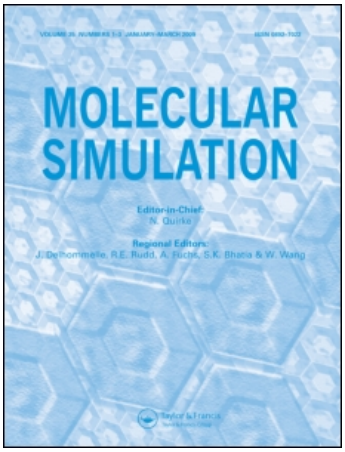

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Kinetic Monte Carlo simulation for the void defects formation in Czochralski silicon growth

Sang Hun Lee[ab]; Hyun Jong Cho[a]; Hyun Jung Oh[a]; Do Hyun Kim[b]
[a] Simulation Part, LG Siltron, Gumi, Gyeongbuk, Republic of Korea [b] Department of Chemical and Biomolecular Engineering, KAIST, Daejeon, Republic of Korea

First published on: 10 September 2009

To cite this Article Lee, Sang Hun , Cho, Hyun Jong , Oh, Hyun Jung and Kim, Do Hyun(2010) 'Kinetic Monte Carlo simulation for the void defects formation in Czochralski silicon growth', Molecular Simulation, 36: 3, 240 — 245, First published on: 10 September 2009 (iFirst)
To link to this Article: DOI: 10.1080/08927020903236348
URL: http://dx.doi.org/10.1080/08927020903236348

Molecular Simulation
Vol. 36, No. 3, March 2010, 240–245

Taylor & Francis
Taylor & Francis Group

Kinetic Monte Carlo simulation for the void defects formation in Czochralski silicon growth

Sang Hun Lee[ab]*, Hyun Jong Cho[a], Hyun Jung Oh[a] and Do Hyun Kim[b]

[a]*Simulation Part, LG Siltron, Imsoodong, Gumi, Gyeongbuk 730-724, Republic of Korea;* [b]*Department of Chemical and Biomolecular Engineering, KAIST, Daejeon 305-701, Republic of Korea*

(*Received 2 April 2009; final version received 3 August 2009*)

The quality of silicon wafers used as substrates for microelectronic devices is measured in terms of the type, size and density of defects formed during crystal growth process. The native point defects such as vacancies and self-interstitials diffuse, react and aggregate to form intrinsic defects in the silicon wafers. We investigated the point defect behaviour using the kinetic lattice Monte Carlo (KLMC) model. The KLMC method has been applied extensively in various forms to the study of microdefects in silicon wafers. The purpose of this paper is to demonstrate the phenomena of void defect formation. The size and density of void defects are usually affected by system temperature, vacancy–vacancy reaction and vacancy–impurity reaction. In this paper, we study the temperature effect and the vacancy concentration effect. The simulation results with various temperatures are well matched with our experimental data, and the relationship between temperature and vacancy density describes well the phenomena of void defect formation. This is the first time such KLMC simulation results have been reported.

Keywords: computer simulation; diffusion; point defects; kinetic lattice Monte Carlo; semiconducting silicon

