From models to mechanisms: defects and charge trapping in amorphous silicon nitride

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Summary

From Models to Mechanisms: Defects and Charge Trapping in Amorphous Silicon Nitride

Altogether, this thesis has advanced the understanding of several long-standing questions surrounding amorphous silicon nitride. Central to the work is the unique electronic structure of a-Si_3N_4 comprising a long Urbach tail in its band gap, which enables the stable localization of charge carriers on a variety of defect sites. This property underpins the success of a-Si_3N_4 as a charge-trapping medium in non-volatile flash memory, where it is exploited commercially with great effectiveness. Conversely, the same localized states require careful consideration when a-Si_3N_4 is employed as a passivation layer or in optoelectronic devices, as they can act as recombination centers, induce carrier scattering, and facilitate charge leakage through trap-assisted tunneling. More recently, a-Si_3N_4 has also been explored as an anode material in conversion-type lithium-ion batteries. Although the material has not been developed with charge-trapping behavior in mind, the findings presented in this thesis suggest that its intricate defect landscape and associated electronic structure nevertheless play an important role in its electrochemical performance.

To unravel the microscopic origins of these phenomena, **CHAPTER 3** presents a systematic assessment of commonly used computational protocols for modeling amorphous solids, identifying typical artifacts and outlining strategies that balance accuracy with computational cost. Focusing on the melt–quench approach, the chapter shows that key structural and physical properties depend sensitively on simulation cell size and cooling rate. Cooling a 280 atom cell at a rate of $1\,\mathrm{K\,ps^{-1}}$ emerges as a reliable compromise, producing ensembles with low and reproducible defect concentrations — an essential prerequisite for a meaningful analysis of the resulting electronic structure.

Building on this foundation, a novel site-specific descriptor is introduced that quantifies the opening angles of coordination polyhedra, providing a simple yet powerful metric for local "defectiveness". This descriptor enables a direct link between local structural motifs and their electronic characteristics, facilitating the identification of trap sites and offering new insights into the mechanisms of charge localization in a-Si_3N_4.

Furthermore, this chapter presents an approach to quantify statistical convergence of structural ensembles by choosing a diverse set of descriptors in order to distinguish typical configurations from outliers. This approach enables the systematic selection of a representative subset for higher-level electronic-structure calculations, thereby capturing the full configurational landscape even when only a sparse sample is treated at the *ab initio* level. Such a hierarchical workflow effectively combines the strengths of classical interatomic potentials with those of *ab initio* methods, maximizing both computational efficiency and the statistical robustness of the resulting analysis.

Modeling external defects in amorphous systems becomes considerably more complex: The absence of symmetry-equivalent sites leads to a vast number of possible configurations with widely varying incorporation patterns. To systematically insert defect atoms, the geometry is subdivided via Voronoi tessellation for the initial guess followed by the subselection strategy used for structural ensembles. This approach constrains the effective search space for defect configurations and enables systematic classification of the resulting structural motifs. The methodology also extends to the incorporation of multiple defects. However, the dependence on sequence of insertion when inserting more than a single defect breaks ergodicity, necessitating a more sophisticated treatment based on a Gaussian Mixture Model. Together, these advances contribute to a coherent framework for understanding the interplay between structure, defects, and electronic behavior in amorphous silicon nitride.

To fully exploit the benefits of hierarchical sampling, robust and well-parameterized interatomic potentials are essential. **CHAPTER 4** introduces a Bayesian Optimization–based scheme that enables a top-down search for purpose-tailored parameters within a chosen force-field framework. Although classical interatomic potentials are generally too simplistic to capture the full underlying physics, the Bayesian Optimization approach identifies parameter sets that reproduce selected observables with unexpectedly high accuracy. This capability makes it possible to leverage the advantages of classical IPs like speed, robustness against extrapolation errors at comparatively low cost, thereby supporting efficient hierarchical sampling of amorphous solids.

