Defect and Diffusion Forum
ISSN: 1662-9507, Vol. 434, pp 93-98
doi:10.4028/p-WmPn6z

Submitted: 2023-09-08
Revised: 2024-04-19
Accepted: 2024-04-19
Online: 2024-08-22

Near-Interface Defect Decomposition during NO Annealing Analyzed by Molecular Dynamics Simulations

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Keywords: 4H-SiC, Oxide interface, NO annealing, molecular dynamics simulation

Abstract. We have used molecular dynamics simulations to investigate the decomposition mechanisms of residual C defects near the interface of 4H-SiC/SiO_2 during NO annealing. We have observed drastically rapid defect decomposition by NO and O_2 mixed gas, which is thermodynamically more realistic, compared with single NO or O_2 gas annealing. We have constructed simplified defect decomposition model. This model numerically reproduced the simulation results, suggesting that multi-step and cooperative reactions caused by the coexistence of NO and O_2 during NO annealing effectively promote the decomposition of residual C defects.

Introduction

Silicon carbide (SiC) has attracted great attention because of its potentially superior properties to Si in terms of high-voltage and high-temperature power device application [1]. The performance of 4H-SiC metal oxide semiconductor field-effect transistors, however, has been limited by the low channel mobility and the threshold voltage instability, which is primarily caused by large amount of interface traps (D_{it}) and/or near interface traps (NITs) [2]. Nitric oxide (NO) annealing is widely known as an effective method for reducing the D_{it} and NITs. One of the key roles of NO annealing is supposed to reduce residual C defects at/near interface, while its microscopic mechanism is still under discussion.

Molecular dynamics (MD) simulation is one of the useful ways to analyze the microscopic mechanisms of defect decompositions. Recently, we have developed an interatomic potential of Si-O-C-N for classical MD simulation in order to investigate the roles of NO annealing at 4H-SiC/SiO_2 interface [3]. In the NO annealing simulation, we have observed the formation of CN defects, which have bonds between C and N atoms. However, the amount of residual C atoms at/near interface has no remarkable reduction, which implies that there is another mechanism to decompose such defects by NO annealing. In this paper, we analyze near-interface defect decomposition by MD simulations under thermodynamically more realistic conditions in order to reveal the decomposition mechanism: we introduced mixed gases composed of NO and O_2 into SiO_2, which would exist in thermal equilibrium conditions at high temperatures.

Methods

We performed classical MD simulations with the LAMMPS package [4]. We utilized our original hybrid charge-transfer-type interatomic potential based on the Tersoff potential. The function form of the potential is the same as described in Ref. [5].

We prepared an atomistic model of near-interface defects according to the flow shown in Fig. 1(a). We first oxidized a 4H-SiC($000\overline{1}$)/SiO_2 interface model [Fig. 1(b)] at 1600 K using the same method as in Ref. [6]. Briefly, O_2 molecules were repeatedly introduced into the region of SiO_2 at a fixed

