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Understanding periodically twinned structure in nano-wires

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ABSTRACT

Using first-principles calculations we have investigated the high stability of twinned nano-wires, which explains why the stacking faults always appear. Furthermore, we present a growth model to describe the formation mechanism of the stacking faults in the compound nano-wire with zinc-blende structure (e.g. SiC). And the model is confirmed by the numerical calculation based on the point charge approximation.

1. Introduction

Recently great effort has been devoted to the synthesis and characterization of nano-wires [1–3], because of their unique electronic, optical, mechanical, and catalytic properties [4–6]. Twinning is the well-known phenomenon in nano-wires, which influence their physical properties and also their performance in application [7–9]. Much experimental and theoretical work showed that in nano-wires with the zinc-blende structure [10–13] the stacking faults appear periodically [14,15]. Strikingly it was found that the thickness of the twinned segment is proportional to the radius of nano-wire [15], which was later confirmed in many other systems such as ZnSe and SiC with zinc-blende structures. Such periodical stacking faults would certainly affect the physical properties of the nano-wires. In fact, in the nano-structural metal the stacking fault can significantly change the mechanical properties [16]. Unfortunately it is not clear why the stacking faults appear periodically, thus it is interesting to study how and why the stacking fault periodically appears in nano-wires. Up to now, several attempts had been made to reveal the formation mechanism of periodically twinned nano-wires and to explain the linear relationship between the thickness of the twinned segment L and the radius R of nanowire. A constant volume model and surface energetic argument were used to explain the experimental results [14,15]. It was also proposed that stacking faults which are formed during the crystallization can decrease the surface energy. But the microscopic mechanism of linear relationship between L and R was not clearly discussed.

In this Letter, based on the first-principles calculation, it is confirmed that the nano-wire of zinc-blende structure (e.g. SiC nano-wire) with periodically appearing stacking faults is energetically stable, which is different from that in the bulk where stacking fault costs energy. Considering that the combination of stacking fault energy and electrostatic energy determines whether a new atomic plane forms a twinned grain boundary, a growth model is further proposed to describe the formation mechanism, which includes the energetic argument and the growth kinetics. As shown later, the present model has revealed the formation mechanism of twinned wire with regular periodicity.

2. First-principles calculation of the relative stability of stacking faults

To get an insight into the relative stability of nano-wires with periodical stacking faults, we carried out the calculation using first-principles pseudo-potential atomic orbital approach within the framework of density functional theory which is based on SIESTA [17,18] and took the SiC nano-wire as an example. The interaction between core and valence electrons is described by Troullier–Martins pseudo-potential [19] and the exchange correlation energy is calculated with generalized gradient approximation (GGA) [20]. The polarization basis set of double-ζ quality for s–p is used. A super-cell of 228 atoms with length of 35 Å in both X and Y directions while 15.05 Å in Z direction is chosen corresponding to the experimental lattice constants of bulk 3C-SiC [21]. The atomic structure of the nano-wire is optimized by the conjugate gradient method until the largest force on each atom is less than 0.05 eV/Å.

It is found that the twinned nano-wire is energetically more stable than the nano-wire without the stacking faults. The binding energy of the nano-wire with stacking faults is ~ 0.01 eV/Å^2

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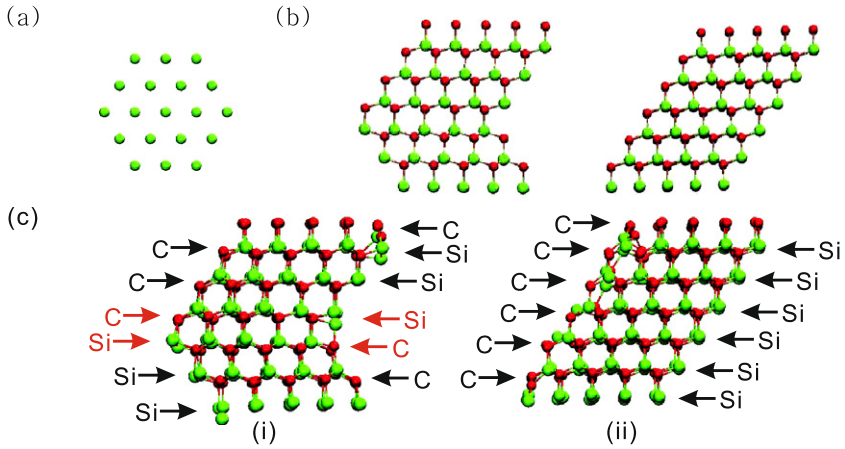

