Planar nucleation and crystallization in the annealing process of ion implanted silicon*

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Abstract: According to thermodynamic and kinetic theory, considering the variation of bulk free energy and superficial energy after nucleation as well as the migration of atoms, we study systematically the planar nucleation and crystallization that relate to two possible transition mechanisms in the annealing process of ion implanted Si: (1) liquid/solid transition: the critical nucleation work is equal to half the increased superficial energy and inversely proportional to the supercooling ΔT. Compared with bulk nucleation, the radius of the critical nucleus decreases by half, and the nucleation rate attains its maximum at $T = T_m/2$. (2) amorphous/crystalline transition: the atoms contained in the critical nucleus and situated on its surface, as well as critical nucleation work, are all directly proportional to the height of the nucleus, and the nucleation barrier is equal to half the superficial energy too. In addition, we take SiGe semiconductor as a specific example for calculation; a value of 0.03 eV/atom is obtained for the elastic strain energy, and a more reasonable result can be gotten after taking into account its effect on transition

Finally, we reach the following conclusion as a result of the calculation: for the annealing of ion implanted Si, no matter what the transition method is—liquid or solid planar nucleation—the recrystallization process is actually carried out layer by layer on the crystal substrate, and the probability of forming a "rod-like" nucleus is much larger than that of a "plate-like" nucleus.

Key words: annealing of ion implanted Si; transition; planar nucleation; liquid phase recrystallization; solid phase recrystallization

DOI: 10.1088/1674-4926/31/8/083001 **PACC:** 6170A; 6460Q; 8130H

1. Introduction

Ion implantation and annealing technology is an important method for semiconductor doping and a vital link in the technology of large scale integrated circuits (LSI), very large scale integrated circuits (VLSI) and optical and electrical integrated circuits (OEIC); it also plays an irreplaceable role in the fields of "impurity engineering" and "energy band engineering"[1−4].

When an ion with high energy bombards the surface of a silicon sheet, it displaces the substrate atom out of a regular lattice position, damages the crystal lattice, and even results in a heavily-doped amorphous layer. In the meantime, many impurity atoms are situated in non-electrical active positions, and annealing is needed for ion implanted silicon. In this annealing process, the silicon sheets are heated to a certain temperature so that the atoms on the surface regain their migrating ability. This may touch off liquid/solid or amorphous/crystalline transitions on the superficial damage layer through nucleation and growth, resulting in the elimination of lattice damage and recovery of the regular arrangement of atoms on the surface[5, 6].

Bulk nucleation theory concerning the liquid/solid transition is a rather mature theory[7], but in the process of annealing to ion implanted Si, recrystallization is usually performed on the crystal substrate layer by layer, because it may be taken as a natural two dimensional nucleus, so bulk nucleation theory has to be revised to a certain extent. On the other hand, for the solid amorphous/crystalline transition, no matter whether bulk or planar nucleation, the theory is still far from mature. In this work, we try to perfect the theoretical problem concerning the annealing of ion implanted silicon through introduction of the concept of planar nucleation. As for solid bulk nucleation, we have given a special discussion of this in another article[8].

2. Theoretical calculation and result discussion

2.1. Planar recrystallization from the liquid phase

In general, the pulse length of a laser is shorter than the rearrangement time of a solid atom, so pulse laser annealing can be realized just through recrystallization from the liquid phase[9]; the mechanism of annealing is that the superficial amorphous layer melts first, and then recrystallizes epitaxially on the crystal substrate, so the solid substrate under the melting layer become a natural two dimensional nucleus.

Supposing that the nucleus is cylinder-like, with a radius r and a height h, when a nucleus is formed on the liquid/solid interface, the variation of total Gibbs free energy in the system can be written as:

$$\Delta G = \Delta G_v \pi r^2 h + (2\pi r h + \pi r^2)\sigma, \tag{1}$$

where ΔG_v is the difference between the Gibbs free energy per unit volume for the liquid and solid phases, and σ is the

* Project supported by the National Natural Science Foundation of China (No. 50804015).
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Received 8 February 2010, revised manuscript received 26 March 2010
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interfacial energy per unit area. In Eq. (1), the first term on the right stands for the decrease of bulk free energy, and the second term stands for the increase of interfacial energy. Because the base of the nucleus is formed directly on the solid substrate, the superficial area of the nucleus just includes the area of the side and the upper face.

