

Atomistic Insights into NH₃ Plasma-Induced Carbon Depletion and Nitrogen Incorporation in SiCOH Low-k Dielectrics

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Abstract—Low-k SiCOH dielectrics are highly susceptible to plasma-induced damage during semiconductor processing, leading to carbon depletion and degradation of electrical performance. While experimental studies have reported carbon loss under NH₃ plasma exposure, the atomistic mechanisms governing these processes remain unclear. In this work, large-scale molecular dynamics (MD) simulations are employed to investigate NH₃ plasma interactions with amorphous SiCOH films. The simulations capture bond-breaking events, fragment desorption, and nitrogen incorporation at the atomic scale. Results reveal that carbon depletion originates from hydrogen-assisted scission of Si-CH₂-Si bridges, accompanied by CH_x fragment removal. Nitrogen is incorporated predominantly in the near-surface region through the formation of Si-bonded NH_x motifs. These findings provide a mechanistic understanding of plasma-induced low-k modification and establish a physics-based framework for interpreting experimentally observed degradation.

Keywords—low-k dielectrics, SiCOH, NH₃ plasma, molecular dynamics, plasma-induced damage

I. INTRODUCTION

Porous SiCOH is widely used as an interlayer dielectric in advanced interconnect structures because its reduced polarizability and engineered free volume lower parasitic capacitance[1]. The same structural features that enable a low dielectric constant, carbon-containing terminal groups, nanoscale pores, and a large internal surface area, also increase sensitivity to reactive plasma species. Plasma-induced removal of hydrophobic carbon groups can increase moisture affinity, modify the local density, and degrade dielectric performance [1]-[4].

X-ray photoelectron spectroscopy and related measurements provide direct evidence of carbon depletion after plasma exposure[2],[3], but they primarily report the cumulative composition after many reaction events. They do not identify which local carbon environments are attacked first, how the SiCOH network reorganizes, or whether nitrogen remains physically trapped or forms chemically integrated configurations. Atomistic simulation therefore provides complementary information by resolving bond scission,

transient fragments, local densification, and the bonding environment of incorporated species.

This work extends our previous plasma-modeling framework [5], [6] to NH₃-plasma interactions with a realistic porous SiCOH model. The objectives are to determine (i) the spatial distribution and atomistic origin of carbon loss, (ii) the evolution of terminal and bridging carbon environments, and (iii) the depth and local bonding states of incorporated nitrogen. The simulation is interpreted as an accelerated sequence of early-stage reaction events; it is not used as a direct clock-to-clock representation of the experimental exposure time.

II. ATOMISTIC MODEL AND SIMULATION METHOD

A. Porous SiCOH Model

The amorphous film contains approximately 5300 Si, O, C, and H atoms in a $40 \times 40 \times 60 \text{ \AA}^3$ simulation cell. The relaxed structure has a density of approximately 1.45 g cm^{-3} and about 20% porosity, with interconnected cavities on the 1–2 nm scale, consistent with reported porous SiOCH film morphologies [7]. The carbon concentration is approximately 18 at.%, representative of plasma-enhanced chemical-vapor-deposited organosilicate films. Hydrogen termination was used to passivate artificial Si and O dangling bonds at pore surfaces and to reproduce hydrophobic carbon-containing environments.

Two characteristic carbon topologies are present, as illustrated in Fig. 1: terminal Si-CH₃-like groups coordinated to one Si atom and bridging Si-CH₂-Si groups coordinated to two Si atoms. Among the carbon environments classified by C-Si coordination, the initial model contains approximately 23% terminal and 77% bridging configurations. This distinction is important because terminal groups are exposed at pore walls, whereas bridging carbon participates directly in the network backbone.

B. Model Validation

The initial structure was checked against available film-level observables before plasma exposure. On a hydrogen-excluded basis, the simulated Si/O/C composition is approximately 33/44/22 at.%, compared with representative XPS values of

31/45/23 at.%. The simulated density and porosity likewise fall within the range expected for porous low-k organosilicate films. Although these comparisons do not uniquely validate every local topology, they ensure that the starting network structure provides a realistic global composition and free-volume distribution for analysis of the subsequent plasma-induced chemistry.

