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An investigation of the rate of Si self-interstitial annihilation at dislocations

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Abstract. Two different approaches are proposed for calculating the dislocation sink efficiency γ for silicon self-interstitials: a numerical calculation and an analytical approach, the results of which are very close. The differences between the calculated and measured values of γ is interpreted in terms of the effective dislocation density, and this new hypothesis is introduced in the analytical model leading in a first approximation to a linear relationship between γ and the proportion of mobile dislocations (via a climbing process).

1. Introduction

It is now well established that investigations of Au [1–3], Pt [3] and Zn [4] diffusion can be used for the study of self-interstitial (Si_i) characteristics in Si, such as their distribution, diffusivity and equilibrium concentration. Dislocations are known to enhance the self-interstitial annihilation rate, which leads to an increase in the impurity concentration if the impurity diffuses via the so-called kick-out mechanism [5]. If, as commonly assumed [5], the rate of Si_i annihilation at dislocations is high enough, the self-interstitial lifetime is controlled by their diffusion to dislocations and should depend only on the dislocation density. However, investigations of gold-diffused crystals have shown [6–9] that in some cases the rate of self-interstitial annihilation at dislocations is much lower in Czochralski-grown (Cz) Si than in floating-zone (FZ) Si. Thus, in such Cz crystals the limiting process for interstitial annihilation is not only the diffusion to sinks but also the capture by dislocations. This means that dislocation climbing in these crystals due to Si_i absorption is strongly restricted. In such cases, measurements of impurity concentration in dislocated samples allowed the self-interstitial absorption by dislocations and its dependence on impurity content, thermal treatment conditions, etc, to be studied. In the present paper, we attempted to work out what it is possible to learn about the dislocation properties from such experiments.

2. Experimental details

The experiments were carried out on FZ (111) boron-doped ($N_A = 1.2 \times 10^{16}$ cm^{-3}) and Cz (001) boron-doped ($N_A = 9 \times 10^{15}$ cm^{-3}) silicon wafers that were 525 μm thick. After chemical etching in CP4, dislocation sources were nucleated by scratching the surface along the sample length parallel to the $\langle 110 \rangle$ direction with a diamond tip subjected to a constant

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load (0.3 N). Then the samples were elastically bent at room temperature in a cantilever mode and were heated under stress at 700 °C for 0.5 h in a pure argon atmosphere. Due to the deformation procedure used, the dislocation density varies along the sample length from 0 to about 10^6 cm^{-2}. A gold layer 100 nm thick was plated by sputtering onto the sample surface, then gold diffusion was performed in the temperature range from 850 to 1000 °C in pure argon. To avoid any surface effect on the gold concentration, a layer 200 μm thick was mechanically removed from the surface, and the new surface was etched in CP4. After selective chemical etching in Sirtl or Secco etchant to reveal the dislocations, Schottky barriers were formed on this surface by thermal evaporation of Al. The ohmic contacts were prepared on the back surface using indium–gallium alloy. The dislocation density was measured inside every diode. The gold concentration was determined as a concentration of donor centres with the energy level $E_t = E_v + 0.34$ eV using the DLTS technique with a lock-in amplifier as a correlator. Some DLTS measurements were performed on as-deformed samples. Due to the clean deformation conditions and relatively small dislocation densities involved, the dislocation-related DLTS peaks were negligible as compared to gold-related ones; therefore the DLTS signal of the dislocations did not influence the gold concentration measurements.

3. Results

In agreement with previous observations [8, 9] the substitutional gold concentration $N^{d}_{Au_s}$ was found to increase with dislocation density following the $(N_D)^{1/2}$-law for both types of sample, and over the whole temperature range used. The gold concentration in the samples with dislocations is given by [5]

$$N^{d}_{Au_s} = N^{lim}_{Au_s}(2D^{*}_{I}t)^{1/2}(\gamma N_D)^{1/2} \tag{1}$$

where $N^{lim}_{Au_s}$ is the solubility limit for substitutional gold at the diffusion temperature, $D^{*}_{I} = N^{eq}_{I}D_I/N^{lim}_{Au_s}$ is the effective diffusivity of Si_i, N^{eq}_{I} and D_I are, respectively, the Si_i equilibrium concentration and the diffusion coefficient, t is the annealing time, and γ is a coefficient describing the efficiency of dislocations as sinks for Si_i. In our experiments we have measured substitutional gold concentrations and dislocation densities. Since $N^{lim}_{Au_s}(2D^{*}_{I})^{1/2}$ has been obtained from measurements of gold concentration in parts of the same sample without dislocations at each temperature studied [9], γ can be obtained directly at each temperature.

