Exo-electron emission during the oxidation of alkalated W(110) surfaces

H. Brenten, H. Müller, W. Maus-Friedrichs, S. Dieckhoff and V. Kempter

Physikalisches Institut der Technischen Universität Clausthal, Leibnizstrasse 4, D-3392 Clausthal-Zellerfeld, Germany

We have investigated the emission of electrons and photons during the oxygenation of submonolayer (coverage $\theta_{Alk} \leq 1$ monolayer (ML)) alkalated W(110) surfaces originating from a non-adiabatic surface reaction. Exo-electron energy distributions have been measured as a function of the alkali-precoverage. The electronic structure is monitored by MIES (metastable impact electron spectroscopy) and UPS as well as WF (work function) measurements. The surface WF turns out to be a crucial parameter in the investigation. An interpretation involving Auger de-excitation into the O_2 molecule affinity level is supported by the results of substituting O_2 by CO molecules in the experiments.

1. Introduction

Considerable effort has been made during the past years to improve the knowledge about the chemical bonding of atoms or molecules to surfaces. Experimental and theoretical efforts so far were mainly concerned with the electronic structure of well characterized adsorbed layers on metal surfaces. Much less is known about the dynamics by which such species are chemisorbed to the surface. Of fundamental interest is the question how a chemical bond of a molecule, as for instance between the two oxygen atoms in O_2, is broken and a new bond between the surface and the resulting oxygen atoms is formed.

It has been recognized from electron energy loss spectroscopy (EELS) studies that negative molecular ions may play an important role in the chemisorption process [1–3]. The negative ion state may be considered as the precursor for dissociative chemisorption: by the transfer of electrons from the surface to the molecular projectile the bonding length is increased and its dissociation energy is lowered, thus facilitating the breaking of the intramolecular bond considerably. Evidence for the ionic nature of the precur-

sor was also provided by recent work on grazing incidence scattering of, in particular, reactive ions, as O_2^+, from metal and semiconductor surfaces [4–7].

The transition to the final chemisorbed state of the system may often proceed via crossings of the various potential surfaces describing the state of the molecule–surface system. If the electron transfer to the molecule is non-adiabatic, e.g., the system does not follow the ground state potential surface of the system, the chemisorption process involves an excited state of the system. A part of the exothermicity of the reaction may then be converted to electronic energy leading to the emission of so-called exo-photons or exo-electrons [8]. Chemiluminescence and exo-electron emission are therefore direct indicators for the occurrence of non-adiabatic processes in molecule–surface collisions. So far several studies dealing with such processes have been reported (see ref. [9] for a list of references).

A recent study [9] has dealt with the exo-electron emission during the interaction of O_2 with Cs films of several monolayers thickness on Ru(001) sufaces. It was proposed that the electron emission is confined to the oxidation stage

where O_2^{2-} becomes transformed into O_2^-, and is caused by an Auger process accompanying the formation of O_2^- from the inpinging O_2 molecules in the neighbourhood of the O_2^{2-} complexes.

We report the exo-electron emission during the oxidation of submonolayer alkalated W(110). Here the formation of O_2^{2-} ions cannot occur because the density of states associated with the alkali atoms in the surface layer (thereafter denoted by surface density of states (SDOS)) is too low. This is concluded from electron spectroscopic results obtained with UPS and MIES [10]. By combining the information from the study of the exo-electron emission and the electron spectroscopic techniques UPS and MIES, we propose a mechanism – similar in general to the one proposed by Kasemo et al. [8] and verified by Böttcher et al. [9], but differing in details from the latter – which is able to explain the exo-electron emission observed above ~ 0.6 ML Cs (in units of the Cs saturation coverage at room temperature).

2. Apparatus and measurements

The experiments have been performed using two different UHV-systems. One is equipped with facilities for UPS and MIES apart from standard tools as AES, LEED and an electrostatic hemispherical analyzer (ESA). The base pressure is better than 5×10^{-11} Torr. A detailed description is found in ref. [12].

