Diffusion-reaction mechanisms of nitriding species in SiO$_2$

W. Orellana, Antônio J. R. da Silva, and A. Fazzio
Instituto de Física, Universidade de São Paulo, C.P. 66318, 05315-970, São Paulo, SP, Brazil
(Dated: February 2, 2008)

We study using first-principles total-energy calculations, diffusion-reaction processes involved in the thermal nitridation of SiO$_2$. We consider NO, NH, N$_2$ and atomic N in different charge states as the nitriding species in α-quartz. Our results show that none of neutral species react with the SiO$_2$ network remaining at interstitial sites. Therefore, they are likely to diffuse through the oxide, incorporating nitrogen at near-interface (Si/SiO$_2$) regions. Whereas, charged species are trapped by the network, nitriding bulk SiO$_2$. For the diffusing species, we find that NH and atomic N show increasing diffusivities with temperatures, whereas for NO and N$_2$ they are relatively constant. This result agree well with the finding of higher N concentration at the Si/SiO$_2$ interface obtained by thermal processing of SiO$_2$ in NH$_3$ as compared with those obtained in N$_2$O. Finally, we discuss spin-dependent incorporation reaction mechanisms of NH and atomic N with the SiO$_2$ network.

PACS numbers: 66.30.Ny, 71.55.Ht, 71.15.Nc, 71.15.Mb

I. INTRODUCTION

Nitried silicon oxide or oxynitride is currently the near-term solution to substitute SiO$_2$ as the gate insulator material for the ultrathin metal-oxide-semiconductors (MOS) technology. Recent studies have suggested that the performance of oxynitride-based MOS devices depends both on the depth concentration and on the distribution of nitrogen into the gate oxide. According to these studies, the best nitrogen profile for an ultrathin gate oxide would have: (i) a small nitrogen concentration near the SiO$_2$/Si interface in order to reduce degradations by hot electrons and (ii) a larger N concentration near the interface between the dielectric and the polycrystalline silicon (poly-Si) gate electrode, in order to minimize dopant diffusion.

The growth of ultrathin oxynitride films depends strongly on the reactant agent (e.g., N$_2$O, NO, NH$_3$) and the technique used. Nitrogen can be incorporated into SiO$_2$ using either thermal oxidation and annealing or chemical and physical deposition methods. Thermal nitridation of SiO$_2$ in N$_2$O generally results in a relatively low N concentration at near-interface (Si/SiO$_2$) region. The nitriding species are originated in the decomposition of the N$_2$O molecule occurring at typical oxidation temperature, these species being the NO and N$_2$ molecules. On the other hand, nitrogen incorporation in SiO$_2$ can also be performed via annealing in a NH$_3$ atmosphere, resulting in a relatively high N concentrations into the films. This method provides both near-interface and near-surface nitridation, which suggests different mechanisms for N incorporation or different nitriding species derived from NH$_3$. The above thermal processing are performed at high temperatures (> 800 °C). Plasma nitridation is a promising method for making ultrathin oxynitride at lower temperatures (~300–400 °C). Higher N concentrations and controlled distribution can be attained with this method, typically using ions and radicals derived from N$_2$ and NH$_3$ as nitrogen sources. Additionally, nitridation by energetic particles (N ions) provides high N concentrations much closer to the near-surface region, with little or no nitrogen at the SiO$_2$/Si interface. Although the nitridation mechanisms to make ultrathin SiO$_2$ films are well known at the several layers level, less is known about the diffusing mechanism of the nitriding species and their reactions with the oxide at the atomic level.

In this work the energetics and diffusing properties of the SiO$_2$ thermal nitridation are studied from first-principles total-energy calculations. We have considered the N$_2$, NH and NO molecules as well as atomic N in different charge states as the nitriding species reacting and diffusing through the SiO$_2$ network. The outline of the paper is as follows. Section II describes the theoretical procedure. Our results for the interaction of the nitriding species with the SiO$_2$ network is presented in Sec. IIIA. The diffusivity of the nitriding species through SiO$_2$ is presented in Sec. IIIB. In Sec. IIIC we discuss the spin-dependent diffusion reactions of NH and atomic N with the SiO$_2$ network. Finally, in Sec. IV we show our conclusions.

