

Interaction of atomic oxygen (N_2O) with a clean Si(001) surface: O adsorption geometries as derived from the O KVV Auger lineshape

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The room temperature adsorption of N_2O on the clean Si(001) 2×1 surface was used as a model system in an Auger electron spectroscopy (AES) study presented in this paper. Earlier experimental and recent theoretical work have provided evidence that this reaction evolves in discernible stages each exhibiting different adsorption geometries for the oxygen atom. In this AES study the intensity ratio of the KL_1L_1 and $\text{KL}_{2,3}\text{L}_{2,3}$ O Auger transitions, α , was measured as a function of the fractional oxygen coverage, θ , and compared with our calculated intensity ratios and binding energy measurements of the O 1s photoelectron from literature. As a result we have found, for the first time, that $\alpha(\theta)$ can be related to a specific adsorption geometry in the submonolayer range. Moreover, we have found experimental evidence for an intermediate stable O adsorption state on the dimer at low coverage ($\theta \leq 0.2$ monolayer), as proposed earlier from theoretical studies.

1. Introduction

Auger electron spectroscopy (AES) can be considered as a standard, low cost and easy to use experimental technique in ultra high vacuum (UHV). Its application includes checking surface cleanliness, determination of fractional elemental surface coverage, θ , and obtaining information about the chemical composition of materials. With AES one can also get a qualitative picture of the nature of the chemical bond, i.e. the electronic structure [1]. For the system silicon–oxygen, for example, much effort has been put into the analysis of the Si LVV Auger lineshape at various oxidation stages (see, e.g. refs. [2,3]). Although interesting results have been achieved, the interpretation of experimental Si LVV Auger spectra is complicated by a concomitant large background signal, as a result of comeasuring (deeper-lying) Si atoms which are not involved in the initial oxygen adsorption. One can overcome this inherent experimental problem by measuring the OKLL Auger spectrum since in oxygen adsorption experiments all O atoms contributing to this lineshape will be involved in the bond on the

surface and will thus participate in the OKLL Auger spectrum. A sensitive quantitative probe of the chemical bond in such an experimental approach is the intensity ratio of the KL_1L_1 and $\text{KL}_{2,3}\text{L}_{2,3}$ O Auger lines, α , introduced by Weissmann [4]. For various elemental oxides Weissmann monitored the ratio α for which a significant variation was observed. His concept is based on the assumption that the charge accumulation on the oxygen atom involved in the oxide is reflected in the (extra) population of the O p-orbitals, or $\text{L}_{2,3}$ energy level. The observed variation of α with compound was therefore explained by the degree of charge transfer characteristic of the chemical bond in which the O atom is involved [4]. This concept of Weissmann seemed to work well on several bulk oxides and carbides [5–7]. Stimulated by these results we were interested in the behaviour of α in the initial adsorption stage of oxygen on clean low Miller index surfaces of Si, as large changes in charge transfer in the Si–O bond may be expected to take place in this region [8–11]. Very recently [12], we reported a significant variation of α in the submonolayer region upon exposing the clean

Si(001) 2×1 surface to O₂ and N₂O. Our experimental data, however, could not be explained satisfactorily by Weissmann's chemical bond ionicity concept. Cluster calculations [13] provided evidence that the bonding configuration of the oxygen atom/molecule in the initial adsorption stage, in particular the O–Si bond distance, has a significant influence on the inter-atomic Auger matrix elements. The inter-atomic Auger transitions, which are usually assumed to be negligible, were shown to play an important role in the observed behaviour of α , as does the core state. From X-ray photoelectron spectroscopy (XPS) studies [14–16], namely, it is well known that the binding energy (BE) of the O 1s electron varies with the (molecular and atomic) oxygen adsorption stage. A change in core state is in general accompanied by relaxation processes which, due to their complex impact, are still not well understood [17]. According to our calculations [13] a relaxation of the core state wavefunction also influences the intensity ratio α for the O Auger transitions. Considering these aspects, it is obvious that the simple chemical bond ionicity concept of Weissmann [4] has only a very limited application. Since the probability of inter-atomic Auger electron emission processes depends sensitively on the degree of the overlap of the oxygen wavefunctions with the silicon wavefunctions [13], the question arises if α can be assigned to a specific O adsorption geometry. Our goal in the present study is to find out in detail if a change in O adsorption geometry manifests itself in the OKLL Auger process. For that purpose we need a model system. As a model system we take the room temperature adsorption of nitrous oxide (N₂O) on Si(001) 2×1 for which both experimental [18] and theoretical [19] work have provided evidence that the adsorption of atomic oxygen as released by this molecule is restricted to the first layer Si atoms leading ultimately to an in-plane configuration of bridge bonded oxygen. Our experimental results concerning this model system published previously [18] indicate that the adsorption of atomic oxygen evolves in distinguishable stages. In order to find out if the stepwise reaction of N₂O with Si(001) 2×1 can also be observed in the $\alpha(\theta)$ curve, the Auger measure-