The main components of the other apparatus in which the exo-emission is studied have been described previously [11]. It consists of a surface ionisation source for alkali ions, an electrostatic hemispherical analyzer and standard equipment for LEED and AES. The base pressure is better than 1×10^{-10} Torr. Cs (K, Na, Li) atoms are offered to a W(110) crystal, held at room temperature during the measuremnets, by means of a dispenser source (SAES getters, Inc.). The partial coverage by Cs (K, Na, Li), θ_{Alk} (in units of adatoms layers at room temperature), is determined by work-function measurements combined with AES results.

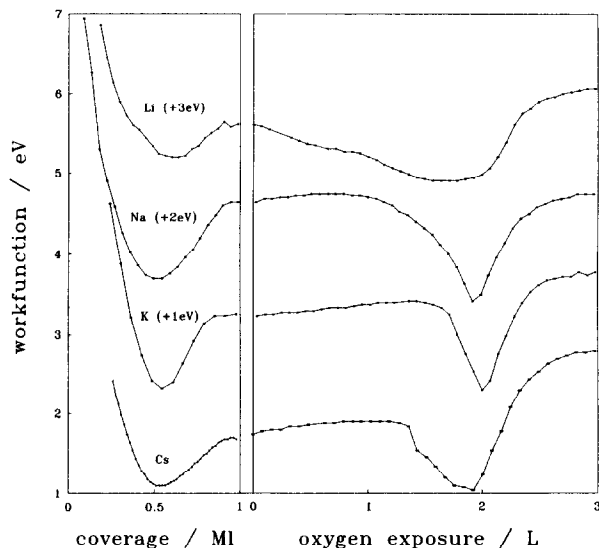Prior to the preparation of the alkali adlayer

Fig. 1. The dependence of the work function of W(110) as a function of the alkali coverage (left) and of the exposure to oxygen at 1 ML precoverage (right).

the cleanliness of the W(110) crystal is routinely checked by WF measurements, AES and ion scattering spectroscopy. O_2 is offered to the alkalated crystal by means of a leak valve. The oxygen partial pressure is chosen to be in the range between 1×10^{-9} and 6×10^{-9} Torr (1 L = 10^{-6} Torr · s). During the oxygenation of the alkalicovered surface energy distributions of the electrons, ejected in the direction of the surface normal, have been measured with the ESA ($\Delta E = 0.2$ eV). Simultaneously there was looked for emitted photons by means of a photo-multiplier with a red-sensitive cathode (type C31034-02, RCA, Inc.).

Fig. 1 shows the WF as a function of O_2 exposure for 1 ML Cs, K, Na and Li covered surfaces. The minimum value of the WF (around 2 L O_2) increases from Cs to Li which will be important in the interpretation of the results for exo-electron emission.

Fig. 2 shows the electron energy spectra, obtained during the oxygenation of a 1 ML Cs-precovered surface, as a function of the O_2 exposure at a partial pressure of 6×10^{-9} Torr. A narrow peak ($\Delta E = 0.5$ eV FWHM) develops only after an oxygen exposure of about 2.5 L. The differ-
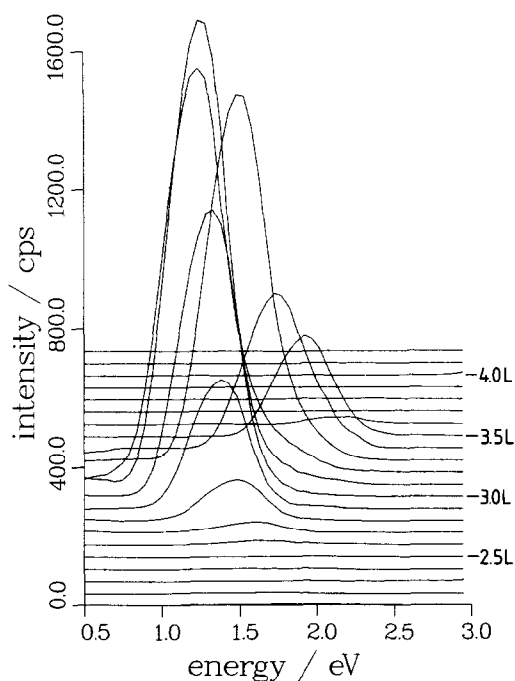
Fig. 2. Exo-electron energy spectra obtained during the oxygenation of a W(110) surface precovered by 1 ML Cs as a function of the O_2 exposure at a partial pressure of 6×10^{-9} Torr.