PACS: 61.50.Ah; 61.72.Cc; 61.72.jd

1. Introduction

Vacancy aggregation in silicon has been studied extensively because void defects are known to be harmful to microelectronic device yield and reliability, particularly gate oxide integrity (GOI) [1,2]. The behaviour of intrinsic point defects in microdefect formation has been researched by many theoretical and experimental studies. Voronkov [3] was the first to connect theoretically point defect dynamics and crystal growth operating conditions, such as crystal pull rate V and cooling rate G, with observable transitions in microdefect structures during crystal growth. His approach pioneered the comprehensive modelling of point defect dynamics. The prediction of defect formation depends on understanding the sensitivity of important features of the microdefects in the silicon crystal to the crystal temperature field and pull rate. Habu et al. [4] and Habu and Tomiura [5] described the dominant point defect species with a two-dimensional (2D) continuum model. Ebe [6] performed analytical calculations on the behaviour of point defects in the growing silicon crystal. The development of these models is only discussed with regard to the native point defects such as vacancy and self-interstitial silicon, but defect species are also created by the combination of native point defects and impurities, such as dopant. Sinno et al. [7] describe an extension including an impurity (boron). Continuum models based on rate equations are most often used to make direct connections to experimental measurements. The kinetic evolution leading to micro-void formation from supersaturation of vacancies is very complex, and the nucleation stage requires an atomic description of the atomic scale phenomena. Molecular dynamics (MD) calculations have been extensively used to explore the fundamental interactions among vacancies. In the results, the cluster formation energy and single-particle dynamics have been gained. Bongiorno and Colombo [8] and Prasad and Sinno [9] used MD to model the energy of vacancy cluster formation and used this information to develop a continuum model of cluster aggregation [10]. Recently, the kinetic lattice Monte Carlo (KLMC) method was used for description of vacancy diffusion and clustering phenomena. La Magna et al. [11] proposed a KLMC method for the description of vacancy diffusion and clustering phenomena. The KLMC method does not make any assumptions about the behaviour of clusters, but shows that particles hop in the simulation domain according to pre-determined rates that depend on their local environment. Unlike the MD method, the KLMC method can provide valuable mesoscopic information that is difficult to obtain experimentally. Haley [12] shows that vacancy clustering behaviour as a function of temperature, concentration and interaction range is well described using the KLMC method. The diffusivity of the vacancies decreased over time as clusters were formed with the

*Corresponding author. Email: gigantic@siltron.co.kr

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020903236348
http://www.informaworld.com

power law. Temperature and vacancy concentration have significant effects.

In this work, we describe void defects formation using the KLMC model. In particular, we show the cluster formation with various temperatures and vacancy concentrations, and we also present the simulation results together with the experimental results corresponding to each simulation to validate our simulations.

2. Simulation model

A detailed study of vacancy cluster thermodynamics, transport and structure is presented based on MD for free energy estimation. MD was performed with the empirical environment dependent interatomic potentials, which has been shown to lead to a very good representation of vacancy cluster properties. MD calculations have been extensively used to explore the fundamental interactions between vacancies. The KLMC model has been widely used to describe the diffusion and clustering of vacancies in a Si lattice [13–15]. A typical move in a KLMC method consists of picking a particular event to execute, and then picking a random vacancy that can execute that event. Once the vacancy move is executed, the hopping rate of the vacancy and its surrounding neighbours are updated to reflect its new environment. The rate of a migration event is then simply given by the following Arrhenius expression:

$$r_i = \nu_0 \exp\left[-\frac{E_i}{k_B T}\right], \tag{1}$$

where ν_0 is the attempting frequency as the prefactor, E_i is the migration energy, k_B is the Boltzmann constant and T is the simulation temperature. $E_i = 0.43$ eV, reported by La Magna et al. [11], and the lattice constant is 5.43 Å. The E_i is for a single vacancy without any interaction. When a vacancy has neighbour vacancies, the E_i changes to ΔE_i that is the energy barrier for a vacancy hop. The energy barriers for a vacancy hop given by Dia et al. [16] are as follows:

$$\Delta E_i = \max\left(0, \Delta E_{\text{hop}} - 0.5 \times \sum_{j=1}^{\text{NN}} \Delta \text{NB}_j E_b^j\right), \tag{2}$$

where E_{hop} is the energy barrier for a single vacancy jump. NN is the nearest-neighbour shell. NB_j is the change in the number of particle–particle bonds with interaction range j. E_b^j is the binding energy of ith vacancy that has a neighbour vacancy j. Bongiorno et al. [17] investigated the formation and binding of vacancy clusters in silicon. Spherical-shaped clusters (SPC) are assumed in this work. The binding energy of nth vacancy added is defined as $E_b(n) = E_f(n-1) + E_f(1) - E_f(n)$. Table 1 shows the formation energy and the binding energy as a function of cluster size (n). In this work, the vacancy–vacancy interaction distance is extended up to the eighth nearest-neighbour shell based on the MD simulation results.

