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Adsorption of nitric oxide on the Si(100)2 × 1 surface: A theoretical and experimental approach

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This paper describes a study concerning the interaction of nitric oxide with the clean Si(100)2 × 1 surface at room temperature. Differential reflectometry in the photon energy range of 2.4–4.4 eV, Auger electron spectroscopy ($KL_{2,3}L_{2,3}$ and $L_{2,3}VV$), and low-energy electron diffraction have been used to investigate experimentally the chemisorption process of NO on the freshly cleaned Si(100)2 × 1 surface. Theoretically, the chemisorption process has been modeled by means of the use of quantum-chemical calculation methods [modified (intermediate) neglect of diatomic overlap, MNDO and MINDO/3]. Within this framework we have calculated the binding energy of several possible adsorption sites and the partial local density of states. The latter has been utilized to simulate the loss-corrected Si $-L_{2,3}VV$ Auger line shape, in the derivative mode, which proved to be a powerful tool for the interpretation of the newly revealed fine structure. The low nitrogen and oxygen coverages (15% of a monolayer) at saturation could be explained by lateral electrostatic repulsion. Also, evidence for molecular adsorption of NO on the Si(100)2 × 1 surface at 300 K has been found. Furthermore, the possibility that a missing-dimer defect could play a role in the adsorption process has been considered.

I. INTRODUCTION

Silicon surfaces are very important as interfaces in electronic devices. The development of complex integrated circuits in the semiconductor industry requires reduction of their dimensions, and the dimensions have become comparable with several fundamental scaling lengths (e.g., the Debye screening length, the diffusion length, and the deBroglie wavelength).[1,2]

In the last few years investigators have become more aware of the special role of structural defects in the characteristic behavior of the surface. Scanning-tunneling-microscopy (STM) investigations of the structure of silicon surfaces gave rise to significant progress in the understanding of the silicon surface, in particular of structural defects on the silicon surfaces.[2,3] Interaction of gases with structural defects may be of considerable interest not only from a scientific point of view but also with respect to technological applications.

In this paper we present a study of the adsorption of NO on the freshly cleaned Si(100)2 × 1 surface, and the role of missing-dimer defects in this process at 300 K. By analyzing the electronic structure of the 2 × 1 reconstructed Si(100) surface and of the NO molecule in combination with quantum-chemical calculations, we were able to describe the adsorption of NO on the Si(100)2 × 1 surface.

In this study nitric oxide has been used as adsorbate, because of the relative simple constitution of the molecule. From the geometric and electronic structure of the Si(100)2 × 1 surface, obtained from experimental results and utilizing quantum-chemical calculations, we suggest that the low coverage of NO chemisorbed on the silicon surface at 300 K, found in experimental results discussed in this paper, is not due to adsorption on missing-dimer defects only. The adsorption of NO predominantly on missing-dimer defects as a consequence of use of the Woodward-Hoffmann rules (WHR) appeared to be not fully correct.[4–6] This is because the model is inadequate to explain the chemical bonding, when effects such as electrostatic interaction and core-core repulsion cannot be neglected. These effects play a dominant role in the adsorption process of NO on the Si(100) surface, as revealed by the quantum-chemical calculations. To our knowledge, this is the first report on the interaction of NO on the Si(100)2 × 1 surface at room temperature, which includes surface defects like missing-dimer defects in theoretical calculations.

The solid-gas interaction has been studied in ultrahigh vacuum (UHV), at 300 K, by Auger-electron spectroscopy (AES), low-energy electron diffraction (LEED), and differential reflectometry (DR). First, with AES (KLL) a quantitative analysis was made of the different types of atoms present in the surface region. The local chemical environment of the NO molecule bonded to the reconstructed silicon surface was analyzed by Si $L_{2,3}VV$ Auger-electron spectroscopy. Second, with LEED one is able to detect the structure of the surface of the sample and its possible changes upon adsorption. Third, with DR *in situ* information about the electronic structure of the surface can be obtained.[7–9] If the wavelength and intensity of the light beam are properly chosen, DR is essential a nonperturbing probe of the adsorption process. In view of recent photoemission results,[10,11] which indicate the existence of a surface state at 2.5 eV below the Fermi energy, E_F, we have performed the reflection experiments in the photon range 2.4–4.4 eV. In Sec. II we present the experimental results. The theoretical calculations are presented in Sec. III. The results of the experiments and calculations will be discussed in Sec. IV. At the end of this paper some concluding remarks will be given.

II. EXPERIMENTAL RESULTS

A. Introduction

In this subsection the experimental results are summarized. Each measurement was repeated several times and showed good reproducibility. The measurements are categorized after the techniques used in this investigation: LEED, AES, and DR. Several measurements were performed to get insight into the adsorption behavior of NO on silicon, such as varying the exposure as a function of pressure and time. In addition, adsorption measurements were done with the surface heated to 550 K. However, our main objective is to describe the adsorption behavior of NO on a Si(100)2×1 reconstructed surface at 300 K.

B. Differential-reflectometry results

Two types of reflectometry measurements have been performed, time dependent at constant photon energy ($h\nu$), and wavelength dependent.

The time-dependent measurements made it possible to study *in situ* the dynamical behavior of the adsorption of NO on the silicon surface. The wavelengths have been tuned to the surface-state transitions of the clean Si(100)2×1 reconstructed surface (Table I). The chemisorption of NO on the surface induces surface-state shifts, and peaks will be seen in the dR/R signal.

From Fig. 1 we can calculate the initial sticking probability, $S(\Theta)$, with $\Theta=0$ (Θ is the NO coverage) assuming a proportional relation between the dR/R signal and the number of surface states which have disappeared:[6–9]

$$dR/R \propto d\Theta/dt = S(\Theta)p\nu/N_0 \ , \qquad (1)$$

where ν is a frequency factor ($=2.56\times10^{20}$ $\mathrm{cm^{-2}\,s^{-1}\,Torr^{-1}}$). N_0 is the number of adsorption sites available to NO on the Si(100) surface [$=14\%$ of 6.78×10^{14} $\mathrm{cm^{-2}}$ (Ref. 12)], $p=3.3\times10^{-8}$ Torr, and t is the time in seconds. For all experiments listed in Table I (where some characteristics are given) the initial sticking probability is about 0.8. The value of the sticking coefficient is merely an estimation, because of the uncertainty of the number of adsorption sites available for the NO molecule. It indicates only that this chemisorption process is rapid, suggesting a high chemical reactivity.

