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Citation: *J. Appl. Phys.* **86**, 1843 (1999); doi: 10.1063/1.370977

View online: <http://dx.doi.org/10.1063/1.370977>

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Hydrogen role on the properties of amorphous silicon nitride

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(Received 3 December 1998; accepted for publication 5 May 1999)

We have developed an interatomic potential to investigate structural properties of hydrogenated amorphous silicon nitride. The interatomic potential used the Tersoff functional form to describe the Si–Si, Si–N, Si–H, N–H, and H–H interactions. The fitting parameters for all these interactions were found with a set of *ab initio* and experimental results of the silicon nitride crystalline phase, and of molecules involving hydrogen. We investigated the structural properties of unhydrogenated and hydrogenated amorphous silicon nitride through Monte Carlo simulations. The results show that depending on the nitrogen content, hydrogen has a different chemical preference to bind to either nitrogen or silicon, which is corroborated by experimental findings. Besides, hydrogen incorporation reduced considerably the concentration of undercoordinated atoms in the material, and consequently the concentration of dangling bonds. © 1999 American Institute of Physics.
[S0021-8979(99)00616-7]

I. INTRODUCTION

Materials with large bulk modulus, comparable to that of diamond, have been focus of interest over the last decades.¹ Of all those prototypical materials, silicon nitride (SiN) has been extensively investigated because of both its mechanical and electronic properties which make it suitable for several applications in the microelectronic industry. Besides its high melting temperature and low mechanical stress, silicon nitride has high dielectric constant and large electronic gap. It has been used in electronic devices as a charge storage medium in memories or as a gate dielectric in thin films.

Amorphous silicon nitride is prepared by chemical vapor deposition using a silane (SiH₄) and ammonia (NH₃) gas mixture at high temperatures, by sputtering silicon in a NH₃ atmosphere, or by plasma deposition from SiH₄-NH₃ or SiH₄-N₂ gas mixtures. Hydrogen is always present in those processes, being incorporated into the samples in high concentrations. For example, silicon nitride prepared by chemical vapor deposition may have up to 40% of hydrogen concentration. Hydrogen changes the electronic and the mechanical properties of the material. It interacts with the dangling bonds which appear in the amorphous silicon nitride matrix. Besides, hydrogen incorporation is known to reduce the hardness of the material.² Since hydrogen affects silicon nitride properties, it is important to understand the microscopic processes of hydrogen incorporation and diffusion inside the material. This becomes essential to improve the properties of microelectronic films.

Theoretical modeling of silicon nitride (*ab initio*^{3,4} and semiempirical^{5–8} methods) provided considerable information about the electronic structure of crystalline and amorphous phases. Although they have been successful in describing some properties, computational cost hinders their extensive use to systems larger than a few hundred atoms.

However, for many systems of interest, thousands of atoms are required for a proper description. This motivated developing interatomic potentials^{9,10} as alternatives in studying structural properties. We have recently developed an interatomic potential to describe silicon nitride systems¹¹ using the Tersoff functional form.¹² It provided a reliable description of amorphous silicon nitride in a wide range of nitrogen contents, from pure silicon to stoichiometric Si₃N₄. Here we extend our model to include the hydrogen interactions, allowing the modeling of hydrogenated silicon nitride. There are other empirical models to describe the Si–H interaction^{13,14} which have been developed to study hydrogen-terminated silicon surfaces. However, to our knowledge our model is the only one which provides an empirical description of SiNH systems. This article is organized as follows: in Sec. II, we discuss the functional form and the fitting strategy to find the best set of parameters for all the interactions. In Sec. III, we test the potential to amorphous SiN_x:H systems using Monte Carlo simulations, and compare the results to available experimental data. We also discuss the structural properties of hydrogenated silicon nitride. In Sec. IV, we present final remarks.

