

ADSORPTION OF ATOMIC AND MOLECULAR OXYGEN ON Si(001) 2×1 :
COVERAGE DEPENDENCE OF THE AUGER O K V V LINESHAPE

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By means of Auger electron spectroscopy (AES) we have monitored the room temperature adsorption of O₂ and N₂O on the clean Si(001) 2×1 surface. We have found, for the first time, a significant variation in the intensity ratio of the K L₁ L₁ and K L₂₃ L₂₃ O Auger lines in the submonolayer range. This variation can be related to a change in bonding configuration of the oxygen atom/molecule in the initial adsorption stage in which the influence of inter-atomic matrix elements of the Auger process cannot be neglected.

THE INITIAL stage of the oxidation of silicon surfaces has been the subject of numerous experimental and theoretical studies. Auger electron spectroscopy (AES) has proven to be a valuable surface analysis technique in these studies. The chemical element specificity combined with low surface destruction makes AES highly suitable to check the surface cleanliness and to determine coverage, an aspect which has shown its importance in a very recent study of Keim and Wormeester concerning the analysis of the atomic nature of 5×1 reconstructed Si(110) [1, 2]. The determination of the oxygen coverage at an initial oxidation stage is usually performed by measuring the peak height ratio of the appropriate Auger transitions in the first derivative of the energy distribution ($dN(E)/d(E)$) of the adsorbate and the substrate. A reference system is needed to define monolayer [ML] coverage in order to be independent from escape depth and matrix elements [3, 4]. If valence electrons are involved in the Auger process not only information about the chemical composition can be derived from AES. Analysis of such Auger line shapes can provide information on the nature of the chemical bond of the elements where the core hole is located. A qualitative picture of the change of the Si L V V line shape upon oxidation has been presented by Keim *et al.* [3, 5–9]. Sasse *et al.* [10–13] have tried to identify the chemical origin of the observed features in these Si L V V spectra by deconvoluting the AES line shape to remove instrumental broadening and plasmon loss structures. The resulting line shape was compared to calculated Auger line shapes of several possible bonding configurations. The calculated Auger spectra were generated with quantum chemical cluster calculations. The limit of this approach was shown in the analysis

of a Si(001) surface oxidized beyond one ML [10]. The complexity of the measured spectrum allowed only a qualitative interpretation of the appearance of four different oxygen bonding configurations.

A more quantitative interpretation of the change of the electronic structure recorded by AES valence band spectroscopy is desired. We shall focus our attention to the O K L L transitions since in oxygen adsorption experiments, all oxygen atoms contributing to this line shape will be involved in the bond of the adsorbed atom on the surface and will thus contribute to the O K L L Auger line shape. In contrast, most Si atoms which contribute to the Si L V V line shape are not involved in the initial adsorption and will therefore give rise to a large background signal. The idea of relating changes in charge transfer to a different chemical bond configuration in the case of AES was presented by Weißmann [14, 15]. With the assumption that changes in the actual charge of an oxygen atom will give rise to a change in the number of the *p*-orbital electrons only, Weißmann obtained the following relationship for the intensities of the structures in the O K L L Auger spectrum:

$$\alpha = \frac{I(K L_1 L_1)}{I(K L_{23} L_{23})} = \frac{2}{(4 + \Delta q)(3 + \Delta q)} \frac{M_{ss}}{M_{pp}} \quad (1)$$

where Δq is the charge transfer to the oxygen atom as a result of the chemical bond and M_{ss} and M_{pp} are the atomic matrix elements of an Auger transition of *s* and *p* electrons, respectively, with $M_{ss}/M_{pp} = 0.72$ [14]. The ratio of these atomic matrix elements is assumed to be independent of the chemical environment [14]. Ascarelli *et al.* [16] and Shul'Ga *et al.* [17] have shown that using this charge concept of Weißmann, there is a linear relation between their experimentally found

intensity ratio α , the relative energy positions of the peaks in the Auger KLL spectrum and the chemical shift in the XPS spectra for several metal oxides and carbides. These effects are all believed to be the result of the charge transfer characteristic of the chemical bond in which the oxygen (or carbon) atom is involved. To a good approximation the shifts recorded are even linear to this charge transfer. Laudet *et al.* [18] recorded the change of the intensity ratio of the O KLL spectrum upon the oxidation of Cu and Al surfaces. From this work it is clear that there is a change in charge during the oxidation process.