II. THEORETICAL METHOD

Our calculations were performed in the framework of the density functional theory, using a basis set of numerical atomic orbitals as implemented in the SIESTA code. We have used a split-valence double-ζ basis set plus the polarization functions as well as standard norm-conserving pseudopotentials. For the exchange-correlation potential we adopt the generalized gradient approximation. We used a 72-atom α-quartz supercell and the Γ point for the Brillouin zone sampling. The positions of all the atoms in the supercell were relaxed until all the force components were smaller than 0.05 eV/Å. We also consider neutral and singly charged species, where the neutrality of the cell is always maintained by introducing a compensating background charge. Spin-polarization effects are included throughout the calcula-
The binding energy of NO$^-$ to two fourfold coordinate Si atoms of SiO$_2$ structure where the N atom of the molecule is bound to the network as well as their diffusivities in Si/SiO$_2$ are considered. Therefore, it may diffuse easily through the oxide reacting with the silicon at the Si/SiO$_2$ interface or escaping from the films.

The N$_2$ molecule is a product of the N$_2$O gas decomposition at typical oxidation temperatures, being introduced in this way into SiO$_2$ in thermal processing. N$_2$ (and atomic N) may also be introduced at lower temperatures by plasma assisted methods. Our results for N$_2$ in SiO$_2$ show that this molecule does not react with the oxide being relatively inert for the three charge states considered. Therefore, it may diffuse easily through the oxide reacting with the silicon at the Si/SiO$_2$ interface or escaping from the films.

The N atom in free space has a quartet ($S=3/2$) state. The difference in energy with respect to the doublet ($S=1/2$) state is calculated to be $\sim 3$ eV. However, for a N atom in the largest interstitial site of SiO$_2$-quartz, this difference in energy between both spin configurations decreases to 1.04 eV, due to the interaction with the crystal field. We find that triplet NH does not react with the SiO$_2$ network remaining relatively inert at the interstitial sites. However, singlet NH reacts quickly with the oxide forming a structure where the N atom of NH binds to both Si and O atoms of the oxide. This incorporation reaction is highly exothermic with an energy gain of 2.04 eV. In Section III C we discuss the possibility that NH might be incorporated in the SiO$_2$ network via a triplet-to-singlet spin exchange.

Singly charged NH molecules are highly reactive in the SiO$_2$ network forming bound configurations as shown in Fig. 1(b) and Fig. 1(c). The binding energies for NH$^-$ and NH$^+$ are 3.2 and 2.7 eV, respectively, which suggest that these configurations are very stable favoring a SiO$_2$ near-surface nitridation. We observe that the NH$^-$ bound configuration is similar to that previously found for NO$^-$. However, the relaxation of the SiO$_2$ network is larger for the NH$^-$ bound configuration [see Fig. 1(b)]. Here, both Si-N bond lengths are about 2.1 Å, whereas the Si-Si distance decreases by about 14% with respect to the perfect SiO$_2$ network showing a strong lattice relaxation. The N-H bond length is found to be 1.04 Å. In the bound NH$^+$ configuration [Fig. 1(c)], the N atom binds to an O atom of the oxide keeping its bond to the H atom. The O-N and N-H bond lengths are 1.43 and 1.05 Å, respectively, forming a O-N-H angle of 103°.
α-quartz, this energy difference decreases to 0.76 eV. We find that quartet N does not react with the SiO₂ network suggesting that it would be a diffusing species. However, doublet N reacts with the oxide being incorporated into SiO₂ network forming a Si-N-O bond. This reaction is exothermic with an energy gain of 0.76 eV. In Section III C, we discuss the possibility that atomic N might be incorporated into the SiO₂ network via a quartet-to-doublet spin exchange.

