

A First-Principle Study of F₂ Selective Etching of Si/SiGe Stacks towards Sub-3 nm Node Transistor Manufacturing

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Abstract—Selective etching of sacrificial SiGe layers in Si/SiGe stacks is a key process in sub-3nm gate-all-around field-effect transistor (GAAFET) fabrication and requires nanometer-scale profile control. Although fluorine-based thermal etching is attractive because it enables isotropic material removal without energetic ion bombardment. However, the atomistic reaction mechanisms governing isotropic thermal etching are still not fully understood. In this work, we investigate the facet- and composition-dependent behavior of F₂ selective etching in Si/SiGe stacked structures using density functional theory (DFT). We evaluate the coupled effects of crystal orientation and Ge concentration on surface reactivity and reaction barriers. The results show that higher Ge concentration lowers the reaction barrier, while the (110) surface consistently exhibits lower barriers than the (111) surface. Among the studied systems, Si₃Ge shows the most favorable etching characteristics across major crystal facets.

Keywords—DFT, Etch Selectivity, Nanosheet Cavity Etch

I. INTRODUCTION

As logic transistors continue to scale toward the sub-3-nm technology node, increasingly stringent requirements are imposed on channel geometry and electrostatic control. Gate-all-around field-effect transistors (GAAFETs) have become an important candidate architecture for advanced logic devices because the gate surrounds the channel provides stronger gate controllability^[1, 2]. In these devices, Si/SiGe stacked structures are commonly used as the starting material platform. The Si layers serve as channel layers, whereas the SiGe layers act as sacrificial layers that need to be selectively removed during subsequent processing.

Therefore, selective etching of sacrificial SiGe layers is a critical process step for forming inner-spacer cavities in GAAFET fabrication^[3]. The geometry of the etched cavity directly determines the inner-spacer structure, the isolation profile between the gate and the source/drain regions, and the final nanosheet channel profile. Poor control of this step may lead to non-uniform cavity depth, Si channel damage, and increased device-to-device variability. As shown in Fig. 1, an ideal etching process requires high SiGe-to-Si selectivity, a well-defined lateral etch front, and a nearly square cavity tip. Therefore, an atomistic understanding of the selective etching mechanism of Si/SiGe stacks is essential for process-window optimization in advanced transistor manufacturing^[4] (Fig. 1).

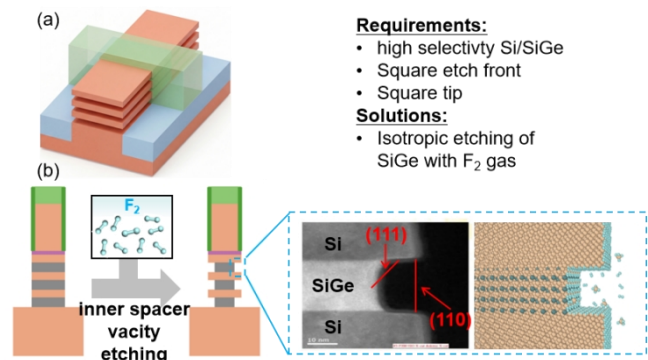


Fig.1 (a) 3D GAAFET structure, (b) Requirements and Atomic-Scale Representation of inner spacer cavity etching

Fluorine-based thermal etching has attracted increasing attention as a promising approach for SiGe sacrificial-layer removal because it can remove surface atoms through dissociative chemisorption without energetic ion bombardment^[5, 6]. Compared with plasma-assisted etching, this process is expected to reduce ion-induced surface damage and provide more controllable isotropic etching, which is beneficial for forming laterally recessed inner-spacer cavities. Previous studies have shown strong crystal-orientation dependence during F₂ etching^[7]. Other studies have also reported that Ge incorporation can influence SiGe-to-Si etch selectivity by modifying the local bonding environment and surface reactivity of SiGe alloys^[8, 9]. However, crystal orientation and Ge concentration are often treated as separate factors, and their coupled influence on F₂-induced surface reactions remains insufficiently understood.

In this work, density functional theory (DFT) calculations are employed to investigate the coupled effects of crystal orientation and Ge concentration during F₂ selective etching of Si/SiGe stacked structures in GAAFET fabrication. Surface models of Si, Si₇Ge, and Si₃Ge are constructed on representative (110) and (111) facets to compare reaction pathways and kinetic barriers. By analyzing F₂-induced surface bond dissociation on these models, this study clarifies how alloy composition and crystal orientation jointly regulate surface reactivity and etching kinetics. The results provide atomistic insight into SiGe sacrificial-layer removal and offer theoretical guidance for profile-controlled cavity etching in advanced GAAFET manufacturing.