ence between the work function of the crystal and the analyzer was overcompensated by biasing the ESA in such a way, that electrons, leaving the crystal with zero kinetic energy arrive at the ESA with approximately 0.5 eV. Therefore the leading edge in the electron spectra represents the global work function of the W(110) crystal. The exo-electron yield increases with decreasing work function, which is in qualitative agreement with previous findings concerning the O_2 + Mg system [13,14] and suggestions made therein. But it is at variance to Böttcher et al. [9], who find an increasing exo-electron yield by oxygenation of 2 to 3 ML Cs-precovered Ru(001) surfaces only after the work function of the crystal has passed its minimum value.

Furthermore, inspection of fig. 2 shows, that the electron spectra have a common leading edge on the high-energy side only until the work-function minimum is reached, which will be of major relevance for the discussion.

Oxygenation of 0.6 ML Cs- and K-covered surfaces causes giant electron currents (up to 2×10^{-11} A as estimated from the spectra obtained with the ESA) as soon as the work-func-
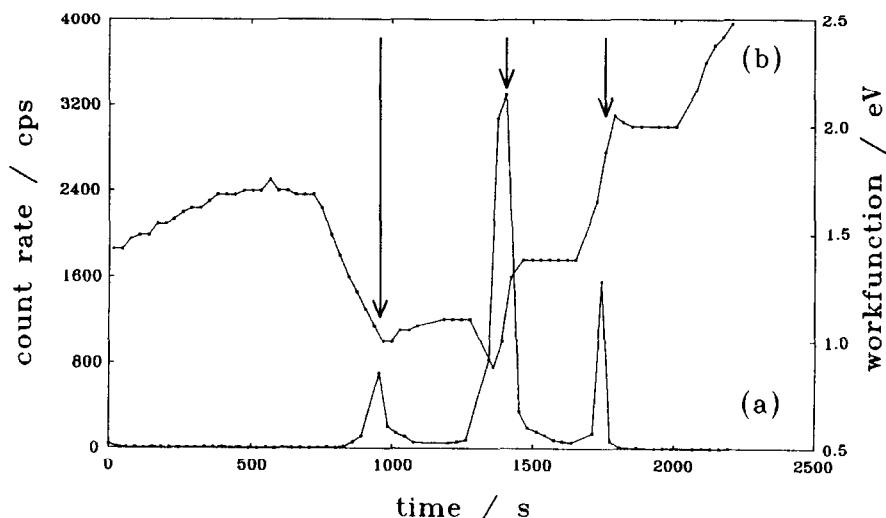

Fig. 3. (a) Exo-electron yield and (b) work function of W(110) precovered by 1 ML Cs as a function of oxygen exposure. Arrows indicate when oxygen exposure was interrupted.

tion minimum is reached at about 2 L O_2 exposure. These electron currents have been proven to be independent of oxygen exposure. Their origin is found in the thermal emission of electrons by a surface with very low WF, prepared in the way described above. According to the Richardson–Dushman equation,

$$I = AK_R T^2\, e^{-e\phi/kT}, \tag{1}$$

where K_R is a material-dependent constant, A is the area of the target and ϕ is the surface work function. For $e\phi = 1.0$ eV and $K_R = 3 \times 10^4$ A/K^2 m^2 for an oxygenated 0.6 ML Cs/W(110) surface at its WF minimum we estimate that one has indeed to expect electron currents of the magnitude mentioned above.

Consequently extreme care has to be taken to separate the exo-electrons accurately from those thermally emitted, even at room temperature. This was done by interrupting the oxygen exposure during the measurements as shown in fig. 3 to make sure, that the analyzed electrons depend on oxygen exposure.

Fig. 4 shows the integrated exo-electron yield as a function of the Cs-precoverage. Open circles represent exo-electron yields obtained with 1.5×10^{-9} Torr O_2 partial pressure and interrupted exposure (see fig. 3), whereas the asterisks mark yields obtained with a continuous oxygen exposure of 6×10^{-9} Torr. Especially for interrupted oxygen exposure a higher integrated exo-electron current is found than for continuous O_2 exposure. A similar result is found by Böttcher et al. [15].

The exo-electron spectrum from a 1 ML K-covered surface shows a peak similar to that of fig. 2 with a width (FWHM) of ~ 0.5 eV, again the peak appears at the WF minimum. From the measurements we estimate the same exo-electron yield as that found for a 1 ML Cs-covered surface, which is of the order of $\sim 2 \times 10^{-6}$ exo-electrons per O_2 molecule. On offering O_2 to a 1 ML Na-covered W(110) surface one can observe exo-electron emission as well, but since the work function does not decrease enough on oxygenation the yield amounts to only 3% as compared to Cs and K. As a consequence a measurement of the electron energy distribution with sufficient energy resolution was not possible and thus the width of the exo-electron peak could not be determined. Li covered W(110) surfaces (≤ 1 ML) did not show up a detectable exo-electron emission.

An explanation is found following the lines of the WF argument mentioned in the context of the Na/W surface, as will be discussed later. We state at this point, that for all investigated sys-
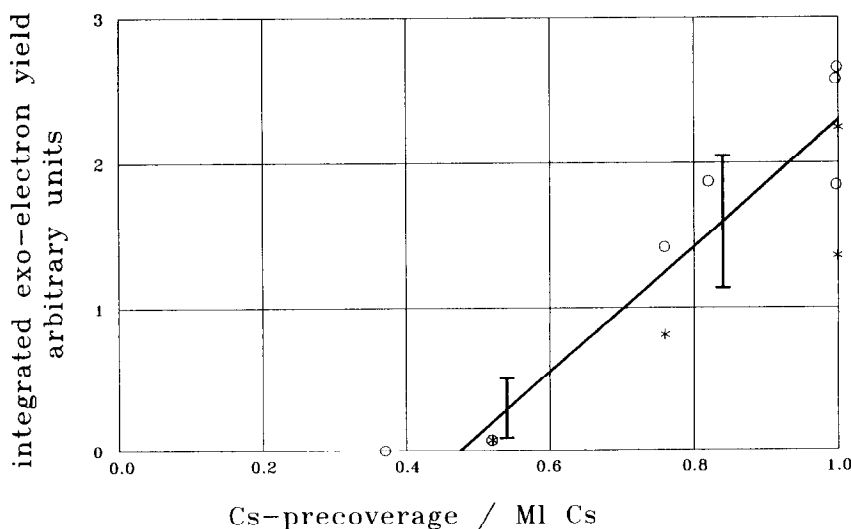

Fig. 4. Exo-electron yield integrated over the entire exposure time to oxygen as a function of the Cs-precoverage.

tems no exo-photon emission was detectable. The upper limit for this process as derived from the efficiency of our photon detection system is 10^{-4} exo-photons per O_2 molecule. Offering CO molecules to a Cs- or K-covered surface did not result in exo-electron emission.

