Phase Field Modeling of the Effects of Gradient Energy Coefficients on the Void-matrix Interface Thickness during Czochralski Silicon Crystal

X. J. Guan[1,2,a,*], J. Wang[1,2,b]

[1]School of Materials Science and Engineering, Shandong University, Jinan 250061, China

[2]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

[a]xjguan@sdu.edu.cn, [b]vwangjin@163.com

* Corresponding author: X J Guan

Keywords: Silicon crystal, Czochralski process, Phase field modeling, Gradient energy coefficient, Void-matrix interface thickness

Abstract. For investigating the effects of gradient energy coefficients on the void-matrix interface thickness during Czochralski silicon single crystal, an established phase field model and the corresponding program code were used to simulate the evolution process of a single void. Based on the given criterion of interface thickness, sixteen simulating cases were performed to study the related influence laws. The results show that the void-matrix interface thickness is influenced by both of the gradient energy coefficients of composition and chemical ordering, and the increases of gradient energy coefficients contribute to the enlargement of interface thickness.

Introduction

With the vigorous development of electronic industry and deepening of society informatization, microelectronic technology plays an increasingly important role at almost every aspect of human activities. Silicon single crystal, whose quality determines the development speed and potentiality of modern electronic information industry, is the basic material in electronic device manufacture. Czochralski (shortly called CZ) crystal growth process is the most common method to obtain silicon single crystal in experimental study and practical production. In CZ process, void-type microdefects form and evolve with pulling crystal, which influence the Gate Oxide Integrity of microelectronic devices. Thus, it is significant to conduct related researches on the dynamics of void evolution during CZ silicon single crystal.

To investigate the dynamics of microdefect evolution and capture the essential features of formation and growth of grown-in microdefect in CZ silicon crystal, different theoretically analytical models and simulation tools were developed. Kulkarni [1] employed the classical nucleation theory and diffusion-limited growth model to predict the microdefect types and their size distribution in silicon crystal. Sinno and Brown [2] used discrete rate equations and Fokker-Planck equations to describe various sizes of microdefect clusters in CZ silicon single crystal. Dai [3] developed a lattice kinetic Monte Carlo model for vacancy aggregation to simulation void growth dynamics in silicon single crystal. We also studied the void evolution in the process of CZ silicon single crystal using phase field method [4, 5].

This paper is concerned of the effects of gradient energy coefficients on the void-matrix interface thickness in phase field model, which is the follow-up work and extension of our previous work [6, 7], in which phase field simulations of the growth dynamics of single void and double

voids during CZ silicon single crystal were reported. Based on the phase field model established previously, the influences of the coefficients on the void-matrix interface thickness are discovered through simulating the single void growth in the process of CZ silicon single crystal.

Simulation Model and Calculation

Phase Field Model. The concerned simulation system is consisted of two phases, that is, the matrix phase containing the supersaturated vacancies and the void one. The vacancy concentration field $c_v(\boldsymbol{r}, t)$ and order parameter field $\phi(\boldsymbol{r}, t)$ were introduced as phase variables to describe the vacancy diffusion and void evolution, where $\boldsymbol{r}$ is spatial position and t is time. In the matrix phase, $\phi = 0$, while in the void phase, $c_v = 1$ and $\phi = 1$. The total free energy function of the system, $E(c_v,\phi,T)$, includes the chemical free energy and gradient energy as follows:

$$E(c_v,\phi,T) = N\int_V (F(c_v,\phi,T)+wg(\phi)+\kappa_v|\nabla c_v|^2+\kappa_\phi|\nabla\phi|^2)dV, \quad (1)$$

where N is the number of the lattice sites per unit volume of the crystal; $F(c_v,\phi,T)$ is the t otal chemical free energy; T is the absolute temperature; $g(\phi)$ is a double-well function relat ed to phase transition barrier; w is a positive constant; $\kappa_v|\nabla c_v|^2$ and $\kappa_\phi|\nabla\phi|^2$ represent the int erfacial energy contributed by the gradients of composition and chemical ordering, respectiv ely, where κ_v and κ_ϕ are gradient energy coefficients. The form of the total chemical free e nergy, $F(c_v,\phi,T)$, and double-well function, $g(\phi)$, are as following, respectively:

