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# Adsorbate-induced buckling switch of Si dimers in dissociated phenylamine on Si(001)

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Using first-principles density-functional calculations, we investigate the adsorption structures of phenylamine, $NH_2(C_6H_5)$, on the Si(001) surface. We find that the N atom initially bonds to the down Si atom of the buckled dimer and subsequently, adsorbed $NH_2(C_6H_5)$ dissociates into $NH(C_6H_5)$ and H species. Unlike the case of ammonia where the buckling of Si dimers remains unchanged through ammonia dissociation, we find that the N-H dissociation in adsorbed phenylamine gives rise to the buckling switch of the neighboring Si dimers, thereby inducing a charge polarization in neighboring dimers such that the electrophilic (down-buckled) and nucleophilic (up-buckled) sides are oriented adjacent to the Si-$NH(C_6H_5)$ and Si-H moieties, respectively. This adsorbate-induced buckling switch in dissociated phenylamine is caused by a greater electronegativity of the phenyl group compared to the H atom in dissociated ammonia.

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## I. INTRODUCTION

Current interest for the adsorption of organic molecules on the Si(001) surface relates to proposed integration of organic-nanostructure devices with traditional semiconductor technology.[1–4] To control and design the formation of organic nanostructures on Si(001), it is essentially required to understand the formation mechanism of such hybrid organic-silicon systems. The Si(001) surface exhibits a surface reconstruction consisting of buckled dimers, where a partial charge transfer occurs from the down Si atom to the up Si atom, therefore being partially positively and negatively charged, respectively.[5] Thus, the electrophilic (nucleophilic) side of impinging molecules is more likely to react with the up (down) Si atom. This selective reaction of molecules with the Si(001) surface has been known to determine the adsorption pattern of molecules.[6,7] For example, the initial reaction of ammonia ($NH_3$) with Si(001) takes place via a precursor in which the lone pair of N atom is attracted to the electron-deficient down Si atom [termed the molecular state, see Fig. 1(a)].[7–12] Subsequently, adsorbed $NH_3$ dissociates into $NH_2$ and H species [termed the dissociative state, see Fig. 1(b)].[7–12] Using a combination of infrared-absorption spectroscopy and density-functional cluster calculations, Queeney *et al.*[7] proposed that the dissociated $NH_2$ and H species induce a charge polarization in neighboring dimers such that the nucleophilic (up-buckled) and electrophilic (down-buckled) sides are oriented adjacent to the Si-$NH_2$ and Si-H moieties, respectively, as shown in Fig. 1(b). As a result, another $NH_3$ adsorption is more likely to occur on the down atom of a neighboring dimer, leading to the distribution of dissociated $NH_2$ species with a "zigzag" pattern on alternating opposite sides of Si dimers [see Fig. 1(c)].[7] The preferential appearance of the zigzag adsorption pattern of dissociated $NH_2$ on Si(001) was also observed by a recent scanning tunneling microscopy (STM) measurement.[13] Thus, it is likely that the charge polarization of the Si(001) substrate plays a crucial role in determining the local ordering of adsorbates.

One would expect that the above-mentioned adsorbate-induced charge polarization of the Si(001) substrate may change in the case that one of the hydrogen atoms of $NH_3$ is replaced by a functional group whose electronegativity is greater than that of the H atom. We here report a theoretical investigation of adsorbate-induced charge polarization in dissociated phenylamine, $NH_2(C_6H_5)$, on Si(001). Similar to ammonia, phenylamine molecule initially forms a dative Si-N bond where the lone-pair state of the N atom participates in bonding to the electron-deficient down Si atom. However, unlike ammonia dissociation showing that the buckling of Si dimers remains unchanged, the up- and down-buckled sides of the neighboring Si dimers are found to be reversed through the N-H dissociation of phenylamine. This adsorbate-induced buckling switch of the neighboring Si dimers in dissociated phenylamine can be explained by the reduced Coulomb interaction between the dissociated

