

# Crystalline and liquid Si<sub>3</sub>N<sub>4</sub> characterization by first-principles molecular dynamics simulations

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**Abstract.** Silicon nitride (Si<sub>3</sub>N<sub>4</sub>) has a wide range of engineering applications where its mechanical and electronic properties can be effectively exploited. In particular, in the microelectronics field, the amorphous silicon nitride films are widely used as charge storage layer in metal-alumina-nitride-oxide nonvolatile memory devices. Atomic structure of amorphous silicon nitride is characterized by an high concentration of traps that control the electric behavior of the final device by the trapping-de-trapping mechanism of the electrical charge occurring in its traps. In order to have a deep understanding of the material properties and, in particular, the nature of the electrical active traps a detailed numerical characterization of the crystalline and liquid phases is mandatory. For these reasons first-principles molecular dynamics simulations are extensively employed to simulate the crystalline Si<sub>3</sub>N<sub>4</sub> in its crystalline and liquid phases. Good agreement with experimental results is obtained in terms of density and formation entalpy. Detailed characterization of c-Si<sub>3</sub>N<sub>4</sub> electronic properties is performed in terms of band structure and band gap. Then constant temperature and constant volume first-principles molecular dynamics is used to disorder a stoichiometric sample of Si<sub>3</sub>N<sub>4</sub>. Extensive molecular dynamics simulations are performed to obtain a reliable liquid sample whose atomic structure does not depend on the starting atomic configuration. Detailed characterization of the atomic structure is achieved in terms of radial distribution functions and total structure factor.

## 1 Introduction

In the recent years new non volatile memory devices have been introduced to overcome the emerging scaling limitation in the standard floating gate approach due for example to the statistical charge injection, cell to cell interference and technology complexity. One of the most promising advanced memory for replacing the NVM-NAND architecture is the so called Charge Trapping Devices [1] based on the discrete trapping of electronic charge in the material defects: in general an amorphous Si<sub>3</sub>N<sub>4</sub> layer of few nanometer has been employed in the actual memory device preparation. Typically silicon nitride layer is deposited at high temperature (> 700 °C) by the help of Chemical Vapour Deposition technique with stoichiometric or Si-rich ratio obtained by changing reactant gas flow rate. Due to the recent technology approach, i.e. 3D geometry shape [2], material intrinsic defects become more relevant than the one produced by implantation damage or induced by spurious element such as Boron or Phosphorus. To explore the formation of a such defects we use a different approach with respect to Ref. [3] based on cluster models taking into account the dynamical evolution at the atomic level of

defects and their environment. Our approach is similar to that one reported in Ref. [4] where first-principles molecular dynamics simulations are used to produce a reliable amorphous sample of Si<sub>3</sub>N<sub>4</sub>. Our approach allows the study of a larger system on longer time scales for a full characterization of the Si<sub>3</sub>N<sub>4</sub> system. After a detailed analysis of the crystalline phase of Si<sub>3</sub>N<sub>4</sub> as reported in section 2, we report a computational procedure to produce a reliable liquid sample (section 3). The characterization of the liquid sample is reported in section 4.

## 2 Si<sub>3</sub>N<sub>4</sub> crystalline $\alpha$ phase

Si<sub>3</sub>N<sub>4</sub> presents two crystalline hexagonal phases:  $\alpha$  (shown in Fig. 1) and  $\beta$  belonging to point group c1 and c6h, respectively. We present results relatively to both phases comparing our results with the experimental ones reported in Ref. [5] and in Ref.[6]. We consider a simulation cell composed by 28 atoms (12 Si and 16 N). At the experimental values of the lattice parameters ( $\alpha$  phase:  $a=7.753$  Å,  $c=5.618$  Å;  $\beta$  phase:  $a=7.706$  Å,  $c=2.909$  Å) we compute the electronic band structures in very good agreement with the experimental results [6]. In Fig. 2 the EDOS of

