Atomistic Study of Amorphous Si-O-X Networks for Plasma Enhanced Atomic Layer Deposition-Produced SiO_2 Films: Illuminating the Structure-Composition-Mechanical and Electrical Property Connections

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1. **Reference:** Dernov, A., Tong, Z., Kumar, R., Agarwal, P., Frauenheim, T., Dumitrică, T.,. *Adv. Theory Simul.* 2022, 5, 2200284. https://doi.org/10.1002/adts.202200284

2. **Density functional-based molecular dynamics predicts densification of amorphous silica by Aluminum addition. Aluminum content promotes dense silica-like fivefold and sixfold coordination defects and shifts the potential energy minima to larger densities than in pristine silica:**

By molecular dynamics (MD) simulations, we have created a large collection of *a*-SiO_2 atomistic models of various densities, Figure 1a. We uncovered that the PE-ALD *a*-SiO_2 correspond to a thermodynamic minima and higher density *a*-SiO_2 are energetically unfavorable. Structurally, they must contain 5-fold coordination defects. Since pressure-driven densification is not compatible to atomic deposition technologies, is there a bottom-up way of driving the formation of 5-fold coordination defects during the *a*-SiO_2 film formation? We have explored this question by studying the effects of modifiers X added during the *a*-SiO_2 film formation. As modifier we have considered Aluminum (Al) because this element is the prevailing impurity in quartz, were AlO_4 tetrahedra are long known. Note that the choice for X must be done with care as not all elements are network forming. For example, fluorine (F) would be an inappropriate choice as it is known from the F doping of silica that F forms SiO_3F thetrahedral units and plays instead a bridging role.

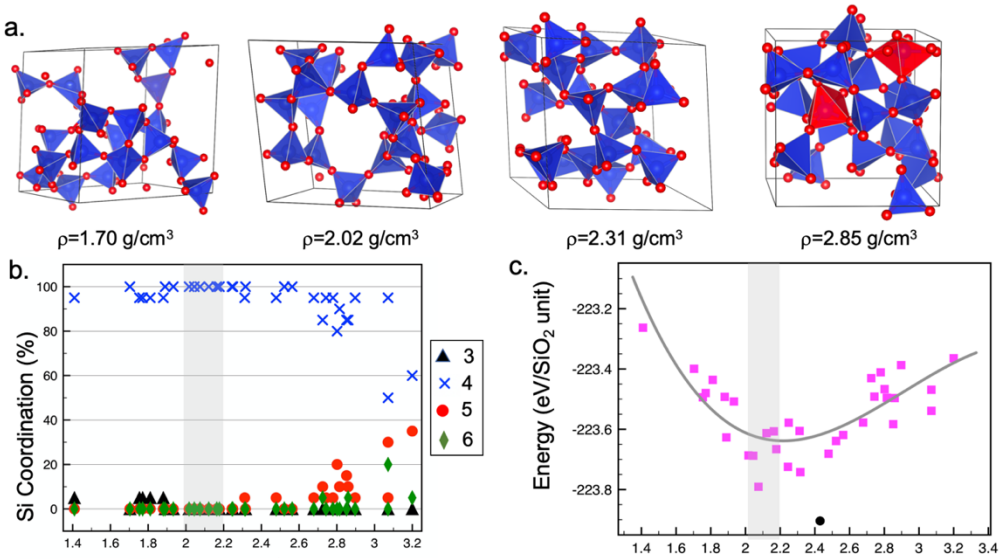

Figure 1*. MD a-SiO_2 models: a) Selected cells comprising 20 SiO_2 units with various ρ. Blue and red colored faces indicate tetrahedra and pentahedra, respectively. b) Coordination of Si atoms and c) total potential energy (squares) vs. ρ for a collection of 33 atomistic models with ρ=1.4-3.2 g/cm^3. The gray line is a polynomial trend line. Alpha-quartz (filled circle) is included for a comparison. The gray shading indicates the density range of a-SiO_2 fabricated by PE-ALD.*

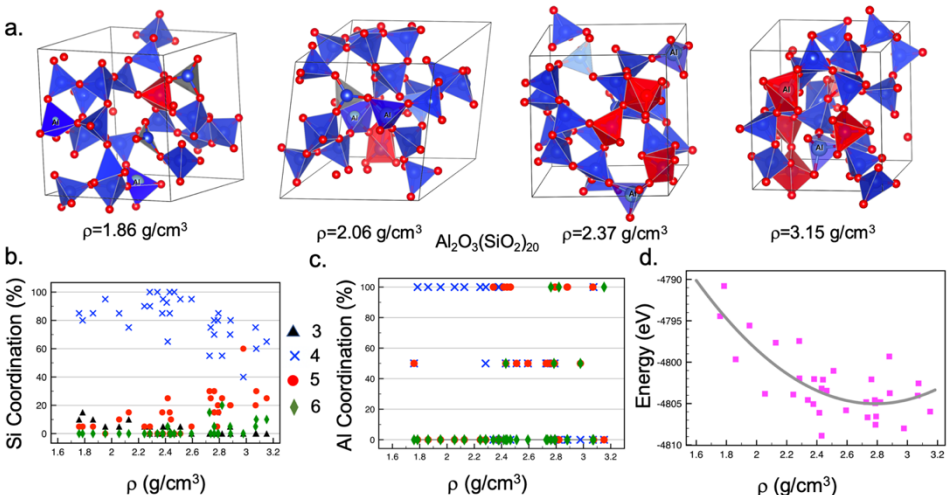

Figure 2. *MD Al_2O_3-a-SiO_2 models: a) Selected unit cells comprising one Al_2O_3 and 20 SiO_2 units with various ρ. Gray, blue, and red colored faces indicate triangles, tetrahedra and pentahedra, respectively. b) Coordination of Si atoms and c) Al atoms, and d) total potential energy (squares) vs. ρ for a collection of 30 atomistic models with 1.7-3.2 g/cm³ densities. The gray line is a polynomial trend line.*

With *X*=Al as the added network forming element, we have performed simulations to shown if this modifier can drive densification through unquenchable coordination defects similar to those observed in *a*-SiO_2 densified under pressure. The obtained Al_2O_3-*a*-SiO_2 models, some presented in Figure 2a, display a qualitatively similar network topology dominated by SiO_4 tetrahedra and Al-centered polyhedra connected through bridging O atoms (red balls). As ρ increases, the Si-O coordination departs more significantly from the ideal one in favor of fivefold and, to a lesser extent, sixfold coordination defects, Figure 3b. Interestingly, Al acts not only as a network former but also as a center for coordination defects: While in the 2-2.2 g/cm³ range the Al-O coordination remains ideal (i.e., Al acts as a network former), above this range it increases to five and even six, Figure 3c. Importantly, the plotted energies, Figure 3d, indicate shifting of the energy minimum to ρ~2.8 g/cm³. This means that these structures are thermodynamically stable at higher density values. Thus, their realization does not necessitate the application of external pressure.

3. The Young's modulus Y and static dielectric constant ε_0 are effectively doubled through densification: