Surface Science 199 (1988) 243–260
North-Holland, Amsterdam

MISSING DIMER DEFECTS INVESTIGATED BY ADSORPTION OF NITRIC OXIDE (NO) ON SILICON (100) 2 × 1

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Received 22 July 1987; accepted for publication 8 February 1988

This paper describes a study concerning the interaction of nitric oxide (NO) with the clean Si(100)2×1 surface in ultra-high vacuum at room temperature. Differential reflectometry (DR) in the photon energy range of 2.4–4.4 eV. Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) have been used to investigate the chemisorption of NO on Si(100)2×1. With this combination of techniques it is possible to make an analysis of the geometric and electronic structure and chemical composition of the surface layer. The aim of the present study was to explain the experimental results of the adsorption of NO on the clean Si(100)2×1 at 300 K. Analysing the electronic and geometric structure of a simplified stepped 2×1 reconstructed Si(100) surface and of the NO molecule in combination with the use of Woodward–Hoffmann rules (WHR) we were able to model a surface defect specific adsorption mechanism. Surface defects such as missing dimer defects seem to play an important role in the adsorption mechanism of NO on the silicon surface. The experimental results are consistent with this developed model. We also suggest a relation between the missing dimer defects and the number of steps on the silicon surface.

1. Introduction

Substantial research has been devoted to the structure of semiconductor surfaces – in particular those of silicon. Silicon surfaces are very important as interfaces in electronic devices. The development of complex integrated circuits in the semiconductor industry needs a more fundamental understanding of interfaces with device dimensions of the order of several fundamental scaling lengths [1].

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

In this paper we want to study the role of missing dimer defects in the adsorption process of NO on the clean Si(100)2 × 1 surface, at 300 K. Analysing the electronic structure of a simplified stepped 2 × 1 reconstructed Si(100) surface and of the NO molecule in combination with the use of Woodward–Hoffmann rules (WHR) we were able to model the influence of

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the missing dimer defects on the adsorption mechanism of NO on the Si(100)2 × 1 surface. By applying the Woodward–Hoffmann rules (WHR) [4,5] we are able to distinguish several kinds of adsorption sites, more or less active with respect to a particular adsorbate. Choosing a particular adsorbate we can expect adsorption predominantly on the active sites, thus discriminating these adsorption sites from others.

In our study nitric oxide (NO) has been used as adsorbate, because of the relative simplicity of the molecule with respect to its orbital symmetry. From the geometric and the electronic structure of the Si(100)2 × 1 surface, and using the WHR, we suggest that NO adsorption on Si(100) is dominated by adsorption on missing dimer defects.

To our knowledge this is the first report on the interaction of NO with the Si(100)2 × 1 surface with respect to surface defects at 300 K.

The solid–gas reactions were studied in ultra-high vacuum (UHV) at 300 K by Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and differential reflectometry (DR). Firstly, with AES a quantitative analysis was made of different types of atoms in the surface regions. Secondly, with LEED one is able to detect the structure of the surface of the sample and its possible change upon adsorption. Thirdly, with DR information about the electronic structure of the silicon surface can be obtained [6–9]. Using DR, electrons are excited from filled to empty (surface states) bands and the experimental data therefore always contain joint properties of both types of bands. One of the advantages using DR rather than AES or LEED is its essentially nonperturbing nature if the wavelength and intensity of the light beam are properly chosen.

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 energy range 2.4–4.4 eV.

In section 2 the experimental techniques are discussed. The experimental results of the adsorption of NO on Si(100)2 × 1 are presented in section 3. The Woodward–Hoffmann rules and their application with respect to the adsorption behaviour of NO on a silicon surface and the discussion of the experimental results with respect to the developed surface model of Si(100)2 × 1 are given in section 4. Concluding remarks are given at the end of this paper (section 5).

2. Experimental

2.1. Equipment

The experimental setup is extensively described elsewhere [6]. Only minor changes have been made. For AES, the primary electrons were accelerated by

a Wallis PM4DCP (10–4000) high voltage unit. The specification of this power supply unit is the same as mentioned in ref. [6]. The LEED equipment is unaltered. The DR setup has been changed, but not significantly. The main improvement is made on the mechanical stability.

2.2. Surface cleaning

The surface cleaning procedure is the same as described in ref. [6]. The samples used in the experiments have the same specifications. The surface was considered to be clean when no elements other than Si could be detected in the KLL Auger spectrum. We estimate that the carbon surface concentration is about 0.001 of a monolayer or less [6].

2.3. Gas handling

The purity of the NO we used was 99.9%. Further, exactly the same gas handling procedure was used as described in ref. [6].

We put stress on the fact that no filaments were lit in the reaction chamber during the adsorption experiments. No AES and LEED experiments were performed during adsorption to avoid electron induced effects. All exposures are given in langmuir units (1 $L = 1.0 \times 10^{-6}$ Torr s). The background pressure is about 6.0×10^{-11} Torr.

The surface region that was analysed was the same for AES, LEED and DR.

3. Results

3.1. Introduction

In this section 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 differential reflectrometry. Several measurements were performed to test the model, such as varying the exposure as function of pressure and time. Also some measurements were done on a surface heated to 550 K during adsorption. The results of these measurements will be mentioned in the discussion. Our main objective is to discuss the adsorption behaviour of NO on a Si(100)2 × 1 surface at room temperature.

3.2. Reflectometry results

Two types of reflectometry measurements were performed: (a) time-dependent reflectometry; and (b) wavelength-dependent reflectometry.

