

# Ab Initio Structure and Energetics for the Molecular and Dissociative Adsorption of NH<sub>3</sub> on Si(100)-2 × 1<sup>†</sup>

Eyal Fattal, Michelle R. Radeke, Gregg Reynolds, and Emily A. Carter\*

Department of Chemistry and Biochemistry, Box 951569, University of California, Los Angeles, Los Angeles, California 90095-1569

Received: April 15, 1997; In Final Form: August 14, 1997<sup>⊗</sup>

We predict the structures and detailed energetics for the dissociative adsorption of NH<sub>3</sub> to form NH<sub>2</sub> and H adsorbed on a single Si dimer on the Si(100)-2 × 1 surface at the MRSDCI (multireference single and double excitation configuration interaction) level of theory. We predict that this dissociation involves two steps: (i) barrierless molecular chemisorption of NH<sub>3</sub> followed by (ii) activated N–H bond cleavage of NH<sub>3(a)</sub> to form NH<sub>2(a)</sub> + H<sub>(a)</sub>. While the second step involves a barrier, its relatively small height renders the overall reaction barrierless. The extremely high adsorption exothermicity (~75 kcal/mol) results in a very high desorption barrier. These results can explain the experimentally determined high sticking probability of NH<sub>3</sub>, the observation of NH<sub>3(a)</sub> at low temperatures, and the observed stability of NH<sub>2(a)</sub> and H<sub>(a)</sub> on the Si(100) surface up to ~600 K. Additionally, our CASSCF level (complete active space self-consistent-field) calculated geometries for the dissociatively adsorbed species agree with structures proposed to explain experimental data.

## Introduction

The Si(100)-2 × 1 surface is the most commonly used surface in device manufacture because of its anisotropic etch properties. Nitridation of this surface creates Si<sub>3</sub>N<sub>4</sub> (silicon nitride) films which are used in integrated circuits as insulating and passivating layers. NH<sub>3</sub> is an excellent nitriding agent for Si(100)-2 × 1: it has a sticking probability of one at 120 K<sup>1</sup> and is reactive at temperatures as low as 80 K.<sup>2–4</sup> The reaction of NH<sub>3</sub> with Si(100)-2 × 1 is potentially useful in the production of the ultrathin, sharp silicon nitride interfaces which are necessary for the next generation of very large scale integrated (VLSI) devices,<sup>5</sup> because this reaction has the interesting property of occurring rapidly only up to a maximum film thickness of 100 Å.<sup>5–8</sup> After this thickness, the growth of the silicon nitride layer becomes much slower, allowing the reaction to be stopped after only a very thin film has been created.

Because the insulating layers required for VLSI devices may be only tens of atoms thick, knowledge of the precise mechanisms for the nitridation process could aid the development of nitridation techniques for creating the thinnest and sharpest interfaces. For nitridation of Si via NH<sub>3</sub>, details of the initial mechanism for the adsorption of NH<sub>3</sub> onto the Si(100)-2 × 1 surface are not known. At temperatures between 80 and 300 K, most experimental studies support some degree of dissociated adsorption of NH<sub>3</sub>,<sup>9</sup> either to NH<sub>2(a)</sub> and H<sub>(a)</sub>,<sup>10</sup> as suggested by the bulk of these studies, or to NH<sub>(a)</sub> and H<sub>(a)</sub>, as found in earlier work.<sup>11</sup> There is also a controversy over the saturation coverage of NH<sub>3</sub> on this surface. A saturation coverage of 0.5 monolayers (ML) or one NH<sub>3</sub> molecule per Si dimer is reported by several experimentalists using electron-stimulated desorption ion angular distributions (ESDIAD) and temperature-programmed desorption (TPD)<sup>1</sup> and X-ray photoelectron spectroscopy (XPS).<sup>2,12</sup> On the other hand experimental data from low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and