Fig. 5 shows MIE spectra obtained during the oxygenation of Cs(0.75 ML)/W(110). Measurements were performed with a He*$(2^3S; 2^1S)$ beam; the $2^3S:2^1S$ ratio is about $7:1$ [16]. As discussed in ref. [10,12] the spectral features are essentially due to the de-excitation of 2^3S atoms; the Fermi energy $E_F(2^3S)$ is located at $E_F = 14.8$ eV. The strong emission near E_F is due to the ionization involving the Cs 6s electrons. The doublet at $E_B = 11.4$; 13 eV is due to Auger de-excitation of He(2^3S) by the Cs $5p_{1/2,3/2}$ electrons. In the early stage of the oxygenation a three-peak oxygen induced structure (labeled $A_{1,2,3}$) with $E_B = 5.8$; 7.5; 9.7 eV appears. With forthgoing oxygenation this structure disappears and the two prominent peaks (labeled O_a and O_s) at $E_B = 6$

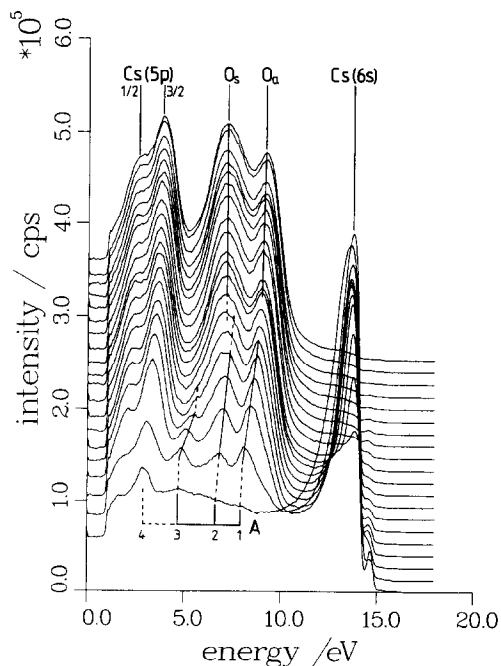Fig. 6. As fig. 5, but for 0.46 ML Cs-precoverage.

Fig. 5. MIE spectra of a W(110) surface precovered by 0.75 ML Cs exposed to oxygen. Oxygen exposure changes by 0.1 L between each two spectra. The bottom curve corresponds to the clean Cs/W(110) surface.
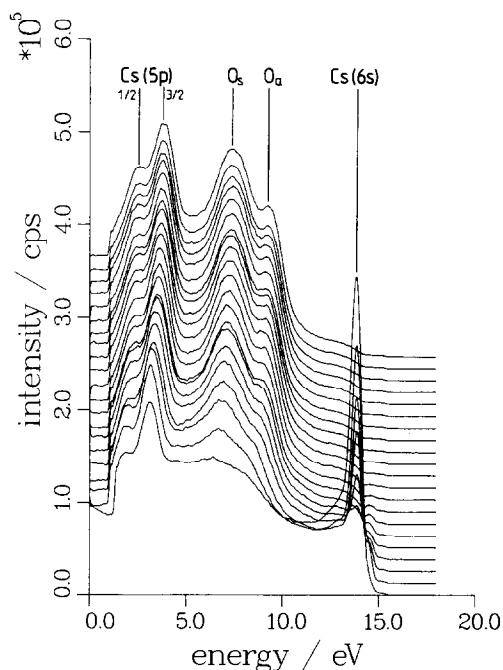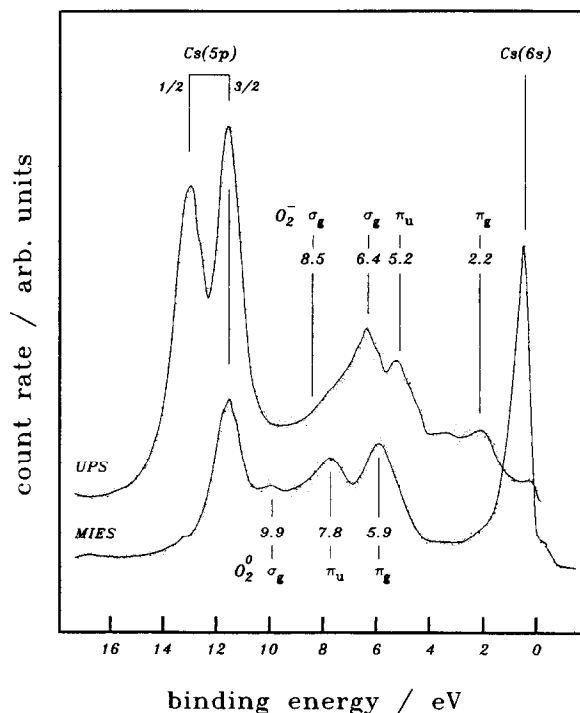
binding energy / eV