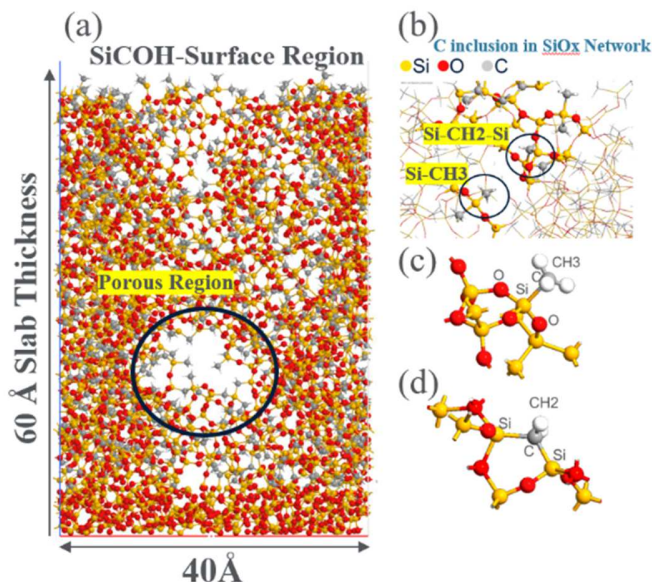


Fig. 1. Atomistic model of porous SiCOH (~20% porosity). (a) Cross-sectional view showing interconnected pores and the exposed surface region. (b) Local Si-CH₃ and Si-CH₂-Si environments. (c), (d) Representative terminal methyl and bridging methylene configurations.

C. Plasma-Impact Molecular Dynamics

Molecular dynamics simulations were performed using the MatterSim machine-learning interatomic potential [8], which provides energy and force predictions without imposing a fixed bonding topology. This enables atomic rearrangement, bond cleavage, and the formation of new local environments involving Si, O, C, H, and N during plasma-impact events.

The porous SiCOH slab was separated from its periodic image by an approximately 50 Å vacuum region along the surface-normal direction, with periodic boundary conditions applied in the lateral directions. A reservoir region was maintained near 500 K to dissipate the heat generated by successive impacts.

NH₃-plasma exposure was represented through sequential impacts of H and NH_x species with an incident kinetic energy of approximately 10 eV, corresponding to the low-energy chemical-interaction regime[9]. Each impact was followed for 0.5 ps and subsequently relaxed for 1.5 ps using 0.25 fs time step. Impact locations were randomized across the lateral surface to sample different pore-wall and surface environments. The impact relaxation cycles were applied in multiple batches, resulting in an accumulated simulation trajectory of approximately 200 ps. The accelerated impact sequence increases the number of observable reaction events within an

accessible trajectory. The resulting trajectory is therefore used to identify atomistic reaction pathways and persistent products, rather than to equate approximately 200 ps of simulation with the experimental process time. Quantitative process-time prediction would require an independently calibrated flux- or dose-based model together with kinetic treatment of rare events.

D. Structural and Chemical Analysis

Carbon loss was determined from the change in the number of carbon atoms remaining in the slab, and element-resolved mass-density profiles were computed along the film-normal direction. Carbon topology was classified using C-Si coordination with a 2.0 Å cutoff. A carbon atom with one Si neighbor was assigned to a terminal CH_x environment, whereas two Si neighbors identified a bridging Si-CH₂-Si environment. Pair-specific nitrogen coordination cutoffs were selected from the first minima of the corresponding partial radial-distribution functions. Each incorporated N atom was subsequently classified according to its Si, C, H, and O neighbor counts to construct the motif statistics.

III. RESULTS AND DISCUSSION

A. Carbon Depletion and Spatial Localization

After the modeled NH₃-plasma exposure, the slab retains 92.9% of its initial carbon population, corresponding to an overall carbon loss of approximately 7.1% (Fig. 2). The depth profile shows that the strongest compositional modification is associated with the exposed side of the porous film, whereas the deeper network remains comparatively stable. Because the simulation contains a finite number of impacts and samples only the early trajectory, the 7.1% value is a response to the selected atomistic dose rather than a prediction of the final loss after the experimental process time.

The important agreement with experiment is therefore qualitative and mechanistic: NH₃-plasma-derived species are capable of removing carbon from porous SiCOH under the modeled conditions. The simulation additionally resolves the local bond-breaking sequence that cannot be determined from an integrated XPS signal alone.

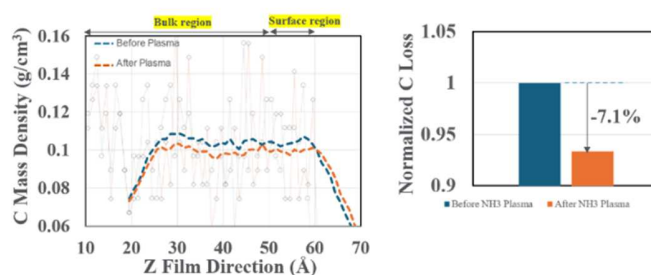


Fig. 2. Carbon mass-density profile before and after NH₃-plasma exposure. The largest change occurs toward the exposed surface, while the inset reports the overall normalized carbon loss (~7.1%) for the modeled impact sequence.

