

Modeling of silicon-nanocrystal formation in amorphous silicon/silicon dioxide multilayer structure

Keyong Chen (陈可勇), Xue Feng (冯雪)*, and Yidong Huang (黄翊东)

State Key Laboratory of Integrated Optoelectronics, Department of Electronic Engineering,
Tsinghua University, Beijing 100084, China

*E-mail: x-feng@tsinghua.edu.cn

Received August 5, 2010

The formation process of silicon-nanocrystals (Si-NCs) in the amorphous silicon/silicon dioxide (a-Si/SiO₂) multilayer structure during thermal annealing is theoretically studied with a modified model based on the Gibbs free energy variation. In this model, the concept of average effective interfacial free energy variation is introduced and the whole formation process consisting of nucleation and subsequent growth is considered. The calculating results indicate that there is a lower limit of the silicon layer thickness for forming Si-NCs in a-Si/SiO₂ multilayer, and the oxide interfaces cannot constrain their lateral growth. Furthermore, by comparing the results for a-Si/SiO₂ and a-Si/SiN_x multilayers, it is found that the constraint on the crystal growth from the dielectric interfaces depends on the difference between interfacial free energies.

OCIS codes: 310.0310, 310.6805.

doi: 10.3788/COL20100812.1199.

Efficient silicon-based light source is one of the most popular topics in the studies on silicon (Si) photonics that has attracted many attentions due to its compatibility with existing semiconductor fabrication techniques. For this topic, various approaches have been explored, such as porous Si^[1,2] and Si nanocrystals (Si-NCs) in bulk Si-rich compounds^[3–5] and multilayers^[6,7]. Among them, Si-NCs are holding the attention for their strong quantum confinement effects with stable optical properties, especially when multilayer structure is considered as a method to independently regulate the size and density of Si-NCs, and improve light emission with substantially lower driving voltage^[6]. Nevertheless, compared with that in bulk Si-rich compounds^[8], the formation of Si-NCs in ultrathin amorphous Si (a-Si) layers covered with thin dielectric layers, such as SiO₂ and Si₃N₄, i.e., a-Si multilayers, has not been widely studied. The existing theories^[9,10] cannot well clarify the whole formation process of Si-NCs in multilayers by modeling nucleation and subsequent growth separately. In this letter, for better understanding and control of the Si-NC formation, a modified model is developed to unify the formation process based on the Gibbs free energy variation. According to the calculations using the proposed model, a lower limit for the a-Si layer thickness and incapability of constraint on the lateral growth of Si-NCs from the oxide interfaces are discovered in a-Si/SiO₂ multilayers. Furthermore, the model could be readily applied to estimate the differences between interfacial free energies, which correspond to different dielectric materials. By comparing the results of a-Si/SiO₂ and a-Si/SiN_x multilayers, we find that the constraint on the Si-NC growth from the dielectric interfaces depends on the difference between interfacial free energies.

In general, the formation of Si-NCs includes nucleation and the following growth, induced either by furnace annealing or pulsed laser^[11]. Nucleation occurs homogeneously in the interior of the uniform amorphous phase or heterogeneously at preferential sites such as impuri-

ties, interfaces, and defects. After nucleation, Si-NCs would grow up with sufficient external thermal energy.

Here, we divide the whole formation process into two successive stages, i.e., pre-touch and post-touch of the dielectric interfaces. The multilayer is simplified as an a-Si/dielectric sandwich structure as shown in Figs. 1 and 2. In the pre-touch stage, a Si-NC is assumed to nucleate symmetrically in the middle of the a-Si layer with spherical shape with radius r . As in Ref. [9], spacing l is introduced to separate the crystal nucleus from the dielectric interfaces. When the Si-NC keeps growing up and intersects the top and bottom interfaces, the post-touch stage will begin. However, it will be shaped like a drum with lateral diameter beyond the layer thickness d . Moreover, we define γ_{ac} as the interfacial free energy per unit area between the a-Si phase and the crystalline Si (c-Si) phase, γ_{dc} as that between the dielectric material and the c-Si phase, and γ_{da} as that between the dielectric material and the a-Si phase. According to the deductions in Ref. [9], we can then achieve the effective interfacial free energies γ_{dc}^{eff} and γ_{da}^{eff} .

