Simulation of Metal-Assisted Halogen-Free Etching of Silicon Using Ruthenium Catalyst

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Introduction
Silicon (Si) is the foundational material of modern micro- and nanotechnology, requiring precise nanoscale etching for device fabrication [1]. Si etching methods include wet chemical etching, metal-assisted chemical etching, and plasma-based techniques such as reactive ion etching (RIE), which enable selective removal of unmasked silicon using metal masks (e.g., Al, Au, Cu) with control over anisotropy, selectivity, and etch rate. Mask-enhanced etching beyond conventional RIE has been reported, where metals such as Al, Cu, Ag, and Au locally enhance Si etching due to an increased local concentration of fluorine radicals near the metal surface, accelerating the formation of volatile silicon tetrafluoride (SiF_4) [2], forming the basis of metal-assisted plasma etching. Plasma etching proceeds through reactive species, including ions and radicals, that remove material from the surface.
Conventional Si etching using fluorinated gases such as SF_6 and CF_4 achieves high etch rates but generates per- and polyfluoroalkyl substances (PFAS) and greenhouse gases. Hydrogen-based plasma etching produces volatile silane (SiH_4) instead of SiF_4 but exhibits low silicon etch rates due to the high activation energy for hydrogen dissociation. In this work, we hypothesize that a catalytic metal such as Ru enhances molecular hydrogen dissociation, generating reactive atomic hydrogen and increasing the Si etch rate.

Result and discussion
H_2 dissociation on a Ru_{14} cluster was investigated by initially placing the H_2 molecule 4.8 Å from the cluster. The calculated reaction energy profile shows a barrierless dissociation process with a final-state energy of -1.8 eV (−0.9 eV per H atom), consistent with reported dissociative adsorption energies of −0.91 eV for H_2 on Ru surfaces [4]. Previous studies of H_2 dissociation on the Si (100) surface have identified intra-dimer and inter-dimer pathways, with the lowest activation barrier associated with the inter-dimer pathway [5].
H_2 dissociation on Si (100) surface and surface with Ru_{14} were also investigated. On the clean Si (100) surface, dissociation proceeds via an activation barrier of E_a = 0.33 eV, consistent with reported DFT values in the range of 0.3–0.7 eV [5], and follows the intra-dimer pathway. In contrast, on the Si–Ru surface, a barrierless dissociation pathway is observed via the inter-dimer configuration. The reaction energies for H_2 dissociation on clean Si and Si–Ru surfaces are −1.86 eV and −1.9 eV, respectively, indicating that Ru promotes efficient hydrogen dissociation and provides a localized source of atomic hydrogen at the metal–silicon interface.
The etching of silicon via the formation of volatile silane (SiH_4) from a clean Si surface was examined by considering two distinct reaction pathways. In the first pathway, a high-energy hydrogen atom originating from the plasma directly attacks a surface-bound SiH_3 species. As shown by the dotted red line in Fig. 2(b), this process leads to silicon etching through a barrierless reaction pathway. In the second pathway, an adsorbed hydrogen atom located on a neighbouring surface Si atom reacts with the adjacent SiH_3 species to form SiH_4. As indicated by the blue line in Fig. 2(b), this reaction proceeds via an activated process and requires overcoming an energy barrier of E_a = 2.3 eV.
In contrast, when a Ru cluster is present on the Si surface, atomic hydrogen binds strongly at the Si-Ru interface, while the SiH_3 species becomes unstable (see Fig. 3), limiting spontaneous formation and desorption of volatile etch products. These results indicate that Ru primarily functions as an efficient hydrogen activation site rather than directly facilitating silicon removal, clarifying its role in halogen-free plasma etching.

Methodology
An Si (100) surface was selected for modelling. The Si slab was generated using the Atomic Simulation Environment (ASE), visualized with VESTA (Fig. 1a), and consisted of 160 atoms, including surface reconstruction on the reactive side and hydrogen passivation of dangling bonds on the backside. A Ru_{14}

cluster with a double-layer hexagonal (hcp-like) structure was modelled using Avogadro (Fig. 1b) [3]. All geometries were fully relaxed to obtain minimum-energy configurations.
All energies and geometries were calculated using density functional theory (DFT) with the Quantum ESPRESSO package. Ultrasoft pseudopotentials from the Quantum ESPRESSO library were employed for all elements. Convergence tests yielded a plane-wave cutoff of 50 Ry for the wavefunction, 500 Ry for the charge density, and a 2 × 2 × 1 k-point mesh. Geometry relaxations used a self-consistency threshold of 1×10^{-6} eV. Minimum-energy paths for H_2 dissociation and etching reactions were determined using the nudged elastic band (NEB) method.

Figure 1. (a) Optimized structure of the Ru_{14} cluster. (b) Optimized structure of the Ru_{14} on the Si (100) surface.

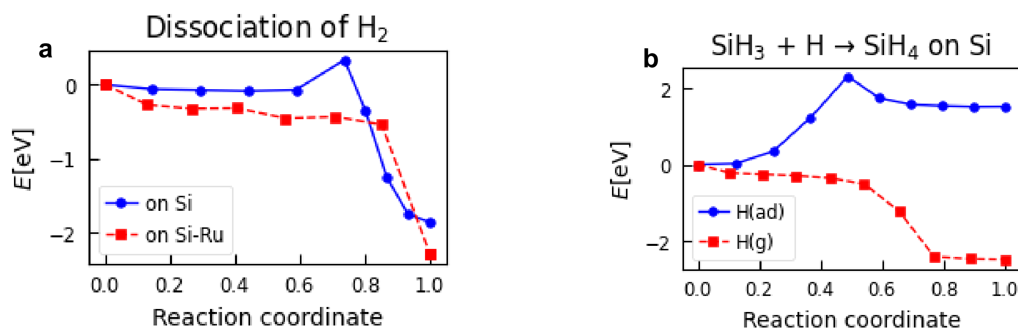

Figure 2. (a) Reaction pathway for H_2 dissociation on clean Si (E_a = 0.33eV), and on the Si–Ru surface (barrierless). (b) Reaction pathway for the etching of Si on the Si surface with hydrogen adsorbed on a neighboring Si atom (E_a = 2.3eV), and with a hydrogen atom originating from the gas phase (barrierless).

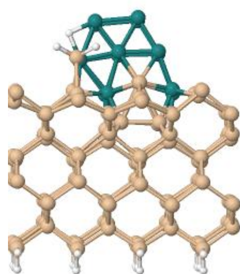

Figure 1. Optimized structure of SiH_3 on Si surface containing Ru_{14} cluster

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