photoemission yield spectroscopy (PYS),<sup>13</sup> as well as XPS<sup>14</sup> suggested that the saturation coverage is 0.25 ML or one NH<sub>3</sub> molecule per two Si dimers. Furthermore, it is not known whether NH<sub>3</sub> desorbs dissociatively on one dimer, as suggested by the ESDIAD data of Yates and co-workers,<sup>1</sup> or across dimer rows, as predicted by the calculations of Zhou et al. using a Si<sub>20</sub>H<sub>18</sub>NH<sub>3</sub> cluster in conjunction with the DV-X $\alpha$  (discrete variational X $\alpha$ ) and semiempirical ASED-MO (atom superposition and electron delocalization—molecular orbital) methods.<sup>15</sup> We have attempted to provide some insight into these questions by looking at the dissociative adsorption of NH<sub>3</sub> on a single Si dimer using the ab initio CASSCF/MRSDCI (complete active space self-consistent field/multireference single and double excitation configuration interaction) level of theory. By comparing our calculated energetics for adsorption/desorption and our predicted geometries of the adsorbates to experimental observations, we can assess the likelihood that NH<sub>3</sub> adsorbs onto the Si(100)-2 × 1 surface through this pathway.

## Method

To model a dimer on the Si(100)-2 × 1 surface, we use a Si<sub>9</sub>H<sub>12</sub> cluster which has been used successfully in previous work to model localized bonding on this surface.<sup>16–19</sup> This cluster is comprised of nine Si atoms embedded in  $\bar{H}$ 's (siligens), which are hydrogen atoms modified to have the electronegativity of bulk Si.<sup>18,19</sup> There are two surface layer Si atoms representing the dimer, four second layer Si atoms, two third layer Si atoms, and one fourth layer Si atom. The terminating siligens are fixed in bulk Si tetrahedral directions at an optimized Si– $\bar{H}$  bond length of 1.729 Å.<sup>18</sup> The siligens serve to keep the subsurface Si's in a tetrahedral, neutral environment, i.e., a mimic of the Si lattice. We have previously presented specifics of the atomic basis sets used for the Si, hydrogen adsorbates, and siligens, as well as the effective core potentials used for the Si atoms.<sup>20</sup> For the N atom in NH<sub>3</sub> and the related adsorbate and TS structures, we use a Dunning/Huzinaga valence double- $\zeta$  basis set<sup>21</sup> and include a 3d polarization function ( $\zeta^d = 0.76$ ) and 2s and 2p diffuse functions ( $\zeta^s = 0.066$  and  $\zeta^p = 0.045$ ). The overall number of atoms in the system is 25, and the total

<sup>†</sup> We dedicate this paper to our dear friend and colleague, Daniel Kivelson, whose wisdom, humor, and collegial nature make the UCLA Chemistry and Biochemistry Department a wonderful place to work.

\* To whom correspondence should be addressed.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, October 1, 1997.

number of electrons treated explicitly is 58 using a total of 133 basis functions.

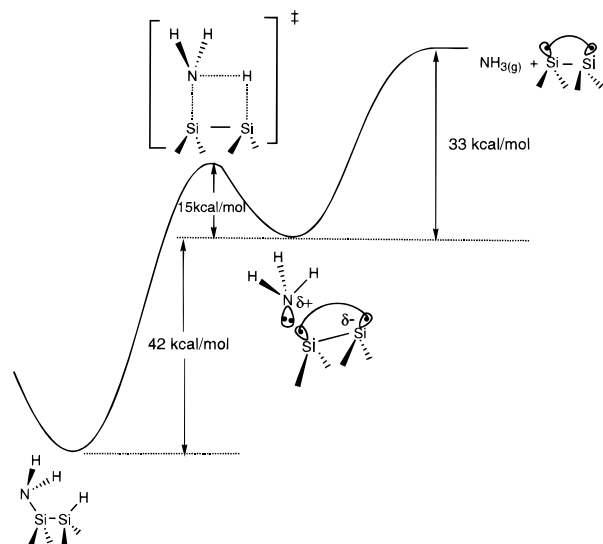
The optimal structures for the molecularly and dissociatively adsorbed NH<sub>3</sub> on the embedded Si cluster, as well as that of the reactants NH<sub>3(g)</sub> + the bare cluster, were determined using the quasi-Newton<sup>22</sup> method, and the TS for dissociative adsorption was searched for using the DIIS-Ridge method.<sup>23</sup> Both methods used CASSCF<sup>24</sup> level energy and gradient calculations. The structures were considered converged when the gradient components of all movable atoms (all nonsilicogens) were minimized to below 10<sup>-3</sup> au. To determine the final energetics, MRSDCI<sup>25</sup> calculations were performed on all the optimized reaction structures. The reference space for the MRSDCI contained all configuration state functions in the 10 electrons in 10 orbitals CAS with coefficients ≥ 0.01. This results in final CI expansions of up to ~6.5 million configuration state functions. On the basis of error analysis done on related systems,<sup>16</sup> we expect MRSDCI barriers to be 2–5 kcal/mol too high and MRSDCI exothermicities to be ~2 kcal/mol too low, which is an acceptable level of accuracy for surface science models.