In KLMC simulations, the diffusion coefficient in each case was computed using the Einstein relation

$$d_V = \frac{1}{6} \lim_{t\to\infty} \sum_{i=1}^{N} \frac{|R_i(t) - R_i(0)|^2}{t}. \tag{3}$$

Here, $R_i(t)$ is the position of the ith atom or vacancy at time t.

The time interval is set by the inverse of the net hopping rate as follows:

$$\Delta t = \frac{1}{\sum_q R_q}, \tag{4}$$

where $R_q = \sum_{i=0} r_i^q$.

The time dependence of diffusivity as a power law of the form is as follows:

$$D(t) = \sim t^{-\gamma}. \tag{5}$$

3. Results and discussion

Void defects are driven by the supersaturation of vacancy in silicon crystals, and the defect formation is easily influenced by temperature and vacancy concentration. The main concern of this study was the temperature effect and the vacancy–vacancy reaction. We used the KLMC method for defect formation with long-range interactions that interact up to the eighth nearest neighbour. The actual simulation volume is $1.6 \times 10^{-16}\,\text{cm}^3$, and the total simulation time is 0.01 s.

3.1 Temperature

The simulations presented in this section were performed with 400 vacancies in a 3D simulation box with 100 unit cells in each dimension, for a vacancy concentration of $2.5 \times 10^{18}/\text{cm}^2$. The system's temperature range for

Table 1. Formation energy and the binding energy as a function of cluster size (n).

Number of vacancies	E_f (eV)	E_b (eV)
1	3.4	
2	5.2	1.6
3	7.14	1.46
4	9.36	1.19
5	10.68	2.08
6	11.27	2.72
7	13.7	1.07
8	14.08	3.04

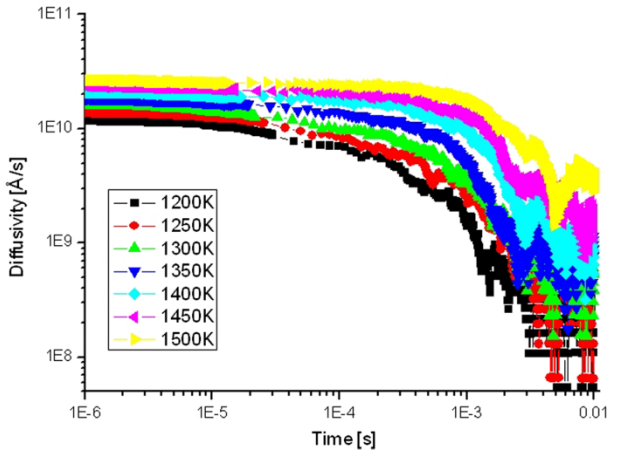

Figure 1. Diffusivity of vacancies for the temperature range 1200–1500 K.