$$F(c_v,\phi,T) = (1-h(\phi))f_m(c_v,T)+h(\phi)f_v(c_v), \quad (2)$$

$$\text{and } g(\phi) = \phi^2-2\phi^3+\phi^4, \quad (3)$$

where $h(\phi)$ is a interpolating function; $f_m(c_v,T)$ and $f_v(c_v)$ are chemical free energy of matrix phase and void one, respectively. They can be got from the following equations:

$$h(\phi) = 3\phi^2-2\phi^3, \quad (4)$$

$$f_m(c_v,T) = (E_{f,v}-k_BT\ln c_{v,0})c_v+k_BT[c_v\ln c_v+(1-c_v)\ln(1-c_v)] \quad (5)$$

$$\text{and } f_v(c_v) = (c_v-1)^2, \quad (6)$$

here $E_{f,v}$ is the vacancy formation energy; k_B is the Boltzmann constant; $c_{v,0}$ is the pre-exponential factor of the thermal equilibrium vacancy concentration in the matrix $c_{v,e} = c_{v,0}\exp(-E_{f,v}/k_BT)$.

The processes of vacancy diffusion and void evolution were described by Cahn-Hilliard conservative field equation [8] and Allen-Cahn non-conservative field equation [9], respectively, i.e.

$$\frac{\partial c_v}{\partial t} = \nabla\cdot M_v\nabla\frac{1}{N}\frac{dE(c_v,f,T)}{dc_v} \quad (7)$$

and $\frac{\partial f}{\partial t} = -L\frac{dE(c_v, f, T)}{df}$ (8)

where $M_v = D_v c_v / k_B T$ is the vacancy mobility, here D_v is the vacancy diffusivity coefficient; L is the free surface mobility.

Initial Conditions and Parameters. The two-dimensional simulation region was divided into isometric grids of $256\Delta x \times 256\Delta x$, where Δx was grid length. There was an isolated void with a radius of $10\Delta x$ at the center of the solution domain, surrounded by the matrix containing uniform vacancies of supersaturated concentration. The initial vacancy concentration and the initial temperature were set to 0.02 and 1385K, respectively. In the simulation, periodic boundary condition was applied, and other simulation parameters were valued based on Table 1 and their physical meanings can be understood in the References [6] and [7].

Void-matrix Interface Thickness. In our previous work [6, 7], it was obtained that there was an interface of some thickness between void phase and matrix one, shown in Fig. 1. In the interface area, $0 < \phi < 1$ and $c_{v,\,near} < c_v < 1$, where $c_{v,\,near}$ is the vacancy concentration of the immediate vicinity of interface in the matrix. However, it is so difficult for phase field modeling to exactly capture the grids nearby the interface whose phase variables are $\phi = 0$ and $c_v = c_{v,\,near}$ or $\phi = 1$ and $c_v = 1$, respectively. Thus, in this paper, we define the total length of counted grids corresponding to $\phi \in [0.05, 0.95]$ as the void-matrix interface thickness, which is similar as the definition of void radius in Reference [6]. The schematic diagram for calculating the interface thickness is shown in Fig. 2.

Table 1 The parameters used in the phase-field simulation

Parameters	Value
$E_{f,v}$ / eV	4
$\Delta\tau$	5.0×10^{-4}
q / K·$\Delta\tau^{-1}$	0.5
D_v	2
L	100
κ_v / eV·l^{*2}	1.0, 2.0, 3.0, 4.0
κ_ϕ / eV·l^{*2}	1.0, 2.0, 3.0, 4.0
w	1
$c_{v,0}$	1.0×10^{11}

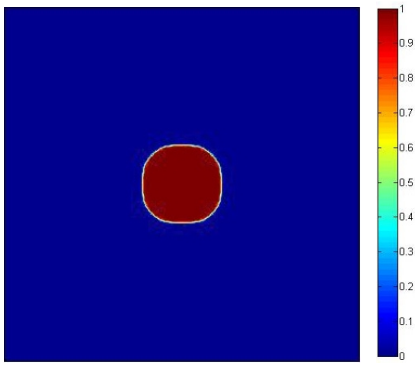

Fig. 1 The order parameter field corresponding to the evolution of void [6]

