Reaction pathway analysis for differences in motion between C-core and Si-core partial dislocation in 3C-SiC

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Abstract
Reaction pathway analysis was carried out to investigate the activation energy barriers of Shockley partial dislocation mobility in 3C-SiC. For each partial dislocation, there are two types of dislocations according to which kind of atom, Si or C, comprises the core edge of the dislocation line. In this paper, the partial dislocation is simulated by Vashishta potential functions. Moreover, the activation energy of kink pair nucleation and kink migration are investigated by reaction pathway analysis. The dependence of the activation energy on the driving shear stress is also discussed. The results show that during kink migration, 30° partial dislocations have a lower activation energy barrier than 90° partial dislocation. And, C-core partial dislocations have a higher activation energy barrier than Si-core dislocations for both degrees of partial dislocations during kink migration and nucleation. This conclusion is consistent with the experimental result that Si-core dislocations migrate more readily than C-core dislocations. Furthermore, we found that partial dislocations with larger distance between the dangling bond atoms along the dislocation line have higher activation energy barriers. Based our calculation results, we propose new models to account for the morphological differences in the dislocation lines.

Key words : Reaction path way, Shockley partial dislocation, Dislocation activation energy barrier, Morphology of dislocation lines, Kink nucleation and migration

1. Introduction

Silicon Carbide is well known as one of the most promising semiconductor material, with a wide bond-gap, high saturation velocity, and high thermal conductivity. Its excellent performance in high temperature makes a great advantage in developing high frequency and high power application (Sasaki, et al., 1984 and Ruff, et al., 1994). Silicon Carbide has more than two hundred and fifty polytypes, the α-silicon carbide is one major type with hexagonal or rhombohedral crystal structure, such as 2H-SiC, 4H-SiC, 6H-SiC. Another major type is β-silicon carbide, the 3C-SiC, which has a lower growth temperature compared with α-silicon carbide and can be grown on silicon substrate by chemical vapor deposition method (CVD). With this lower formation temperature, 3C-SiC can be grown with a larger wafer diameter compared with other polytypes. The larger diameter of silicon carbide wafer is important in the semiconductor device manufacture.

During the growth of 3C-SiC on silicon, lattice mismatch caused by the difference in lattice constant and thermal misfit due to the differences in thermal expansion coefficient will contribute to large residual stress (Nagasawa and Yagi., 1997, Sun, et al., 2012, Veprek, et al., 2009, Zielinski, et al., 2007, Severino, et al., 2007). This stress can induce a high dislocation density and wafer warpage in device manufacture. In addition, dislocation nucleation and propagation is thought to be one of the main factors of the wafer warpage. Therefore, the dislocation analysis is necessary to have a good understanding of how to reduce dislocation density and the wafer warpage. There are two types of dislocations in 3C-SiC due to which kind of atoms constitute the dislocation line, i.e. Si-core and C-core. Moreover, all dislocations in all SiC polytypes are dissociated into two partials. Thus the screw dislocation is
dissociated into two 30° partials, the 60° dislocation is dissociated into a 90° and a 30° partial (Pirouz and Yang, 1993). There have been many controversies about which kind of partial dislocation move easier. As we know, in crystals where the lattice resistance (i.e., Peierls stress) is large, dislocation moves by kink pair nucleation and migration. And the activation energy barriers of the kink pair nucleation and migration are used to see whether the C-core or the Si-core dislocation move easier. Therefore, by investigating these activation energies, which kind of partial dislocation has higher activation energy barrier can be illustrated.