clustering was 1200–1500 K [18–20]. Figure 1 shows the diffusivity of vacancies over time. The initial constant diffusivity, indicating free vacancy diffusion, leads to decreasing diffusivity, as clusters form. The diffusivity of vacancies decreases at a power law with exponent $\gamma = 1.1 \pm 0.2$ and the power law exponent is greater at the specific temperature range of 1400–1350 K. This means that the clustering phenomena are vigorous in this temperature range. This result is in good agreement with our experimental results [18]. Compared with the conditions in Haley's research [12], this study focussed on the clustering temperature range and allowed a wider range of vacancy concentration, but the trend agrees well with Haley's research. Figure 2 shows the formation of vacancy clusters for the temperature range. Figure 2(a) shows the number of clusters over time. The number increased and then gradually decreased as the time increased, because small clusters merged with other clusters or resolved into the free vacancies. At higher temperatures, small clusters initially formed and dissolved easily into free vacancies, but they remained for a relatively long time at lower temperatures. Figure 2(b) shows the mean size of clusters over time. At higher temperatures, the free vacancies diffuse rapidly so large clusters are formed quickly by capturing the free vacancies. Therefore, the size tends to be larger on average than those formed at lower temperatures. The mean size of clusters continuously increases over time by capturing the free vacancies. Figure 3 shows a comparison between simulation results and previous experimental results [18]. In our experiment, the behaviour of the grown-in defects is well explained by a growth halt test that is a temporary stop test of the crystal pulling rate. The pulling rate was dropped abruptly from 0.8 to 0.04 mm/min near the ingot position of 60 cm of 6″ crystal for 60 min. The crystal stayed 60 min more at a specific temperature depending on the crystal's position. After the crystal was grown, the distribution of void defects was changed, and the temperature dependency of void defects was well explained by the density and size of the void defects in the halted crystal. The temperatures of the crystals at the different positions were calculated using global heat transfer simulation. Figure 3(a) is a graph comparing the void defect density from the experiment and the cluster density of the KLMC simulation results. Figure 3(b) is a graph comparing the void defect size from the experiment and the mean cluster size of the KLMC simulation results. Because of the different scales of both systems, we could not directly compare the void defects with the vacancy clusters, but the temperature dependencies of both cases are well matched. The temperature dependencies of clustering are important in controlling the clustering phenomena during an experiment.

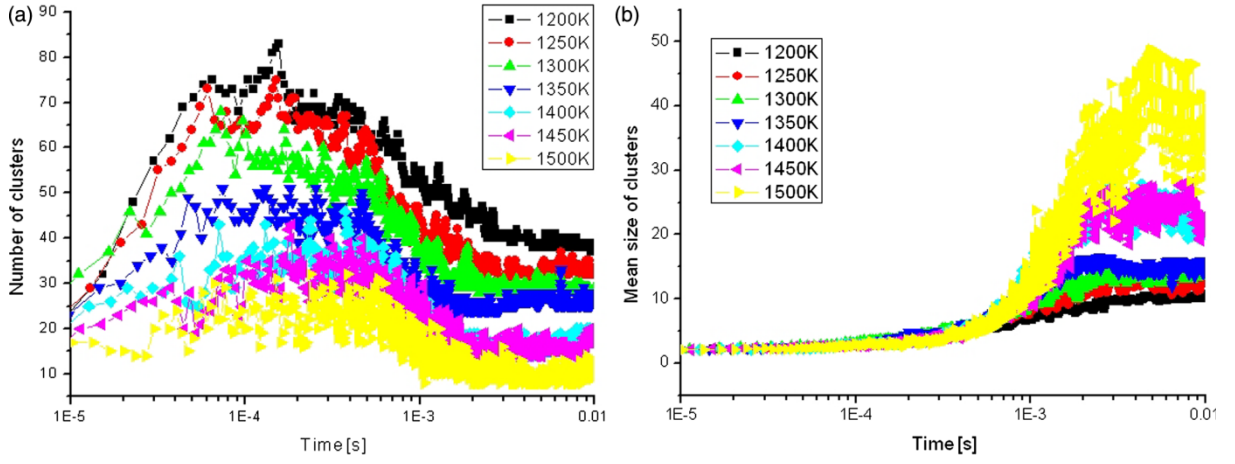

Figure 2. Formation of vacancy clusters for the temperature range 1200–1500 K: (a) number of clusters and (b) mean size of clusters as a function of time.

