

Emission of Exoelectrons during Oxidation of Cs via Thermal Activation of a Metastable O_2^- Surface Species

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 (Received 1 October 1993)

Exposure of Cs surfaces to O_2 causes the emission of exoelectrons. With a Cs monolayer on Ru(0001) the maximum yield is observed with an already partly oxidized surface on which a metastable O_2^- species could be identified. Thermally activated transformation (with an activation energy of 0.8 eV) of this phase leads to dissociation accompanied by exoelectron emission via Auger deexcitation.

PACS numbers: 79.75.+g, 78.60.Fi, 79.20.Nc, 82.65.Pa

Oxidation of alkali metals is found to be accompanied by emission of electrons ("exoelectrons") indicating the possibility for a nonadiabatic channel which enables transformation of the reaction enthalpy into electronic excitation [1,2]. The subsequent deexcitation step is thought to be an Auger deexcitation process in which an empty hole state on the oxygen species with an energy below the Fermi level (representing the electronic excitation and being derived from the affinity level of the interacting particle) is filled by electronic transition from the solid whereby the energy is released to another electron which eventually may escape into the vacuum where it may be detected [3]. Previous studies with the oxidation of thick (i.e., bulk) Cs films revealed that electron emission was essentially confined to the last step of oxidation, namely, formally the transformation of Cs_2O_2 into CsO_2 . A pronounced influence of the sample temperature suggested that a thermally activated surface process is involved and it was speculated that it creates an activated site on the surface which upon collision of an incoming O_2 molecule gives rise to exoelectron emission [4]. Although a kinetic model was proposed which was able to reproduce the recorded kinetics rather satisfactorily, the actual nature of the thermally activated step remained unclear. Subsequent experiments on the oxidation of Na films [5] revealed a quite similar behavior of this system. In addition, it was demonstrated that exoelectron emission is by no means restricted to the formation of bulk oxides, but may even occur with submonolayer quantities of an alkali metal chemisorbed on a transition metal substrate. Recent experiments on the interaction of NO with a Cs monolayer revealed that the thermal pretreatment of the mixed adlayer was of decisive importance for the yield of exoelectrons suggesting the participation of (unidentified) metastable surface phases [6].

The present work reports on investigations with a Cs monolayer chemisorbed on a Ru(0001) surface, and the actual transformations occurring on the surface associated with the emission of exoelectrons are elucidated in some detail. In particular, it will be demonstrated that in this system exoemission need not be an instantaneous process linked with the impact of a particle from the gas phase, but that it involves a well-defined metastable sur-

face species which acts as "precursor" and undergoes thermally activated transformation. The annealing of an oxidized surface yields electron emission known as "glow curves" observed in thermoluminescence [7] or thermally stimulated exoelectron emission [8] and is related to the disappearance of a molecular O_2^- species from the top-most layer.

The starting situation was a well-ordered Cs monolayer on Ru(0001) which is characterized by an ordered $\sqrt{3} \times \sqrt{3} R 30^\circ$ phase in which the Cs atoms (5.3×10^{14} atoms/cm²) are located in threefold coordinated sites and form a hexagonal densely packed overlayer [9]. Upon exposure to O_2 at $T \geq 300$ K the work function $\Delta\Phi$ starts to decrease and passes through a minimum while simultaneously exoelectron emission begins, increases in intensity, and reaches a maximum just at the $\Delta\Phi$ minimum which quantity was thus found to be a convenient measure for calibration of the oxygen exposure with this system (see Fig. 1).

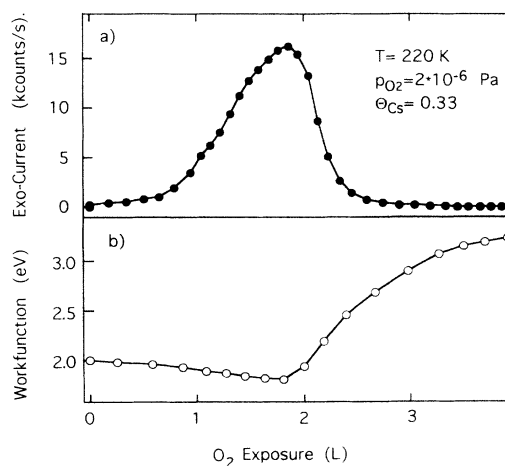


FIG. 1. Typical exoemission experiment on the oxidation of a monolayer of Cs on Ru(0001) at 220 K as a function of O_2 exposure (1 L = 1.3×10^{-4} Pas). (a) Exoelectron current where 1×10^4 counts/s correspond to about 0.5 nA/m² of current density; (b) work function change $\Delta\Phi$ as measured by the kinetic energy of the exoelectrons ($\Phi_0 = 2.0 \pm 0.1$ eV).

