PHYSICAL REVIEW B VOLUME 54, NUMBER 8 15 AUGUST 1996-II

Attenuation of low-energy (<10 eV) O^+ ions in transmission through adsorbed alkali-metal layers

V. N. Ageev, N. D. Potekhina, and B. V. Yakshinskii
A. F. Ioffe Physical-Technical Institute, Academy of Sciences, St. Petersburg, Russia

M. Akbulut and T. E. Madey*
Department of Physics and Astronomy and Laboratory for Surface Modification, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08855

(Received 15 April 1996; revised manuscript received 8 May 1996)

We report the transmission of low-energy (<10 eV) O^+ ions through adsorbed alkali-metal (Li, Na, K, and Cs) overlayers on an oxidized tungsten substrate. We find that the O^+ yield is attenuated by the alkali-metal overlayers. For $\Theta > 0.3$ ML, we derive attenuation cross sections of $(18\pm 2)\times 10^{-15}$ cm^2 for Cs, $(13\pm 1)\times 10^{-15}$ cm^2 for K, $(5\pm 1)\times 10^{-15}$ cm^2 for Na, and $(3.3\pm 0.3)\times 10^{-15}$ cm^2 for Li. We attribute the attenuation of O^+ in alkali-metal films for $\Theta > 0.3$ ML mainly to resonance electron tunneling from adsorbed alkali-metal atoms to excited states of oxygen. [S0163-1829(96)50732-0]

In DIET (desorption induced by electronic transitions), the depth of origin of desorbing ions is a fundamental issue.[1–3] That is, what are the processes and properties that determine the survival probability of ions excited below the surface of a solid? Recently, in order to identify the dominant processes that limit the survival probability of low-energy ions created below the surface, the transmission of low-energy (<10 eV) ions (e.g., O^+, F^+, F^-) through ultrathin atomic (e.g., Ar, Kr, Xe) and molecular (e.g., H_2O, NH_3) films several monolayers thick have been systematically studied.[1–3] These studies have revealed that elastic scattering and charge-transfer processes are the dominant processes in determining the attenuation of the ions created below the overlayer films; these processes depend strongly on the overlayer electronic and chemical properties as well as the nature of the ion and its kinetic energy.

In this work, we present systematic measurements of the transmission of O^+ ions through an ultrathin film of metal atoms, i.e., alkali-metal overlayers having thicknesses $\leqslant 1$ ML. We generate well-defined O^+ beams by electron bombardment of a oxidized tungsten surface. We find that for alkali-metal coverages $\Theta \geqslant 0.3$ ML on the oxidized tungsten surface, the O^+ yield is attenuated strongly, and the attenuation is exponential. The attenuation of O^+ is strongest for Cs, while the attenuation of O^+ is lowest for Li.

The experimental setup is described in detail elsewhere.[4] In short, the experiments are performed in an ultrahigh vacuum (UHV) chamber (base pressure: $\sim 2\times 10^{-11}$ Torr) equipped with instrumentation for surface analysis including ESD (electron stimulated desorption), surface ionization (SI), and TDS (thermal desorption spectroscopy). ESD measurements are performed using a static magnetic mass spectrometer combined with a retarding field analyzer. A textured tungsten ribbon with a predominantly (100) oriented surface is used as the sample. The sample is cleaned by annealing in an oxygen atmosphere at 1700 K; oxygen is admitted by thermal decomposition of barium peroxide. In order to form an ultrathin oxide film the sample is heated in oxygen (600 Langmuir) at 1500 K. Based on the results of earlier studies, we assume that the stoichiometry of the oxidized W(100) surface is approximately $WO_{2\text{-}3}$. Electron bombardment of this surface by a 100-eV electron beam produces a well-defined O^+ ESD ion beam having a peak energy of ~ 7 eV. During the ESD measurements a very low electron current density ($\sim 10^{-6}$ A/cm^2) at electron energy $\leqslant 100$ eV is used to minimize electron-induced thermal desorption of overlayer atoms.