II. THE INTERATOMIC POTENTIAL

Interatomic potentials for silicon nitride have been developed previously.^{9,10} Although those models have been successful in describing some properties of the crystalline phase, their transferability to structures away from those used in the fitting remains untested. We have recently developed an interatomic potential for silicon nitride¹¹ using the Tersoff functional form.¹⁶ Our model provided a considerable improvement in modeling amorphous silicon nitride in a wide range of nitrogen contents as compared to other empirical models. The Tersoff potential,¹² originally developed for pure silicon, is a bond-order potential composed of a two-

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TABLE I. Best set of the parameters that define the Si–Si, Si–N, Si–H, and N–H interactions.

| | N | Si | H |
|---------------------------------|---------------------------|--------------------------|---------|
| A (eV) | 6.36814×10^3 | 1.8308×10^3 | 86.7120 |
| B (eV) | 5.11760×10^2 | 4.7118×10^2 | 43.5310 |
| λ (\AA^{-1}) | 5.43673 | 2.4799 | 3.7879 |
| μ (\AA^{-1}) | 2.70000 | 1.7322 | 1.9800 |
| β | 5.29380×10^{-3} | 1.1000×10^{-6} | 4.0000 |
| n | 1.33041 | 7.8734×10^{-1} | 1.00 |
| c | 2.03120×10^4 | 1.0039×10^5 | 0.00 |
| d | 2.55103×10^1 | 1.6217×10^1 | 1.00 |
| h | -5.62390×10^{-1} | -5.9825×10^{-1} | 1.00 |
| R (\AA) | 1.80 | 2.70 | 0.80 |
| S (\AA) | 2.10 | 3.00 | 1.00 |
| χ | | | |
| N | 0.00 | 0.65 | 0.76 |
| Si | 0.65 | 1.00 | 0.78 |
| H | 0.76 | 0.78 | 1.00 |

body expansion with an implicit angular dependence on the local environment. This model was later extended to C, Ge, and their alloys.¹⁶

Here our model¹¹ is extended to describe the Si–H, N–H, and H–H interactions using the original Tersoff functional form. The fitting parameters for those interactions were found using a database which included *ab initio* and experimental results of a few molecules. The database included the experimental bond energy, interatomic distance and vibrational wave number of the H₂ molecule¹⁷ to describe the H–H bond. For the Si–H bond, we used the binding energy and interatomic distance of the SiH₄ molecule,¹⁸ while for the N–H bond, we used the NH(SiH₃)₂ molecule.¹⁹ The best set of parameters for hydrogen is determined by a least-squares approach.²⁰ For the Si–Si interaction, we took the parameters from the original Tersoff potential,¹⁶ while for the Si–N interaction, we took the parameters previously fitted by us.¹¹ Table I presents the best set of parameters for all the interactions. The parameters for the Si–H (and N–H) interaction may be computed by combining the parameters for Si and H (N and H) in the way developed by Tersoff.¹⁶ Here the parameters R and S for the hydrogen interactions were not obtained arbitrarily during the fitting procedure. They were chosen such that the cut-off function falls smoothly from 1 to 0 between the first and second nearest neighbors.

Table II gives the properties of some molecules computed using this empirical model as compared to experimental or theoretical data. The table also includes those molecules from the database. Overall, the results using this interatomic potential are in good agreement with experimental or theoretical data.

There are other empirical models for the Si–H interactions: one model can be described as a modified Tersoff potential¹³ while the other model is an extension of the Brenner potential.^{14,15} Both models have been fitted to a number of Si_{*m*}H_{*n*} molecules and have been used to study hydrogen-terminated silicon surfaces. Our model provides an overall poorer description of Si_{*m*}H_{*n*} molecules than those

TABLE II. Properties of some molecules Si_{*n*}H_{*m*}N_{*k*} using this interatomic potential as compared to experimental data and *ab initio* calculations. Energies are in eV, distances in \AA , force constants in N/cm, and vibrational wave numbers in cm⁻¹.

| | Expt./theory | This work |
|------------------------------------|---------------------------------|-----------------------|
| H ₂ | | |
| $E_{\text{H-H}}$ | 4.8 eV ^a | 4.8 eV |
| $r_{\text{H-H}}$ | 0.74 \AA ^a | 0.74 \AA |
| K | 5.75N/cm ^a | 5.77N/cm |
| SiH ₄ | | |
| $E_{\text{Si-H}}$ | 3.42 eV ^a | 3.30 eV |
| $r_{\text{Si-H}}$ | 1.48 \AA ^a | 1.44 \AA |
| $\theta_{\text{H-Si-H}}$ | 109.5° ^a | 109° |
| ν | 2100 cm ^{-1b} | 2206 cm ⁻¹ |
| NH(SiH ₃) ₂ | | |
| $E_{\text{N-H}}$ | 4.05 eV ^c | 3.98 eV |
| $r_{\text{N-H}}$ | 0.995 \AA ^c | 1.15 \AA |
| $\theta_{\text{Si-N-H}}$ | 117° ^c | 120° |
| Si ₂ H ₆ | | |
| $E_{\text{Si-H}}$ | | 3.30 eV |
| $r_{\text{Si-H}}$ | 1.49 \AA ^d | 1.44 \AA |
| $\theta_{\text{H-Si-H}}$ | 109.5° | 109° |
| ν | 2155 cm ^{-1e} | 2206 cm ⁻¹ |
| SiH ₃ | | |
| $E_{\text{Si-H}}$ | 3.25 eV ^a | 3.33 eV |
| $r_{\text{Si-H}}$ | 1.48 \AA ^f | 1.43 \AA |
| $\theta_{\text{H-Si-H}}$ | 110.5° ^g | 119° |
| ν | 1955 cm ^{-1h} | 2155 cm ⁻¹ |
| Si ₂ H ₄ | | |
| $E_{\text{Si-H}}$ | | 3.35 eV |
| $r_{\text{Si-H}}$ | 1.48 \AA ^f | 1.43 \AA |
| $\theta_{\text{H-Si-H}}$ | 112.8° ^g | 119° |
| ν | | 2155 cm ⁻¹ |
| SiH | | |
| $E_{\text{Si-H}}$ | 3.14 eV ^f | 3.35 eV |
| $r_{\text{Si-H}}$ | 1.51 \AA ^b | 1.44 \AA |
| ν | 2042 cm ^{-1b} | 2155 cm ⁻¹ |

^aReference 15.

^bReference 29.

^cReference 17.

^dReference 30.

^eReference 31.

^fReference 32.

^gReference 33.

^hReference 34.

models.^{13,14} The Murty–Atwater model used a modified Tersoff functional form to describe the Si–H and H–H interactions, and the original functional form for the Si–Si interactions. That model required more than 40 fitting parameters to describe the Si–H and H–H interactions. In contrast, our model has the advantage of using exactly the original functional form for all interactions, and describes not only the H–H and Si–H interactions, but also the Si–N and N–H interactions. Besides, our model requires only 13 additional parameters to describe all these interactions, and was fitted to a considerably smaller database.

III. STRUCTURAL PROPERTIES OF HYDROGENATED SILICON NITRIDE

In a previous study,¹¹ we discussed a theoretical modeling of amorphous silicon nitride having only Si and N species. Here we present a more realistic modeling by including

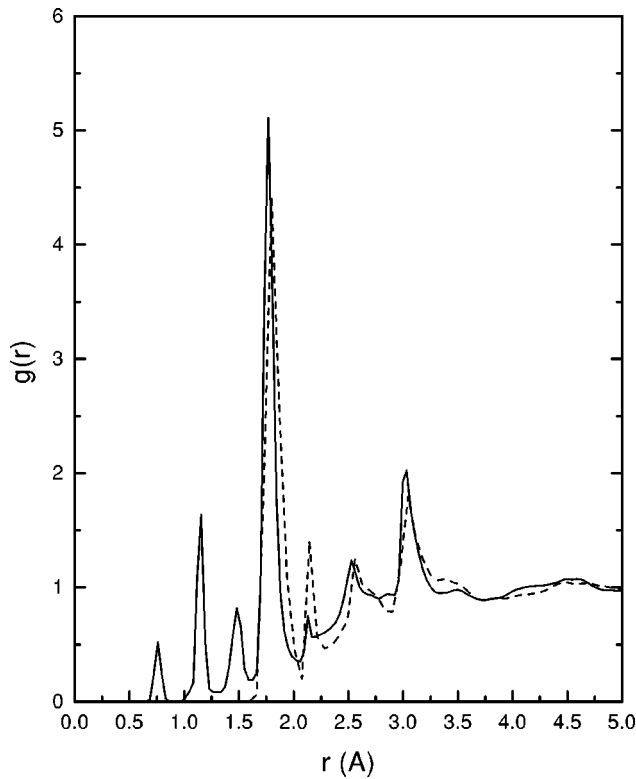


FIG. 1. Total correlation function $g(r)$ for amorphous silicon nitride: unhydrogenated $a\text{-SiN}_{1.33}$ (dashed line) and hydrogenated $a\text{-SiN}_{1.33}$ (full line).