Singly charged N atoms are highly reactive in SiO₂. N⁻ binds to a fourfold coordinate Si atom forming an additional Si-N bond of 1.85 Å, as shown in Fig. 1(d). The N atom has a binding energy of 2.2 eV. On the other hand, N⁺ binds to an oxygen forming a O-N bond, as shown in Fig. 1(e). We find a O-N bond length of 1.39 Å with a N binding energy of 1.1 eV.

As a general trend, we can say that because of the ionic character of SiO₂, charged species are trapped by the network. The positively (negatively) charged NO, NH and N species attach to O (Si) atoms of the oxide, forming strong bonds, with binding energies ranging from 1 to 3 eV. This suggests a mechanism for the high-density bulk and near-surface nitridation. On the other hand, the neutral species in their ground-state spin configurations do not react with the SiO₂ network. Therefore, they are able to diffuse through the oxide.

### B. Diffusion of nitriding species in SiO₂

We calculate the diffusion coefficient for the neutral species hopping through the larger channel of α-quartz, normal to the c-axis. To calculate the migration barriers, we have followed the same procedure as described in our previous calculation of the O₂ diffusion in α-quartz. We fix one atom of the molecules at several points along the pathway joining neighboring interstitial sites of α-quartz where the distance between them is ~5 Å. All other atoms of the systems are allowed to relax. Our results for the total energy variations along this diffusion path are shown in Fig. 2(a). Here, the zero distance indicates approximately the center of the largest interstitial site and the arrow, the place of closest approach to the network. As a general trend, we find an anisotropic energy profile through the migration path which can be associated to the asymmetry of neighboring interstitial sites. Fig. 2(a) shows the calculated total-energy variations of difusing NO and N₂; we observe that these species show similar global minima and height barriers along the pathway. However, N₂ exhibits two local minima not found in the NO pathway, showing that the interactions between the crystal field and the molecular orbitals of the diffusing species may affect the diffusion energy profile. Nevertheless, we must consider that uncertainties are introduced by fixing one atom of the molecules in order to map the diffusion energy profiles. For NH and atomic N we find lower-energy barriers and shorter distances between minima, as compared with NO and N₂ (see Fig. 2), suggesting higher diffusivities for these species.

We estimate the thermal diffusion coefficient or diffusivity for the nitriding species using the Arrhenius law, given by

$$D(T) = D_0 \exp\left(-\frac{E_a}{kT}\right).$$  \hspace{1cm} (1)

Here, the prefactor is defined by $D_0 = \frac{1}{6}\nu$ for a three-dimensional migration path, where $l$ is the hopping distance between minima and $\nu$ is the attempt frequency, $kT$ the Boltzmann constant times the temperature, and $E_a$ is the highest energy barrier of the migration path. $\nu$ is calculated from the energy profile of each species at the interstitial site (approximately the zero distance in Fig. 2), using the harmonic approximation, whereas $E_a$ and $l$ are obtained directly from the same figure. Tab. II lists the values of these quantities as well as our results.

| Species | $E_a$ (eV) | $l$ (Å) | $\nu \times 10^{13}$ sec⁻¹ | $D_0 \times 10^{-4}$ cm²/sec |
|---------|-----------|--------|----------------------|-----------------------------|
| NO      | 0.95      | 4.7    | 2.26                 | 8.32                        |
| N₂      | 0.95      | 4.8    | 2.38                 | 9.14                        |
| NH      | 0.48      | 2.8    | 3.67                 | 4.79                        |
| N       | 0.60      | 3.6    | 3.41                 | 7.37                        |
for the prefactor of each nitriding species. It is worth pointing out that we have considered a very specific migration pathway through α-quartz. Other pathways may result in different migration barriers and diffusivities. In fact, recent calculations have shown major differences in the diffusivity of atomic hydrogen in different crystalline structures of SiO$_2$.\cite{Kumar:2010aa,Heinrich:2013aa} However, we find that our approach is valid to obtain informations on the relative diffusivities of the species under consideration.