ments as described in ref. [18] from which the α data have been published [12], were repeated using an Auger spectrometer equipped with a cylindrical mirror analyser (CMA), so as to obtain OKLL Auger spectra with the best possible signal-to-noise (S/N) ratio down to 0.05 monolayer (ML) oxygen coverage.

In this paper we will show that α is a valuable tool in studies which are directed towards the characterization of the O adsorption geometry on clean surfaces of Si.

2. Experimental

The nitrous oxide adsorption experiments were performed in a stainless steel UHV system described previously [20] with facilities for AES, spectroscopic ellipsometry, surface conduction measurements and ion bombardment. The procedures for gas handling, surface cleaning by simultaneous argon ion bombardment and annealing (SIBA) were identical to those described earlier [18]. The fractional oxygen coverage, θ , was determined following the method of Keim [21] in which the ratio of the OKL_{2,3}L_{2,3} and the SiLVV Auger peak to peak (p–p) heights, h_O/h_{Si} , at the saturation coverage of N₂O on Si(001) at 300 K is assumed to correspond with $\theta = 0.85 \pm 0.10$ ML. We note that the determination of the oxygen coverage in the submonolayer region using these peaks may not provide the correct θ since the OKL_{2,3}L_{2,3} peak intensity is modulated by the chemical bond. Nevertheless, we can determine an order of successive stages of oxidation from the O/Si p–p ratio. The Auger spectra were recorded in the first derivative of the energy distribution, $d(EN(E))/dE$, using a primary beam energy of 2000 eV, a primary beam current density of about $1 \times 10^4 \mu\text{A cm}^{-2}$, 4 V_{p–p} modulation voltage applied to the CMA, a sweep rate of 0.2 eV s^{–1} and a lock-in time constant of 3 s. Under these conditions the relatively low intensity OKL₁L₁ Auger peak could be resolved down to about 0.05 ML oxygen coverage. Fig. 1 shows the OKLL Auger spectrum recorded at 0.33 ML oxygen coverage in which α is defined as the ratio of the indicated KL₁L₁ and KL_{2,3}L_{2,3} p–p

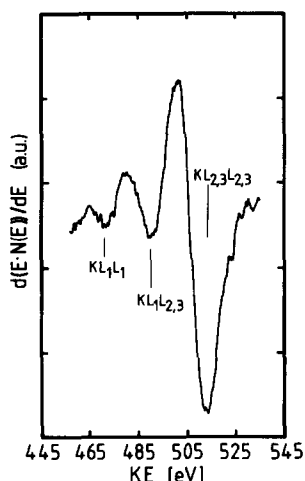


Fig. 1. Oxygen KLL Auger spectrum recorded at a fractional oxygen coverage, $\theta = 0.33$ ML. α is defined as the ratio of the KL_{1L_1} and $KL_{2,3L_{2,3}}$ p-p heights.

heights. The silicon sample ($8 \times 30 \times 0.3$ mm³) was made out of a $2000 \Omega \cdot \text{cm}$, nominally flat p-type crystal in the $\langle 001 \rangle$ orientation. Each AES data point was obtained after exposing the cleaned Si surface to a single N₂O dose in order to avoid electron beam induced effects.