Fig. 1. (a) Top view of single atomic layer of the initial SiC nano-wire structure used in first-principles calculation. (b) Side view of the initial SiC nano-wire structures used in first-principles calculation. (c) Relaxed atomic structure of SiC nano-wires. The surface atoms are labeled by arrows. It shows that the element of surface atoms of the twinned SiC nano-wire changes periodically, which play a key role to the stability of the nano-wire. (i) Atomic structure of twinned SiC nano-wires. The surface relaxation near the stacking fault is labeled by red arrows, which shows the significant relaxation of surface atoms and the surface atoms change periodically. (ii) Atomic structure of SiC nano-wires without any stacking faults.

higher than that without the stacking faults. This result clearly explains why the stacking faults always appear in the compound nano-wire. For comparison the stacking fault energy in the bulk phase 6H-SiC is also calculated. It is ~ 0.0005 eV/Å^2, which is one order of magnitude less than the calculated value in nano-wire. And the experimental value is even smaller (0.0002 eV/Å^2) [22]. Since the binding energy of stacking fault in the nano-wire is much lager than that in the bulk, i.e., the energy of stacking fault near the center of the wire is negligible, it is reasonable to assume that the surface area near the stacking faults plays a key role in the stability of the twinned nano-wire, thus the stacking fault energy could be proportional to radius. In fact as shown in Fig. 1, one can easily find that a significant relaxation of surface atoms occurs near the stacking faults, resulting in that the stacking faults energy in a nano-wire is proportional to the radius of nano-wire.

3. The epitaxial growth model

3.1. Model description and numerical verification

The growth model is used to explain the formation mechanism of compound nano-wire with zinc-blende structure, such as SiC, ZnSe.... In these compounds, the bonding among atoms shows both covalent and ionic character, which involves charge transfer and results in both cation and anion. For instance, in SiC, due to the difference of electronegativity between Si and C, some electrons would transfer from Si to C atoms. C atom carries negative charge as an anion and Si atom carries positive charge as a cation. Therefore, in this system the electrostatic energy is the significant part of the total energy of the nano-wire and especially the surface charge interaction plays a key role in the stability of the nano-wire. Since the crystallization takes place epitaxially at the end of nano-wire, when a new atomic layer is added on, either twinned grain boundary in AaBbCc + Bb stacking sequence or a perfect atomic layer in AaBbCc + Aa stacking sequence can emerge, which is energetically determined by the sum of stacking fault energy and electrostatic energy. Here the electrostatic energy is defined as the potential energy of all the ions in the nano-wires and the stacking fault energy is defined as the extra energy which is used to form a twinned grain boundary. As mentioned in the previous section, stacking fault energy can be approximately assumed to have linear relationship with the radius of the nano-wire, i.e., the stacking fault energy can be written as

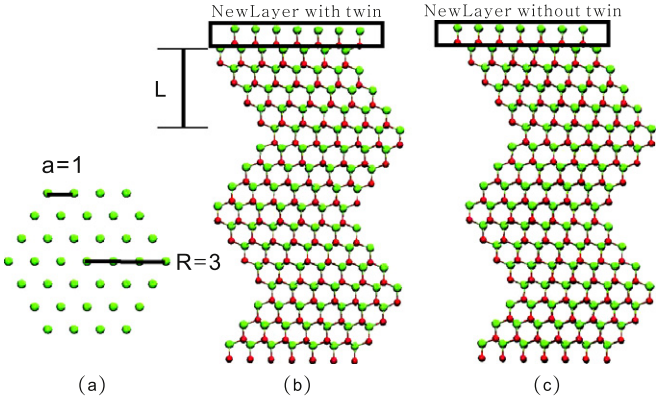

Fig. 2. Schematic structure of nano-wire used in numerical calculation of the model. (a) Top view of single atomic layer of the nano-wire with the radius R of 3 and the lattice constant a of 1. (b) Nano-wire with one additional layer which cause a twinned grain boundary. The segment thickness of the nano-wire L is 3.27 (4 layers) in the figure. (c) Nano-wire with one additional layer which doesn't cause a twinned grain boundary.

$$E_t(R) \approx \gamma R + \tau, \tag{1}$$

where R is the radius of nano-wire, γ and τ are constants.