It may be proved that the nucleation rate of a "rod-like" nucleus is much higher than that of a "plate-like" nucleus in the case of planar nucleation from the liquid phase[8], that is, $r \ll 2h$, so the area of the upper face can be neglected, and Equation (1) may be simplified as:

$$\Delta G = \Delta G_{\rm v}\pi r^2 h + 2\pi r h\sigma. \quad (2)$$

Letting $\frac{{\rm d}\Delta G}{{\rm d}r}\Big|_{r_{\rm c}} = 0$, we can obtain the radius of the critical nucleus:

$$r_{\rm c} = -\frac{\sigma}{\Delta G_{\rm v}}. \quad (3)$$

Compared with bulk nucleation, the radius of the critical nucleus is reduced by half[7], meaning that nucleation becomes easier as planar nucleation.

Substituting Eq. (3) into Eq. (2), we can get the critical nucleation work:

$$\Delta G_{\rm c} = -\frac{\pi\sigma^2 h}{\Delta G_{\rm v}} = \frac{1}{2}(2\pi r_{\rm c} h)\sigma. \quad (4)$$

We can see from Eq. (4) that the critical nucleation work is equal to half the increased superficial energy after nucleation, which tells us that, in the case of planar nucleation, the free energy difference between the liquid and solid phases can only compensate half of the superficial energy, while another half comes from the energy fluctuation in the system itself. This conclusion is also different from that of bulk nucleation[7].

According to thermodynamic theory, the relationship between $\Delta G_{\rm c}$ and supercooling ΔT is[7]:

$$\Delta G_{\rm v} = -\frac{L_{\rm m}\Delta T}{T_{\rm m}}, \quad (5)$$

where $L_{\rm m}$ is the transition latent heat per unit volume, and $T_{\rm m}$ is the melting point

Substituting Eq. (5) into Eqs. (3) and (4), and letting $T_{\rm r} = T/T_{\rm m}$, called the reduced temperature, we have:

$$r_{\rm c} = \frac{\sigma T_{\rm m}}{L_{\rm m}\Delta T} = \frac{\sigma}{L_{\rm m}(1-T_{\rm r})}, \quad (6)$$

$$\Delta G_{\rm c} = \frac{\pi\sigma^2 h T_{\rm m}}{L_{\rm m}\Delta T} = \frac{\pi\sigma^2 h}{L_{\rm m}(1-T_{\rm r})}. \quad (7)$$

In Eq. (7), we can see that the critical nucleation work of planar nucleation is inversely proportional to ΔT, which is different from bulk nucleation where it is inversely proportional to ΔT^2 [7]. Moreover, $\Delta G_{\rm c}$ is directly proportional to h, which means that the higher the nucleus is, the more difficulty with which it forms.

The expression of nucleation rate for planar nucleation can be written as[8]:

$$I_{\rm s} = Zsv_0 n_0 {\rm e}^{-\frac{\Delta G_{\rm c}}{kT}}{\rm e}^{-\frac{\Delta G_{\rm a}}{kT}}, \quad (8)$$

Table 1. Relationship between nucleation rate and height.

h (nm)	A_0 (cm^{-2})	$I_{\rm sm}$ (cm$^{-2}\cdot$s^{-1})
0.5	2.5×10^{15}	1.25×10^{14}
1	5×10^{15}	2.5×10^{-1}

where $\Delta G_{\rm a}$ stands for the energy barrier to be overcome when an atom diffuses from the liquid to the nucleus, because the nature of melting semiconductor materials is similar to that of metals; $\Delta G_{\rm a}$ is the same order as kT[7]. So as an estimation, we can let ${\rm e}^{-\frac{\Delta G_{\rm a}}{kT}} \approx 1$ approximately, and the physical meanings of other constants and their values for silicon are as follows:

Z is the Zeldowich factor: $Z = 0.05$ [10]. s is the number of atoms adjacent to the critical nucleus: $s = 10^2$[10]. v_0 is the frequency of atomic vibration: $v_0 = 10^{13}$ s^{-1}[9]. n_0 is the atomic numerical density in the original phase: $n_0 = 5 \times 10^{28}$ m^{-3}[11]. $\sigma = 0.736$ J/m^3[11]. $T_{\rm m} = 1700$ K[11].