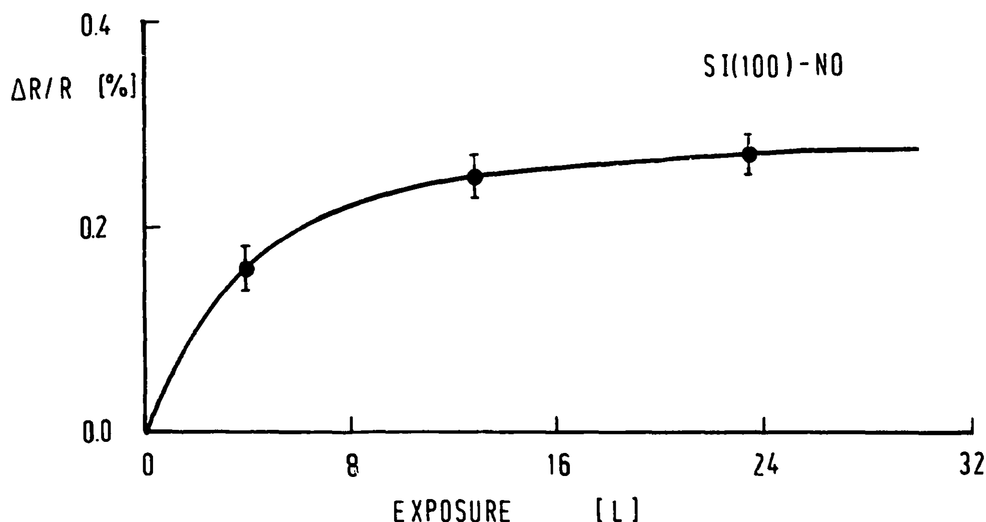

Fig. 1. Relative initial change in reflectivity versus NO exposure at $h\nu = 3.93$ eV and at room temperature. The pressure during the exposure is 3.3×10^{-8} Torr.

The time-dependent measurements made it possible to study in situ the dynamical behaviour of the adsorption of NO on the silicon surface. The wavelengths involved in these measurements are tuned on surface state transitions of the Si(100)2 × 1 surface. The chemisorption of NO on the surface induces surface state shifts, and peaks will be seen in the $\mathrm{d}R/R$ signal. From fig. 1, we can calculate the initial sticking probability, $S(\theta)$, with $\theta = 0$, assuming a proportional relation between the $\mathrm{d}R/R$ signal and the number of surface states which disappear:

$$\mathrm{d}R/R \propto \mathrm{d}\theta/\mathrm{d}t = S(\theta)p\nu/N_0, \tag{1}$$

where ν is a frequency factor ($= 2.56 \times 10^{20}$ cm^{-2} s^{-2} Torr^{-2}). N_0 is the number of adsorption sites available to NO on the Si(100) surface ($= 14\%$ of 6.78×10^{14} cm^{-2}), $p = 2.5 \times 10^{-8}$ Torr and t is the time in seconds. For all experiments listed in table 1 (where some characteristics are given) the initial sticking probability is ~ 0.8. Some important features involved in these measurements are:

- No pressure dependence in the range $1.0 \times 10^{-5} \leq p \leq 1.0 \times 10^{-7}$ Torr at a constant exposure (2500 L) (see fig. 2 dashed line). The sample is saturated

Table 1

Wavelength (nm)	Energy (eV)	Bond associated with [6]
316	3.93	Filled dimer, second layer
323	3.85	Filled dimer, first layer
355	3.50	b-type dimer
428	2.90	Filled dangling bond

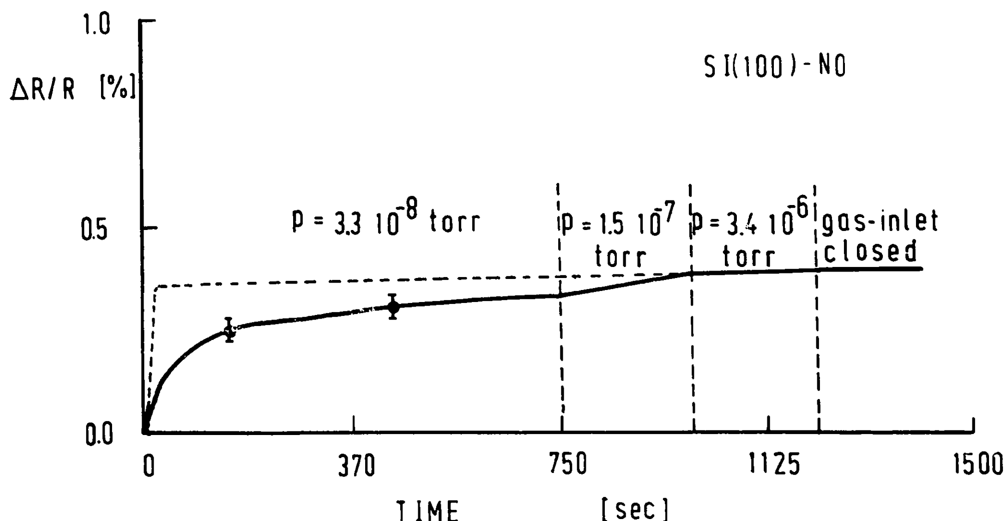

Fig. 2. Relative change in reflectivity versus NO exposure at $h\nu = 3.93$ eV and at room temperatures as a function of time and pressure. (a) Influence of the exposure at very low pressures on the time dependent dR/R signal. The corresponding pressures are indicated in this figure (solid line). (b) The same as (a) for pressures between 1.0×10^{-5} and 1.0×10^{-7} Torr (dashed line).

within a few seconds at a pressure of 3.4×10^{-6} Torr. However, a very weak pressure dependence is seen at low pressures ($1.0 \times 10^{-8} \le p \le 1.0 \times 10^{-7}$ Torr) (see fig. 2 solid line).