Since the formation of stacking faults costs energy E_t, it prevents the structure of nano-wire becoming wurtzite structure. But the absolute value of electrostatic energy difference $\Delta E(R, L)$ between AaBbCc + Aa stacking sequence (Fig. 2(c)) and AaBbCc + Bb stacking sequence (Fig. 2(b)), which makes the new layer of nano-wire trend to form a twinned grain boundary, becomes larger during the growth of new segment of the nano-wire with radius R. When the thickness of new segment reaches segment thickness L, the absolute value of electrostatic energy difference $\Delta E(R, L)$ will be larger than stacking fault energy E_t slightly. Then a twinned grain boundary is formed. So we can use the equation

$$\Delta E(R, L) + E_t(R) = 0 \tag{2}$$

to get the relationship between the segment thickness L and the radius R. Here, the value of the electrostatic energy difference term $\Delta E(R, L)$ is negative, which makes the new layer of nano-wire trends to form a twinned grain boundary. The value of the stacking fault energy term E_t is positive, which wants to keep the zinc-blende structure.

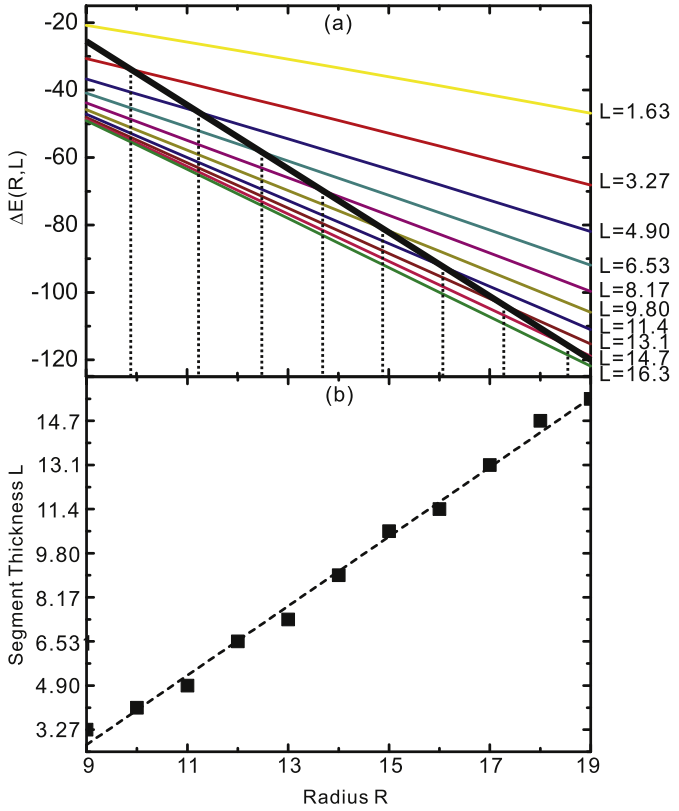

Fig. 3. (a) Numerical results of electrostatic energy and stacking fault energy based on point charge model. The thick black line denotes the negative value of stacking fault energy $-E_t$, with the slope $-\gamma$ of -9.5 and intercept $-\tau$ of 60.5. And $1/4\pi\epsilon_0$ is set to 1 to define the unit of energy. The colored line shows electrostatic energy difference ΔE for different L. The intersection point of thick black line and colored line shows the solution of Eq. (2). (b) The black points are the solution got from (a) which shows the relationship between radius and segment thickness. We have shifted the values of solutions to the realistic values, i.e., we ensure that the solutions correspond to the nano-wires, of which the number of atom layers of one segment and atoms of one layer is integer. The dashed line is the result of linear fitting. It is shown that the segment thickness L has the linear relationship with radius R.