Alkali-metal atoms are deposited onto the oxidized tungsten surface at 300 K from directly heated evaporators by decomposition of the corresponding chromates. Impurities in the alkali-metal fluxes are found to be less than 0.1%. The exposures of alkali metal are determined from the deposition time under constant alkali flux, and the concentrations of alkali metal on the oxidized tungsten surface are determined by means of thermal desorption spectroscopy. The alkali-metal fluxes are determined by measuring the total alkali-ion current during surface ionization at the sample surface. 1 ML of Li or Na corresponds to 1×10^{15} atoms/cm^2; 1 ML of K or Cs corresponds to 5×10^{14} atoms/cm^2.[4]

Figure 1 shows a semilogarithmic plot of the normalized ESD O^+ yield (q^+/q_0^+) as a function of alkali-metal concentration N on the oxidized tungsten surface. Note that q_0^+ denotes the value of the total O^+ signal obtained from the oxidized tungsten in the absence of alkali metal, whereas q^+ denotes the O^+ yield in the presence of alkali metal on the oxidized tungsten surface. The data of Fig. 1 show that in the presence of the alkali-metal overlayers the O^+ signal is attenuated. However, in the alkali coverage range $\Theta < 0.3$ ML (low-coverage regime) the attenuation of the O^+ signal is lower than the attenuation of O^+ for alkali coverage 0.3 ML$<\Theta<$0.8 ML (high-coverage regime). As seen in Fig. 1, the decrease in the O^+ yield is roughly exponentially dependent on alkali-metal coverages ($\Theta > 0.3$ ML) and the slope is most steep for Cs and least steep for Li. We suggest that the exponential attenuation is mainly due to the overlapping of the effective interaction area of neighbor-

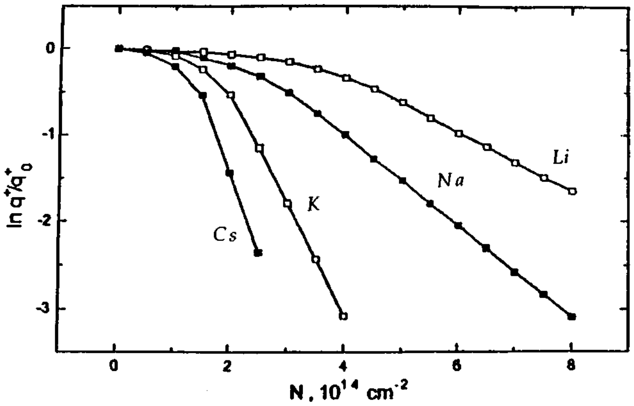

FIG. 1. Normalized O$^+$ yield as a function of concentration of Li, Na, K, and Cs adsorbed on an oxidized tungsten surface. The data are plotted semilogarithmically and normalized to 0 for the clean surface value.

ing overlayer atoms with increasing coverage, as suggested earlier by Akbulut *et al.*[5] for the attenuation of O$^+$ ions in an H_2 ^{18}O overlayer.

We can derive an attenuation cross section of O$^+$, σ, using the equation[6]

$$q^+ = q_0^+ \exp(-\sigma N). \tag{1}$$

For the exponential regime (high alkali coverage), we calculate the attenuation cross sections of O$^+$ to be

$$(18\pm 2)\times 10^{-15}\ \text{cm}^2 \quad \text{for Cs,}$$

$$(13\pm 1)\times 10^{-15}\ \text{cm}^2 \quad \text{for K,}$$

$$(5\pm 1)\times 10^{-15}\ \text{cm}^2 \quad \text{for Na,}$$

$$(3.3\pm 0.3)\times 10^{-15}\ \text{cm}^2 \quad \text{for Li.}$$

For low alkali concentration ($\Theta < 0.3$ ML), the attenuation cross section of O$^+$ is found to be $(4\pm 1)\times 10^{-16}$ cm^2 for all alkali-metal overlayers.

We now discuss the factors that may contribute to the attenuation of O$^+$ in the presence of alkali overlayers. First, we begin by considering several ''initial state'' effects that may influence the rate at which O$^+$ ions are generated by electron bombardment: (a) shielding of the substrate from the electron beam by elastic electron scattering from the alkali overlayers, (b) electron energy loss due to inelastic scattering by the alkali overlayers, and (c) change in the local electronic structure of the substrate upon adsorption of alkali metal on the oxidized W.