To adequately describe the reaction path for dissociative adsorption, a 10-orbital, 10-electron CAS was found to be necessary. For the desorbed and molecularly adsorbed structures, the orbitals involved in the CAS were the two surface Si dangling bonds, the correlated N lone pair described by two orbitals, and the three N–H bonds and their respective antibonding orbitals. The CAS for the dissociatively adsorbed structure included the Si–N and Si–H bonding and antibonding orbitals, the two N–H bonding and antibonding orbitals, and the correlated N lone pair described by two orbitals. All CASSCF energy and gradient calculations were performed using the program HONDO.<sup>26</sup>

The calculations were performed within C<sub>s</sub> symmetry. To verify that this was not a restriction, initially all geometry optimizations as well as the beginning of the saddle point search were carried out using no symmetry constraints. In all of these cases, the structures evolved into ones that were C<sub>s</sub> symmetric and exactly matched the results obtained when the C<sub>s</sub> symmetry restriction was imposed. Because inclusion of symmetry can considerably speed up calculations, at the point the TS geometry developed C<sub>s</sub> symmetry, we continued the search using this symmetry. The speedup obtained using symmetry is especially important in a situation such as this where the CAS is large, making the CASSCF energy and gradient calculations computationally intensive. For consistency in comparing the energetics, structures of both adsorbed and the desorbed minima were also optimized using C<sub>s</sub> symmetry, and all MRSDCI calculations were done using this symmetry.

## Results and Discussion

The reaction path and predicted MRSDCI energetics for the adsorption of NH<sub>3</sub> onto a single dimer are depicted in Figure 1. The dissociation of NH<sub>3</sub> on the surface involves two stages. First, we find that gaseous NH<sub>3</sub> adsorbs molecularly on the surface with no barrier and a 0 K well depth of 32 kcal/mol. Second, the molecularly adsorbed NH<sub>3</sub> dissociates to NH<sub>2(a)</sub> + H<sub>(a)</sub>. This dissociation is activated, with a barrier of 15 kcal/mol. The exothermicity of the reaction of molecularly adsorbed NH<sub>3</sub> converting to the dissociated NH<sub>2(a)</sub> + H<sub>(a)</sub> is 43 kcal/mol. The overall exothermicity from gaseous NH<sub>3</sub> and a bare Si surface is predicted to be 75 kcal/mol. Since the intermediate barrier lies 17 kcal/mol below the energy of the reactants, this highly exothermic reaction has no overall barrier to dissociative chemisorption. Only in the case where 17 kcal/mol translational