– No dependence on the exposure (L) at a constant pressure $p = 2.5 \times 10^{-6}$ Torr in the range 200 L $\le$ exposure $\le 2.0 \times 10^{6}$ L.

– For exposures at very high pressures ($p > 1.0 \times 10^{-4}$) new phenomena are introduced which can be attributed to adsorbate–adsorbate interaction. The existence of a new peak at 69 eV in the Si $L_{2,3}VV$ AES spectrum at room temperature strongly suggests that dissociation of NO occurs at room temperature [12].

– The height of the dR/R signal depends strongly on the quality of the cleaning procedure. The concentration of NO on a sputtered-only surface was twice as high as on an annealed surface.

– dR/R measurements tuned on the wavelength of the optical transition which probes the second layer dimers show a small increase of the signal (0.04%) after initial adsorption. This suggests that two characteristic time constants must be involved at this wavelength.

– The initial behaviour 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 measurements. We see a peak at 3.93 eV.

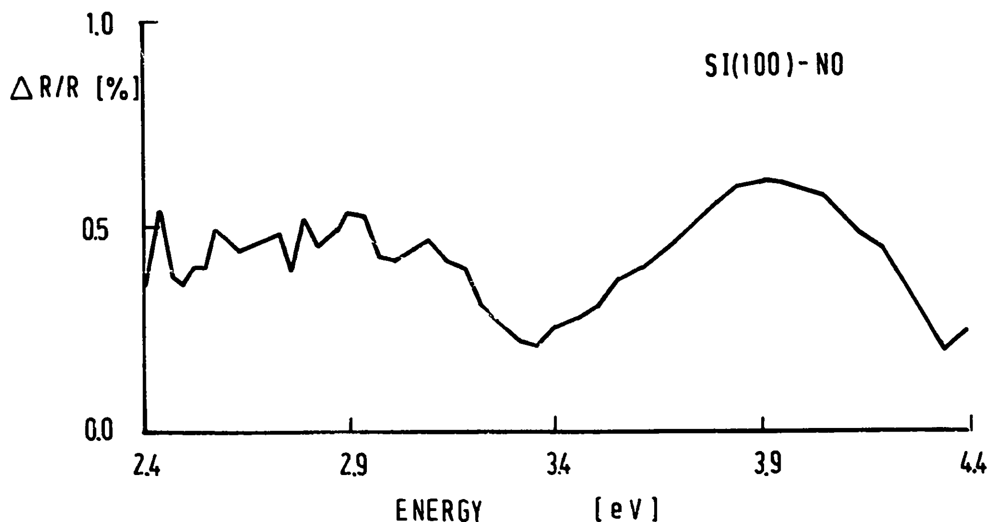

Fig. 3. Relative change in reflectivity versus $\mathrm{d}R/R(h\nu)$ before and after exposing a clean Si(100) surface to 1000 L NO. The pressure during exposure is 3.4×10^{-6} Torr.

We also observe a significant shoulder at 3.4–3.65 eV. An interesting fine-structure is seen in the lower energy part of the spectrum. This structure is reported in an earlier paper [13], however, not recognized as fine-structure.

3.3. AES results

We used AES (KLL) to detect the amount of N and O adsorbed, either molecular or (partly) dissociative on the silicon surface after an exposure of 2500 L. We saw, using the same qualitative method as used by Keim et al. [6], an amount of $7\pm1\%$ oxygen and $7\pm1\%$ nitrogen. Upon adsorption at a sample temperature of 550 K the concentration of nitrogen increases to 12%. While the oxygen concentrations remains the same at 7%. Heating the sample after adsorption to 1100 K only nitrogen is detected at the same rate as before heating. No oxygen is detected anymore.

3.4. LEED results

LEED measurements are only used as a "fingerprint" technique. The results are: After an exposure of NO the LEED 2×1 two domain structure has not changed (apart from a very small increase of the background relative to the 2×1 spots of the LEED pattern) even twelve hours after adsorption had taken place. The LEED pattern does not change when the sample is heated to 1100 K after adsorption either.

4. Discussion

4.1. Structural model

4.1.1. Introduction

In recent years the clean Si(100) surface has been the subject of many experimental an theoretical studies [14–19]. The ideal unrelaxed Si(100) surface is highly unstable [14,15] and the surface therefore reconstructs.

Low energy electron diffraction (LEED) experiments show a (2 × 1) diffraction pattern, indicating a doubling of the surface periodicity in one direction. Other LEED investigations [20,21] and helium diffraction experiments [22] showed that the reconstruction is closer to a c(4 × 2) structure (under optimal conditions) and indicated that p(2 × 2) and possible c(2 × 2) regions also exist on the surface, the (2 × 1) reconstruction, however, being dominant.

Many structural models have been proposed to explain the LEED results. The (2 × 1) reconstruction has been described in terms of:
- the vacancy model [23];
- the paring model [23,24];
- the conjugated chain model [25];
- more recently by the dimer model [15,17,26];
- and very recently by Northrup in his π-bonded chain model [27].

From all these models the dimer model, which appears to explain most of the experimental results, is most widely supported. The first three models were found to be incompatible with angle resolved photoemission spectroscopy (ARUPS) data [28]. Recently STM [2,3] showed that only the dimer model is consistent with the experimental results. Therefore we prefer the dimer model to Northrup's π-bonded chain model. In the following section we shall discuss the dimer model.