TABLE I. Surface-state transitions.

Wavelength (nm)	Energy (eV)	Bond associated with
316	3.93	filled dimer, 2nd layer[a]
323	3.85	filled dimer, 1st layer[b]
355	3.50	*B*-type dimer[a]
428	2.90	filled dangling bond[b]

[a] Reference 4.

[b] Reference 7.

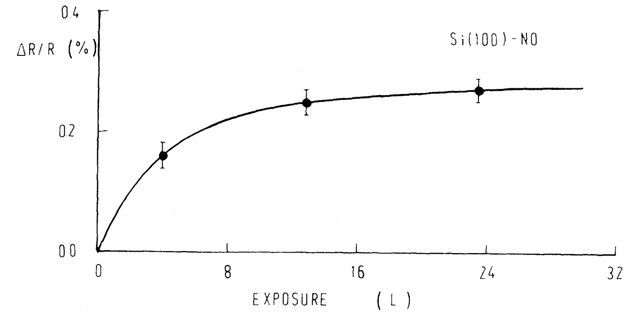

FIG. 1. Relative initial change in reflectivity vs NO exposure at $h\nu=3.93$ eV at room temperature. The pressure during the exposure was 3.3×10^{-8} Torr.

Some important features involved in these measurements are the following.

(1) No pressure dependence in the range $1.0\times10^{-5}\leq p\leq1.0\times10^{-7}$ Torr at a constant exposure (2500 L where 1 L$=10^{-6}$ Torr s) (see Fig. 2., dashed line). The sample is saturated at a pressure of 3.4×10^{-6} Torr within a few seconds. However, a very weak pressure dependence can be seen at low pressures ($1.0\times10^{-8}\leq p\leq1.0\times10^{-7}$ Torr) (see Fig. 2, solid line).

(2) No dependence of exposure (L) at a constant pressure $p=3.4\times10^{-6}$ Torr in the range of 200 exposure $\leq2.0\times10^{6}$ L.

(3) For exposures at very high pressures ($p>1.0\times10^{-4}$ Torr) new phenomena occur which may be attributed to adsorbate-adsorbate interaction.

(4) The height of the dR/R signal recorded at the wavelength used (Table I) strongly depends on the quality of the cleaning procedure. The concentration of NO on a "sputtered-only" surface was approximately twice as high as on a sputtered and annealed surface.

(5) dR/R measurements tuned to the wavelength of the optical transition which probes the second-layer di-

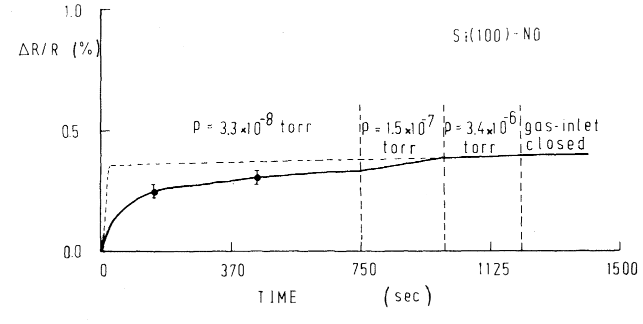

FIG. 2. Relative change in reflectivity vs NO exposure at $h\nu=3.93$ eV and at room temperature with varying pressure values during time as indicated. Influence of the exposure at very low pressures on the time-dependent dR/R signal is depicted by the solid line. The corresponding pressures are listed in the figure. For pressures between 1.0×10^{-5} and 1.0×10^{-7} Torr no dependence on the pressure is observed (dashed line).

mers show a small increase of the signal (0.04%) after the initial adsorption for about 1 h after the evacuation of the vacuum chamber. This suggests that two characteristic time constants could be involved at this wavelength.

(6) The initial behavior of the dR/R signal is the same for all wavelengths used in the time-dependent measurements.

The wavelength-dependent measurements are shown in Fig. 3. These measurements show the relative difference in reflectivity, dR/R, as a function of the photon energy before and after exposing a clean Si(100) surface to NO. This spectrum is the average of four independent measurements. We see a peak at 3.93 eV. We also observe a significant asymmetrical shoulder at 3.4–3.65 eV. An interesting fine structure can be observed in the lower-energy part of the spectrum. This structure is reported in an earlier paper,[13] but was not recognized as fine structure.

C. AES and LEED results

We used AES ($KL_{2,3}L_{2,3}$ and $L_{2,3}VV$) measurements to detect the amount of N and O adsorbed, either molecular or (partly) dissociated on the silicon surface and to obtain information about the chemical bonding after an exposure of 2500 L. Using the qualitative method described by Ref. 12, we obtained a coverage of 7±1 % oxygen and 7±1 % nitrogen. Upon adsorption at a sample temperature of 550 K the concentration of nitrogen increases to 12%, whereas the oxygen concentration remains the same at 7%. If the sample is heated to 1100 K after adsorption, nitrogen is detected in the same amount as before heating; no oxygen is detected after heating.

Relevant information concerning the chemical bonding can be extracted from the Si $L_{2,3}VV$ Auger spectra in the range 40–85 eV.[7] In this energy range of emerging electrons the information depth is about 2 atomic layers.[12] Recently, it has been shown that careful measurements of the Si $L_{2,3}VV$ Auger spectra in this energy range can lead to more definite conclusions about the binding state of an element adsorbed on the silicon surface.[7,14,15] By analyzing the loss-corrected Auger line shape in the derivative mode, $dA(E)/dE$, additional features can be revealed, which are directly comparable with quantum-chemical calculations.[16]

The $L_{2,3}VV$ Auger spectra between 40 and 85 eV of the several adsorption experiments are shown in Fig. 4. The $L_{2,3}VV$ spectrum of a freshly cleaned silicon surface is shown in Fig. 4(a). We could resolve peaks at 43, 54, 74, 81, and 91.8 eV. The 91.8 eV is not shown in Fig. 4.