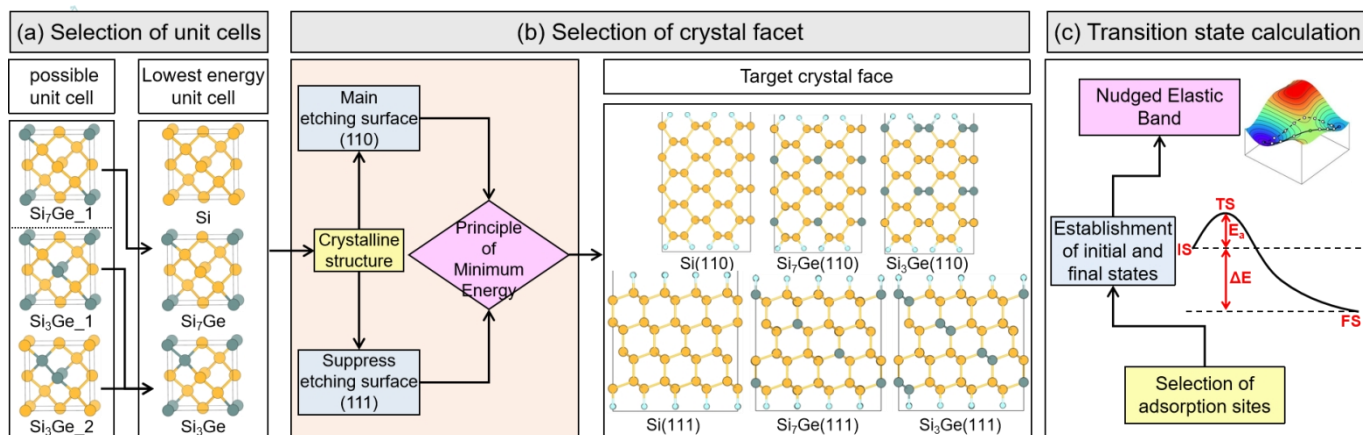


Fig.2 A First-Principles-Based Modeling Approach for SiGe Etching Selectivity Prediction. (a) Selection of unit cells, (b) Selection of crystal face, (c) Transition state calculation.

II. COMPUTATIONAL MODELING

This section presents the mechanistic analysis of F_2 etching on Si and SiGe surfaces, including surface model construction and the first-principles calculation workflow, as illustrated in (Fig. 2).

A. Modeling Structures

To investigate F_2 etching under the coupled effects of crystal orientation and Ge concentration, surface models of Si, Si_7Ge , and Si_3Ge were constructed on representative crystal facets. These three compositions describe the evolution from pure Si to Ge-containing SiGe alloys and were used to examine how Ge incorporation modifies the local surface bonding environment during fluorine-based etching.

For each Ge concentration, possible bulk unit-cell configurations were first considered, and the most stable structure with the lowest energy was selected as the initial structure for subsequent surface model construction. Based on the optimized bulk structures, the (110) and (111) facets were cleaved to build slab models. These two facets were selected because they represent different etching characteristics during Si/SiGe cavity formation. The (110) facet is generally regarded as the primary etching surface and is expected to exhibit higher surface reactivity, whereas the (111) facet is usually more stable and shows higher reaction barriers and lower etching rates. Therefore, comparing these two facets enables the evaluation of crystal-orientation-dependent etching behavior.

After surface cleavage, fully fluorinated surface configurations were further constructed and optimized. For each composition and facet, the fully fluorinated surface configuration with the lowest surface energy was selected as the corresponding slab model. Through this model construction strategy, the effects of Ge concentration and crystal orientation on F_2 -induced surface bond dissociation can be systematically compared.

B. Computational Methodology

All density functional theory (DFT) and climbing-image nudged elastic band (CI-NEB) calculations were performed using the CP2K package. The exchange-correlation energy

was described by the Perdew - Burke - Ernzerhof (PBE) functional, and long-range dispersion interactions were included using the DFT-D3(BJ) correction. The DZVP-MOLOPT-SR-GTH basis set and GTH-PBE pseudopotentials were adopted for all atomic species. The electronic density was represented using a five-level multigrid scheme, with a plane-wave cutoff of 600 Ry and a relative cutoff of 35 Ry. Spin polarization was treated within the unrestricted Kohn - Sham formalism.

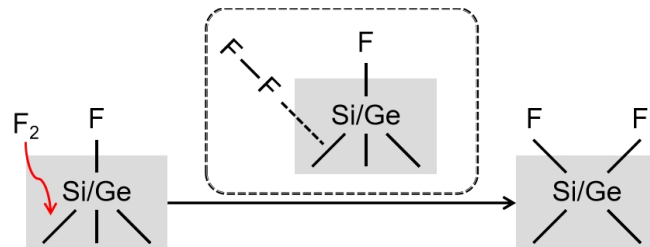


Fig.3 Schematic Illustration of Fluorine Etching on SiGe Surface

The calculations focused on the key surface reaction step in F_2 thermal etching, namely surface bond dissociation and the corresponding transition state, as illustrated in (Fig. 3). In the fluorinated surface environment, the removal of a surface atom is closely related to the breaking of local surface bonds. Therefore, this elementary step directly reflects the kinetic difficulty of chemical etching on different Si/SiGe surfaces.

