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AN INVESTIGATION OF THE INTERACTION OF N_2O WITH THE Si(111)-7 × 7 SURFACE USING AES AND OPTICAL REFLECTOMETRY; A COMPARISON WITH O_2

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At 300 K, N_2O decomposes into N_2, leaving behind atomic oxygen at the Si(111)-7 × 7 surface. Decomposition at two different sites is proposed, having the overall initial reaction probability: $s(0) = (6.7 \pm 0.7) \times 10^{-6}$. $SiO_x (x \sim 1)$ bonds are predominantly formed, saturation occurring at monolayer coverage. This oxygen monolayer appears to completely prevent further oxygen uptake by additional N_2O or O_2 exposures, in contrast with the adsorption behaviour of O_2 on Si(111)-7 × 7, which exhibits slow sorption beyond one monolayer.

1. Introduction

The oxidation of the Si(111) crystal face has been the subject of numerous investigations. Recent result [1–3] indicate that the initial chemisorption of molecular oxygen on Si(111) is complex. The combined use of both molecular (O_2) and atomic (N_2O) oxygen gives a better understanding of the mechanism of the oxygen chemisorption process on clean silicon surfaces. This method has also been successfully applied to metal surfaces [4].

N_2O appears to be an attractive proposition for the production of an atomic oxygen adlayer on silicon surfaces due to its low bond dissociation energy ($D(N_2–O) = 1.677$ eV [5]). This paper presents results showing the respective adsorption and decomposition of O_2 and N_2O on a clean Si(111)-7 × 7 surface at 300 K and a comparison of the adsorption behaviour of both gases.

2. Experimental results

2.1. General remarks

The experiments were performed in a stainless steel UHV system described previously [6], with additional facilities for AES–LEED (four-grid retarding

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field analyser) and ion-bombardment. Reflectivity measurements were performed with the automatic reflectometer [7] in the 1.0–3.0 eV photon-energy region. Adsorption experiments were initiated from a clean Si(111)-7×7 surface. O_2 and N_2O were admitted in single doses. During all adsorption experiments no filaments were lit in the reaction chamber.

2.2. Adsorption of O_2

The reflectivity measurements [8] are not shown here. Fig. 1a shows the measured oxygen intensity as a function of exposure. The oxygen intensity is displayed as the ratio, h_O/h_{Si}, of the oxygen (510 eV) to the silicon (92 eV)