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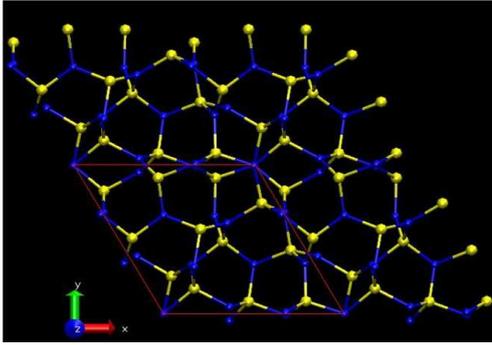


Fig. 1. Structure of  $\text{Si}_3\text{N}_4$  crystalline  $\alpha$  phase

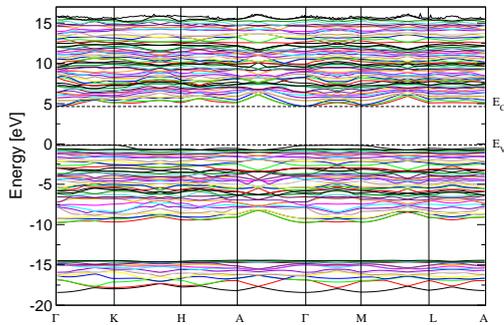


Fig. 2. Calculated band for crystalline  $\alpha$  phase  $\text{Si}_3\text{N}_4$

the crystalline  $\alpha$  phase is reported. The band gap is formed between  $\Gamma$  and K points in good agreement with Ref. [6]. In Fig. 3 we report the calculated total density of electronic states where an HUMO-LUMO band gap of 4.63 eV is found. This value is in good agreement, within 8% of error, with the experimental one (4.9-5.1 eV) [6].

### 3 Simulation modeling approach for liquid phase generation

To produce a reliable liquid configuration, extensive first-principles Molecular Dynamic simulations have been performed by using the standard Car-Parrinello method [7]. All calculations are performed at constant volume on a system of 223 atoms: Si-N mixture with a ratio of  $r = [\text{N}]/[\text{Si}] = 1.347$  in order to increase the probability to find point defects. The periodically cubic cell has a size of 13.91 Å corresponding to the experimental density of amorphous  $\text{Si}_3\text{N}_4$  phase (3.1 g/cm<sup>3</sup>) at room temperature. The starting configuration has been chosen by randomly generating the coordinates of each atom discarding positions with

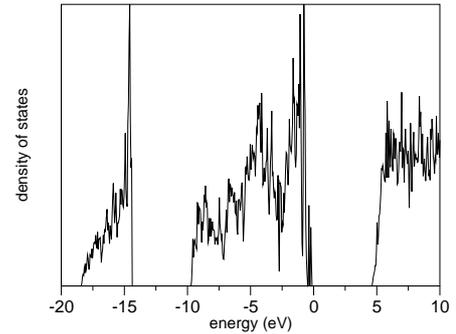


Fig. 3. Calculated DOS for crystalline  $\alpha$  phase  $\text{Si}_3\text{N}_4$

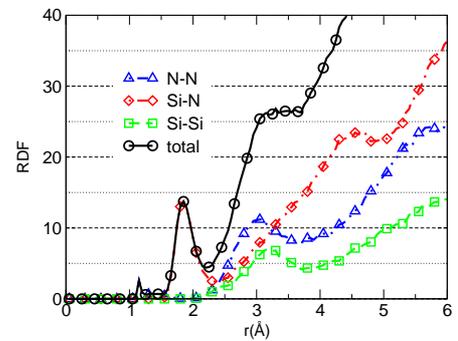
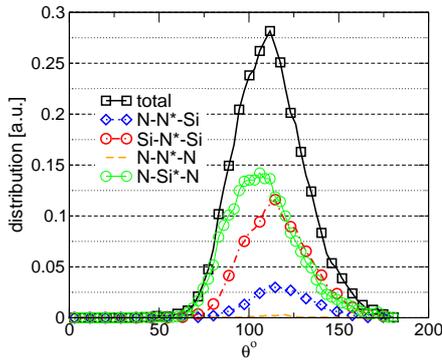


