}/kT)$, where $G_{eff} = H_{eff} - TS_{eff}$ has been interpreted either as the

*Reported at the 8th Yugoslav Conference on the Physics of Condensed Matter, Poreč, 21—24 Sept. 1982.

effective free energy for $(\text{Fe}^{\text{I}} - \text{V})$ pair formation, *LKS*-model B⁵⁾). In a model favouring self-interstitials- I_{Si} as dominant lattice defects in thermal equilibrium above 1000 K^{6,7)} the G_{eff} has been associated with the reaction $\text{Fe}^{\text{S}} + \text{I}_{\text{Si}} \rightarrow \text{Fe}^{\text{I}}$, *AGS*-model⁷⁾). All these models require the vacancies and/or self-interstitials to be major point defects created in equilibrium concentration at high temperatures. In investigating the behaviour of iron in silicon the special attention was paid to the position of iron atoms within the crystal lattice as well as to the correlation of these positions with self-defects. The iron has been considered as an amphoteric impurity existing in substitutional and interstitial lattice positions^{1,2,8,9,10)}, or as an impurity which easily enters into silicon and precipitates in some lattice disturbances^{1,5)}.

In order to prove the above mentioned models many experimental works have been done in which the thermal treatment of silicon was combined with irradiation. Namely, the quenched silicon specimens containing predicted equilibrium concentrations of Fe^{S} and Fe^{I} were exposed to certain fluences of ^{60}Co gamma rays or reactor neutrons when an increase of Fe^{I} as a product of Fe^{S} interaction with the radiation has been expecting. As the increase of the iron interstitial concentration during the irradiation was not observed by *ESR* one can suspect the existence of substitutional iron when the dissociative mechanism of iron diffusion in silicon could be suspected too.

The aim of this work is further study of iron behaviour in silicon, with a special consideration of the following questions: Whether the Fe^{S} really exists or not; using its relation to Fe^{I} the mechanism of iron diffusion and the problem of single-vacancies existence in silicon at high temperatures is considered. If the self-interstitials are predominant defects in equilibrium concentrations at diffusion temperatures, what is their relation to the diffused-in iron. During the diffusion,

which must occur via an interstitial mechanism, self-interstitials may interact with iron interstitials making the $(\text{Fe}^{\text{I}}-\text{I}_{\text{Si}})$ complex. The question is whether these complexes represent the origin of further growing of micro-defects observed by *TEM*^{11,12)}.

2. Experimental

The Fe^{I} was identified by the $E_{\text{v}} + 0.4$ eV energy level in the forbidden band^{10,13)} and more reliably by *ESR* resonance line at 9.27 GHz ($g = 2.07$)^{5,10,14)}. The interstitial iron was observed almost in all thermally treated silicon specimens quenched rapidly from high temperatures^{5,8,14,15)}. Some of the results indicate iron as a common impurity in as-grown silicon single-crystals^{5,16)} while other suggest iron as impurity diffused-in from ambient sources during a high temperature treatment^{9,10)}. The latter suggestion seems to be the correct one. Namely, it has been shown recently¹⁷⁾ that iron is not the native impurity in silicon; it originates from ambient sources being introduced in the specimens by diffusion. The appropriate procedure has been developed to protect the silicon specimens against the contamination by iron during the heating performance¹⁷⁾ making the study of quenched specimens properties with and without iron more accurate. These results are illustratively shown in Fig. 1 which represents *ESR*-absorption lines of Fe^{I} in quenched silicon specimens. All the *ESR* measurements were performed using *VARIAN X-band ESR* spectrometer and the intensity of Fe^{I} spec-

trum was derived from the first derivative of the absorption lines recorded at the liquid nitrogen temperature (77 K). The atmosphere as a mixture of hydrochloride and argon seems to be quite good to protect the silicon specimens against the contamination by iron from ambient sources (Absence of *ESR* spectrum of Fe^1 on the curve 2).

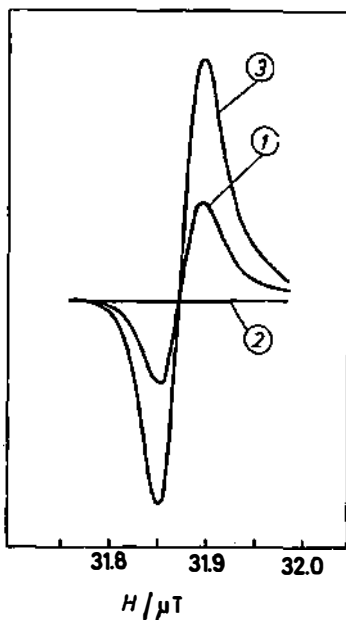


Fig. 1. The *ESR*-absorption lines of quenched silicon specimens: (1) Specimen heated in the original ambient and argon atmosphere; (2) Specimen heated in the stream of $\text{CH}_4 + \text{Ar}$; and (3) Specimen deliberately coated by iron (FeCl_3 or $^{59}\text{FeCl}_3$) and heated in $\text{HCl} + \text{Ar}$ ¹⁷⁾.