hydrogen, which is generally present in amorphous silicon nitride in high concentrations.²¹ The simulations were performed using the Monte Carlo method²² with periodic boundary conditions and up to 3000 atoms depending on the nitrogen and hydrogen concentrations of each system. The internal stress was released by allowing volume relaxation (NPT ensemble)^{22,23} during the simulations. For each system, the simulation started at a very high temperature ($T > 6000$ K), when the material was essentially liquid. Then, the tem-

perature was slowly reduced (by 5%) in a simulated annealing scheme until it reached room temperature (300 K). Then the statistical properties were computed over several configurations. The properties of the $a\text{-SiN}_x$ and $a\text{-SiN}_x\text{:H}$ systems were compared to recent experimental data.²⁴

In crystalline silicon nitride (Si_3N_4),^{25–27} a N atom binds to three Si first neighbors in a near planar structure (sp^2 hybridization). A Si atom binds to four N first neighbors in a near tetrahedral structure (sp^3 hybridization). In the amorphous phase for the stoichiometric Si_3N_4 , nitrogen has a chemical preference to bind to three silicon, but silicon may bind to other silicon atoms. The local order of amorphous and crystalline phases, described by the total correlation function, are equivalent.⁵ However, in the random network of the amorphous matrix, some dangling bonds may form as a result of the deformed structure. These dangling bond centers, which are related to undercoordinated Si and N atoms, create electronic levels in the gap of the material. Hydrogen incorporation can passivate these dangling bonds.

Figure 1 shows the total radial distribution function $g(r)$ for hydrogenated (10%) and unhydrogenated $\text{SiN}_{1.33}$. For the unhydrogenated silicon nitride the first peak corresponds to the Si–N bonds. This peak is found at 1.73 Å in excellent agreement with experimental data of 1.729 Å reached by neutron scattering.²⁸ A second peak around 2.60 Å corresponds to Si–Si bonds which are still present even at such high nitrogen concentration. A third peak, around 3.1 Å, corresponds predominantly to N–N second neighbors. A small peak around 2.2 Å can also be observed. This peak comes from undercoordinated Si and N atoms. As can be observed in the figure, hydrogenation practically removes this peak. For the hydrogenated silicon nitride, the $g(r)$ changes as a result of hydrogen binding to N or Si atoms. The large peak around 1.73 Å keeps its height and radial position. The three small peaks below 1.73 Å correspond to H–H (0.75 Å), N–H (1.15 Å), and Si–H (1.50 Å) bonds.

