

Mechanisms of HfSe₂ layer-by-layer oxidation and clean van der Waals interface formation with 2D semiconductors: First-principles molecular dynamics simulation study

Joonho Park

School of Electrical Engineering

Korea Advanced Institute of Science and Technology (KAIST)

South Korea

hopefulp@kaist.ac.kr

Yong-Hoon Kim*

School of Electrical Engineering

Korea Advanced Institute of Science and Technology (KAIST)

South Korea

y.h.kim@kaist.ac.kr

Abstract— The principle of layer-by-layer (LbL) oxidation for forming homogeneous native oxides and high- κ /2D semiconductor gate stacks (HfO₂/HfSe₂) is elucidated via first-principles simulations. Plasma oxidation is modeled by inserting oxygen atoms onto HfSe₂ monolayer and at the interface of the partially oxidized HfSe_xO_y/HfSe₂. To preserve the incident oxygen atom velocities and capture local thermal effects due to oxidation, microcanonical (NVE) molecular dynamics is applied, resulting in high transient temperatures. The system is then quenched to 500 K via canonical (NVT) dynamics. This alternating NVE-NVT scheme enables complete oxidation of the top HfSe₂ layer while preserving the bottom layer intact, thereby validating the LbL mechanism. This study provides atomic-scale insight into the formation of native oxide/2D-semiconductor interfaces for next-generation gate stacks.

Keywords— NVE-NVT protocol, 2D gate stack, native oxidation

I. INTRODUCTION

As Si-based devices approach their scaling limits, two-dimensional (2D) semiconductors such as transition metal dichalcogenides (TMDs) offer advantages like atomic thinness, superior electrostatic control, and potential for further miniaturization. Although 2D semiconductor devices using a native oxide gate stack are under development [1, 2], challenges persist in synthesis, contact resistance, and interface control. Recently, native high- κ dielectrics such as HfO₂ on HfSe₂ have demonstrated promising device characteristics, including low gate leakage and steep subthreshold slopes (SS) [3]. While extensive simulations exist for Si oxidation [4, 5], equivalent studies on HfSe₂ are lacking [3, 6].

This work explores native oxide growth and clean vdW interface formation in 2D gate stacks via *ab-initio* molecular dynamics (AIMD) simulation. A monolayer HfSe₂ is partially oxidized using oxygen atom insertions to model plasma oxidation, and then interfaced with monolayers of HfSe₂ [7]. The oxidation kinetics, interface quality, and layer-by-layer (LbL) mechanism are evaluated in atomic detail.

II. METHODS

Density functional theory (DFT) calculations were performed using the VASP package [8], employing the PBE exchange-correlation functional [9] and PAW pseudopotentials. Van der Waals interactions were included via Grimme's DFT-D3 correction [10]. A kinetic energy

cutoff of 500 eV was used, with energy and force convergence set to 10^{-4} eV and 0.01 eV/Å, respectively. For molecular dynamics, a 1 fs timestep was adopted. Brillouin zone sampling used a $2 \times 4 \times 1$ k-point mesh for crystal supercells and Γ -point sampling for amorphous systems.

In oxygen plasma, neutral oxygen atoms are several orders of magnitude more abundant than ionized species such as O⁺ and O⁻ [11]. Among neutral atoms, singlet oxygen atom (¹D) has 2 eV higher than triplet state (³P), making it more reactive during HfSe₂ oxidation. The oxidation energy of O (¹D) on the pristine HfSe₂ is about 7 eV and it reacts with HfSe₂ barrierlessly. To approximate plasma oxidation while maintaining feasible computational cost, multiple (3 ~ 6) oxygen atoms were introduced simultaneously in each oxidation MD simulation. Those singlet oxygen atoms were randomly distributed 4 Å above the surface, with > 5 Å spacing between them. While the initial velocities follow a Maxwell-Boltzmann distribution at 500 K (matching low-temperature plasma condition), only the velocity component normal to the surface was retained for incident oxygen atoms. To capture local heating effects during oxidation, NVE ensemble dynamics were applied for a few picoseconds, resulting in significant temperature increases due to the highly exothermic oxidation of HfSe₂. Selenium atoms were often expelled from bridged sites, floating atop the Hf-O network. After removing these atoms, the system was quenched to 500 K via NVT dynamics using a Nosé–Hoover thermostat. This NVE-NVT protocol was repeated throughout the oxidation procedure, with a timestep of 1 fs. Γ -point sampling was used during AIMD to simulate amorphization.