The silicon specimens ($15 \times 2 \times 1 \text{ mm}^3$) were cut from $\langle 111 \rangle$ -oriented wafers* of the following characteristics: *p*-type Si (B-doped), resistivity $50 \Omega \cdot \text{cm}$, *EPD* (etch-pit density) = 0; *n*-type Si (P-doped), resistivity $50 \Omega \cdot \text{cm}$, *EPD* = 0; *p*-type Si (B-doped), resistivity $1000 \Omega \cdot \text{cm}$, *EPD* = 10^3 cm^{-2} . The FeCl_3 and $^{59}\text{FeCl}_3$ as iron sources for diffusion were used. The diffusion temperature was within the region of 800–1500 K. The distribution of diffused-in iron throughout the whole specimen as a function of diffusion temperature and time were determined by measuring the residual activity of ^{59}Fe as defined by Sieble¹⁸⁾. The diffusion profile of Fe^1 in the quenched specimens was determined by measuring the *ESR*-lines, the intensity of which is proportional to the concentration of iron interstitials. The quenching of specimens after the diffusion was performed by rapid cooling of specimens from high temperatures down to the cooled water or to liquid nitrogen. The estimated initial cooling rate was $10^4 \text{ }^\circ\text{C/s}$.

*Si single-crystals produced by *WACKER-Chemie GMBH, W. Germany*.

3. Results and discussion

The ^{59}Fe profiles as a function of diffusion depth for various temperatures are shown in Fig. 2. The distribution of iron over the diffusion depth clearly indicates the presence of two components, one as fast component and the other near the sample surface ($x = 0$) which is almost temperature independent. The diffu-

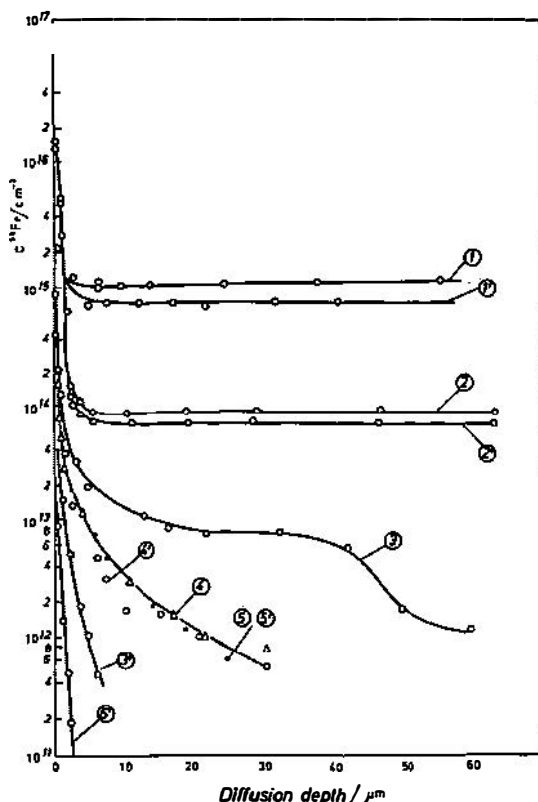


Fig. 2. The concentration of ^{59}Fe versus diffusion depth for the specimens of *p*-type Si, $50\ \Omega \cdot \text{cm}$, $EPD = 0$; (1) 1458 K, 30 min; (2) 1263 K, 30 min; (3) 883 K, 120 min; (4) 1163 K, 30 min.; (5) 1018 K, 120 min. For the specimens of *n*-type Si, $50\ \Omega \cdot \text{cm}$, $EPD = 0$: (1') 1458 K, 30 min.; (2') 1263 K, 30 min; (3') 883 K, 120 min; (4') 1163 K, 30 min; (5') 1018 K, 120 min; (6') 785 K, 120 min.