3. Results and discussion

Fig. 2a (filled circles) shows the intensity ratio α as a function of the fractional oxygen coverage θ . From this figure three distinct adsorption stages can be discerned, the initial stage from 0 to about 0.2 ML, followed by the second ranging to $\theta = 0.6$, and the final stage from 0.6 to 0.85 ML. Curve b of fig. 2, previously published [18] and identical to the one obtained with the CMA (this work), shows θ , as derived from the ratio $h_{\text{O}}/h_{\text{Si}}$ as a function of nitrous oxide exposure. Also taken from ref. [18] is fig. 2c which shows the relative change of the sample surface optical reflectivity, $\Delta R/R$, with exposure at photon energies of 2.90 eV (DB) and 3.85 eV (DM). The DM curve corresponds with the removal of the Si-Si dimers as the formation of bridge bonded oxygen proceeds, the accompanying saturation of dangling bonds is depicted by the DB curve. Fig. 2 has

been composed of curves a, b and c in such a way that the relation between $\alpha(\theta)$ and $(\theta, \Delta R/R)$ with exposure is clear at a glance. The two solid lines in fig. 2a which mark the transition from one adsorption stage into the other have been extended to (b) and (c). From fig. 2 it can be seen that the adsorption stages as indicated in curve a are in agreement with those obtained earlier (curve b, and curve DM and DB in (c)). According to our model of the dissociative reaction of N₂O with the Si(001) 2×1 surface [18] (see curve DM and DB of fig. 2c) oxygen goes into a bridging position between top layer Si atoms in the initial oxidation stage by decomposition at the Si-Si dimer bonds (1st stage), the initial reaction probability being $(2.4 \pm 0.2) \times 10^{-5}$, followed by additional uptake of atomic oxygen via attachment of the dangling bonds of the top layer Si atoms whose position has moved considerably to the nearest neighbour (nn) Si atoms forming the Si/O\Si configuration as well (2nd stage), and ultimately leading to a complete saturation of first the dimer and then the dangling bond orbitals (3rd stage). For a view of the schematic model for the successive uptake of atomic oxygen (O) on a clean Si(001) 2×1 surface, we refer to fig. 14 of ref. [18].

3.1. Stage I

The spectroscopic differential reflectivity (SDR) measurements [18] indicate that in this stage the adsorption of oxygen atoms occurs at only one specific site (fig. 2c), as the optical activity is narrowed to one region. XPS investigations dealing with the room temperature adsorption of nitrous oxide on Si(001) 2×1 [16] indicate that the BE of the O 1s electron, centered around 531.7 ± 0.2 eV at fractional oxygen coverages below about 0.2 ML, has an undetectable shift which implies that the O core state does not change significantly in this region. Our theoretical calculations of the OKLL Auger lineshape show that a contraction of the O core hole wave function can lower the value of α [13]. However, as the BE of the O 1s electron does not change within the S/N ratio [16], it is unlikely that α will decrease significantly in the first stage as a result

of this effect. Reducing the Si–O bond length leads to a decrease in α , as a change in the overlap of the O and nn Si atom will influence the strength of the inter atomic Auger transitions [13]. That this aspect is responsible for the observed decrease in α is supported by theoretical studies concerning the adsorption of atomic oxygen on the 2×1 reconstructed Si(001) surface [19,22]. These studies reveal without exception that atomic oxygen is adsorbed at the dimer bridge site, with a Si–O bond length varying from 1.63 [19] to 1.68 Å [22]. However, the same studies

also show that the stable bridge bonded configuration at the dimer may be preceded by a metastable state in which the Si–O distance is in the range of 1.8–1.9 Å. Our experimentally observed decrease of α therefore strongly suggests that in the first adsorption stage this metastable state exists as an intermediate stable state which is completely transformed into a stable state at 0.2 ML, characterized by a large Si/O\Si bond angle. We prefer to call it an intermediate stable state as it is not modified by intensive electron bombardment (total dose about 5×10^{19} elec-