Substituting Eq. (7) into Eq. (8) and letting $\frac{{\rm d}I_{\rm s}}{{\rm d}T_{\rm r}}\Big|_{T_{\rm rm}} = 0$, we can get that the reduced temperature corresponding to the maximum nucleation rate is $T_{\rm rm} = 1/2$, that is, $T = T_{\rm m}/2$; this temperature is just included among the extent fitting for annealing of ion implanted silicon ($T_{\rm m}/3 < T < 2T_{\rm m}/3$)[11].

Substituting $T_{\rm r} = 1/2$ and related constants into Eqs. (6)–(8) respectively, we have:

$$r_{\rm cm} = \frac{2\sigma}{L_{\rm m}} = 0.35\ {\rm nm},$$
$$\Delta G_{\rm cm} = 2\frac{\pi\sigma^2 h}{L_{\rm m}} = \frac{1}{2}(2\pi r_{\rm cm} h)\sigma,$$
$$I_{\rm sm} = 2.5 \times 10^{42} h {\rm e}^{-6.9\times 10^{10} h}. \quad (9)$$

We can calculate the nucleation rate corresponding to a nucleus of different heights, taking $h = 0.5$ nm and 1 nm as examples. The results are listed in Table 1.

Here, $A_0 = n_0 h$ is the superficial atomic density

We can see from the data in Table 1 that for a nucleus whose height is 1 nm, $I_{\rm sm}/A_0$, defined as nucleation probability per unit time, approaches zero, but when $h = 0.5$ nm, this nucleation probability is up to 5%. Because the atomic radius of Si is 0.146 nm[12], the mean atomic distance is nearly 0.27 nm[12]; moreover, the condition $r \ll 2h$ has to be considered for a "rod-like" nucleus, so we start our calculation from a nucleus height $h = 0.5$ nm, which is actually slightly thicker than a monoatomic layer. Therefore, this tells us that for the annealing of a Si sheet through the liquid phase mechanism, its recrystallization process is mainly performed layer by layer on the crystal substrate.

2.2. Planar recrystallization from the solid phase

For conventional furnace annealing, or CW laser and electron beam annealing, as well as rapid thermal annealing and so on, because of the rather longer annealing time, the same temperature in the whole Si sheet may be attained, and it is impossible to perform liquid phase recrystallization unless the whole Si sheet is melted, so its annealing mechanism can merely be solid phase recrystallization. However, solid phase recrystallization only fits the case where the thickness of the film is less than 300 nm; when it is thicker than 300 nm, annealing can be realized just through liquid phase recrystallization[9]. The

Table 2. Calculation results of a nucleus whose height is 0.5 nm and 1 nm.

h (nm)	A_0 (cm^{-2})	i_c	O_{i_c}	ΔG_{i_c} (eV)	I_s ($cm^{-2} \cdot s^{-1}$)	r_c (nm)
0.5	2.5×10^{15}	11.4	16.3	1.14	2.5×10^{7}	0.38
1.0	5×10^{15}	22.8	32.6	2.28	5×10^{2}	0.38

thickness of the ion implanted amorphous layer is usually thinner than 300 nm, so for the annealing of ion implanted Si, solid phase epitaxy recrystallization is an important way of annealing.

Supposing that a cylindrical nucleus with a radius r and a height h is formed on the crystal substrate, it contains i atoms and O_i of them locate on its surface, the mean distance of the atom is a, Δg_v and σ_{ca} represent the free energy difference and the interfacial energy of an atom respectively as the amorphous/crystalline transition occurs, when an atomic group is formed from the amorphous phase, its increment of free energy is:

$$\Delta G_i = -\Delta g_v i + \sigma_{ca} O_i, \tag{10}$$

where $i = \frac{\pi r^2 h}{a^3}$, or

$$r = \frac{1}{\sqrt{\pi h}} a^{3/2} i^{1/2}, \tag{11}$$

$$O_i = \frac{2\pi r h + \pi r^2}{a^2}. \tag{12}$$

Similar to liquid phase planar nucleation, we can prove that in the circumstances of solid phase planar nucleation, the probability of forming a "rod-like" nucleus is much higher than the probability of forming a "plate-like" nucleus[8], that is, $r \ll 2h$. So we may neglect the area of the upper face, and Equation (12) can be simplified as:

$$O_i = \frac{2\pi r h}{a^2}. \tag{13}$$

Substituting Eqs. (11) and (13) into Eq. (10), we have:

$$\Delta G_i = -\Delta g_v i + 2\sigma_{ca} \sqrt{\frac{\pi h}{a}} i^{1/2}. \tag{14}$$