For FZ Si, γ was found to be equal to about 0.1 and to be practically independent of the diffusion temperature (γ might slightly decrease as the diffusion temperature increases). For Cz Si, γ was always smaller than that for FZ Si at every temperature and its temperature dependence is much more pronounced (figure 1). In fact, for Cz crystals, γ was found to increase with temperature and its Arrhenius curve showed an activation energy of about 1–1.5 eV.

4. Discussion

The increase of the gold concentration with dislocation density as $(N_D)^{1/2}$ demonstrates that, for both types of crystal, the Si_i annihilation is controlled mainly by dislocations, and that the theory developed for gold diffusion in crystals with dislocations [5] can be used. In the framework of this model the gold concentration depends on the self-interstitial lifetime, which is assumed to be equal to $\tau = (\gamma N_D D^{*}_{I})^{-1}$. Therefore to understand the reasons for

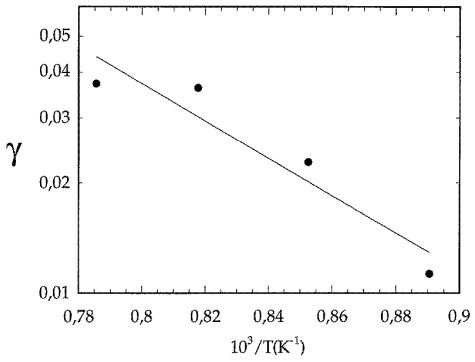

Figure 1. The measured sink efficiency γ as a function of temperature for Czochralski-grown silicon.

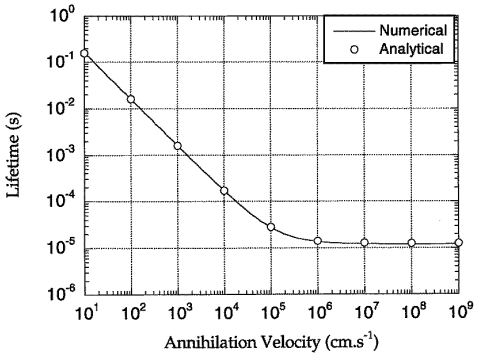

Figure 2. A comparison between numerical (line) and analytical (empty circles) calculations of the Si_i lifetime for various annihilation rates. $a = 1$ nm; $N_D = 10^6$ cm^{-2}.

the decrease in γ it is necessary to calculate the self-interstitial lifetime in the samples with dislocations as a function of dislocation characteristics. In the common case with randomly distributed dislocations it seems hopeless to make such calculations. But we propose that for the dislocation structure used, two methods of calculation presented below will give a good approximation to the real situation.

The first method consists in a numerical calculation of the self-interstitial distribution under the assumptions that all dislocations are parallel, they form a regular square grid with a distance between them of $h = (N_D)^{-1/2}$, the dislocation capture radius is a, the rate of self-interstitial annihilation at the surface of cylinder with this radius is S_{an}, and self-interstitial annihilation in the bulk can be neglected. To reduce the problem, we can consider just one square with a side equal to h and with a dislocation at its centre. It is obvious that the self-interstitial flow through the square boundaries is equal to 0, which gives us the boundary condition for a solution of the diffusion equation. The problem has been solved using finite-difference schemes on a special nonuniform grid [10]. Then the effective self-interstitial lifetime can be obtained using the relation

$$N_I^{av} = \int N_I(x, y)\ \mathrm{d}x\ \mathrm{d}y = g\tau \tag{2}$$

where N_I^{av} is the average concentration of self-interstitials, $N_I(x, y)$ is their calculated distribution, and g is the self-interstitial generation rate which was assumed to be homogeneous in the bulk. The calculated dependence of the effective Si_i lifetime on the surface recombination rate for $a = 1$ nm and a dislocation density $N_D = 10^6$ cm^{-2} is presented in figure 2.

