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On the mechanism of ion stimulated desorption of O^+ from transition-metal surfaces

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Abstract

The O^+ ion desorbs from oxygenated V, Cr and Ta surfaces by He^+ irradiation due to the internal potential energy of He^+ . The O^+ ion (the Ne^+ ion) is neutralized completely (survives considerably) at the V and Ta surfaces in the ion-scattering experiment because the valence holes have a much shorter lifetime than the core hole. From these facts, we can deduce that the stimulated desorption of O^+ should not be caused by the valence holes but is more likely initiated by the O 2s core-hole state. The core-excited oxygen, formed via quasisonant charge exchange with primary He^+ , is ionized because of the intraatomic Auger decay after breakage of the chemisorptive bond, which is essential for escape of very slow secondary O^+ ions from the efficient resonance neutralization. (Int J Mass Spectrom 202 (2000) 199–205) © 2000 Elsevier Science B.V.

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1. Introduction

Understanding the mechanism of ion emission from solid surfaces is of crucial importance for the development of surface analysis techniques, such as electron and photon stimulated desorption (ESD and PSD) and secondary ion mass spectrometry (SIMS). In ESD and PSD, the F^+ and O^+ ions are known to be ejected efficiently from surfaces of transition-metal oxides. Knotek and Feibelman [1] postulated simple coulombic ejection, which occurs when oxygen (and fluorine) in the ionic lattice of TiO_2 is converted into a positive ion as a result of the interatomic Auger decay of the Ti 3p core hole. The Knotek–Feibelman

mechanism was generalized to elucidate O^+ desorption from oxygenated metal surfaces, where the 2-hole 1-electron (2h1e) or 2-hole (2h) states caused by the Auger decay of a deep core hole initiates the O^+ desorption [2–6]. This mechanism, termed Auger stimulated desorption (ASD), assumes localization of the valence holes in a metal–oxygen bond orbital for a considerably long time (10^{-14} – 10^{-13} s).

In SIMS, secondary ions arise from complex mixture of collisional dynamics and electronic transitions, but a considerable contribution of the potential energy of primary ions to ionic desorption of surface atoms has been suspected on the analogy of ESD and PSD. This particular phenomenon has been termed ion-stimulated desorption (ISD) [7–10]. However, the conversion mechanism of primary ion's potential energy into kinetic and potential energies of desorbing

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surface atoms is still an open question. Very recently, the O^+ ion was found to desorb efficiently from the $TiO_2(110)$ surface by He^+ irradiation, but very little O^+ was emitted from surfaces of simple ionic compounds such as MgO , Al_2O_3 and SiO_2 [11]; the O^+ ion is initiated by formation of a $O\ 2s$ core-hole state having antibonding characteristics, followed by ionization via intraatomic Auger decay. Thus, the mechanism of stimulated desorption of secondary ions is currently under debate, and hence, more systematic investigation is indispensable.

In this article, we study secondary ion emission from oxygenated metal surfaces such as V, Cr and Ta by He^+ irradiation. So far, most of the previous studies in ESD, PSD and ISD have focused on the initiating event of desorption, i.e., the nature of the antibonding state. In reality, however, the ions desorbing from the surface should suffer efficient neutralization on the outgoing trajectory, which may determine the occurrence of the ionic desorption more conclusively. Hence, more insight into the mechanism of stimulated ion desorption would be gained from the point of view of ion neutralization at a surface. To clarify the mechanism of ion emission from surfaces, low-energy O^+ and Ne^+ ions are scattered from the V and Ta surfaces and the results are compared with those of ISD O^+ emission.

2. Experiment

The experiments were made in an ultrahigh vacuum (UHV) chamber (base pressure of 2×10^{-10} Torr) equipped with facilities for standard surface characterization. The He^+ , Ne^+ and O^+ beams extracted from a discharge were mass analyzed by using a Wien filter. The surfaces were bombarded by the ions with an incidence angle of 20° from the surface normal, and the scattered and sputtered ions normal to the surface were detected by means of a hemispheric electrostatic energy analyzer (ESA) operating with a constant pass energy mode (the energy resolution of 2 eV). The experimental setup has been described elsewhere [12]. In the present experiment, the primary ion was chopped by an electrostatic deflector into