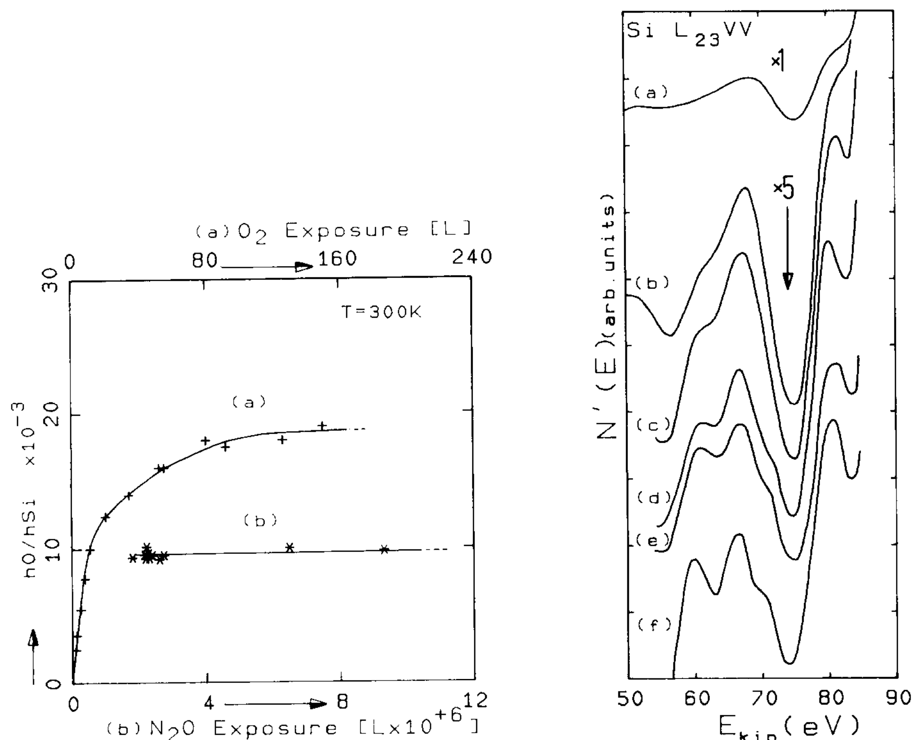

Fig. 1. Auger oxygen signal, h_O/h_{Si}, as a function of exposure of (a) O_2 and (b) N_2O to Si(111)-7×7 at 300 K. The data in (b) were recorded after saturation of the surface. Primary beam energy: 2 keV, primary current density: ~ 3.5 μA mm^{-2}; modulation voltage: 9 V peak-to-peak.

Fig. 2. Si $L_{23}VV$ spectrum for five chemisorption stages of oxygen on silicon. Minimal beam effects: (a) the clean Si surface; the surface exposed to (b) 1.7 L O_2, (c) 4.8 L O_2, (d) 11 L O_2, (e) 19 L O_2, (f) 175 L O_2. Modulation voltage: 2 V peak-to-peak.

peak-to-peak height, from the second derivative Auger spectra. The adsorption of oxygen is characterised by a rapid uptake followed by a slow sorption process and finally saturation after ~ 200 L (1 langmuir = 1×10^{-6} Torr s). The $L_{23}VV$ line in the second derivative mode for several stages of chemisorption of oxygen, ranging from a clean through to an almost saturated surface is shown in fig. 2. New peaks emerge at 83, 63 and ~ 70 eV, the last appearing at ~ 11 L.

2.3. Decomposition of N_2O

No nitrogen was detected in the Auger spectra, confirming that the overall reaction is: $N_2O \rightarrow N_2^{\nearrow} + O_{ad}$. Our interest was focussed on the kinetics of the N_2O decomposition at the two different adsorption sites of the Si(111)7 × 7 surface [6]. The relative change in reflectivity, $\Delta R/R$, as a function of exposure at $h\nu = 2.45$ eV (main peak) and 1.76 eV (secondary peak), is shown in fig. 3; the insert gives the peak positions as a function of $h\nu$. The measurements at 1.76 eV are corrected for the contribution from the main peak.

