SURFACE SCIENCE LETTERS

DECOMPOSITION OF N_2O ON THE $\text{Si}(100)2 \times 1$ AND $\text{Si}(111)7 \times 7$ SURFACES: DETERMINATION OF THE DENSITY OF BROKEN BONDS

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This paper reports on the site-specific decomposition behaviour of N_2O on the clean $\text{Si}(100)2 \times 1$ and $\text{Si}(111)7 \times 7$ surfaces at room temperature, studied by spectroscopic differential reflectometry (SDR) and Auger electron spectroscopy (AES). It has been established that Si–O bond formation occurs at the top layer Si atoms, mainly via attachment of the unsaturated broken bonds. In this way it is possible to determine the density of broken (dangling) bonds at the clean Si surface. Our results confirm the high dangling bond density at the 2×1 reconstructed $\text{Si}(100)$ surface for which we assume a defect density of $15 \pm 10\%$. The density of dangling bonds per 7×7 unit cell (49 atoms), 23 ± 4 , is in agreement with the established 19 as revealed by current imaging tunneling spectroscopy (CITS).

1. Introduction

Various methods have been used to obtain information about the electronic structure of the clean low-Miller index surfaces of silicon, e.g. photoemission spectroscopy (PES), current imaging tunneling spectroscopy (CITS) and spectroscopic differential reflectometry (SDR). Direct information can be obtained about the occupied and unoccupied surface states using, respectively, photoemission and inverse photoemission spectroscopy, the latter being very difficult to use as a routine technique [1]. Although with CITS both types of surface states can be measured, the sensitivity around the Fermi energy E_F is, at least for semiconductor surfaces, very low [2]. On the other hand, adsorption studies are frequently performed to characterize the electronic structure of the clean surface, e.g. oxygen adsorption is used to generate a bulk-like electronic structure in the surface region. The difference between the clean and the adsorbed state serves to identify the electronic structure of the clean surface (see, e.g. refs. [3–13]). During oxygen adsorption the reflectometric parameter, $\Delta R/R$, is continuously followed [6,7,9,10–13]. By means of SDR the excitation of electrons from filled to empty surface states is investigated and information is obtained containing joint properties of both types of bands. One of the advantages of SDR is its essentially non-perturbing nature

if the wavelength and intensity of the light beam are properly chosen. In comparison with CITS, the transitions in SDR are threshold energy differences that need not to occur at the Γ point of the surface Brillouin zone, which is emphasized in the tunneling spectrum. Furthermore, SDR is sensitive for surface states up to E_F .

By exposing the carefully cleaned (by simultaneous ion bombardment and annealing [9–12,14]) Si(100)2 × 1 surface to nitrous oxide [10] SDR has revealed several types of dangling bond surface states in addition to the dimer bond surface state, which is in agreement with literature (see, e.g. ref. [10] and references therein). The significance of the use of nitrous oxide in studies dealing with the initial oxidation behaviour of clean Si surfaces is that the N₂O molecule supplies only one oxygen atom after the dissociative adsorption, i.e., $\text{N}_2\text{O}(\text{gas}) \rightarrow \text{O}_{\text{ad}} + \text{N}_2(\text{gas})$, thus excluding the possibility of complex molecular adsorption. This phenomenon has been observed on the three low-Miller index surfaces of silicon [9–11]. Moreover, we have shown that the reaction of N₂O with the Si(100)2 × 1 [10], Si(111)7 × 7 [9] and Si(110)5 × 1 [11] surfaces is very site-specific; Si–O bond formation occurs at the toplayer Si atoms, mainly via attachment of the dangling bonds, and in the case of the 2 × 1 reconstructed Si(100) surface also via attachment of the “dangling bonds” which constitute the dimer by breaking this dimer bond [10]. Supporting evidence has been given both experimentally by high energy-resolution Auger electron spectroscopy (AES) [10–12], and theoretically by semi-empirical quantum chemical cluster calculations [15].

Since the dissociative reaction of the N₂O molecule seems to limit itself to the dangling bond sites, the question arises if we can use this reaction as a method to determine the density of broken bonds on clean Si surfaces.

In this Letter it will be shown that this method can contribute to a better understanding of the clean reconstructed Si surfaces; our results confirm the high dangling bond density at the Si(100)2 × 1 surface. On the other hand, the applicability of our method is demonstrated by studying the well characterized Si(111)7 × 7 surface which has a very low number of broken bonds per unit cell.