As with thick Cs films, the kinetics as well as total yield of exoelectron emission were revealed to be markedly influenced by the sample temperature, indicating the operation of competing reaction channels [4,6]. If in an experiment as displayed in Fig. 1 the oxygen dosage is switched off at the maximum of the exoemission and the surface is annealed with a constant heating rate, electron emission is observed again, as is shown in Fig. 2(a). This effect is definitely not due to thermionic electron emission, since the emission current shows a maximum (at 260 K) instead of continuously rising with temperature while the work function changes by no more than 0.05 eV. A series of similar experiments with variation of the heating rate β revealed a shift of the temperature of maximum emission, T_m , analogous to the situation with a thermally activated desorption process in thermal desorption spectroscopy (TDS). This indicates that the emission of exoelectrons is associated with a transformation of the surface *after* adsorption of oxygen.

In analogy to the analysis of TDS data, a plot of $\ln(T_m^2/\beta)$ versus $1/T_m$ yields a straight line from whose slope an activation energy $E^* = 0.8 \pm 0.1$ eV is derived.

The changes of the electronic properties of the outermost atomic layer associated with this transformation are reflected by the electron energy distributions recorded by metastable deexcitation spectroscopy (MDS). The spec-

tra reproduced in the inset of Fig. 2(b) were taken at the beginning and at the end of the glow curve of Fig. 2(a) by using singlet 2^1S_0 He* atoms as primary particles. These spectra consist of a main peak together with a satellite at higher kinetic energies. Both peaks reflect He* deexcitation that involves an electron from the Fermi level of the substrate which is Cs 6s derived. While the satellite at higher kinetic energies is associated with the decay of a 2^1S_0 singlet, the main peak reflects 2^3S_1 triplet deexcitation. This indicates that the incident He* singlet atoms are largely converted into triplet atoms at alkali metal surfaces prior to deexcitation which then give rise to the main peak [10]. Figure 2(b) shows the variation of the total intensity of the main (i.e., triplet) peak upon raising the temperature which strongly increases and exhibits a point of inflection around 260 K where the maximum occurs in Fig. 2(a). This result indicates that the thermally activated emission of exoelectrons is accompanied by a structural transformation of the surface in which a larger proportion of not yet completely oxidized Cs atoms becomes exposed to the vacuum. Since this process was found to be associated with no noticeable release of O₂ (or O) into the gas phase, it is suggested that it comprises migration of oxygen species below the plane formed by the Cs atoms which thereby become more accessible to probing by the He* atoms. Both sets of data in Fig. 2 can be satisfactorily fitted by a model based on second order kinetics as will be described in detail elsewhere [11].

The $\sqrt{3} \times \sqrt{3} R 30^\circ$ low-energy electron diffraction (LEED) pattern of the pure Cs monolayer changes into a diffuse pattern of a split 2×2 phase upon the O₂ exposure under discussion at 220 K with a Cs:O stoichiometry around 2:3, i.e., nominally between that of the bulk compounds Cs₂O₂ and CsO₂, although the actual structure of this overlayer is of course quite different. This transforms into a well-ordered $\sqrt{21} \times \sqrt{21} R 10.9^\circ$ structure upon annealing to 300 K. Hence the transformation of the adlayer can also be related to a reorganization of its long-range order.

