Computational Materials Science 148 (2018) 165–175

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Modeling amorphous silicon nitride: A comparative study of empirical potentials

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ARTICLE INFO

Article history:
Received 14 September 2017
Received in revised form 4 December 2017
Accepted 5 December 2017

Keywords:
Amorphous material
Silicon nitride
Density functional theory
Empirical potential
Molecular dynamics
Enthalpy of formation

ABSTRACT

We perform a comparative study of empirical potentials for atomistic simulations of amorphous silicon nitride (a-Si_3N_4). We choose 5 different parameterizations of the Tersoff potential, the Marian-Gastreich two-body (MG2) and three-body (MG3) potential, the Vashishta (V) potential, and the Garofalini (SG) potential. Amorphous models of Si_3N_4, comprising of 448 atoms, are generated by each empirical potential using a melt-and-quench procedure. Subsequently, models are optimized using Density Functional Theory calculations, and structures resulting from these DFT optimizations are compared. We emphasize local coordination of atoms and the enthalpies of formation (ΔH_f) relative to crystalline β-Si_3N_4. The SG and MG2 potentials prove to be best options for modeling of a-Si_3N_4. Models generated with these potentials are close to their DFT local minimum, exhibit the smallest number of defects, and have realistic enthalpies of formation.

1. Introduction

Silicon nitride is a ceramic material with diverse applications owing to its good mechanical and electrical properties [1]. Dense sintered Si_3N_4 components exhibit high thermal strength and fracture toughness and are used in many engineering applications [2,3]. Thin films of amorphous silicon nitride, have a high dielectric constant and are applied in microelectronics [4–7] Thick films of Si_3N_4 are promising materials for non-linear optical applications [8,9]. Moreover, Si_3N_4 is an environmental barrier coating material due to its oxidation resistance up to 1500 °C [10]. Silicon nitride also exhibits great biocompatibility and is used as bearings for total hip and knee joint replacement in orthopedics [11].

There is extensive work in computational modeling of amorphous silicon nitride (a-Si_3N_4). The first study was reported by Ohdomari et. al. who constructed a continuous random network ball-and-stick model [12]. A Keating type potential was applied to relax these models and radial distribution functions characterized the local environment of atoms. Umesaki et al. used a Busing-type pair potential to model a-Si_3N_4 by molecular dynamic (MD) simulations [13]. Their models consisted of SiN_4 tetrahedral units with few structural defects, and the radial distribution function (RDF) as well as the structure factor agreed well with experimental data.

Development of a Tersoff potential to model a-Si_3N_4 was first pursued by Kroll [14]. Seven different parameterizations for the N atom were proposed and used together with the original Si parameters by Tersoff [15,16]. Adopting one of these parameter sets, Matsunaga studied a variety of silicon nitride ceramics including amorphous SiCN, SiBN and Si_3N_4 ceramics [17,18]. Brito-Mota et al. proposed an alternative parameter set for N and studied local geometry and bonding in a-SiN_x ($0 < x < 1.6$) materials [19,20]. The parameterization of Brito-Mota was later augmented to study hydrogen interactions in a-SiN_x:H systems [21]. Vashishta et. al. developed a Si—N interaction potential including charges, polarizabilities, and bond angle terms. This potential was used to model multi-million atom models of a-Si_3N_4 and study nano-indentation, crack propagation, and various mechanical properties of a-Si_3N_4 [22–26]. As part of their efforts to model SiBN ceramics, Marian et. al. proposed a two-body potential for interactions involving Si, B and N [27]. This potential reproduced structure, vibrational and elastic properties of crystalline Si_3N_4 and BN, and was used to model mixtures of these two systems, particularly $Si_3B_3N_7$. The same authors also suggested a more elaborate three-body potential for modeling SiBN materials [28]. Completing this brief survey, Garofalini et. al. developed an interaction potential for modeling inter-granular films in Si_3N_4 ceramics [29,30].

Given several empirical potentials available for modeling Si_3N_4, an obvious question is: which is the best? Since all the potential models outlined have been fitted to properties of α- and β-Si_3N_4, they describe these crystalline structures quite well. However,

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https://doi.org/10.1016/j.commatsci.2017.12.008
0927-0256/

these potentials are also used to model amorphous silicon nitride, and while transferability is commonly assumed, it is, by no means, guaranteed to work. Therefore, our goal is to compare these different empirical potentials with respect to their ability to provide sound models of amorphous silicon nitride. Our comparison is facilitated through Density Functional Theory (DFT) calculations, which provide a rigorous assessment of every structure generated by each empirical potential within one common method.

The next section will provide a brief description of the individual empirical potentials. We then describe the computational approach that we use for structure generation and DFT calculations. In the result section we emphasize local atomic arrangements and structural changes happening during DFT optimizations as well as the enthalpy of formation.

2. Interatomic potentials

In this section we briefly describe the analytical form of each empirical potential and their parameters.