Letting $\frac{d\Delta G_i}{di}\Big|_{i_c} = 0$, we can obtain the atom number contained in the critical atomic group.

$$i_c = \left(\frac{\sigma_{ca}}{\Delta g_v}\right)^2 \frac{\pi h}{a}. \tag{15}$$

Substituting i_c into Eqs. (11), (13) and (10), we can get a group of formulae as follows.

$$r_c = \frac{\sigma_{ca}}{\Delta g_v}, \tag{16}$$

$$O_{i_c} = 2\frac{\pi h}{a}\frac{\sigma_{ca}}{\Delta g_v}, \tag{17}$$

$$\Delta G_{i_c} = \frac{\pi h}{a}\frac{\sigma_{ca}^2}{\Delta g_v} = \frac{1}{2} O_{i_c} \sigma_{ca}. \tag{18}$$

We can see from Eq. (18) that the nucleation barrier is equal to half the increasing superficial energy, which is in agreement with the conclusion of liquid phase nucleation.

We can see through the above calculation that the atom number contained in the critical nucleus and situated on its surface, as well as the critical nucleation work, are all directly proportional to its height, so the higher the nucleus is, the lower the number is.

Some constants for silicon are as follows:

Δg_v = 0.1 eV/atom[9, 12], a = 0.27 nm[12], σ_{ca} = 0.14 eV/atom[12].

Substituting these into Eqs. (15)–(18), we can get:

$i_c = 22.8h$, r_c = 0.38 nm, $O_{i_c} = 32.6h$, $\Delta G_{i_c} = 2.28h$ eV, where the unit of h is nm.

Similar to liquid phase planar nucleation, the nucleation rate of solid phase planar nucleation is:

$$I_s = Zsv_0 n_0 e^{-\frac{\Delta G_{i_c}}{kT}} e^{-\frac{\Delta G_a}{kT}} \tag{19}$$

With the exception of v_0 and ΔG_a, the values of the other quantities are all identical to those in Eq. (8); because of the solid phase annealing, the order of ΔG_a is no longer the same as kT, and the frequency of atom vibration lowers greatly too, of course, compared with the liquid phase, atomic migration will be more difficult.

Take h = 0.5 nm and h = 1 nm as examples, ΔG_a = 2.35 eV[9], $v_0 = 2 \times 10^4\ s^{-1}$[9], and assume T = 1300 K. Substituting them into the above relative formula gives the calculation results listed in Table 2.

Because a "rod-like" nucleus has to meet the condition of $r \ll 2h$, our calculation starts from h = 0.5 nm. We can see from the data in Table 2 that the nucleation rate of a 0.5 nm high nucleus is 5 orders more than that of a 1 nm high nucleus, from which we see that for solid annealing of ion implanted silicon, its recrystallization process is also basically performed layer by layer on the crystal substrate.

2.3. Influence of elastic strain energy

We can see from the calculation data in Table 2 that $i_c < O_{i_c}$; this result is clearly not reasonable, and it can be revised by taking the influence of elastic strain energy into account.

In the process of solid transition, because of the different specific volumes and structures, the emergence of the nucleus usually causes lattice distortion in the nucleus itself and in the original phase around it, which results in the emergence of elastic strain energy. The larger the elastic energy is, the higher the nucleation barrier is, in other words, in the case where the other conditions are the same, the nucleus with smaller elastic energy will form first, so elastic energy is also an important factor influencing nucleus formation, because it emerges just in the solid transition. Therefore, only when we study the process of solid phase recrystallization does elastic strain energy have to be considered.