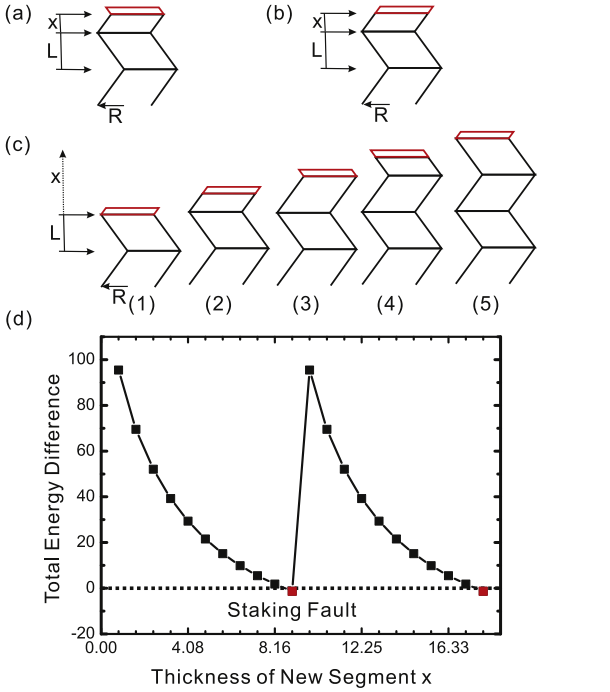

Fig. 4. (a) Twinned nano-wire with a new atomic layer with stacking fault. (b) Twinned nano-wire with a new atomic layer without stacking fault. The electrostatic energy difference $\Delta\varepsilon(R, L, x)$ is equal to the energy difference between configuration (a) and configuration (b), where R is the radius, L is the segment thickness and x is the thickness of new segment. (c) Growth process of SiC nano-wire, which depends on the total energy difference of the model $\Delta E_{tot} = \Delta\varepsilon(R, L, x) + E_t(R)$. (d) The total energy difference ΔE_{tot} is a function of the thickness of new segment x, where the radius $R = 14$ and the segment thickness $L = 8.98$ (11 layers). When the total energy difference is equal to zero, a new twinned grain boundary is formed.

Before analyzing the growth process of nano-wire quantitatively, we performed numerical calculation based on the point charge model to show the linear relationship first. Here each ion, i.e. the charged atom, is taken as a point charge. For simplicity, it is assumed that each atom carries equal electric charge. The calculation is based on the structure model shown in Fig. 2(b), (c). The number of atom-layer is large enough ($N \geqslant 1000$) to ensure the convergence of ΔE. Meanwhile the lattice constant, the charge on each atom and the coefficient $1/4\pi\epsilon_0$ are all set to 1.

In order to get the solution of Eq. (2), we calculated the energy difference $\Delta E(R, L)$ and negative stacking fault energy $-E_t(R)$ numerically and plotted them (Fig. 3(a)). Here we determine the slope $-\gamma$ and intercept $-\tau$ of $-E_t(R)$ are -9.5 and 60.5 respectively. The thick black line denotes the negative value of stacking fault energy as a function of radius R. Each of colored lines denotes the electrostatic energy difference ΔE as a function of radius R for different segment thickness L. The intersections of colored lines and thick black line show the solution of Eq. (2) (Fig. 3(b)). The solution really shows the linear relationship between the segment thickness L and radius R. It is worth to note another feature of ΔE shown in Fig. 3. When L approaches to infinity the value of ΔE will approach to a constant.

In order to show the process of twinning formation more clearly we calculated the electrostatic energy difference $\Delta\varepsilon(R, L, x)$ between the new atomic layer with stacking fault (Fig. 4(a)) and the new atomic layer without stacking fault (Fig. 4(b)), where R is the radius, L is the segment thickness and x is the thickness of new segment. By the definition the relationship between energy difference $\Delta\varepsilon(R, L, x)$ and $\Delta E(R, L)$ is $\Delta E(R, L) = \Delta\varepsilon(R, L, 0)$. Obviously the total energy difference ΔE_{tot} between the structures of Fig. 4(a) and Fig. 4(b) is the sum of energy difference $\Delta\varepsilon(R, L, x)$ and $E_t(R)$. When ΔE_{tot} is equal to zero the stacking fault energy cannot keep the zinc-blende structure and a twinned grain boundary could be formed. We take the nano-wire with radius of 14 and segment thickness of 8.98 (11 layers) as an example, which is a solution of Eq. (2) (Fig. 3). Fig. 4(d) shows the total energy difference ΔE_{tot} as a function of the thickness of new segment x. During the growth of the nano-wire the total energy difference becomes lower and lower until it becomes zero (Fig. 4(c) (1)–(2)). Then a twinned grain boundary is formed and the sign of surface charge reverses owing to the variation of surface-atom element. So the value of total energy difference ΔE_{tot} will be larger than zero again (Fig. 4(c) (3)). A new segment is formed and the previous process repeated (Fig. 4(c) (4)–(6)). Finally it results in a periodically twinned nano-wire.