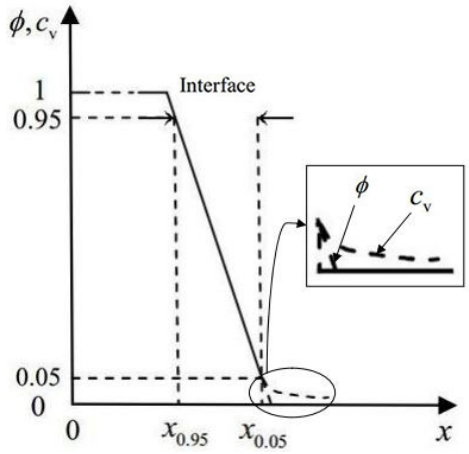

Fig. 2 Schematic diagram of calculating void-matrix interface thickness

The interface thickness changes with different κ_v and κ_ϕ were studied during single void growth. The results at twenty moments corresponding to the time steps of the multiple of 1500 were recorded and counted in each simulation, and their mean value, $L_{t,\phi}$, was calculated and treated as the interface thickness under current condition. Besides, for the sake of illustrating the change degree of the interface thickness in every simulation, the variance of the twenty thickness values, σ_{th}, was also calculated. It should be emphasized here that the initial interface thickness was all set to $2\Delta x$ in order to eliminate its influence on the simulation output.

Results and Discussion

As seen in Table 2, the values of simulated void-matrix interface thickness, $L_{t,\phi}$, vary in some degree with the different gradient energy parameters. With the enlargement of κ_v and κ_ϕ, $L_{t,\phi}$ increases and its changing degree is influenced by them. For the sake of illustrating the inner relationship between $L_{t,\phi}$ and the gradient energy parameters, image visualization was conducted that the data listed in Table 2 were transferred into functional image, as shown in Fig. 3. It is seen from Fig. 3 (a) that $L_{t,\phi}$ is a function of κ_v and κ_ϕ and its image is approximately a plane in three-dimensional space. The image is further fitted into a plane with binary linear function in Fig. 3 (b), and its mathematical expression is:

$$L_{t,\phi} = 0.8536\kappa_\phi + 0.1379\kappa_v + 2.2071. \quad (9)$$

Table 2 Mean values of the simulated interface thickness, $L_{t,\phi}$ [Δx]

κ_v [eV·l^{*2}] \ κ_ϕ [eV·l^{*2}]	1.0	2.0	3.0	4.0
1.0	3.0503	4.1806	4.9546	5.6330
2.0	3.3082	4.3263	5.1406	5.8264
3.0	3.3332	4.4745	5.2738	5.9633
4.0	3.4924	4.5615	5.3808	6.0744

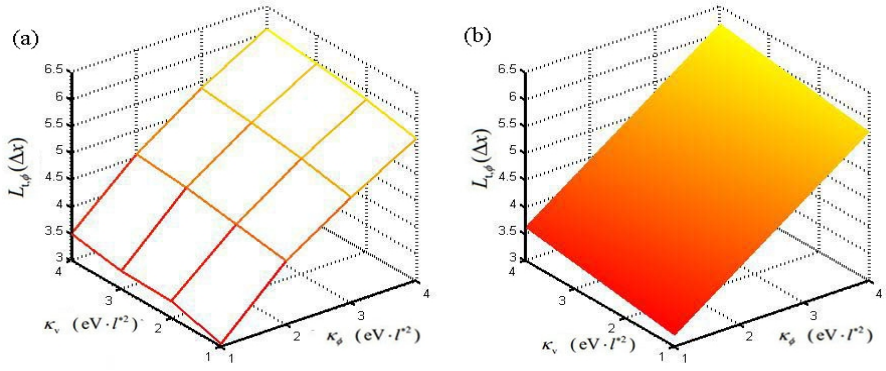

Fig. 3 Interface thickness, $L_{t,\phi}$, as a function of k_f and k_v (a) initial three-dimensional functional image; (b) fitting three-dimensional functional image

The variance values of twenty interface thickness values, $\sigma_{th,}$, obtained in each simulating case with certain values of κ_v and κ_ϕ were listed in Table 3. It is apparent that the variance values are all little compared with the values of $L_{t,\phi}$, which indicates that the void-matrix interface thickness basically remains invariant during the void growth. Hence, the void-matrix interface thickness does not depend on simulating time and only relates to the gradient energy coefficients. Also, it further illustrates that it is advisable to choose the mean value of the simulated thickness, $L_{t,\phi}$, as the indicator to evaluate the effects of the gradient energy coefficients on interface thickness.

