IRON AS AN IMPURITY IN SILICON

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Abstract: The behaviour of Fe in Si has been studied by Fe^{59} radioactive tracers method and ESR measurement of Fe-interstitial resonant line. The major quantity of Fe^{59} precipitates on the specimens surfaces ($6 \times 10^{16} cm^{-3}$). The interstitial mechanism of iron diffusion in Si is proposed. The concentration of diffused-in Fe^{59} depends on the concentration of native iron which is present in almost all Si crystals. At room temperature, unstable Fe interstitials do not interact with selfinterstitials and vacancies produced by Co^{60} gamma rays.

1. INTRODUCTION

The behaviour of Fe in Si has recently aroused a considerable interest. Firstly, the Fe contamination on Si surface diffuses with ease into the bulk and precipitates in the regions without any recognizable disturbances. Secondly, Fe in Si is highly suitable for obtaining information on the nature of dominant intrinsic defects by studying quenched-in Fe interstitial which could be identified by its electronic level, $E_V + 0.4$ eV /1/ or,more specifically, by its ESR signal at $g = 2.070$ /2/. The absence of this signal in the slowly cooled solid solution of Fe in Si indicates that under the nearly equilibrium conditions Fe is either incorporated substitutionally or precipitated. In rapidly quenched specimens from temperatures above 1000 K, a detectable fraction of Fe atoms is found as Fe^{o} in interstitial sites of Td symmetry /3,4/.

If Fe exists in Si in both substitutional Fe^{s} and interstitial Fe^{i} positions, than it diffuses via dissociative mechanism described by $Fe^{i} + V \rightleftarrows Fe^{s}$. This mechanism requires vacancies to be lattice defects in equilibrium at high temperatures. Collins and Carlson /5/ discovered that Fe^{59} tracers diffuse into Si via two different mechanisms. The faster one is assigned to the diffusion of Fe interstitials and the slower component to the diffusion of substitutional Fe atoms via selfinterstitials or/and vacancies. These contradictions should be solved precisely if the general controversy in the nature of intrinsic defects in equilibrium at high temperatures were to be solved. Whereas some authors /7,8/ maintain that in Si the thermal defects are vacancies, the Stuttgart group /9,10,11,12,15/ pointed out that experimental evidences favour selfinterstitials.

The aim of our work is to give some contribution to solving the mentioned controversy using the diffusion of Fe^{59} tracers and gamma rays irradiation of specimens under various conditions, as well as the ESR measurements.

2. EXPERIMENTAL

The used Si specimens were cut from /111/ oriented dislocation free wafers with a resistivity of 5 Ohm. cm (p-type Si, boron doped), and 50 Ohm. cm (n-type Si, phosphorus doped). The $FeCl_3$, $Fe^{59}Cl_3$ and metallic Fe deposited on the specimens surface were used as impurity sources for diffusion of Fe in Si. Generally, the specimens after coating with Fe were encapsulated in the evacuated quartz ampula heated at diffusion temperatures (1200-1500 K) during 30 minutes, and then quenched by dropping the ampula into the water bath. Similar procedure has been performed for the controlling specimens that are used to compare the properties of the quenched specimens with and without iron.

The concentration of the diffused-in iron vs. diffusion depth was determined by Fe^{59} tracers method, for both p-type Si and n-type Si, quenched from high temperatures. The properties of interstitial Fe^{o} were studied by ESR-spectrometry in an X-band cavity ($V = 9.27$ GHz) at the liquid nitrogen temperature. Some of the quenched specimens with the diffused-in Fe have been irradiated at room temperature by Co^{60} gamma rays (4×10^{12} photons $cm^{-2}s^{-1}$). The ESR signal of Fe^{o} has been controlled after certain radiation doses in order to correlate its variation with intrinsic lattice defects formed by gamma rays.

3. RESULTS AND DISCUSSION

Fig. 1 shows the concentration of the radioactive iron, Fe^{59}, as a function of a diffusion depth for p-type Si (curves 1 and 3) and n-type Si (curves 2 and 4), for the diffusion performed in 30 minutes at temperatures 990°C and 1185°C, respectively. These data indicate that two species of iron might be present: the "slow" one with max. Fe^{59} concentration at zero depth about $6 \times 10^{16} cm^{-3}$ which is almost temperature independent, and the fast one with Fe^{59} concentration extrapolated to zero depth of about $2\text{-}3 \times 10^{11} cm^{-3}$ at 990°C and $3\text{-}4 \times 10^{12} cm^{-3}$ at 1185°C.

Because of the temperature independence of the diffusion depth we assumed that the "slow" diffused-in component belongs to Fe^{59} precipitated on the specimens surface. We have proved this assumption by diffusing Fe^{59} under the same conditions into two identical specimens which are different only in the grade of surface polishing. The results are also shown in Fig. 1. We established that the "diffusion" depth of the slow Fe^{59} component is twice smaller in the specimen with better polished surface(points in squares) as compared with the same for specimen having a low grade of surfac- polishing(point in circles).