Fig. 7. MIE and UP spectra of a W(110) surface precovered by 1 ML Cs exposed to 1 L oxygen as a function of the binding energy with respect to the Fermi level.

and 8 eV remain. The change in the spectra occurs when the WF minimum is passed. It should be remembered that the WF and exo-emission results were collected with different apparatus; this implies that the WF minima will not necessarily occur at identical exposures. Corresponding MIE spectra for 0.46 ML Cs-precoverage are shown in fig. 6. In contrast to fig. 5 structure A (E_B = 5.8; 7.9; 9.7 eV) is not found.

Fig. 7 compares MIE and UP spectra obtained from a W(110) surface precovered by 1 ML Cs and subjected to about 1 L O_2 exposure. The oxygen-induced structure in the UP spectra can be identified on the basis of the results of Wijers et al. [17] and Bertel et al. [18] as due to the ionization of MOs π_g, π_u and σ_g O_2^- with peaks at E_B = 2.2; 5.2; 6.4; 8.5 eV, respectively. The MIE spectra show (weakly !) the features due to O_2^- ionization as well, but the dominant part of the spectrum differs in peak positions as well as in their relative intensities.

3. Interpretation

The MIES results will be described in detail in ref. [20] and can be summarized as follows:

For alkali precoverages below 0.5 ML the O_2 molecule will dissociate when coming into contact with the reactive W(110) surface leading to the peaks labeled O_s and O_a, respectively. For precoverages above 0.5 ML and oxygen exposures < 1 L the initial step in the oxygenation process is the transfer of electrons from the Cs adlayer to the impinging O_2 molecules. The charge density underneath the alkali adlayer is high enough to accommodate the oxygen as O_2^- ions proven by UPS results (see fig. 7).

On top of the surface the charge transfer is less efficient because of the lower charge density; the adsorbed oxygen species still resembles the free O_2 molecule. The equilibrium internuclear distance has increased, partly due to the charge transfer and partly due to the interaction with the adatoms. Therefore we expect the MIE spectra to be essentially due to a Franck–Condon transition $O_2^0 \rightarrow O_2^+$ at an enlarged internuclear distance. If we anticipate an unrelaxed internuclear distance

of about 1.4 Å (instead of the 1.2 Å in the free O_2) we predict four peaks which should be roughly spaced by 2 eV each. The MIES results show 3 peaks which are spaced by 1.8 and 2.2 eV; the fourth peak may very well be hidden under the strong Cs $5p_{3/2}$ emission.

It is evident that the exo-emission must be correlated to the exposure range where the first step is the transfer of electrons to the impinging O_2 molecules. However, it is not seen with detectable intensity over the entire exposure range where O_2^- ions are present. It is limited mainly to the exposure range around the WF minimum (see fig. 1).

For oxygen exposures > 1 L the alkali valence electrons become involved into the bonding of the oxygen and the density of states associated with the alkali atoms will be reduced considerably. As a consequence the size of the alkali species shrinks and the substrate becomes again accessible for oxygen attack [19]. When this happens, the surface WF rises by ~ 1.2 eV (see fig. 1). In this exposure range the two peaks O_a and O_s known from fig. 6 appear again (see fig. 5). O_a has increased because the number of alkali sites to which oxygen may be bound has increased as compared to fig. 6. Also the emission induced by the ionization of the Cs 6s electrons begins to disappear indicating that all valence electrons are involved in binding the oxygen.