Figures 2(a) and 2(b) show the average coordination

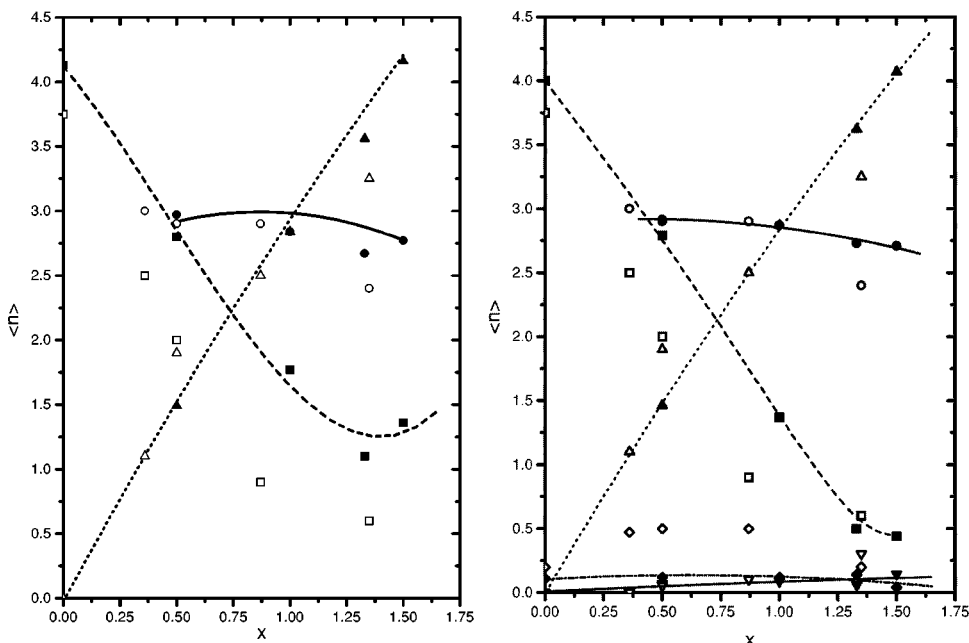


FIG. 2. Average coordination number at Si and N sites as a function of nitrogen content (x). The simulation results (full symbols) are compared to experimental data (open symbols) (see Ref. 24): (a) unhydrogenated and (b) hydrogenated (10% hydrogen atomic concentration) silicon nitride. (a) and (b) show $n_{\text{Si}}(\text{Si})$ (\square), $n_{\text{N}}(\text{Si})$ (\triangle), $n_{\text{Si}}(\text{N})$ (\circ). (b) also shows $n_{\text{H}}(\text{N})$ (∇) and $n_{\text{H}}(\text{Si})$ (\diamond).

numbers on the Si and N centers for different nitrogen contents as compared to experimental results.²⁴ Those experiments obtained indirectly the density of bonds and the mean number of nearest neighbors of the Si and N atoms by combining x-ray photoemission spectroscopy, electron-energy-loss spectroscopy, and optical absorption. The figures show the coordination $n_A(B)$, the average number of nearest neighbors A around atom type B . This coordination is defined as the average number of neighbors inside the radial distribution function up to the covalent radius of that specific atom. In the case of unhydrogenated silicon nitride [Fig. 2(a)], at $x=0$ (*a*-Si), each Si atom has an average coordination of 4.1. As x increases, the N atoms compete with Si atoms to form bonds, and the coordination n_{Si} (Si) drops from 4.1 to about 0.9 at $x=1.5$. On the other hand, the coordination n_{N} (Si) grows linearly from zero to four. The coordination n_{Si} (N) is about 3.0 for all the range of x . This behavior is consistent with the fact that N atom has a chemical preference to bind to three Si atoms.²⁹ Although Fig. 2(a) shows the correct trends for the average coordinations, all the theoretical coordinations are an overestimation of the experimental data. This may be explained because the samples, in which the experiments were performed, had considerably high hydrogen concentrations. Since hydrogen competes with the other atoms to form bonds, a more realistic comparison should also include hydrogen. That result is shown in Fig. 2(b), which presents n_{Si} (N), n_{Si} (Si), n_{N} (Si), n_{H} (N), and n_{H} (Si). The hydrogen incorporation does not change the overall trends of the coordinations. The hydrogen causes a decrease in the n_{Si} (N), n_{N} (Si), and n_{Si} (Si) coordinations. This is because hydrogen competes with Si–N and Si–Si bonds in order to form Si–H and N–H bonds. Figure 2(b) also shows the competition between the Si–H and N–H bonds. For low nitrogen contents ($x < 1.25$), hydrogen has a preference to bind to silicon rather than to nitrogen, and $n_{\text{H}}(\text{Si}) > n_{\text{H}}(\text{N})$. This chemical preference switches at $x \approx 1.25$, which is in good agreement with the experimental data.²⁴

We also studied the role of hydrogen in removing dangling bonds in the amorphous silicon nitride. We performed the calculations using $\text{SiN}_{1.33}\text{H}_y$ for several hydrogen contents ($0\% < y < 40\%$). The simulation for each hydrogen content started at a very high temperature, which was slowly reduced in a simulated annealing process. The statistical properties of the system were computed for room temperature. Figure 3 shows the concentration of undercoordinated silicon and nitrogen atoms as a function of hydrogen content. We defined that an atom is undercoordinated, and therefore has at least one dangling bond, when its coordination is lower than three for nitrogen and four for silicon. A nitrogen atom may bind to a silicon atom (this bond is in average 1.75 Å) or to a hydrogen atom (this bond is in average 1.15 Å). Here we do not consider the N–N bonds, which are unlikely in a stable amorphous silicon nitride. We define that there is a bond between a nitrogen atom and another atom when they are closer than a certain cut-off radius. We chose this cut-off radius to be 10% longer than the largest average bond distance of a specific specie. This essentially considers all atoms inside the first peak in the radial distribution function. In the