III. RESULTS & DISCUSSION

1. NVE Dynamics

Fig. 1 shows the NVE dynamics from the second cycle of the NVE-NVT simulation, in which six incident oxygen atoms collide with a partially oxidized HfSe₂ monolayer (Hf₂₄Se₄₅O₆) while preserving local heating in the microcanonical ensemble. The system uses a 3×4 orthorhombic HfSe₂ supercell (Hf₂₄Se₄₈), and after the first NVE-NVT cycle, three Se atoms are removed.

In the time profiles of the NVE simulation in **Fig. 1a**, the potential energy (red line) rapidly decreases within the first few tenths of a picoseconds (ps) as the incident oxygen atoms impinge on the surface and stabilize, releasing ~20 eV. The kinetic energy (blue line) increases by a comparable amount,

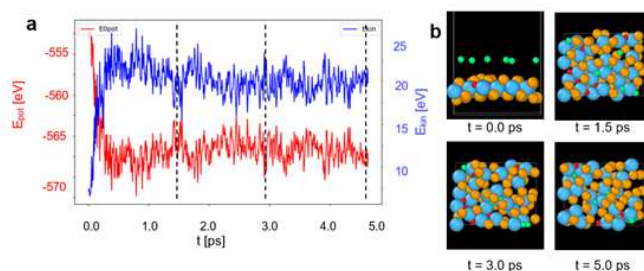


Fig 2. NVE dynamics for the oxidation reaction of the partially oxidized HfSe₂. (a) Time profiles of potential (red line) and kinetic energy (blue line) for NVE dynamics. (b) Snapshots of the system at several time steps denoted as dashed line in (a). At the start of the simulation ($t = 0.0$ ps), six oxygen atoms (green) are inserted 4 Å above the surface and spaced more than 5 Å apart. By 1.5 ps, the newly inserted oxygen atoms become stabilized between Hf atoms and remain coordinated without escaping those sites thereafter. Color scheme: Hf (cyan), Se (dark yellow), O (red) and incident O (green).

maintaining total energy conservation. Based on the oxidation energy of ~ 7 eV per oxygen and a total of six O atoms, the expected total oxidation energy (~ 42 eV) is roughly equally divided between potential and kinetic contribution, consistent with the equipartition theorem.

Fig. 1b represents atomic snapshots during the 5 ps molecular dynamics (MD) simulation. By 1.5 ps, all the incident oxygen atoms (green) occupy stable bridging positions between three Hf atoms (triply-bridged). After stabilization, the local configurations remain unchanged up to 5.0 ps. Since the oxygen atoms rapidly settle into stable configuration during the NVE step, the simulation can be efficiently stopped and followed by a 1 ps NVT quenching step down to the reference temperature of 500 K. The strong binding of oxygen and the fast kinetics enable an efficient ab initio MD simulation of the oxidation process, producing amorphous HfO₂ structure with minimal computational cost.

2. NVE-NVT Protocol

In **Fig. 2a**, NVE-NVT protocol is applied to the oxidation of a HfSe₂ monolayer. Each cycle (pale green background) involves oxygen insertion during NVE step (red box), followed by floating Se atom removal and NVT quenching (blue box). Repeated application of this cycle (striped arrow) ultimately leads to a fully oxidized, amorphous HfO₂. Notably, the final structure of NVE step becomes the starting configuration for the subsequent NVT step, after removing loosely bound Se atoms. **Fig. 3** illustrates the simulation workflow in detail.

In the first cycle, a cluster of three Se atoms forms on the surface and fly away due to the thermal energy released from oxidation, resulting in partially oxidized model of O₆ (Hf₂₄Se₄₅O₆). During HfSe₂ oxidation, oxygen atoms spontaneously and barrierlessly occupy bridging sites between Hf atoms. Concurrently, Se atoms are expelled from the triply-bridged sites and migrate to form clusters atop Hf atoms. The significant heat generated promotes strong atomic vibrations, enabling oxygen penetration and oxidation on both surfaces of the monolayer.

After removing Se atoms, the system undergoes a 1ps quenching process via NVT dynamics using Nosé–Hoover thermostat, cooling it from the elevated temperature back to the reference temperature of 500 K. This stabilizes the highly excited system. The NVE-NVT protocol is then applied iteratively until O₃₆ model (Hf₂₄Se₂₈O₃₆) is obtained.