We have measured the O KLL Auger lineshapes in the initial oxidation stage on the clean (111), (110) and (001) surfaces of Si. In these experiments O₂ as well as N₂O have been used to oxidize the clean Si surface at room temperature. In this paper the N₂O/O₂ adsorption measurements on the Si(001)2 × 1 surface will be discussed, those on the other two will be published elsewhere. For the experimental details we refer to [3]. The intensity ratio α of equation (1) was determined as a function of the oxygen coverage and is depicted in Fig. 1. The coverage was determined following the method of Keim [4] in which 1 ML is defined as the ratio of the O K L₂₃ L₂₃ and the Si L V V Auger peak to peak (*pp*) heights at the saturation coverage of N₂O on Si(001) at 300 K, with a correction for defects at the surface. It is obvious from this paper that the determination of the coverage in the submonolayer region using these peaks cannot give the correct coverage since the O K L₂₃ L₂₃ peak intensity is modulated by the chemical bond. Nevertheless, we can determine an order of successive stages of

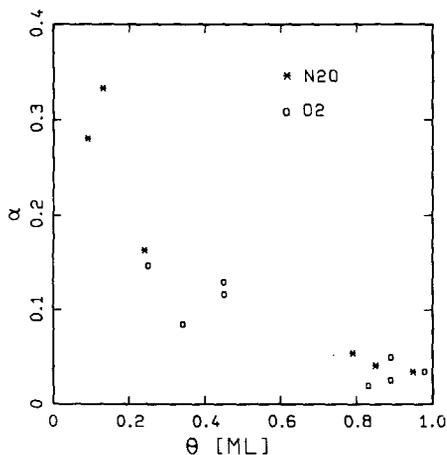


Fig. 1. Ratio α of the O K L₁ L₁ and K L₂₃ L₂₃ Auger *pp* heights in the first derivative of the energy distribution ($dN(E)/dE$) as a function of fractional oxygen coverage (θ) on Si(001)2 × 1.

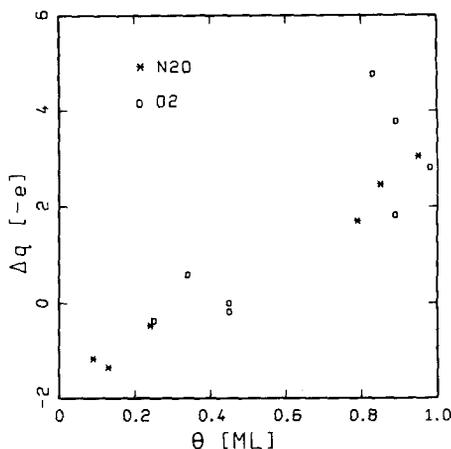


Fig. 2. Charge transfer (Δq), according to equation (1), as a function of fractional oxygen coverage (θ) on the Si(001)2 × 1 surface derived from the data in Fig. 1. In the high coverage region the bounds of experimental error are relatively large because of the low signal-to-noise ratio.

oxidation from the O/Si *pp* ratio. From Fig. 1 it is clear that the ratio α changes dramatically in the very early adsorption stage, without a significant difference between O₂ and N₂O. Beyond ML coverage the surface shows a steady state bonding configuration. Similar results have been obtained for the adsorption of molecular oxygen and nitrous oxide on the (110) and (111) surfaces of Si. To our knowledge we are the first to report this change in the ratio of the O KLL Auger peaks as a function of the oxidation stage of an Si surface in the submonolayer region.

The parameter α is in the view of Weißmann [14, 15] a direct measure of the atomic charge per oxygen atom bonded at the surface, whose quantity has been depicted in Fig. 2 using equation (1). The charge transfer in the final stage as seen in Fig. 2 results in the previously reported formation [19] of a negative charge density accumulation in the near surface region. Work function measurements [20] also show a change in the formed dipole layer, but this change is partly due to the interaction between the dipoles, which is the result of the formation of Si-O bonds. Also subsurface oxidation will lead to interpretation problems, not present in the local probe of the atomic additional charge within the frame of equation (1). The increase of the charge at the oxygen atom will also change the electrostatic field at the surface which may certainly cause the activation barrier for oxygen chemisorption to increase as a function of coverage as suggested by Gupta *et al.* [21]. The change in the atomic charge is in the view of Grunthaner *et al.*

[22] due to geometric effects. Using X-ray Photo Electron Spectroscopy (XPS) Grunthaner and coworkers [22] recorded the O 1s and Si 2p spectra of a Si-SiO₂ interface. Their O 1s electron distribution showed two distinct peaks that were related to two different bond angles of the Si-O bond. The difference in binding energy was calculated by relating the charge transfer in the Si-O bond, as a result of a bond angle variation of several species of *a*-SiO₂, to an energy shift in the XPS spectrum. Their calculations for quartz have shown to give an extensive change in charge transfer through variation of the Si-O-Si bond angle. Quantum chemical cluster calculations can also easily be done for the partially oxidized Si(001) surface. These calculations for atomic oxygen by Smith and Wander [23] and molecular oxygen by Zheng and Smith [24] not only confirm the reaction path mechanism of N₂O and O₂ on Si(001), respectively, as proposed by Keim *et al.* [3], But also show a change in the geometric position of the oxygen atom in the Si-O-Si bond as the chemisorption proceeds. Furthermore, the theoretical work of Zheng and Smith [24] shows that in the initial stage molecular oxygen adsorption on the Si(001) surface is dissociative with the oxygen atoms occupying sites between first layer Si atoms, a configuration which is similar to the one when the same surface is exposed to nitrous oxide [3, 23]. This finding forms a natural explanation for our experimental observation that, at least in the initial adsorption stage, there is no significant difference between O₂ and N₂O in the α versus θ curve as depicted in Fig. 1. The non-static position of the oxygen atom on the Si surface upon adsorption was also experimentally observed by Schaefer and Göpel [25]. Their High Resolution Electron Energy Loss (HREELS) measurements show a remarkable change in the frequency of one of the modes observed. This change is linear with coverage in the measured 0.2 to 0.6 ML range ($T = 300$ K), indicating a stronger bond strength as the oxidation proceeds. Their measurements also show a change in the position of the O 1s XPS peak upon oxidation. According to Ascarelli and Shul'Ga [17] this change has the same origin as the change in α as presented in Fig. 1.