Figure 3 shows the diffusivities of the nitriding species in α-quartz as calculated from Eq. 1, for a range of temperatures typically used in thermal and plasma assisted methods. Here we observe that NH and atomic N have the higher diffusivities in α-quartz with increasing temperatures as compared with NO and N$_2$, which suggest that they would be the best thermally-activated diffusing species in SiO$_2$ and the most efficient for Si/SiO$_2$ interface nitridation, as compared with NO and N$_2$. According to our results, the ratio between NH and NO diffusivities at 800°C is estimated to be $D_{\text{NH}}/D_{\text{NO}} \approx 90$. Assuming that NH and NO are the main diffusing species, our results agree well with the experimental finding of higher N concentrations at the interface obtained by thermal nitridation of SiO$_2$ in NH$_3$ as compared with thermal nitridation in NO.\cite{Veprek:2011aa,Chen:2012aa}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig3}
\caption{Calculated diffusivities ($D$) of the nitriding species in α-quartz as a function of typical plasma assisted and thermal processing temperatures.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig4}
\caption{Triplet ($S = 1$) and singlet ($S = 0$) total-energy curves along the reaction pathway ($d$ in the inset figure) for the NH molecule approaching the SiO$_2$ network. The zero distance is the equilibrium position of NH in the largest interstitial site of α-quartz where its corresponding total energy is chosen as the zero energy of the system.}
\end{figure}

C. Spin-dependent diffusion reactions of NH and N in SiO$_2$

As mentioned above, NH in the triplet state does not react with the SiO$_2$ network remaining inert at interstitial sites. However, singlet NH reacts easily with the oxide being incorporated into the network. Because of this spin-dependent reaction of NH with the SiO$_2$ network, we study the possibility that a diffusing NH may suffer a triplet-to-singlet spin conversion while approaching the oxide, resulting in its incorporation into the network. For this, we compute the potential-energy surface (PES) along a pathway joining the equilibrium position of interstitial NH and a Si-O bond of the SiO$_2$ network, for both triplet and singlet spin states, as shown in Fig. 4. The triplet PES in the figure is depicted along a direction perpendicular to the diffusion pathway shown in Fig. 2, however, both pathways intercept at the interstitial equilibrium configuration of NH (zero distance in Fig. 4). The probability that the system changes from the triplet to the singlet PES may be estimated by the Landau-Zener theory. This theory has been recently used to describe spin effects in the adsorption of O$_2$ in the Si(001) surface\cite{Hartog:2010aa} and the O$_2$ incorporation reaction in the Si/SiO$_2$ interface.\cite{Hartog:2010aa} Considering that the NH is initially in the triplet diffusion PES, and is evolving towards the crossing region with a velocity $v$, the probability for a conversion to the singlet PES ($P_{ts}$) may be approximated by

\begin{equation}
    P_{ts} = 2 \left[ 1 - \exp(-V^2/\hbar |F_1 - F_2|) \right],
\end{equation}

where $V$ is the triplet-to-singlet spin-orbit matrix element of NH ($X^3\Sigma^- \rightarrow b^1\Sigma^+$) of 65.1 cm$^{-1}$,\cite{Hartog:2010aa} $F_1$ and $F_2$ are the slopes of the two PES at the crossing point and $\hbar$ is the Planck’s constant. $v$ is estimated from the NH center-of-mass thermal velocity at 800 °C, a typical annealing temperature. $F_1$ and $F_2$ are obtained from the triplet and singlet curves at the crossing region (see Fig. 2). Thus, the probability for a triplet-to-singlet conversion is found to be $P_{ts} = 9.3 \times 10^{-4}$. This means that triplet NH in a single passage through the crossing point has a small probability to change to the singlet PES. However, as the system is thermally activated, many pas-
sages of NH through the crossing point will be performed. In order to quantify the spin-conversion events for NH molecules approaching the SiO$_2$ network at a given temperature, we estimate the ratio between the rate of NH following the triplet diffusion PES ($\Gamma_{ts}$) and the rate of NH changing from triplet to singlet PES at the crossing point ($\Gamma_{ts}$). Assuming that the thermally-activated systems follow the Arrhenius law, the reaction rates can be written as