2.1. Tersoff potential

The Tersoff potential is based on the concept that the strength of a bond between two atoms depends on their local environment [15,16]. The potential is short-ranged, with only the first coordination shell included, and consists of two-body and three-body terms. It was originally developed to model single element semiconductors such as Si, Ge, and C, but soon was applied to binary systems such as SiC [31]. The key-idea of the Tersoff potential is its "transferability"; eleven (11) parameters are developed for each element, only once. Parameters for interaction in compound systems are then governed by simple rules of mixture. This approach, ideally, eliminates the work to find new parameter sets for every new combination of elements. Practically, the potential still uses two unique parameters for each binary combination of elements, χ_{ij} and ω_{ij}, which can be used to tailor hetero-atomic interaction. The explicit functional form of the potential is given in the Appendix A.

Tersoff-parameters for modeling of Si_3N_4 have been developed by Kroll and by Brito-Mota et al. [14,20]. Kroll followed the original idea of Tersoff and fitted potential parameters for N using structure and elastic data for hypothetical phases of nitrogen only. Unique parameters for C—N and Si—N interaction were subsequently fitted using experimental and computed data of C_3N_4 and Si_3N_4 crystalline structures. A variety of parameter sets were proposed and analyzed [14]. Three suitable sets are shown in Table 1 (labels 001-1, 001-2, 002-1). Brito-Mota et al., on the other hand, optimized their parameter set for N—N and for Si—N interaction simultaneously using experimental and computed data available for β-Si_3N_4, the N_2 molecule and trisilylamine molecule, Si_3NH_9. The parameters (label BM) are included in Table 1. The parameter set used by Matsunaga et al. is identical with set 001-1 of Kroll; with the exception that one of the unique binary parameters (ω_{ij}) was set to 1 [18]. It is listed as an independent set (label mat) in Table 1. For all Tersoff potential parameterizations, the attractive part of homo-atomic interactions Si—Si and N—N is set to zero for modeling of Si_3N_4. Hence, Si—Si and N—N interactions are repulsive up to the defined cutoff distance.

2.2. Marian-Gastreich two-body potential (MG2) [27].

The MG2 potential was originally developed for modeling of SiBN ceramics [27]. For our study, we use its portion relating to SiN systems only. The potential consists of two-body terms only: attractive Morse-type for Si—N, screened Coulomb repulsion for Si—Si and N—N, and an additional dispersion term for N—N interactions. A taper function provides a cutoff at a distance of 5.8 Å. The explicit form of the potential together with parameters is given in the Appendix A. The absence of a three-body term in covalently bonded systems makes the MG2 potential unique in comparison to all other empirical potentials considered in this study.

2.3. The Marian-Gastreich three-body potential (MG3) [28]

Soon after the MG2 potential, the same authors developed a three-body potential for modeling of SiBN ceramics [28]. The MG3 potential includes charges, attractive Coulomb interactions and a Stillinger-Weber-type angular term [32]. A smooth cutoff of the potential limits its range to 8 Å. Si—Si and N—N interactions are repulsive up to the cutoff. We use only the portion relating to SiN systems in this work. The analytical form of the potential together with parameters is given in the Appendix A.

2.4. The Vashishta potential (V) [22]

The Vashishta potential is another approach involving two-body and three-body terms. It includes steric repulsion, screened Coulomb interaction, and screened charge-dipole interactions. A three-body Stillinger-Weber-type angular term accounts for bond bending effects [32]. The two-body part of the potential has a cutoff distance of 5.5 Å, while the three-body part is short-ranged with a cutoff of 2.6 Å. Homo-atomic interactions of Si—Si and N—N are defined repulsive. The analytical form of the potential along with its parameters is included in the Appendix A.

Table 1
Tersoff potential parameter sets for N: 001-1, 001-2, 002-1 by Kroll, BM by Brito-Mota et al. and mat by Matsunaga [14,17,20]. The sets 001-1 and 001-2 differ only in choice of the unique binary parameters $\chi_{Si\text{-}N}$ and $\omega_{Si\text{-}N}$. The parameter set mat is identical to 001-1 except for $\omega_{Si\text{-}N}$ (set to 1 in mat).

Parameters	001-1	001-2	002-1	Mat	BM
A [eV]	11,000	11,000	8860.0	11,000	6368.14
B [eV]	219.45	219.45	197.09	219.45	511.760
λ [$Å^{-1}$]	5.7708	5.7708	5.5237	5.7708	5.43673
μ $Å^{-1}$]	2.5115	2.5115	2.3704	2.5115	2.70
β [10^{-2}]	10.562	10.562	5.8175	10.562	0.529380
n	12.4498	12.4498	8.2773	12.4498	1.33041
c	79,934	79,934	79,126	79,934	20312.0
d	134.32	134.32	112	134.32	25.5103
h	−0.99734	−0.99734	−0.99995	−0.99734	−0.562390
χ_{Si-N}	0.91736	0.88779	0.85758	0.91736	0.65
ω_{Si-N}	1.0993	0.98426	0.66175	1*	1.00
R (pm)	180				
S (pm)	210				