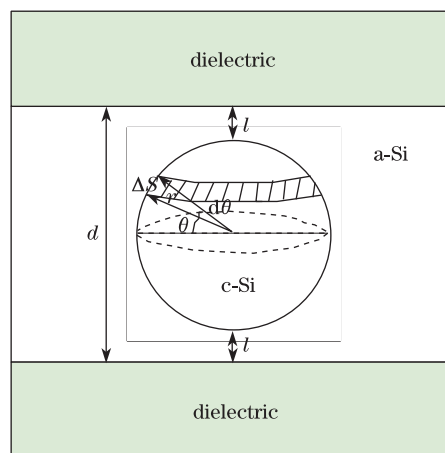


Fig. 1. Schematic diagram of the Si-NC in the pre-touch stage.

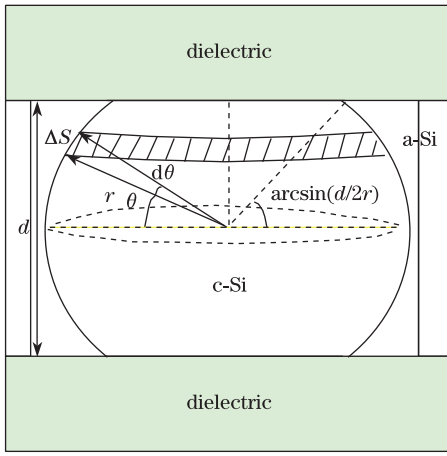


Fig. 2. Schematic diagram of the Si-NC in the post-touch stage.

$$\gamma_{dc}^{\text{eff}} = \gamma_{ac} + (\gamma_{dc} - \gamma_{ac})e^{-l/l_0}, \quad (1)$$

$$\gamma_{da}^{\text{eff}} = \gamma_{da}e^{-l/l_0}, \quad (2)$$

where the spacing distance between the crystal nucleus and the dielectric interface $l = d/2 - r$, and l_0 is the screening length that is strongly associated with the interatomic force between the dielectric material and c-Si or a-Si. In the longitudinal direction, the effective interfacial free energy variation $\Delta\gamma_{\perp}^{\text{eff}}$ is given by $\gamma_{dc}^{\text{eff}} - \gamma_{da}^{\text{eff}}$, while the interfacial free energy variation remains constant as γ_{ac} in the latitudinal direction. Then we introduce the average effective interfacial free energy variation $\overline{\Delta\gamma}^{\text{eff}}$ which

equals $(\Delta\gamma_{\perp}^{\text{eff}} + \gamma_{ac})/2$, and assume that the variation is isotropic. Therefore, the crystal surface at the same distance from the closer dielectric interface has the same interfacial free energy variation of $\overline{\Delta\gamma}^{\text{eff}}$ in any direction.

With the above assumptions, the Gibbs free energy variations of the Si-NC in the pre-touch and post-touch stages can be derived:

$$\Delta G_{\text{pre-touch}} = -\Delta G_{ac}V + \sum \overline{\Delta\gamma}^{\text{eff}} \Delta S (r \leq d/2), \quad (3)$$

$$\begin{aligned} \Delta G_{\text{post-touch}} = & -\Delta G_{ac}V + \sum \overline{\Delta\gamma}^{\text{eff}} \Delta S \\ & + (\gamma_{dc} - \gamma_{da})S (r \geq d/2), \end{aligned} \quad (4)$$

where

$$\begin{aligned} \overline{\Delta\gamma}^{\text{eff}} = & (\Delta\gamma_{\perp}^{\text{eff}} + \gamma_{ac})/2 = (\gamma_{dc}^{\text{eff}} - \gamma_{da}^{\text{eff}} + \gamma_{ac})/2 \\ = & \gamma_{ac} + \frac{\gamma_{dc} - \gamma_{da} - \gamma_{ac}}{2} e^{-(d/2-r)/l_0}, \end{aligned} \quad (5)$$

and ΔG_{ac} is the difference between the Gibbs free energies per unit volume of amorphous and crystalline bulk phase, V is the volume of the crystal cluster, S is the sum of contact areas between the cluster and the upper/lower dielectric interfaces, and ΔS is the ribbon-like area element of its spherical surface, which stands for a region with approximately the same interfacial free energy variation of $\overline{\Delta\gamma}^{\text{eff}}$. This can be regarded as a pure mathematical technique. Using integral calculus, we can further deduce the following results from Eqs. (3)–(5):

