Nucleation barrier of voids and dislocation loops in silicon

T. Y. Tan, P. Plekhanov, and U. M. Gösele
Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708-0300

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We have calculated the nucleation energy barrier of voids and vacancy (V) type dislocation loops in Si under V-supersaturation conditions. The barrier of V-type dislocation loops is higher than that of voids by more than one order of magnitude, with the former exceeding 35 eV at attainable V-supersaturation levels. Thus, voids can be nucleated, but not dislocation loops. This provides an explanation for the observations that, in Si crystals grown under V-supersaturation conditions, voids exist but V-type dislocation loops do not. Voids seriously degrade the Si device gate oxide integrity. It is highly probable that the D-type swirl defects in Si are nanoscopic voids. Our calculated results have also provided information for limiting the formation temperature range of the D-swirl defects to be lower than ~1050 °C, and the Si V formation enthalpy to be above ~3.0 eV. © 1997 American Institute of Physics. [S0003-6951(97)04513-0]

In the ultralarge scale integration regime, very large diameter (up to 30 cm or beyond) Czochralski (CZ) Si crystal wafers will be used to increase manufacturing productivity. Also, very thin thermal SiO₂ films (under ~10 nm) will be used as gate insulators to enhance performances of the field effect transistors and capacitors. Recent studies using such wafers and SiO₂ films revealed that the gate oxide integrity may be degraded by the D-type swirl defects, a kind of grown-in point defect clusters in pristine Si crystals. In severe cases, a gate oxide may break down at only ~1/4 of the normal thermal SiO₂ breakdown strength, with the responsible defects being voids in Si reaching ~100 nm in size. When unaltered by processing, these voids are polyhedral-shaped consisting of thin oxide covered planes. They are suggested to be large-sized polyhedral-shaped consisting of thin oxide covered planes. They are suggested to be large-sized voids with oxide covered internal voids in FZ Si. Since CZ Si also contains oxygen, the nucleation of swirl defects is dependent upon the crystal growth rate and the thermal gradient ∇ at the Si crystal-melt interface, via the factor υ/∇. A small υ/∇ value leads to an I supersaturation, causing A defects to form, while a large υ/∇ value leads to a V supersaturation, causing D defects to form. From the gate oxide integrity study and related results, it may be inferred that D defects are nanoscale voids in FZ Si. Since CZ Si also contains oxygen, D defects in CZ Si should be small voids with oxide covered internal surfaces.

Thus, during Si crystal growth, the two-dimensional extended defect I-type dislocation loops form under I supersaturation, while the three-dimensional extended defect voids form under V supersaturation. The reason that these two kinds of defects are totally different in morphology must be related to the energetic factors governing their nucleation and growth processes. Without involving impurities, formation of I-type dislocation loops can substantially reduce an I supersaturation, but not large-sized I-type three-dimensional extended defects such as an I "self-precipitate," since it will incur a tremendously large strain energy in Si. Under V supersaturation, both dislocation loops and voids can form. Voids possess a surface energy but will not incur a large strain in Si. Thus, it is important to know whether formation of voids or formation of V-type dislocations is the dominant process under V-supersaturation conditions. In the present letter we show that formation of voids is favored over V-type dislocation loops via a nucleation barrier energy difference.

We examine the defect nucleation problem using the classical nucleation theory for the homogeneous process. Consider first that a V-type edge dislocation loop which may also contain an intrinsic stacking fault (SF). To form a loop of radius r_b, the crystal free energy is increased by πr_b²γ + 2πr_b(Γ/L), where γ is the intrinsic SF energy density, Γ/L is the edge dislocation energy per unit length given by Γ/L = μb²/2(4πr_b), and μ is the Si shear modulus. The loop is favored over a void of radius r_d, the crystal free energy is increased by 4πr_d²γ + πr_d²G, where r_d is the radius of the dislocation loop. The number of V consumed in forming the loop is πr_b²/2(4πr_b), and the net Si crystal free energy change is

$$\Delta G_d = \frac{\mu b^2}{2(1-\nu)} \left( \ln \frac{8a r_d}{b} \right) - \frac{\pi r_b^2}{\Omega} k_b T \ln \frac{C_V}{C_V^0}. \quad (1)$$
This energy is zero for \( r_v = 0 \), rises to a maximum at the critical size \( r_v = r_v^* \), and then decreases. At the energy maximum, the condition \( d(\Delta G_v)/dr_v = 0 \) yields

\[
2\pi r_v^* \gamma + \frac{\mu b^2}{2(1 - \nu)} \ln \frac{8\alpha r_v^*}{b - 2\pi r_v^* k_BT} b \ln \frac{C_v}{C_v^{eq}} = 0.
\]

(2)

\[
\Delta G_v^* = \pi (r_v^*)^2 \gamma + \frac{\mu b^2}{2(1 - \nu)} \ln \left( \frac{8\alpha r_v^*}{b - 1} \right) - \pi (r_v^*)^2 k_BT \ln \frac{C_v}{C_v^{eq}}.
\]