Fig. 4. Radial distribution function for the liquid  $\text{Si}_3\text{N}_4$

distance less than 1.74 Å from every other atom. This procedure assures a faster and more accurate thermalization process. Norm conserving pseudopotentials are used in conjunction with a generalized gradient approximation (GGA) for the exchange and correlation part of the total energy. The wave functions are expanded in plane waves at the  $\gamma$  point of the supercell. A cutoff of 140 Ry yields converged properties for simple molecules (SiSi, NN and SiN dimers) and reproduce accurately electronic properties of the crystalline phases, as shown in the previous section. A temperature control is implemented for both ionic and electronic degrees of freedom by using the Nosé-Hoover thermostats. A simulation time of about 5 ps is used to thermalize the disordered system at high temperature ( $T = 3200$  K) to assure that the system has lost memory of its initial conditions. Physical quantities are then calculated and averaged on a trajectory lasting about 7 ps at the temperature  $T = 1800$  K.

### 4 $\text{Si}_3\text{N}_4$ liquid phase characterization

To analyze the short-range order of the obtained liquid phase we have calculated the total radial distribution

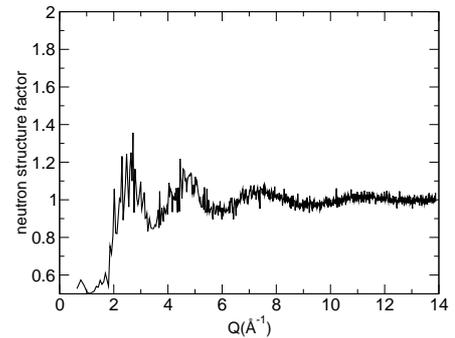


**Fig. 5.** Calculated angular distribution for the liquid  $\text{Si}_3\text{N}_4$

function, reported in Fig. 4. The comparison with the experimental one reported in Ref. [8] confirms the reliability of our numerical model. It is interesting to note that our model well reproduce the very first peak at 1.15 Å. Partial radial distribution functions reported in Fig.4 reveal the origin of this first peak in the total one. This peak is not related to the presence of hydrogen in the sample as explained in Ref. [4] but to the presence of small but not negligible quantity of N-N bonds. The distance distribution for S-N bond is picked at 1.80 Å, for Si-Si at 2.38 Å while in the case of N-N bond at 1.15 Å and 2.73 Å.

The angular distribution is shown in Fig. 5. The N-Si-N distribution has a peak at  $106.5^\circ$  very close to the peculiar value of regular tetraedra. The Si-N-Si has instead a pick at  $115^\circ$  indicating the presence of planar  $\text{NSi}_3$  units. Both Figures 4 and 5 confirm the picture of a liquid system composed essentially by Si atoms fourfold coordinated and only few threefold and fivefold coordinated. On the contrary, almost all the nitrogen atoms are bound to three silicon atoms. Homopolar bonds are essentially due to nitrogen atoms. Thus the liquid  $\text{Si}_3\text{N}_4$  system can not be considered completely chemically ordered. This picture explains the great interest of this system for applications in microelectronics.

To verify the reliability of our approach also on long length atomic scales, we have computed the structure factor. The calculated structure factor is shown in Fig.6. The agreement is very good over the entire  $k$  range with experimental results reported in Ref. [8, 4], the position of maxima and minima being accurately reproduced. As expected, the shape of the structure factor of our liquid sample is less structured than the experimental one obtained on an amorphous system. In particular the width of the peaks is more pronounced and their height significantly lower.



**Fig. 6.** Neutron structure factor for the liquid  $\text{Si}_3\text{N}_4$

## 5 Conclusion and further work

In this paper our first goal has been to achieve a precise characterization of the liquid atomic structure of the  $\text{Si}_3\text{N}_4$  system. This liquid sample, that we have demonstrated a reliable representation of the real liquid phase of the  $\text{Si}_3\text{N}_4$  system, can be considered a good starting point for the obtention of the amorphous phase. We have shown that our theoretical approach is able to model accurately all the main features of the liquid system both in the short and long range length scales. Moreover we are confident that this procedure can be applied successfully to produce and characterize the amorphous phase. This approach will allow to study accurately the relation between atomic scale intrinsic defects and the macroscopic structural and electronic properties of the  $\text{Si}_3\text{N}_4$  system.

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