$$\Delta G_{\text{pre-touch}} = -\Delta G_{ac}V + \int_{-\pi/2}^{+\pi/2} \left[\gamma_{ac} + \frac{\gamma_{dc} - \gamma_{da} - \gamma_{ac}}{2} e^{-(d/2-r \sin \theta)/l_0} \right] (2\pi r \cos \theta) r d\theta, \quad (6)$$

$$\Delta G_{\text{post-touch}} = -\Delta G_{ac}V + \int_{-\arcsin(d/2r)}^{+\arcsin(d/2r)} \left[\gamma_{ac} + \frac{\gamma_{dc} - \gamma_{da} - \gamma_{ac}}{2} e^{-(d/2-r \sin \theta)/l_0} \right] (2\pi r \cos \theta) r d\theta + (\gamma_{dc} - \gamma_{da})S, \quad (7)$$

and then

$$\Delta G_{\text{pre-touch}} = -\Delta G_{ac} \times \frac{4}{3} \pi r^3 + \{ \gamma_{ac} \times 4\pi r^2 + (\gamma_{dc} - \gamma_{da} - \gamma_{ac}) \times 4\pi r l_0 \times [e^{-(d/2-r)/l_0} - e^{-d/2l_0}] \}, \quad (8)$$

$$\begin{aligned} \Delta G_{\text{post-touch}} = & -\Delta G_{ac} \times \left(\pi r^2 d - \frac{\pi d^3}{12} \right) + [\gamma_{ac} \times 2\pi r d + (\gamma_{dc} - \gamma_{da} - \gamma_{ac}) \times 4\pi r l_0 \times (1 - e^{-d/2l_0})] \\ & + (\gamma_{dc} - \gamma_{da}) \times 2\pi \left(r^2 - \frac{d^2}{4} \right). \end{aligned} \quad (9)$$

So far, the relationships between the Gibbs free energy variation and the crystal size as well as the layer thickness have been obtained. In Eqs. (8) and (9), the first negative terms in the right hand show the energy that would be released by forming the crystal volume while the remaining positive terms show the energy that would be consumed to form the crystal surface interfacing with the ambient. As a result, the Gibbs free energy variation reveals the overall energy gain or cost during the Si-NC formation. Additionally, the impact of the dielectric lay-

ers on the formation is just embodied in $\gamma_{dc} - \gamma_{da}$.

With Eqs. (8) and (9), the layer-thickness dependence of the Gibbs free energy variations in the two stages can be solved numerically. Here, we adopt the parameter values from Ref. [9] for a common multilayer structure of a-Si/SiO₂ as seen in Table 1.

In the pre-touch stage, the maximum of $\Delta G_{\text{pre-touch}}$ is defined as the nucleation barrier, denoted as ΔG_c . The corresponding nucleus size is the critical radius r_c . When $r \geq r_c$, Si-NC can be formed; otherwise the crystal

Table 1. Parameter Values for a-Si/SiO₂ and a-Si/SiN_x Multilayers

Multilayer Structure	ΔG_{ac} (eV/nm ³)	γ_{ac} (eV/nm ²)	$\gamma_{dc} - \gamma_{da}$ (eV/nm ²)	l_0 (nm)
a-Si/SiO ₂	5.081	1.440	2.491	0.64
a-Si/SiN _x	8.85	1.46	151.1	0.64

The parameter values for a-Si/SiO₂ and a-Si/SiN_x multilayers are obtained from Refs. [10] and [11], respectively. But for a-Si/SiN_x multilayers, l_0 is set to 0.64 nm in our model.

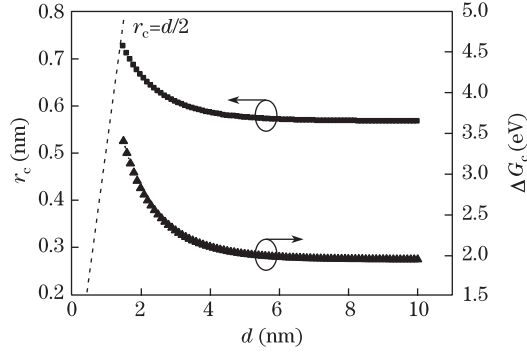


Fig. 3. Nucleation barrier ΔG_c and corresponding critical radius r_c versus a-Si layer thickness d in the pre-touch stage for a-Si/SiO₂ multilayers.