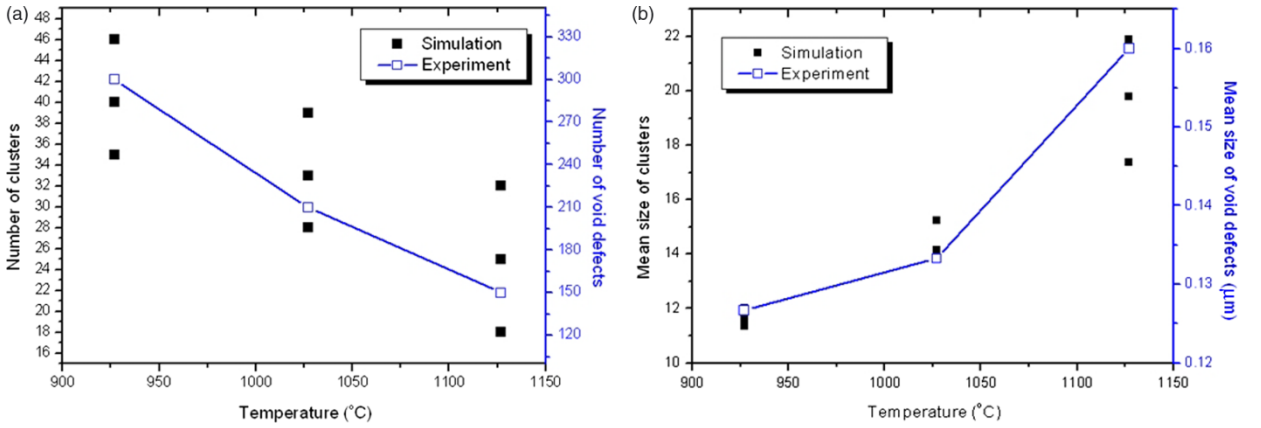

Figure 3. Comparison between the experimental results and the KLMC simulation results: (a) comparison between the void defect density from experiment and cluster density of the KLMC simulation result and (b) comparison between the void defect size from experiment and mean cluster size of the KLMC simulation result.

3.2 Vacancy concentration

The simulations presented in this section were performed with different numbers of vacancies in a 3D simulation box with 100 unit cells in each dimension, for a vacancy concentration range of $0.5–3.5 \times 10^{18}$ atoms/cm^2. The defect formation phenomenon was different compared with previous research [12], because of higher system temperature. Figure 4 shows the diffusivity of the vacancies over time. Except for a vacancy concentration of 0.5×10^{18} atoms/cm^2, the diffusivity decreased as clusters were formed with the power law exponent $\gamma = 1.3 \pm 0.2$, in which the higher values correspond to higher concentrations. This means that the clusters were formed quickly and trapped more vacancies at higher concentrations. However, the diffusivity remains constant over time at 0.5×10^{18} atoms/cm^2. Because the system did not have enough vacancy to form a stable cluster at 1500 K, a cluster was not formed.

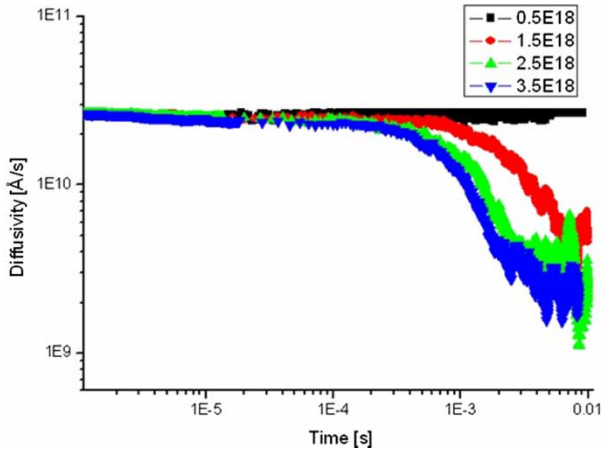

Figure 4. Diffusivity of vacancies for the vacancy concentration range $0.5–3.5 \times 10^{18}$ atoms/cm^3.