$$\Gamma_t = \Gamma_0 \exp(-\Delta E_t/kT)$$

and

$$\Gamma_{ts} = \Gamma_0 [\exp(-\Delta E_p/kT)] \times P_{ts}. \quad (4)$$

Here, $\Gamma_0$ is the frequency prefactor; $\Delta E_t$ is the energy barrier for the triplet diffusion PES obtained from Fig. 2(b) ($\Delta E_t = 0.5$ eV) and $\Delta E_p$ is the energy difference between the lowest-energy equilibrium configuration of the triplet NH and the crossing point, obtained from Fig. 4 ($\Delta E_p = 0.1$ eV). For a temperature of 800 °C, we obtain for our calculated $P_{ts}$, that $\Gamma_t/\Gamma_{ts} \simeq 14$, which indicates that NH will proceed preferentially along the triplet diffusion PES.

As the incorporation of NH into the oxide due to the spin exchange is also likely to occur (an average of one in 14 events), we study three possible thermally-activated diffusion-reaction mechanisms for an incorporated singlet NH at 800 °C: (i) NH diffuses along the SiO$_2$ network by a hopping mechanism. The rate is estimated by Eq. 8 substituting $\Delta E_t$ by a calculated hopping energy barrier ($\Delta E_h = 2.2$ eV). We find a hopping rate of $\Gamma_h = \Gamma_0 (4.6 \times 10^{-11})$. (ii) NH is released from the network following the singlet PES. This reaction rate is estimated by

$$\Gamma_s = \Gamma_0 [\exp(-\Delta E_s/kT)] \times (1 - P_{ts}), \quad (5)$$

where $\Delta E_s$ is the singlet PES energy barrier obtained from Fig. 4 ($\Delta E_s = 2.0$ eV). We find that $\Gamma_s = \Gamma_0 (4.0 \times 10^{-10})$. (iii) NH is released from the network changing from the singlet to the triplet PES at the crossing point. The reaction rate is estimated by Eq. 8 where $\Delta E_p$ is now the difference between the energies at the singlet-triplet crossing point and at the incorporated NH equilibrium configuration, obtained from Fig. 4 ($\Delta E_p = 1.05$ eV). We find that $\Gamma_{st} = \Gamma_0 (1.1 \times 10^{-8})$. According to these results, the most likely diffusion mechanism for an incorporated singlet NH in SiO$_2$ would be mediated by the reaction (iii), i.e., NH leaves the network changing from the singlet to the triplet PES at the crossing point and then diffuses through SiO$_2$ as a triplet NH. The two other mechanisms are less likely, as can be verified by the ratios $\Gamma_{st}/\Gamma_s \approx 240$ and $\Gamma_{st}/\Gamma_s \approx 28$.