CHAPTER 5 presents a comprehensive structural ensemble of a-Si_3N_4, whereby the statistical convergence of the sampling has been carefully monitored according to the methodology described in the previous chapter. This ensemble is used to identify a representative subset of structures, which is then examined in the $-1/0/+1$ charge states at the HSE06 level. These calculations reveal that the mid-gap states near the valence- and conduction-band edges originate from Anderson-like states localized on undercoordinated nitrogen and silicon atoms known as N- and K-centers, respectively. They act as precursor sites for hole and electron trapping, in agreement with the prevailing hypotheses in the literature.

Electron trapping at pre-existing K-centers typically involves minimal structural relaxation and yields moderate trapping energies (on average −0.6 eV), enabling reversible charging-discharging cycles. However, trapping at K-centers is only the case in 31 % of the samples. Owing to the pronounced Urbach tails at both band edges, localized states also arise on a variety of structural motifs, consistently associated with distorted SiN_4 tetrahedra. Upon charging, electrons localize on these sites, amplifying the distortion toward a pseudo–trigonal-bipyramidal coordination in which the trapped electron effectively occupies one of the polyhedral positions. In extreme cases, this distortion can rupture a strained Si–N bond, creating a new N-center while the electron localizes on the resulting threefold-coordinated Si atom. A third trapping motif involves two adjacent Si atoms that jointly localize the electron, forming a $N_3Si{-}SiN_{x\in\{3,4\}}$-type trap reminiscent of the onset of Si–Si bond formation.

Since a-Si_3N_4 encompasses a wide, continuous distribution of deformed coordination polyhedra, even small simulation cells contain several trap precursor sites. The sequence in which they are occupied is therefore determined by their relative energy level and predicting these is not straightforward. Accordingly, instances were found in which electrons are trapped at intrinsic precursor sites despite the presence of a nearby K-center. Trapping energies span a wide range between −2.83 eV to −0.20 eV with a mean of −0.73 eV, with the deepest traps being partially irreversible due to the severe structural rearrangement.

Crucially, these findings provide a vector why charge trapping remains prevalent in a-Si_3N_4 even under conditions where chemical intuition would predict passivation of coordination defects, *e.g.*, in the presence of hydrogen or oxygen and after high-temperature annealing.

The alternative trapping pathways uncovered here demonstrate that electron injection can reversibly create K-centers and subsequently heal them upon discharging. This self-induced, reversible trapping mechanism provides a microscopic rationale for the exceptional reliability of SiN_x-based charge-trapping memory technologies.

In practice, a-Si_3N_4 is rarely used in its pristine form. Hydrogen and oxygen are typically present in thin films, whether unintentionally incorporated during growth or deliberately added to passivate the network and tune its electronic properties. Hydrogen effectively terminates dangling N- and Si-bonds, suppressing mid-gap states and lowering the density of electrically active defects. As such, it is widely considered a universal panacea in different contexts ranging from the prevention of charge trapping entirely up to adjustment of trapping behavior.

The models presented in **CHAPTER 6**, however, reveal the multifaceted role of hydrogen in a-Si_3N_4. While the passivation of coordination defects proceeds as intended, hydrogen acts as a donor/acceptor depending on whether it is bound to N or Si, respectively. More critically, hydrogen can insert into Si–N bonds, which in extreme cases leads to bond rupture. This process proceeds *via* a backside attack on the silicon atom, inverting the local tetrahedral geometry and generating a dangling nitrogen bond. This has two major implications: First, the resulting N-center constitutes a new intrinsic defect capable of trapping a hole, meaning that hydrogen insertion can paradoxically create additional defect states that would require further hydrogen to passivate. Second, because hydrogen binds to only a single neighbor, its incorporation disrupts the connectivity of the amorphous network. At elevated concentrations, such network-breaking events compromise the mechanical integrity of the material and thus offer a plausible microscopic pathway for hydrogen-induced embrittlement.