pulses of 100 ns in width and 40 kHz in frequency, so that the mass of sputtered secondary ions was analyzed by the time-of-flight (TOF) technique. Thus, the yield of secondary ions at a desired kinetic energy was obtained by integrating the specific ion peaks in the TOF ion mass spectrum (TOF-IMS). The energy distribution of the mass-selected secondary ions was measured by scanning the kinetic energy of ESA. To avoid a sample damage, the ion beam current was reduced to below 5 nA/cm^2 and each TOF-IMS was accumulated for 10 s. The polycrystalline samples of V and Cr were prepared by a procedure of sputtering and annealing (1500 K) in UHV. The polycrystalline Ta foil ($50\ \mu\text{m}$ in thickness) was heated by electron bombardment to a temperature of 2500 K. The V and Cr surface exhibited a trace of oxygen peak in low-energy He^+ ion scattering, but no oxygen was detected at the cleaned Ta surface. For oxygenation, a research grade O_2 gas (99.999 %) from a glass bottle was introduced through a variable leak valve. The measurements of the TOF-IMS spectra were made at room temperature.

3. Experimental results

Figure 1 shows the energy distributions of secondary ions ejected from the oxygenated (100 L) V, Cr and Ta surfaces by 2-keV He^+ ion bombardment. The intensities are normalized relative to each other through the ion beam current. The clean surfaces exhibit very little secondary ion yields, but the yields are increased markedly upon oxygenation of the surface. All of the surfaces examined were saturated with oxygen as revealed by the evolution of the secondary ions intensity. The O^+ ions have a considerably narrow energy distribution ($E < 10\text{ eV}$) relative to the V^+ and VO^+ ions. The high energy tail of the secondary ions is due to kinetic sputtering while the low-energy peak of the O^+ ion is characteristic of noncollisional potential sputtering [7,10]. Note that the peak position of O^+ from the oxygenated Ta surface (7 eV) is apparently higher than that from the V and Cr surfaces (4 eV). The O^+ energy distribution from the $TiO_2(110)$ surface [11] is almost identical to

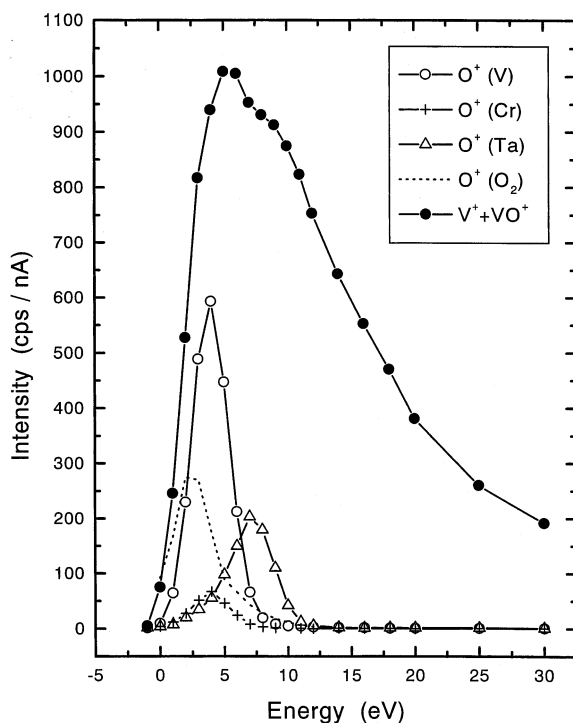


Fig. 1. Energy distributions of secondary O^+ ions ejected from the oxygenated (100 L O_2 exposure) V, Cr and Ta surfaces, together with the secondary V^+ and VO^+ ions. The energy distribution of the O^+ ions by excitation of the O_2 gas (1×10^{-5} Torr) is shown by a dotted line.

that from the oxygenated V and Cr surfaces. To elucidate the different energy distributions of the O^+ ions, the gas-phase O_2 molecule was excited by the He^+ ions; the experiments were made by backfilling the UHV chamber with the O_2 gas up to 1×10^{-5} Torr and the ejected ions were detected under the same configurations.