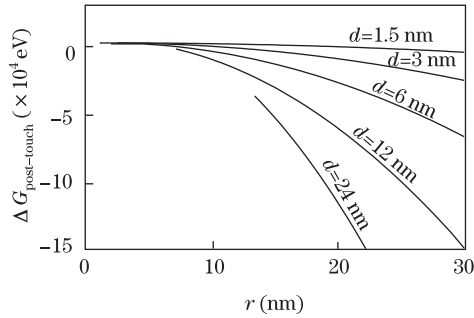


Fig. 4. Gibbs free energy variation in the post-touch stage $\Delta G_{\text{post-touch}}$ versus lateral radius r of the crystal cluster with various a-Si layer thicknesses d from 1.5 to 24 nm for a-Si/SiO₂ multilayers.

nucleus would be unstable with the tendency to shrink. We acquire ΔG_c by searching the maximum of $\Delta G_{\text{pre-touch}}$ with varying radii of Si-NC at a certain thickness of a-Si layer. The calculated ΔG_c and the corresponding r_c versus the layer thickness d are plotted in Fig. 3. The figure shows a cross point of the line $r_c = d/2$ (dash) and the curve of r_c , which significantly indicates a lower limit (~ 1.5 nm) of the layer thickness for the Si-NC formation under the condition of $r_c \leq d/2$ or equivalently $l \geq 0$ that must be implemented in our model. In addition, the thinner the Si layer, the higher the nucleation barrier or thermal energy that would be required for the nucleation.

Consequently, only when the a-Si layer thickness is no smaller than the limit can the post-touch stage occur. In the post-touch stage, the values of $\Delta G_{\text{post-touch}}$ are calculated with various r , subjected to $d \geq 1.5$ nm. Figure 4 displays that $\Delta G_{\text{post-touch}}$ is negative and decreases with increasing crystal radius, which indicates that the Si-NC tends to grow up with no lateral constraint from

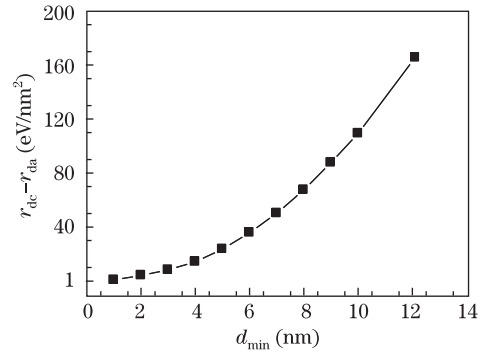


Fig. 5. Difference between the interfacial free energies γ_{dc} and γ_{da} versus lower limit of the a-Si layer thickness d_{min} .

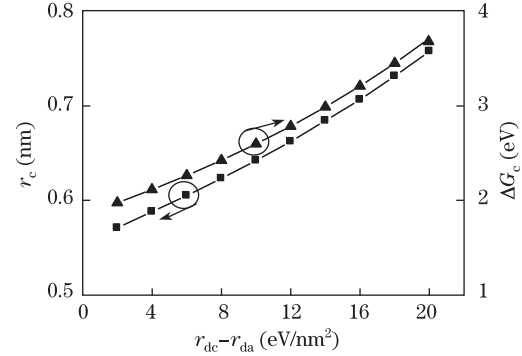


Fig. 6. Nucleation barrier ΔG_c and corresponding critical radius r_c versus difference between the interfacial free energies γ_{dc} and γ_{da} with the a-Si layer thickness d of 3 nm for a-Si/SiO₂ multilayers.

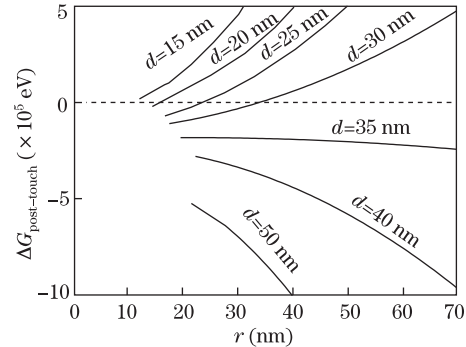


Fig. 7. Gibbs free energy variation in the post-touch stage $\Delta G_{\text{post-touch}}$ versus lateral radius r of the crystal cluster with various a-Si layer thicknesses d from 15 to 50 nm for a-Si/SiN_x multilayers.

the oxide interfaces as the formation is favored.