Figure 4(b) shows the spectrum for NO adsorption at 300 K on Si(100). When the pressure is kept constant (3.4×10^{-6} Torr) we obtain similar Si $L_{2,3}VV$ Auger spectra for exposures between 2.0×10^{2} and 2.0×10^{4} L. The main peak at 91 eV is shifted downwards by 1 eV. Because of adsorption of NO at the silicon surface new peaks are observed at 62 and 83 eV.

When the sample, heated at 550 K, was exposed to 2.0×10^{3} L NO [Fig. 4(c)], the same peaks were observed as in Fig. 4(b), as well as a new peak at 69 eV.

After having exposed the sample to NO at 550 K, the sample was heated to 1100 K. The Auger transition at 69 eV disappeared, but other transitions still could be observed [Fig. 4(d)].

LEED measurements are only used as a "fingerprint" technique. The results are as follows. After NO exposure (300 K) the LEED 2×1 two-domain structure has not changed (apart from a very small increase of the background relative to the 2×1 two-domain spots of the LEED pattern of the atomically clean Si(100) surface). Twelve hours after adsorption had taken place still no changes were observed. The LEED pattern did not change either when the sample was heated to 1100 K after adsorption.

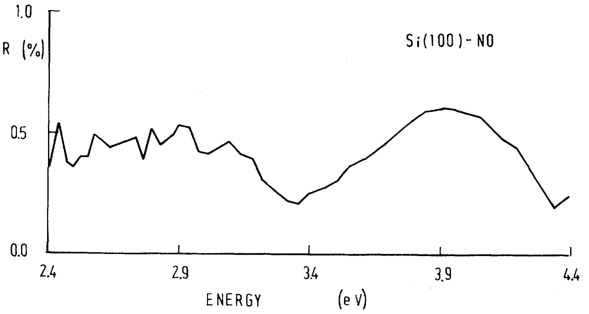

FIG. 3. Relative change in reflectivity vs $h\nu$ before and after exposing a clean Si(100)2×1 reconstructed surface to 1000 L NO. The pressure during exposure is 3.4×10^{-6} Torr.

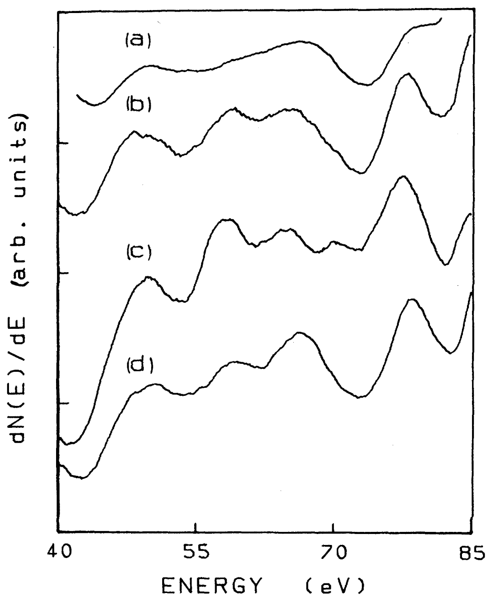

FIG. 4. Si $L_{2,3}VV$ spectra of (a) clean Si(100); (b) Si(100) exposed to 2.0×10^{3} L NO at 300 K; (c) Si(100) exposed to 2.0×10^{3} L NO at 550 K; (d) Si(100) surface in (c) followed by heating to 1100 K.

III. THEORETICAL CALCULATIONS

A. Introduction

The linear-combination-of-atomic-orbitals molecular-orbital (LCAO-MO) theory and its applications to molecules are well known.[15] For our partial LDOS calculations we have adapted the semiempirical quantum-chemical method MINDO/3 (modified intermediate neglect of diatomic orbitals).[16,17] The bonding energy and geometry are obtained with the modified neglect of diatomic orbitals (MNDO) scheme. This scheme has been proven to be superior to MINDO/3 with respect to bonding energies and bonding configuration.[17]

In our calculation method the Si(100)2×1 reconstructed surface is represented by finite clusters. For the subsurface atoms the ideal bulk geometry of silicon (i.e., $d_{\text{Si-Si}} = 2.35$ Å, and tetrahedral angles) has been used, whereas the surface atoms are subject to an asymmetric 2×1 reconstruction[18,19] as used by Kunjunny and Ferry.[20]

To avoid the generation of fictitious surface states, which could interact with the real surface states, thus severely affecting the final results,[21] we used hydrogen atoms to terminate the silicon substrate and obtain boundary conditions of sufficient quality. The value attributed to the Si—H bond length has been the subject of debate.[21,22] We have adapted the value $d_{\text{Si-H}} = 1.41$ Å recently found by Estreicher.[22]

For the nitric oxide adsorption we used the $Si_{22}H_{18}(NO)$ and the $Si_{20}H_{18}(NO)$ clusters (see Fig. 5). The latter is used to model the chemisorption of the NO molecule on a missing-dimer defect (dimer in the second layer). Furthermore, smaller clusters were used to assure convergence of the results as a function of the cluster size.

B. Bonding energies and geometry: MNDO

Analogous to chemisorption of O_2 on the Si(100) surface,[17] we studied three possible molecular adsorption sites: (a) on top of a dangling bond; (b) in a bridge position with the N and O atoms bonded to the silicon dimer atoms; (c) in a bridge position with the N atom bonded to the dimer and with the O atom dangling (see Fig. 6).

After the geometry has been optimized, we calculate the binding energies using the same procedure as described by Barone.[17] All calculations were performed within the framework of the restricted Hartree-Fock (RHF) method, because of the large clusters needed for modeling the adsorption process. We have assumed that the error in the binding energy within the RHF scheme at larger clusters will be constant. This assumption has been checked for several clusters of different sizes and the error appeared to be of the same order as the accuracy of the MNDO method (±0.5 eV for the binding energies).

