Effect of nitrogen doping on the dislocation behaviors of 4H-SiC

Rong Wang[1], Xiaoshuang Liu[1, 2], Jiajun Li[1], Hao Luo[1, 2], Guang Yang[3], Deren Yang[1, 2], and Xiaodong Pi[1, 2]

[1]Hangzhou Innovation Center, Zhejiang University, Hangzhou, 311200, China, rong_wang@zju.edu.cn

[2]State Key Laboratory of Silicon Materials and School of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, China, xdpi@zju.edu.cn

[3]Center for Optoelectronics Materials and Devices, Department of Phy4H-SiCs, Zhejiang Sci-Tech University, Hangzhou 310018, China

2022 6th IEEE Electron Devices Technology & Manufacturing Conference (EDTM) | 978-1-6654-2178-2/22/$31.00 ©2022 IEEE | DOI: 10.1109/EDTM53872.2022.9798310

Abstract

We demonstrate that nitrogen (N) dopants are prone to spontaneously decorate the most important dislocation of basal plane dislocation (BPD) during the N doping of 4H silicon carbide (4H-SiC). The N decoration shifts the acceptor-like states of BPDs to donor-like states, which results in the donor-like character of BPDs in N-doped 4H-SiC. Kinetically, N decoration enhances the slip and piling up of BPDs, reducing the hardness, elastic modulus and fracture toughness of 4H-SiC.

(Keywords: 4H-SiC, doping and dislocations)

Introduction

4H silicon carbide (4H-SiC) has been attracting great attention in high power and high frequency electronics, owning to the advantages of wide bandgap, high breakdown electric field strength and high thermal conductivity [1,2]. Nitrogen (N) doping is well known to tune the electrical properties of 4H-SiC. The concentration of N in n-type 4H-SiC is larger than 10^{19} cm^{-3}. It is reasonable to expect that the high-concentration N would interplay with dislocations, and change dislocation behaviors in 4H-SiC. However, the interaction between N and dislocations, as well as its effect on the electronic and mechanical properties of dislocations are still ambiguous, which significantly hinders the optimization of processing of 4H-SiC substrates and impedes the understanding on the electron-transport mechanism of 4H-SiC based power devices.

In this work, taking the most important dislocation of BPD as an example, we demonstrate that N dopants are prone to spontaneously decorate BPDs during the N doping of 4H-SiC. BPDs create acceptor-like states in undoped 4H-SiC, while act as donors in N-doped 4H-SiC. The electron transfer from the defect states of intrinsic vacancy clusters to the unoccupied defect states of BPDs gives rise to the acceptor-like behavior of BPDs in undoped 4H-SiC. Upon N decoration, the accumulation of N dopants gives rise to the donor-like behavior of BPDs in N-doped 4H-SiC. Kinetically, we find that the N decoration enhances the slip and piling up of BPDs, which reduces the hardness, elastic modulus and fracture toughness of 4H-SiC. Our work not only help the understanding of electron-transport mechanism of 4H-SiC based power devices, but also pave the way for the design of processing of 4H-SiC wafers.

Results and discussion

A. *N decoration of BPDs*

We firstly calculate the formation energy of BPDs in 4H-SiC. Fig. 1 displays the relaxed supercell containing a typical BPD in 4H-SiC.

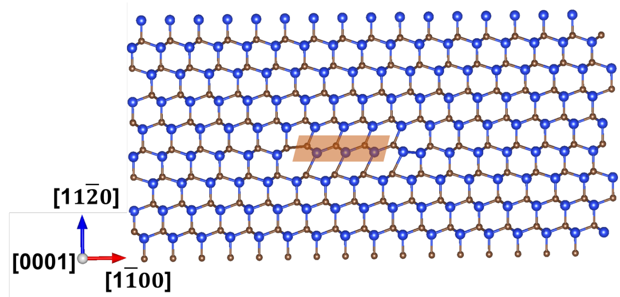

Fig. 1: Relaxed 4H-SiC supercell containing a BPD. The red region denotes the BPD.

During N doping, the N substitution of C can happen either at the core of the BPD or inside the bulk region of 4H-SiC. The formation energies of N_C at the supercell of 4H-SiC containing a BPD is calculated by:

$$\Delta H_f(BPD) = E_t(BPD) - E_t(host) + \sum n_i(\mu_i + E_i) \quad (1)$$

where $E_t(BPD)$ and $E_t(host)$ are total energies of the 4H-SiC host with and without the BPD, respectively. n_i is the number of constituent i transferred from the supercell to the reservoir during the formation of the BPD, μ_i is the chemical potential of constituent i referenced to its elemental phase with energy E_i. As shown in Fig. 2, the positive value of N_C located at the perfect region away from the BPD indicates that it costs energy to

Authorized licensed use limited to: Xiamen University. Downloaded on April 11,2024 at 12:39:31 UTC from IEEE Xplore. Restrictions apply.

substitute C atoms at the perfect region away from the BPD of 4H-SiC. However, when N substitutes C atom at the core of the BPD, the value of formation energy of N_C becomes negative. When the number of N atoms decorating the BPD core increases from 1 to the maximum of 6, the formation energies of N_C continuously decrease. This indicates that N atoms prefer to decorate the cores of BPDs during the N doping of 4H-SiC. Only when the decoration becomes saturated, N atoms begin to substitute C at the perfect region of 4H-SiC.