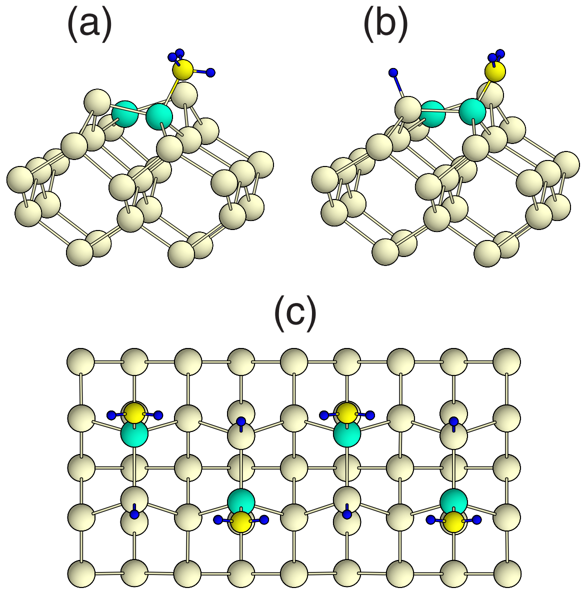

FIG. 1. (Color online) Optimized geometry of adsorbed ammonia on Si(001): (a) the molecular state, (b) the dissociative state, and (c) the full-covered dissociative state. The circles represent Si, N, and H atoms with decreasing size. For distinction, the down Si atoms are drawn in gray.

Si-NH($C_6H_5$) moiety and the down Si atom of neighboring dimers. Such an adsorbate-induced buckling switch generated by the presence of the functional group with a greater electronegativity is found to be more conspicuous in diphenylamine dissociation compared to phenylamine dissociation because of the increase in the number of phenyl rings.

## II. METHODS

The total-energy and force calculations were performed by using first-principles density-functional theory[14,15] within the generalized-gradient approximation. We used the exchange-correlation functional of Perdew *et al.*[16] for the generalized-gradient approximation. The C and N (Si and H) atoms are described by ultrasoft[17] (norm-conversing[18]) pseudopotentials. The surface is modeled by a periodic slab geometry. Each slab contains six Si atomic layers and the bottom Si layer is passivated by two H atoms per Si atom. The thickness of the vacuum region between these slabs is about 14 Å and phenylamine molecules are adsorbed on the unpassivated side of the slab. We employed a $2\times4$ unit cell that involved four dimers along the dimer row. The electronic wave functions were expanded in a plane-wave basis set using a cutoff of 25 Ry and the electron density was obtained from the wave functions at two $k$ points in the surface Brillouin zone of the $2\times4$ unit cell. All the atoms except the bottom two Si layers were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force component were less than 1 mRy/bohr. Our calculation scheme has been successfully applied for the adsorption and reaction of various organic molecules on Si(001).[19]

## III. RESULTS

We first determine the atomic structure of adsorbed phenylamine on the Si(001) surface within the molecular and dissociative states. Each optimized structure is shown in Fig. 2. The calculated adsorption energies ($E_{\text{ads}}$) for the two states are given in Table I, together with the present and previous[7–12] ones for the case of ammonia. We find that the dissociative state has an adsorption energy of 1.85 eV, larger than that ($E_{\text{ads}}=0.91$ eV) of the molecular state. This tendency for the greater stability of the dissociative state compared to the molecular one is similar to the case of ammonia where the molecular (dissociative) state has adsorption energies ranging from 0.94 (1.86) to 1.31 (2.30) eV, see Table I.[8–12] In the molecular state [Fig. 2(a)], phenylamine adsorbs on the down atom of the buckled Si dimer, where the height difference $\Delta h$ of the up and down atoms is 0.44 Å, much reduced compared to $\Delta h=0.73$ Å of the neighboring dimers or $\Delta h=0.77$ Å at a clean Si(001) surface. However, in the dissociative state [Fig. 2(b)] the N-bonded Si atom becomes higher than the H-bonded Si atom by $\Delta h=0.06$ Å, thereby leading to the up-buckled side of the dimer to the Si-NH($C_6H_5$) moiety. In order to reduce the Coulomb interaction between the dissociated Si-NH($C_6H_5$) moiety and the neighboring dimers, the up-buckled sides of the neighboring dimers are oriented opposed to the Si-NH($C_6H_5$) moiety [see Fig. 2(b)]. This alternating buckled-dimer configuration is found to be more stable by $\Delta E_{\text{ads}}=0.10$ eV than its opposite configuration [see Fig. 2(c)] where the up-buckled sides of neighboring dimers are placed on the same side of the Si-NH($C_6H_5$) moiety. Thus, in contrast with ammonia dissociation where the initial alternating buckled-dimer configuration of the Si(001) surface does not change, phenylamine dissociation dramatically changes the buckling configuration of the neighboring Si dimers.