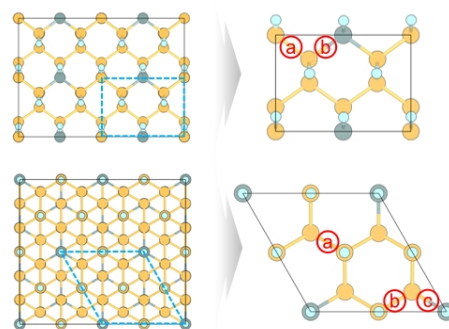


Fig.4 Etching sites of Si_7Ge (110) and (111) Crystal facets

This reaction step was selected as the main object of analysis because it provides a clear and comparable

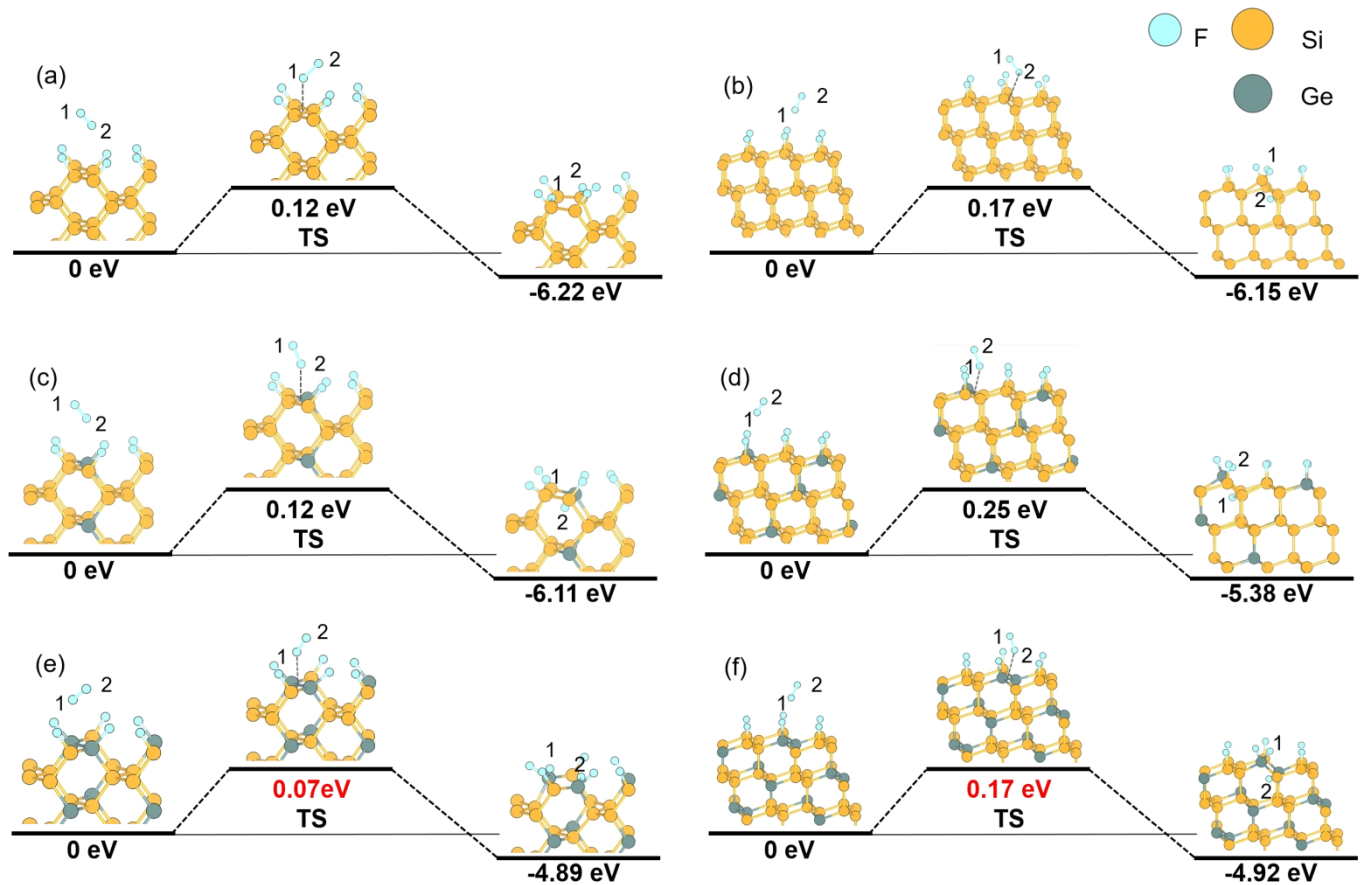


Fig.5 Reaction pathway of the F₂ etching fluorinated surface. TS stands for transition state. (a) Si(110), (b) Si(111), (c) Si₇Ge(110), (d) Si₇Ge(111), (e) Si₃Ge(110), (f) Si₃Ge(111).