The O^+ ions are emitted from the gas-phase O_2 molecule as well. As shown by a dotted line in Fig. 1, the O^+ intensity from the O_2 molecule is peaked at a lower kinetic energy position than that from the oxygenated transition-metal surfaces. The O^+ ions should be ejected from the specific bonds (or “diatomic molecules”) such as O–O, V–O, Cr–O and Ta–O. Assuming that the internal energy used for dissociation is identical and is shared with the molecular counterpart, the higher kinetic energy of O^+ results from the molecule with a heavier counterpart because

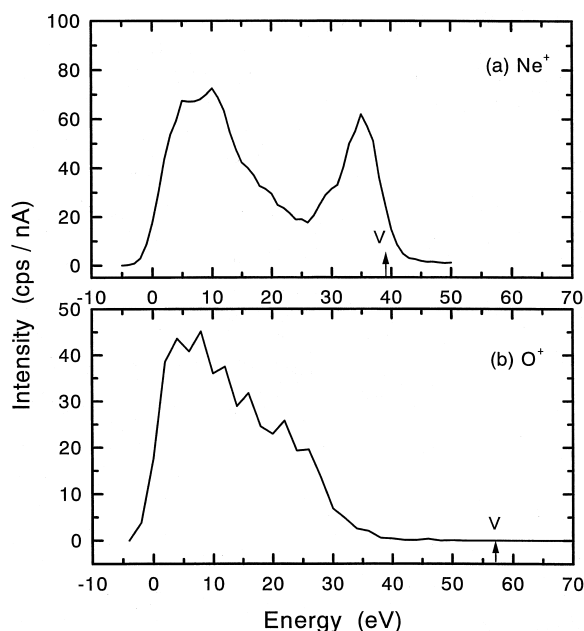


Fig. 2. Energy spectra of positive ions from the clean V surface by incidence of (a) Ne^+ and (b) O^+ ions with the primary energy of 200 eV. The intensities are normalized through the ion beam current. The scattered primary ions appear around the ideal binary collision energy indicated by arrows on the abscissa whereas the sputtered secondary ions have a lower kinetic energy extending to 0 eV.

it carries less kinetic energy than the lighter one. This explains the observed energy distributions of O^+ qualitatively, but this might be a rough estimate because the dissociation energy itself should be dependent upon the nature of the possible antibonding state. A knowledge of the potential energy surface is indispensable for quantitative discussion of the kinetic energy distribution of O^+ .

The experiments of ion scattering were performed to evaluate the ion neutralization effects. Figs. 2 and 3 show the energy spectra of positive ions ejected from the clean V and Ta surfaces, respectively, by irradiation with the O^+ and Ne^+ ions of 200 eV. The measurements were made without chopping the beam, and hence the energy distributions of both scattered and sputtered ions were obtained without mass separation. The scattered primary ions, if they survived neutralization via single collision with the topmost layer of atoms, should exhibit surface peaks near the

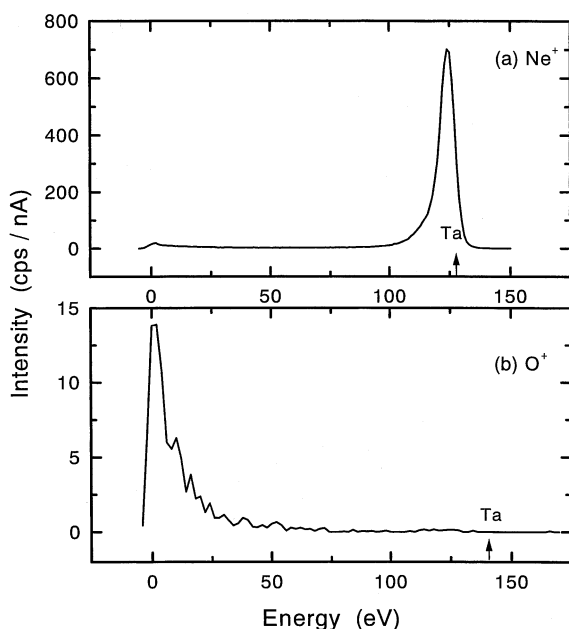


Fig. 3. Energy spectra of positive ions from the clean Ta surface by incidence of (a) Ne^+ and (b) O^+ ions with the primary energy of 200 eV. The intensities are normalized through the ion beam current. The scattered primary ions appear around the ideal binary collision energy indicated by arrows on the abscissa whereas the sputtered secondary ions have a lower kinetic energy extending to 0 eV.

ideal binary collision energy indicated by arrows on the abscissa, whereas the secondary ions appear with a smaller kinetic energy reaching 0 eV [11,12]. The scattered Ne^+ ion shows a clear surface peak but the surface peak of scattered O^+ is almost missing, indicating that the O^+ ion undergoes very efficient neutralization at the surface.