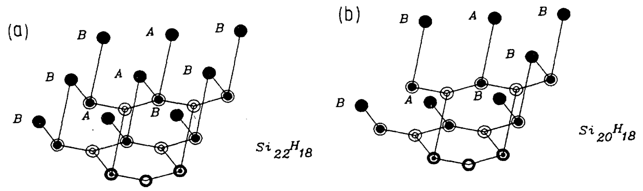

FIG. 5. (a) The $Si_{22}H_{18}$ cluster. (b) The $Si_{20}H_{18}$ cluster. The silicon atoms symbolized the same way are constituted in the same plane. The unsaturated states below the first layer are saturated with hydrogen atoms and are not drawn for convenience.

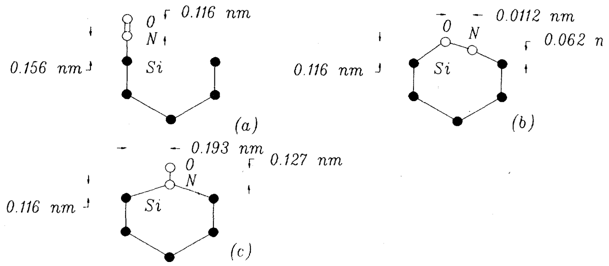

FIG. 6. Equilibrium geometries for NO on Si(100)2×1: (a) on top; (b) and (c) in a bridges configuration.

Chemisorption on the dimer in a bridge position with the nitrogen atom only bonded to this dimer appeared to be most stable. The results are listed in Table II.

Next, the calculations for NO on the stable site [Fig. 5(b)] are performed for larger clusters (see Table III). The binding energy increases with the cluster size. This phenomenon is yet not fully understood and is under investigation. By increasing cluster size we found also the same trend for oxygen using Barone's[17] model. The net charge transfer is larger than in the case of atomic O chemisorbed on a localized site of the Si(100) surface.

We also calculated the binding energies in the case of dissociation of the NO molecule. In all cases we found high energy barriers and therefore dissociation is not likely to occur, which is consistent with earlier experimental results.[6,12]

C. PLDOS of the silicon atom bonded to the NO molecule

In Fig. 7 we depict the partial (LDOS) calculations of Si (NO) on a first- and second-layer dimer, respectively. To our knowledge there exist no previous valence-band DOS calculations of the Si/NO interface, and thus we cannot make any comparison with results reported by others.

TABLE II. Bonding energies (ΔE) in eV and net charges on N (q_N) and O (q_O) for molecular adsorption of NO on the Si(100) surface for different sites.

Site	ΔE (eV)	q_N ($\lvert e \rvert$)	q_O ($\lvert e \rvert$)
on top[a]	0.26	−0.08	−0.14
bridge [Fig. 6(b)]	−1.92	−0.66	−0.23
bridge [Fig. 6(c)]	1.01	−0.77	−0.32

[a]This is not an equilibrium value, as the optimization failed.

TABLE III. Bonding energies (ΔE) in eV and net charges on N (q_N) and O (q_O) for molecular adsorption of NO on the Si(100) surface at the most stable site [Fig. 6(b)] for different cluster size.

Cluster (RHF)	ΔE (eV)	q_N ($\lvert e \rvert$)	q_O ($\lvert e \rvert$)
Si_9H_{12}	−1.92	−0.66	−0.23
$Si_{13}H_{12}$	−2.48	−0.71	−0.26
$Si_{22}H_{18}$	−3.83	−0.76	−0.40

IV. DISCUSSION OF THE RESULTS

A. DR

In this section we will try to explain the experimental and calculated results presented in the preceding section. The peaks in the reflectivity spectrum (Fig. 3) can be interpreted as surface-state transitions from a filled surface state to an empty one. Keim *et al.*[7] showed that their phenomenological interpretation of the DR spectra, neglecting other kinds of optical excitations, is very useful to obtain information about the reactivity of the dangling and dimer bonds on the Si(100)2×1 reconstructed surface. Their interpretation is based on the existence of surface states at about 2.5 eV below the Fermy energy, E_F. This existence is confirmed by theoretical calculations and experimental results.[10,23] These states are identified with filled-dimer-bond surface state. Keim *et al.*[7] interpreted the peak at 3.85 eV as a surface transition from a filled dimer bond to an empty dimer bond at about 1.5 eV above E_F. This dimer bond is geometrically situated at the first surface layer. Therefore, we suggest that the peak at 3.93 eV in Fig. 3 can be attributed to a dimer-bond surface-state transition. The shift of 0.08 eV from 3.85 to 3.93 eV can be explained as due to the different surface potential, because the charge transfer from the silicon surface to the adsorbate is larger than for SiO. Furthermore, this shift may also be explained by adsorption on the second-layer dimer, because of its dispersion due to a different bonding of the dimer in the second layer.