B. Evolution of Carbon Bond Topology

The C-Si coordination distribution changes systematically during plasma exposure. The fraction of single-Si-coordinated carbon increases from 0.216 to 0.260, while the double-Si-coordinated fraction decreases from 0.7159 to 0.668 (Fig. 3). These changes correspond to approximately +4.6 and -4.8 percentage points, respectively. Because the statistics are

evaluated for the carbon atoms remaining in the structure, the apparent rise in terminal CH_x character does not indicate net creation of carbon or methyl groups.

Trajectory inspection shows that incident hydrogen can attack a bridging Si-CH₂-Si environment and cleave one of the Si-C bonds. The surviving carbon then becomes single-Si-coordinated and can acquire additional hydrogen, producing a terminal CH_x fragment. Continued reaction can detach the fragment from the network and allow desorption. Thus, the paired decrease in bridging carbon and increase in terminal character represents network fragmentation preceding carbon removal. The local network is simultaneously left with under-coordinated Si sites that can be passivated by H or react with nitrogen-containing species.

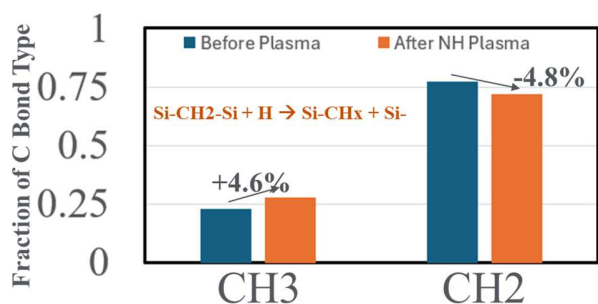


Fig. 3. Evolution of carbon bonding environments under NH₃-plasma exposure. Depletion of bridging Si-CH₂-Si configurations and the corresponding increase in terminal CH_x character indicate hydrogen-assisted bridge cleavage and network restructuring.

C. Nitrogen Incorporation Depth

Nitrogen introduced by the NH_x-containing impact sequence is not distributed uniformly through the slab. As shown in Fig. 4, the N mass-density profile is concentrated within approximately the top 15 Å of the exposed region and decays rapidly toward the interior. A small number of nitrogen atoms appear at greater depth where open pore channels provide direct access, but the dominant response remains surface-localized within the 200 ps trajectory.

This profile indicates that the initial incorporation mechanism is controlled by reactions at accessible pore-wall sites rather than by homogeneous bulk diffusion. Longer process exposure can increase dose and modify the accessible depth, but the present simulations establish the location and chemistry of the earliest stable N-containing products.

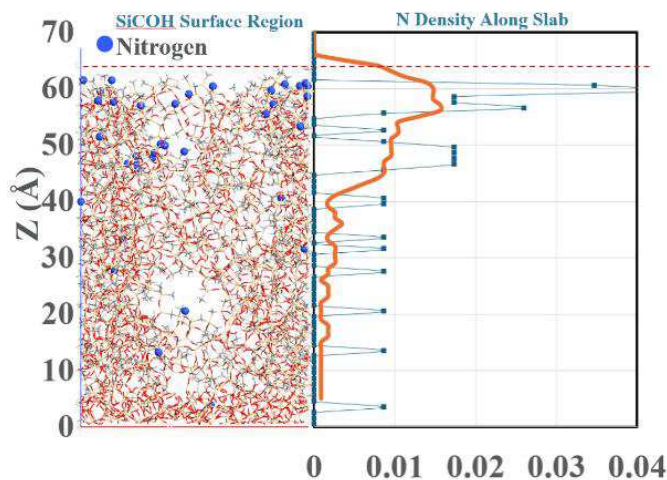


Fig. 4. Depth-resolved nitrogen distribution following NH₃-plasma exposure. Nitrogen atoms are shown in blue, and the N mass-density profile indicates that incorporation is concentrated primarily within the top ~15 Å, with limited penetration into the deeper film during the simulated trajectory.

D. Local Nitrogen Bonding Environments

A total of 36 incorporated nitrogen atoms were analyzed in the final structure. Their first coordination shell contains 42 Si, 34 H, and 10 C neighbors, corresponding to average coordination values of 1.17 Si, 0.94 H, and 0.28 C per N atom. No persistent N-O coordination is detected within the selected bonding cutoff. The absence of N-O motifs indicates that nitrogen incorporation is not primarily mediated by oxide-like bonding in the simulated chemistry.

