

Defect Centers in $a\text{-SiN}_x$: Electronic and Structural Properties

F. de Brito Mota,

Instituto de Física da UFBA, CEP 40210-340, Salvador, BA, Brazil

J. F. Justo and A. Fazzio

Instituto de Física da Universidade de São Paulo, CP 66318, CEP 05315-970, São Paulo, SP, Brazil

Received on 23 April, 2001

By combining *ab initio* methods and interatomic potentials, we investigated the electronic and the structural properties of amorphous silicon nitride. Our results show the trends on the electronic band structure of SiN_x ($0.5 < x < 1.8$) as the nitrogen content changes, and are in good agreement with the experimental data. Hydrogenation of the systems was found to considerably reduce the number of energy levels in the gap. The energy levels which appeared in the materials band gap were compared to the electrically active centers, which have been identified by electron-paramagnetic resonance experiments.

Amorphous silicon nitride ($a\text{-SiN}$) is a material of unique electronic properties, such as large electronic gap, and high dielectric constant. Due to these superior electronic properties, it has been used in microelectronic devices as a gate dielectric in thin film transistors or as a charge storage medium in non-volatile memories. Although considerable effort has been spent in studying silicon nitride, a number of issues related to its microscopic properties remain unaddressed.

Over the last decade, SiN has been investigated by several theoretical methods [2, 3, 4, 5]. Those investigations used parameter-dependent models, providing only a qualitative description of the physical properties of the systems. Tight-binding models [5], for example, introduced unphysical shifts in the electronic energy levels, in order to reproduce the experimental electronic band structure. Amorphous silicon nitride have not been investigated by parameter-free *ab initio* methods so far. Here we combined interatomic potentials [2, 4] with *ab initio* methods to investigate the electronic properties of unhydrogenated and hydrogenated amorphous silicon nitride in a wide range of nitrogen contents. The results were compared to available experimental data.

Atomistic simulations based on *ab initio* methods have been a formidable task, specially in the case of disordered systems. In order to overcome such computational difficulties, we used interatomic potentials [2, 4] to generate the initial amorphous configurations. These were used as input configurations to the *ab initio* simulations, when full relaxation, based on the Hellmann-Feynman forces, could be performed. This procedure has been shown to reduce considerably the computa-

tional cost in finding the equilibrium configurations [6, 7, 8]. However, this procedure would only speed up the simulations if the interatomic potentials are transferable, i.e., they can provide a realistic description of the amorphous systems. We have recently developed an interatomic potential which describes accurately the structural properties of silicon nitride in a wide range of nitrogen contents [2, 4]. The amorphous configurations were generated using that interatomic potential combined with Monte Carlo simulations in a simulated annealing procedure. The relaxation of both the atomic positions and the cell volume were allowed in the simulated annealing.

The *ab initio* calculations [9] were performed within the local density approximation. The Kohn-Sham equations were solved using the Car-Parrinello scheme with separable pseudopotentials [10]. The basis set was expanded in plane-waves, with kinetic energy up to 65 *Ry*. The nuclear positions were fully relaxed in the *ab initio* calculations until the Hellmann-Feynman forces were down to 10^{-3} a.u. The large unit cell comprised 66 atoms for all nitrogen and hydrogen contents. The Brillouin zone was sampled by the Γ -point. Our investigations considered only one atomic configuration for each nitrogen content ($a\text{-SiN}_x$, $x = 0.5, 1.0, 1.33, 1.5, \text{ and } 1.8$). Still we expected to provide a reasonably good sampling of an amorphous silicon nitride. To certify that we in fact generated realistic samples, we computed the pair correlation function and the average coordination numbers. For all nitrogen contents, a first peak appears around 1.75 Å which corresponds to Si-N bonds, while a second peak appears around 2.5 Å, corresponding to Si-Si bonds, both in good agree-

ment with the experimental data [11]. For the average coordination number at Si and N sites [2], our results agree very well with the experimental data [12] for several nitrogen contents. Since the local order determines most of the electronic properties of the material, our *ab initio* calculations should provide a realistic description of the electronic band structure of *a*-SiN.

Generally, the electronic density of states (DOS) of amorphous semiconductors obtained by theoretical modeling present a large number of gap levels. Several authors have used some artifacts to “clean” the gap from those spurious levels. In *a*-Si, the gap levels have been removed by removing the atoms which presented dangling bonds, and passivating the remaining bonds with H [13]. On the other hand, we removed the gap levels by introducing hydrogen in the sample, performed a simulated annealing with interatomic potentials, and then performed the *ab initio* calculations. Our procedure was less artificial than others [13, 14], although also less effective in removing the gap levels.

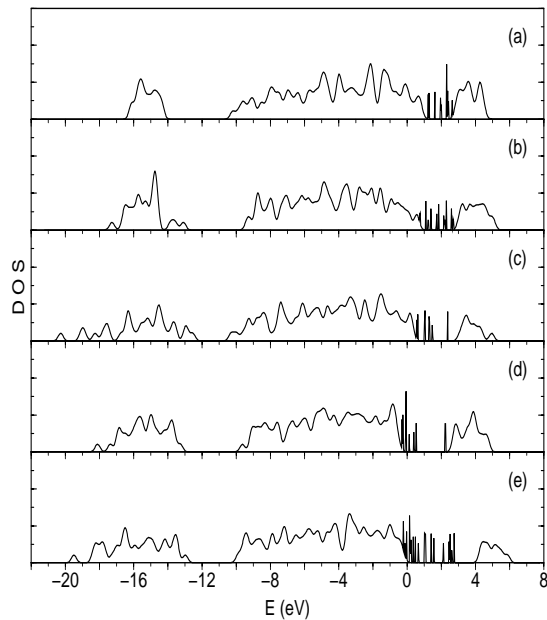


Figure 1. Theoretical total density of states of *a*-SiN_x:H. The figure shows the DOS for (a) $x = 0.5$, (b) $x = 1.0$, (c) $x = 1.33$, (d) $x = 1.5$, and (e) $x = 1.8$.

Fig. 1 shows the calculated DOS for the *a*-SiN_x:H ($0 < x < 1.8$) with 18% of hydrogen atomic concentration. For $x = 1.33$, the DOS is equivalent to that of the crystalline β -Si₃N₄. The first region of the valence band (VB), corresponding to the N-2s states, is between -20.0 eV and -12.5 eV. The second region of the VB, between -10.5 and 1.5 eV, is formed by levels coming from the hybridization of the N-2p and Si-3p states. The top of valence band is formed by the N $p\pi$ lone pairs. The gap is found to be 2.0 eV. The energy gap increases with increasing nitrogen concentration, resulting from the replacement of Si-Si bonds, located

in the top of the VB, by Si-N bonds; and by the displacement of the bottom of the conduction band, due to the substitution of Si-Si anti-bonding states by Si-N anti-bonding ones.

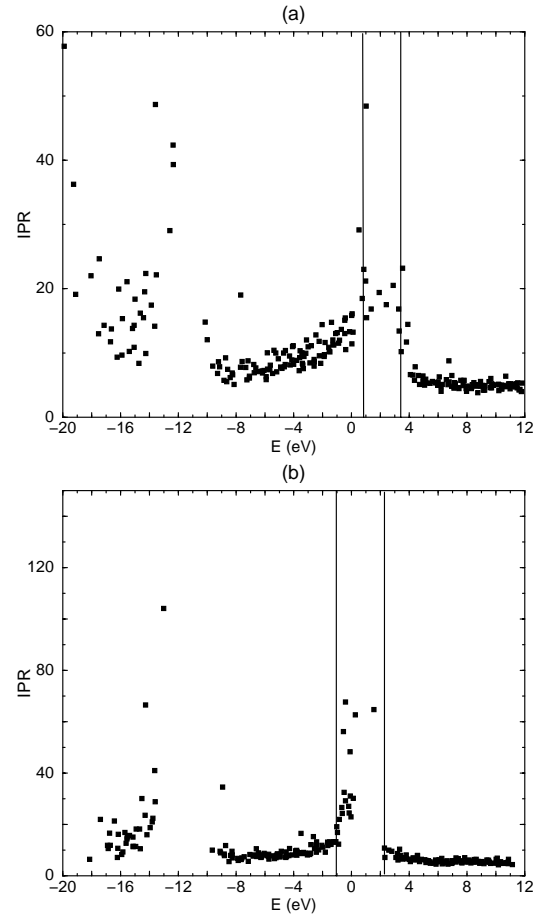


Figure 2. Inverse participation ratio (IPR) for all energy levels in *a*-SiN_x:H. The figure shows the IPR for (a) $x = 1.33$ and (b) $x = 1.5$.

The gap was determined by analyzing the localization degree of the states near the band edges. The localization of each electronic state was quantified by the inverse participation ratio (IPR). The IPR of an orbital $\psi_n(\vec{r}_i)$, $I(\psi_n)$, is defined by:

$$I(\psi_n) = N \frac{\sum_{i=1}^N |\psi_n(\vec{r}_i)|^4}{\left[\sum_{i=1}^N |\psi_n(\vec{r}_i)|^2 \right]^2}, \quad (1)$$

where N is the number of volume elements in the cell and i is the index of the volume element. The IPR is large for highly localized states and small for delocalized states.

The IPR can identify a level as belonging to the band (delocalized), to the band-tail (partially localized), or to the gap (highly localized). Fig. 2 shows the IPR for all states in *a*-SiN_x:H for two nitrogen contents. The large IPR for the states in the bottom of the valence band is result of the localized character of the

N-2s states. For all nitrogen contents, the closer the states are from the gap, the larger is the IPR. Fig. 3 shows the theoretical gap as function of nitrogen contents obtained by the IPR. The figure also shows the experimental optical gap [12, 15, 16]. Our results give the correct trend: the electronic gap increases with the nitrogen content. Our results also show that the electronic gap increases faster with x for $x > 1$ than for $x < 1$, also in agreement with the experimental findings. However, our results underestimate the gap for all nitrogen contents, which results from the known limitation of the density functional theory in describing excited states.

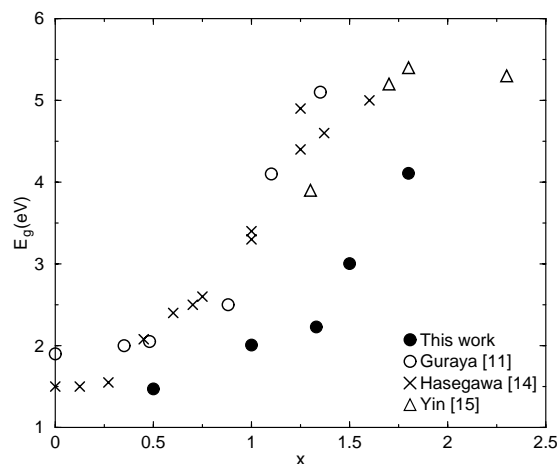


Figure 3. Electronic energy gap (E_g) versus the nitrogen content (x). The figure also shows the experimental optical gap [12, 15, 16]. Energies are in eV.

Electron paramagnetic resonance (EPR) experiments have measured several paramagnetic centers in silicon nitride which have been identified to undercoordinated atoms. A center which generates an energy level in the middle of the gap has been interpreted as due to a three-fold coordinated silicon atom (K -center) [17]. A center which generates an energy level in the bottom of the gap has been interpreted as due to a two-fold coordinated nitrogen atom (N_2 -center) [17]. We investigated the properties of the gap levels in a -SiN_{1.5} which presented large IPR, and compared their electronic spatial distribution with the characteristics of the known EPR centers. We could identify both centers in our investigation. A level at $E_v + 2.48$ eV (E_v is the top of valence band), and therefore close to the conduction band, clearly shows a dangling bond characteristic, with the electronic charge localized around a silicon atom. This level is consistent with the K -center identified by EPR [17]. A level at $E_v + 0.45$ eV, near the valence band, shows a dangling bond characteristic, with the electronic charge localized around a nitrogen atom. This level is consistent with the N_2 -center identified by EPR [17].

In summary, we have used *ab initio* calculations to investigate the electronic properties of hydrogenated amorphous silicon nitride for several nitrogen concen-

trations. All of our results were in good agreement with available experimental data. The inverse participation ratio allowed to identify the spatial localization of the all the energy levels. This shows that the IPR can be an effective tool to investigate deep levels in amorphous materials even when using small simulation cells. Additionally, we have theoretically identified the electronic active centers which appear in the gap in a realistic sample of amorphous silicon nitride. Those levels were correlated to the known EPR results, namely, the undercoordinated Si and N atoms.

Acknowledgments

FBM and JFJ acknowledge partial support from Brazilian agencies PRODOC/CADCT-BA and FAPESP, respectively. The calculations were performed at the Computer Center of the UFBA.

References

- [1] F. H. P. M. Habraken and A. E. T. Kuiper, *Mat. Science Eng. R* **12**, 123 (1994).
- [2] F. de Brito Mota, J. F. Justo, and A. Fazzio, *Phys. Rev. B* **58**, 8323 (1998).
- [3] F. de Brito Mota, J. F. Justo, and A. Fazzio, *Int. J. Quant. Chem.* **70**, 973 (1998).
- [4] F. de Brito Mota, J. F. Justo, and A. Fazzio, *J. Appl. Phys* **86**, 4249 (1999).
- [5] J. Robertson, *Philos. Mag. B* **63**, 47 (1991).
- [6] J. F. Justo, M. de Koning, W. Cai, and V. V. Bulatov, *Phys. Rev. Lett.* **84**, 2172 (2000).
- [7] J. F. Justo, A. Fazzio, and A. Antonelli, *J. Phys.: Condens. Matter* **12**, 10039 (2000).
- [8] J. F. Justo, A. Antonelli, and A. Fazzio, *Solid State Commun.* **118**, 651 (2001).
- [9] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, *Comput. Phys. Commun.* **107**, 187 (1997).
- [10] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- [11] T. Aiyama, T. Fukunaga, K. Niihara and K. Susuki, *J. Non-Cryst. Solids* **33**, 131 (1979).
- [12] M. M. Guraya, H. Ascolani, G. Zampieri, J. I. Cisneros, J. H. Dias da Silva, and M. P. Cantão, *Phys. Rev. B* **42**, 5677 (1990). *Phys. Rev. B* **62**, 4477 (2000).
- [13] P. A. Fedders, D. A. Drabold, and S. Nakhmanson, *Phys. Rev. B* **58**, 15624 (1998).
- [14] J. J. Dong and D. A. Drabold, *Phys. Rev. Lett.* **80**, 1928 (1998).
- [15] S. Hasegawa, M. Matuura, and Y. Kurata, *Appl. Phys. Lett.* **49**, 1272 (1986).
- [16] Z. Yin and F. W. Smith, *J. Non-Cryst. Solids* **137**, 879 (1991).
- [17] W. L. Warren, J. Kanicki, J. Robertson, and P. M. Lenahan, *Appl. Phys. Lett.* **59**, 1699 (1991).