

MECHANISM OF MOLECULE MIGRATION OF CARBON AND SILICON MONOXIDES IN SILICON CARBIDE CRYSTAL

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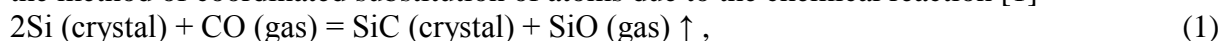
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Abstract. The main processes occurring during the migration of molecules of carbon monoxide CO and silicon monoxide SiO gases through a layer of monocrystalline silicon carbide SiC of a cubic polytype have been described by the *ab initio* methods. This problem arises when a single-crystal SiC layer is grown by the method of coordinated substitution of atoms due to the chemical reaction of a crystalline silicon substrate with the CO gas. The reaction products are epitaxial SiC layer and SiO gas. It has been shown that CO and SiO molecules decompose into separate atoms in the SiC crystal. The Oxygen atoms migrate through interstices only in the [110] direction (activation energy is 2.6 eV). The Si and C atoms transit by the vacancy mechanism in the corresponding SiC sublattices with activation energies of 3.6 eV and 3.9 eV respectively (and also only in the [110] direction).

Keywords: silicon carbide, epitaxy, diffusion, *ab initio* modelling

1. Introduction

During the growth of the epitaxial film of silicon carbide (SiC) from a silicon (Si) crystal by the method of coordinated substitution of atoms due to the chemical reaction [1]



the transport of carbon monoxide (CO) reagent gas and silicon monoxide (SiO) reaction product gas through the SiC layer plays a key role in determining the growth rate of SiC. At present, neither the mechanisms of diffusion of CO and SiO through SiC nor the corresponding values of the diffusion coefficients or the diffusion activation energies are known. It is not even known what stage limits the growth rate of SiC. In order to investigate these questions, all the main processes of transport of CO and SiO gases through the SiC layer have been modeled in this work by the methods of quantum chemistry.

2. Modeling methods

For the modeling, the Medea-Vasp package was used, which applies pseudopotentials for the projected augmented wave (PAW) method [2,3]. In all calculations, the density functional method with a plane-wave basis was used, and the exchange-correlation energy was calculated in the framework of the SCAN meta-functional approximation [4-6], which essentially refines the generalized gradient approximation (GGA). The cutoff energy of the plane waves was 400 eV in all calculations.

A supercell of $8.72 \times 6.17 \times 9.25 \text{ \AA}^3$ of 48 independent atoms of silicon carbide of the cubic SiC-3C polytype was used for the modeling. The supercell was oriented so that the *x*-axis was directed along [001], the *y*-axis was along $[\bar{1}10]$, and the *z*-axis was along [110].

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The size of the supercell in the [110] direction was specially chosen to be the largest and equal to 3 periods in this direction since the atoms move mainly along [110]. The integration in the first Brillouin zone was carried out over k-points in $3 \times 4 \times 3$ Monkhorst-Pack grid. The studies have shown that CO and SiO molecules, once inside the SiC crystal, immediately decompose into separate atoms, since the size of the voids in SiC is too small for them. The oxygen atom, in principle, can move in different directions, however, the activation energy of migration in the direction [110] turned out to be much less than in other directions. In quantum chemistry, the migration process is best described by the method of nudged elastic band (NEB) [7,8]. The idea of this method is that knowing the initial and final positions of the atoms, one can freeze the system and introduce additional forces that will direct the atoms from the initial state to the final state. If certain conditions are met, the system will follow the minimal energy pathway (MEP) [8]. This is such a path of a system transformation that any local change in the path leads to an increase in the energy of the system in the vicinity of a given point of the path. In other words, this is the path of the fastest descent from the initial configuration of atoms to the final configuration, i.e. the most probable path of atomic migration in this case. Accordingly, the cross-section of the potential energy surface along the transformation path is the energy profile of this process.

3. Modeling results

The NEB calculation gives the energy profile of the oxygen atom moving in cubic SiC for one period of 3.08 Å in the [110] direction, as shown in Fig. 1.