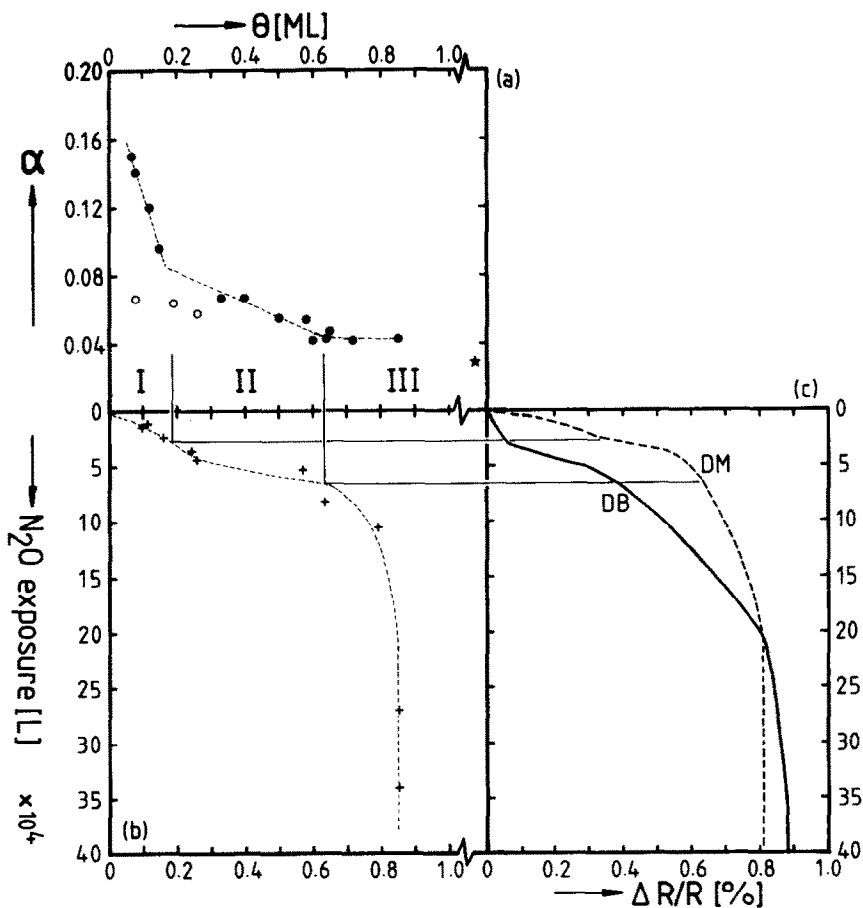


Fig. 2. (a) The intensity ratio, α , as a function of the fractional oxygen coverage θ upon exposing the Si(001) 2×1 surface at 300 K to N_2O (filled circles). The open circles represent $\alpha(\theta)$ data obtained after exposing the same surface at 100 K to O_2 . α representing the native oxide layer on Si(001) is depicted by the asterisk. (b) θ as derived from the normalized oxygen Auger signal, h_O/h_{Si} , as a function of N_2O exposure (adapted from ref. [18]). (c) The relative change in reflectivity, $\Delta R/R$, versus N_2O exposure at photon energies of 2.90 eV (DB) and at 3.85 eV (DM). The curves are taken from ref. [18]. The two solid lines in fig. 2a mark the transition from one adsorption stage into the other, and have been extended to (b) and (c).

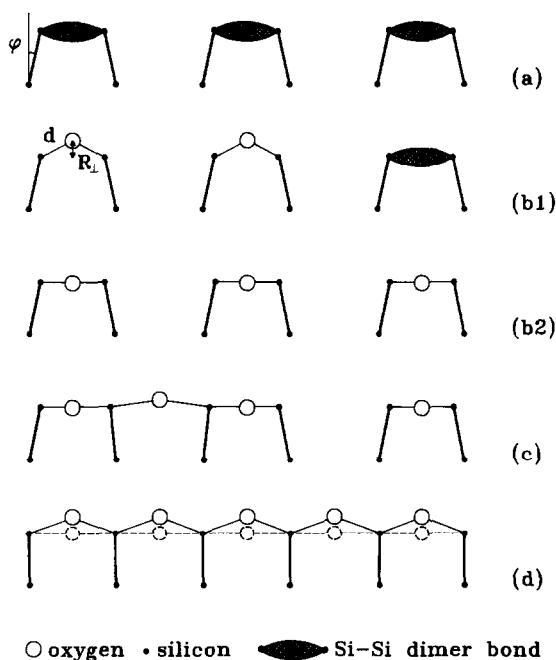


Fig. 3. Schematic model for the successive uptake of atomic oxygen (O) as a result of the decomposition of N_2O on a clean Si(001) 2×1 surface. For simplification a side view of this surface with symmetric dimers is presented (a). All displacements in (a) through (d) have been drawn to scale using the results of ref. [19]. The stable (in-plane) adsorption geometry at saturation as found by ref. [22] has been indicated by the dashed lines.