The electron spectroscopy results suggest that O_2^- ions are responsible for the exo-electron emission. However it should be kept in mind that MIES-UPS furnish informations about the final state of charge transfer process while the exo-emission depend upon intermediate states of the chemisorption process. In the following we adopt a mechanism proposed by Kasemo et al. [8] and recently applied to exo-electron emission during the oxygenation of thick Cs films by Böttcher et al. [9,15]:

The potential surface of the O_2–surface system is crossed by the surface describing the O_2^-–surface interaction. Some fraction of the colliding O_2 molecules does not follow the adiabatic ground state surface, e.g., the resonant electron transfer from the surface to the O_2 molecule will not take place at the crossing of the surfaces. The

reason for that maybe the reduced free-electron density at the Fermi level caused by the binding of the oxygen. In the early stages of the oxygenation (below 2 L oxygen exposure) the probability for resonant electron transfer from the surface to the O_2 is still so high that the system will follow the adiabatic ground state surface with practically unity probability. If the formation of O_2^- occurs by an Auger process involving two surface electrons, exo-electrons will be ejected provided the excitation energy is larger than the WF. This process becomes only likely when the SDOS and therefore the probability for the competing resonant electron transfer are reduced sufficiently (see above and Böttcher [9]). Unfavourable orientation of the impining O_2 molecule with respect to the surface could be an additional reason in preventing resonance capture to the O_2 affinity level.

From the UPS results of fig. 7 we estimate that the maximum excitation energy E_a is approximately 2.2 eV close to the surface (the binding energy of the highest occupied molecular orbital $\pi_g O_2^-$ is ~ 2.2 eV with respect to the Fermi level). It follows that the maximum kinetic energy of the electron (with respect to the low energy cut-off of the spectra) will be $E_a -$ WF which is about 1 eV because the minimum WF upon oxygenation is ~ 1.2 eV for Cs/W(110). Indeed we measure a total width of the spectra of about 1.0 eV.

When the oxygen exposure increases further, the WF increases drastically (fig. 1). At the same time the SDOS both below and above the Fermi level decreases because all alkali electrons are involved in the binding of the oxygen. This is reflected in the exo-electron spectra of fig. 2: the decrease of the electron intensity is due to the decrease of the SDOS which leads to a reduction of the probability for the Auger process and the increasing WF causes the narrowing of the spectra. However, the leading edge on the high-energy side does not retain its position beyond the WF minimum as expected for an Auger process. This could however be due to the change in electronic structure at the surface (transition from molecular to atomic adsorption) with ongoing O_2

exposure which may increase the available excitation energy E_a to some extent.

The model explains the threshold coverage (~ 0.5 ML) as due to the onset of O_2^- formation. At smaller precoverages only atomic adsorption is observed, and the potential surfaces of the system obviously do not offer a possibility for a nonadiabatic behavior of the system which is prerequisite for the electron formation. The different behavior observed for alkalis others than K and Cs and the strong decrease of the exo-intensity when going from Cs and K to Li, follows from the less drastic reduction of the WF upon oxygenation. In all cases including Li and Na the MIE and UP spectra suggest formation of O_2^- underneath the surface layer in the initial phase of the oxygenation; for Na and Li O_2^- formation does even occur on top of the surface which is sampled by MIES [20].

The mechanism of ref. [8] is also consistent with the fact that we do not observe exo-emission when offering CO molecules to alkalated surfaces: the WF decrease upon CO exposure is not sufficient to allow for the emission of electrons via an Auger process even if a curve crossing as discussed for O_2 would occur. The available energy would only be sufficient to excite electrons into empty states above the Fermi level.