When the new phase and original phase are coherent or semicoherent, the expression of the volume density of coherent elastic strain energy can be written as[10]:

Table 3. Calculation results for two different height critical nuclei after considering elastic strain energy.

h (nm)	A_0 (cm^{-2})	i_c	O_{i_c}	ΔG_{i_c} (eV)	I_s (cm$^{-2}\cdot$s^{-1})	r_c (nm)
0.5	2.5×10^{15}	23.16	23.16	1.63	2.5×10^{5}	0.54
1.0	5×10^{15}	46.52	46.52	3.26	5×10^{-2}	0.54

$$E_c = \frac{\varepsilon_\alpha \delta^2}{1-v}\phi(c/a). \quad (20)$$

When the new phase and original phase are incoherent, the coherent strain energy disappears, but owing to different specific volumes, the volume strain energy still exists.

Nabarro has given the volume elastic strain energy per unit volume[7].

$$E_v = \frac{2}{3}\mu \Delta^2 f(c/a). \quad (21)$$

In the above two equations, $\phi(c/a)$ and $f(c/a)$ stand for a formal factor, whose values are within the extent of 0.75–1 according to different nucleus forms[7], δ and Δ are the misfit quantity of the lattice or volume respectively, μ stands for the shear modulus, ε_α stands for the isotropical elastic modulus of elemental material (Si), and v is the Poisson ratio.

Generally speaking, for a semiconductor in a partly relaxed state, $\Delta^2 \ll \delta^2$, so $E_v \ll E_c$, the elastic strain energy per unit volume $E = E_c + E_v \approx E_c$, and the elastic strain energy per atom $\varepsilon_c = \frac{E}{n_0}$.

Taking SiGe semiconductor as an example: $\varepsilon_\alpha = 10^{11}$ N/m^2[11], μ = 39.8 GPa[13], v = 0.274[14, 15], δ = 4.18%[14].

Letting $\phi(c/a) = 1$ and substituting it into Eq. (20), we can obtain $\varepsilon_c = 0.03$ eV/atom. Comparing this with the free energy of transition (0.1 eV/atom), it can no longer be neglected.

The influence of elastic strain energy on solid planar nucleation can be reflected just by changing Δg_v in Eqs. (15)–(18) into $\Delta g_v - \varepsilon_c$, and we can get a group of formulae as follows.

$$i_c = \left(\frac{\sigma_{ca}}{\Delta g_v - \varepsilon_c}\right)^2 \frac{\pi h}{a} = 46.52h, \quad (22)$$

$$r_c = \frac{\sigma_{ca}}{\Delta g_v - \varepsilon_c} a = 0.54 \text{ nm}, \quad (23)$$

$$O_{i_c} = 2\frac{\pi h}{a}\frac{\sigma_{ca}}{\Delta g_v - \varepsilon_c} = 46.52h, \quad (24)$$

$$\Delta G_{i_c} = \frac{\pi h}{a}\frac{\sigma_{ca}^2}{\Delta g_v - \varepsilon_c} = 3.26h. \quad (25)$$

According to the above formula and Eq. (19), we also do a calculation for an h = 0.5 and 1 nm nucleus. The results are listed in Table 3.

Comparing the data in Tables 2 and 3, we can see that after considering the influence of elastic strain energy, both the critical nucleus radius and the atom number contained in it increase, and the nucleation rate decreases, which means that nucleation is more difficult. This conclusion is in agreement with our previous experimental results where a relatively longer annealing time is needed for a Si sheet implanted by Ge+[15, 16]. Moreover, $i_c = O_{i_c}$, telling us that under the circumstances of planar nucleation, no matter what the height of the nucleus is, all of its atoms are basically situated on its surface. Because the nucleation rate forming a 0.5 nm high nucleus is 7 orders more than that forming a 1 nm high nucleus, we can infer that after considering the influence of elastic strain energy, the conclusion that the process of solid phase recrystallization is performed layer by layer on the crystal substrate is also unchanged.

3. Conclusion

In this work, we study in depth the planar nucleation theory in the transition process, including liquid/solid and amorphous/crystalline transition relative to the annealing of ion implanted Si; the following main conclusions are reached:

(1) Liquid phase planar nucleation: compared with bulk nucleation, the radius of the critical nucleus decreases by half, the critical nucleation work is inversely proportional to the supercooling ΔT and is equal to half the increasing superficial energy owing to nucleation, and the reduced temperature corresponding to the maximum nucleation rate is T_{rm} = 1/2, that is, $T = T_m/2$.