In the second approach we assumed that all self-interstitials generated inside a cylinder with radius $R = (\pi N_D)^{-1/2}$ can annihilate only at a dislocation situated along the axis of this cylinder. In this case we can write for the Si_i flow through the surface of a cylinder of radius r

$$2\pi r \frac{\partial N_I}{\partial r} D_I^* = g\pi(R^2 - r^2) \tag{3}$$

and by integration of (3) we obtain

$$N_I = \frac{g}{2D_I^*}\left(R^2 \ln r - \frac{r^2}{2} + A\right). \tag{4}$$

The constant A can be determined from the boundary condition

$$\left(D_{\mathrm{I}}^{*}\frac{\partial N_{\mathrm{I}}}{\partial r}\right)_{r=a} = N_{\mathrm{I}}S_{\mathrm{an}}$$

and for $a \ll R$ it is

$$A = R^2\left(\frac{D_{\mathrm{I}}^{*}}{aS_{\mathrm{an}}} - \ln a\right) \tag{5}$$

thus giving

$$N_{\mathrm{I}} = \frac{g}{2D_{\mathrm{I}}^{*}}\left(R^2\ln\frac{r}{a} - \frac{r^2}{2} + R^2\frac{D_{\mathrm{I}}^{*}}{aS_{\mathrm{an}}}\right). \tag{6}$$

Using the relation

$$N_{\mathrm{I}}^{\mathrm{av}} = \tau g = \frac{1}{\pi R^2}\int_a^R N_{\mathrm{I}}(r)\,2\pi r\ \mathrm{d}r \tag{7}$$

we obtain the following relation for τ:

$$\tau = \frac{R^2}{2D_{\mathrm{I}}^{*}}\left(\ln\frac{R}{a} - \frac{3}{4} + \frac{D_{\mathrm{I}}^{*}}{aS_{\mathrm{an}}}\right). \tag{8}$$

The results of calculations using (8) for the same parameters as used for numerical calculations are also presented in figure 2. A comparison of results reveals a very good correlation between the τ-values obtained using these two approaches. If γ is assumed in accordance with [5] to be equal to $(\tau N_{\mathrm{D}}D_{\mathrm{I}}^{*})^{-1}$, then for such an arrangement of dislocations

$$\gamma = 2\pi\left(\ln\frac{R}{a} - \frac{3}{4} + \frac{D_{\mathrm{I}}^{*}}{aS_{\mathrm{an}}}\right)^{-1} = 4\pi\left[-\ln(\pi a^2N_{\mathrm{D}}) - \frac{3}{2} + 2\frac{D_{\mathrm{I}}^{*}}{aS_{\mathrm{an}}}\right]^{-1} \tag{9}$$

and is indeed close to 1. Thus if $2D_{\mathrm{I}}^{*}/(aS_{\mathrm{an}})$ is low enough, we can take into account just the first term in square brackets of (9), and for $N_{\mathrm{D}} = 10^6$ cm^{-2} we find that γ is equal to 0.73 for $a = 0.5$ nm and equal to 0.80 for $a = 1$ nm.

From (9) it is easy to see that in the common case the decrease of the γ-value may formally be correlated with a decrease of the effective dislocation density $N_{\mathrm{D}}^{\mathrm{eff}}$ ($N_{\mathrm{D}}^{\mathrm{eff}} < N_{\mathrm{D}}$) which is able to annihilate $\mathrm{Si_i}$, or with a reduction of the annihilation rate at any dislocation site (a decrease of a or S_{an}). The first case assumes that only some fraction of the dislocations can climb, i.e. that dislocation climbing is essentially inhomogeneous; the second one means that the gold diffusion leads to approximately homogeneous climbing along a dislocation but with a decreased rate of self-interstitial annihilation. As seen from figure 2, if a decrease of about a factor of ten (as for FZ Si) or about two orders of magnitude (as for Cz Si) is associated with a decrease of S_{an}, to change τ from its saturated value to a value ten times higher it is necessary to drop the annihilation rate down by two to three orders of magnitude. Such a drop in S_{an} can be associated with a potential barrier for self-interstitials, e.g. due to the elastic stress created by impurities gathered by dislocations or with dislocation locking by impurities. Such a locking of moving dislocations was observed in Si with high oxygen concentration [11]. But in gold diffusion experiments the rate of dislocation climbing is very small; therefore it seems more probable that oxygen gettered by dislocations precipitates, forming obstacles to climbing.