However, few studies have been reported on the activation energy barrier of the partial dislocations in 3C-SiC. Blumenau et al. (2002, 2003) had investigated the activation energy barrier of 90° partial dislocation and asymmetrical 30° partial dislocation structure respectively with about 500 atoms by DFTB (density function based tight binding method) and AIMPRO (ab initio modelling program). They indicated that all the polytypes of silicon carbide have similar dislocation core structure and broadly similar kink migration energy based on the assumption that similar kink migration process must occur in them. However, their conclusion that the C-core partial dislocation has a lower activation energy barrier is in contrast with the experimental observations (Lara, et al., 2012, Ning, et al., 1996, Idrissi, et al., 2007 and Ha, et al., 2003). Ning et al. pointed out that Si-core partial dislocation nucleated before C-core partial dislocation by TEM observation above 1300 °C. Idrissi et al., and Lancin et al., also observed that the C-core partial dislocation segments were produced and immobile after the Si-core partial dislocations moved a long distance around 1100 °C. Lara showed that at temperature higher than Tc~993 °C, most of the basal dislocations dissociated into two partials that glide simultaneously, and the Si-core partial dislocation was leading while the C-core partial dislocation is trailing. These experimental data indicate that the Si-core partial dislocations have a higher mobility than C-core partial dislocations. The dislocation mobility is activated with energy Q as Eq. (1)

\[ v_{dis} \propto e^{-Q/kT} \]  

(1)

Q is given as \( Q = 2E_f + w_m \) for short dislocation segments, and \( E_f + w_m \) for long segments (Hirth J.P. and Lothe J., 1982). \( E_f \) represents the activation energy barrier of the kink nucleation, and \( w_m \) represents the activation energy barrier of the kink migration. Therefore, the Si-core partial dislocations move easier by a lower activation energy barrier than C-core partial dislocations. Opposite results to those of Blumenau et al. (2002, 2003) may be caused if the size of the model employed by these authors in their numerical simulation was larger. Therefore, atomic simulation with more atoms based on empirical potential is needed. Sun et al. (2013) showed that the Si-core dislocation has lower activation energy and may result in athermal strains during glide-set partial nucleation from sharp corners. This conclusion agrees with the previously-mentioned experimental data. In order to figure out which kind of partial dislocation has a higher mobility, we use the reaction pathway analysis based on Climbing Image Nudged Elastic Band (CI-NEB) method to investigate the partial dislocation mobility difference between C-core and Si-core in 3C-SiC.

2. Model and simulation methods

The simulation model is schematically shown in Fig. 1. The model size is 9.60×22.2×2.26nm\(^3\), including 46,656 atoms. The coordinate axes are [11-2], [-110], [111] along X, Y, Z directions. We created the dislocation on the slip plane (111), with the burgers vector \( b_{90} = a_0/[11\bar{2}] \) and \( b_{30} = a_0/[1\bar{2}1] \) (\( a_0 = 0.458nm \)). Shear stress \( \sigma_{xz} \) was applied by displacing top and bottom atoms to X and –X directions. Periodic boundary condition is applied in Y direction. In addition, Vashishta potential function (Vashishta, et al., 2007) was used to represent the 3C-SiC in this simulation, which can reproduces the stacking fault energy calculated by DFT (Shimojo, et al., 2001). Therefore, with the combination of molecular dynamics and conjugate gradient method, several stable configurations of 30° and 90° partial dislocations with different kink pair widths were obtained. Based on these configurations, we performed reaction pathway analysis (Izumi and Yip, 2008, Shima, et al., 2010) based on CI-NEB method to identify the activation energy barriers of kink nucleation and migration for these different kinds of dislocations.
Fig. 1 Schematic representation of the simulation model. The yellow line represents the kink which glides on (111) plane.

(a) 90° Partial dislocation Si-core  (b) 90° Partial dislocation C-core

(c) 30° Partial dislocation Si-core  (d) 30° Partial dislocation C-core

Fig. 2 The relaxed core structure of the Shockley partial dislocation in {111} plane of 3C-SiC. The larger atoms represent silicon while the smaller ones represent carbon. For each partial dislocation, the upper Fig. shows a projection along the dislocation line while the bottom Fig. shows the projection onto (111) glide plane with the [110] dislocation line vertical in the Fig. (a), (b) show the 90° partial dislocation core structure of Si-core and C-core respectively. (c), (d) show the 30° partial dislocation core structures of Si-core and C-core respectively. The stacking fault area is shown by shadow area. The dash yellow lines show the distance between the dangling bond atoms along the dislocation line.
Fig. 2 shows the dislocation core structure’s projection onto (111) and (110) planes with different direction of Si-core and C-core respectively. Along the dislocation line, two layers of atoms shown by green balls represent the atom with three-fold coordination while the other atoms have four-fold coordination. The larger atom represents silicon, the smaller one represents carbon. In this paper, we focus on the unreconstructed dislocation types, for the reason that these structures have lower activation energy barrier compare with reconstructed dislocation (Savini, et al., 2007a, 2007b). Moreover, Vashishta potential function can’t reproduce the reconstructed dislocation structure.