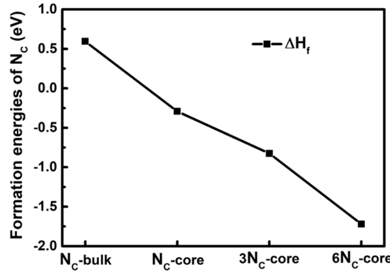

Fig. 2: Calculated formation energies (ΔH_f) of N_C as functions of the number of N_C at the bulk region of 4H-SiC and that at the core of the BPD.

In order to verify the decoration of N at BPDs, we then calculate the binding energy (E_b) of the nN_C-BPD (n=1-6) complex by:

$$E_b(nN_C - BPD) = [n\Delta H_f(N_C) + \Delta H_f(BPD) - \Delta H_f(nN_C - BPD)]/n \quad (2)$$

The calculated values of E_b are all positive, indicating that once N atoms decorate BPDs, the N_C-BPD complex is strong against decomposition.

Next, we investigate the electronic properties of BPDs in 4H-SiC. As shown in Fig. 3, the BPD creates two defect levels in the bandgap of 4H-SiC. Single-particle analysis indicates that the defect level above the VBM of 4H-SiC is fully occupied by electrons, while the defect level below the CBM is empty. The empty defect level of BPD under the CBM of 4H-SiC is capable of accepting electrons excited from the mid-gap state of vacancy clusters. The electron transfer process gives rise to the acceptor-like behavior of BPDs in undoped 4H-SiC. For N-doped 4H-SiC, the defect level above the VBM of 4H-SiC slightly shifts to higher energy. Meanwhile, two separate defect levels are created under the CBM of 4H-SiC (Fig. 3). In N-doped 4H-SiC, because N dopants prefers to segregate at BPDs. The positively charged N dopants give rise to the donor-like behavior of the N-decorated BPDs. The excess electron of N_C at the core of the BPD would either transfer to the CBM, or to the so-called 'perfect region' where also exists high density of vacancy clusters.

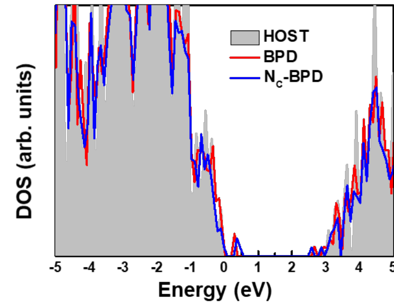

Fig. 3: Calculated DOSs of 4H-SiC, the pure BPD, and N_C-decorated BPD.

B. Effect of N decoration on the electronic properties of BPDs

The electronic properties of BPDs are analyzed by detecting the contact potential difference (V_{CPD}) between the tip and the etched 4H-SiC by the Kelvin probe force microscopy (KPFM) approach. The surface potential mapping of the BPD in undoped 4H-SiC is shown in Fig. 4(a). With the assistance of band-diagram analysis, we find that the local Fermi energy of the BPD is lower than the perfect region of 4H-SiC. The lower local Fermi energy of the BPD indicates that BPDs create acceptor-like defect states in undoped 4H-SiC, the charge transfer from perfect regions to BPDs and thus the electron-accumulation at BPDs lowers the local Fermi energy of the BPD in undoped 4H-SiC.

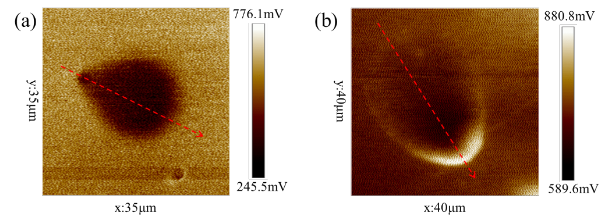

Fig. 4: Surface potential of a representative BPD in (a) undoped and (b) N-doped 4H-SiC.

For N-doped 4H-SiC, the local potentials of BPDs are also lower than that of the perfect region. Interestingly, we find that the local potential for the peripheral region surrounding the core of the BPD in N-doped 4H-SiC is remarkably higher than those of other regions [Fig. 4(b)]. This indicates that BPDs in N-doped 4H-SiC create donor-like states in N-doped 4H-SiC. Upon N doping, the local Fermi energy of BPDs shift to higher positions in the bandgap of 4H-SiC. This verifies first-principles results that N decoration at BPDs causes the donor-like behavior of BPDs in n-type 4H-SiC.

Authorized licensed use limited to: Xiamen University. Downloaded on April 11,2024 at 12:39:31 UTC from IEEE Xplore. Restrictions apply.