Consider the possible effect of elastic backscattering of primary electrons from the adsorbed layers on the measured attenuation of O$^+$.[5] In an earlier study, Yu[7] has investigated ESD O$^+$ and O$^-$ yields from an oxygen chemisorbed Mo(100) surface as a function of Cs overlayer coverage, for thicknesses less than a monolayer. Yu has found that at low Cs coverages the O$^-$ yield increases, whereas the O$^+$ yield decreases slightly, and at high Cs coverages both ESD O$^+$ and O$^-$ yields are strongly attenuated. The author suggested that shielding of the oxygen atoms from the incident 200-eV electrons by elastic electron scattering from the Cs overlayer may be the reason for the high-coverage attenuation. However, it is known that for electrons having kinetic energy >100 eV, the elastic backscattering and large angle scattering probability from a surface are very low, so that the attenuation of the $\sim$100-eV electron beam by elastic backscattering in the overlayer probably has little influence on the measured attenuation of O$^+$. As discussed in detail in Ref. 6, we do not consider that primary electron energy loss in the alkali overlayers is a dominant process in the attenuation of O$^+$.

If adsorption of alkali metal affects the electronic structure of the substrate significantly, this could influence the initial ESD O$^+$ yields. Recent experimental studies[8,9] on adsorption of alkali-metal atoms on TiO_2 surfaces have revealed that alkali adsorption is accompanied by charge transfer into Ti 3*d* band-gap states at low alkali coverages (<0.4 ML); the alkali-metal adsorbate is adsorbed ionically on TiO_2 for coverages up to the value at which the work function of the substrate is reduced to its minimum value. The adsorbed alkali species become neutral adatoms with increasing coverage. The dependence of the observed work-function change on the alkali-metal coverage reflects this electronic behavior.

Ageev *et al.*[4,10] have shown that the Li$^+$, Na$^+$, and Cs$^+$ ESD signals obtained from alkali-metal adsorbed on an oxidized W surface depend strongly on alkali-metal coverages; the ESD alkali-metal–ion signals increase steeply in the alkali coverage range 0–0.3 ML, and then decrease for alkali coverage >0.3 ML. This result is consistent with the interpretation that adsorbed alkali-metal atoms on the oxidized W surface are ionic in nature in the low-coverage regime (<0.3 ML), and become metallic with increasing coverage. This is very consistent with the results of adsorption of alkali-metal atoms on TiO_2.

As shown in Fig. 1, the O$^+$ attenuation cross sections are comparatively low ($\sim 4\times 10^{-16}$ cm^2) in the low-alkali-coverage regime. Although adsorption of alkali metal may affect the electronic structure of the oxidized tungsten substrate due to charge transfer at low coverages (<0.3 ML), the O$^+$ ESD mechanism does not appear to be significantly affected upon adsorption of alkali-metal atoms. Based on the above discussion, we conclude that initial-state effects may contribute to O$^+$ attenuation at low coverages, but are probably not the dominant processes that determine the attenuation of O$^+$ in the presence of high coverages of alkali overlayers.

We now consider final-state effects. The measured O$^+$ attenuation in the alkali overlayers may be due to elastic scattering between desorbing O$^+$ ions with the overlayer atoms and/or due to inelastic scattering such as charge-transfer neutralization of O$^+$. Let us first consider elastic scattering processes. If desorbing O$^+$ ions are elastically backscattered or scattered through such a large angle by alkali atoms that they cannot escape from the surface, the measured O$^+$ signal is attenuated.[5] If O$^+$ ions scattered in the forward direction can escape from the surface, they are not attenuated. Recently, Ageev[11] has shown, by using a model based on elastic backscattering and local surface field relaxation, that the larger the mass of the overlayer atom, the smaller the O$^+$ attenuation cross section. However, our present observation shows that the attenuation cross section of O$^+$ increases with increasing overlayer alkali atom mass. In fact, the measured O^+ attenuation cross sections are much too large to be realistic for elastic backscattering and large-angle scattering, for which smaller impact parameters are necessary. Therefore, we do not believe that elastic scattering processes are the dominant processes in determining the attenuation of O^+ through the alkali overlayers.

We focus now on inelastic processes such as energy-loss processes and charge-transfer neutralization of the desorbing O^+ ions. The inelastic energy losses to the lattice vibrations (phonons), or through excitation or ionization of the overlayer atoms, are not expected to be important processes in our experiment, because the energy of an O^+ ion is so low (<10 eV) and the overlayers so dispersed.[6] However, charge transfer can be a very important mechanism for loss of O^+ signal. If desorbing O^+ ions undergo one-electron charge transfer processes, the O^+ ions are converted to neutral species; the measured O^+ signal is attenuated.

We consider two possible charge-transfer processes in the presence of alkali overlayers: (a) electron tunneling from the substrate to O^+ and (b) charge transfer from an adsorbed alkali-metal atom to O^+.

Consider first the possibility of charge transfer from the substrate to desorbing O^+ ions. It is well known that adsorption of alkali-metal atoms on a metal or oxide surface decreases the work function of the surface significantly.[12] It is possible that the attenuation of O^+ is caused mainly by resonance electron tunneling from the oxidized tungsten surface to O^* $^3S_1$ and O^* $^5S_2$ excited states of oxygen with excitation energies of $\sim$4.09 eV and 4.4 eV, respectively.[13] The work function of the oxidized tungsten surface, ϕ_w, is about 6 eV.[14] Since our ultrathin oxide film is only a few monolayers thick, we assume that the top of the valence band lies at or just below the Fermi level.

In the vicinity of a surface, the energy levels of the excited states of an atom are expected to shift upward due to the image potential.[15] Hence, during O^+-ion desorption from the oxidized tungsten, the resonance electron tunneling from the oxidized W surface to the O^* $^3S_1$ and O^* $^5S_2$ excited states of O^+ is expected to have very low probability, because the excited states lie always above the Fermi level of the substrate. However, adsorption of alkali metal on the oxidized surface can make resonance tunneling possible, because adsorption of alkali metal on the surface leads to a decrease in the work function, and may affect the excited-state energy level of the desorbing ions.[12] Since the dipole moment of adsorbed Cs is larger than that of Li, a smaller Cs coverage than that of Li is necessary to produce the same work-function change. This effect is clearly noticeable at low coverages, because the work function decreases rapidly with increasing coverage from 0 to 0.3 ML.[9] Hence, if the resonance electron tunneling from the valence band of the substrate to the excited states of O^+ ions were a dominant process we would expect a strong attenuation of O^+ yield at low coverages. However, as seen in Fig. 1, the attenuation of O^+ is not very substantial in the low-alkali-metal coverage $\theta<0.3$ μL, which implies a low resonance tunneling probability.

Adsorbed alkali metals become more metallic for $\Theta>0.3$ ML. Hence, for $\theta>0.3$ ML, the excited states of oxygen may couple strongly with the valence band of the alkali-covered substrate,[16] so that resonance electron tunneling from the substrate to the excited states of O^+ ions becomes possible. In this coverage regime, the work function of the substrate is expected to change relatively little until the bulk value of the alkali work function is reached. In addition, for $\Theta>0.3$ ML, the change in work function is not expected to be very different for the various alkali overlayers. We conclude that, for $\Theta>0.3$ ML, resonance electron tunneling from the low work-function substrate to the excited states of O^+ ions may contribute to the attenuation of O^+ ions in the alkali-metal overlayers, but it is not the dominant process.

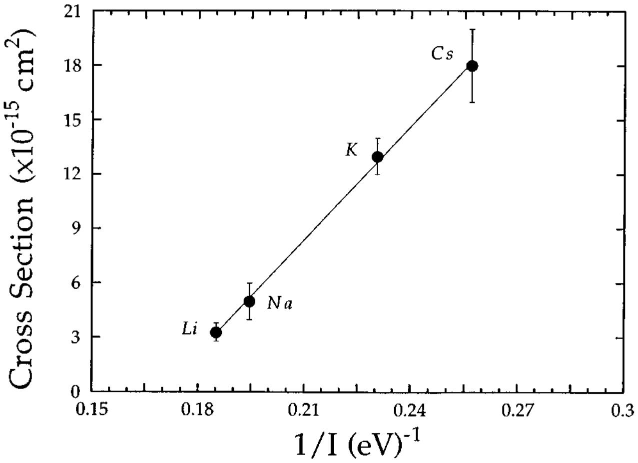

FIG. 2. Measured O^+ attenuation cross sections in the Li, Na, K, and Cs overlayers as a function of reciprocal ionization potential of gaseous alkali-metal atom.