Figure 5 shows the formation of the vacancy clusters over time with various vacancy concentrations. Figure 5(a) shows the number of clusters over time. It increased and then gradually decreased over time, because small clusters merged with other clusters or they were resolved into the free vacancies. The number of clusters was proportional to the vacancy concentration. Figure 5(b) shows the mean size of the clusters over time. Once a free vacancy was formed in a cluster, the diffusivity decreased dramatically, such that it became difficult to move and merge with neighbouring clusters. In the authors' system, the mean size of the clusters was mainly affected by the number of free vacancies. If two systems of identical number of free vacancies existed, the systems with fewer clusters grow more than other systems with a greater number of clusters. As mentioned, a cluster does not form at 0.5×10^{18} atoms/cm^2. To form a stable cluster, a system in higher temperature needs higher vacancy concentration.

Figure 6 shows the formation of the clusters according to various temperatures and vacancy concentrations. The system's temperature range was from 1200 to 1500 K and its vacancy concentration range was from 0.5 to 3.5×10^{18} atoms/cm^3. The contour plot in Figure 6(a) explains the number of clusters according to the temperatures and the vacancy concentrations. The number of clusters increased with the decrease in the temperature and with the increase in the vacancy concentration. Figure 6(b) shows the mean size of the clusters according to the temperatures and the vacancy concentrations. The mean size of the clusters increased with an increase in the temperature and a decrease in the vacancy concentration. However, a stable cluster needs a higher vacancy concentration at a higher temperature. For example, a cluster was formed in a low vacancy concentration condition (0.5×10^{18} atoms/cm^3) at 1200 K, but did not form at 1500 K. These results imply that the void defect

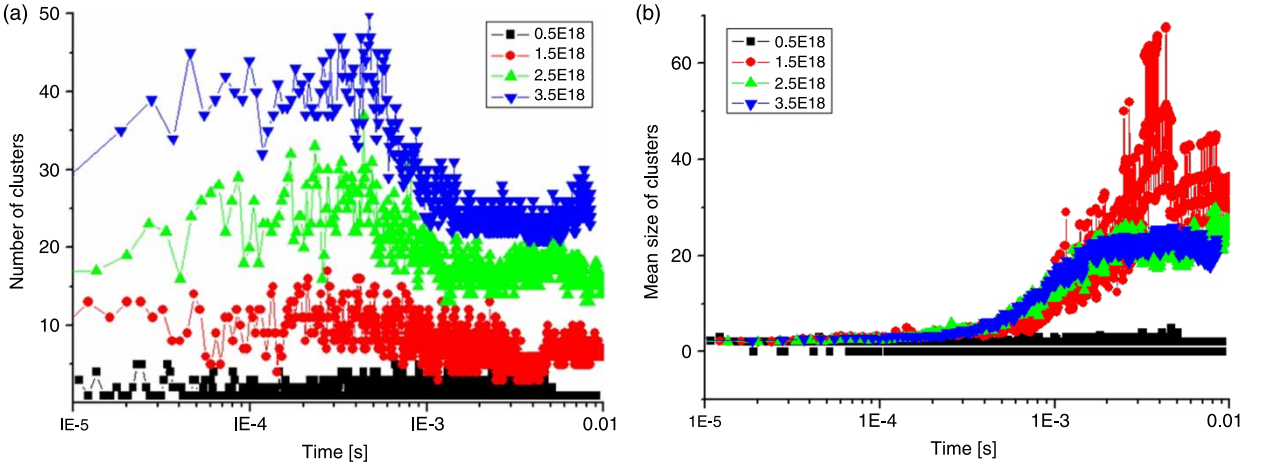

Figure 5. Formation of vacancy clusters for the vacancy concentration range $0.5–3.5 \times 10^{18}$ atoms/cm^3: (a) number of clusters and (b) mean size of clusters as a function of time.

density and size can be controlled by changing the system temperature and the vacancy concentration.