Under this assumption the dislocation–oxygen interaction decreases the fraction of dislocations which can climb. In fact, some distribution of distances between oxygen-related obstacles exists, and thus only dislocation segments whose length exceeds some

critical value can climb. Let us denote as k the ratio between the total length of such mobile segments and the total dislocation length, so k can be expressed by

$$k = N_{\mathrm{D}}^{\mathrm{eff}}/N_{\mathrm{D}}. \tag{10}$$

Then replacing N_{D} by $N_{\mathrm{D}}^{\mathrm{eff}}$ in (8) gives

$$\gamma = 4\pi k\left[-\ln(\pi a^2 k N_D) - \frac{3}{2} + 2\frac{D_{\mathrm{I}}^*}{aS_{\mathrm{an}}}\right]^{-1}. \tag{11}$$

If k is small enough and the average length of the climbing segments of dislocations is much smaller than the distance between these segments, it would be better to describe the dislocation-related self-interstitial sink geometry in terms of spherical particles with radius b being present in a concentration C_{D}. If n is the number of climbing segments per unit length of dislocation, then $C_{\mathrm{D}} = nN_{\mathrm{D}}$. The average distance between defects R_{s} can be obtained from the relation

$$\frac{4}{3}\pi R_{\mathrm{s}}^3 C_{\mathrm{D}} = 1. \tag{12}$$

So from (12)

$$R_{\mathrm{s}} = \sqrt[3]{\frac{3}{4\pi C_{\mathrm{D}}}} = \sqrt[3]{\frac{3}{4\pi n N_{\mathrm{D}}}} = \sqrt[3]{\frac{3b}{2\pi k N_{\mathrm{D}}}} \tag{13}$$

where $k = N_{\mathrm{D}}^{\mathrm{eff}}/N_{\mathrm{D}} = 2bn$. In this case the diffusion equation can be solved in a way similar to that used for long dislocations, and for γ we obtain

$$\gamma = 3b\left[R_{\mathrm{s}}^3 N_{\mathrm{D}}\left(1 - 1.8\frac{b}{R_{\mathrm{s}}} + \frac{D_{\mathrm{I}}^*}{S_{\mathrm{an}}b}\right)\right]^{-1} = 2\pi k\left[1 - 1.8b\sqrt[3]{\frac{2\pi k N_{\mathrm{D}}}{3b}} + \frac{D_{\mathrm{I}}^*}{S_{\mathrm{an}}b}\right]^{-1}. \tag{14}$$

It is easy to see from (11) and (14) that in a first approximation k is proportional to γ and can be evaluated using experimental data for γ. For high values of S_{an} and taking $a = b$, the ratio between k-values obtained using these two approaches is about eight. Relation (11) gives for k, in the samples doped with boron to a concentration of about 10^{16} cm^{-3}, a value of about 0.1 for FZ Si over the whole temperature range used, and about 10^{-2} at 850 °C for Cz Si. Using (14) gives values eight times higher for k, but for these values it seems that relation (11) is preferable, and relation (14) should be used for smaller values of k. Thus in FZ Si only 10% of dislocations are mobile. In Cz Si the proportion of mobile dislocations is even ten times smaller at 850 °C, and increases exponentially with temperature. This increase can be explained by a temperature-stimulated release of dislocation segments from oxygen-related obstacles.

5. Conclusion

From the solution of the diffusion equation for self-interstitials, the relationship between (i) the dislocation efficiency γ as a sink for self-interstitials and (ii) the dislocation capture radius and recombination rate has been obtained. It has been shown that using the relation obtained for small values of γ the proportion of dislocations which can climb in gold diffusion conditions due to absorption of self-interstitials can be estimated.

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