(3)

The quantity \( \Delta G_v^* \) is the energy barrier preventing loop nucleation from occurring. Consider now the nucleation of voids. To form a spherical-shaped void of radius \( r_v \), the crystal free energy is increased by \( 4\pi r_v^2 \sigma \), where \( \sigma \) is the Si surface energy density. In analogy to the dislocation case, the formation of the void leads to a decrease of the crystal free energy by \( (4\pi r_v^3/3! \) k\( b \) T \( \ln (C_v/C_v^{eq}) \)). Thus, the net Si crystal free energy change is

\[
\Delta G_v = 4\pi r_v^2 \sigma - \frac{4\pi r_v^3}{3} k_BT \ln \left( \frac{C_v}{C_v^{eq}} \right).
\]

(4)

This energy is zero for \( r_v = 0 \), rises to a maximum at the critical size \( r_v = r_v^* \), and then decreases. At the energy maximum, the condition \( d(\Delta G_v)/dr_v = 0 \) yields

\[
r_v^* = \frac{2\pi \sigma}{3} k_BT \ln \left( \frac{C_v}{C_v^{eq}} \right),
\]

(5)

\[
\Delta G_v^* = \frac{16\pi}{3} \Omega^2 \sigma^3 \left[ k_BT \ln \left( \frac{C_v}{C_v^{eq}} \right) \right]^2.
\]

(6)

Using the V-supersaturation value \( C_v/C_v^{eq} \) as the independent variable, we have calculated the critical values of \( r \) and \( \Delta G \) for both the dislocation and the void cases, respectively, using Eqs. (2) and (3), and Eqs. (5) and (6), from 900 to 1200 °C. The materials parameters used are \( \Omega = 2 \times 10^{-23} \text{ cm}^3 \), \( \sigma = 1230 \text{ ergs cm}^{-2} \), and \( \gamma = 60 \text{ ergs cm}^{-2} \) for the faulted dislocation loop and 0 ergs cm\(^{-2} \) for the perfect dislocation loop. \( \mu = 6.45 \times 10^{11} \text{ dyn cm}^{-2} \), \( \nu = 0.228 \), \( \alpha = 4 \), \( b = 3.135 \times 10^{-8} \text{ cm} \) for the faulted (111)/3 Frank partial dislocation loop, and 3.84 \times 10^{-8} \text{ cm} \) for the (110)/2 perfect loop. The results are fairly insensitive to temperature changes, and those on \( \Delta G^* \) for the 1000 °C case are shown in Fig. 1. It is seen that \( \Delta G_v^* \) values of voids are smaller than \( \Delta G_d^* \) values of both faulted and perfect dislocation loops by more than one order of magnitude. Thus, the possibility of nucleating V-type dislocation loops can be ruled out, because of competition by voids, and because the \( \Delta G_v^* \) values are excessively large. For defect formation temperatures assumed to be at or higher than 900 °C, the attainable \( C_v/C_v^{eq} \) value cannot exceed \( 10^5 \), to be discussed shortly with Fig. 2. Now, from Fig. 1 it is seen that the loop nucleation barrier exceeds \( \sim 35 \text{ eV} \). To obtain Fig. 1, the used \( \sigma \) value of 1230 ergs cm\(^{-2} \) is that of the Si \{111\} surface.\(^{17} \) If the Si \{100\} \( \sigma \) value of 2130 ergs cm\(^{-2} \) is used, \( \Delta G_v^* \) values become larger, but still a few times smaller than those of dislocation loops. The used \( \gamma \) value is that of the extrinsic SF. The intrinsic SF \( \gamma \) value is not known, but it is larger than that of the extrinsic SF. Hence, it is even harder to nucleate a faulted loop than our calculated result has indicated. Our results on dislocation loops shown in Fig. 1 are also applicable to the nucleation of A defects in the I-supersaturation case. Since the loop nucleation barrier did not drop below \( \sim 10 \text{ eV} \) even for a supersaturation value of \( C/C^{eq} = 10^{10} \), it is unlikely that A defects can be homogeneously nucleated. As indicated by the swirl distribution pattern, the A defects are most likely nucleated heterogeneously, e.g., with the less well defined B defects as precursors.\(^{18} \)

As voids grow large, however, they will become higher in energy than perfect dislocation loops accommodating the same number of \( V \), but not that of faulted loops. This is because the void energy is proportional to \( r_v^2 \), that of a perfect loop to \( r_d \ln (r_d) \), and that of a faulted loop to both kinds of terms. Thus, surpassing a critical size, voids should collapse into perfect dislocation loops. In the present study we have found that when the number of \( V \) contained in the defects exceeded \( \sim 8 \times 10^5 \), corresponding to a void larger than \( r_v \sim 70 \text{ nm} \) and a perfect loop larger than \( r_d \sim 1 \mu \text{m} \), the void energy becomes larger than that of a perfect dislocation loop. No such loops have been observed, probably for two reasons: (i) collapsing a void into a dislocation loop needs the surmounting of a nucleation barrier which may not be attainable, for the observed void size of \( \sim 100 \text{ nm} \) is very close to this critical value and there will hence not be a sufficiently large driving force; (ii) the observed void surfaces are covered by oxides which have probably provided a stabilization effect.