Figure 5 combines representative atomistic configurations with the normalized motif occurrence. Si-bonded NH_x structures dominate, particularly NH-Si₂ and NH₂-Si environments, followed by mixed NH-Si-C configurations. The preference for Si-bonded nitrogen environments is consistent with related modeling of NH₃-based treatment of porous SiOCH, which reported NH_x adsorption and the formation of Si-N, and C-N bonding configurations [10]. Less frequent C-rich or higher-Si-coordination motifs are also present. These local structures show that nitrogen is chemically integrated into newly created or under-coordinated network sites rather than remaining exclusively as weakly trapped NH_x fragments. The mixed Si-C-N states further connect nitrogen uptake to the same carbon-network restructuring responsible for depletion.

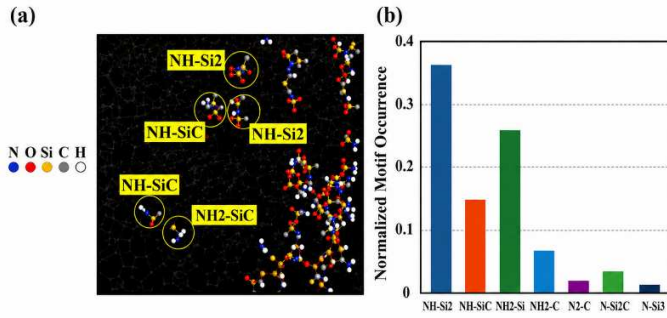


Fig. 5. Local nitrogen bonding environments after NH₃-plasma exposure. (a) Representative Si-bonded NH_x and mixed Si-C-N configurations. (b) Normalized occurrence of the principal motifs, showing that Si-coordinated NH_x environments dominate the incorporated nitrogen population.

E. Coupled Carbon-Nitrogen Reaction Picture

The carbon and nitrogen analyses are mutually consistent rather than independent observations. Cleavage of a Si-CH₂-Si bridge removes one network connection and produces a reactive Si-centered site. Hydrogen can terminate that site, but an incident NH_x species can also form a Si-N bond and remain incorporated. The predominance of NH-Si₂ and NH₂-Si motifs therefore reflects the availability of under-coordinated Si generated during carbon-network fragmentation. Mixed NH-Si-C configurations occur where nitrogen is stabilized adjacent to a surviving carbon-containing segment.

This coupled picture also explains why nitrogen is concentrated near the same surface-accessible region in which carbon depletion is initiated. Open pores increase the number of reachable internal surfaces, but penetration is not unlimited: reactive species are consumed at pore walls, and local densification or passivation can reduce access to deeper sites. The present trajectory does not establish whether the modified layer becomes fully self-limiting at long process time, but it identifies the atomic processes that could produce such behavior.

F. Timescale Interpretation and Material Implications

The simulation and experiment probe complementary regimes. Experiment integrates a continuous plasma flux over seconds and measures the cumulative compositional response, whereas molecular dynamics resolves individual impacts, bond rearrangements, and desorption events over picoseconds. Extending the MD trajectory alone would not establish a unique conversion from simulation time to process time because the correspondence also depends on incident flux, radical-to-ion ratio, energy distribution, surface-site saturation, and evolving transport through the modified layer.

Within this scope, the simulations identify a coupled mechanism: hydrogen-assisted cleavage removes carbon-containing bridges, and the resulting reactive sites facilitate stabilization of Si-bonded nitrogen. Carbon depletion reduces hydrophobic CH_x content, while NH_x incorporation introduces

more polar local bonding environments. Both effects can modify the dielectric response and moisture sensitivity of the near-surface region, although direct calculation of the dielectric constant and process-time kinetics is beyond the present study.

IV. CONCLUSION

Large-scale atomistic simulations reveal the early-stage mechanism of NH₃-plasma modification in porous SiCOH. Carbon loss is initiated by hydrogen-assisted cleavage of Si-CH₂-Si bridges, which increases terminal CH_x character among the surviving carbon population before fragment desorption. Nitrogen incorporation is concentrated near the exposed surface and occurs predominantly through Si-bonded NH_x motifs, with negligible persistent N-O bonding. The combined depth, coordination, and motif analyses connect experimentally observed carbon depletion to a specific atomistic sequence of network fragmentation and chemical incorporation. The framework provides a physically interpretable basis for future dose-dependent modeling and for evaluating plasma conditions that minimize low-k damage.

Future work will extend the impact-dose series, repeat the calculation over independent porous structures, and evaluate the dielectric response of the modified region. Coupling the atomistic event statistics to a kinetic or flux-based model will be required to predict carbon loss and nitrogen uptake on the experimental time scale. These extensions can convert the present mechanistic picture into a quantitative process-structure-property relationship.

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