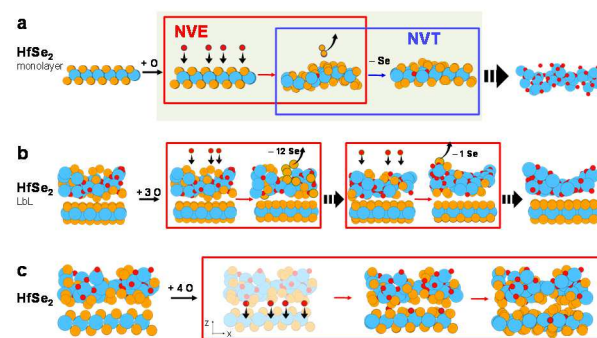


Fig 1. NVE-NVT protocol for the oxidation of HfSe₂ monolayer and bilayer under weak and strong power condition. (a) The NVE-NVT protocol (pale green background) consists of an NVE oxidation step (red box) where several oxygen atoms are inserted above the surface, followed by an NVT quenching step (blue box) after the removal of floating Se atoms. This process cools the system to the reference temperature of 500 K. Repeated application of this cycle (striped arrow) results in the completely oxidized HfSe₂ into amorphous HfO₂. (b) The partially oxidized O₃₆ model (Hf₂₄Se₂₈O₃₆) is stacked on pristine HfSe₂, forming an interface model that undergoes further oxidation via additional oxygen insertion during the NVE step. Successive NVE-NVT cycles results in an amorphous HfO₂/HfSe₂ structure with a preserved van der Waals (vdW) gap. (c) In the strong power condition, oxygen atoms are dropped onto the pristine bottom layer, resulting in the contaminated interface which breaks the layer-by-layer (LbL) oxidation mechanism. Color scheme: Hf (cyan), Se (brown), and O (red).

During Se atom removal, special care must be taken to exclude only floating Se atoms that are not at bridge sites. In the second NVE-NVT cycle, Hf atoms with more than three O coordination begins to align vertically. This behavior reflects the inherent three-dimensional crystal of HfO₂, where half of the oxygen atoms occupy tetrahedral sites and the remainder reside at triangular site. This vertical alignment of Hf atoms eventually results in voids forming on HfSe₂ surface, as shown in the last figure of O₃₆ model in **Fig. 3**. These voids act as channels that facilitate further oxygen insertion or Se extraction from deeper layers. Therefore, during multilayer oxidation, these void channels remain critical for continued oxidation and structural evolution.

3. Layer-by-Layer Oxidation

In **Fig. 2b**, the partially oxidized O₃₆ model is stacked on pristine HfSe₂, and then subjected to further top-surface oxidation using NVE-NVT protocol. This demonstrates the progressive formation of a homogeneous gate stack via layer-by-layer (LbL) oxidation of HfSe₂, ultimately resulting in the formation of amorphous-HfO₂/HfSe₂ with van der Waals (vdW) gap. [3]

Fig 4. presents detailed reaction mechanism underlying LbL oxidation under low-power plasma conditions. [3] Due to the monolayer thickness of the amorphous oxide, a high density of dangling bonds observed on the Hf atoms. In bulk HfO₂, Hf atoms typically exhibit a coordination number (CN) of seven, while surface Hf atoms have CN of five or six. However, in this ultrathin HfO₂ structure, all Hf atoms are exposed on either the upper or lower surfaces, resulting in an even higher density of dangling bonds. To address this, four additional oxygen atoms are introduced beyond the stoichiometric ratio, consistent with the oxygen-rich