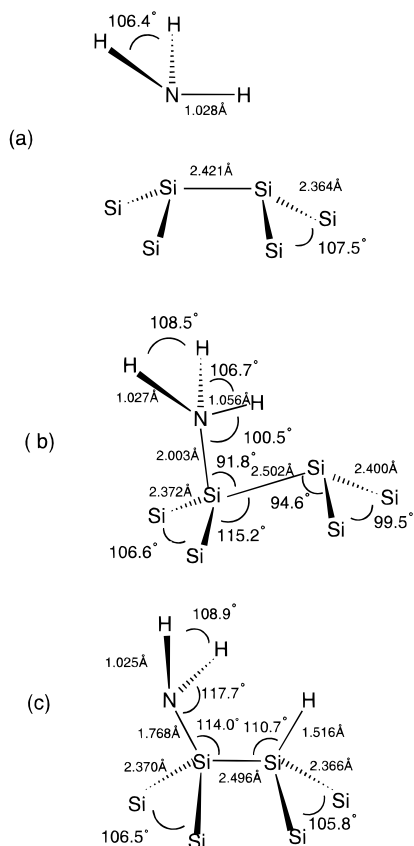


**Figure 1.** Predicted energetics for the molecular and dissociative adsorption of NH<sub>3</sub> onto a single silicon dimer on the Si(100)-2 × 1 surface.

energy acquired by NH<sub>3(g)</sub> would be absorbed by Si lattice phonons will NH<sub>3</sub> be trapped in the molecular state. There is some evidence for this at very low temperatures, as discussed below.

Our results agree with the following experimental observations: (i) Molecularly adsorbed NH<sub>3</sub> has been observed by ultraviolet photoelectron spectroscopy (UPS) to be stable up to ~120 K, but even at 80 K, a fraction has converted to NH<sub>2(a)</sub> + H<sub>(a)</sub>, with this fraction increasing as the surface is heated.<sup>4</sup> The presence of both NH<sub>3(a)</sub> and NH<sub>2(a)</sub> + H<sub>(a)</sub> at 80 K is consistent with the idea that overall dissociative adsorption is barrierless while there remains some probability of metastable NH<sub>3(a)</sub> formation. (ii) NH<sub>3</sub> adsorbs with a sticking coefficient of 1 at low temperatures (120 K),<sup>1</sup> consistent with a barrierless, highly exothermic reaction. (iii) The large barrier (~75 kcal/mol) that we calculate for NH<sub>2(a)</sub> + H<sub>(a)</sub> recombination is in accord with experimental observations that NH<sub>2(a)</sub> is stable up to ~600 K,<sup>1,27</sup> above which temperature NH<sub>3(g)</sub> is produced through NH<sub>2(a)</sub> and H<sub>(a)</sub> recombination.

Our CASSCF geometries for gaseous NH<sub>3</sub>, molecularly adsorbed NH<sub>3</sub>, and the dissociatively adsorbed NH<sub>2(a)</sub> + H<sub>(a)</sub> on the embedded cluster are shown Figure 2 (only the first two layers are shown). Our calculations predict that the molecularly adsorbed NH<sub>3</sub> bonds via charge transfer to the surface (Figure 2b) with approximately half an electron transferred to both surface and subsurface Si atoms. This effectively reduces the inherent repulsion between the NH<sub>3</sub> lone pair and the Si dangling bond and also yields an asymmetric dimer configuration with the more negatively charged Si dimer atom buckled upward, as expected.<sup>28</sup> In the dissociatively adsorbed structure (Figure 2c), the hydrogens on the NH<sub>2(a)</sub> (amino group) point inward toward the dimer bond and upward away from the surface. We determined that this configuration is energetically preferred over having the H atoms in the amino ligand angled outward away from the dimer bond and downward toward the surface, by using both possible conformations as initial guesses in our optimization of this structure. The optimized structure we obtained for dissociatively adsorbed NH<sub>3</sub> is identical in nature to the structure Yates and co-workers proposed to explain their ESDIAD data<sup>1</sup> and to the structure suggested by Fujisawa et al. to fit their high-resolution electron energy loss spectroscopy (HREELS) data.<sup>29</sup> Moreover, the tilt angle of the Si–N bond from the surface predicted by us (66.0°), Moriarty and Smith (67.3°),<sup>29</sup>



