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Nucleation and growth of vacancy agglomeration in CZ silicon crystals

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Abstract When concentration of vacancies in a CZ silicon crystal is defined by molar fraction X_B, the degree of super-saturation σ is given by $[X_B - X_{BS}]/X_{BS} = X_B/X_{BS} - 1 = \ln (X_B/X_{BS})$ because X_B/X_{BS} is nearly equal to unity. Here, X_{BS} is the saturated concentration of vacancies in a silicon crystal and X_B is a little larger than X_{BS}. According to Bragg-Williams approximation, the chemical potential of the vacancies in the crystal is given by $\mu_B = \mu^0 + RT \ln X_B + RT \ln \gamma$, where R is the gas constant, T is temperature, μ^0 is an ideal chemical potential of the vacancies and γ is an adjustable parameter similar to the activity of solute in a solution. Thus, $\sigma(T)$ is equal to $(\mu_B - \mu_{BS})/RT$. Driving force of nucleation for the vacancy agglomeration will be proportional to the chemical potential difference $(\mu_B - \mu_{BS})$ or $\sigma(T)$, while growth of the vacancy agglomeration is proportional to diffusion of the vacancies and grad μ_B.

1. Introduction

Vacancy agglomeration and oxygen precipitate in CZ silicon crystals are still very important problems although they have been researched by Voronkov [1, 2] and others [3,4]. The phenomena are discussed here based on Bragg-Williams approximation.

2. Analytical study

2.1. Degree of super-saturation

When concentration of vacancies in a CZ silicon crystal is defined by the molar fraction:

$$X_B = n_B/(n_A + n_B) = N_B/(N_A + N_B), \tag{1}$$

the degree of super-saturation is given by

$$\sigma(T) = [X_B - X_{BS}]/X_{BS} = X_B/X_{BS} - 1 = \ln (X_B/X_{BS}) \tag{2}$$

because X_B/X_{BS} is nearly equal to unity. Here, n_{BS} is the saturation concentration of vacancies in a silicon crystal of n_A moles at temperature T, n_B is a little larger than n_{BS} for a super-saturation where $N_A = N_o n_A$, $N_{BS} = N_o n_{BS}$, $N_B = N_o n_B$ and N_o is Avogadro's number. According to Bragg-Williams approximation, the chemical potential of the vacancies is given by

$$\mu_B = \mu^0 + RT \ln X_B + RT \ln \gamma, \tag{3}$$

where R is the gas constant, μ^0 is an ideal chemical potential of the vacancies and γ is an adjustable parameter similar to the activity coefficient of solute in a regular solution [5]. Thus, we have

$$\sigma(T) = (\mu_B - \mu_{BS})/RT. \tag{4}$$

2.2. Nucleation

The probability p that one of the lattice points is occupied by a vacancy is given by

$$p = N_B/(N_A + N_B) = X_B, \tag{5}$$

Thus the probability P that this point is occupied by a vacancy in excess of its thermal equilibrium is given by

$$P = p\,(N_B - N_{BS})/N_B = (N_B - N_{BS})/(N_A + N_B) = X_B - X_{BS} = \sigma(T)\, X_{BS}. \tag{6}$$

Assuming that excess α vacancies will successively merge, they will act as a nucleus for vacancy agglomeration. The probability of the nucleus formation is equal to P^α and thus the generation rate of the nuclei is given by

$$\partial m/\partial t = (P\, \nu\, e^{-U/kT})^\alpha = [\sigma(T)\, X_{BS}\, \nu\, e^{-U/kT}]^\alpha, \tag{7}$$

where m is the number of nuclei, U is the formation energy of a vacancy, ν is its frequency factor and k is Boltzmann factor [5].

2.3. Diffusion of vacancies

Diffusion flow density of the vacancies is given by

$$j = D_o\, e^{-E/kT} \text{ grad } \mu_B = D \text{ grad } \mu_B, \tag{8}$$

where D is the diffusion constant of vacancies, E is the

activation energy and D_o is the pre-diffusion constant.