However, the difference between the interfacial free energies γ_{dc} and γ_{da} , $\gamma_{dc} - \gamma_{da}$, related to a certain dielectric layer, is not a well-known parameter and is usually obtained by fitting experimental data. With our model, its value could be simply derived from the lower limit d_{min} of the a-Si layer thickness, as shown in Fig. 5. It can be found that $\gamma_{dc} - \gamma_{da}$ increases with d_{min} and on the other hand, nucleation barrier and critical radius increase with $\gamma_{dc} - \gamma_{da}$, as displayed in Fig. 6. Therefore, for those dielectric layers that cause higher energy consumption to expand the crystal surface, the layer thickness would affect the Si-NC formation more dramatically.

The proposed model could also be used for other a-Si

multilayer structures. With the use of the parameter values from Ref. [10] as also seen in Table 1, we analyze the Si-NC formation in a-Si/SiN_x multilayers. According to the trends of $\Delta G_{\text{post-touch}}$ in Fig. 7, the lateral growth of the Si-NC would be constrained by the nitride interfaces when the a-Si layer thickness is below ~ 35 nm, since $\Delta G_{\text{post-touch}}$ moves from negative to positive with the crystal growing and the formation is not favorable in the end. Such results are consistent with those in Ref. [10]. Meanwhile, the lower limit for the layer thickness could be estimated as > 4 nm from Fig. 5. However, Si-NCs have been experimentally observed while the layer thickness is below that limit^[10]. It may be attributed to the effects for nonstoichiometry of the dielectric layer (SiN_x, $x < 4/3$), including the silicon diffusion, bond relaxation, and rearrangement during high-temperature annealing, and the reduced inhomogeneous interfacial strain. These effects are not included in our model and may weaken the influence of the nitride interfaces and the limitation to the a-Si layer thickness. The value of $\gamma_{\text{dc}} - \gamma_{\text{da}}$ for a-Si/SiN_x (151.1 eV/nm²) is consequently much higher than that for a-Si/SiO₂ (2.491 eV/nm²). In short, according to the calculating results for both multilayers, there remains a lower bound for the a-Si layer thickness but the constraint on the Si-NC growth from the dielectric interfaces would depend on the difference of $\gamma_{\text{dc}} - \gamma_{\text{da}}$.

In conclusion, we investigate the whole formation process of Si-NCs in a-Si/SiO₂ multilayers from nucleation to following growth with a modified model based on the Gibbs free energy variation. The calculating results indicate that there is a lower limit for the a-Si layer thickness below which the Si-NC formation cannot occur for a-Si/SiO₂ multilayers and the lateral growth of Si-NCs cannot be constrained by the oxide interfaces, which should

be accounted in order to better regulate the size and density of Si-NCs in the multilayer structure and further exploit as much as possible the luminescent potential of Si quantum dots.

This work was supported by the National Natural Science Foundation of China (No. 60877023) and the National "973" Program of China (No. 2007CB307004).

References

1. L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
2. X. Lu, J. Hou, M. Xiang, Z. Jia, and F. Zhong, *Chin. Opt. Lett.* **8**, 618 (2010).
3. M. Molinari, H. Rinnert, and M. Vergnat, *Appl. Phys. Lett.* **82**, 3877 (2003).
4. H. Zhang, L. Lin, and S. Jiang, *Chin. Opt. Lett.* **7**, 332 (2009).
5. M. Xie, Z. Yuan, B. Qian, and L. Pavesi, *Chin. Opt. Lett.* **7**, 319 (2009).
6. M. Wang, A. Anopchenko, A. Marconi, E. Moser, S. Prezioso, L. Pavesi, G. Pucker, P. Bellutti, and L. Vanzetti, *Physica E* **41**, 912 (2009).
7. F. Delachat, M. Carrada, G. Ferblantier, A. Slaoui, C. Bonafos, S. Schamm, and H. Rinnert, *Physica E* **41**, 994 (2009).
8. C. Spinella, S. Lombardo, and F. Priolo, *J. Appl. Phys.* **84**, 5383 (1998).
9. M. Zacharias and P. Streitenberger, *Phys. Rev. B* **62**, 8391 (2000).
10. L. Zhang, K. Chen, L. Wang, W. Li, J. Xu, X. Huang, and K. Chen, *J. Phys.: Condens. Matter* **14**, 10083 (2002).
11. K. Chen, X. Huang, J. Xu, and D. Feng, *Appl. Phys. Lett.* **61**, 2069 (1992).