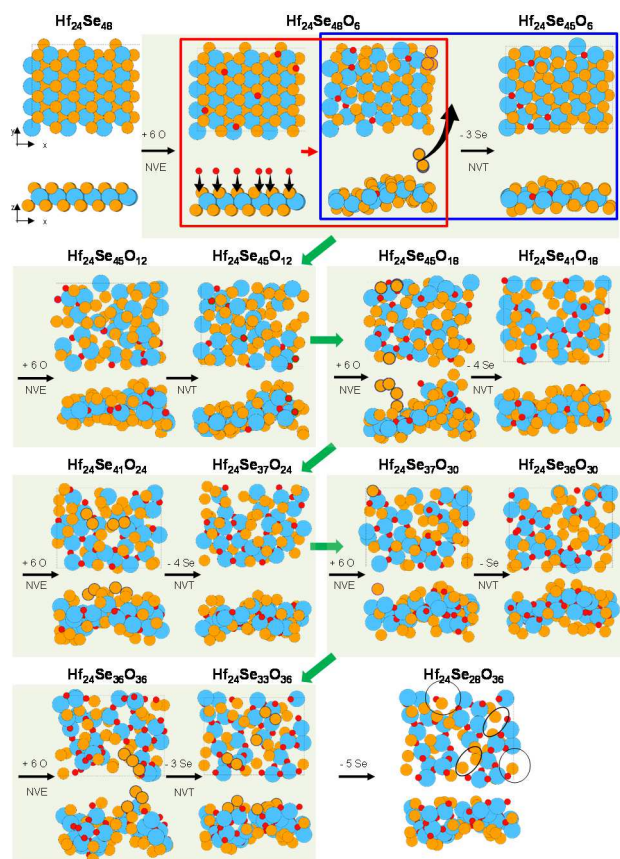


Fig 3. NVE-NVT dynamics for oxidation of HfSe₂ monolayer. In every NVE step, six oxygen atoms are inserted above the surface. Each NVE-NVT cycle is highlighted by pale green background. After six NVE-NVT cycles, partially oxidized O₃₆ model (Hf₂₄Se₂₈O₃₆) is obtained. Red and blue boxes in the first cycle indicate the NVE and NVT steps, respectively. Color scheme: Hf (cyan), Se (brown), and O (red).

condition of plasma oxidation. In the forth cycle, three oxygen atoms are inserted at the oxide/HfSe₂ interface with upward velocities, specifically targeting the passivation of vacancy sites on the bottom surface of the oxide layer. This approach accelerates the passivating process, which would otherwise be limited by slow diffusion of oxygen from the oxygen-rich region to oxygen-poor region. Through these technical measures, an amorphous HfO₂ with a preserved van der Waals gap above the pristine HfSe₂ layer was successfully achieved, consistent with experimental observation. [3]

4. Breaking Layer-by-Layer Oxidation Condition

Fig. 2c illustrates the oxidation process at the O₃₆ model/HfSe₂ interfaces under high-power plasma condition. Unlike the earlier simulations (**Fig. 2b** and **4**), where oxygen atoms were deposited only on the top surface, this scenario involves direct insertion of four oxygen atoms at the interface, directed toward the underlying HfSe₂ layer. Upon impact, the oxygen atoms penetrate the bottom layer, leading to contamination of the interface. Even only one oxygen atom could oxidize the underlying pristine layer.

Therefore, precise experimental control is essential to maintain a clean interface during the fabrication of homogeneous gate stack based on HfSe_2 . It is worth noting that heterogeneous gate stack precursors such as $\text{HfSe}_2/\text{MoS}_2$ and $\text{HfSe}_2/\text{WSe}_2$ may exhibit different behaviors under oxygen plasma, depending on the reactivity of the respective

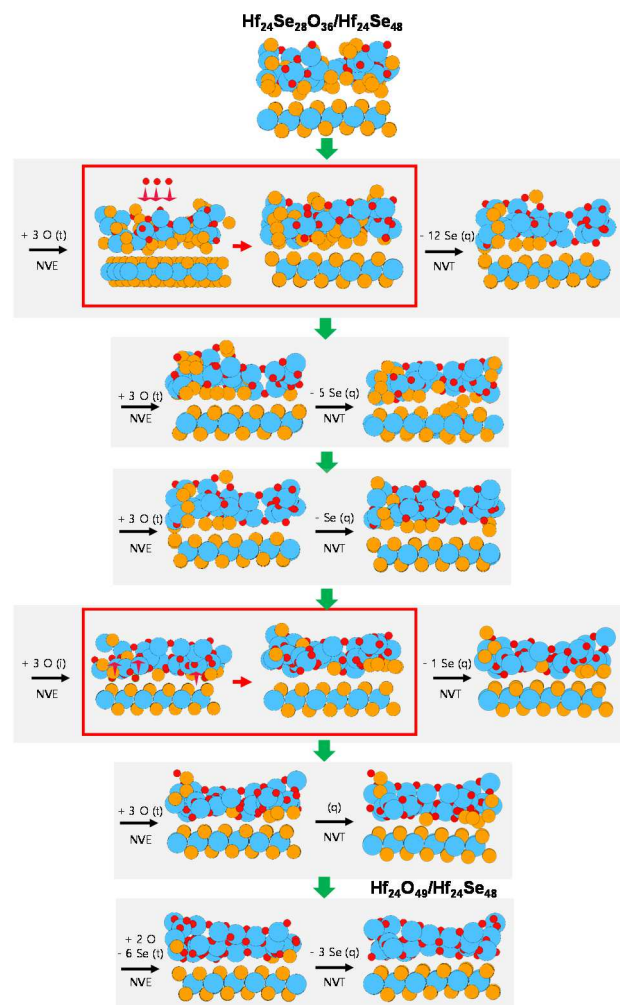


Fig 4. NVE-NVT dynamics for oxidation of HfSe₂ bilayer of O₃₆ model (Hf₄Se₂₈O₃₆)/HfSe₂. The interface model undergoes further oxidation through insertion of three oxygen atoms during each NVE step. Repeated NVE-NVT cycles produce an amorphous HfO₂/HfSe₂ structure with a well-defined van der Waals (vdW) gap. Color scheme: Hf (cyan), Se (brown), and O (red).