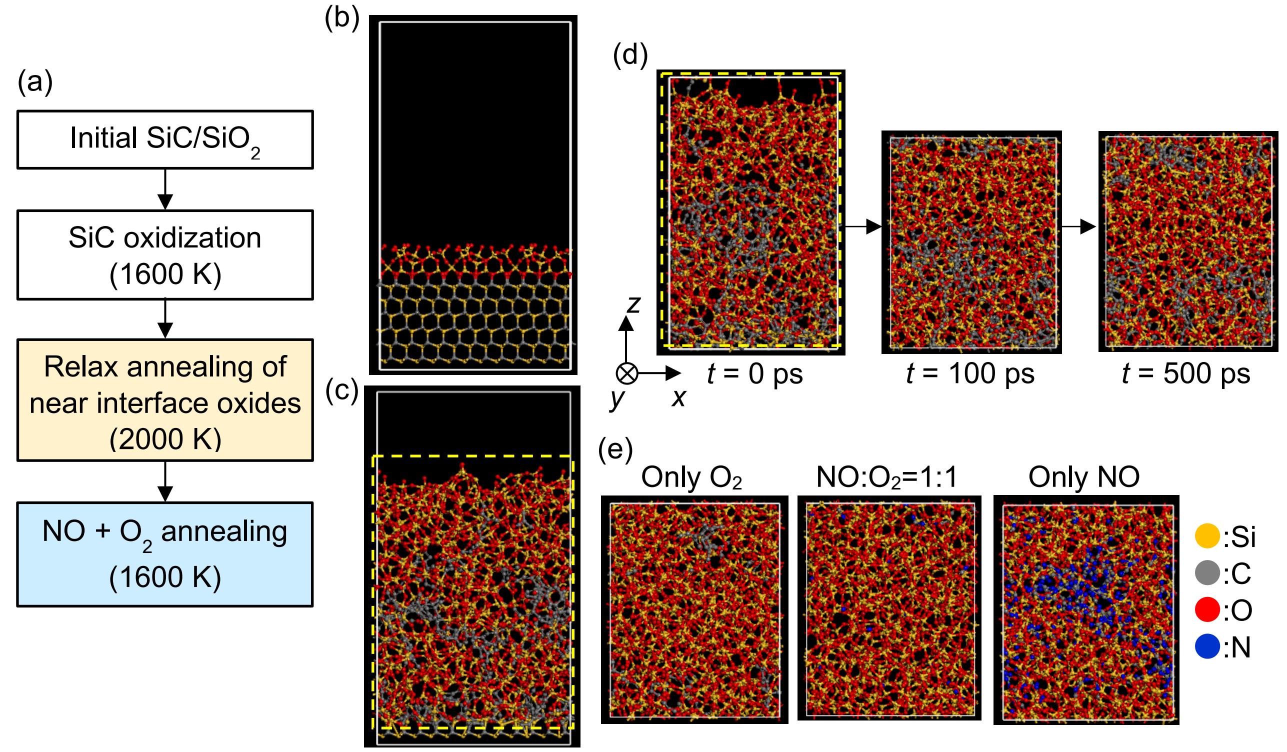

Fig. 1. (a) Computational flow of defect decomposition simulation. Cross sections of (b) initial 4H-$SiC(000\bar{1})/SiO_2$ interface, and (c) after SiC oxidization by O_2. (d) Snapshots of relax annealing. (e) Cross sections after mixed gas annealing simulations. Yellow, red, grey, and bule circles represent Si, O, C, and N atoms, respectively.

density of 1 molecule/nm^3. These O_2 molecules reacted with 4H-SiC at the interface. The positions of the molecules were randomly selected from a region 1.8 Å away from all existing atoms. The bottom layer of SiC was fixed to maintain the vaccume slab model. In our all simulations, unreacted or decomposed gases such as O_2 and CO were excluded at every 1 ps. The time step was set to 0.5 fs.

After the full oxidization of unfixed SiC layers [Fig. 1(c)], the SiO_2 region (yellow dashed box) including residual C defects was extracted and was compressed to reproduce the experimental density of SiO_2 [Fig. 1(d)]. The typical density of amorphous SiO_2 is 2.0-2.2 g/cm^3 while the density of SiO_2 obtained by the oxidization simulation was 1.7 g/cm^3. We speculate that this difference originates from the faster oxidization rate than experiments. In order to compensate for this mismatch, we increased the density of SiO_2 during relaxing annealing of near-interface oxides: after 1 ps of MD simulation under the NVT ensemble at 2000 K, the cell length in z-axis direction [normal to the 4H-SiC/SiO_2 interface, Fig. 1(d)] was compressed by a factor of 0.997544. Repeating this flow 100 times, the z-axis length was eventually compressed from 46 Å to 36 Å. Following this compressive relaxation, we performed MD simulation of 400 ps at 2000 K to relieve the internal stresses. This relax annealing increased the density to 2.1 g/cm^3.

Finally, we repeatedly introduced mixed gases, which were composed of NO and O_2 molecules to react with the near-interface defects at 1600 K. The composition of the gases was varied as NO: O_2 = 1:0, 9:1, 3:1, 1:1, 1:3, 1:9, and 0:1, where the total gas density was kept constant at 1 molecule/nm^3. The decomposed or unreacted gases such as CO_x and NO_x were removed at regular intervals in order to evaluate the decomposition rate. In Fig. 1(e), we show typical examples of cross sections after mixed gas or single gas annealing for 2000 ps. The remaining amounts of defects and their chemical bonding apparently depend on the composition of mixed gas, which we discuss in more detail below.

Results and Discussion

Figure 2(a) displays the amount of C atoms in the cell obtained from NO + O_2 annealing MD simulations. Since the model no longer contained the 4H-SiC substrate, the amount of C atoms can be regarded as the amount of the residual C defects. Although they decomposed even in single gas ($NO:O_2$ = 1:0 or 0:1), their decomposition was drastically faster in mixed gas. The decomposition rate was maximum in the range of $NO:O_2$ = 1:3 to 3:1.

Although the decomposition rate seems to be nearly identical in the range of $NO:O_2$ = 1:3 to 3:1, the amount of N atoms depends on the composition of the mixed gas as shown in Fig. 2(b). As we introduced more NO molecules, the incorporation of N increased. At the same time, it was found that the amount of N reached a maximum before t = 500 ps in the mixed gas annealing, and then monotonically decreased.