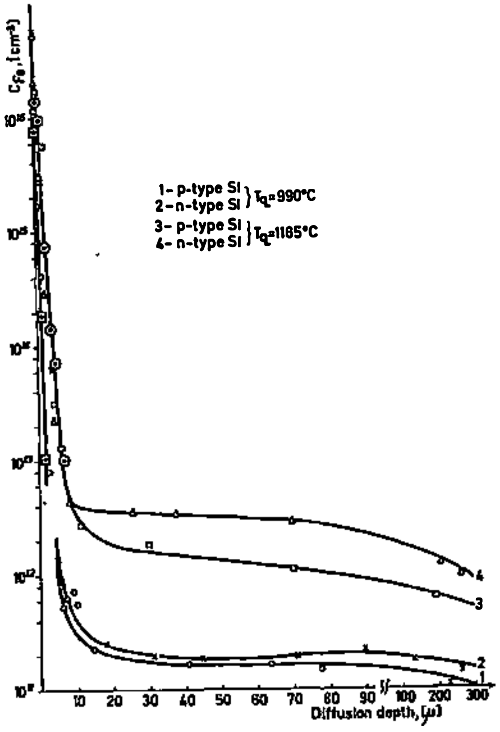

Fig. 1. The concentration of Fe^{59} vs. Diffusion depth

The fast diffused-in component was assigned to Fe^{59} interstitials identified by ESR-resonante line(g= 2.070, v= 9.27 GHz) which is generaly used in the study of Fe^{o} in Si /2,3,13,14/.The concentration of interstital Fe^{59} is far below the already established solid solubility of Fe in Si which is,depending on the temperature,-rom 10^{13} to 10^{17} cm^{-3} /4,5,6,13/.Such a low concentration could be explaned in two different ways.Firstly,because of the low quenching rate the major quantity of iron may precipitate on the cpecimen surface during the cooling.Secondly,the concentration of the diffused-in Fe^{59} could be limited by the quantity of native iron introduced into the crystals during their growth.Namely,when the native iron moves rapidly from precipitates(until they become emptied) to the interstitial sites upon heat treatment, the outside iron can enter only in a quantity to reach the solid solubility of Fe characteristic for the actual temperature.While the concentration of native iron remains constant,the concentration of Fe^{59} increases with increasing of the diffusion temperature since the Fe solubility increases too.The ESR data are consistent with the second explanation.

The temperature dependence of solid solubility of interstitial Fe, as it is already known /3/, obeys the Arrhenius law, where the Gibbs free energy has been interpreted either as the Gibbs free energy of solution of Fe interstitials (LKC-model B) /13/, or as the

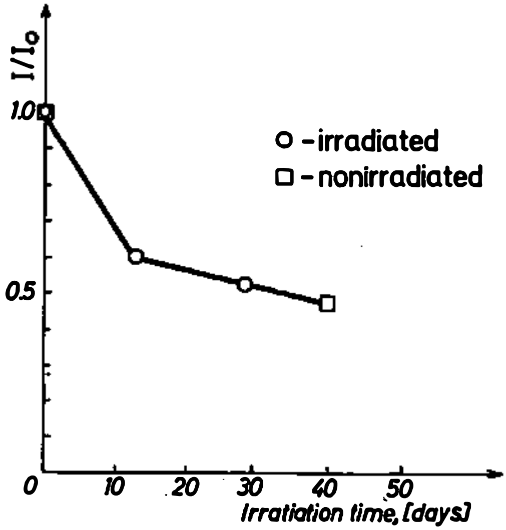

Fig. 2. Relative intensity of ESR resonant line of Fe^o vs. time for irradiated and nonirradiated specimens of p-type Si

effective Gibbs free energy of the decay process of supersaturated concentration of selfinterstitials, which are taken to be dominant defects at high temperatures in Si. If the substitutionally dissolved iron exists, the mentioned decay occures via reaction: selfinterstitial + substitutionally dissolved $Fe^S \rightarrow$ interstitial Fe^o (model FGS) /15/.

In order to give some contribution in considering the above models, we performed an experiment based on the following assumptions: If the quenched specimens Fe^S and Fe^i are in equilibrium and if the intrinsic lattice defects are introduced by the appropriate irradiation (electrons or gamma rays), than one can expect the next reactions to occur: Fe^S + selfinterstitial$\rightarrow Fe^i$ (ESR-line increases), reaction similar as for Al in Si (16); and/or Fe^i + vacancy $\rightarrow Fe^S$ (ESR-line decreasing). We used two similar specimens quenched after an iron diffusion from the same temperature and one of them has been irradiated by Co^{60} gamma ray's at room temperature. The results of irradiation are shown in Fig. 2. As it can be seen, the concentration of Fe^o decreases permanently in the same way for irradiated and controlling specimen. This process which is not affected by intrinsic lattice defects induced by radiation could be explained only as the precipitation of interstitial iron, even at room temperature.

Finally, the results of this work can be summarized as follows:

- Iron diffuses into Si via an interstitial mechanism;
- Concentration of the diffused-in iron depends very much on the concentration of native iron which is present almost in all Si crystals;
- The intrinsic lattice defects (vacancies and selfinterstitials) induced by Co^{60} gamma rays at room temperature do not remarcably interact with Fe interstitials;
- The absence of substitutional iron does not exclude selfinterstitials to be predominant defects at quenching temperatures above 1ooo°C; on the contrary, the existence of vacancies is questionable.

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