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Ab initio molecular dynamics simulation of a pressure induced zinc blende to rocksalt phase transition in SiC

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Abstract

The high-pressure induced phase transformation from the zinc blende to rocksalt structure in SiC has been studied by the *ab initio* molecular dynamics method. The simulations showed that SiC passes through a tetragonal intermediate state before transforming to a monoclinic phase at 160 GPa. The mechanism for this phase transformation agrees well with recent *ab initio* MD simulations, in which the applied pressure was as high as ~ 600 GPa, but in the present study the transformation occurs at much lower pressure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is well known that, under ambient pressure, highly covalent compounds favor the lower coordination structures, such as fourfold coordinated zinc blende (ZB) and wurtzite structures, whereas highly ionic materials prefer the higher coordination structures (for example, sixfold coordinated rocksalt (RS) and eightfold coordinated CsCl structures). As pressure is increased, the covalent compounds can transform into the higher coordination phases. During the past several years, high-pressure induced phase transition from ZB to RS structure in semiconductors has been extensively studied. Experimentally, picosecond time-resolved optical spectroscopy coupled with shock wave techniques [1–3] and shape changes determined by x-ray diffraction [4] can provide direct probes on intermediate metastable states formed during the high-pressure phase transition. On the other hand, the molecular dynamics (MD) method [5] and *ab initio* periodic density functional theory [6–11] have played significant roles in the study of high-pressure phase transition. Recently, the *ab initio* molecular dynamics methods [12–14] (AIMD) that combine first-principles with MD methodology have been employed to explore the mechanism for high-pressure induced phase transition.

The phase transition from ZB to RS structure in silicon carbide (SiC) is one of the most intensively studied in high-

pressure physics. The technological interest in SiC is mainly motivated by its electronic and optical device applications, as well as its nuclear applications, because of its outstanding mechanical and electronic properties, such as high thermal conductivity, high melting temperature, large bulk modulus, large band gap, and low dielectric constant [15]. Also, microelectronic devices made of SiC can be used under extreme conditions of high-power, high-temperature, high-frequency, and radiation [15]. During the last few decades, a number of experimental and theoretical studies on the high-pressure phase transition in SiC have been reported. X-ray diffraction measurements [16] and shock compression experiments [17] suggested that a transformation from ZB to RS structure in SiC takes place above 100 GPa. Theoretically, the transition pressure has been predicted to be around 60 GPa based on *ab initio* pseudopotential calculations [15, 18, 19]. Despite great efforts devoted to understanding the structural transformation under high-pressure, the nature of the transition pathways and intermediate states remains controversial. In earlier first-principles calculations it was proposed that the ZB \rightarrow RS phase transformation would pass through a rhombohedral $R3m$ intermediate transition state with one formula unit per primitive unit cell [6, 15]. Based on MD simulations within a new interatomic potential scheme, Shimojo *et al* [5] suggested that the atomistic mechanism for the structural transformation involves a cubic-to-monoclinic