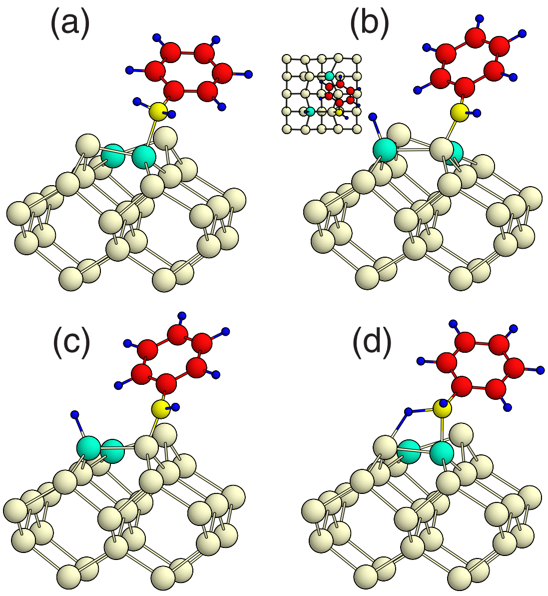

FIG. 2. (Color online) Optimized geometry of adsorbed phenylamine on Si(001): (a) the molecular state, (b) the dissociative state where the up-buckled sides of neighboring dimers are oriented opposed to the Si-NH($C_6H_5$) moiety, (c) the dissociative state where the up-buckled sides of neighboring dimers are placed on the same side of the Si-NH($C_6H_5$) moiety, and (d) the transition state. The inset in (b) shows the top view. The circles represent Si, C, N, and H atoms with decreasing size. For distinction, the down Si atoms are drawn in gray.

It has been well established by a number of experimental works[20–23] that phenylamine on Si(001) chemisorbs dissociatively via cleavage of one N-H bond, retaining the aromatic character after bonding to the surface. To examine the cleavage of the N-H bond, we optimize the structure by using the gradient projection method[24] where only the distance $d_{\text{N-H}}$ between the N atom and the dissociated H atom is constrained. Hellmann-Feynman forces are used for the relaxation of all the atomic positions as well as the N-H bond angles for the constrained N-H distance. In this way, we calculate the minimum-energy pathway of N-H dissociation as a function of increasing distance $d_{\text{N-H}}$. We find that the adsorption energy of the transition state [see Fig. 2(d)] is 0.14 eV, which is 0.77 eV smaller than $E_{\text{ads}}=0.91$ eV of the molecular state, yielding an energy barrier ($E_b$) of 0.77 eV from the molecular to the dissociative state. By using an Arrhenius-type activation process with a typical vibration frequency of $\sim10^{13}$ Hz for the pre-exponential factor, we estimate that at a temperature of 300 K the reaction rate for the N-H dissociation is $\sim1.2\ \text{s}^{-1}$. We note that at room temperature the dynamic flipping motion of buckled Si dimers is facile.[25] Therefore, we also calculate the energy barrier for

