Effect of Nitrogen and Aluminium on Silicon Carbide Polytype Stability

S. Nishizawa 1* and F. Mercier 2

1) Research Institute for Applied Mechanics, Kyushu University, 6-1 Kasuga-koen,
Kasuga, Fukuoka 816-8580, Japan

2) Université Grenoble Alpes, CNRS, Grenoble INP, SIMAP, 1340 Rue de la Piscine,
BP 75, F-38402, Saint Martin d'Hères, France

* Corresponding author

*e-mail: s.nishizawa@riam.kyushu-u.ac.jp

Abstract

In this study, effects of nitrogen and aluminium dopant on the SiC crystal structure and polytype stability were investigated by density functional theory. With taking account of the stacking energy of additional bilayer, the carbon terminated surface as seed surface with nitrogen doped condition is the only condition of 4H single polytype SiC growth. Under the other conditions, polytype conversion and inclusion might occur.

Keywords:

A1. Crystal structure, A2. Growth from vapor, A2. Single crystal growth,
B2. Semiconducting silicon compounds

Highlights:

- Effect of dopant on the bulk properties on SiC is small.
- Effect of dopant on the surface features on SiC is large.
- Only the stacking energy can explain the polytype stability of SiC growth.

1. Introduction

Silicon carbide is a potentially useful material for power devices in the post-silicon era, due to its wider bandgap and higher electrical breakdown field than those of silicon. Silicon carbide shows a wide variety of polytypes with different stacking sequences, such as 3C, 4H, 6H, etc, and each polytype has specific physical and electrical properties, and 4H-SiC is best-desired for power device applications. In sublimation growth of SiC, it was reported that in order to grow 4H-SiC, the carbon terminated surface should be used as a seed surface, and nitrogen doping conditions are strongly recommended [1]. But these growth conditions have been established by experiments long performed so far, and the microscopic mechanism of crystal growths under those conditions still remain unclear.

The authors previously investigated the stability of undoped SiC polytypes by using density functional theory (DFT) calculation, and reported that the energy differences among SiC polytypes are enhanced at the surface with respect to the bulk, and the surface has a predominant role on the determination of SiC polytype [2]. In the present study, the nitrogen and aluminium dopant effects on the SiC polytype stability are investigated. Based on DFT calculations, an atomic-scale mechanism of the

common 4H-SiC polytype growth onto the carbon terminated surface under nitrogen doping conditions are discussed.

2. Effect of dopants on bulk crystal properties

2.1 Effect of doping concentration on the lattice constant

In order to investigate the effect of doping concentration on the lattice constant, the first principle calculations in the scheme of the density functional theory were carried out by CASTEP using super supercells with 64 atoms as same as those in the previous work [2]. For SiC, nitrogen and aluminium are used as n-type and p-type dopant impurities. Based on the site-competition theory, nitrogen and aluminium substitute carbon and silicon, respectively [3]. In this study, the concentration of nitrogen in C-site and aluminium in Si-site were varied in the range 10^{18} - 10^{21} atoms/cm³. Fig.1 shows the lattice constants of 4H-SiC as a function of the impurity concentration [4]. The calculated results agree well with the room temperature data found in experiments [5]. In this study, the effect of temperature did not considered. From Fig.1(a), the c-lattice constant is almost constant in the range from 5×10^{18} to 1×10^{19} atoms/cm³, whereas the c-lattice constant decreases as increasing the nitrogen concentration above 2×10^{19} atoms/cm³. The a-lattice constant decreases as increasing

