



# Model form uncertainty versus intrinsic atomic variability in amorphous silicon oxides and nitrides



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## ABSTRACT

We quantify uncertainties in density functional theory predictions of several fundamental materials properties of amorphous dielectrics focusing on those that arise from the intrinsic atomic variability of the glass structures and those stemming from approximations in the theory. The intrinsic, or aleatoric, uncertainties are quantified by performing calculations over ensembles of structures obtained by annealing independent liquid samples. We estimate model form, or epistemic, uncertainties by comparing results from two exchange and correlation functionals that exhibit different bonding characteristics: the local density approximation (that typically overbinds), and the generalized gradient approximation (that often underbinds). In the case of density, bulk modulus, and point defect formation energies predictions obtained from systems containing between 72 and 192 atoms, typical of current state-of-the-art calculations, show that the intrinsic variability in the atomic structure leads to uncertainties a factor of two to four times greater than those originating from model form. While model form discrepancies remain important, our results emphasize the importance of using ensembles of structures to make predictions of amorphous materials. The use of such probabilistic atomic-level data as input in multiscale materials or device models is critical for predictions with quantified uncertainties but also to uncover how atomic variability affects device performance.

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## 1. Introduction

Predictive modeling and simulation has the potential to revolutionize the design, optimization and certification of materials, devices and structures [1]. Realizing the full potential of these techniques requires rigorous uncertainty quantification in the predictions that would enable simulation data-informed decision-making; see, for example, [2–4]. In this paper we quantify uncertainties and variability in first-principles calculations using density functional theory; this is important because this technique is often used as the foundation of multiscale materials modeling efforts [5,6]. In general, uncertainties in the predictions of a simulation arise either from known variability in an input quantity (aleatoric uncertainty) or due to a lack of knowledge (epistemic uncertainty) [7]. Uncertainties in density functional theory predictions of materials properties have multiple origins and their relative importance depends on the specific application. However, two sources of uncertainties dominate predictions in most cases: (i) simplifications in the atomic structure used (e.g. simplified

model structures, lack of defects) and (ii) those arising from physical approximations made in the theory (epistemic). In the case of DFT predictions of total energies the latter is the choice of exchange and correlation functional [8,9]. In the cases of interest in this paper, involving amorphous systems, the uncertainties associated with the atomistic structures are aleatoric in nature (i.e. they are inherent and cannot be reduced). Other sources of uncertainty in DFT calculations include those associated with numerical approximations (such as basis sets, pseudopotentials and grids for numerical integrations); these are often called verification uncertainties and an excellent description of them can be found in Ref. [9]. In this paper we focus on the first two types described (those associated with the atomic structure and those associated with approximations in the theory) since they are of a fundamental nature and pervasive in DFT applications. We characterize how these uncertainties affect the prediction of bulk properties (density and bulk modulus) and point defect formation energy in amorphous dielectrics of technological interest.

In amorphous materials, variability at the atomic-structure level can be classified into two types: (i) one is intrinsic, associated with the glassy network, and leads to property variability from point to point in the same sample and from sample to sample;

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(ii) a second kind depends on processing conditions and can lead to significant changes in properties; see Ref. [10] and references therein. The second kind has been particularly challenging to capture in simulations.

Amorphous dielectrics, such as silicon oxides ( $a\text{-SiO}_2$ ) and nitrides ( $a\text{-Si}_3\text{N}_4$ ), are used in a range of electronic applications spanning individual memory [11] and transistor [12] devices, to entire integrated circuits, [13] solar cells [14,15] and micro-electromechanical systems [16,17]. The electronic properties of these materials govern device performance and can only be quantitatively understood by studying accurate atomic scale models including defects. Structurally, these materials are characterized by a random network lacking long-range order and specific short-range connectivity features that are inherently variable, resulting in distributions of properties.

Computational techniques have become a useful and cost-effective way to predict the materials properties of a wide range of materials; in particular, multiscale approaches have been recently used to predict ensembles of low energy  $a\text{-SiO}_2$  [6,18] and  $a\text{-Si}_3\text{N}_4$  [10,19] structures and their properties. At the heart of these predictions is density functional theory (DFT) [20], a quantum mechanical based technique that provides a good balance between accuracy and computational efficiency for a large variety of ground state properties of condensed matter systems [9]. The input to DFT is an exchange and correlation functional that is only known approximately and, thus, leads to epistemic uncertainties. Here we present a quantitative comparison between the model form uncertainty in DFT and the intrinsic topological variability present in amorphous  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  materials prepared by annealing molten samples.

The remainder of the manuscript is organized in the following manner. Section 2 discusses simulation details focusing on the approximations made in the exchange and correlation functional and an overview of those that are used in the present work. In Section 3 we discuss the results of our distributions of calculated densities, bulk moduli, and formation energies for  $a\text{-SiO}_2$  and  $a\text{-Si}_3\text{N}_4$  ensembles. Section 4 then summarizes with our conclusions.