**Figure 2.** Calculated geometries for (a)  $\text{NH}_3(\text{g})$  and the bare Si embedded cluster, (b) molecularly chemisorbed  $\text{NH}_3$  on the cluster, and (c) the dissociative chemisorption products  $\text{NH}_2(\text{a}) + \text{H}(\text{a})$  on the embedded cluster. Note: only Si atoms in the top two layers of the embedded cluster are shown.

and Zhou et al.<sup>15</sup> ( $65^\circ$ ) is in agreement with the experimental results of Fujisawa et al., which suggest that this angle is  $70^\circ$ .<sup>30</sup> (Yates and co-workers assumed Si(100)- $2 \times 1$ :F bond angles in their ESDIAD analysis.<sup>1</sup>) The trigonal-pyramidal orientation of the Si– $\text{NH}_2(\text{a})$  group in the geometry predicted by us and proposed by Yates and co-workers<sup>1</sup> and Fujisawa et al.<sup>30</sup> also agrees with the calculations of Zhou et al.<sup>15</sup> However, this prediction is contrary to the planar structure calculated by Moriarty and Smith using semiempirical methods.<sup>29</sup> A trigonal-pyramidal structure, in which the H atoms in the amino group are aimed inward toward the Si dimer bond, allows the N lone pair to point outward away from the dimer bond and the other adsorbate H atom, thus minimizing steric repulsions. Instead, the N lone pair is directed toward the Si dimer bond in the neighboring dimer row, which is over  $5 \text{ \AA}$  away, and thus unlikely to have any significant repulsive interactions. The planar structure for the amino predicted by Moriarty and Smith<sup>29</sup> is at odds with what one would expect for N in this type of chemical environment as well as with other theoretical calculations and experimental data and therefore seems to be an artifact of the semiempirical methods used.

From our calculations, we have found that dissociative adsorption onto a single Si dimer is in agreement with experimental observations. However, Zhou et al.<sup>15</sup> calculate a negligible barrier to adsorption for dissociative adsorption (as  $\text{NH}_2(\text{a})$  and  $\text{H}(\text{a})$ ) across neighboring dimer rows. We cannot rule out the possibility of adsorption occurring via this pathway, since we have not examined the energetics for this mechanism. At the present time, however, it is not feasible to use CASSCF/MRSDCI level calculations on a cluster large enough to test this adsorption pathway. Nevertheless, we can point out that the much longer N–H distance (the bond between the N in the

adsorbed amino group and the adsorbed hydrogen) required in a TS bridging two dimer rows (which are over  $5 \text{ \AA}$  apart) would presumably make this TS significantly less energetically favorable to form from adsorbing  $\text{NH}_3(\text{g})$  (with N–H bond lengths of  $\sim 1 \text{ \AA}$ ) than in the dissociative chemisorption across one Si dimer (with Si–Si bond lengths of  $\sim 2.4 \text{ \AA}$ ), as suggested herein.

## Conclusions

Our calculations show that the detailed energetics and structures for the adsorption/desorption of  $\text{NH}_3$  onto a single Si dimer are consistent with experimental data. We suggest that the mechanism for the dissociative adsorption of  $\text{NH}_3$  to give  $\text{NH}_2(\text{a}) + \text{H}(\text{a})$  occurs via molecular adsorption of  $\text{NH}_3$  with no overall barrier. Metastable  $\text{NH}_3(\text{a})$  is strongly bound with respect to desorption ( $32 \text{ kcal/mol}$ ), with a lower barrier to dissociate an N–H bond ( $15 \text{ kcal/mol}$ ), which explains why  $\text{NH}_2(\text{a}) + \text{H}(\text{a})$  is readily formed and also why  $\text{NH}_3(\text{a})$  is observed at low temperatures. We predict a highly exothermic ( $75 \text{ kcal/mol}$ ) reaction to form  $\text{NH}_2(\text{a}) + \text{H}(\text{a})$ , consistent with the observed stability of  $\text{NH}_2(\text{a})$  and the unit sticking probability of  $\text{NH}_3$ . Our predicted geometry for the dissociated structure agrees with the geometry proposed by Fujisawa et al.<sup>30</sup> and Yates and co-workers<sup>1</sup> based on their experimental data. The mechanism of one  $\text{NH}_3$  adsorbing onto a single Si dimer, minimizing lateral repulsions by having the  $\text{NH}_2$  group point toward the middle of the dimer, supports a saturation coverage for  $\text{NH}_3$  of  $0.5 \text{ ML}$ . This picture also concurs with STM (scanning tunneling microscopy) data which suggest that Si(100) maintain  $2 \times 1$  symmetry during  $\text{NH}_3$  adsorption, implying that the dimer rows are left intact.<sup>3,31</sup>