We have also used our calculated results to estimate the void nucleation temperature range, the required \( C_v/C_v^{eq} \) value range, and the \( V \) formation enthalpy range. The available thermal energy for nucleating voids (or other extended defects) in Si will not exceed \( \sim 50 \text{ kBT} \).\(^{19} \) This is an estimate obtained from the critical void nuclei density expression

\[
\text{FIG. 1. Calculated critical nuclei activation free energy } \Delta G^* \text{ (in eV) of nucleating } V \text{-type dislocation loops and voids as functions of the } V \text{-supersaturation value } C_v/C_v^{eq}. \text{ For dislocations, both (110)/2 perfect} \text{ dislocation loops and (111)/3 faulted Frank partial dislocation loops have been considered.}
\]
temperature has been given as ~900 °C, \( ^{20} \) (ii) low temperature (4 K) electron irradiation produced \( V \) migrates with \( h_{V}^{m} \leq 0.5 \text{ eV} \) between 80 and 100 K, \( ^{21} \) and (ii) a recent theoretically calculated \( V \) formation enthalpy is 3.65 eV. \( ^{22} \)

In summary, we have calculated the energy barrier values for nucleating void and \( V \)-type dislocation loop in Si. The needed activation energy for void nucleation is approximately one order of magnitude smaller than that of nucleating \( V \)-type dislocation loops. Thus, void formation is favored over forming dislocation. This is consistent with the observations that, instead of dislocation loops, voids are the dominant \( V \)-type extended defects in Si crystals grown under \( V \)-supersaturation conditions. Apparently, the \( D \)-type swirl defects are nanoscopic voids to begin with. Our calculated results have also provided information for limiting the formation temperature range of the \( D \)-swirl defects to be lower than ~1050 °C, and the Si \( V \) formation enthalpy to be above ~3.0 eV.

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\[ C_{V}^{eq} = C_{o} \exp \left( -\frac{\Delta G_{V}^{eq}}{k_{B}T} \right), \]

where \( C_{o} \) is the void nucleation site density taken to be the Si lattice density, \( 5 \times 10^{22} \text{ cm}^{-3} \). For voids to be present, at least one nucleus must have formed in a fairly large crystal, e.g., of the size 1 cm\(^3\). Thus, by letting \( C_{o}^{f} = 1 \text{ cm}^{-3} \), one obtains \( \Delta G_{V}^{eq} \approx 50 k_{B}T \). This estimate is said to be the available thermal energy for nucleation to occur. \( ^{19} \) Around 1000 °C, for \( C_{o}^{f} \) differing from 1 cm\(^{-3}\) by \( 10^{\pm 4} \) times, the error in the estimated \( \Delta G_{V}^{eq} \) values is \( \pm 1 \text{ eV} \). Assuming that the defect formation temperature is in the range of ~900–1200 °C, then \( \Delta G_{V}^{eq} \) should be below \( \approx 5-6 \text{ eV} \), and it is thus seen from Fig. 1 that \( C_{V}^{eq} / C_{V}^{f} \) should be above \( \approx 1 \times 10^{3} \). The Si self-diffusion coefficient due to the \( V \) contribution is characterized by an activation enthalpy of \( h_{V}^{SD} = h_{V}^{f} + h_{V}^{m} = 4.0 \text{ eV} \), \( ^{13} \) where \( h_{V}^{f} \) and \( h_{V}^{m} \) are, respectively, the \( V \) formation and migration enthalpies. Presently, the values of \( h_{V}^{f} \) and \( h_{V}^{m} \) are not independently known, and we can use the attainable \( C_{V}^{eq} / C_{V}^{f} \) value range at the void nucleation temperature \( T \) to estimate the \( h_{V}^{f} \) value range. This is carried out using \( C_{V}(T) = C_{V}^{eq}(T_{m}) \), by assuming that \( C_{V} \) at the Si melting temperature \( T_{m} \) just after a crystal section has grown is the thermal equilibrium value \( C_{V}^{eq}(T_{m}) \), and it is frozen in when the crystal section is cooled to lower temperatures. Figure 2 shows the calculated results. From Fig. 2, we see, in mutual consistency, that: (i) the void nucleation temperature should be lower than ~1050 °C; (ii) the maximum attainable \( C_{V}^{eq} / C_{V}^{f} \) value is \( \approx 10^{5} \) for letting 900 °C to be the minimum defect formation temperature, and (iii) the \( h_{V}^{f} \) value should be larger than ~3.0 eV. These findings appear to be reasonable in view of the facts that: (i) the \( D \)-defect formation