## 2. Methods

### 2.1. Density functional theory and model form approximations

The DFT method we use involves self-consistently solving the Kohn–Sham equations, equivalent to the many-body Schrödinger equation for ground state total energy calculations except that the  $3N$  spatial coordinates of  $N$  electrons are replaced with a three spatial coordinate electronic density,  $n(\mathbf{r})$ . This is achieved by replacing the  $N$  interacting electron potential with an effective potential of non-interacting particles. Interactions between electrons other than those in the classical mean field Hartree term and the effect of the anti-symmetric nature of the electronic wave function are accounted for in a density-dependent exchange–correlation functional ( $E_{xc}$ ). The exact form of this functional is not known but several approximations have been formulated [21–28] whose success depends upon the material system being studied, and often they are derived for specific systems of interest. Two of the most commonly used and widely applicable functional approximations are the local density approximation (LDA) and the generalized gradient approximation (GGA). LDA assumes that the functional energy ( $E_{xc}^{LDA}$ ) at any point in space  $\mathbf{r}$  is dependent only on the density at that point, and GGA assumes that the energy ( $E_{xc}^{GGA}$ ) is also dependent on the gradient of the density ( $\nabla n(\mathbf{r})$ ). That is

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r}) e_{xc}^{LDA}[n(\mathbf{r})] d\mathbf{r} \quad (1)$$

$$E_{xc}^{GGA}[n(\mathbf{r}), \nabla n(\mathbf{r})] = \int n(\mathbf{r}) e_{xc}^{GGA}[n(\mathbf{r}), \nabla n(\mathbf{r})] d\mathbf{r} \quad (2)$$

where  $e_{xc}[n(\mathbf{r})] = e_x[n(\mathbf{r})] + e_c[n(\mathbf{r})]$  can be split into its respective exchange and correlation contributions, and  $F_{xc}$  is known as the enhancement factor. An analytic form for  $e_x$  exists [20,29], however none exists for  $e_c$  and this is typically fit to a combination of theoretical and experimental data. Although a few common fits exist [22,30,31], we use the fitting of Perdew and Zunger [23] to the first principles homogenous electron gas calculations of Ceperley and Alder [32] for the correlation contribution to this term. The enhancement factor for GGA is not unique and several forms exist, parameterized both empirically from experiments [26] and non-empirically from first-principles [24,31,33]. For our calculations we use the non-empirical parameterization of Perdew, Burke and Ernzerhof (PBE) [24]. These choices are implemented in most DFT codes and are therefore readily available in the scientific community, as well as being the most commonly used for the dielectric materials [34–37] under investigation in this study. All calculations are performed using SeqQuest [38], a Gaussian basis set code that expands the Kohn–Sham orbitals with double-zeta plus polarization basis sets. For the LDA calculations, silicon atoms are treated with Hamann type norm-conserving pseudopotentials [33] and Troullier/Martins type pseudopotentials [39] are used for the oxygen and nitrogen atoms. GGA calculations employ a new form of Hamann pseudopotentials [40] for silicon and again Troullier/Martins type [39] for oxygen and nitrogen. Each calculation was performed on systems sufficiently large that the  $\Gamma$ -point was adequate for Brillouin-zone integration [18].

### 2.2. Ensembles of amorphous structures and property calculations

Stoichiometric samples of 72-atom and 192-atom  $a\text{-SiO}_2$ , as well as 112-atom  $a\text{-Si}_3\text{N}_4$  samples were generated using reactive molecular dynamics annealing followed by DFT relaxation as described in Refs. [18] and [10] respectively. The samples were equilibrated at a temperature higher than the predetermined melting point and ensembles of statistically independent samples were annealed to room temperature using empirical force fields. This resulted in an ensemble of 234 independent MD structures; 60 samples of each size of  $a\text{-SiO}_2$  and 114 samples of  $a\text{-Si}_3\text{N}_4$ . The use of cooling rates significantly slower than in prior theoretical studies led to relatively small defect populations and the generation of defect-free, amorphous structures. The resulting structures were fully relaxed using DFT with respect to atomic coordinates and cell parameters (all six degrees of freedom – three lattice parameters and three angles – where treated independently). A stress threshold of 0.5 GPa was used for cell relaxations. A detailed description of structural generation characterization for both  $a\text{-SiO}_2$  and  $a\text{-Si}_3\text{N}_4$  can be found in Refs. [18] and [10], respectively. We note that while all the  $a\text{-SiO}_2$  structures were obtained under nominally identical conditions the  $a\text{-Si}_3\text{N}_4$  are annealed at different densities to mimic different processing conditions.

The bulk moduli of the  $a\text{-Si}_3\text{N}_4$  ensemble were obtained from energy–volume relationships obtained by isotropically straining the relaxed structures. The simulation cell lengths were strained in the range  $-3\%$  to  $+6\%$  keeping cell angles fixed and relaxing atomic positions. We computed the bulk modulus of each structure by fitting a quadratic equation of state to the resulting energy–volume data. Energy–volume data for each individual structure is provided in the [Supplementary Material](#).

Point defects in these materials dominate their performance and degradation [9] and significant efforts have been devoted to their identification and characterization. Formation energies per point defect pair are calculated with reference to the average energy of all defect-free amorphous networks. In our

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