In order to analyze the bonding state of N atoms, we counted the number of bond patterns of N atoms. In Fig. 2(c), we show the main bonding patterns that appeared at more than 10 sites at a given time for $NO:O_2$ = 1:1. The bonding patters are denoted by $Si_aO_bC_cN_d$, which means that a specific N atom is bonded to a Si atom(s), b O atom(s), c C atom(s), and d N atom(s), respectively. For example, when an N atom is bonded to one Si atom and one C atom as shown in Fig. 2(d), we consider that there is one bond pattern of $Si_1O_0C_1N_0$. We found that all of the N atoms had some bonds with C atoms except for unreacted NO molecules, corresponding to $Si_0O_1C_0N_0$.

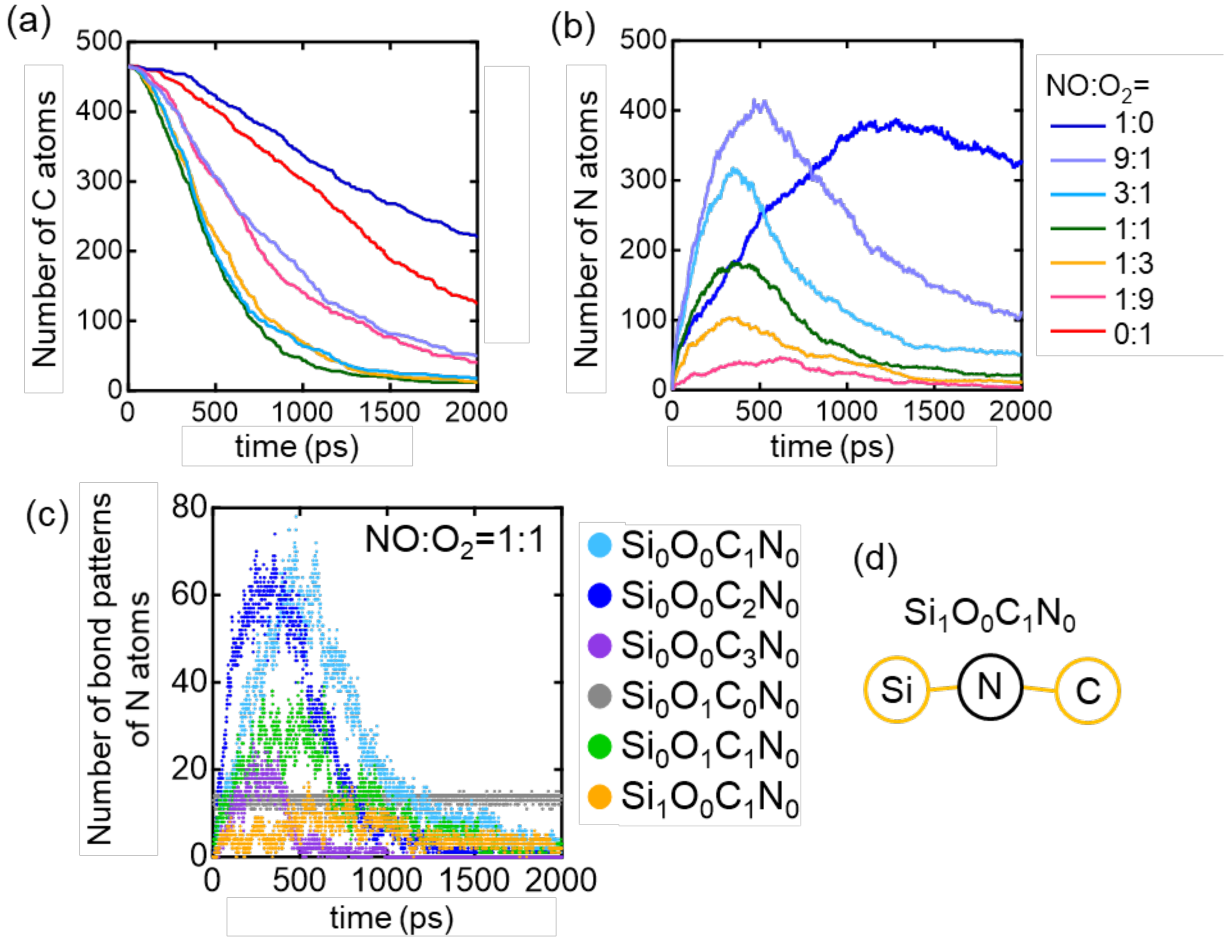

Fig. 2. Numbers of (a) C and (b) N atoms in SiO_2 calculated from molecular dynamics simulations with various mixed gases composed of NO and O_2. (c) Number of bond patterns of N atoms during mixed gas annealing composed of $NO:O_2$ = 1:1. (d) Schematics of a bond pattern of N atoms in the case of $Si_1O_0C_1N_0$.