4. Discussion

The secondary ion yields from the elemental metal surfaces are very small, but the yield of the cationic ions such as V^+ , Cr^+ and Ta^+ increases markedly upon oxygenation. This kind of behavior has been explained successfully by the bond-breaking mechanism of the secondary ion formation [13]; the cationic species such as V^+ (ionization potential of 6.7 eV) can be emitted from the partly ionic V–O bond with

the aid of atomic collision for bond breakage. In order for negatively charged species to be emitted as cations, more than two valence electrons should be excited. The F^+ ion can be emitted from the CaF_2 surfaces by He^+ bombardment because two valence electrons are excited via the electron promotion mechanism during violent collision between F^- and He^0 backscattered from the solid [14,15]. In the present experiment, this channel is not open, as evidenced by the absence of the high-energy tail of O^+ in Fig. 1. This is partly because two-electron excitation is not enough to create O^+ from chemisorbed oxygen, which has a most-probable charge state between -1 and -2 . Also likely is that the sputtered O^+ ion, if any, is neutralized at the metal surfaces with a much higher probability than at the highly ionic compound surface.

As far as the noncollisional ion desorption is concerned, the creation of the $2h1e$ or $2h$ state due to the deep core-hole decay has been assumed as an initiating event of the O^+ desorption [5,6]. The same initial state occurs by He^+ excitation since the Auger decay of the He^+ $1s$ hole results in the $2h$ state. If these holes are localized in a V–O (Ta–O and Cr–O) bond orbital with a bonding character, an antibonding configuration can be produced. The desorption may occur provided that these holes are localized for the time necessary for desorption (10^{-14} – 10^{-13} s). Such localization of the valence holes is realized for isolated gas-phase molecules or highly ionic compound surfaces with a narrow bandwidth. At a metal surface, the lifetime of the holes as estimated from the width of the valence band is as small as 10^{-16} s, so that the localization of the valence holes should not occur. Indeed, this is manifested itself in the occurrence of the complete neutralization of the energetic O^+ ions scattered from the Ta and V surfaces (see Figs. 2 and 3). As shown in Fig. 4, the O $2p$ orbital merges into the valence-band orbitals during the transient chemisorption and the holes in the primary O^+ ion can readily diffuse into the band via the resonance tunneling during the ion-surface interaction time (in the 10^{-15} s range) [16]. The same hole diffusion should occur for stimulated desorption of O^+ if it is initiated by the $2h$ or $2h1e$ state. Thus, the O^+ ions hardly