**Note Added in Proof.** Subsequent to the submission of this paper, a photoelectron diffraction study<sup>32</sup> determined the Si–N and N–Si–Si bond length and angle to be  $1.73 \pm 0.08 \text{ \AA}$  and  $111 \pm 4^\circ$  for dissociatively adsorbed  $\text{NH}_3$  on Si(100)- $2 \times 1$ . These values are in excellent agreement with our predictions shown in Figure 2c.

**Acknowledgment.** This work was primarily supported by the Air Force Office of Scientific Research. E.A.C. also acknowledges the Camille and Henry Dreyfus Foundation and the Alfred P. Sloan Foundation for Teacher–Scholar and Research Fellow Awards, respectively. M.R.R. acknowledges the UCLA Gregory Award for Excellence in Research. We also thank Dr. Antonio da Silva for help at the end of this project.

## References and Notes

- (1) Taylor, A.; Wallace, R. M.; Choyke, W. J.; Dresser, M. J.; Yates, J. T., Jr., *Surf. Sci. Lett.* **1989**, *215*, L286. Dresser, M. J.; Taylor, P. A.; Wallace, R. M.; Choyke, W. J.; Yates, J. T., Jr. *Surf. Sci.* **1989**, *218*, 75.
- (2) Dufour, G.; Rochet, F.; Roulet, H.; Sirotti, F. *Surf. Sci.* **1994**, *304*, 33.
- (3) Avouris, Ph.; Bozso, F.; Hamers, R. J. *J. Vac. Sci. Technol. B* **1987**, *5*, 1387.
- (4) Bischoff, J. L.; Lutz, F.; Bolmont, D.; Kubler, L. *Surf. Sci. Lett.* **1991**, *248*, L240.
- (5) Moslehi, M. M.; Saraswat, K. C. *IEEE Trans. Electron Devices* **1985**, *32*, 106.
- (6) Glachant, A.; Saidi, D. *J. Vac. Sci. Technol. B* **1985**, *3*, 985.
- (7) Bischoff, J. L.; Kubler, L.; Bolmont, D. *Surf. Sci.* **1989**, *209*, 115–130.
- (8) Peden, C. H. F.; Rogers, J. W., Jr.; Shinn, N. D.; Kidd, K. B.; Tsang, K. L. *Phys. Rev. B* **1993**, *47*, 15622 and references therein.
- (9) Johnson et al. (Johnson, A. L.; Walczak, M. M.; Madey, T. E. *Langmuir* **1988**, *4*, 277) using electron-stimulated desorption ion angular distributions (ESDIAD) and ref 14 using ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS).
- (10) Reference 30 using high-resolution electron energy loss spectroscopy (HREELS); ref 1 using ESDIAD and temperature-programmed