unit-cell transformation and a relative shift of the Si and C sublattices in the [100] direction, in contrast to the traditional $R3m$ mechanism. Subsequently, an orthorhombic intermediate state was revealed by least-enthalpy calculations employing a periodic linear combination of the atomic orbitals method in conjunction with the density-lowest-combinations of atomic orbitals functional method [7]. The new transformation pathway was found to be energetically favored over the traditional $R3m$ mechanism. However, the symmetry of the orthorhombic intermediate state of $Pmm2$ was questioned by Mato *et al* [20, 21], who pointed out that the space group symmetry of the intermediate structure should be $Imm2$ rather than $Pmm2$, which was later supported by Catti [22]. On the other hand, Miao *et al* [21] claimed that the unit cell of the intermediate state of SiC is not primitive orthorhombic, but body centered orthorhombic, while Catti argued [23] that this is not correct. Miao and Lambrecht [10] pointed out that the orthorhombic path is very close to a slightly generalized monoclinic path, which was found to have the lowest transition barrier. They also suggested that the high-pressure ZB \rightarrow RS transitions in different semiconductors, such as CdS, ZnTe, InAs, and SiC, pass through a universal monoclinic transition state [11]. Recently, using a constant-pressure *ab initio* technique Durandurdu [12] revealed that the pressure induced phase transition in SiC is based on a tetragonal and an orthorhombic intermediate state, and the space groups of the intermediate states were determined to be $I\bar{4}m2$ and $Imm2$. However, the applied transition pressure was very high, up to 600 GPa, which is significantly higher than the experimental measurement of ~ 100 GPa [16, 17]. In our previous study on the high-pressure induced phase transition from hexagonal wurtzite to the rocksalt structure in both SiC and GaN [14], we found that such high pressure could change the phase transition mechanism. Although these previous experimental and theoretical studies provide important insights into the zinc blende to rocksalt phase transition under high pressure in 3C-SiC, the fundamental mechanism of the pressure induced phase transformation demands further investigation. In the present study, *ab initio* MD methods are employed to establish the transition mechanism for ZB \rightarrow RS phase transformation in SiC.

2. Computational details

Density functional theory calculations within the framework of the localized density approximation [24] have been carried out using SIESTA [25] code in SiC. The electron-ion interactions were described by normconserving Troullier-Martins [26] pseudopotentials. In our *ab initio* constant-pressure MD simulations of 64 atom configurations, the convergence of our calculations has been tested, and we found that Γ -point sampling in the Brillouin zone, single- ζ basis sets, and a 90 Ryd cutoff for the real space mesh can give good converged results. The system was first equilibrated at 300 K and zero pressure. The external pressure was applied via the method of Parrinello and Rahman [27] and increased with an increment of 10 GPa. The equilibration period is 2000 time steps for each increment, with a time step of 1 fs. However, a large number

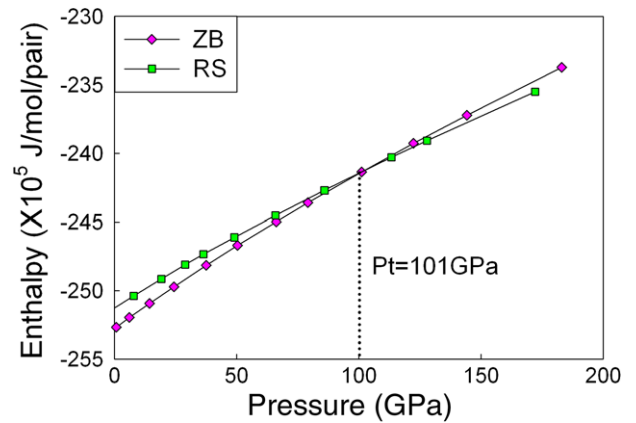


Figure 1. The calculated enthalpies of SiC in ZB and RS phases as a function of pressure.

of time steps up to 6000 were simulated when the pressure was close to the transition pressure.

3. Results and discussions

The optimized lattice constant for the zinc blende SiC is 4.45 Å, in reasonable agreement with the experimental value of 4.36 Å [28], respectively. Figure 1 illustrates the calculated enthalpies of SiC in ZB and RS phases as a function of pressure obtained from single point energy calculations. The ZB \rightarrow RS structural phase transition pressure is predicted to be 101 GPa, which is in excellent agreement with experimental measurements [16] but differs greatly from previous first-principles calculations [15, 19]. In our *ab initio* molecular dynamics simulations, a slightly higher pressure is applied to accelerate the phase transformation, analogous to MD simulations of the melting behavior [29]. The system remains in the zinc blende structure for pressures up to 150 GPa, and the phase transition from the ZB to RS structure takes place when the pressure is increased to 160 GPa.