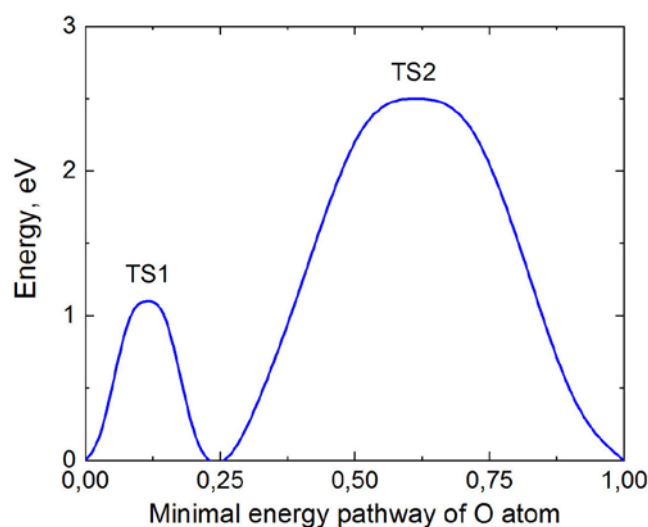


Fig. 1. The energy profile of the process of migration of an oxygen atom in SiC-3C in the [110] direction for one lattice period. The energy barriers corresponding to the two transition states TS1 and TS2 are equal to 1.1 eV and 2.5 eV, respectively

The height of the activation barrier for the migration of the O atom in cubic SiC in the [110] direction is 2.5 eV. In order for the forces acting on the atoms to be less than $0.05 \text{ eV}/\text{Å}$, it took 50 iterations with 15 images in the NEB method. Atomic configurations corresponding to the initial, final, intermediate, and two transition states TS1 and TS2 are shown in Fig. 2.



Fig. 2. The geometrical configuration of atoms corresponding to 5 ground states (3 energy minimums and 2 saddle points TS1 and TS2) during the migration of an oxygen atom in SiC-3C in the [110] direction for one lattice period of 3.08 Å. Atoms Si, C, O are signed by letters

The highest barrier for the migration of the O atom corresponds to the TS2 state, in which the O atom forms a single bond with the Si atom (Fig. 2). The length of this bond is 1.58 Å, i.e. it is stretched by about 5%, which provides the migration barrier. Analysis of the spectrum of the natural frequencies of the TS2 configuration shows that the spectrum contains a single negative (imaginary) frequency equal to -600 cm^{-1} . This proves that the TS2 configuration is indeed a transition state in the process of migration of the O atom in the [110] direction. In other directions, the migration activation energy is noticeably higher; therefore, the migration most likely occurs only in the [110] direction constituting six equivalent directions in the SiC-3C crystal.

Similar calculations by the NEB method show that Si and C atoms practically cannot migrate through SiC interstices since the migration energy exceeds 8 eV. Therefore, the main mechanism of migration of these atoms is the vacancy one. There are a sufficiently large number of vacancies in the Si and C sublattices due to the SiC synthesis mechanism for the following reasons. First, the chemical adsorption of a CO molecule on a SiC notch leads to the formation of a silicon vacancy V_{Si} that immediately begins to migrate to the SiC/Si interface where the drain is located. Second, the substitution of a Si atom by a C atom in silicon at the SiC/Si interface leads to the formation of a carbon vacancy in SiC, since the C atom has left SiC, and the entered Si atom will fall sooner or later into the silicon vacancy. The carbon vacancy migrates from the SiC/Si interface to the SiC surface, where a C atom from the CO molecule will fall into it sooner or later. Third, after a part of Si atoms in silicon is substituted by C, the silicon lattice will “collapse,” since the volume of the SiC-3C cell is half the size of the Si cell. In such event, very strong compressive stresses arise and actuate the effect of upward diffusion leading to the formation of additional silicon vacancies [9]. In addition, it was shown in the paper [10] that it is favorable for a silicon vacancy to transform into a carbon vacancy plus the C_{Si} antisite, i.e. the carbon atom located on the site of the silicon atom. However, for this to happen, it is necessary to overcome the barrier of 3.1 eV. The antisite is an immobile structure, while the carbon vacancy after transformation continues to move toward the SiC surface. Thus, there are two gases of vacancies, silicon V_{Si} and carbon V_{C} , which interact with each other.

The energy profiles of the migration of silicon and carbon vacancies in SiC-3C in different directions have been calculated by the NEB method. As in the case of O atoms, the smallest migration barrier happened to be in the [110] direction. Figure 3 shows the dependences of the system energy on the minimal energy pathway for the V_{Si} and V_{C} vacancies in the [110] direction. The largest energy barrier of migration, equal to 3.9 eV, corresponds to the migration of the carbon vacancy (Fig. 3).