TABLE I. Calculated adsorption energies (in eV/molecule) for the molecular and dissociative states of adsorbed ammonia, phenylamine, and diphenylamine on Si(001). The height difference (in Å) between the H-bonded and N-bonded Si atoms in each dissociative state is also given.

| | Molecular state | Dissociative state | $\Delta h$ |
|---|---|---|---|
| Ammonia | 1.20 (1.13[a], 0.94[b], 1.21[c], 1.31[d]) | 1.86 (2.21[a], 2.30[b], 1.99[c], 2.06[d]) | −0.03 (−0.04 [e]) |
| Phenylamine | 0.91 | 1.85 | 0.06 |
| Diphenylamine | 0.38 | 1.50 | 0.10 |

[a] Reference 8.
[b] Reference 9.
[c] Reference 10.
[d] Reference 11.
[e] Reference 12.

the N-H dissociation from the molecular state in which the orientation of neighboring dimers is flipped before dissociation. For this, we obtain $E_b = 0.67$ eV, giving rise to a reaction rate of $\sim 85\ \mathrm{s}^{-1}$ at 300 K. These results indicate that phenylamine dissociation is feasible at room temperature, consistent with the experimental measurements[20–23] of N-H dissociation at room temperature.

In Table I, we find the height difference $\Delta h$ of the up and down atoms within the reacted Si dimer for dissociated ammonia [Fig. 1(b)] and phenylamine [Fig. 2(b)]. The values of $\Delta h$ for the two cases are −0.03 and 0.06 Å, respectively. Here, the negative (positive) sign indicates that the N-bonded Si atom is lower (higher) than the H-bonded Si atom. This height difference may exhibit the different charge characters of the reacted dimer. As shown in Figs. 3(a) and 3(b), there is somewhat different charge polarity of the dimer bond between dissociated ammonia and phenylamine. In dissociated ammonia, a positive charge polarity exists on the N-bonded Si atom whereas in dissociated phenylamine, the charge polarity on the N-bonded Si atom is reversed to be slightly negative. We note that, in the case that the buckling of neighboring dimers changes as in Fig. 2(c), the slightly up-buckled side (with $\Delta h = 0.05$ Å) of the reacted dimer is located on the Si-NH($C_6H_5$) moiety. Thus, we can say that in dissociated phenylamine, the slightly up(down)-buckled side of the reacted dimer is always located on the Si-NH($C_6H_5$) (Si-H) moiety, independent of the buckling configuration of neighboring dimers.

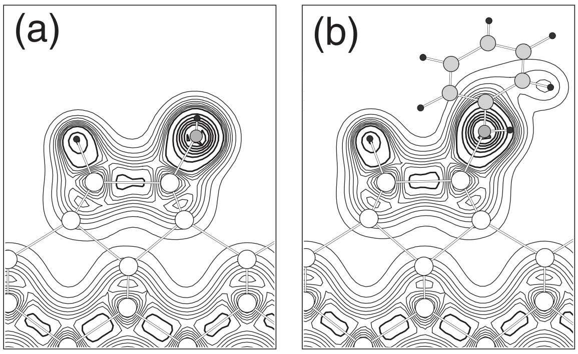

FIG. 3. Calculated charge densities for dissociated (a) ammonia [Fig. 1(b)] and (b) phenylamine [Fig. 2(b)]. The first thin line is at 7.5 millielectron/bohr$^3$ with spacings of 7.5 millielectron/bohr$^3$ and the first thick line is at 75 millielectron/bohr$^3$ with a spacing of 75 millielectron/bohr$^3$ between thick lines. The plots are drawn in a vertical plane containing the Si dimer.

On the basis of our findings, the buckling configuration of the reacted and neighboring dimers can be influenced by the functional groups of adsorbate molecules. We note that the phenyl group in the dissociated NH($C_6H_5$) species has a greater electronegativity compared to the H atom in the dissociated $NH_2$ species. Hence, the former species pull the electrons from the N-bonded Si atom, thereby giving rise to the buckling switch of the neighboring dimers to reduce the Coulomb interaction between the dissociated Si-NH($C_6H_5$) moiety and the neighboring dimers.