The geometrical structures before and after the phase transition and the changes of the local bonding for ZB and RS states are shown in figure 2. Before the phase transition, the Si1 atom is fourfold coordinated to the four carbon atoms (C1–C4) and the other two carbon atoms (C5–C6) are far away. The bond length between the Si1 and the four carbon atoms is 1.698 Å, and the distance between the Si1 and C5 (or C6) is 3.282 Å. After the phase transition, the silicon atoms become sixfold coordinated, and the bond length between the Si1 and the six carbon atoms is 1.878 Å. Further analysis shows that there is no bond breaking involved in the phase transformation, which is consistent with the MD simulations reported by Shimojo *et al* [5].

The time evolutions of the simulation cell lengths and angles at 160 GPa for zinc blende SiC are shown in figures 3(a) and (b), in which the A , B , C cell vectors are along the [100], [010] and [001] directions in the B3 phase, respectively. It can be seen from figures 3(a) and (b) that, before the structural phase transformation, the three cell lengths are equal to each other ($|A| = |B| = |C|$), and the three angles between

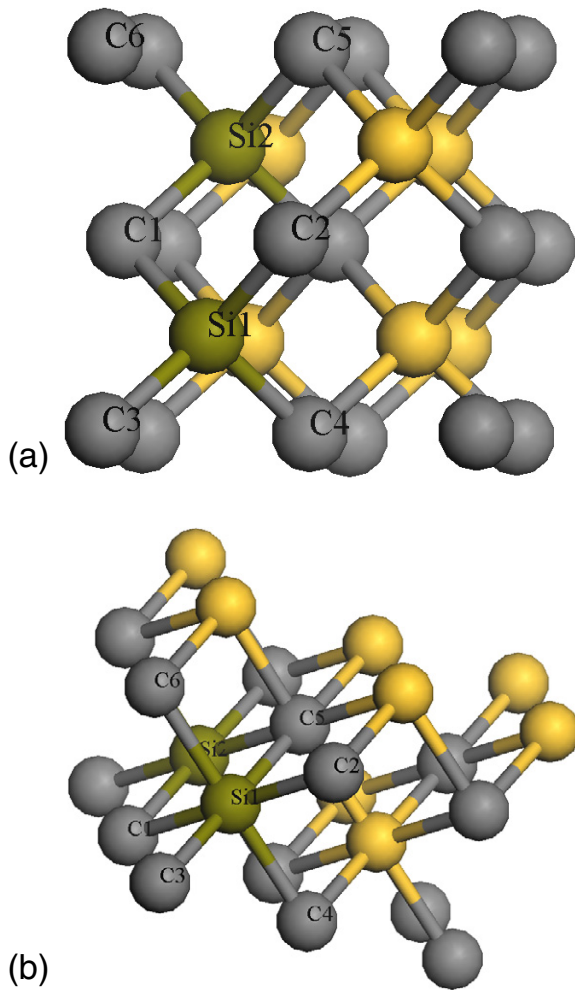


Figure 2. The geometrical structures before (a) and after (b) the transition and the changes of the local bonding for ZB and RS states.

the cell vectors are all right angles ($\alpha = \beta = \gamma = 90^\circ$). As soon as the structural phase transformation begins to take place (at $t = 0.44$ ps), the C cell length decreases considerably, with small variations of the A and B cell vectors. At this stage, all the cell angles change slightly and the MD cell remains cubic, corresponding to a tetragonal intermediate state ($|A| = |B| \neq |C|$, $\alpha = \beta = \gamma = 90^\circ$). At $t = 0.62$ ps the γ angle starts to increase continuously, leading to an intermediate state with monoclinic symmetry ($|A| = |B| \neq |C|$, $\alpha = \beta = 90^\circ \neq \gamma$). Subsequently, the increase in the A cell length and decrease in the B cell length occur simultaneously (at $t = 0.69$ ps), accompanied by an increase in the α and β angles. As the phase transition is completed, the three angles become equal to each other, while the B and C cell lengths are much smaller than the A cell length ($|A| \neq |B| = |C|$, $\alpha = \beta = \gamma \neq 90^\circ$), corresponding to a triclinic structure. However, in the simulation cell each atom is sixfold coordinated and a rocksalt structure is clearly formed, as shown in figure 2(b). This is different from our previous study on the high-pressure induced wurtzite to rocksalt structural transition in SiC [14], where a rocksalt structure is formed in a cubic simulation cell. This difference may be due to the different initial configurations and transition mechanisms in wurtzite and zinc blende SiC.