4. Conclusion

The formation of void defects could be represented by vacancy cluster formations in silicon. It was investigated using the KLMC method, which is effective for estimating the void defects formation in silicon crystal. We studied the vacancy clustering behaviour as a function of temperature and as a vacancy–vacancy reaction. First, we analysed the effect of temperature on the void formation. We show that the clustering phenomenon is vigorous at a specific temperature range (1400–1350 K), that larger clusters were generated at higher temperatures, and that smaller clusters were generated at lower temperatures. This phenomenon is in good agreement with the previous experimental results [18]. Second, we analysed the vacancy concentration effect on the void formation. The number of clusters is proportional to the vacancy concentration, and the mean size of the clusters is not proportional to the vacancy concentration because the mean size of the clusters is mainly affected by the number of free vacancies. In this specific case, a vacancy could not form a cluster if the system had a low vacancy concentration (0.5×10^{18} atoms/cm^3) and a high temperature (1500 K). This means that a system with a higher temperature needs a higher vacancy concentration to form a stable cluster. Our conclusion is that the cluster formation according to various temperatures and various vacancy concentrations could explain the defect formations in real systems; this implies that the void defect density and size can be controlled by changing the system temperature and the vacancy concentration. The KLMC method can provide valuable mesoscopic information about void defect formation. These kinds of KLMC results had not previously been reported.

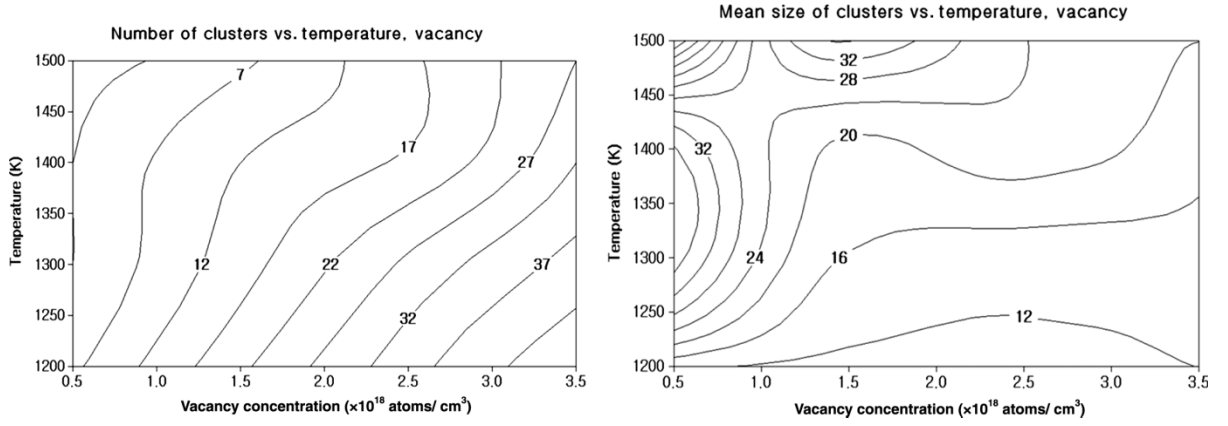

Figure 6. Formation of vacancy clusters according to various temperatures and vacancy concentrations: (a) number of clusters and (b) mean size of clusters as a function of time.

References

[1] E. Dornberger, D. Temmler, and W. von Ammon, *Defects in silicon crystals and their impact on DRAM device characteristics*, J. Electrochem. Soc. 149 (2002), pp. G226–G231.

[2] R. Winkler and G. Behnke, *Gate oxide quality related to bulk properties and its influence on DRAM device performance*, in *Semiconductor Silicon 1994*, H.R. Huff, W. Berghol, and K. Sumino, eds., The Electrochemical Society, Pennington, NJ, 1994, pp. 973–986.

[3] V.V. Voronkov, *The mechanism of swirl defects formation in silicon*, J. Crystal Growth 59 (1982), pp. 625–643.