sion profile of ^{59}Fe in two specimens of Si from the same ingots (*p*-type Si, resistivity $50\ \Omega \cdot \text{cm}$, $EPD = 0$) which are different only in the grade of surface polishing, is shown in Fig. 3. Curve one belongs to the specimen with more relief surface (polished by carborundum powder 600 mesh and etched during 20 s in CP-4 solution). The diffusion profile of iron in the specimen with smoother surface is presented as curve two in Fig. 3. As the diffusion of iron was performed in both specimens under the same conditions ($T_D = 1473\ \text{K}$, $t_D = 30\ \text{min}$) the established difference in iron distribution near the zero depth is explained by different states of specimens surfaces. The iron is partly dissolved

through the whole specimens volume and partly is precipitated on the surface which, in dislocation free specimens, represents the most disordered state. In order to see the effect of dislocations on the iron precipitation process the diffusion, procedure was carried out in two specimens, one dislocation-free and the other with $EPD = 10^3 \text{ cm}^{-2}$, ($T_D = 1458 \text{ K}$, $t_D = 1800 \text{ s}$). The results of this experiment are shown in Fig. 4. It is clear that diffusion profile of iron in the specimen with $EPD = 10^3 \text{ cm}^{-2}$, similar to those earlier obtained^{1,2)}, depends very much on the dislocation density. The major quantity of iron is precipitated on dislocations the presence of which has a great influence on the distribution of iron interstitials as a fast diffusive component.

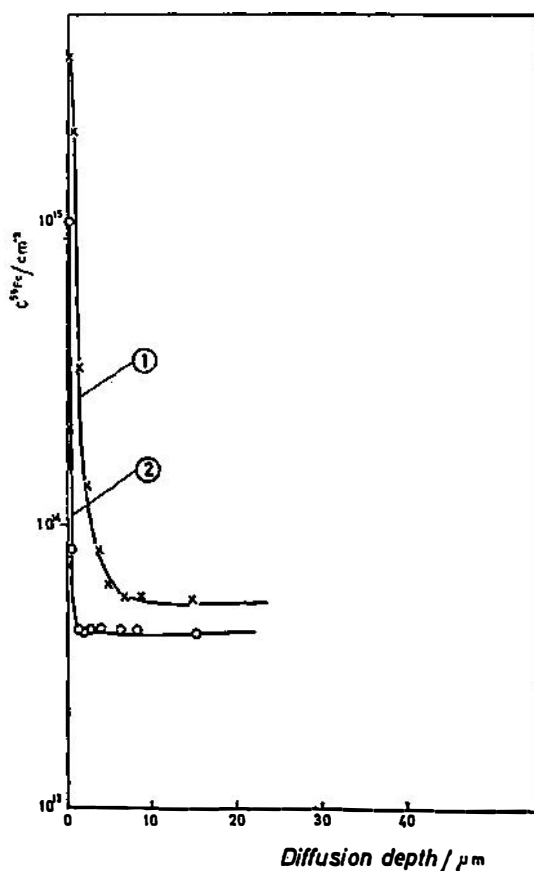


Fig. 3. The effect of surface state on the ^{59}Fe diffusion profile: (1) Specimen etched in CP-4 solution during 20 s; (2) Specimen etched in CP-4 during 100 s (Etching temperature was 0°C). Diffusion temperature $T_D = 1473 \text{ K}$ and time $t_D = 1800 \text{ s}$.

Considering the experimental data from Figs. 2, 3 and 4 it can be concluded that in dislocation-free silicon specimens the diffusion of iron occurs via a mechanism, presumably interstitial mechanism. It was established that during the

diffusion performance finishing, a certain quantity of iron precipitates on the surfaces. It was also shown that the dislocations act as more effective precipitation centers for iron interstitials.

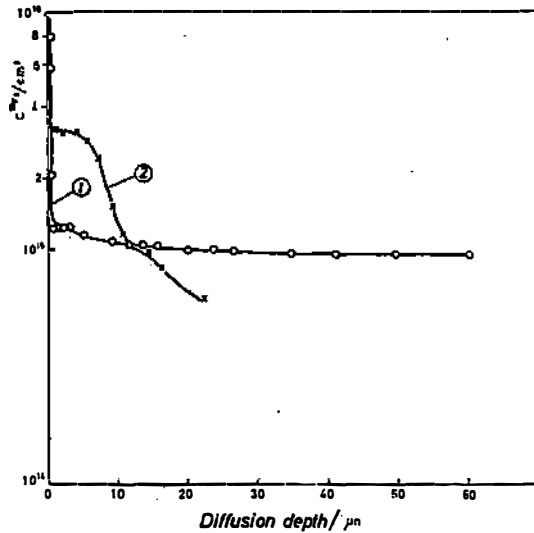


Fig. 4. The effect of dislocations on the diffusion profile of iron: (1) Diffusion profile in the specimen of Si with $EPD = 0$; (2) Diffusion profile in the specimen of Si with $EPD = 10^3 \text{ cm}^{-2}$.