Similarly to NH, we find a spin-dependent diffusion reaction for atomic N with the SiO$_2$ network. According to our results, the N atom in the ground quartet state does not react with the network remaining at interstitial sites, whereas, in the doublet state, the N atom is incorporated between a Si-O bond forming a structure similar to the peroxyxyl bridge of oxygen$^{20}$. Therefore, we examine the possibility that the N atom, initially in the quartet state, changes the spin configuration to the doublet one, resulting in its incorporation into the oxide. Following the same procedure described above for NH, we compute the quartet and doublet PES for the N atom approaching the SiO$_2$ network. Our results are shown in Fig. 5. From Eq. 8 we obtain the probability for the spin conversion using for $V$ the quartet-to-doublet spin-orbit matrix element of the N atom ($^2P \rightarrow ^2P$), obtained from spectroscopy data of 13.8 cm$^{-1}$. Thus, we find a quartet-to-doublet conversion probability $P_{qd} = 1.6 \times 10^{-5}$. This probability corresponds to a single passage of the N atom through the crossing point. To estimate the number of spin-conversion events of thermally activated N atoms approaching the SiO$_2$ network, we calculate the ratio between the rate of N following the quartet diffusion PES ($\Gamma_q$) and the rate of N changing from doublet to singlet PES at the crossing point ($\Gamma_{qd}$). To calculate $\Gamma_q$ we use Eqs. 8 substituting $\Delta E_t$ by the energy barrier for the quartet diffusion PES obtained from Fig. 4(b) ($\Delta E_q = 0.6$ eV). $\Gamma_{qd}$ was estimated by Eqs. 8 substituting $P_{ts}$ by $P_{qd}$ and using $\Delta E_p = 0.6$ eV, the difference between the energies at the interstitial site and at the quartet-doublet crossing point, obtained from Fig. 5. For a temperature of 800 °C, we find that $\Gamma_q/\Gamma_{qd} \approx 6 \times 10^4$. This results indicates that the N atom will most likely proceed along the quartet PES, i.e., it diffuses through the SiO$_2$ essentially without reacting with the network.

Although very unlikely, the reaction of a doublet N with the oxide due to the spin exchange may also occur. Again, following the same procedure described for NH, we have three possibilities for the doublet N
diffusion-reaction mechanism once it is incorporated into the oxide: (i) The incorporated N diffuses through the SiO$_2$ network by a hopping mechanism. From Eq. 8 substituting $\Delta E_0$ by the calculated hopping energy barrier ($\Delta E_h = 1.8$ eV), we find a reaction rate of $\Gamma_h = \Gamma_0 (3.5 \times 10^{-9})$. (ii) $N$ is released from the network following the doublet PES. From Eq. 4 substituting $\Delta E_d$ by the doublet PES energy barrier, obtained from Fig. 6 ($\Delta E_d = 0.9$ eV), and $P_{ts}$ by $P_{qd}$, we find $\Gamma_d = \Gamma_0 (5.9 \times 10^{-8})$. (iii) $N$ is released from the network changing from the doublet to the quartet PES at the crossing point. From Eq. 4 substituting $P_{ts}$ by $P_{qd}$ and using $\Delta E_b = 0.6$ eV, the difference between the energies at the interstitial site and at the quartet-doublet crossing point, obtained from Fig. 5 we find $\Gamma_{dq} = \Gamma_0 (2.4 \times 10^{-8})$. Therefore, if a N atom is incorporated into the oxide by a quartet-to-doublet spin exchange, a rare event, it will be released from the network following the singlet PES, according to the reaction (ii). However, as the incorporation reaction of the doublet N is exothermic, it will be reincorporated into the network if the timescale for relaxation back to the quartet ground state is long enough. Finally, we find that the other two possible reactions are very unlikely as can be verified by the ratios $\Gamma_d/\Gamma_h \approx 1.7 \times 10^4$ and $\Gamma_d/\Gamma_{dq} \approx 2.5 \times 10^3$.

**IV. CONCLUSIONS**

We conclude that because of the ionic character of SiO$_2$, charged species are trapped by the network, where positive (negative) species tend to attach to oxygen (silicon) atoms, forming strong bonds with binding energies as high as 3 eV. This suggests a mechanism for the N incorporation in bulk SiO$_2$ observed in plasma assisted method, which would be associated to charged species surviving the first stages of the incorporation reactions occurring at the surface. Of course, these charged species may also transfer the charge to the network becoming neutral. According to our results, neutral species do not react with the network remaining at interstitial sites, therefore, they would be diffusing species in SiO$_2$ able to reach the Si/SiO$_2$ interface.