C. Effect of N decoration on the kinetic behaviors of BPDs

We then use the nanoindentation to investigate the effect of N decoration on the kinetic behaviors of BPDs, and thus the mechanical properties of 4H-SiC. As tabulated in Table 1, the hardness, elastic modulus and fracture toughness of N-doped 4H-SiC are all smaller than that of undoped 4H-SiC.

Table 1. Crack lengths (*c*), indentation fracture toughness (K_{IC}) for undoped 4H-SiC and N-doped 4H-SiC.

Sample	undoped 4H-SiC	N-doped 4H-SiC
Crack length (μm)	6.66±0.34	7.36±0.36
K_{IC} (MPa m$^{1/2}$)	2.35±0.01	1.74±0.01

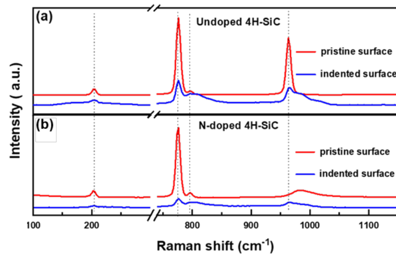

Fig. 5: Raman spectra obtained at a pristine surface and indented surface for (a) undoped 4H-SiC, and (b) N-doped 4H-SiC.

Micro-Raman spectroscopy measurements were then carried out to clarify the effect of N on the kinetic behaviors of BPDs and the lattice distortions of the indented region were investigated by. For nanoindentated undoped 4H-SiC, the intensities of both the FLO peak and FTO peak decrease, as a result of atomic displacement during nanoindentation. The change for the intensity of the FTO (796 cm^{-1}) may be attributed to either a phase transition or a severely lattice distortion. This indicates that amorphization or the polymorph transition occurs during the indentation. For N-doped 4H-SiC the peak of the FLO mode notably shifts to higher wavenumbers, as a result of increasing electron concentration in N-doped 4H-SiC. The high concentration of N also results in the lattice distortion, which broadens the peak of the FTA mode in highly N-doped 4H-SiC. The indentation induced amorphization or polymorph transition increases in the order of N-doped 4H-SiC and undoped 4H-SiC. TEM observations also verifies that high-density BPDs appears in nanoindented *n*-type 4H-SiC (Fig. 6).

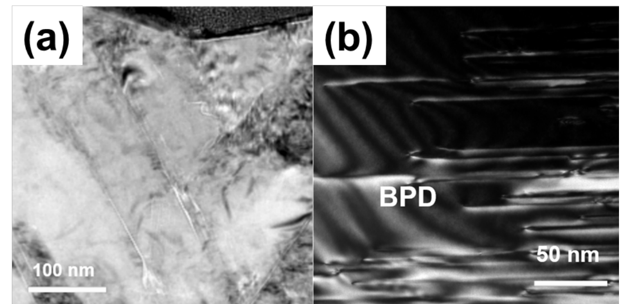

Fig. 6: (a) Cross-sectional TEM image of an indent imprint in undoped 4H-SiC. The indenter is indicated by the white triangle. (b) is the Zoom-in images for the region containing high-density BPDs.

Conclusion

In conclusion, we have demonstrated that N dopants are prone to spontaneously decorate BPDs during the N doping of 4H-SiC. The N decoration shifts the acceptor-like states of BPDs to donor-like states, which results in the donor-like character of BPDs in N-doped 4H-SiC. Kinetically, N decoration enhances the slip and piling up of BPDs, reducing the hardness, elastic modulus and fracture toughness of 4H-SiC.

Acknowledgments

This work is supported by National Key Research and Development Program of China (Grant Nos. 2017YFA0205704, 2018YFB2200101), Natural Science Foundation of China (Grant Nos. 91964107, 61774133), Fundamental Research Funds for the Central Universities (Grant No. 2018XZZX003-02), Natural Science Foundation of China for Innovative Research Groups (Grant No. 61721005) and Zhejiang University Education Foundation Global Partnership Fund.

References

[1] T. Kimoto, J. A. Cooper, “Fundamentals of silicon carbide technology: growth, characterization, devices, and applications,” John Wiley & Sons Singapore Pte. Ltd (2014)

[2] J. Li, R. Wang, H. Luo, G. Yang, Y. Zhang, D. Yang, X. Pi, “Nitrogen Decoration of Basal Plane Dislocations in 4H-SiC”, submitted (2021).

[3] H. Luo, J. Li, G. Yang, Y. Zhang, R. Zhu, Y. Zhang, R. Wang, D. Yang, X. Pi, “Electronic and optical properties of threading dislocations in 4H-SiC”, submitted (2021).

[4] X. Liu, J. Zhang, B. Xu, Y. Lu, Y. Zhang, R. Wang, D. Yang, X. Pi, “Doping-dependent deformation of 4H-SiC”, submitted (2021).

Authorized licensed use limited to: Xiamen University. Downloaded on April 11,2024 at 12:39:31 UTC from IEEE Xplore. Restrictions apply.