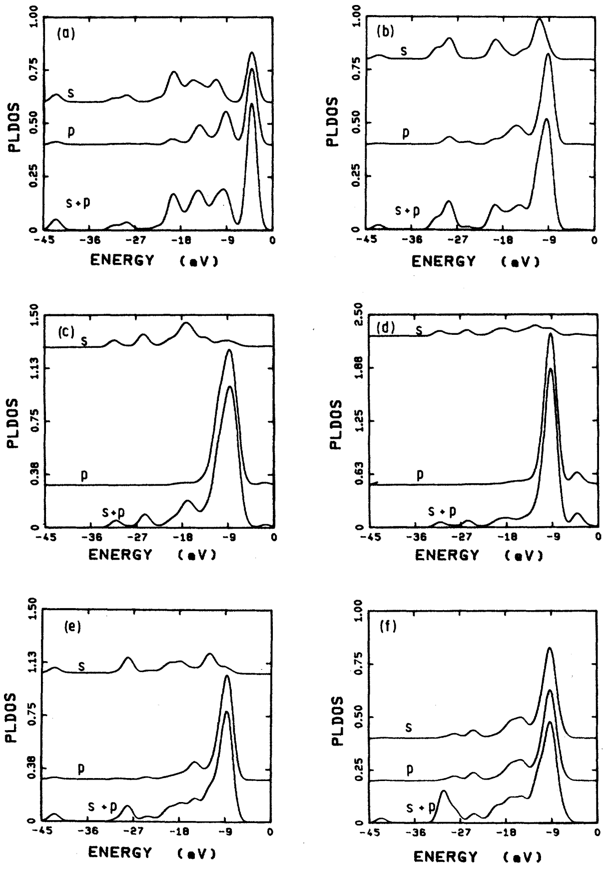

FIG. 7. The partial LDOS of the silicon atoms coordinated to the NO molecule in the first-layer dimer. (a) up atom; (b) down atom; (c) backbond connected to the up atom; (d) backbond connected to the down atom. (e) and (f) the partial LDOS of the silicon atoms coordinated to the NO molecule in the second-layer dimer. The vacuum energy is taken as zero.

The pronounced shoulder (the asymmetric part of the peak) at the lower-energy side of the spectrum is believed to be caused by adsorption on dimer states also (e.g., first- and second-layer dimers and dimers near steps of type *B*). This suggestion is supported by two arguments. (i) The dimer connected to a step of type *B* and a dimer in the first layer will have weaker binding with NO than a second-layer dimer, due to core-core repulsion of the first-layer silicon atoms. (ii) The initial sticking probability of the main peak and the shoulder are the same. The same kind of initial chemical bonding is expected.

At the lower-energy side of the spectrum we observe an offset with some fine structure. The absence of a distinct peak at 2.9 eV strongly suggests that no dangling bonds are involved in the chemisorption process. Mixing of bulk bands with the dangling bond is not likely, because of the lack of geometrical overlap of the electronic structure of a dangling bond with a bulk state.

The fine structure observed must be due to a different kind of optical excitation mechanism. The observation of the same initial sticking probability for photon energies related to this fine structure assumes a relation with the dimer adsorption. The fine structure is also observed for molecular oxygen adsorbed on Si(111)7×7 at 300 K, but not on Ge(111).[13] This phenomenon is under investigation by members of our group.

Furthermore, the high sticking probability (0.8) in combination with a relatively exposure- and pressure-independent adsorption suggest a chemical reaction with almost no energy barrier involved.

B. AES (*KLL*) and LEED

The concentration of N and O on the Si(100)2×1 after room-temperature adsorption of NO is 7±1% of the number of atoms of one monolayer for both atoms. This concentration did not change over a large exposure-pressure variation at a constant exposure of 2500 L nor with exposure variation at a constant pressure of 3.4×10^{-6} Torr. From these results we cannot conclude if NO, at 300 K, is adsorbed molecularly or (partly) dissociatively on the silicon surface. When adsorption occurs at a sample temperature of 550 K the concentration of nitrogen increases at 12%, while that of oxygen remains constant (7%), which is an indication of partial dissociation. Upon heating the sample after adsorption to 1100 K only nitrogen is detected, in the same amount as before heating. The disappearance of oxygen adsorbed either molecularly or atomically from the surface at high temperatures ($T > 950$ K) is well established as SiO etching.[23,24] The very low concentration of N and O on the surface at 300 K suggests that dangling bonds and first-layer dimers are not fully active as adsorption sites.

C. AES (*LVV*)

The Si $L_{2,3}VV$ Auger spectrum of a freshly cleaned silicon surface [Fig. 4(a)] shows well-resolved peaks at 43, 54, 74, 81, and 91.8 eV. The peaks at 81 and 91.8 eV are associated with real $L_{2,3}VV$ Auger transitions.[25] The 91.8-eV peak is called the Si main peak for the Si—Si bond. The peak at 74 eV is the first plasmon-loss peak of the main peak.[26-28] It is suggested that the 54-eV peak is the second-order plasmon-loss peak of the main peak,[25,28] but this is not generally accepted.[26] The Coster-Kronig transition ($L_1L_{2,3}V$) can be related to the peak at 43 eV.[25]

Figure 4(b) shows the spectrum for NO adsorption at 300 K on Si(100). When the pressure is kept constant (3.4×10^{-6} Torr) we obtained similar Si $L_{2,3}VV$ Auger spectra for exposures between 2.0×10^2 and 2.0×10^4 L. The main peak at 91.8 eV is shifted downwards by 1 eV. Due to adsorption of NO at a silicon surface new peaks are observed at 62 and 83 eV. The 83-eV peak as well as the 62-eV peak is well known in $L_{2,3}VV$ Auger measurements of nitridation on the Si(111) surface,[29-32] however, the Si $L_{2,3}VV$ Auger transition at 83 and 62 eV can also be assigned to the Si—O bond.[7] The broadening of the Auger transition at 83 eV in Fig. 4(b), relative to Fig. 4(c), suggests that two adjacent peaks are involved. This can be attributed to different chemical compounds of Si-N in Fig. 4(b) (first- or second-layer adsorption) or to adsorption of oxygen due to partial dissociation of NO at step edges or defects, which appear to be rather active chemically.[33,34] Also, the influence of the primary electron beam can cause partial dissociation of the NO molecule and can be responsible for the slight distortion of the Auger line shape at 83 eV. Therefore, we believe that, at 300 K, both bonds could contribute to the 62-eV peak as well as to the 83-eV peak. The low coverage of nitrogen and oxygen on the silicon surface and the high reactivity of atomic nitrogen and oxygen make an overall dissociation of NO unlikely. Although we cannot exclude a contribution of Si—O bonds, we believe that these bonds play a minor role in the adsorption process and that the chemisorption process is predominantly molecular.