trons/cm²). Our previous work [18] already indicated thermal stability of the atomic oxygen adlayer at all stages up to 700 K, which is again proof of purely bridge bonded oxygen. In fig. 3 we show a schematic model for the uptake of atomic oxygen (O) via decomposition of N_2O on an ideal clean Si(001) 2×1 surface. For simplification we present a side view of this surface with symmetric dimers. Fig. 3b2 then shows the formation of bridge bonded O on the dimers, preceded by an intermediate stable state (b1). All displacements, i.e. Si–O distance, d , dimer tilt angle, ϕ , with respect to the surface normal, and the vertical distance of the adsorbed oxygen atom relative to the adjacent Si atoms to which it is bonded, R_{\perp} , have been drawn to scale using the results of Smith and Wander [19] ((a)–(d), solid lines) and Miyamoto and Oshiyama [22] ((d), dashed line). There are two main differences between the two

models. Whereas Smith and Wander [19] take a constant dimer tilt angle for both the metastable and stable dimer bridge site ((b1) and (b2) of fig. 3, respectively), Miyamoto and Oshiyama [22] obtain a larger ϕ for the metastable state due to a reduced dimer bond length. The second difference concerns the value of R_{\perp} in the high coverage case; whereas ref. [22] reports an in-plane configuration, the authors of ref. [19] find a R_{\perp} of 0.725 Å. Further information is given in the figure caption.

Supporting evidence for the existence of purely bridge bonded oxygen at the dimer sites is provided by a comparison with the following experimental results: fig. 2a shows in addition to the N_2O exposure data, α values in the range of 0.05–0.3 ML obtained by exposing a clean Si(001) 2×1 surface, at 100 K, to O_2 (open circles). These data have been taken from a study in which α is determined as a function of O_2 exposure at low surface temperature. A complete account of this study will be published elsewhere [23]. From fig. 2a it can be seen that the O_2 exposure α values in stage I are significantly lower than the corresponding N_2O data, suggesting the existence of oxygen adsorbate geometries which are expected at more advanced adsorption stages (see the discussion of stage II). From O_2 adsorption studies on silicon surfaces it is well known that at low sample temperatures the adsorption of O_2 is partly dissociative [24–27], resulting in more or less complex (and metastable molecular-like) adsorbate structures, including penetration of oxygen into the Si lattice [24,25]. The formation of oxygen adsorbate geometries in stage I (fig. 2a) which resemble those at more advanced N_2O adsorption stages, i.e. stage II and III (see the discussion below), is therefore highly probable. Our comparative study – O_2 and N_2O – also shows that the bridge bonded O adsorption geometry at the dimer site (stage I) obtained from the chemisorption of atomic oxygen is stable against intensive electron bombardment.

3.2. Stage II

Whereas the initial adsorption of O can be described by a simple reaction mechanism, that is

Si/O\Si formation at dimer bridge sites only (see fig. 3b), the second stage from about 0.2 to 0.6 ML atomic oxygen coverage is characterized by at least two adsorption geometries as predicted experimentally (see fig. 14 of ref. [18]) and found by calculations [19]. Most relevant in stage II, in particular at the onset, are the non-dimer bridge sites between two nn reacted dimer sites (fig. 3b) which are now prone to the uptake of oxygen to form bridge bonded oxygen, as depicted in fig. 3c. The 2nd adsorption stage is accompanied by an increase in Si-O bond length, d , on the reacted dimer site and an increase of the Si/O\Si bond angle as a result of Si/O\Si bond formation at non-dimer bridge sites. A previous high resolution electron energy loss (HREELS) study dealing with the room temperature adsorption of O₂ on Si(001)2 × 1 [14,15] has provided evidence for a change in O adsorption geometry in the range of $0.2 \leq \theta \leq 0.6$ ML, the change in the frequency of one of the observed modes being interpreted as a continuous increase in Si/O\Si bond angle as the oxidation proceeds. The adsorption characteristics of O₂ is in this region comparable to N₂O [12]. Since in stage II at least two different (bridge bonded) O adsorption geometries are likely to coexist [18], we may assume that during stage II the Si-O bond distance continuously changes until at saturation both dimer and non-dimer sites become equivalent (see fig. 3d). Because of the increase in coordination number of the O atoms around one silicon atom we may also expect the charge accumulation on the O atom to vary with θ . Changes in charge transfer in this coverage region were indeed observed in XPS studies by a shift in BE of the O 1s photoelectron upon exposing Si(001)2 × 1 to O₂ [15] or N₂O [16]. However, the XPS data of Namiki et al. [16] were interpreted as a coexistence of Si-O and Si/O\Si species already far below saturation, a result which was comparable to the O₂ exposure XPS data [15], but incompatible with our results (ref. [18] and this work) and theoretical work [19] which show that Si/O\Si is the most appropriate geometry at all stages up to saturation.