- desorption (TPD); Larsson, C. U. S.; Flodström, A. S. *Surf. Sci.* **1991**, *241*, 353 using HREELS, ref 12 using XPS; ref 7 and Kubler, L.; Bischoff, J. L.; Bolmont, D. *Phys. Rev. B* **1988**, *38*, 13113 using XPS; Bischoff, J. L.; Kubler, L.; Bolmont, D.; Sebénne, C. A.; Lacharme, J.-P.; Bonnet, J. E.; Hricovini, K. *Surf. Sci.* **1993**, *293*, 35 using angle-resolved XPS; ref 27 using static secondary ion mass spectroscopy (SSIMS); ref 2 using XPS.
- (11) Bozso, F.; Avouris, Ph. *Phys. Rev. B* **1988**, *38*, 3937 and ref 14 using UPS and XPS.
- (12) Larsson, C. U. S.; Andersson, C. B. M.; Prince, N. P.; Flodström, A. S. *Surf. Sci.* **1992**, *271*, 349.
- (13) Chérif, S. M.; Lacharme, J.-P.; Sebénne, C. A. *Appl. Surf. Sci.* **1992**, *56*, 777. Chérif, S. M.; Lacharme, J.-P.; Sebénne, C. A. *Surf. Sci.* **1991**, *251/252*, 737; **1992**, *262*, 33.
- (14) Hlil, K.; Kubler, L.; Bischoff, J. L.; Bolmont, D. *Phys. Rev. B* **1987**, *35*, 5913.
- (15) Zhou, R. H.; Cao, P. L.; Fu, S. B. *Surf. Sci.* **1991**, *249*, 129.
- (16) Radeke, M. R.; Carter, E. A. *Surf. Sci. Lett.* **1996**, *355*, L289.
- Radeke, M. R.; Carter, E. A. *Phys. Rev. B* **1996**, *54*, 11803.
- (17) Wu, C. J.; Carter, E. A. *Chem. Phys. Lett.* **1991**, *185*, 172. Wu, C. J.; Carter, E. A. *J. Am. Chem. Soc.* **1991**, *113*, 9065. Wu, C. J.; Carter, E. A. *Phys. Rev. B* **1992**, *46*, 4651. Wu, C. J.; Carter, E. A. *Surf. Sci.* **1993**, *295*, 64.
- (18) Wu, C. J.; Carter, E. A.; *Phys. Rev. B* **1992**, *45*, 9065.
- (19) Redondo, Goddard, W. A., III, *J. Vac. Sci. Technol.* **1982**, *21*, 344.
- (20) Wu, C. J.; Ionova, I. V.; Carter, E. A. *Surf. Sci.* **1993**, *295*, 64.
- (21) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. Dunning, T. H., Jr., Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977; p 1.
- (22) Fletcher, *Practical Methods of Optimization*; Wiley: New York, 1987.
- (23) Ionova, I. V.; Carter, E. A.; *J. Chem. Phys.* **1993**, *98*, 6377; **1995**, *103*, 5437.
- (24) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399.
- (25) Siegbahn, E. M. *J. Chem. Phys.* **1980**, *74*, 1647.
- (26) Dupuis, A. Marquez, Davidson, E. R. *HONDO 95.3 from CHEM-Station*; IBM Corporation: Kingston, NY, 1995.
- (27) Zhou, X.-L.; Flores, C. R.; White, J. M. *Surf. Sci. Lett.* **1992**, *268*, L267.
- (28) Landmark, E.; Karlsson, C. J.; Chao, Y.-C.; Uhrberg, R. I. G. *Phys. Rev. Lett.* **1992**, *69*, 1588.
- (29) Moriarty, N. W.; Smith, P. V. *Surf. Sci.* **1992**, *265*, 168.
- (30) Fujisawa, M.; Taguchi, Y.; Kuwahara, Y.; Onchi, M.; Nishijima, M. *Phys. Rev. B* **1989**, *39*, 12918.
- (31) Hamers, R. J.; Avouris, Ph. Bozso, F. *Phys. Rev. Lett.* **1987**, *59*, 2071. Avouris, Ph.; Bozso, F. *J. Vac. Sci. Technol. A* **1988**, *6*, 508.
- (32) Franco, N.; Avila, J.; Davila, M. E.; Asensio, M. C.; Woodruff, D. P.; Schaff, O.; Fernandez, V.; Schindler, K.-M.; Fritzsche, N.; Bradshaw, A. M. *Phys. Rev. Lett.* **1997**, *79*, 673.