[4] R. Habu, T. Iwasaki, H. Harada, and A. Tomiura, *Diffusion behavior of point defects in Si crystal during melt growth IV: Numerical analysis*, Jpn J. Appl. Phys. 33 (1994), pp. 1234–1242.

[5] R. Habu and A. Tomiura, *Distribution of grown-in crystal defects in silicon crystals formed by point defect diffusion during melt-growth: Disappearance of the oxidation induced stacking faults-ring*, Jpn J. Appl. Phys. 35 (1996), pp. 1–9.

[6] T. Ebe, *Factors determining the saturation of point defects in growing silicon crystals*, J. Crystal Growth 203 (1999), pp. 387–399.

[7] T. Sinno, H. Susanto, R.A. Brown, W.V. Amon, and E. Dornberger, *Boron retarded self-interstitial diffusion in Czochralski growth of silicon crystals and its role in oxidation-induced stacking-fault ring dynamics*, Appl. Phys. Lett. 75 (1999), pp. 1544–1546.

[8] A. Bongiorno and L. Colombo, *Interaction between a monovacancy and a vacancy cluster in silicon*, Phys. Rev. B 57 (1998), pp. 8767–8769.

[9] M. Prasad and T. Sinno, *Internally consistent approach for modeling solid-state aggregation. 1. Atomistic calculations of vacancy clustering in silicon*, Phys. Rev. B 68 (2003), 045206.

[10] M. Prasad and T. Sinno, *Internally consistent approach for modeling solid-state aggregation. 2. Mean-field representation of atomistic processes*, Phys. Rev. B 68 (2003), 045207.

[11] A. La Magna, S. Coffa, and L. Colombo, *A lattice kinetic Monte Carlo code for the description of vacancy diffusion and self-organization in Si*, Nucl. Instr. Meth. B 148 (1999), pp. 262–267.

[12] B.P. Haley, *Vacancy clustering and diffusion in silicon: Kinetic lattice Monte Carlo simulations*, Phys. Rev. B 74 (2006), 045217.

[13] L. Pelaz, L.A. Marques, M. Aboy, and J. Barbolla, *Atomistic modeling of amorphization and recrystallization in silicon*, Appl. Phys. Lett. 82 (2003), pp. 2038–2040.

[14] M. Aboy, L. Pelaz, L.A. Marques, L. Enriquez, and J. Barbolla, *Atomistic analysis of defect evolution and transient enhanced diffusion in silicon*, J. Appl. Phys. 94 (2003), pp. 1013–1018.

[15] R. Pinacho, P. Castrillo, M. Jaraiz, I. Martin-Bragado, and J. Barbolla, *Carbon in silicon: Modeling of diffusion and clustering mechanisms*, J. Appl. Phys. 92 (2002), pp. 1582–1587.

[16] J. Dia, J.M. Kanter, S.S. Kapur, W.D. Seider, and T. Sinno, *A lattice kinetic Monte Carlo study of void morphological evolution during silicon crystal growth*, Mol. Sim. 33 (2007), pp. 733–745.

[17] A. Bongiorno, L. Colombo, and T. Diaz De La Rubia, *Structural and binding properties of vacancy clusters in silicon*, Europhys. Lett. 43 (1998), pp. 695–700.

[18] B.M. Park and I.S. Choi, *Formation behavior of grown-in defects in a vacancy-rich Cz-Si crystal*, The ECS Proceedings Series, PV 2000-17, 2000, p. 19.

[19] V.V. Voronkov and R. Falster, *Grown-in microdefects, residual vacancies and oxygen precipitation bands in Czochralski silicon*, J. Crystal Growth 204 (1999), pp. 462–474.

[20] M. Hourai, H. Nishikawa, T. Tanaka, S. Umeno, E. Asayama, T. Nomachi, and G. Kelly, *Nature and generation of grown-in defects in Czochralski silicon crystal*, Electrochem. Soc. Proc. 98-1 (1998), pp. 453–467.