In this simulation, Atomeye (Li, 2003) is used to visualize the structure configuration, and the average Si-C bond length is around 1.86 Å. Moreover, 2.16 Å is set up to decide whether the Si-C bond will be shown in the visualization. The dislocation structure characters are also shown in Fig. 2. For 90° partial dislocation structure, with 0.3 GPa driving shear stress, the dangling bond atoms along the dislocation line area are separated by 2.50 Å for C-core, and 2.28 Å for Si-core under 0.3 GPa driving shear stress. For 30° partial dislocation, the distance between the dangling bond atoms along the dislocation line is 3.18 Å for Si-core and 3.31 Å for C-core under 1.8 GPa. All of these distances between the dangling bond atoms along the dislocation line are shown in Fig. 2 by dash yellow lines.

3. Results and discussion

3.1 90° partial dislocation

For the 90° partial dislocation, the kink nucleation and kink migration were analyzed for both C-core and Si-core. Fig. 3 shows kink migration paths for C-core and Si-core. Here, we focus on one side of the kink for the symmetric structure of the kink pair in 90° partial dislocations. The kink pair of width 12 is shown in Fig. 4. The width is counted by the number of dangling bond atoms along dislocation line between the positive and negative kinks. In Si-core partial dislocation, during the kink migration, the carbon atom marked with small black arrow moves to elongate kink width, while the silicon atom moves in the C-core partial dislocation. The dependence of activation energy on the driving shear stress was investigated which is summarized in Fig. 5.
These results show that the C-core has a higher activation energy barrier. In addition, the activation energy difference of kink migration is $0.15 \pm 0.03 \text{eV}$ between the two types $90^\circ$ partial dislocations under different driving shear stresses. However, the previous simulation given by Blumenau et al. (2002, 2003) with DFTB and Savini et al. (2007a, 2007b) with DFT showed that C-core has lower activation energy barrier in $90^\circ$ partial dislocation. This difference could be caused by the simulation method that DFT and DFTB systems can't run with more than thousands of atoms because of the computation capacity. Moreover, without the reaction path way analysis result would include large numerical error.

Fig. 4 Kink pair structure for C-core $90^\circ$ partial dislocation with a width of 12. The width is measured by the number of dangling bond atoms along the kink. The black arrows show the direction of kink migration. The kink pair width increases after the kink migration.

The kink nucleation path of $90^\circ$ partial dislocation is shown in Fig. 6, while the kink nucleation activation energy as a function of driving shear stress is summarized in Fig. 7. These results indicate that the Si-core $90^\circ$ partial dislocation has a lower activation energy barrier than C-core $90^\circ$ partial dislocation. This conclusion is also consistent with experimental data (Lara, et al., 2012) that, above the critical temperature, the C-core and the Si-core partial dislocation glide simultaneously with a small separation between them, and Si-core partial dislocation is the leading partial dislocation. What's more, based on the reaction path way analysis in Fig. 4, we can see that the atom marked with a small black arrow moves, breaks one Si-C bond and forms a new one during kink migration. Simultaneously, two atom marked by black arrow move in sequence during kink nucleation. The motion of atoms around the kink during kink nucleation and kink migration are quite similar. The similarity of these processes implies that the C-core $90^\circ$ partial dislocation has lower activation energy for both nucleation and migration as compared to the Si-core $90^\circ$
partial dislocation. In other words, it is not possible that the C-core partial dislocation can have a higher activation energy for nucleation but a lower activation energy for migration compared to those for the Si-core partial dislocation. In addition, considering with characteristic of the dislocation core structure, shown in Fig. 2, the partial dislocation with a larger separation between the dangling bond atoms along the dislocation line also has higher activation energy. This consistence may suggest that based on characteristic of dislocation core structure, we can predict which kind of 90° partial dislocations has a lower activation energy barrier. Nonetheless, this hypothesis should be based on that the empirical potential which was carried out in the simulation can represent SiC well.