3.2. Analytical derivation

Besides the numerical verification the linear relationship between radius and segment thickness can also be qualitatively derived. In order to get the analytical form of $\Delta E(R, L)$ which depends on radius R, segment thickness L and lattice constant a. The asymptotic behaviour of $\Delta E(R, L)$ should be made clear. Because of the electron-neutrality of the nano-wire, the electrostatic interaction is screened and the value of the electrostatic energy should be proportional to the size of nano-wire when it approaches to

infinity. As mentioned previously [14], only the polarized charge located on the surface plays a key role. Therefore when the radius R tends to infinity the energy difference of one atom-layer ΔE will be proportional to the radius R (Fig. 3(a)). And since $\Delta E(R, L)$ is the electrostatic energy difference, it must be proportional to the inverse of lattice constant a^{-1} and the square of charge carried by each atom Q^2. So the electrostatic energy difference can be written as

$$\Delta E(R, L) = \frac{Q^2 R}{a^2} \widetilde{\mathcal{F}}(R, L, a). \tag{3}$$

Since the radius R of nano-wire is obviously proportional to lattice constant a, the factor $(Q^2 R)/(a^2)$ is proportional to R, a^{-1} and Q^2, which is the same to the asymptotic behaviour of energy difference $\Delta E(R, L)$. Therefore the function $\widetilde{\mathcal{F}}(R, L, a)$ is a bounded and dimensionless function. We can use first order approximation of Taylor expansion to evaluate the function $\widetilde{\mathcal{F}}(R, L, a)$ safely. For convenience we substitute the variables $(L/R, a/L, a/R)$ for the variables (R, L, a) and define

$$\mathcal{F}\left(\frac{L}{R}, \frac{a}{L}, \frac{a}{R}\right) = \widetilde{\mathcal{F}}(R, L, a). \tag{4}$$

Given to Eq. (3) and Eq. (4) we get

$$\Delta E(R, L) = \frac{Q^2 R}{a^2} \mathcal{F}\left(\frac{L}{R}, \frac{a}{L}, \frac{a}{R}\right). \tag{5}$$

Considering that the lattice constant a is much smaller than the radius R and the segment thickness L, we can use the first order approximation of a Taylor expansion and write the function $\Delta E(R, L)$ as

$$\Delta E(R, L) \sim \frac{Q^2 R}{a^2}\left(\mathcal{F}_0 - \alpha \frac{a}{L} - \beta \frac{a}{R}\right) \tag{6}$$

where $\mathcal{F}_0(L/R) = \mathcal{F}_0(L/R, 0, 0)$, α and β are coefficients of Taylor expansion. And we take them as approximately constant functions. Substituting the left side of Eq. (2) by Eq. (6) and Eq. (1), we have

$$\frac{Q^2 R}{a^2}\left(\mathcal{F}_0 - \alpha \frac{a}{L} - \beta \frac{a}{R}\right) + \gamma R + \tau = 0. \tag{7}$$

And the equivalent form of Eq. (7) is

$$R = \frac{L}{\alpha}\left(\frac{\tau a}{Q^2} - \beta\right) + \frac{RL}{\alpha a}\left(\mathcal{F}_0 + \frac{\gamma a^2}{Q^2}\right). \tag{8}$$

If the stacking fault can be formed in the nano-wire system with different radius, the increase rate of the energy difference $\Delta E(R)$ and stacking fault energy $E_t(R)$ should be in the same order. Otherwise, as shown in Fig. 3, Eq. (2) will not have any solution with large R and the nano-wire with large radius would be of zinc-blende or wurtzite structure without stacking faults. Therefore the sum of one degree term coefficients of $\Delta E(R)$ in Eq. (6) and one degree term coefficients of $E_t(R)$ in Eq. (1) is approximately equal to zero.

$$\frac{Q^2}{a^2}\mathcal{F}_0 \approx -\gamma. \tag{9}$$

Given this approximation (Eq. (9)) the relationship between radius and segment thickness Eq. (8) can be reduced to

$$R \sim \frac{L}{\alpha}\left(\frac{\tau a}{Q^2} - \beta\right). \tag{10}$$

Obviously it arrives at linear relationship between the thickness of segment and the radius, consistent with the numerical results in previous section.

4. Summary

Using first-principles method we have confirmed that the stacking fault does show high stability in compound semiconductor nano-wire, which is different from the bulk phase where stacking faults usually decrease the stability. Based on the competition of stacking fault energy and electrostatic energy, a growth model has been proposed to understand the appearance of stacking faults and the linear relationship between the thickness of segment and radius of compound semiconductor nano-wire with zinc-blende structure is further verified, which is in agreement with experimental observation. In these kinds of nano-wires the electrostatic energy makes the nano-wire trend to form stacking faults but the stacking fault energy prevents it. During the growth of nano-wire the stacking fault energy keeps constant. But the value of electrostatic energy difference which depends on the thick of the new segment becomes larger and goes back to its initial value after the formation of stacking faults. So the stacking faults appear periodically. Numerical calculation is also performed based on the point charge approximation, which does lead to a linear relationship between radius R and thickness L. We believe the present study provided mechanism to understand the formation of periodically twinned nano-wire.

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