the nitrogen concentration, above 5×10^{18} atoms/cm³. From Fig.1(b), the a-lattice constant is almost constant over the whole range of the aluminium concentration. The c-lattice constant increases as increasing the aluminium concentration above of 1×10^{19} atoms/cm³. In Fig.2, the nitrogen and aluminium doping effects on crystal structure were summarized [4]. Fig.2(a) shows the impurity effects on the crystal structure. We define the term hexagonality as c/na in Fig.2 where a, c and n are the c-lattice constant, the a-lattice constant, and the stacking sequence period, respectively. In the case of 4H-SiC, $n=4$. From Fig.2(a), c/na starts increasing at an impurity concentration of around 1×10^{19} atoms/cm³. However, the c/na decreases as increasing the nitrogen concentration in the range over a value of 2×10^{20} atoms/cm³. From the experiments reported so far, it has been known that heavily nitrogen doping causes stacking faults, and changes the crystal structure [6]. The calculation results of a-lattice and c/na dependencies on the nitrogen concentration show similar relation qualitatively. Fig.2(b) summaries the effects of nitrogen and aluminium doping on the bulk crystal structure, schematically. Nitrogen has an effect of the compression on the a-axis, leading to the enhancement of hexagonality, c/na . Aluminum also give rise to the enhancement of the hexagonality, but instead, it is caused by the effect of the c-axis expansion induced by aluminum doping.

2.2 Effect of dopants on bulk energy

In this section, we define the term “ bulk exagonality” of each polytype by adopting of Jagodzinski’s “h-k” notation [7]. As shown in Fig.3, the bulk hexagonality is equal to $h/(h+k)$, ie. 0, 0.33, 0.5 and 1 for 3C, 6H, 4H and 2H polytypes, respectively. The bulk energies for various polytypes were also calculated by CASTEP [2]. 3C bulk energy is -263.2523 eV/atoms. Fig.4 shows the bulk energy differences relative to the 3C structure for 6H, 4H and 2H with and without heavily level doping of nitrogen and aluminium of around 4×10^{20} atoms/cm³ which can make clear the effect of dopants. For the undoped cases, it is pointed out that 2H SiC shows a larger positive bulk energy, compared to the other polytypes of SiC. It means that 2H SiC is less stable than the others [2]. From Fig.4, aluminium doping has little effect on the bulk energy of all polytypes. On the other hand, nitrogen doping gives large positive bulk energy values for of all polytypes. In addition, the difference of bulk energy between nitrogen doped and undoped SiC increases with increasing the bulk hexagonality. It can be concluded that from the view point of bulk energy, nitrogen doping stabilies polytype structures with lower bulk hexagonalities, i.e. 3C(stable) < 6H < 4H < 2H (unstable). However, this conclusion does not agree with the experimental results, that is, nitrogen doping

stabilises 4H compared to 6H [1]. The bulk energy is therefore not an appropriate parameter to discuss the SiC polytype stability. From Fig.4, it is also said that the annealing process, which is commonly used in other materials as a post processes for structural homogenization is not effective to realis desired SiC polytypes.

3. Effect of dopants on stacking energy

3.1 Effect of dopants on surface stacking site

In this section, SiC polytypes with nitrogen and aluminium doping concentrations of 4×10^{20} atoms/cm³ were subjected to calculations with the procedure described in [2]. Fig.5 explains how the dopant element is incorporated in the crystal structure. In Fig.5, the light and dark gray colored small spheres correspond to silicon and carbon atoms, respectively. The bottom surface is terminated by H atoms. Dopant elements were considered to exist in the surface bilayer. According to the site competition theory [3], nitrogen substitutes carbon, and aluminium substitutes silicon of the surface bilayer. We calculated the stacking energy difference for two cases where the dopant atoms occupy h and k sites in the surface bilayer. Fig.6 shows the effect of the dopants on the stacking energy difference between h and k site occupations, indicating, in the case of silicon terminated surface, the nitrogen (aluminium) dopant

makes $E_h - E_k$ larger (smaller) with respect with the undoped case. It means that for the Si-terminated surface, the nitrogen (aluminium) dopant increases (decreases) the tendency of the k-site occupation. On the other hand, in the case of the carbon terminated surface, the nitrogen (aluminium) dopant makes $E_h - E_k$ smaller (larger) with respect with the undoped case. It means that for the C-terminated surface, nitrogen (aluminium) dopant increases (decreases) the tendency of the h-site occupation. In other words, the nitrogen dopant makes the absolute value of $E_h - E_k$ larger, and the aluminium dopant makes it smaller. So, the nitrogen dopant has a stabilizing effect of k-site stacking for the Si-surface and h-site stacking for the C-surface, respectively. As a result, nitrogen makes bulk hexagonality smaller because of the enhancement of k numbers in the case of the silicon terminated surface, whereas nitrogen makes bulk hexagonality larger because of the enhancement of h-site stacking for the carbon terminated surface. As you can easily anticipate from our results, small values of $E_h - E_k$ for aluminum doping will cause a disturbance for stacking in bilayer formation.