These results suggest that the amount of N incorporation corresponds to the amount of CN defects formed by the reaction of residual C with NO molecules. Thus the amount of CN defects varies with the composition of NO:O_2, while the decomposition rate of C atoms remains almost constant in the range of NO:O_2 = 1:3 to 3:1. This implies that some reaction processes are in balance with each other.

In order to analyze these processes, we constructed a simplified defect decomposition model as shown in Fig. 3(a): the CN defects formed by NO are instantly decomposed by O_2, resulting in more pronounced reduction of defects than decomposed by only O_2 or NO. In this model, O_2 molecules can decompose C defects with C-C bonds slowly, but can decompose C-N defects quickly. On the other hand, NO can quickly transform C defects into CN defects, but it takes time to decompose them into CO_2 or CO. Thus, the reaction-promoting mechanism is a combination of both NO-enhancing and NO-decelerating mechanisms working in concert, and the decomposition rate appears to be nearly constant at a NO/O_2 mixing ratio where the two mechanism are balanced with each other.

In order to confirm the validity of this model, the following four reaction processes were extracted:

$$\text{C defects} + \text{NO} \rightarrow \text{CN defects}. \quad (1)$$

$$\text{C defects} + O_2 \rightarrow CO_x. \quad (2)$$

$$\text{CN defects} + O_2 \rightarrow CO_x + NO_x. \quad (3)$$

$$\text{CN defects} + O_2 \rightarrow NO_x + \text{C defects}. \quad (4)$$

Reaction (1) represents the transformation of C defects to CN defects by NO molecules, while reactions (2) and (3) denote the decomposition of C and CN defects by O_2 molecules, respectively. Reaction (4) is the reverse reaction of reaction (1) caused by O_2 molecules. In this model, we ignored other reactions such as decomposition of CN defect by NO molecules because their reactions are supposed to be too slow to promote the decomposition. The time evolution of the amount of C and N atoms ([C] and [N]) can be expressed using the amount of C and CN defects ([C defects] and [CN defects]) and reaction rate constants (k_1, k_2, k_3, and k_4) of the above extracted reactions as follows.

$$d[\mathrm{C}]/dt = -k_2[\text{C defects}] - k_3[\text{CN defects}]. \quad (5)$$

$$d[\mathrm{N}]/dt = k_1[\text{C defects}] - k_3[\text{CN defects}] - k_4[\text{CN defects}]. \quad (6)$$

Here, Eq. 5 shows that reaction (2) and (3) decompose C or CN defects into CO or CO_2, which are removed from the simulation cell. Equation 6 represents that reaction (1) promotes the incorporation of N through transforming C defects into CN defects, while reaction (3) and (4) decomposed CN defects into NO_x. It is reasonable to assume that [C] is equal to [C defects] at $t = 0$ since there is no N atoms at the beginning of the mixed gas annealing. If we ignore the N incorporation in Si-O networks and unreacted NO molecules, all of the N atoms are in CN defects, where [N] and [CN defects] can be regarded as equal. In addition, we can also assume that the reaction rate constant k_i is proportional to the density of each introduced gas: k_1 is proportional to the density of introduced NO molecules, and k_2, k_3, and k_4 are proportional to the density of introduced O_2 molecules.

Assuming the above conditions, we numerically solved the reaction Eqs. 5 and 6, confirming qualitative reproductions of C decomposition and N incorporation observed in MD simulations as shown in Figs. 3(b) and 3(c), respectively.

The results suggest that the multi-step and cooperative reactions caused by the coexistence of NO and O_2 promote the decomposition of residual C defects more effectively than reactions by only O_2, which correspond to thermal oxidization. We speculate that such difference in decomposition rates between C defects and CN defects might be attributed to the different charge bias in these defects brought by N atoms. The observed microscopic mechanism would lead further improvement of 4H-SiC/SiO_2 interface by NO annealing.