4.1.2. Dimer model

In the dimer model, two surface atoms form a dimer bond. These dimer bonds can be distinguished in a symmetric and an asymmetric configuration. A symmetric dimer, however, yields a metallic surface electronic structure which is not in agreement with experimental results [14,15]. However, Redondo and Goddard [29], using cluster calculations, found semiconducting surface states for symmetric dimers. We can therefore not entirely exclude symmetric dimers, but asymmetric dimers are more widely accepted and much theoretical [14–19] and experimental [2,3,20–22] evidence is found to support this asymmetric dimer model.

4.1.3. Missing dimer defects

Missing dimer defects, i.e. a first layer dimer is missing, appear to have an non-negligible influence on the surface. Pandey [30] proposed a new model

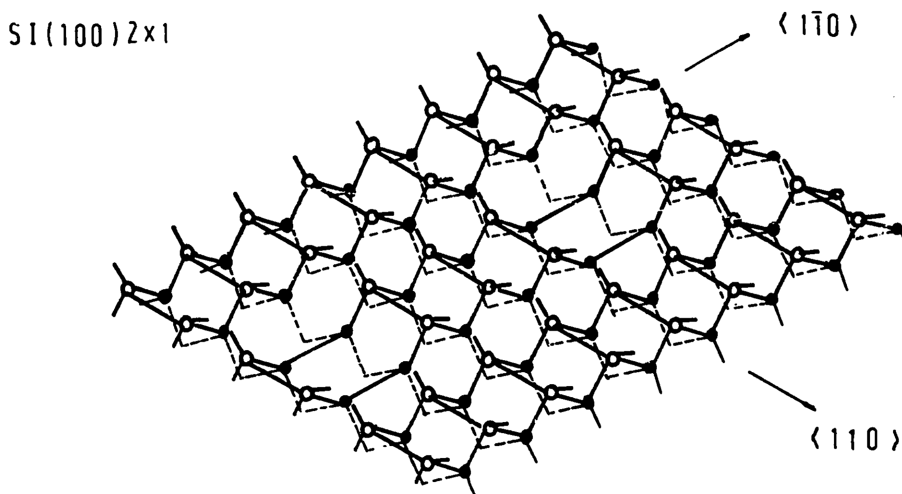

Fig. 4. Simplified model of a missing dimer defect in the 2×1 reconstructed Si(100) surface.

that is based on dimers and missing dimer defects. He proposed that individual vacancy defects stabilize the Si(100) surface: when a surface dimer is removed, two dangling bonds are removed leaving a new dangling bond on each of four second-layer atoms (see fig. 4). These second-layer atoms can translate parallel to ⟨1$\bar{1}$0⟩ (i.e. perpendicular to the first-layer dimers) and form two second-layer dimers. As long as the elastic strain field of the defects do not overlap, the total energy should decrease. Pandey estimated that the structure with the lowest energy would be formed when approximately every fourth dimer was missing producing a defect density of the order of 25% of the amount of surface dimers. Very recently this model has been supported by Martin et al. [31] and by Aruga and Murata [32].

When we consider a surface consisting of both dimers and missing dimer defects we are still considering an "ideal" surface. Under experimental conditions we are always dealing with surfaces which contain all kinds of steps, contaminations, etc.

On the surface there will be a significant number of monatomic steps neglecting contaminations and steps which consists of more than one atomic layer [22]. The step density is in general a function of the cleaning procedure and sample preparation. Before we can analyse the influence of bonding of these monatomic steps we need to model its structure. Therefore we propose a simplified structural model of monatomic steps on the Si(100)2 × 1 surface (fig. 5). In this model we can distinguish four kinds of steps.

(A) Step along ⟨110⟩. The atoms forming the lower step edge are not involved in a dimer bond.
(B) Step along ⟨110⟩. The atoms forming the lower step edge are involved in a dimer bond.
(C) Step along ⟨1$\bar{1}$0⟩. The atoms forming the upper step edge are involved in a dimer bond.

(D) Step along ⟨1$\bar{1}$0⟩. The atoms forming the upper step edge are not involved in a dimer bond.

Steps A to C are also found in ref. [3]. Step D is not mentioned in ref. [3]. From an energetically point of view this kind of step is not very likely. This step probably, will be buckled, which agrees with the STM measurements.

4.1.4. Steps and missing dimers: a relation?

As said before, missing dimer defects cause elastic strains. Because of these strains, missing dimer defects cannot come too close to each other. Taking this into account, Pandey [30] estimates only 25% of the dimers was missing (12.5% of a monolayer of atoms). However, Pandey considered a stepless surface. In experiments one deals with a stepped surface. The configuration of some steps, especially B, C-type steps (see fig. 5), resembles part of the configuration of missing dimer defects. Like missing dimers, these steps must cause elastic strains, so that steps and missing dimers cannot come too close to each other. This is comfirmed by the buckling of symmetric dimers or stabilization of asymmetric dimers (no flipping anymore) near step edges, as can be seen on STM topographs [2,3].

The relation between the concentration of missing dimer defects and steps has never been investigated, as far as we know. To support the suggestion of a relation between the concentration of missing dimer defects and steps we made a comparision between the density of steps (from literature) and the density of missing dimer defects, found by measurements [3,31] as well as by calculation [30]. The values used for this comparison are collected in table 2. Al percentages are related to the number of atoms in one monolayer of silicon.