2.4. Growth of the nuclei

Since a nucleus will grow into a vacancy agglomeration due to diffusion of the vacancies, the growth is an irreversible or nonequilibrium process governed by Onsager's relation. The vacancy and heat flow densities in a crystal, **j** and **q**, are respectively given by

$$-\mathbf{j} = L_{11}(\text{grad}\ \mu_B)/T + L_{12}\ \text{grad}(1/T) \quad (9a)$$

$$\mathbf{q} = L_{21}(\text{grad}\ \mu_B)/T + L_{22}\ \text{grad}(1/T). \quad (9b)$$

where L_{ij} is the Onsager coefficients and their mutual interaction coefficients are related as $L_{12}(\mathbf{B}) = L_{21}(-\mathbf{B})$ under a magnetic flux density: **B**.

On a growing interface of the vacancy agglomeration, the following relation exists.

$$\mathbf{q} + Q\,\mathbf{j} = \mathbf{q}_D, \quad (10)$$

where Q is the heat of vacancy formation. $\mathbf{q}_D$ is the heat flow density within the vacancy agglomeration and is given by

$$\mathbf{q}_D = L_D\ \text{grad}(1/T_D), \quad (11)$$

where T_D is the temperature within the agglomeration.

The thermal conductivity of a CZ Si crystal and that within an agglomeration are respectively given by

$$\chi = [L_{11}L_{22} - (L_{12})^2]/(L_{11}T^2) \quad (12a)$$

$$\chi_D = L_D/T_D^2. \quad (12b)$$

By substitution of Eqs. (9.b) and (11) into eq. (10), we have

$$Q\,\mathbf{j} = -L_{21}(\text{grad}\ \mu_B)/T - L_{22}\ \text{grad}(1/T) + L_D\ \text{grad}(1/T_D) \quad (13)$$

By elimination of (grad μ_B)/T in eq. (13) using eq. (9a), we have

$$\mathbf{j} = L_{11}(\chi\ \text{grad}\ T - \chi_D\ \text{grad}\ T_D)/(Q\ L_{11} - L_{12}) \quad (14)$$

using eqs. (12a and b). The deposition rate of vacancies: $\partial N_B/\partial t$ is related to

$$\partial N_B/\partial t + \text{div}\ \mathbf{j} = 0 \quad (15)$$

under assumption that the continuity relation of incompressible particles is formed. By substitution of eq. (14) into eq. (15), the growth rate is given by

$$\partial N_B/\partial t = -L_{11}(\chi\ \Delta T - \chi_D\ \Delta T_D)/(Q\ L_{11} - L_{12}) \quad (16)$$

Since agglomerated vacancies will make a cavity, we have the following equation:

$$\Delta T_D = 0 \quad (17)$$

Therefore, the agglomeration rate of vacancy [6] is given by

$$\partial\ N_B/\partial t = -L_{11}\chi\ \Delta T/(Q\ L_{11} - L_{12}) \quad (18)$$

3. Discussion and conclusions

1) The number of nuclei: m is linearly proportional to the duration when the crystal is kept at temperature T. While the nucleation rate: $\partial m/\partial t$ is drastically dependent upon the degree of super-saturation: $\sigma(T)$ as indicated in eq. (7), longer duration time at a fairly low temperature will create numerous nuclei for the vacancy agglomeration. However, very low temperature inhibits the nucleation process because the probability of positional exchange between vacancies and atoms is reduced.

2) Growth of the nuclei is caused by diffusion of the vacancies and then higher temperature will be more beneficial as discussed in eq. (8), but the nucleation rate will be lower because of decreasing $\sigma(T)$.

3) Equation (18) is a typical diffusion equation or Poisson's equation, which can be analytically and numerically solved.

4) From eq. (18), the vacancy flows concentrate at pointed ends, the tips of octahedral pyramidal cavities such as COP and LSTD, which are edges of negative crystals [7], and the periphery of thin plates such as stacking faults.

5) From a viewpoint of growth of "negative" crystals, the re-entrant angle is so effective for reducing nucleation difficulties that twinning with the negative crystals is frequently observed [7].

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