2. Si(100)2 × 1

In the dimer model [16,17] of the 2 × 1 reconstructed Si(100) surface alternate rows of surface Si atoms move towards each other to form Si–Si dimers. In the dimerized surface there is still one dangling bond per surface Si atom. Recent STM studies [18–20] have confirmed the basic dimer model. It is also well established that the real Si(100)2 × 1 surface may have a defect density ranging from 5 to 25% [13,19,21], most of which is due to missing dimers [19]. In ref. [10] it has been shown that the room temperature

decomposition of N_2O on the $Si(100)2 \times 1$ surface terminates after a complete removal of the dangling and dimer bond surface states. The amount of chemisorbed oxygen, as shown to be in a bridging position between toplayer Si atoms [10]^{#1}, is therefore linearly proportional to the total number of dangling and dimer bonds present at the surface. AES was used to monitor the total amount of oxygen adsorbed at discrete stages, relevant parameter being the normalized oxygen Auger signal, $h_O/h_{Si(100)}$, with a value at saturation, $h_O/h_{Si(100) \text{ sat}} = 14.7 \pm 0.5$ [10]. If we assume a defect density of $15 \pm 10\%$ [13,19,21,22], it follows from the SDR and AES results that saturation of the $Si(100)2 \times 1$ surface by atomic oxygen (as released by N_2O) occurs at 0.85 ± 0.10 monolayer (ML) coverage, which implies that $85 \pm 10\%$ of the surface Si atoms have one dangling bond.

3. $Si(111)7 \times 7$

SDR measurements exhibited a complete removal of the dangling bond surface states upon exposing the $Si(111)7 \times 7$ surface, cleaned in the same way as the $Si(100)2 \times 1$ surface [9–12,14], to N_2O [9]. The number of $Si(111)7 \times 7$ surface atoms in terms of (111) monolayers ($1 \text{ ML} = 7.84 \times 10^{14}$ atoms per cm^2) which have a dangling bond is therefore given by the ratio of the normalized oxygen Auger signal at saturation, $h_O/h_{Si(111) \text{ sat}}$, which is 9.5 ± 0.5 [9], and $h_O/h_{Si(100) \text{ sat}}$, which is 14.7 ± 0.5 at 0.85 ± 0.10 ML oxygen coverage, corrected for the difference in Si surface atom density between the $Si(111)$ and $Si(100)$ unreconstructed unit cells. The result is 23 ± 4 dangling bonds per 7×7 unit cell (49 atoms), which, within the bounds of experimental error, is in agreement with the established 19 dangling bonds as measured by CITS [20,23,24]. Both CITS [20,23,24] and PES [1] revealed a backbond state at about -1.7 eV below E_F which can be related to the Si–Si backbonds surrounding the adatoms [20,23–26]. Additional decomposition of N_2O at these backbond sites leading to bridge bonded oxygen atoms, as observed by a recent X-ray photoelectron spectroscopy (XPS) study [27], may explain the difference in “dangling bond” density. Because of the limited photon energy range used during the N_2O adsorption experiments on the $Si(111)7 \times 7$ surface [9], the optical transitions originating from this energetically deep-lying back-bond state could, however, not be observed.

^{#1} According to our model of the dissociative adsorption of N_2O on the $Si(100)2 \times 1$ surface [10], oxygen goes into a bridging position between toplayer Si atoms in the initial oxidation stage by decomposing at the Si–Si dimer bonds, followed by atomic oxygen uptake via attachment of the dangling bonds of the toplayer Si atoms whose position has moved considerably to the nearest neighbour Si atoms forming the Si–O–Si configuration as well.

4. Conclusion

The present paper demonstrates that the site-specific decomposition of N₂O is an important complementary tool in clarifying the electronic structure of at least the Si(100)2 × 1 and Si(111)7 × 7 surfaces. This approach has also been successfully applied to the Si(110)5 × 1 surface [11,12,28,29], for which we found a reduction in dangling bond density (using the Si(100)2 × 1 surface as reference) of the same order of magnitude as for the Si(111)7 × 7 surface. This result is in favour of the idea that adatom-like structures exist at the reconstructed Si(110) surface, as proposed by the authors of a recent scanning tunneling microscopy (STM) study [30]. Similar research on the clean low-Miller index surfaces of germanium using SDR, AES, LEED, and in addition spectroscopic ellipsometry, XPS and STM, is in progress in our laboratory.

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