surfaces. These variations in oxidation dynamics will be explored in the future works.

This study demonstrates that the strong binding energies, rapid kinetics, and favorable structural evolution observed in simulations support the feasibility of engineering native-oxide gate stacks with tailored interface properties using ab initio molecular dynamics guided by NVE-NVT protocols. However, maintaining a vdW interface through layer-by-layer (LbL) oxidation in the homogeneous $\text{HfO}_2/\text{HfSe}_2$ gate stack requires precise control of experimental conditions.

ACKNOWLEDGMENT

This work was supported by SK hynix Inc and the National Research Foundation of Korea (RS-2023-NR077013, RS-2023-00253716). Computational resources were provided by KISTI Supercomputing Center (KSC-2025-CRE-0599).

REFERENCES

- [1] M. J. Mleczko *et al.*, "HfSe₂ and ZrSe₂ : Two-dimensional semiconductors with native high- κ oxides," *Science Advances*, vol. 3, no. 8, p. e1700481, August 2017, doi: 10.1126/sciadv.1700481.
- [2] G. Mirabelli *et al.*, "Air sensitivity of MoS₂, MoSe₂, MoTe₂, HfS₂, and HfSe₂," *Journal of Applied Physics*, vol. 120, no. 12, 2016, doi: 10.1063/1.4963290.
- [3] T. Kang *et al.*, "High- κ Dielectric (HfO₂)/2D Semiconductor (HfSe₂) Gate Stack for Low-Power Steep-Switching Computing Devices," *Advanced Materials*, vol. 36, no. 26, pp. 2312747, 2024, doi: 10.1002/adma.202312747.
- [4] M. Jech, A. M. El-Sayed, S. Tyaginov, A. L. Shluger, and T. Grasser, "Ab initio treatment of silicon-hydrogen bond rupture at Si/SiO₂ interfaces," *Physical Review B*, vol. 100, no. 19, 2019, doi: 10.1103/PhysRevB.100.195302.
- [5] L. Cvitkovich, D. Waldhör, A. M. El-Sayed, M. Jech, C. Wilhelmer, and T. Grasser, "Dynamic modeling of Si(100) thermal oxidation: Oxidation mechanisms and realistic amorphous interface generation," *Applied Surface Science*, vol. 610, 2023, doi: 10.1016/j.apsusc.2022.155378.
- [6] S. Lai *et al.*, "HfO₂ /HfS₂ hybrid heterostructure fabricated via controllable chemical conversion of two-dimensional HfS₂," *Nanoscale*, vol. 10, no. 39, pp. 18758–18766, 2018, doi: 10.1039/C8NR06020G.
- [7] C. H. Lee *et al.*, "Atomically thin p-n junctions with van der Waals heterointerfaces," *Nature Nanotechnology*, vol. 9, no. 9, pp. 676–681, 2014, doi: 10.1038/nnano.2014.150.
- [8] G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set," *Physical Review B*, vol. 54, no. 16, pp. 11169–11186, 1996, doi: 10.1103/PhysRevB.54.11169.
- [9] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized Gradient Approximation Made Simple," *Physical Review Letters*, vol. 77, no. 18, pp. 3865–3868, 1996. [Online]. Available: <http://link.aps.org/doi/10.1103/PhysRevLett.77.3865>.
- [10] S. Grimme, S. Ehrlich, and L. Goerigk, "Effect of the damping function in dispersion corrected density functional theory," *Journal of computational chemistry*, vol. 32, no. 7, pp. 1456–1465, 2011, doi: 10.1002/jcc.21759.
- [11] A. Schütze, J. Y. Jeong, S. E. Babayan, J. Park, G. S. Selwyn, and R. F. Hicks, "The Atmospheric-Pressure Plasma Jet: A Review and Comparison to Other Plasma Sources," in "IEEE TRANSACTIONS ON PLASMA SCIENCE," 1998, vol. 26.