3.2 30° partial dislocation

For the unsymmetrical kink structure of 30° partial dislocation, there are two different activation energy barriers for the left and right kink (LK and RK) respectively. Their activation energy difference is caused by structure difference of RK and LK. Fig. 8 shows the kink migration path of LK and RK for Si-core and C-core partial dislocation. The
migration mechanism of LK is more complex compared with RK because of the structure difference. In LK migration path, the atom marked by black arrow is the major moving part while two atoms are shifting during the RK migration path. Fig. 9 and Fig. 10 represent the dependence of activation energy on the driving shear stress of LK and RK. Notice that, for 30° partial dislocation kink migration simulation, only the high driving shear stress region is given. For the reason that, in low stress region, we can’t get stable dislocation structure which probably due to the interatomic potential problem. These simulation results show that the Si-core 30° degree partial dislocation has a lower activation energy barrier compared with C-core 30° partial dislocation. And, the energy difference between the C-core and Si-core is around 0.07eV for LK, while the difference for RK is 0.13eV. Moreover, RK has a higher the activation energy barrier than LK. Compared with previous numerical study, our conclusion that LK has a lower activation energy barrier in C-core 30° partial dislocation is consistent with Savini’s first-principle simulation (Savini, et al., 2007a, 2007b). However, as regards the activation energy barrier of LK and RK in Si-core 30° partial dislocation, we have a contrary conclusion. Savini pointed out that, for Si-core 30° partial dislocation, the activation energy barrier for LK is 0.08eV and that for RK is 0.06eV. But in the present work, the saddle point energy is calculated to be 0.07eV and 0.152eV for LK and RK, respectively. Considering the structure similarity of RK for Si-core and C-core in 30° partial dislocation, the difference of migration activation energy of RK in C-core and Si-core should not be so large. Moreover, Savini’s simulation result of the kink nucleation activation energy in 30° partial dislocation showed an opposite conclusion about the dislocation mobility compared with previous experimental results (Idrissi, et al., 2007 and Ha, et al., 2003). Besides, as mentioned at the end of section 3.1, there is also a consistency with the fact that, for both the dislocation nucleation and migration, the partial dislocations with a larger separation between dangling bonds have a higher activation energy barrier than the partial dislocations with a smaller separation.

![Fig. 8 Kink migration paths for 30° partial dislocations. The first and second row show the left and right kink (LK and RK) migration path respectively for the Si-core glide set 30° partial dislocation. The third and fourth row show the left and right kink (LK and RK) migration path respectively for the C-core glide set 30° partial dislocation. The atom marked by black arrow is the major moving part in LK migration while two atoms shift during the RK migration path. The light blue lines show the changing of the kink pair width during kink migration.](image-url)
Fig. 11 shows the kink nucleation path of 30° partial dislocation under a specific driving shear stress. Notice that, the configurations of point 1 and point 2 do not represent the saddle point configuration in the reaction path. These two configurations are used to give a better illustration that, for each core of 30° partial dislocation, one RK and two LKs migrate in sequence to complete the kink nucleation process. Indeed, these migration processes are not exactly the same compared with the RK and LK migrations which are mentioned in Fig. 8. But, they have similarity in the migration mechanism of the major moving part. Moreover, the C-core and Si-core 30° kink nucleation paths are simulated with driving shear stresses of 3.0 GPa and 2.34 GPa respectively. The activation energy barriers are 1.03 eV and 1.04 eV for C-core and Si-core. It is well-known that the activation energy barrier decrease as the driving shear stress increase. Therefore, we can conclude that in the 30° partial dislocation kink nucleation the Si-core has a lower activation energy barrier than C-core 30° partial dislocation. The previous first-principle calculation that was done by Savini et al. (2007a, 2007b) showed that the kink formation energy barriers are 1.48 eV and 2.12 eV for C-core and Si-core in 30° partial dislocations respectively. Our conclusion about which type of 30° partial dislocation has lower action energy barrier is contradicted to that of Savini’s. This contradiction might be caused by the size of the model employed in the numerical simulation. In summary, the kink nucleation in 30° partial dislocation has a higher activation energy barrier than the 90° partial dislocation. At the same time, for kink migration, the 30° partial dislocation has a lower activation energy barrier compared with the 90° partial dislocation.
3.3 Morphology of partial dislocations