CHAPTER 7 covers the nature of oxygen defects in a-Si_3N_4 focusing on oxygen interstitials (O_i) and substitutions (O_N). Thermodynamically, SiO_2 is favored over Si_3N_4, which is confirmed by virtually all substitutions exhibiting negative defect formation energies (-1.26 eV on average). Likewise, O_i atoms bind strongly to a-Si_3N_4 and even inserting into Si–N bonds if the network permits. Once incorporated, O_N adopts a silica-like Si–O–Si configuration. Due to oxygen's lower valency compared to nitrogen, this substitution creates a formally undercoordinated Si atom acting as a new K-center competing with the native ones for trapping electrons. However, the adjacent O_N atom stabilizes the former electrostatically, turning them into shallow traps that are filled only after the lower-lying intrinsic states. This behavior aligns with experimental observations showing enhanced carrier mobility in SiN_xO_y films, where the presence of additional shallow states promotes trap-assisted tunneling.

Contrary to its oxophilic character discussed above, a-Si_3N_4 is widely used as a passivation layer and is well known for its remarkable oxidation resistance. To understand this behavior, Chapter 7 presents a series of nudged-elastic band calculations exploring the transition of O_i defects to O_N defects. Surprisingly, the formation of an Si$-O_N-$Si bridge proceeds with only a moderate barrier of 1.01 eV to 2.05 eV, producing a nitrogen interstitial (N_i) as a byproduct. The N_i retains two of its original Si–N bonds by forming an N–N linkage, thereby remaining firmly bound to the amorphous network. The subsequent conversion of this $Si_2N_i-NSi_2$ species into a gaseous $N_{2(g)}$ to be removed from the reaction site turns out to be the step with the highest barrier. This is due to the multitude of Si–N bonds that need to be broken simultaneously and the creation of a nitrogen vacancy. Although the presence of a second oxygen atom can lower the barrier by inserting into the emerging vacancy or reacting with the N_i itself, the inherently low diffusivity of oxygen in a-Si_3N_4 raises the question how accessible these reaction pathways actually are. Nevertheless, these mechanisms rationalize the unusual high abundance of NO_x species found in the product gas mixture.

Finally, **CHAPTER 8** investigates a-Si_3N_4 as an emerging conversion-type anode where lithium incorporation drives the formation of a structurally robust matrix and active phases. Analogously to hydrogen, Li donates its valence electron to the conduction-band minimum according to $Li^0 \rightarrow Li^+ + e^-$, after which the resulting Li^+ coordinates to nearby nitrogen atoms while the electron localizes in one of the native trap states of a-Si_3N_4. With only a few exceptions, the mid-gap electronic structure is therefore still governed by the intrinsic defect states of the host material. Insertion of a second Li atom follows the same mechanism, where the electron occupies the same trap state forming a bipolaron. This bipolaron subsequently relaxes into a $N_3Si-SiN_{x\in\{3,4\}}$ configuration previously identified in Chapter 5 whose electronic state lies deep within the valence band, rendering the process irreversible. Adding more Li atoms continues this pattern: Each subsequently added Li donates its electron to the lowest-energy available trap, bipolarons form, and these relax into stable deep

states. Once all structural precursors capable of hosting such deep traps are consumed, further trapping events become progressively shallower.

Major implications emerge from these results. Charge trapping directly drives the structural transformation of a-Si_3N_4 during the initial lithiation through the formation of polarons and bipolarons. These charge-induced modifications lead to the formation of a Li–Si–N matrix that stabilizes the anode framework. The matrix formation is linked to the emergence of Si-rich regions that act as precursors to the electrochemically active phase converting electronically active polarons to inactive bipolaron states. The transition from electronically active polarons to bipolarons thus establishes a direct connection between charge localization and matrix formation. Taken together, these findings recast charge trapping in a-Si_3N_4: Rather than being an incidental by-product of lithiation, it emerges as a central and potentially tunable parameter in the design of high-performance conversion-type anodes.