The saturated values of ^{59}Fe concentration representing the total concentration of diffused-in iron, and the relative height for ESR -resonant lines, proportional to the concentration of ^{59}Fe interstitials as functions of reciprocal diffusion temperature are shown in Fig. 5. The slope of the curve from ESR data estimated to be 1.11 eV may be considered as an effective free energy of iron interstitials solubility in silicon. The ^{59}Fe data presented as the other curve indicate the larger effective free energy of about 1.78 eV. These data show that the amount of dissolved iron exists either as the substitutional iron- Fe^s or as the iron bonded with crystals imperfections such as the impurities of the acceptor type and point defects created at high temperatures which might be single vacancies and/or self-interstitials.

The numerous attempts have been made to identify the Fe^s in silicon in order to prove the dissociative mechanism of iron diffusion and its amphoteric character. It was assumed that substitutional iron, if exists, interacting with recoiled radiation-formed self-interstitials, could be dislocated into interstitial positions giving than a contribution to the intensity of ESR line. The quenched silicon specimens with diffused-in iron were irradiated by certain fluences of ^{60}Co gamma rays and by reactor neutrons in order to observe the reaction $\text{Fe}^s + \text{I}_{\text{Si}} \xrightarrow{\gamma, n} \text{Fe}^i$. However, the experiments performed to confirm this reaction failed either because Fe^s does not exist or the process of Fe^i creation by radiation is suppressed by iron precipitation and/or association with lattice defects. The above experimental results suspecting the dissociative mechanism favour the interstitial mechanism

of iron diffusion in silicon. It means that single-vacancies as lattice defects the iron interstitials may associate with would be excluded from further consideration, particularly when the diffusion has to be performed above 1000 K. Above this

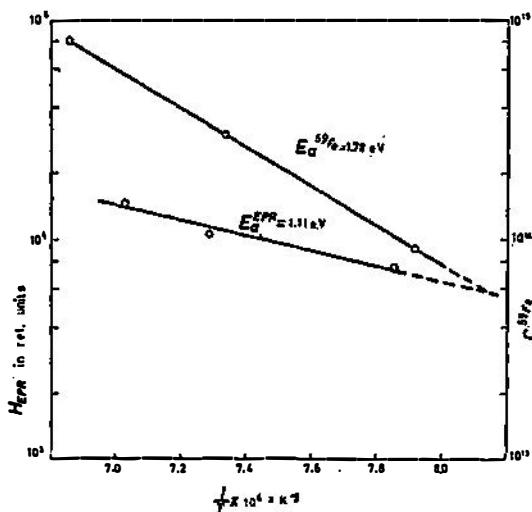


Fig. 5. The concentration of diffused-in iron versus the reciprocal diffusion temperature as determined by ^{59}Fe tracer and by ESR-resonant line of Fe^{I} .

temperature there are predictions^{6,7)} favouring self-interstitials to be predominant thermal defects in equilibrium concentration. So the above mentioned associations of iron which should be in an equilibrium with the dissolved iron interstitials may be regarded as a complex consisting of iron and self-interstitial originating from the reaction $\text{Fe}^{\text{I}} + \text{I}_{\text{Si}} \rightleftharpoons (\text{Fe}^{\text{I}} - \text{I}_{\text{Si}})$. These complexes in some respect could be considered as the geneses of further growing of micro-defects already observed in quenched silicon by the transmission electron microscopy (TEM)^{11,12)}. Having in mind the fact that Fe^{I} migrates as positive ion at high temperatures and if the assumption of $(\text{Fe}^{\text{I}} - \text{I}_{\text{Si}})$ pairs formation is correct, than the self-interstitials could be considered as negatively charged thermal defects able to associate with mobile iron interstitials via the coulombic attraction. The cross section for this reaction must be considerably large because of the great mobility of both self-interstitials and iron interstitials at high temperatures.

As a suggestion for further work it would be useful to reconsider the electrical properties of quenched silicon with and without diffused-in iron in order to establish the origin of $E + 0.4 \text{ eV}$ energy level which has been assigned to many defects as to iron interstitial^{10,13)}, to self-interstitial¹⁹⁾, to aluminium interstitial²⁰⁾ etc.