When the sample, heated at 550 K, was exposed to 2.0×10^3 L NO [Fig. 4(c)], the same peaks were observed as in Fig. 4(b), but also a new peak emerges at 69 eV. In Ref. 7 and references therein, it was argued that this peak can be associated with the forming of a more bulklike oxide. This bulklike oxide can be formed, after dissociation of the NO molecule, by diffusion of atomic oxygen through the surface layer.[35,36] The absence of the Auger transition at 69 eV in the $L_{2,3}VV$ spectrum at 300 K [Fig. 4(b)] suggests, therefore, molecular adsorption of NO. That dissociation may occur is also consistent with the *KLL* Auger measurements, which yield a concentration of the 12±1% nitrogen and 7±1% oxygen on the silicon surface. These percentages agree with the results of Wiggins *et al.*[37] for the Si(111) surface. The difference in the oxygen and nitrogen concentrations on the surface can be explained by the increase of the thermal energy of the system through heating of the silicon sample, when new adsorption sites become available due to desorption of SiO.[37]

After exposing the sample to NO at 550 K, the sample was heated to 1100 K. The Auger transition at 69 eV disappeared, but other peaks still could be observed [Fig. 4(d)]. No oxygen could be detected with Auger *KLL* measurements. The amount of nitrogen (12%) remained the same. These peaks can be completely attributed to Si—N bonds, because of the desorption of oxygen as SiO.[37] The broadening of the 83-eV peak in Fig. 4(d) became significantly smaller than curve (b) of Fig. 4, which supports the suggestion of the existence of two adjacent peaks at 83 eV at 300 K. The slope of the curve in the lower-energy part of the Si $L_{2,3}VV$ Auger spectra increases after adsorption of NO. An enlargement of the secondary background is responsible for this phenomenon.[12] The difference in the background between the clean silicon surface and the silicon surface after adsorption of NO can be explained by the change in the surface potential due to the chemisorption of NO molecules.[28] This observation is consistent with the calculations, which show a significant charge transfer to the adsorbate (Table III).

Correction for the secondary background in Figs. 4(b) and 4(d) leads to almost similar spectra, only the shape of the 83-eV peak being slightly different. The observation is consistent with the proposed adsorption site on top, with only the nitrogen atom bonded to the silicon atoms of a first- or second-layer dimer, and supports the suggestion of molecular adsorption.

The Auger transitions, at 54 and 74 eV which appear in all spectra of Fig. 4 are not well understood yet. The 74-eV peak can be associated with first-order plasmon loss, but the difference in its shape could be a sign that Si—N bonds as well as Si—O bonds are involved in this transition also.

In summary, we conclude that at room temperature NO is adsorbed as a molecule at the Si(100)2×1 surface. Furthermore, it is argued that the broader Auger transition at 83 eV, at 300 K, may be composed of more than one peak. Dissociation of the NO molecule is observed during adsorption when the sample is heated to 500 K.

D. Binding-energy calculations

In this subsection we discuss the results for the binding energies and equilibrium geometries for NO on the Si(100) surface for different adsorption sites. We tested our MNDO program by reproducing the results of

Barone[17] in the case of adsorption of atomic oxygen on the silicon (100) surface. Note that we compare the total energy of the substrate plus adsorbate with the total energy of a reconstructed surface plus an adsorbate in the gaseous molecular state at infinity. A negative binding energy means that the bond is stable.

For the calculation of the adsorption of NO on the silicon surface we have distinguished adsorption at the first and second layers (missing-dimer defects).

The results for the first-layer adsorption are listed in Tables II and III. We found the bridge site of Fig. 6(c) to be stable. The value of the binding energy is approximately twice as small as in the case of adsorption of molecular oxygen.[16,17] Furthermore, we found that the electron affinity of the NO molecule is rather large compared to that of the oxygen molecule adsorbed on the same site and in the same configuration.[16,17] This results in a highly ionic site at the surface, which will be subject to electrostatic lateral repulsion with next-neighbor adsorption sites. First-order estimation of this lateral electrostatic interaction for two chemisorbed NO molecules, equal to a coverage of approximately 25% of the surface dimers, reveals an energy which is of the same order as the binding energy of the NO molecule to the silicon surface. Although we cannot neglect local space-charge screening[38] as a possible explanation, we believe that this electrostatic repulsion is responsible for the experimentally observed low coverage of nitrogen and oxygen on the Si(100) surface.

The results of the calculation of the adsorption of the NO molecule on the second layer at a missing-dimer defect are listed in Table IV. A perspective view of the important adsorption sites within the $Si_{20}H_{18}$ cluster is found in Fig. 8. We found, similar to the adsorption at the first-layer dimer, that adsorption on top with the nitrogen atom bonded to the silicon atoms (sites II–IV) is stable. However, the most stable configuration (site IV) is tilted by 45° to the normal of the silicon surface. This tilting is caused by an asymmetrical core-core repulsion of the silicon atoms at the first atomic layer, because a missing-dimer defect consists of two dimers at the second layer and only one is subject to chemisorption. This chemisorbed NO molecule is situated asymmetrically with respect to the edges of the missing-dimer defect. Site I, proposed in earlier work,[6] is not stable. This is due to the strong core-core repulsion associated with this site. The binding energies show that bonding at a missing-dimer defect is about as stable as at a dimer on the first layer.

TABLE IV. Bonding energies (ΔE) in eV and net charges on N (q_N) and O (q_O) for molecular adsorption of NO on a missing-dimer defect on the Si(100)2$\times$1 reconstructed surface.

Cluster (Fig. 8)	ΔE (eV)	q_N ($\lvert e \rvert$)	q_O ($\lvert e \rvert$)
I	10.65	−0.48	−0.17
II[a]	−0.28		
III[a]	−0.10		
IV	−3.37	−0.78	−0.23

[a] This cluster geometry, which is not an equilibrium geometry, was only subject to energy minimizing and the full calculation has not been performed.