X-ray photoelectron spectroscopy (XPS) from the O 1s core level region shows that the phase formed at 200 K exhibits spectral features composed of two peaks centered at 531.8 and 529.6 eV, respectively [Fig. 3(a)]. Heating up to 300 K causes less than 10% loss in total intensity (presumably because of oxygen migration below the Cs layer) and a substantial variation in the relative proportions of the two species [Fig. 3(b)]. Following corresponding reports in the literature [12] we assign the peak at 531.8 eV binding energy to a molecular and that at 529.6 eV to an atomic oxygen species. The XPS data thus suggest that the thermally activated transformation is associated with dissociation of an O₂-type surface intermediate.

More direct identification of these surface species was achieved by recording vibrational spectra by means of high resolution energy loss spectra (HREELS). Expo-

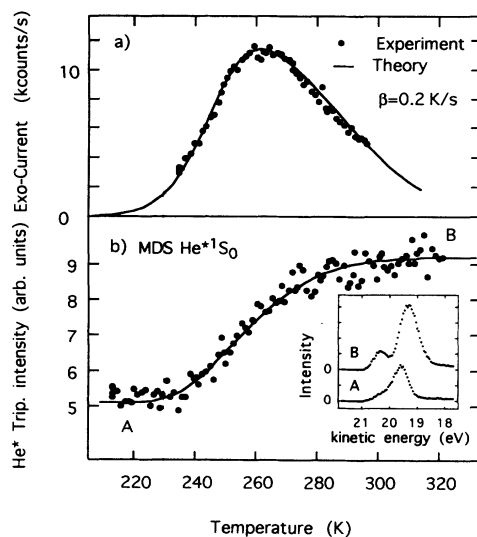


FIG. 2. Comparison of thermally stimulated exoelectron emission and He* metastable deexcitation intensities from the Fermi level on an oxidized monolayer of Cs at the work function minimum (heating rate $\beta = 0.2$ K/s). Note no O₂ was admitted to the gas phase. (a) Exoelectron current (b) intensity of the He triplet deexcitation from the Fermi level as a function of temperature indicating increasing access of He* to the Cs atoms. The inset shows two He* spectra before (A) and after (B) annealing at 220 K. The solid line mimics a thermally activated second order process with the same parameters for (a) and (b), where in (b) the integral of (a) is shown.

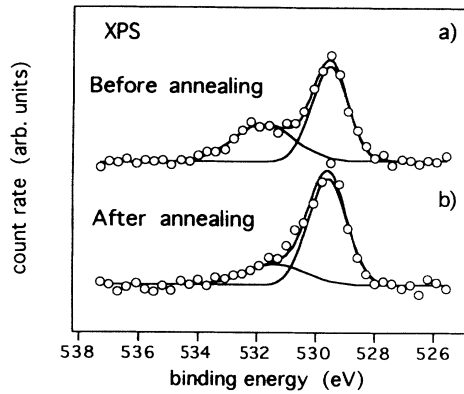


FIG. 3. XPS Mg $K\alpha$ excited O $1s$ spectra (a) cold surface (220 K); (b) annealing removes a large portion of the molecular species at higher binding energy.

sure of a Cs monolayer on Ru(0001) to O_2 at 90 K causes at first dissociative chemisorption, characterized by Cs-O and Ru-O vibrational energies of 28 and about 60 meV, respectively [13]. This is consistent with the structure of the $\sqrt{3}\times\sqrt{3}R30^\circ$ Cs+O/Ru(0001) phase as analyzed by LEED [14] in which the O atoms are in close contact with both Cs and Ru atoms and form a plane below that of the centers of the Cs adlayer. Further exposure then leads to the additional appearance of peaks at 140.3 meV assigned to the stretching vibration of an O_2^- species with overtones at 278.4, 414, and 546 meV, and at 15 meV attributed to the vibration against the substrate [15]. The identification of this species as superoxo (O_2^-) ion was based on the fact that bulk superoxides such as KO_2 or RbO_2 with well-defined structures exhibit quite similar values for the O-O stretching vibration and compares well with recent observations of Hock *et al.* [16]. These superoxo species are presumably located on top of the overlayer as depicted schematically in the inset of Fig. 4(a).