3.2 Effect of dopant on polytype stability

Fig.7(a)-(c) summarize the energy difference between various polytypes determined from our stacking energy calculations. From stacking energy calculations,

among the 2 possible polytype stacking (h or k), the one leading to the replication of the polytype was selected. Then, mean values of the different substructures for the each polytype were plotted. Negative values mean that the first polytype is more stable than the second polytype. In Fig.7, all the possible surfaces given in Table 1 in Ref.[2] were considered. From Fig.7, only the case of nitrogen doping combined with the carbon terminated surface gives higher stability of 4H polytype compared with the cases for 6H and 3C. All the others cases shows that 4H is unstable, or 4H has a similar stability with 6H and 3C such as the case of undoped C-terminated seed surface. This means that in order to grow 4H-SiC, carbon terminated surface should be used as the seed surface and nitrogen should be added as a dopant. This condition well agrees with the experiments regarding 6H to 4H polytype conversion [1, 8] as well as 4H single polytype growth. And even for the growths using 4H-SiC seeded crystals, the silicon terminated surface is not suitable to grow 4H-SiC, because of the large possibility of the 6H and 3C polytype conversion and/or the formation of inclusions [1]. For 6H-SiC growth, the Si terminated surface is more suitable than the carbon terminated surface, but there is a possibility of 3C inclusions. Fig.7 also shows that there is no window for the aluminium doped 4H single polytype growth condition due to higher stability of 6H and 3C in the conditions we demonstrated in this study. This means that aluminium

doped 4H-SiC is difficult to grow with keeping its polytype stability.

4. Conclusion

In this paper, the effects of nitrogen and aluminium doping on the crystal structure and the polytype stability were investigated by calculations of the lattice constant, the bulk crystal energy and the stacking energy of bilayer added on the surface. Both nitrogen and aluminium dopants have effects on the hexagonality (c/a) enhancement. The nitrogen dopant makes the a -lattice constant smaller, and the aluminium dopant makes the c -lattice constant larger. The nitrogen dopant also makes the bulk energy larger for all polytypes. These results can not explain the experiments reported so far. Our stacking energy calculations show that 4H-SiC growth is stable on the carbon terminated surface under nitrogen doping conditions in agreement with the experimental facts. Silicon carbide is grown by ad-atom and/or bilayer deposition, not by solidification, and structural properties for surface bilayers are therefore more important than bulk properties to determine the polytype stability during the growth.

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Figure captions

Fig. 1 Effect of dopant on lattice constant of 4H-SiC

(a) Nitrogen doping (b) Aluminium doping

Fig.2 Effect of dopant on hexagonality of 4H-SiC

(a) c/na (b) schematic drawing

Fig.3 Bulk hexagonality of SiC

Fig.4 Bulk energy difference. Undoped case taken from [2]

Fig.5 Example of a structure for the DFT calculation with nitrogen/aluminium dopant. The position of dopants are circled.

Fig.6 Stability of the additional bilayer stacking. h and k subscripts mean the hexagonal and cubic orientation with respect to the surface bilayer.

(a) silicon terminated surface (b) carbon terminated surface

Fig.7 Stability diagram between the polytype.

(a) Between 6H and 4H (b) Between 4H and 3C (c) Between 6H and 3C

(a)

(b)

Fig. 1

(a)

(b)

Fig. 2

**Percentage of hexagonal stacking
“h” in the [0001] direction**

Fig.3

Fig. 4

Fig. 5

(a)

(b)

Fig. 6

(a)

(b)

(c)

Fig. 7