The structures before, during, and after the phase transition are all quenched using the AIMD method. It is shown that the intermediate states are very stable, in which the global structure is tetragonal and the local structure is fourfold coordinated. To check whether there are finite size effects for our simulations, we performed additional calculations of the ZB to RS phase transition using 128 atoms. It turns out that the results are nearly the same, showing that there are no finite size effects.

The observation that the ZB \rightarrow RS phase transition in SiC occurs first via a tetragonal intermediate state and then an intermediate monoclinic phase does not support the previous suggestions of rhombohedral $R3m$ intermediate transition states [6, 15]. The present simulations also differ from a generally accepted model that the high-pressure ZB \rightarrow RS transitions in different semiconductors go through a universal monoclinic transition state [5, 7, 11, 20–23]. In these other MD and first-principles calculations, no intermediate tetragonal state was observed. Our results agree well with recent constant-pressure *ab initio* MD simulations in SiC [12], where a very high pressure (about 600 GPa) was applied in the simulations, and it was suggested that the pressure induced phase transition in SiC is based on intermediate tetragonal (space group: $I\bar{4}m2$) and orthorhombic (space group: $Imm2$) states. These other results all differ from our previous study on the high-pressure induced wurtzite to rocksalt structural transition in SiC [14], where a tetragonal intermediate structure was observed under a pressure of 140 GPa, somewhat similar to the present study. On the other hand, Durandurdu [30] proposed that wurtzite SiC exhibits phase transformation via a hexagonal phase first and then an orthorhombic intermediate state at pressures of 600–700 GPa. Such a discrepancy has been attributed to the over-applied pressure in their simulations, which may change the transition mechanism.

Following the transition path from zinc blende to rocksalt structure, we calculated the enthalpy ($H = E + PV$) of a series of atomic configurations at the transition pressure using the AIMD method. The variation of enthalpies with time evolution is presented in figure 4. The energy barrier is determined to be 0.424×10^5 J/mol/pair for phase transition in SiC, differing greatly from the value of 0.7×10^5 J/mol/pair obtained from first-principles density functional calculations [13]. However, the energy barrier for the zinc blende to rocksalt transition from the present study is slightly lower than that determined previously, 0.54×10^5 J/mol/pair, for the wurtzite to rocksalt transition using similar methodology. The lower energy barrier in the present study is consistent with a faster transition time.

The structural transition mechanism from a fourfold coordinated structure to a sixfold coordinated structure has been demonstrated by Shimojo *et al* [5]. In their MD simulations, it was proposed that when the structural transformation starts, the zinc blende structure is compressed in one direction, and one angle between the MD cell vectors is decreased from 90° to about 70° . Meanwhile, the Si and C sublattices shift relatively to each other along the [100] direction in the original zinc blende structure, and the [110] direction in the transformed rocksalt structure. The AIMD simulations performed by Durandurdu [12] showed that the lattice structure is simultaneously compressed along the [010]