We estimate the diffusivities of neutral species through $\alpha$-quartz. Our results show that NH and atomic N have increasing diffusivities with temperature, and the highest one among the nitriding species, suggesting that they would be efficient for near interface nitridation. This result is in good agreement with the finding of high N concentration at the Si/SiO$_2$ interface obtained by thermal processing in NH$_3$. On the other hand, NO and N$_2$ show relatively constant diffusivities in $\alpha$-quartz for the same range of temperatures. This result is also in good agreement with the finding of relatively low N concentration at the Si/SiO$_2$ interface obtained by thermal processing in N$_2$O, which is the main source of NO and N$_2$ species.

We also study the incorporation reaction of NH and atomic N with the SiO$_2$ network driven by a spin exchange mechanism. We find that, for a typical annealing temperature ($T = 800$ °C), a NH molecule diffusing through the triplet PES will have, on average, one in fourteen possibilities to be incorporated into the network by a triplet-to-singlet conversion. The incorporated singlet NH will most likely return to the triplet PES after an inverse spin conversion. We also find that atomic N may be incorporated into the network by a quartet-to-doublet conversion while diffusing through the quartz PES, however, only an average of one in $6 \times 10^4$ events will be successful. If this rare event occurs, the incorporated N will be released from the network following the doublet PES and, subsequently, reincorporated into the network due to the doublet exothermic process. However, this mechanism will be valid if the timescale for the relaxation to the quartet ground state is long enough.

**Acknowledgments**

This work was supported by FAPESP and CNPq. We also would like to thank to CENAPAD-SP for computer time.

---

*Electronic address: wmmomunoz@if.usp.br*

1. M.L. Green, E.P. Gusev, R. Degraeve, and E.L. Garfulkel, J. Appl. Phys. 90, 2057 (2001).
2. E. Cartier, D.A. Buchanan, and G.J. Dunn, Appl. Phys. Lett. 64, 901 (1994).
3. D. Wristers, L.K. Han, T. Chen, H.H. Wang, and D.L. Kwong, Appl. Phys. Lett. 68, 2094 (1996).
4. K.A. Ellis and R.A. Buhrman, IBM J. Res. Develop. 43, 287 (1999).
5. I.J.R. Baumvol, Surf. Sci. Rep. 49, 5 (1999).
6. H.C. Lu, E.P. Gusev, E. Garfunkel, B.W. Busch, T. Gustafsson, T.W. Sorsch, and M.L. Green, J. Appl. Phys. 87, 1550 (2000).
7. K. Watanabe and T. Tatsumi, Appl. Phys. Lett. 76, 2940 (2000).
8. E.P. Gusev, D.A. Buchanan, P. Jamison, T.H. Zabel, and M. Copel, Microelectron. Eng. 48, 67 (1999).
9. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
10. P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B 53, 10441 (1996).
11. N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
12. J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
13. W. Orellana, A. J. R. da Silva, and A. Fazzio, Phys. Rev. Lett. 90, 16103 (2003).
14. W. Orellana, A. J. R. da Silva, and A. Fazzio, Phys. Rev.
Lett. 87, 155901 (2001).
15 A. Bongiorno, L. Colombo, and M.I. Trioni, J. Non-Cryst. Solids 216, 30 (1997).
16 B. Tuttle, Phys. Rev. B 61, 4417 (2000).
17 C. Zener, Proc. R. Soc. London, Ser. A137, 696 (1932).
18 K. Kato, T. Uda, and K. Terakura, Phys. Rev. Lett. 80, 2000 (1996).
19 D.R. Yarkony, J. Chem. Phys. 92, 320 (1990).
20 D.R. Hamann, Phys. Rev. Lett. 81, 3447 (1998).