In Eq. 9, the fitting coefficients in front of κ_v and κ_ϕ are all positive, which demonstrates that the interface thickness, $L_{t,\phi}$, is positively related to the gradient energy coefficients, namely, the increase of κ_v and κ_ϕ cause its enlargement. Basically, the two coefficients can be regarded as the weights of κ_v and κ_ϕ to $L_{t,\phi}$, and 0.8536 > 0.1379 indicates that the influence of κ_ϕ on $L_{t,\phi}$ overweighs that of κ_v in same change range.

Table 3 Variance values of the calculated interface thickness, σ_{th} $[(\Delta x)^2]$

κ_v [eV·l^{*2}] \ κ_ϕ [eV·l^{*2}]	1.0	2.0	3.0	4.0
1.0	0.0192	0.0112	0.0065	0.0044
2.0	0.0212	0.0050	0.0105	0.0098
3.0	0.0096	0.0069	0.0123	0.0120
4.0	0.0081	0.0041	0.0081	0.0123

It is known from Eq. 1, Eq. 7 and Eq. 8 that the increases of κ_v and κ_ϕ make $E(c_v,\phi,T)$ and $\delta E(c_v,\phi,T)$ enlarge, which strengthens the changing rates to decrease vacancy concentration in matrix and increase the region of order parameter varying, that is, the tendencies of vacancy diffusion an order parameter changes become stronger. Hence, the void-matrix interface thickness, $L_{t,\phi}$, corresponding to the region of order parameter varying increases. Obviously, the relatively stronger influence of κ_ϕ on $L_{t,\phi}$ is attributed to that the interface thickness is determined by the gradient energy coefficients and is characterized by the number of counting grids corresponding to the order parameter values in a setting region. Therefore, in simulating void evolution during CZ silicon single crystal, the varieties of gradient energy coefficients cause the change of the void-matrix interface thickness, but do not affect the law of void growth, so that they can be chosen as adjusting parameters to control the interface thickness.

Conclusions

The effects of gradient energy coefficients on the void-matrix interface thickness have been studied using an established phase field model and related program codes for simulating the void evolution in the process of Cz silicon single crystal. The interface thickness enlarges with the increases of both them, and the effect of the gradients energy coefficient of vacancy concentration is relatively stronger compared with the gradients energy coefficient of order parameter. It can obtain the reasonable and stable interface thickness to adjust the gradients energy coefficients in simulating void evolution during CZ silicon single crystal.

Acknowledgments

This work is financially supported by the Open Project from State Key Laboratory of Crystal Materials in Shandong University (grant no. KF1303).

References

[1] M. S. Kulkarni, V. V. Voronkov, R. Falster, Quantification of defect dynamics in unsteady-state and steady-state Czochralski growth of monocrystalline silicon，J. Electrochem. Soc. 151(2004) 663-678.

[2] T. Sinno, R.A. Brown, Modeling microdefect formation in Czochralski silicon, J. Electrochem. Soc. 146(1999) 2300-2312.

[3] J. Dai, W.D. Seider, T. Sinno, A lattice kinetic Monte Carlo study of void morphological evolution during silicon crystal growth, Mol. Simulat. 33(2007) 733-745.

[4] Q. K. Zeng, X. J. Guan, Z. B. Pan, Phase field model of the dynamics of growth in voids during Czochralski silicon crystal growth, J. Synth. Cryst. 41(2012) 888-895.

[5] X. Y. Zhang, X. J. Guan, Q. K. Zeng, Phase field modeling of void dynamics during CZ silicon growth with radial vacancy diffusion, J. Xuzhou Inst. Techno. 28(2013) 41-45.

[6] J. Wang, X. J. Guan, X. Y. Zhang, Growth dynamics of single void during Czochralski silicon crystal growth using phase-field modeling, Appl. Mech. Mater. 576(2014) 3-7.

[7] X. J. Guan, J. Wang, X. Y. Zhang, Phase-field simulation for the growth dynamics of double voids during czochralski silicon crystal growth, J. Synth. Cryst. 44(2015) 1207-1212.

[8] J. W. Cahn, J. E. Hilliardl Free energy of a nonuniform system: Ⅰ interfacial free energy, J. Chem. Phys. 28(1958) 258-267.

[9] S. M. Allen, J. W. Cahn, Theory for Antiphase Boundary Motion and Its Application to Antiphase Domain Coarsening, Acta Metall. 27(1979) 1085-1095.