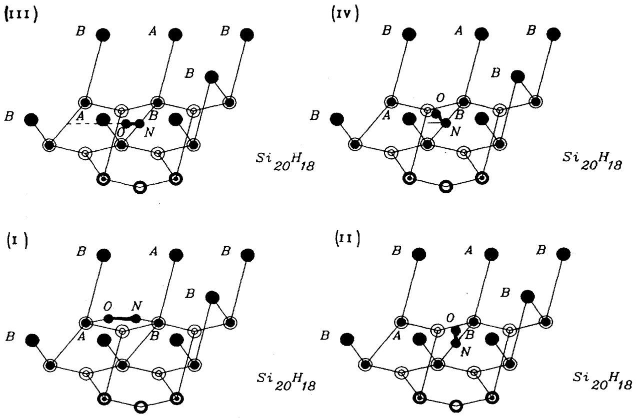

FIG. 8. Cluster geometries for the molecular adsorption of NO on a missing dimer. The silicon atoms symbolized the same way are constituted in the same plane. The unsaturated states below the first layer are saturated with hydrogen atoms and are not drawn for convenience.

E. Comparison of calculated and measured $dA(E)/dE$

The derivative Auger line shape can be simulated by using the partial local density of states calculated in Sec. III C and an estimation of the angular-momentum-weighted Auger matrix elements. These angular-momentum-weighted Auger matrix elements are approximated by the ratio of the possible decay channels (*pp* 46, *sp* 24, *ss* 3) of the two electron Auger process,[11,12] which do not vary much as function of energy.[4,5,16]

In Fig. 9 we present the calculated $dA(E)/dE$ spectra of the silicon/NO interface with a NO molecule bonded to the first- and second-layer dimers. The spectrum can be compared directly with our measured energy-loss-corrected Si $L_{2,3}VV$ Auger spectrum.

The experimentally obtained loss-corrected Si $L_{2,3}VV$ Auger spectra, $dA(E)/dE$, are presented in Fig. 10 and the peak positions (eV) are listed in Table V.

The difference between the features in (B) and (C) in Table V can only be due to the dissociation of the NO molecule at 550 K, because the coverage of nitrogen and oxygen atoms on the silicon surface remains approximately the same. The difference between features (C) and (D) of Table V is completely due to the disappearance of oxygen on the silicon surface at 1100 K.

Relating to the 84-eV feature to Si—O bonds we observe a shoulder in curve (b) of Fig. 4 at this energy level. In curve (b) of Fig. 10 (left), this structure becomes more pronounced and disappears at curve (c) (left). This supports the suggestion that the features at about 83 eV in the $dN(E)/dE$ spectrum (Fig. 4) of silicon upon chemisorption of nitric oxide at 300 K could be composed of two adjacent peaks related to Si—N and Si—O bonds. However, the similarity of the spectra (A) and (C) supports the existence of the proposed molecular adsorption features. The high reactivity of dissociated atomic oxy-

TABLE V. Si_3 $L_{2,3}VV$ spectra of (A) clean Si(100); (B) Si(100) exposed to 2.0×10^3 L NO at 300 K; (C) Si(100) exposed to 2.0×10^3 L NO at 550 K; (D) Si(100) surface in (C) heated to 1050 K after finishing the exposure.

					Experimental results							
(A)			91.9		86.5	82.3	79.0	74.0	71.3		65.6	
(B)		93.4	91.4	88.5	85.0	81.6	77.9	73.8	70.5	67.3[a]	64.2[a]	
(C)	97.5[a]	95.0	90.3	87.6	84.2	81.0	77.4	73.6	69.6[a]	67.5	64.8	62.8
(D)	97.5[a]	93.6	91.7		85.8	81.8	77.0	74.0[a]	70.7[a]	68.2[a]	65.0	62.0
					Calculated results (first-layer dimer)							
up atom		95.1	90.1		85.0		79.5	74.7		68.8		62.1
down atom		94.8	90.2		83.6		79.5		70.9			63.1
backbond	98.4		92.0			81.1		74.5		68.5		
backbond		95.2	90.5			81.1	78.6	73.4		68.3		
					Calculated results (second-layer dimer)							
up atom		96.2	91.4		84.2		79.8	74.0	71.1			62.9
down atom		95.0	90.5		83.2			74.7	69.7			62.4

[a] Weak features.

gen on the Si(100) surface would induce a dangling-bond peak in the dR/R spectrum, and induce distortions in the 2×1 two-domain LEED pattern, which was not observed. Moreover, higher coverages of nitrogen and oxygen should be expected than the observed approximately 15% of a monolayer.

The peaks at approximately 88 eV [Figs. 10(a) and 10(b) (left)] can be entirely attributed to adsorption of oxygen to the silicon surface. This is in agreement with the results of Sasse *et al.*,[39] where a feature at about 87 eV has been observed. The shift of 1 eV could be caused by changes in the bonding configuration from predominantly molecular adsorbed oxygen to atomic.

The theoretical results of the molecular chemisorption stage can only resemble a part of the experimental spectrum, because the experimental derivative line shape, $dA(E)/dE$, is a weighted sum of the clean reconstructed silicon surface atoms coordinated to other silicon atoms and of silicon atoms coordinated to the nitrogen atom of