Although the concept of Weißmann [14, 15] seems to be able to explain the change in the observed ratio α as a change in the charge transfer of the Si-O bond upon oxidation, this is not a satisfying explanation. In Fig. 2 is shown that the charge transfer, as derived from the data in Fig. 1 using equation (1), accompanied by the variation of α is at least 2 electrons. To our opinion, this is physically unlikely. In the very initial stage of oxidation, the adsorbed oxygen atom even seems to show a deficit of electrons. We

performed MNDO (Modified Neglect of Diatomic Overlap) cluster calculations on a Si₉H₁₂O cluster simulating the adsorption of oxygen on the Si(001) surface leading to bridge bonded oxygen between first layer Si atoms which is the most likely adsorption geometry (see, e.g. [23, 24] and references therein). These calculations show only a relatively small change in the additional charge of the O atom if the O atom is varied in position (R_{\perp}) between -1.2 and 1.2 Å below and above the surface defined by the first layer Si atoms, as can be seen in Table 1. We calculated both local ($\Delta q_L(-e)$) and Mulliken ($\Delta q_M(-e)$) populations for the determination of the charge at the oxygen atom. From Table 1 the question arises what charge should be taken as probed by Auger, i.e. the local or the Mulliken charge [26], or even something else since both $\Delta q_L(-e)$ and $\Delta q_M(-e)$ cannot explain our experimentally derived charge transfer data (Fig. 2) for a bridge bonded oxygen geometry on the dimer site. The reason for the discrepancy between calculated variation of the charge and the resulting O KLL Auger intensity ratio $\alpha_{L,M}$ (Table 1), and that measured (Fig. 2 and Fig. 1, respectively) could therefore originate from the description of the Auger process. It seems that the interpretation of O KLL Auger line shapes in terms of local or Mulliken charge is not sufficient. The change of the chemical bond observed is quite likely to be due to a geometric change of the oxygen atom as might be concluded from the work of Schaefer and Göpel [25] and Grunthaner *et al.* [22]. Calculations of Smith and Wander [23] also predict a different equilibrium position of the O atom on the Si(001) surface at 0.5 ML and 1 ML. As a result of this different geometrical

Table 1. Change in the local ($\Delta q_L(-e)$) and Mulliken charge ($\Delta q_M(-e)$) of the oxygen atom upon variation of the oxygen distance to the surface (R_{\perp}), and the resulting O KLL Auger intensity ratio α_L and α_M , respectively, according to equation (1)

R_{\perp} (Å)	$\Delta q_L(-e)$	α_L	$\Delta q_M(-e)$	α_M
-1.20	0.585	0.087	0.724	0.081
-0.80	0.570	0.087	0.777	0.079
-0.40	0.398	0.095	0.731	0.080
-0.05	0.332	0.098	0.718	0.081
0.10	0.312	0.099	0.709	0.082
0.20	0.305	0.100	0.703	0.082
0.30	0.300	0.100	0.697	0.082
0.40	0.299	0.100	0.690	0.082
0.50	0.300	0.100	0.680	0.082
0.80	0.303	0.100	0.635	0.084
1.20	0.278	0.102	0.531	0.089

position the overlap of the oxygen wavefunctions with the Si wavefunctions is changed. This means that the influence of the chemical bond on the Auger lineshape, i.e. the matrix elements, should be evaluated in a more rigorous way, taking into account the influence of the distance between neighbour atoms on the Auger matrix elements. Preliminary results from cluster calculations reveal a significant influence of inter-atomic matrix elements on the Auger process for well defined possible adsorption geometries. These results, showing the change of the inter-atomic matrix elements of the Auger process upon a change in overlap between neighbouring atoms, i.e. the influence of adsorbate geometry on the Auger lineshape, will be published elsewhere [27]. We will show that the matrix elements of the Auger process depend on more than the charge transfer of a chemical bond only as is the assumption in equation (1). The oxygen adsorption on the clean Si surface seems to provide a test case for the description of the Auger process when different chemical bonds are involved.

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