(2) Solid phase planar nucleation: i_c is the atom number contained in the critical nucleus and O_{i_c} is the atom number located on its surface; as well as the critical nucleation work being directly proportional to its height, the nucleation barrier is also equal to half the increasing superficial energy, but $i_c < O_{i_c}$, which is not reasonable.

(3) Influence of elastic strain energy on solid planar nucleation: taking SiGe semiconductor as a specific example, we have obtained that the value of elastic strain energy is equal to 0.03 eV/atom when the amorphous/crystalline transition occurs; this is not negligible relative to the free energy of transition. After considering the influence of elastic stain energy on solid planar recrystallization, we can obtain a reasonable result that no matter what the height of the nucleus is, all of its atoms basically locate on its surface, moreover, nucleation becomes more difficult, which results in the decreasing of nucleation rate.

(4) It does not matter whether liquid phase planar nucleation or solid phase planar nucleation occurs, and no matter whether the influence of elastic strain energy on nucleation is considered or not, we can reach the same conclusion: for the annealing of ion implanted silicon, its planar recrystallization process is performed layer by layer on the crystal substrate.

References

[1] Sawana K, Fukumoto A, Hoshi Y, et al. Strained Si n-channel metal–oxide–semiconductor field-effect-transistors formed on very thin SiGe relaxed layer fabricated by ion implantation technique. Appl Phys Lett, 2007, 90(20): 202101

[2] Ziegler J F. Handbook of ion implantation. New York: North Holland, Elsevier Science Publishers, 1992

[3] Yang Hui, Zhang Enxia, Zhang Zhengxuan. Effects of Si ion implantation on total dose radiation properties of SIMOX SOI ma-

terials. Chinese Journal of Semiconductors, 2007, 28(3): 323 (in Chinese)
[4] Camillo-Castillo R A, Law M E, Jones K S, et al. Kinetics of the end of range damage dissolution in flash-assisted rapid thermal processing. Appl Phys Lett, 2006, 82(23): 232104
[5] Ferri M, Solmi S, Nobili D, et al. Damage and recovery in boron doped silicon on insulator layer after high energy Si^+ implantation. J Appl Phys, 2006, 100(3): 033711
[6] Zhang R, Rozgonyi G A, Yakimov E, et al. Impact of thermal annealing on deep-level defect in strained Si/SiGe heterostructure. J Appl Phys, 2008, 103(10): 103506
[7] Shi Deke. Basis of material science. Beijing: China Machine Press, 2003
[8] Luo Yimin. Research on annealing of ion implanted silicon and thermodynamics in the process of annealing. PhD Dissertation, Central South University, Changsha, 2010 (in Chinese)
[9] Poate J M, Mayer J W. Laser annealing of semiconductor. New York: Academic Press, Inc, 1982
[10] Feng D. Metallic physics: 2nd volume, transition. Beijing: Science Press, 2000
[11] Wang Zhanguo, Chen Liquan, Tu Hailing. China materials engineering canon, Vol.11–information functional materials (volume 1). Beijing: Chemical Industry Press, 2006
[12] Spinella C, Lombardo S, Priolo F. Crystal grain nucleation. J Appl Phys, 1998, 84(10): 5383
[13] Vjihara T, Sazaki G, Fujiwara K, et al. Physical model for the evolution of solid-liquid interfacial tension in silicon. J Appl Phys, 2001, 90(2): 750
[14] Xu Zhenjia. Surface science aspects of current semiconductor materials. Beijing: Peking University Press, 2002
[15] Luo Yimin, Chen Zhenhua, Huang Peiyun. Annealing behavior of $Si_{1-x}Ge_x$/Si heterostructure formed by Ge^+ implantation. Journal of Central South University, 2005, 36(4): 560 (in Chinese)
[16] Luo Yimin, Chen Zhenhua, Huang Peiyun. Research on rapid thermal annealing of high dose Ge^+ implantation into silicon. Mater Rev, 2004, 18(7): 101 (in Chinese)