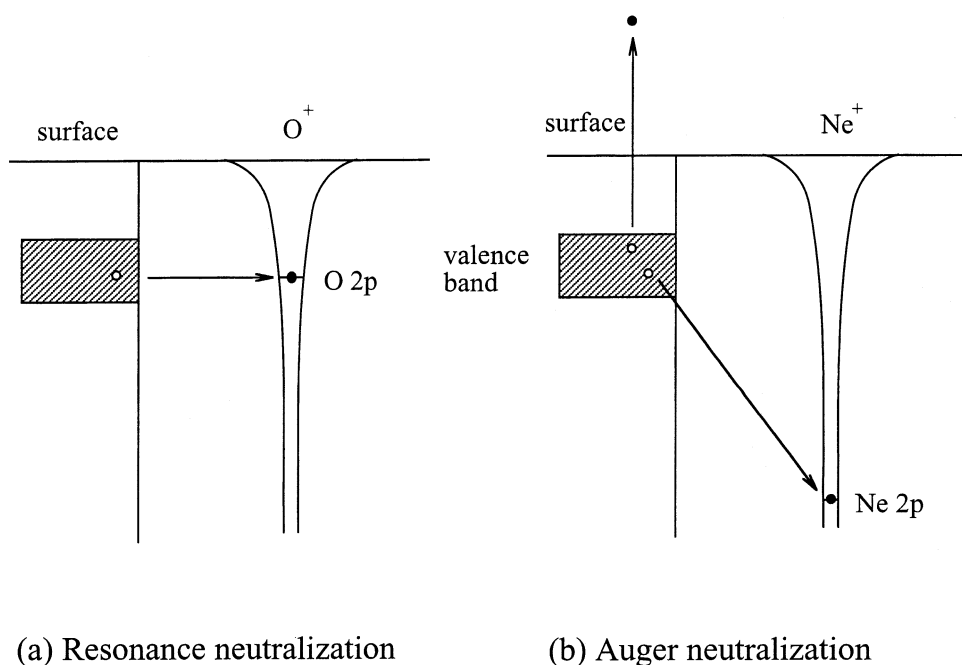


Fig. 4. The energy diagrams for resonance and Auger neutralization. The O 2p valence holes decay via the one-electron resonance tunneling during transient chemisorption on metal surfaces, whereas the Ne 2p hole decays via the two-electron Auger process.

emerge from the valence holes, especially at metal surfaces and, hence, the conventional picture of ASD may not be true.

It should be noticed that a considerable amount of the Ne^+ ions can be scattered from the metal surfaces without neutralization. This is because the Ne^+ 2p hole decays via the Auger process (see Fig. 4); the lifetime of the Auger decay (10^{-14} s) is much longer than that of the resonant tunneling and is almost comparable to the interaction time of slow secondary ions with solid surfaces. In this context, the creation of the core hole rather than the valence O 2p holes is responsible for the O^+ desorption [11]. The O 2s hole (the binding energy of -26 eV) can be formed via the quasisonant charge exchange with the He^+ 1s state (-24.6 eV). The ionization of core-excited oxygen occurs due to the intraatomic Auger decay on the outgoing trajectory after breakage of the strong chemisorptive bond, thereby avoiding efficient resonance neutralization. Thus, the creation of the long-lived O 2s hole state is essential for the O^+ desorption. This mechanism is termed resonant

ion-stimulated desorption (RISD). The scheme of electron transitions in RISD is schematically shown in Fig. 5, together with that in ASD.

The above-mentioned mechanism should be true not only for ISD but also for ESD and PSD. In any case, the acquisition of the kinetic energy is another prerequisite for ion desorption to occur. Probably, a sudden formation of a core hole induces rearrangement of the valence electrons to screen a positive charge, during which the antibonding valence-orbital configuration occurs. The oxygen acquires kinetic energy in the course of lengthening of the bond. In fact, it is revealed that the creation of the core hole in highly correlated transition-metal compounds such as TiO_2 and SrTiO_3 induces rearrangement of the valence orbitals into the antibonding configuration [17]. In the study of gas-phase dissociation of simple molecules, some indications are presented which manifest that the core-hole state has the antibonding character and hence the dissociation of molecules or the movement of constituent atoms is induced prior to Auger decay of the core hole [18,19]. The core-hole