We cannot simply add the number of measured steps and measured missing

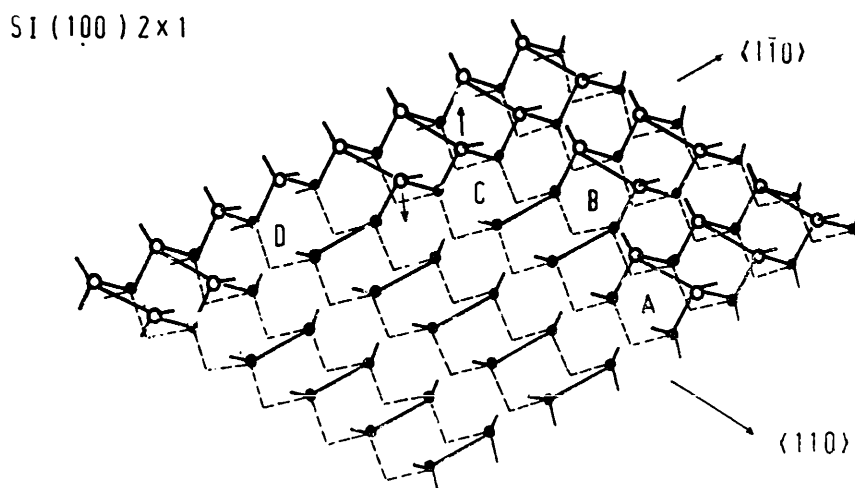

Fig. 5. Simplified model of a stepped 2×1 reconstructed Si(100) surface. The types of step-edges are explained in the text. The possibility of buckling of the dimers in the neighbourhood of steps is ignored.

Table 2
Values of step and missing dimer densities

	Density (percentage of 1st layer atoms)	Ref.
Measurement		
Missing dimer defects	5–8	[3,31]
Steps	10–14	[3,33]
Calculation		
Missing dimer defects	12.5	[30]

dimer defects. The missing dimer defect can be seen as a combination of one step down and one step up within a very small area. The elastic strain caused by a step (within one dimer row) is therefore approximately half as large as the elastic strain caused by a single missing dimer defect. So, in order to compare the values of the steps and missing dimer defects, we have to divide the amount of steps by two. Adding the measured percentage of missing dimer defects and half of the measured percentage of steps, we arrive, to a first order, at 10 to 15% of the number of first layer atoms. This is in good agreement with the calculation of Pandey [30]. Care must be taken in this comparision, because the step density is a function of the sample preparation. We want to suggest only, that to our opinion, there must be a relation between the missing dimer defects and the step density. Further investigation should be done on this very interesting subject.

4.2. Woodward–Hoffmann rules

4.2.1. Introduction

To describe why the NO molecule can or cannot be bound to a specific site on the silicon (100)2 × 1 surface, we need to consider a microscopic model. The Woodward–Hoffmann rules give an explanation, why some of the sites on the surface are involved in bonding while others are not, without elaborate numerical calculations. This method is widely used by chemists to explain chemical reaction kinetics. In the gas–solid interface this method is not common practice. Banholzer et al. [34] applied the WHR to explain the adsorption of NO on a platinum surface. We shall adapt this method to model the reactivity of NO to the several possible adsorption sites on the Si(100)2 × 1 surface.

4.2.2. The orbital symmetry conservation model

When the NO approaches a surface, the microscopic structure of the Si(100)2 × 1 surface as described in section 4.1 becomes important. In determining the influence of structural properties on the rates of reactions

Woodward and Hoffmann [4] and Fukui [35] made important progress. They found that while the bond energy can play an important role, most often orbital symmetry constraints play an even more important role. They developed rules (WHR) which are based on the conservation of orbital symmetry to model chemical bonding.

In short, the orbital symmetry constraint model can be described as follows: As a chemisorption process proceeds, there is a net transfer of electrons from "donor" to "acceptor" molecular orbitals, provided there is an overlap of these orbitals. If the donor and the acceptor molecular orbitals have the same symmetry, then a direct transfer of electrons is possible. In this case the activation energy for the reaction will be low. However, if the donor and acceptor orbitals are of different symmetry, the direct transfer of electrons is forbidden. A significant activation barrier is often associated with this process [4].

4.2.3. Application of the WHR to NO on Si(100)2×1

In order to predict molecular adsorption behaviour we have to distinguish between the following cases:

- If there can be enough overlap of orbitals of the NO molecule and the silicon surface (if bonding is geometrically possible).
- If overlapping orbitals have the same symmetry.

Two kinds of adsorption must be considered:

- molecular adsorption;
- atomic adsorption (dissociative adsorption).

For dissociation, electron transfer to the empty antibonding orbital is necessary to supply enough energy for dissociation. As is standard in the analysis of uni-molecular reactions, the NO dissociation step will be modelled as transfer of electrons from the bonding orbitals of NO to the surface, and from the surface to the antibonding orbitals of the NO. If it is assumed that the oxygen and nitrogen end up with closed shells, then the $S \rightarrow \sigma^*$ and $S \rightarrow \pi^*$ transfers will dominate (S = surface) [36].

Before we can apply the WHR we need to simplify the orbital configuration of the silicon surface. We use the following simplifications and assumptions:

(1) The dimer is assumed to be symmetric. In asymmetric, buckled and non-buckled dimers the charge shift and change in geometry are too small to have a significant influence on the results of the orbital symmetry conservation model [14–16,30].

(2) We categorize the valence orbitals on the silicon surface into three groups [37]: (i) dangling bonds: p_z-like; (ii) dimer bonds: Si–Si bonds in the same layer as the dangling bonds ($p_{x,y}$-like); (iii) backbonds: Si–Si bonds between atoms in adjacent layers (S-like).

(3) The silicon valence orbitals are ordered by energy level. A dangling bond will have the highest energy. A dimer bond has a lower energy. The $3\sigma_p$

orbital, formed from $3p_x$, $3p_x$ orbitals has a lower energy than the $3\pi_x$ orbital formed from $3p_y$, $3p_y$, as is usual. All valence electrons of silicon have a higher energy than they would have in the empty NO $2\sigma_p^*$ or nearly empty NO $2\pi_p^*$ state. In case of sufficient overlap electron transfer is expected, without the need of activation energy.