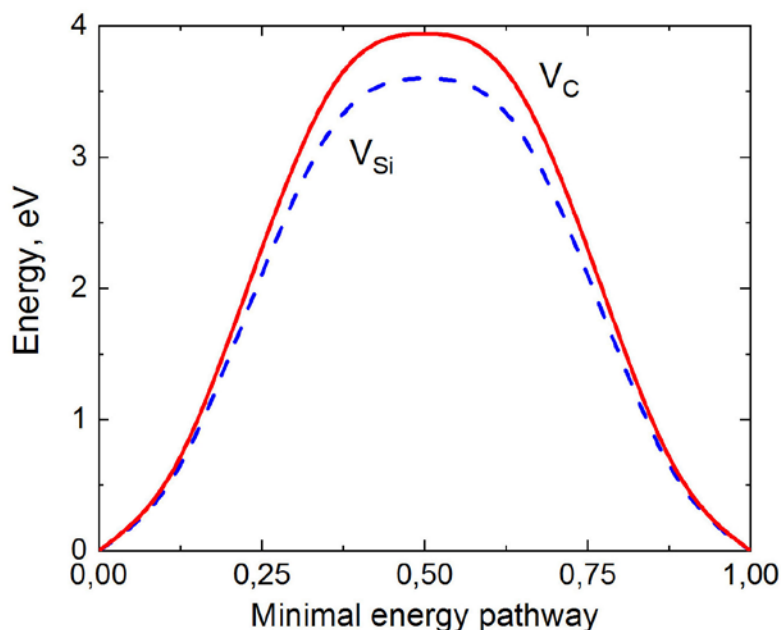


Fig. 3. The energy profile of the migration process of silicon V_{Si} and carbon V_C vacancies in SiC-3C in the [110] direction for one lattice period. The energy barriers for V_{Si} and V_C are 3.6 eV and 3.9 eV, respectively

Therefore, in pure SiC at low temperatures, it is carbon vacancies that limit the growth of the SiC film (the energy barrier of the chemical reaction itself is 2.6 eV [11]). However, for doped materials, as well as with increasing temperature, the situation may change. For example, if the original silicon is doped with boron, then the activation barrier for the migration of silicon vacancies may increase and they will begin to limit the growth of SiC. In addition, if the temperature rises to 1100 – 1200 °C, a significant part of silicon vacancies will turn into carbon vacancies plus immobile carbon structures (antisites) constituting almost a flat cluster of 4 C atoms (the activation energy of this process is 3.1 eV [10]). In this case, silicon vacancies limit the growth of SiC, since the product of the concentration of silicon vacancies and their mobility is less than that for carbon vacancies. Apparently, this case is most often observed in practice, since these carbon structures are detected both by infrared spectroscopy (they give a new line of 960 cm^{-1}) [10] and ellipsometry that allows to measure their volume concentration [10]. Usually, the concentration is in the range of 1 – 3%, depending on the type and degree of doping of the original silicon [10]. If silicon vacancies limit the SiC growth, then the reaction product SiO will accumulate inside the SiC layer, failing to escape. Sometimes this leads to microexplosions of the SiC layer, resembling a volcanic eruption. Such “eruptions” are regularly detected experimentally at low CO pressures [1].

4. Conclusion

In summary, in the present work, we have shown by quantum chemistry methods that V_{Si} and V_C vacancies play a key role in the kinetics of the reaction (1). The transport of the CO reagent gas to the reaction zone and the transport of the SiO reaction product gas from the reaction zone are carried out only in the [110] direction and directions equivalent to it, i.e. in the direction of the SiC channels. The migration of CO and SiO molecules is equivalent to the migration of the O atom and the V_{Si} and V_C vacancies, since it is not necessary for the Si and C atoms to migrate, because the O atom easily forms a chemical bond with any atoms of the SiC crystal. The energy barrier of the migration of vacancies is more than 2 times lower than the barrier of the migration of atoms, and it is equal to 3.6 eV for V_{Si} and 3.9 eV for V_C in the

ideal crystal. Therefore, at low temperatures, the SiC synthesis is limited by the migration of V_C . In a SiC-3C crystal containing twin boundaries, the migration barriers can be 10 – 20% lower. Starting with a temperature of 1100 – 1200 °C, a significant part of silicon vacancies turns to carbon vacancies plus immobile carbon structures (the activation energy of this process is 3.1 eV). Therefore, a lack of silicon vacancies can limit the SiC synthesis. In this case, in SiC synthesized by the method of coordinated substitution of atoms, there are both carbon clusters and traces of microexplosions caused by the accumulation of a large amount of SiO inside the SiC layer. Both features are determined experimentally at low CO pressures.

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