The interpretation of $\alpha(\theta)$ in the second stage is complicated by the fact that in addition to

changes in d (the formation of Si/O\Si bonds in between the nn reacted dimer sites is accompanied by an increase in d of the bridge bonded oxygen species at the dimer site), the core state changes as observed by XPS [16]. The increase in d alone would result in an increase of α [13]. The shift in BE can however, compensate this increase. Our theoretical work showed that a contraction of the O 1s orbital leads to a significant decrease of α [13]. The smaller rate of change of α with θ in stage II as compared with stage I can therefore be attributed to a partial compensation of the increase in d by a contraction of the O 1s orbital.

In view of the above discussion, it would be very useful to measure in the same experiment the BE of the O 1s photoelectron – in particular in stage II – and α , so as to obtain insight into the contribution of the core hole to α . These experiments should be accompanied by a theoretical calculation of the OKLL Auger lineshapes in which the electron distribution, extending as far as nn and next nn atoms surrounding the oxygen atom and the core hole at this oxygen atom, is explicitly taken into account. An investigation into the influence of a specific adsorption geometry on the core state wavefunction by means of the MNDO quantum chemical cluster approach [13] is not feasible. For that purpose an ab initio method is required. In future calculations one should also consider the relaxation of the Si/O\Si bridge bonded species at the reacted nn dimer sites upon adsorption, as this aspect may be an important factor in the adsorption process, like the actual dimer tilt of the clean surface.

3.3. Stage III

Finally, in the 3rd stage in which mainly non-dimer bridge bonded oxygen is formed via attachment of the dangling bonds (see curve DB of fig. 2c), so that dimer and non-dimer sites become equivalent, the rate of change of α with θ is almost zero (fig. 2a). From the XPS results of Namiki et al. [17] it can be derived that the O core state continues to change upto saturation (about ML coverage). Our results (stage III of fig.

2a) therefore strongly suggest that the decrease of α due to a contraction of the core hole is compensated by an increase of α because of a decrease in overlap of the O and nn Si atom. This would favour an O adsorption geometry in the high coverage case with a relatively large Si–O bond length as calculated by Smith and Wander [19] (see fig. 3d). They found at this stage a bond length of 2.05 Å (with $R_{\perp} = 0.725$ Å) which is 0.13 Å larger than that found by Miyamoto and Oshiyama [22]. That the adsorption geometry at saturation (fig. 3d) is not the ultimate relaxed configuration (the most stable configuration is vitreous silica [24]) can be seen from the data point α in the right bottom corner of fig. 2a (asterisk). It represents the native oxide layer on Si(001) and is significantly smaller than the one at the saturation coverage of 0.85 ± 0.10 ML (stage III). In a native oxide layer, which can be considered as a compressed phase of SiO₂ [24], SiO₄ structures will be present which have a mean Si–O bond distance of 1.62 Å as in vitreous silica or even smaller [24]. This distance is at least 16–21% shorter than d in fig. 3d (stage III, saturation). Due to the larger overlap of the O and nn Si atom and higher degree of ionicity of the Si–O bond, α (native oxide) is expected to be smaller, as illustrated by our experiment.

4. Conclusion

We have presented evidence that the combination of measuring the intensity ratio α of the KL₁L₁ and KL_{2,3}L_{2,3} O Auger lines and the chemical shift in BE of the O 1s core electron can provide quantitative information about the change in the oxygen adsorbate structure during N₂O exposure. Theoretical evaluation of the O adsorption process, using the MNDO quantum chemical cluster method, has revealed that the Si–O bond distance has a significant impact on α . As a result we have been able to give an accurate description of the adsorption behaviour of N₂O on the Si(001)2 × 1 surface in the initial stage ($\theta < 0.2$ ML) in which an intermediate stable state exists. The method of OKLL Auger lineshape analysis, however, seems to be seriously limited at more

advanced adsorption stages, e.g. stage III, at which almost no variation of α with θ is observed although the adsorption geometry continuously changes. With future – ab initio – calculations in which the O core state is explicitly incorporated, it should be possible to describe this adsorption process at all stages. Our results encourage us to expect similar use of the KL₁L₁ and KL_{2,3}L_{2,3} Auger intensity ratio for N, F, and C on well defined elemental surfaces, provided that for each solid/gas system a simple model reaction is available to calibrate the α data against.

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