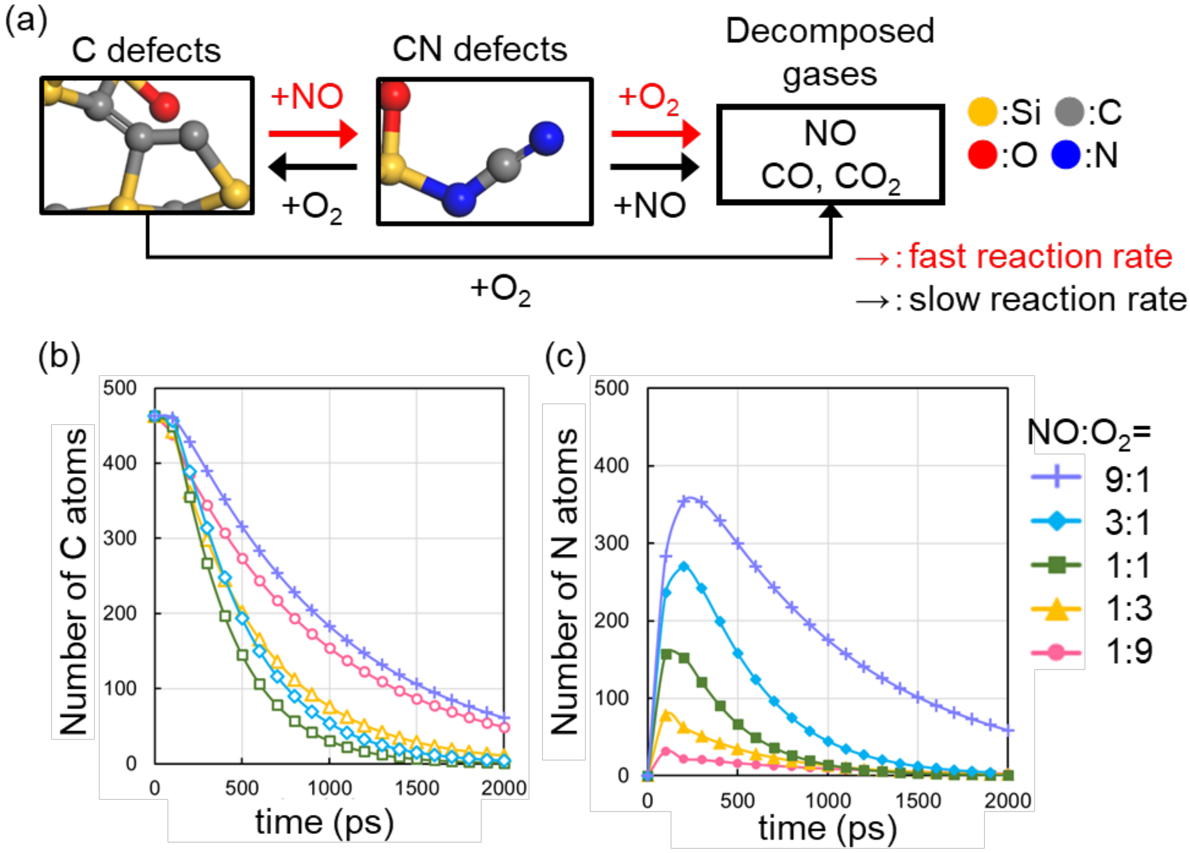

Fig. 3. (a) Schematics of simplified defect decomposition model in NO and O_2. Numbers of (b) C and (c) N atoms in SiO_2 calculated by the simplified model.

There are numerous experimental reports that consider the optimal conditions for NO annealing [1]. On the other hand, there are few cases where the ratio of NO to O_2 has been studied in detail. The effects of NO annealing have been primarily focused on the role of NO alone [7], and a systematic understanding considering the ratio of NO to O_2 is still lacking. This may be due to the difficulty of accurately extracting the mixed gas decomposition enhancement in experiments, since the absolute amount of NO also changes when the ratio of NO to O_2 is altered. However, in experiments where the temperature or type of gas such as NO or N_2O was varied, not only the absolute amount of NO but also the ratio of NO to O_2 should change due to the thermal equilibrium reaction. A more detailed evaluation of the relationship between the gas composition during the NO annealing and the electrical characteristics of the device is expected to provide useful insights into further understanding of interfacial reactions.

Summary

We have used molecular dynamics simulations to investigate the decomposition mechanisms of residual C defects near the interface of 4H-SiC/SiO_2 during NO annealing. By introducing thermodynamically realistic situation of NO/O_2 mixed gas, we have observed drastically rapid defect decomposition compared with the single gas annealing. We have constructed simplified defect decomposition model. This model numerically reproduced the simulation results, suggesting that multi-step and cooperative reactions caused by the coexistence of NO and O_2 are the key roles of NO annealing to reduce the residual C defects more effectively than reactions by single NO or O_2 gas. The uncovered microscopic mechanism would lead further improvement of 4H-SiC/SiO_2 interface by NO annealing.

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