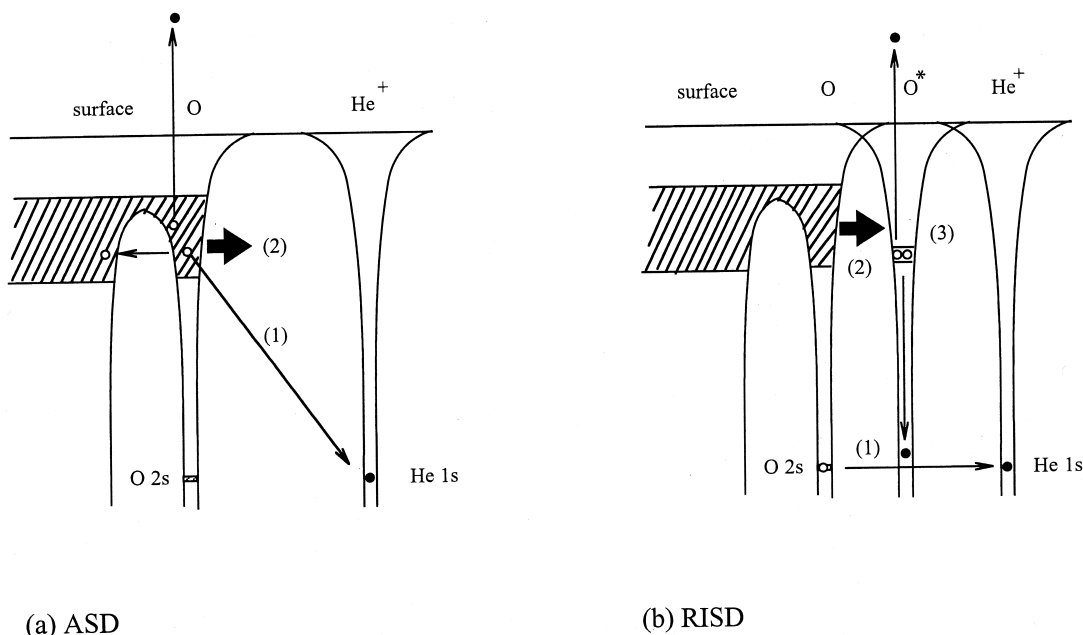


Fig. 5. The energy diagrams for (a) the Auger stimulated desorption (ASD) and (b) the resonant ion-stimulated desorption (RISD). In RISD, the resonant hole exchange between He⁺ 1s and O 2s initiates the event and the desorption of the core-excited O atom (O*) follows. Finally, the ionization of O* occurs on the outgoing trajectory via the intraatomic Auger decay of the O 2s hole. The reneutralization of the resulting O⁺ ion is reduced by the occurrence of the ionization after breakage of the strong chemisorptive bond. In ASD, two valence holes due to Auger decay of the He⁺ 1s hole might initiate the event. However, the valence holes are rather short lived because of the rapid diffusion into the band, so that the O⁺ desorption may hardly result.

state is rather long lived (10^{-14} – 10^{-13} s), so that the oxygen can gain a large kinetic energy. This is indeed necessary not only for bond breakage but also for the resulting ion to overcome the attractive force by the image charge.

The O atoms adsorbed on a surface should be desorbed more easily than those incorporated in the substrate. Indeed, slight heating of the oxygenated transition-metal surfaces (800 K) decreases the O⁺ yield significantly despite the fact that the oxygen still remains on the surface. This is because the O species adsorbed on a lower coordination site (probably with a single bond) is preferentially emitted as the O⁺ ions, whereas the oxygen in the stable oxide form is hardly desorbed as an ion.

Regarding ion species other than O⁺, the F⁺ ion is known to be emitted very efficiently in ISD and ESD [15], but, to my best knowledge, the potential sputtering of C⁺ and N⁺ is not reported to occur [10]. The

fluorine is most likely in the charge state of -1 on a surface and, hence, the F⁺ emission occurs due to the loss of two electrons. In this context, the C and N atoms are less charged on a surface, so that the desorption of C⁺ or N⁺ would occur more easily. In reality, however, the C (N) 2s state is shallower than the O 2s and F 2s states so that it usually takes part in the valence orbitals. In such a situation, the lifetime of the holes is too short for ionic desorption to occur. On the other hand, the H⁺ emission might occur even from the valence holes state provided that they are created in the bonding 3σ orbital of the OH species, as inferred from the fact that the H⁺ ion survives neutralization during collision with oxygen in the H⁺ scattering experiment [20,21]. This is not only because the velocity of the H⁺ ion is faster than the other species, but also because the surface molecule is formed in the transient OH species [16,20], which prevents the holes from diffusion into the valence

band considerably. Even in this case, however, it is more likely that the hole creation in the 2σ orbital of the OH species (having the O 2s character) initiates the event and the H^+ ion is formed as a consequence of the interatomic Auger decay during the breakage of the OH bond [22].

5. Conclusion

The conversion mechanism of the internal potential energy of He^+ into desorption of the O^+ ions has been investigated at the oxygen-adsorbed V, Cr and Ta surfaces. In the ion-scattering experiments, the O^+ ions with the valence holes hardly emerge from the metal surfaces because of the occurrence of the efficient resonance neutralization whereas the Ne^+ ion, undergoing the Auger decay, can survive neutralization considerably. This fact clearly shows that the creation of two valence holes as a consequence of the Auger decay of the deep core hole should not cause the O^+ desorption. It is concluded that the formation of the O 2s hole resulting from the quasisonant charge exchange with the He^+ 1s state is the initiating event and the oxygen desorption occurs from the long-lived core-hole state having the antibonding characteristic. The O^+ ion is finally formed via the Auger decay of the O 2s hole on the way out from the surface after breakage of the chemisorptive bond.

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