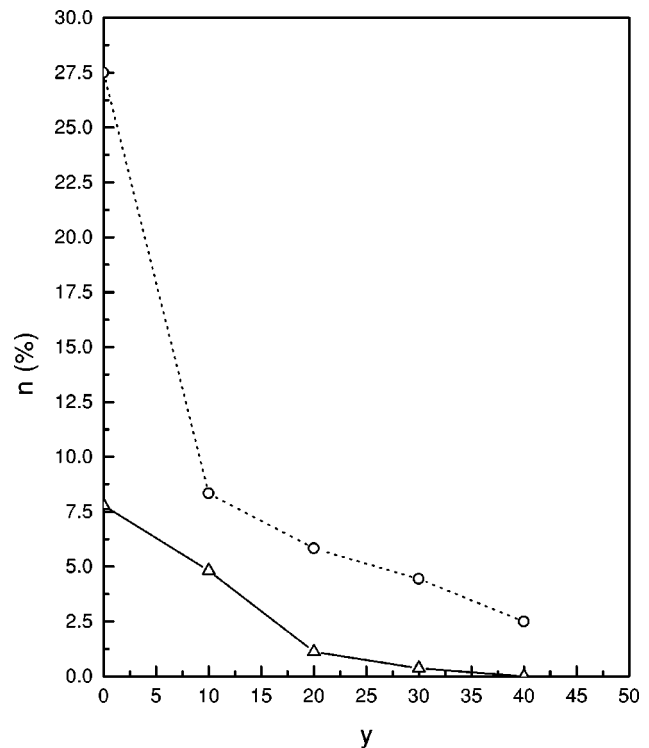


FIG. 3. Concentration of undercoordinated Si (Δ) and N (\circ) atoms as function of hydrogen content y (in at. %).

case of a nitrogen atom, we consider that all atoms inside 1.90 Å are neighbors. A silicon atom may bind to another silicon atom (this bond is in average 2.35 Å), to a nitrogen atom (this bond is in average 1.75 Å), or to a hydrogen atom (this bond is in average 1.50 Å). In the case of silicon, we consider that all atoms within 2.60 Å are neighbors. Figure 3 shows that the concentrations of undercoordinated silicon and nitrogen atoms drop drastically as one increases the hydrogen content in the material. However, the nitrogen dangling bond concentration drops considerably faster than the silicon dangling bond concentration.

We may relate the concentration of dangling bonds to the concentration of energy gap levels and consequently to the electronic activity of the material. Several dangling bond centers have been identified in amorphous silicon nitride.³⁰ The two most important are the K and N₂ centers. The K center is related to a silicon atom bonded to three nitrogen atoms with one dangling bond. The N₂ center is related to a nitrogen atom bonded to two silicon atoms with one dangling bond. Hydrogen incorporation passivates these centers, removing gap levels in the material. Therefore, the results presented in Fig. 3 may be compared in the future to experimental results of the electronic activity of amorphous silicon nitride as function of hydrogen incorporation in the sample.

IV. CONCLUSIONS

In summary, we have developed an interatomic potential to describe hydrogenated silicon nitride systems using the Tersoff functional form. The model provided a reasonably good description of bond energies and bond lengths for several molecules. The model also provided a reliable descrip-

tion of amorphous silicon nitride over a wide range of configurations and nitrogen and hydrogen contents.

The role of hydrogen on the structural properties of hydrogenated amorphous silicon nitride was investigated. For low nitrogen concentrations, hydrogen has a chemical preference to bind to silicon atoms. On the other hand, for high nitrogen contents hydrogen atoms bind preferentially to nitrogen. Hydrogen incorporation to silicon nitride provided a drastic reduction in the dangling bond concentration of both silicon and nitrogen atoms. However, hydrogen appears to be more effective in passivating nitrogen dangling bonds than silicon dangling bonds. This may in part explain why it is more difficult to experimentally detect the nitrogen dangling bond (N_2) center than the silicon dangling bond (K) center.

The good transferability of the model would allow the study of a number of systems in which thousands of atoms (or more) are required. The Si/SiN interface, for example, has been the focus of attention over the last few years. As these interfaces are formed, as a result of growth of one material over the other, several dangling bond centers appear there. These dangling bonds result from the mismatch between the two lattices. Hydrogen may passivate these dangling bonds and therefore stabilize the interface. Understanding these passivation processes may be crucial to improve the quality of devices which use these interfaces.

ACKNOWLEDGMENTS

Partial support was provided to F.B.M. and A.F. by Brazilian agencies Capes and CNPq. J.F.J. and A.F. acknowledge support from FAPESP.

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