In 1981, using an in-situ TEM technique, Hirsch et al. (1981) pointed out that the morphology of 90° partial and 30° partial dislocation lines are different, the 90° partial dislocation line was found to be cusped as a zigzagged line while the 30° partial dislocation line was smooth and straight. Since then, researchers have tried to find a connection between the morphology of the partial dislocation line and the types of dislocation line, such as different core nature or the types of partial dislocations (e.g., 30°, 90°). Ning and Pirouz (1996) and Stahlbush et al. (2004) showed that, in their observation, all the Si-core partial dislocation had a smooth shape while the C-core partial dislocation were zigzagged. They attribute the dislocation line morphology difference to their core nature. On the other hand, Pilyankevich et al. (1982, 1984) and Maeda et al. (1988) attribute the different morphologies of partial dislocations to their Burgers vector. After that, Mussi et al. (2007) and Lancin et al. (2009) found that C-core partial dislocation could be either straight or zigzagged. Their experimental results showed that the core nature of partial dislocations cannot be deduced from the morphology of the dislocation line. Until now, this controversy is still going on, and most of the research in this area is experimental. We have not seen any theoretical computation performed that has provided an understanding of the partial dislocation line morphology. Here, based on the reaction path analysis of the partial dislocation activation energy, we propose new models to describe this morphology difference.

For representing the kink nucleation and migration paths in part 3.1, we conclude that, migration and nucleation have similarities in terms of the motion of atoms at and near the dislocation core. Fig. 12 shows a comparison of the minimum energy path for kink nucleation and migration in 90° partial dislocation. Notice that in the kink nucleation path, the activation energy barrier for saddle point 1 is almost the same ($E_1 \approx E_s$) as the kink migration energy. This means that if for kink migration, part of the kink nucleation process has also been produced. Moreover, think of the activation energy as a pulse, if the pulse is not large enough to cover the barrier for saddle point 2 but large enough to cover saddle point 1, the existence of the local minimum which is marked by a red spot in Fig. 12 can insure that the kink has the probability to be stable with this configuration. In other words, the kink migration and nucleation have the same probability to be generated. Of course, in this case the kink nucleation process is not finished within a local minimum configuration. Based on the above, we propose a mechanism for the 90° partial dislocation kink propagation in Fig. 13. Once the 90° partial dislocation kink is nucleated, there are several possible activation energy barriers. Here, D1 and D3 present the probability for kink migration; D2 means the probability for a new kink nucleating from the top of the original one while D4 means the probability for another new kink to nucleate on the remaining dislocation line.
We already know that, the activation energy barrier for the saddle point 1 is almost the same \( E_1 \approx E_s \) compared with the kink migration activation energy. These similar activation energy barriers indicate that the kink migration and part of the kink nucleation can be produced with similar possibilities. In addition, for the structure’s symmetric character, we get that D1= D3. Based on the above, we conclude that about the possibility for four different kind of kink movement direction: D1= D3 ≈ D2 ≈ D4. This conclusion shows that, if the 90° partial dislocation kink has enough energy to be migrated, a part of the kink nucleation can be nucleated too. Therefore, the 90° partial dislocation lines have a zigzagged morphology.