It is noteworthy in dissociated phenylamine that the down Si atom of neighboring dimers is located in the same side of the dissociated Si-NH($C_6H_5$) moiety [see Fig. 2(b)]. Therefore, if another phenylamine adsorbs on neighboring dimers, it is more likely to occur on the same side of the dissociated NH($C_6H_5$) species. In this sense, the dissociated NH($C_6H_5$) species would not exhibit the zigzag pattern [see Fig. 1(c)] as observed[7,13] in ammonia dissociation on Si(001). According to the STM measurement of Rummel and Ziegler,[22] the dissociated NH($C_6H_5$) species were observed to occupy every other Si dimer along the dimer row, indicating that the saturation coverage of phenylamine would be 0.5 monolayer, i.e., one molecule per two Si dimers. To explain this saturation coverage, they suggested that one-monolayer coverage would not be realizable because of a steric hindrance of adsorbed molecules.[22] As shown in the inset of Fig. 2(b), the dissociated phenylamine reaches laterally to the neighboring dimer. This geometrical feature of dissociated phenylamine possibly blocks a subsequent adsorption on a dimer adjacent to a dissociation site, consistent with the STM data of Rummel and Ziegler.[22]

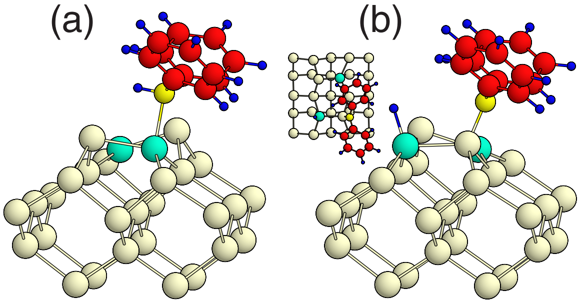

FIG. 4. (Color online) Optimized geometry of adsorbed diphenylamine on Si(001): (a) the molecular state and (b) the dissociative state. The inset in (b) shows the top view. The circles represent Si, C, N, and H atoms with decreasing size. For distinction, the down Si atoms are drawn in gray.

In addition, we examine the adsorbate-induced buckling switch in dissociated diphenylamine, $NH(C_6H_5)_2$, on Si(001). We find that the molecular [Fig. 4(a)] and dissociative [Fig. 4(b)] states of adsorbed diphenylamine have adsorption energies of 0.38 and 1.50 eV, respectively, smaller than the corresponding ones (0.91 and 1.85 eV) of adsorbed phenylamine. This indicates that the bonding of diphenylamine to the surface is weaker than that of phenylamine. However, similar to phenylamine dissociation, diphenylamine dissociation reverses the buckling configuration of the neighboring Si dimers [see Fig. 4(b)]. In the molecular state, the N-bonded Si atom lies 0.36 Å below the up Si atom bonding to it but in the dissociative state, it becomes higher than the H-bonded Si atom by $\Delta h = 0.10$ Å. It is noticeable that this value of $\Delta h$ in dissociated diphenylamine is greater than that (0.06 Å) in dissociated phenylamine, indicating an enhanced adsorbate-induced buckling in diphenylamine dissociation because of the increase in the number of phenyl rings.

## IV. SUMMARY

We have performed first-principles density-functional calculations for the adsorption structures of phenylamine on the Si(001) surface. Our calculations predicted that the dissociation of phenylamine reverses the buckling configuration of the neighboring Si dimers. This adsorbate-induced buckling switch of the neighboring Si dimers in dissociated phenylamine can be explained in terms of the reduced Coulomb interaction between the dissociated Si-$NH(C_6H_5)$ moiety and the neighboring dimers.

## ACKNOWLEDGMENTS

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