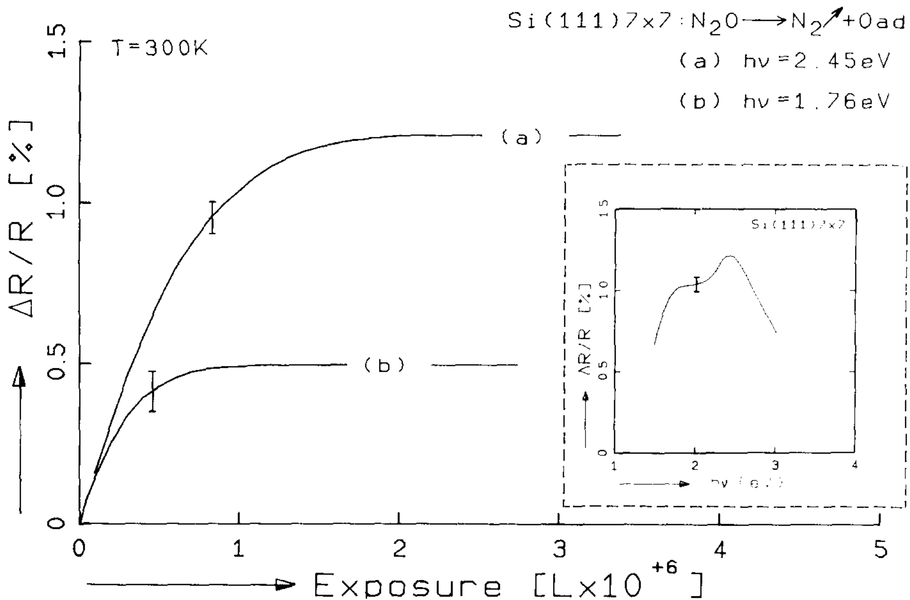

Fig. 3. The relative change in reflectivity $\Delta R/R$ versus N_2O exposure for fixed photon energies at 300 K. The insert shows the relative difference in reflectivity $\Delta R/R$ before and after decomposition of N_2O on the clean Si(111)-7×7 surface up to saturation as a function of the photon energy $h\nu$ at 300 K. The figure exhibits peaks at 2.45 and 1.76 eV, which compares favourably with fig. 2 from ref. [6].

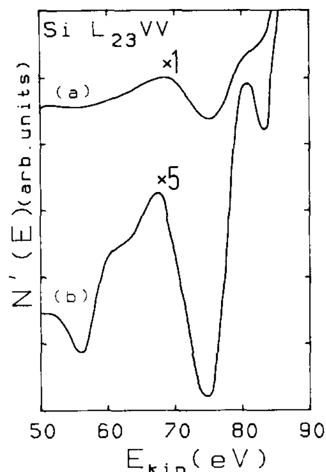

Fig. 4. Si $L_{23}VV$ spectrum (a) of the clean surface, (b) after saturation of the surface with atomic oxygen by the decomposition of N_2O. Modulation voltage: 2 V peak-to-peak. The $L_{23}VV$ line shape (b) does not change upon additional N_2O exposures (up to $\sim 10^7$ L) or O_2 exposure (up to $\sim 10^3$ L).

Both peaks give information about the disappearance of surface states [9], which may be identified with atomic oxygen adsorption on sites 1 (main peak) and sites 2 (secondary peak), see section 3. Saturation of the silicon surface occurs at $\sim 2 \times 10^6$ L (fig. 3). Fig. 1b shows the ratio h_O/h_{Si} in the Auger spectra as a function of exposure, taken after saturation up to $\sim 10^7$ L; beyond 2×10^6 L no further oxygen uptake occurs. The corresponding Si $L_{23}VV$ spectrum (fig. 4) exhibits no change in line shape for exposures $> 2 \times 10^6$ L. A distinct peak at 83 eV and a smaller one at 63 eV are the only new features.

3. Discussion

It is assumed that saturation of the fast O_2 adsorption stage in fig. 1a, after (8.5 ± 0.5) L, corresponds to monolayer coverage, i.e. one oxygen atom per silicon surface atom [10]; $h_O/h_{Si} = \sim 9.5 \times 10^{-3}$ rel. units at $\theta = 1$. A calculation using simple adsorption kinetics [11] gives the initial sticking probability, $s_0 = 0.13 \pm 0.01$.

The reaction probability, s, of N_2O (fig. 5) is defined as the number of adsorbed oxygen atoms per incident N_2O molecule on sites 1 and 2 respectively. Recently [6] the disappearance of the two peaks in fig. 2 from ref. [6] were interpreted (using the Haneman model [12] for the Si(111) surface) with oxygen adsorption on raised and lowered surface atoms. This model is, however, currently under discussion [13], so we think it more appropriate to