![Energy vs Reaction coordinate](image1.png)

**Fig.12** Minimum energy path for kink nucleation and migration in 90° partial dislocations under a driving shear stress of 0.3 GPa. The red spot shows the local minimum in the kink nucleation path. The light blue line show the value difference between the saddle point in kink migration and saddle point 1 in kink nucleation is very small. In kink nucleation path, \( E_1 \) represents the activation energy barriers for saddle point1 while \( E_2 \) represents the activation energy barriers from the local minimum spot to saddle point 2. \( E_s \) represents the activation energy barriers for kink migration. And, \( E_1 \approx E_s > E_2 \).

![Energy vs Reaction coordinate](image2.png)

**Fig.13** Kink propagation mechanism for 90° partial dislocation. D1, D2, D3 and D4 show the possibility for each direction which the kink can migration in. With the similar possibility each direction, the 90° partial dislocation line could have a zigzagged morphology.

The kink propagation mechanism for 30° partial dislocation is different. In Fig. 14, we show the minimum energy path way for the kink nucleation with a driving shear stress of 3.0 GPa and migration of RK and LK with a driving shear stress of 2.3 GPa. In the 30° partial dislocation kink nucleation path, there is only one saddle point, no local minimum. And the large difference of the activation energy barriers between the kink nucleation and migration indicate that once the kink is nucleated, both LK and RK can migrate freely while the kink still does not have enough energy to nucleate a second kink. Moreover, since the activation barrier of RK is about 10 times that of LK, we propose that after nucleation, the kink prefers to migrate because of the lower activation energy of LK.
Fig. 15 shows the schematic representation of the glide energetic configuration, beginning from kink pair nucleation with different widths. Once the kink nucleation process is finished, for 90° partial dislocation, the kink can migrate in two directions. For the symmetric kink pair character of 90° partial dislocation, no matter which direction the kink migrates, the energy curve in Fig. 15 would be the same because of the same activation energy barrier for RK and LK. However, for the 30° partial dislocation as mentioned in last paragraph that the LK kink prefers to migrate because of its lower migration activation energy after the kink nucleation process is finished. This glide process is showed in Fig 15 (b). Combination with the large difference in activation energy barrier for kink nucleation and migration, we propose that during the 30° partial dislocation propagation, once the LK is nucleated, it prefers to continue migrating since its migration energy is lower than that of RK. And the large difference of activation energy barrier between kink nucleation and migration can induce that the kink can keep migrating until the energy is large enough to nucleate a new kink. In this way, the 30° partial dislocation lines always have a smooth morphology. This kink propagation mechanism for 30° partial dislocation is shown in Fig 16. We emphasize again that all the above analysis applies to the unreconstructed dislocation lines.
This analysis method can also apply to other kinds of dislocations. For example, reconstructed partial dislocations could have totally different nucleation paths. Dislocation lines with the following characters: a local minimum exist in the paths and their kink migration activation energy barrier is close to the barrier to reach the local minimum could have a zigzagged morphology. Due to the existence of both unreconstructed and reconstructed partial dislocation lines with different propagation mechanisms, we cannot simply attribute the morphology difference to their core nature or their Burgers vector. This can also explain why previous investigators reached opposite conclusions.

4. Conclusion

The reaction pathway analysis is applied to study on the activation energy barrier of 30° and 90° partial dislocations mobility in 3C-SiC. The simulation results show that, C-core partial dislocation has a higher activation energy barrier for kink migration and kink nucleation than Si-core for both 30° and 90° partial dislocations. The conclusion about which kind of dislocation moves easier for a lower activation energy barrier is in agreement with previous experimental studies (Lara, et al., 2012, Ning, et al., 1996, Idrissi, et al., 2007 and Ha, et al., 2003). Besides we also found that the partial dislocation with a larger distance between the dangling bond atoms along the dislocation line also has a higher activation energy barrier for both 30° and 90° partial dislocations. Moreover, based on the activation energy barrier calculation, we propose new models to explain the morphological character of different partial
dislocation lines. We propose that the 30° partial dislocation prefer to be smooth because of the large activation energy difference between kink nucleation and kink migration. And the 90° partial dislocation lines prefer to be zigzagged for the reason that the 90° partial dislocation lines have the possibility to migrate and nucleate simultaneously.

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