(4) Assuming an unchanged character of orbitals, we isolate one pair of silicon atoms, and regard it as a diatomic molecule which cannot be reached from the bottom. Only in one case we will have to include the influence of a second dimer pair (see below).

(5) Of the important silicon and NO orbitals we draw pictures of the atomic orbitals forming the molecular orbitals of the NO or Si–Si molecule, taking into account their relative orientation of the sign of their wave functions (see fig. 6). Dangling bonds are drawn single because they do not form a molecular orbital together with another dangling bond.

(6) The N side of the molecule binds to the silicon atom. Shustorovich [38] deduces an expression proving the NO molecules should be coordinated to a metal via N, because N has the larger heat of chemisorption.

(7) The bondings shown in figs. 7a–7d are not expected for geometrical reasons: the Si 3σ bond and the Si $3\sigma_p$ bond are shielded by the dangling and dimer bonds. In figs. 7c–7f dimer bonds are involved in the bonding. At terraces the dimer bond is shielded by the dangling bonds, therefore no molecular adsorption is possible at the first layer dimers. This is not the case

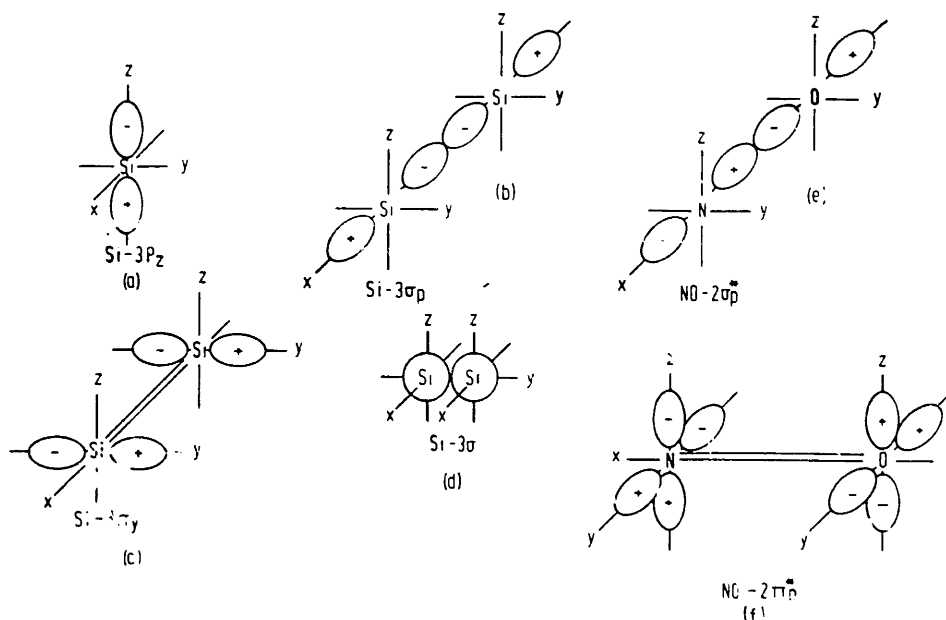

Fig. 6. The important atomic orbitals of the Si, N and O atoms are drawn schematically forming the molecular orbitals of the N–O and Si–Si molecule taking into account their relative orientation of the sign of their wave functions. The dangling bond has been drawn single because it does not form molecular orbitals together with an other dangling bond.

for missing dimer defects and steps of type B (figs. 7e and 7f), when approaching on the top of the dimers. The dangling bonds at the top of the silicon surface are easy to reach for the NO molecule and therefore bonding is geometrically possible (see figs. 7g and 7h). Therefore adsorption on the sites