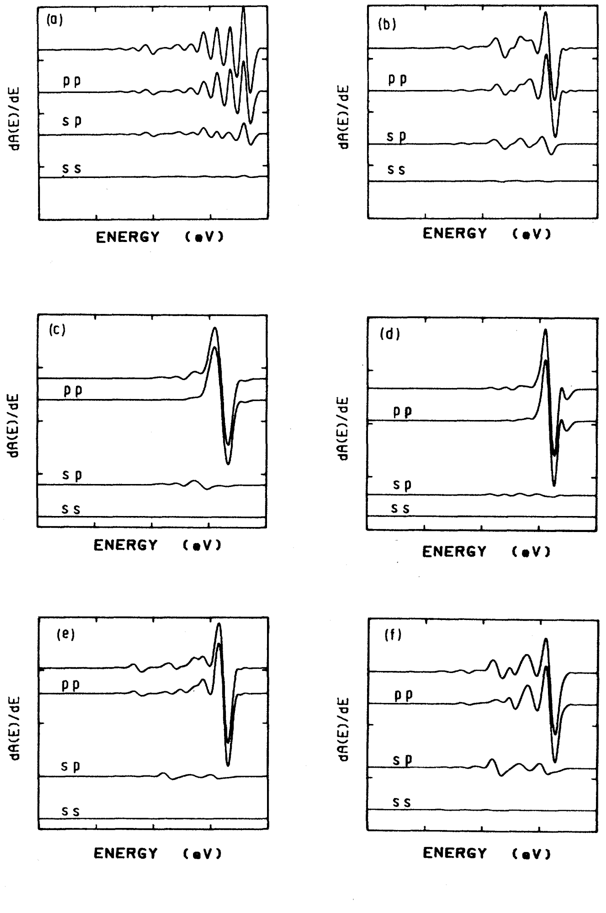

FIG. 9. The calculated Auger line shape, $dA(E)/dE$, of Si-NO (a)–(d) First-layer dimer: (a) up atom; (b) down atom; (c) backbond connected to the up atom (d) backbond connected to the down atom. (e) and (f) Second-layer dimer. The width of the kinetic energy axis is 60 eV. The zero of the axis depends on the energy of the core hole and the effective value for the work function of the surface and the detector.

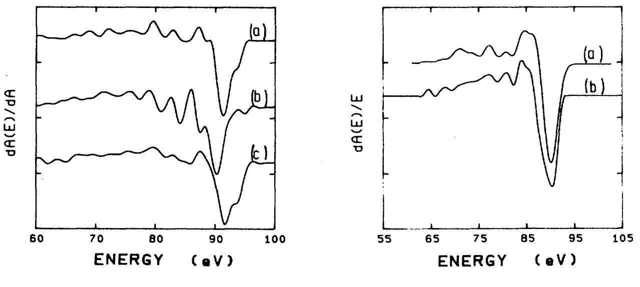

FIG. 10. Experimentally obtained $dA(E)/dA$ spectra. Left: (a) Si(100) exposed to 2.0×10^3 L NO at 300 K; (b) Si(100) exposed to 2.0×10^3 L NO at 550 K; (c) Si(100) surface heated to 1100 K after finishing the exposure. Right; (a) the calculated $dA(E)/dE$ of the clean Si(100) surface (Ref. 16); (b) the experimentally obtained $dA(E)/dE$ of the clean Si(100) surface (Ref. 16).

TABLE VI. Peak positions (in eV) of the LDOS for silicon atoms coordinated to the NO molecule. (a) First-layer dimer. (b) Second-layer dimer. The vacuum energy is taken as zero.

(a) First-layer dimer										
up atom		−4.0	−9.6	−14.4		−19.3		−28.6	−30.7[a]	−42.5
down atom		−4.0[a]	−9.4	−14.6		−19.4	−25.0[a]	−28.6	−30.7	−42.6
backbond (up)	−1.5		−8.4		−16.9	−20.0[a]	−25.3		−31.0	
backbond (down)		−4.0	−9.1		−18.1		−25.5		−31.0	
(b) Second-layer dimer										
up atom			−8.6	−14.8	−17.5	−19.7	−24.2	−28.1		−42.6
down atom			−9.2	−16.0	−16.8	−19.7	−24.3	−28.1	−30.2	−42.6

[a] Weak features.

the NO molecule. Furthermore, at adsorption temperatures higher than 300 K, SiO_x and SiN_x units will also influence this weighted sum.

Therefore, it only makes sense to compare curve (a) of Fig. 10 (left) with the calculated results. Of particular interest is the question if we can discriminate between NO adsorbed on the first- or second-layer dimer. However, the correlation between the calculated spectra makes it impossible to draw definite conclusions about a predominant adsorption site.

From the LDOS (Table VI) we observe relatively strong *p*-like valence-electron distribution at the backbond atoms and a relatively strong *s*-like valence-electron distribution at the atoms in first- and second-layer dimer. This suggests a charge transfer of predominantly *s*-type electrons to the dimer atoms. Furthermore, a peculiar enhancement of the *p*-type electrons at the backbond atoms is observed, which is not understood yet and will be subject to further investigation.

V. CONCLUDING REMARKS

The aim of this paper—to study, experimentally and theoretically, the chemisorption of a NO molecule on the Si(100)2×1 reconstructed surface at 300 K, under UHV conditions, to get a description of the adsorption process of NO on the Si(100)2×1 surface—has been achieved. New developments in signal processing improved the resolution of the Auger spectra. Moreover, modeling the half-infinite silicon surface with a finite cluster we could interpret the resolved peaks in terms of the local electron distribution governed by the chemical structure of the chemisorbed silicon surface.

We summarize the main conclusions of the chemisorption process of the NO molecule on the freshly cleaned Si(100)2×1 surface at 300 K.

Predominantly molecular adsorption of NO on the Si(100) surface at room temperature at two sites: on top on the first-layer dimer and on missing-dimer defects with only the nitrogen molecule bonded to silicon atoms. Molecular adsorption is in agreement with the quantum-chemical calculation which reveals a high energy barrier for dissociation. Dissociation of the NO molecule occurs at adsorption on a silicon sample heated to 550 K.

From quantum-chemical calculations to active sites are proposed: on top of a first- and second-layer dimer with the nitrogen atom coordinated to the silicon atoms, and the oxygen atom in a dangling position.

Only a submonolayer coverage (15%) can be obtained during adsorption at 300 K for a large range of pressures and exposures.

The LEED (2×1 two-domain) pattern does not change upon heating the surface after adsorption.

The electron affinity after molecular adsorption of NO is higher than in the case of molecular adsorption of O_2.

The binding energy of the NO molecule is about twice as small as that of the oxygen molecule bonded on the same site.

The very low saturation coverage can be explained by lateral repulsion due to electrostatic interaction, which is of the same order of magnitude as the binding energy of NO to the silicon surface.

Although the derivative of the loss-corrected experimental Auger line shapes reveals fine structure, at present no conclusive determination can be made between adsorption at the first- or second-layer dimer.

Quantum-chemical calculations modeling the partial local density of states of the half-infinite silicon surface and the adsorption process in combination with experimental results for studying gas-solid interactions have proven to be powerful. Further development of these types of calculations in modeling all kind of local phenomena is recommended.

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