4. Summary

The emission of electrons and photons was studied during the oxygenation of submonolayer alkalated (Li, Na, K, Cs) W(110) surfaces. Electron emission was observed for Na, K and Cs. For W(110) precovered by Cs and K the intensity was strong enough to carry out detailed studies: the electron emission yield was measured as a function of the alkali precoverage. A rather well-defined threshold was observed at 0.5 ML Cs-precoverage. Energy distributions were measured as a function of the precoverage for Cs and K. The spectra are less than 1 eV wide and essentially confined to kinetic energies below 2.5 eV. The yield is $\sim 2 \times 10^{-6}$ exo-electrons per O_2 molecule

for the W(110) surface precovered by 1 ML of Cs or K at room temperature.

The electronic structure of the oxygenized surface was monitored by UPS, MIES and WF measurements. The combined results are consistent with the assumption that the exo-electron emission is caused by an Auger transition from filled levels just below the E_F into the O_2 affinity level.

Exo-photons could not be detected under the chosen conditions (oxygen partial pressure below 10^{-8} Torr); the probability for this process is lower than 10^{-4} exo-photons per O_2 molecule.

Acknowledgements

References

[1] J.L. Gland, B.A. Sexton and G.B. Fisher, Surf. Sci. 95 (1980) 587.

[2] C. Backx, C.P.M. de Groot and P. Biloen, Surf. Sci. 104 (1981) 300.

[3] C.T. Campbell and M.T. Paffet, Surf. Sci. 143 (1984) 517.

[4] P. Haochang, T.C.M. Horn and A.W. Kleyn, Phys. Rev. Lett. 57 (1986) 3035.

[5] P.H.F. Reijnen, P.J. van den Hoek, A.W. Kleyn, U. Imke and K.J. Snowdon, Surf. Sci. 221 (1989) 427.

[6] S. Schubert, U. Imke and W. Heiland, Vacuum 41 (1990) 252.

[7] J. Rechtien, U. Imke, K.J. Snowdon, P.H.F. Reijnen, P.J. van den Hoek, A.W. Kleyn and A. Namiki, Surf. Sci. 227 (1990) 35.

[8] B. Kasemo, E. Törnquist, J.K. Nørskov and B.I. Lundqvist, Surf. Sci. 89 (1979) 554.

[9] A. Böttcher, R. Imbeck, A. Morgante and G. Ertl, Phys. Rev. Lett. 65 (1990) 2035.

[10] W. Maus-Friedrichs, S. Dieckhoff, M. Wehrhahn and V. Kempter, Surf. Sci. 253 (1991) 137.

[11] H. Schall, W. Huber, H. Hoermann, W. Maus-Friedrichs and V. Kempter, Surf. Sci. 210 (1989) 163.

[12] W. Maus-Friedrichs, M. Wehrhahn, S. Dieckhoff and V. Kempter, Surf. Sci. 237 (1990) 257.

[13] G.C. Allen, P.M. Tucker, B.E. Heyden and D.F. Klemperer, Surf. Sci. 102 (1981) 207.

[14] T.F. Gesell, E.T. Arakawa and T.A. Callcott, Surf. Sci. 129 (1988) 399.

[15] A. Böttcher, R. Grobecker, R. Imbeck and A. Morgante, J. Chem. Phys. 95 (1991) 3756.

[16] H. Hotop, E. Kolb and J. Lorenzen, J. Electron. Spectrosc. Relat. Phenom. 16 (1979) 213.

[17] G. Wijers, M.R. Adriens and B. Feuerbacher, Surf. Sci. 80 (1979) 317.

[18] E. Bertel, F.P. Netzer, G. Rosina and H. Saalfeld, Phys. Rev. B 39 (1989) 6082.

[19] B. Woratschek et al., J. Chem. Phys. 86 (1987) 2411.

[20] W. Maus-Friedrichs, S. Dieckhoff and V. Kempter, Surf. Sci, to be published.