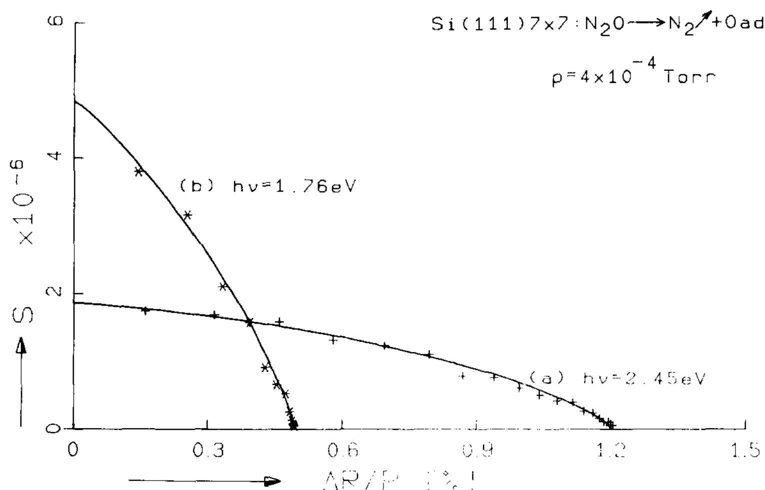

Fig. 5. Reaction probability s for the N_2O decomposition at: (a) site 1 and (b) site 2 on the clean Si(111)-7×7 surface as a function of $\Delta R/R$ (oxygen coverage), derived from reflectometric measurements (fig. 3). The solid lines represent eq. (1) with (a) $K_1 = 0.4$ and (b) $K = 0.6$ at 300 K.

interpret the disappearance of the two peaks in fig. 3 (insert) with oxygen adsorption on sites 1 (main peak) and 2 (secondary peak). The existence of two distinct adsorption sites was recently supported by an infrared study of Chabal et al. [14]. Assuming an equal density of sites, it is possible to correlate the relative change in reflectivity at 2.45 and 1.76 eV with the fractional coverage per type of site, θ_i ($i = 1, 2$). At saturation, the number of oxygen atoms on each site type is 3.92×10^{14} cm^{-2}. Fig. 5 shows, for each site, the line of best fit with the measured data. These lines may be described using the rate equation for adsorption on a single site via a mobile precursor state, where the reflection probability of gasmolecules is independent of θ_i as outlined by Kohrt and Gomer [15]:

$$S_i(\theta') = S_i(0)\left[1 + K_i\theta_i'/(1 - \theta_i')\right]^{-1}, \tag{1}$$

where $\theta_i' = \theta_i/\theta_i(\text{sat})$ ($i = 1, 2$) and the constant K_i is related to the probabilities of chemisorption (P_{a_i}), desorption of the precursor molecules from empty chemisorption sites (P_{d_i}) and filled sites (P_{d_i}'), through: $K_i = P_{d_i}'/(P_{a_i} + P_{d_i})$. The initial reaction probabilities on sites 1 and 2, are given by $s_1(0)$ and $s_2(0)$, where $s_1() = (1.9 \pm 0.1) \times 10^{-6}$ and $s_2(0) = (4.8 \pm 0.7) \times 10^{-6}$, indicating a preference for the N_2O molecule to decompose on site 2, or alternately, a difference in density between the two sites. The relatively large error in $s_0(0)$ (about 15%) mainly arises from the fact that due to strong overlapping of both peaks (fig. 3, insert) correction for the contribution due to the main peak by

extrapolation can only be a best estimate. Assuming an equal site density, a difference in surface lifetime for the N_2O molecule as a mobile precursor and/or a difference in activation energy for decomposition of the N_2O molecule on these sites may explain why $s_2(0)$ and $s_2(0)$ have different values. We may speculate that since eq. (1) fits the observed kinetic results this could imply the existence of two independent arrays of definite adsorption centers. Comparison of h_O/h_{Si} between the curves a (at saturation of the fast adsorption stage) and b in fig. 1 allows us to infer that decomposition of N_2O leads ultimately to a monatomic oxygen layer. This adlayer appears chemically stable against additional O_2 exposures up to $\sim 10^3$ L since no change is induced in either the Si $L_{23}VV$ line shape in fig. 4b, or h_O/h_{Si} in fig. 1b. O_2 adsorption, in contrast, exhibits slow sorption beyond one monolayer (fig. 1a) [16], the dangling bond surface states being quenched after ~ 19 L [6,8].