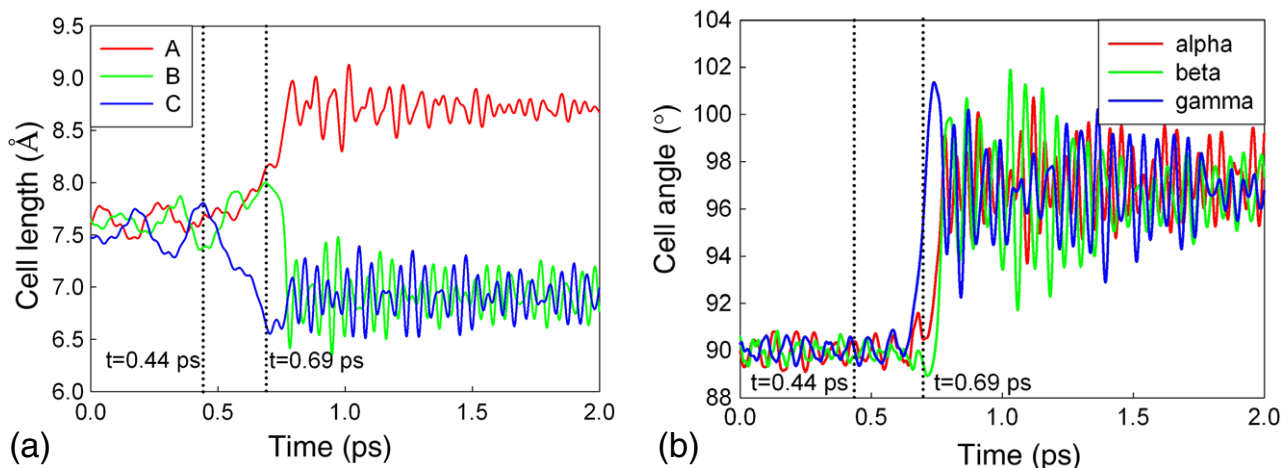


Figure 3. (a) Variation of the MD cell vectors as a function of time at 160 GPa in SiC; (b) variation of the MD cell angles as a function of time at 160 GPa in SiC.

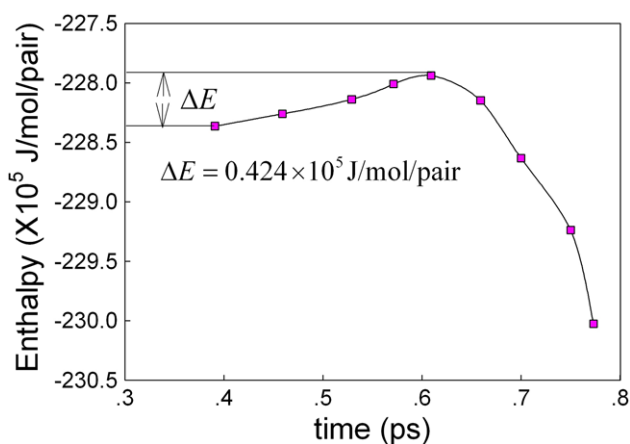


Figure 4. Variation of the enthalpies with the time change at 160 GPa for SiC.

direction and elongated along the other directions, which leads to the onset of a phase transformation in SiC. This differs somewhat from our *ab initio* MD simulations. The present results show that during the structural transformation the zinc blende structure is mainly compressed along the [001] direction, accompanied by one angle between the MD cell vectors increasing from 90° to about 100° . This leads to a tetragonal phase first and then a monoclinic phase. After the transition barrier is overcome, the intermediate phase is mainly expanded along the [100] direction and compressed along the [010] direction. Accompanied by this deformation, the two angles between the MD cell vectors are increased from 90° to about 100° . As a consequence of these motions, each atom is sixfold coordinated and the rocksalt structure is formed.

4. Conclusion

In conclusion, high-pressure induced ZB \rightarrow RS phase transformation in SiC has been investigated by the *ab initio* MD method. The transition pressure is predicted

to be 101 GPa, in excellent agreement with experimental measurement. Our simulations showed that under 160 GPa the ZB \rightarrow RS phase transition in SiC occurs first via a tetragonal intermediate state and then a monoclinic phase, which differs from some previous MD and first-principles calculations. However, our results agree well with the recent constant-pressure *ab initio* MD simulations that predicted the same transition path, but under much higher applied pressure (~ 600 GPa). The energy barrier is determined to be 0.424×10^5 J/mol/pair for phase transition in SiC, differing greatly from the value of 0.7×10^5 J/mol/pair obtained from first-principles density functional calculations.

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