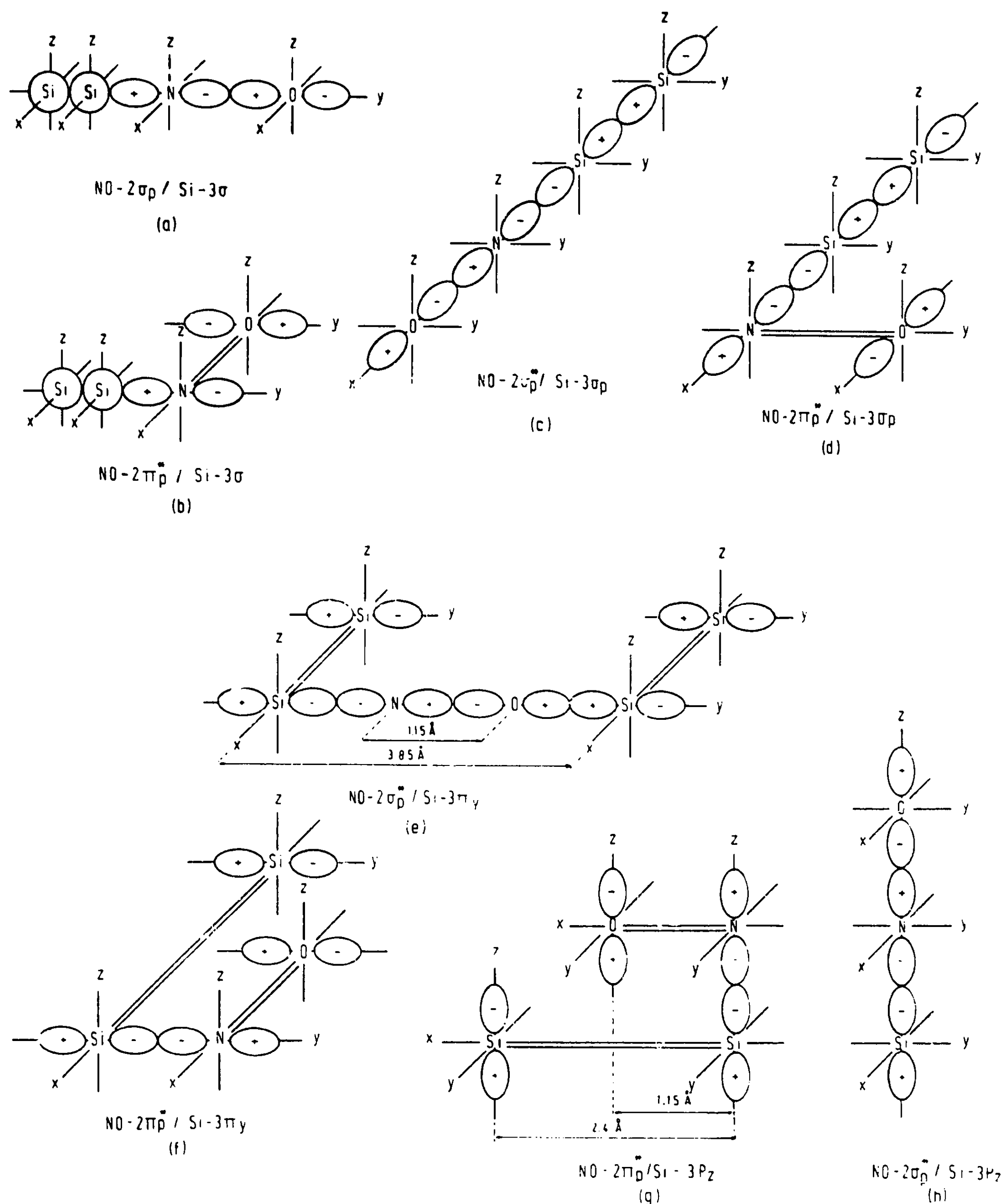

Fig. 7. All combinations of (partly) filled silicon valence orbitals and (partly) empty NO valence orbitals. The pictures are not drawn to scale, unless it is necessary for a good understanding (then values of the distances are added). The only important features in these pictures are the character of the bonds and their mutual orientation.

shown in figs. 7e–7h are geometrically allowed, and dimer bonding only on missing dimer defects and steps of type B.

Different bondings will have different energies. These bonding energies are expected to be of the same order, except the adsorption mechanism in fig. 7e, because two bonds are involved in stead of one in other bonding geometries. This bonding is the most complicated one and we will have a closer look to this bonding-type. Of both dimers involved in the bonding the one electron of the half filled Si $3\pi_y$ orbital is transferred to the empty NO $2\sigma_p^*$, which becomes a filled orbital. For dissociation the NO $2\pi_p^*$ orbital needs to be filled too. It is not expected that the electrons needed can be supplied by overlap with silicon atoms. However, the bonding of the Si π_y and the NO $2\sigma_p^*$ orbital may yield enough energy for the bond NO molecule to be excited to fill the $2\pi_\pi^*$ orbital and thus dissociate. In that case the N atom is bound on a silicon atom. The O atom is being bound on a silicon atom on the adjacent dimer. Another remark, it seems that on the two dimer bonds two NO molecules can be bound, however, we must remember that the Si $3\pi_y$ orbital is though to be only half filled and thus, the two Si $3\pi_y$ orbitals have only enough electrons to fill one NO $2\sigma_p^*$ orbital. In conclusion:
- Several kinds of molecular bonding can be expected.
- Dimer bonding is only possible at missing dimer defects and B-type steps.
- The bonding shown in fig. 7e is energetically highly favourable.
- Dissociative bonding is possible at missing dimer defects and B-type steps.

4.3. Discussion of the results

4.3.1. dR results

In this section we will try to explain the experimental results with our proposed models, formulated in sections 4.1 and 4.2. The peaks shown in the relative difference in reflectivity, $dR/R(h\nu)$, can be interpreted as surface state transitions [6]. However, care must be taken in attributing above band gap structure in the differential reflection spectrum completely to surface states [39]. The convolution properties of the joint density of states strongly suggest a transition from a local filled state in the valence band to a local unfilled state situated in the conduction band. Otherwise, no small peaks could be observed in these reflection spectra. Broad peaks, therefore must be attributed to a different optical excitation mechanism such as, mixing of bulk bands with local structures or local space charge effects.

Optical excitation mechanisms such as excitonic effects, bulk-like Franz–Keldysh effect, and surface state screening do not play a significant role in our results (see ref. [6], and references therein). These excitation mechanisms are still not fully understood and care must be taken to exclude them from the discussion.

Theoretical calculations and experimental results [10,40] confirm the existence of a surface state at ~ 2.5 eV below the Fermi energy, E_F. This state is

attributed to a filled dimer bond surface state. Keim et al. [6] interpreted the peak at 3.85 eV as surface transition from a filled dimer bond to a empty dimer bond ~ 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, which is situated at the second surface layer. The shift of 0.08 eV from 3.85 to 3.93 eV can be explained due to a stronger bonding of a second layer dimer.

The pronounced shoulder (the asymmetric part of the peak) and the lower energy side of the peak is believed to occur by adsorption on B-type steps (fig. 5). This idea is supported by two arguments. (i) The dimer in the B-type step is geometrically situated at the first surface layer and therefore a shift to the lower energy side of the spectrum is expected. (ii) The initial sticking probabilities 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 thereon added a fine-structure. The missing of a pronounced 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 geometrically overlap of the electronic structure of a surface state 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 dynamical behaviour of this fine-structure assumes a relation with the missing dimer adsorption. This fine-structure is also observed for molecular oxygen adsorption on Si(111)7 × 7 at room temperature, but not on Ge(111) [13,41]. We do not have a sufficient explanation for this phenomenon yet. Further investigation will be necessary.