This value shows reasonable agreement with that from Hollinger and Himpsel [2], who have further shown that, upon O_2 adsorption, four oxidation states of Si can be detected before all surface states are quenched [2,3]. This implies that the oxygen atoms are not all initially connected through the silicon dangling bond, but that oxide-like Si–O–Si chains are also formed. Thus completion of monolayer coverage is determined at an earlier stage when using AES (this work) which, unlike reflectometry [6,8], measures the entire oxygen content of the adsorbed layer. This is further supported by the Si $L_{23}VV$ spectra (figs. 2e and 4b), which were taken just after quenching of the dangling bond surface states. Whereas both curves exhibit additional structure at 83 and 63 eV, curve e displays structure at ~ 70 eV not existing in curve b, further the peak at 63 eV in curve e is more pronounced than in curve b. Lang et al. [17] argue that the presence of fine structure with peaks at 61 and 66 eV can be attributed to a precursor state of silica. In our spectra (fig. 2e–2g) these two peaks occur at 63 and ~ 70 eV, probably due to sample charging effects and different experimental arrangement. In the exposure region used there is no evidence that SiO_2 has formed. The 83 eV peak is usually attributed to an intermediate oxidation stage, SiO_x, with $x \sim 1$ (ref. [17] and references therein). In view of the above results, decomposition of N_2O leads to oxygen atoms mainly connected through the silicon dangling bonds, monolayer coverage occurring when all dangling bonds are quenched. This monatomic oxygen layer appears to completely prevent further oxygen uptake by additional N_2O or O_2 exposures. O_2 adsorption, however, seems to be a more complicated process. The evidence suggest that determination of monolayer coverage using optical methods may not be unambiguous.

References

[1] H. Ibach, H.D. Bruchman and H. Wagner, Appl. Phys. A29 (1982) 113.
[2] G. Hollinger and F.J. Himpsel, J. Vacuum Sci. Technol. A1 (1983) 640.
[3] G. Hollinger and F.J. Himpsel, Phys. Rev. B28 (1983) 3651.

[4] F.H.P.M. Habraken, Thesis, University of Utrecht, Utrecht (1980).
[5] G. Herzberg, Electronic Spectra of Polyatomic Molecules (Van Nostrand, New York, 1966).
[6] P.E. Wierenga, A. van Silfhout and M.J. Sparnaay, Surface Sci. 87 (1979) 43.
[7] K.O. van der Werf and P.E. Wierenga, Polytech. Tijdschr. Electrotech. Electron. 35 (1980) 400, 464, 512.
[8] The reflectometric measurements of oxygen adsorption on the clean Si(111)-7 × 7 surface were re-done. The results are in good agreement with those from Wierenga et al. [6], i.e. all dangling bond surface states are quenched after ~ 19 L.
[9] F. Meyer, E.E. de Kluizenaar and G.A. Bootsma, Surface Sci. 27 (1971) 88.
[10] A.H. Boonstra, Philips Res. Rept. Suppl. 3 (1968).
[11] R. Dorn, H. Lüth and H. Ibach, Surface Sci. 42 (1974) 583.
[12] D. Haneman, Phys. Rev. 121 (1961) 1093.
[13] A. Kahn, Surface Sci. Rept. 3 (1983) 275.
[14] Y.J. Chabal, G.S. Higashi and S.B. Christman, Phys. Rev. B28 (1983) 4472.
[15] C. Kohrt and R. Gomer, J. Chem. Phys. 52 (1970) 3283.
[16] S.E. Goodnick, W. Porod, R.O. Grondin, S.M. Goodnick, C.W. Wilmsen and D.K. Ferry, J. Vacuum Sci. Technol. B1 (1983) 767.
[17] B. Lang, P. Scholler and B. Carrière, Surface Sci. 99 (1980) 103.