The energies of the overtones reflect the anharmonicity of the interatomic potential of the O_2^- species. Assuming a Morse potential leads to a value for the dissociation energy $D=3.9\pm 0.3$ eV, which is close to that for the free ion (4.1 eV). This result suggests that coupling of the O_2^- species to the surface is only weak and mainly electrostatic in nature. In particular, it rules out substantial occupation of its affinity level which is strongly antibonding with respect to the O-O bond. The proximity of the metallic surface will certainly cause an energetic lowering of this level due to image force effects, but the operation of the partly oxidized Cs overlayer as a "spacer" keeps it still above the Fermi level.

Annealing the sample to 300 K causes complete disappearance of the band assigned to the O_2^- stretch vibration and an increase of the intensity of the Cs-O band [Fig. 4(b)]. This indicates directly that the chemical transformation associated with exoelectron emission has

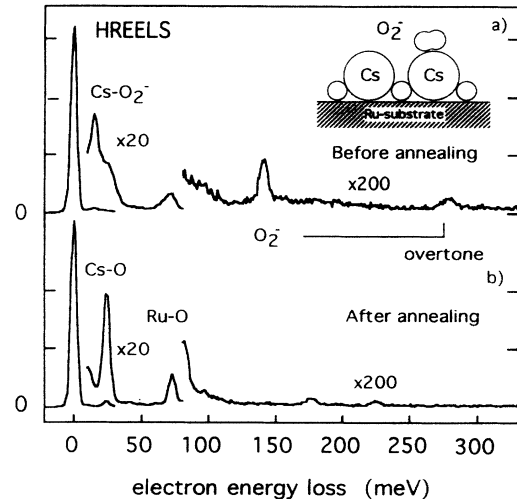


FIG. 4. HREELS $E_p=5$ eV. The CsO_2^- (15 meV) and the O_2^- (140 meV) related loss features in (a) disappear on annealing the sample (b).

to be identified with thermally activated dissociation of the surface superoxo species. The activation energy derived for this process (0.8 eV) is much lower than the dissociation energy for the O_2^- species derived from the anharmonicity of the stretching frequency (3.9 eV). It is hence concluded that the observed exoelectron emission is not a consequence of direct dissociation of the O_2^- species into O^-+O . The derived activation energy of 0.8 eV characterizes a structural transformation by which the O_2^- species comes closer to the metallic surface so that orbital overlap causes further lowering of its affinity level below the Fermi level accompanied by additional electron transfer and subsequent dissociation. Recent calculations with O_2-Li_n systems revealed the formation of O_2^{2-} at close distances for which bond dissociation proceeds without any noticeable energetic barrier [17]. In the present case the highly exothermic coupling of the fragments of dissociation to the metallic substrate will again be accompanied by the "sudden" creation of a hole state below E_F which may be deexcited by an Auger process eventually leading to exoelectron emission.

In another recent series of experiments with the same system, ejection of O^- ions was detected at small exposures which rapidly decayed with progressing oxidation [18]. At these early stages no metastable O_2^- species may be formed but rather direct transformation of the incident oxygen molecules into O_2^{2-} . A small fraction of the latter with their molecular axis along the surface normal may release one of the O^- fragments into the gas phase. A partly oxidized surface will, as demonstrated here, lead to the formation of metastable O_2^- intermediates whose coupling and orientation to the surface will prevent any O^- ejection upon dissociation following further electron uptake. Emission of exoelectrons will al-

ways be strongly competed by adiabatic reaction channels, and the relative probabilities will be sensitively affected by the actual nuclear motions and electronic interactions. It hence becomes plausible that the probability for exoelectron emission in the stage of reaction proceeding through metastable O_2^- species is different from that in which the incident O_2 molecules become doubly ionized and dissociate directly. In this way it can be rationalized why with the present system the yield of exoelectrons is very low with a clean surface and increases with progressing oxidation.

The present findings are compatible with the previous suggestion that exoelectron emission with the oxidation of thick Cs films is essentially confined to that stage in which the superoxide is formed. The results presented here enable more detailed elucidation of the decisive step and show that the exoemission proceeds via dissociation of a metastable O_2^- superoxo species on a preoxidized surface.

We thank G. Glaefke in Rostock and R. Monnier in Zürich for fruitful discussions and J. Osterwalder for some beam time at ESCA II in Fribourg. T.G. acknowledges an Alexander von Humboldt scholarship.

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