4. Conclusion

The ESR data about Fe^{I} and ^{59}Fe data about the total concentration of Fe in quenched silicon in their qualitative significance as presented in this work,

gave a few essential conclusive remark. The distribution of iron concentration versus the diffusion depth as well as the irradiation data when the reaction $Fe^s + I_{Si} \xrightarrow{\gamma, \beta} Fe^i$ has not been confirmed suggest an interstitial mechanism of iron diffusion in silicon. The earlier proposed dissociative mechanism based on the assumption that single-vacancies are dominant thermal defects in equilibrium at diffusion temperatures and that iron behaves as an amphoteric impurity in silicon should be suspected. The dissolved iron interstitials precipitate easily on the dislocation-free specimens surfaces and more effectively on the dislocations if they are present in as-grown single-crystals of silicon. In dislocation-free specimens and in the specimens containing a certain dislocation density the diffusion profiles of diffused-in iron are obtained to be quite different. So one would be very careful in the quantitative treatment of diffusion mechanism of iron in silicon which is very specific in the specimens with and without dislocations. It was established that a quantity of diffused iron interstitial is associated with thermal defects i. e. with self-interstitials that are presumed to be the dominant lattice defect in equilibrium at diffusion temperatures. The proposed complex of iron with self-interstitial, $(Fe^i - I_{Si})$ has been considered as a geneses for further growing of micro-defects already observed in quenched silicon by TEM.

References

- 1) D. J. Struthers, J. Appl. Phys. **27** (1956) 1560;
- 2) B. C. Collings and O. R. Carlson, Phys. Rev. **108** (1957) 1409;
- 3) J. B. Masters, Sol. State Comm. **9** (1971) 283;
- 4) A. J. Van Vechten, Inst. Phys. Conf. Ser. **23** (1974) 2•2;
- 5) Y. H. Lee, R. L. Kleinhenz and J. W. Aorbett, Appl. Phys. Lett. **31** (1977) 142;
- 6) A. Seeger, W. Frank and V. Gösele, I. P. C. Ser. **46** (1979) 148;
- 7) W. Frank, V. Gösele and A. Seeger, Inst. Phys. Conf. Ser. **46** (1979) 514;
- 8) T. N. Bendik and S. L. Milevskii, Dokl. Akad. Nauk SSSR **195** (1970) 107;
- 9) E. Weber and G. H. Roitte, Appl. Phys. Letters **33** (1978) 433;
- 10) H. Feichtinger, Inst. Phys. Conf. Ser. **46** (1978) 528;
- 11) A. Cullis and L. Katz, Phil. Mag., Vol. **30** (1974) 529;
- 12) D. Kostoski, M. Stojić, V. Spirić and F. Phillipp, Fizika **12** (1980) Suppl. 1;
- 13) A. I. Dyatlov, L. M. Kapitanova, A. A. Lebelev, M. A. Pogorski and T. A. Sloposlinikova, Phys. Semicond. **11** (1977) 951;
- 14) H. H. Woodbury and W. G. Ludwig, Phys. Rev. **117** (1960) 102;
- 15) W. G. Ludwig and H. H. Woodbury, Sol. Stat. Phys. **13** (1962) 223;
- 16) A. Mayer, Solid State Technol. **15** (1972) 38;
- 17) M. Stojić, Phys. Stat. Sol. (a) **70** (1982) K 39;
- 18) P. Seibel, Int. J. Appl. Radiant. Isotopes **15** (1964) 697;
- 19) W. Frank, Inst. Phys. Conf. Ser. **23** (1975) 23;
- 20) M. Cherki and A. H. Kalma, Phys. Rev. **B1** (1970) 647.

GVOŽĐE U SILICIJUMU I NJEGOV ODNOS PREMA TERMIČKIM
DEFEKTIMA

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Originalni naučni rad

Osobine gvožđa u zakaljenim monokristalima silicijuma i njegov odnos prema termičkim defektima proučavani su metodom radioaktivnog obeleživača i ESR-spektroskopijom. Ustanovljeno je da gvožđe difunduje u silicijumu intersticijalnim mehanizmom. U procesu kaljenja gvožđe delimično ispada iz rastvora i precipitira na površini uzorka i znatno efikasnije na dislokacijama. Precipitacija posebno na dislokacijama bitno utiče na profil difundovanog gvožđa. Izvesna količina intersticijalnog gvožđa asocira s termičkim defektima tj. sa sopstvenim intersticijama gradeći ($Fe^I - I_{Si}$) parove. Smatra se da su ti parovi centri daljnjeg rasta mikrodefekata koji su ranije otkriveni u zakaljenom silicijumu metodom transmise elektronske mikroskopije.