descriptor for evaluating etching behavior. A lower bond-dissociation barrier indicates that the surface atom can be removed more easily during thermal etching, whereas a higher barrier suggests stronger resistance to etching. By focusing on the transition state associated with surface bond dissociation, the calculation can capture the rate-limiting feature of F₂-induced surface reactions and allow a direct comparison among different compositions and crystal facets.

Therefore, the reaction barrier obtained from this process was used as the main indicator for comparing the etching kinetics of Si, Si₇Ge, and Si₃Ge surfaces. This approach makes it possible to evaluate how Ge concentration and crystal orientation influence the ease of surface atom removal at the atomic scale.

For each slab model, representative etching sites were selected from the local atomic arrangements of the fully fluorinated surfaces, as shown in (Fig. 4). These sites were used to represent typical local coordination environments under different crystal orientations and Ge concentrations. Specifically, they include different Si-related and Ge-related bonding configurations, allowing the influence of local alloy composition on F₂-induced surface bond dissociation to be analyzed. By using these representative sites as initial configurations, the subsequent reaction-path calculations can reflect the characteristic surface reactivity of different compositions and crystal facets.

The transition states of F₂-induced surface bond dissociation were then determined using the CI-NEB method. For each reaction pathway, the initial state corresponds to the

stable fluorinated surface configuration before bond dissociation. The energy difference between the initial state and the transition state was defined as the reaction barrier. A lower reaction barrier indicates that surface bond dissociation is kinetically more favorable, whereas a higher barrier suggests stronger resistance to etching. Therefore, by comparing the calculated reaction barriers for different compositions and crystal facets, the coupled effects of Ge concentration and crystal orientation on surface reactivity and etching kinetics can be systematically analyzed.

III. RESULTS AND DISCUSSION

To evaluate the effect of Ge concentration on F₂ selective etching, the calculated reaction barriers were compared for Si, Si₇Ge, and Si₃Ge surfaces (Table 1). The results show that the Ge-containing systems exhibit more favorable bond-dissociation behavior than pure Si. Among all systems considered, Si₃Ge shows the lowest reaction barriers on both the (110) and (111) surfaces, indicating that a higher Ge content can facilitate F₂-induced surface bond breaking. From a kinetic perspective, the reduced reaction barrier suggests that Ge incorporation promotes the removal of surface atoms and enhances the etching tendency of SiGe relative to Si.

The influence of crystal orientation was further analyzed by comparing the reaction barriers of the (110) and (111) facets for each composition. For all studied compositions, the reaction barrier on the (111) surface is higher than that on the corresponding (110) surface. This trend indicates that the (111) facet is more resistant to F₂-induced bond dissociation

and therefore exhibits slower etching kinetics. In contrast, the lower barriers on the (110) surface suggest stronger surface reactivity, making it more favorable for thermal etching. This facet-dependent behavior is consistent with the role of crystal orientation in controlling cavity profile evolution during Si/SiGe selective etching.

Table.1 Initial-state, final-state, and transition-state energies, as well as energy barriers, on the (110) and (111) surfaces of Si, Si₇Ge, and Si₃Ge

	Initial state energy(eV)	Final state energy(eV)	Transition state energy(eV)	Energy barrier(eV)
Si(110)	-36199.51	-36205.73	-36199.39	0.12
Si(111)	-36198.93	-36205.08	-36198.75	0.17
Si₇Ge(110)	-36191.74	-36197.85	-36191.62	0.12
Si₇Ge(111)	-36191.22	-36196.60	-36190.97	0.25
Si₃Ge(110)	-36184.13	-36188.98	-36184.07	0.07
Si₃Ge(111)	-36183.57	-36188.49	-36183.40	0.17

Overall, this DFT study clarifies the coupled roles of Ge concentration and crystal orientation in F₂ selective etching of Si/SiGe stacked structures, as summarized in (Fig. 5). Ge incorporation lowers the reaction barriers, especially for the Ge-rich Si₃Ge composition, while the (110) facets are consistently more reactive than the corresponding (111) facets. These findings indicate that Si₃Ge provides the most favorable overall etching characteristics among the studied systems. Therefore, Si₃Ge can be regarded as a promising sacrificial-layer composition window for profile-controlled cavity etching in advanced GAAFET manufacturing.

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