4.3.2. AES (KLL) results

The concentration of N and O on the Si(100)2 × 1 surface, at 300 K, is $7 \pm 1\%$ of the number of atoms of one monolayer. This concentration is calculated with the same quantitative method as used by Keim et al. [6]. This concentration did not change if the exposure pressure was varied in the range $1.0 \times 10^{-5} \leq p \leq 1.0 \times 10^{-8}$ Torr at a constant exposure (2500 L). The concentration of N and O is also independent of the exposure between 200 and 2.0×10^6 L with a constant pressure of 2.5×10^{-6} Torr. From these results we cannot conclude if NO, at 300 K, is adsorbed, either molecularly or (partly) dissociatively on the silicon surface. Upon adsorption at a sample temperature of 550 K the concentration of nitrogen increases to 12%, while oxygen remains the same (7%), thus at least partly dissociation must take place. Upon heating the sample after adsorption to 1100 K only nitrogen is detected at the same rate as before heating. No oxygen is detected anymore. The disappearance of adsorbed oxygen, molecularly or atomic, on the surface at high temperatures

(> 950 K) is well establish as SiO etching [42,43]. The very low concentration of N and O, at 300 K, on the surface suggests that dangling bonds or first layer dimers are not or not fully active as adsorption sites. However, as WHR does not exclude adsorption on dangling bonds, we believe, that there is no NO adsorption on this surface state. This lack of dangling bond adsorption must be explained from the adsorption energy. The molecule may be so loosely bounded that collisions and vibrations cause desorption of the molecules. Besides this, it can be concluded from the amount of adsorbed NO (14%) in relation to the number of dangling bonds on Si(100)2 × 1 surface that adsorption is not likely to take place at the dangling bonds. First layer dimers are not active as adsorption sites. This will be discussed in the next section.

4.3.3. LEED results

After exposures of NO as described in section 3.4, the LEED 2 × 1 two domain pattern did not change. The dimer bonding on the Si(100) surface is responsible for the 2 × 1 structure, therefore an unaltered LEED pattern suggests that the dimer bonds are not broken due to NO adsorption. This observation is consistent with the expectations formulated by the WHR. Adsorption of NO on first layer dimers on the Si(100) surface can be excluded.

4.4. Adsorption on defect sites

Excluding the dangling bonds and first layer dimers, adsorption can still take place on second layer dimers at missing dimer defect sites, steps or at back bonds.

From application of the orbital symmetry conservation model to the adsorption of NO on Si(100)2 × 1 surface (see section 4.2.2) it can be concluded that adsorption can very well take place at the second layer dimers, indicated above. This is confirmed by the rapid, abruptly stopping increase of the time-dependent $\mathrm{d}R/R$ signal, which indicates a reaction with no (or very low) activation energy and a limited number of sites available. We believe that all second layer dimers are easily occupied. That NO molecules are easily adsorbed at these sites is also in agreement with the pressure independence of the $\mathrm{d}R/R$ signal. The constant value of the $\mathrm{d}R/R$ signal after stopping the exposure indicates that the adsorption is strong enough to be resistant against pumping, etc. The AES results again confirm this conclusion: the amount of adsorbed NO molecules on the Si(100) surface equals the amount of missing dimer defects (5–8%), as expected to occur at our stepped surface.

We believe that B-type steps are also active in the adsorption process as is supported by the experimental results. The amount of B-type steps (being only a part of the total amount of steps: 2–10% according to ref. [31]; 5% according to ref. [6]) is too little compared to the uncertainties involved in the determination of the amount of missing dimer defects, to draw a definite conclusion

about their involvement in the adsorption process. Another indication that the adsorption takes place at defect files is the observation that the dR/R signal increases when defects are purposely made by sputtering, or when the surface is less thoroughly prepared.

The expectation that NO dissociates can be checked by considering the AES results. At room temperature, the amount of N and O is equal, so although dissociation might occur, the total molecular adsorption is not in disagreement with the AES results. However, the absence of the 69 eV peak in the Si $L_{2,3}VV$ Auger spectrum strongly supports the idea of molecular adsorption [12]. At higher temperatures and at higher exposure pressures ($p > 1.0 \times 10^{-5}$ Torr) different amounts of N and O were observed, which is in agreement with other investigations [42,43] and also other sites than missing dimers could be activated.

Another argument why dissociation of the NO molecule on the Si(100)2 × 1 surface is not likely is the observation of Keim et al. [6] that atomic oxygen will break the dimer bonds in the first atomic layer and distort the 2 × 1 two domain LEED pattern.

In summary the experimental results of the adsorption of NO on the clean Si(100)2 × 1 surface, at 300 K, can be explained in terms of adsorption, predominately on missing dimer defects.

5. Concluding remarks

The most important conclusion of this paper is that on a atomically clean Si(100)2 × 1 surface adsorption of NO, at 300 K, mainly occurs on missing dimer defects.

Another important conclusion is that WHR can give a global insight into the local adsorption process on silicon surfaces.

The suggestion of the existence of a relation between steps and missing dimer defects should stimulate theorists to perform calculations on stepped surfaces. Surface reconstruction means also lowering the surface free energy and therefore steps should influence the reconstruction. The existence of buckling and non-buckling dimers on Si(100)2 × 1 as observed by STM [3] supports this idea.

Acknowledgement

The authors wish to thank Dr. E.G. Keim and Professor Dr. M.J. Sparnaay for their stimulating discussions, and reading this paper thoroughly before publishing. We also wish to thank Ir. D.G. Lakerveld for performing the Auger measurements.

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