We now consider the attenuation of O^+ on the basis of a model involving one-electron charge transfer between an alkali-metal atom and an O^+ ion. In the low-coverage regime ($\Theta<0.3$ ML) adsorbed alkali-metal atoms are expected to be ionic, and we do not expect charge transfer between an alkali ion and a desorbing O^+ ion. This is consistent with our observed results; for $\Theta<0.3$ ML, the O^+ attenuation cross section is comparatively low. However, in the coverage regime $\Theta>0.3$ ML, alkali-metal atoms are metallic, and a charge-transfer reaction between an adsorbed alkali-metal atom and a desorbing O^+ ion is possible. Note also that the magnitude of the O^+ attenuation cross sections in the alkali overlayers ($18\text{–}3\times10^{-15}$ cm^2) is comparable with the typical gas-phase resonance charge-transfer cross sections ($1\times10^{-14}\text{–}1\times10^{-15}$ cm^2) at low energy (<10 eV).[17]

The gas-phase excitation energies of O^* $^3S_1$ and O^* $^5S_2$ are very close to the ionization energies of the alkali-metal atoms (3.9–5.4 eV). Near the surface, the energy levels of adsorbed alkali atoms and desorbing ions shift and broaden.[12] We expect that the energy levels of the excited states of atomic oxygen and the ionization levels of adsorbed alkali metals can overlap at some ion-surface distance, because of the level shift and broadening. This makes resonance electron tunneling from alkali-metal atom to desorbing O^+ possible. Rapp and Francis[18] have shown that a resonance charge-transfer reaction (zero energy defect reaction, $\Delta E\approx0$ eV) depends strongly on the ionization potential of the electron transferred during collision: the resonance charge transfer cross section is inversely proportional to the ionization potential of the colliding particles. This implies that the lower the tunneling barrier (ionization potential), the higher the tunneling rate. Since the O^+ attenuation cross section increases with decreasing alkali ionization energy, it is possible that resonance charge transfer from alkali metal to an excited state of O^+ can be the dominant process in determining the O^+ attenuation in the alkali overlayer.

Figure 2 shows a plot of the O^+ attenuation cross sections for high alkali coverages as a function of reciprocal of alkali ionization potential in the gas phase. As shown in Fig. 2, the O^+ cross section increases linearly with the reciprocal of the ionization energy. If the O^+ attenuation is mainly due to a one-electron resonance charge-transfer process, we expect this kind of relationship from the theory.[18] It is interesting to note that the straight line intersects the horizontal axis at 0.17 eV^{-1}. The inverse of this value corresponds to the critical ionization potential of ~ 5.9 eV, which is close to the work function of the clean oxidized tungsten (~ 6 eV).[14]

In conclusion, we have found that less than a monolayer of alkali-metal (Li, Na, K, or Cs) overlayer attenuates the O^+ ESD yield from an oxidized W surface almost completely; for $\Theta > 0.3$ ML, the attenuation of O^+ is strongest for Cs overlayers ($\sim 18 \times 10^{-15}$ cm^2), while it is lowest for Li ($\sim 3 \times 10^{-15}$ cm^2). Resonance electron tunneling from adsorbed alkali-metal atoms appears to be the dominant factor influencing the transmission of low-energy (< 10 eV) O^+ through fractional monolayer films of Li, Na, K, and Cs. There is a correlation between the ionization potential of the alkali metal and the O^+ attenuation cross sections for high alkali coverages ($\Theta > 0.3$ ML), which is consistent with the resonance one-electron charge-transfer model.

This work was supported by the Russian Fundamental Research Foundation through Grant No. 95-02-04081-*a* and the U.S. National Science Foundation (NSF), Grant No. CHE-9408367.

---

*Author to whom correspondence should be addressed.

[1] M. Akbulut, N. J. Sack, and T. E. Madey, Phys. Rev. Lett. **75**, 3414 (1995).

[2] N. J. Sack, M. Akbulut, and T. E. Madey, Phys. Rev. Lett. **73**, 794 (1994).

[3] T. E. Madey, N. J. Sack, and M. Akbulut, Nucl. Instrum. Methods Phys. Res. B **100**, 309 (1995).

[4] V. N. Ageev, O. P. Burmistrova, and B. V. Yakshinskii, Surf. Sci. **194**, 101 (1988).

[5] M. Akbulut, N. J. Sack, and T. E. Madey, J. Chem. Phys. **103**, 2202 (1995).

[6] N. J. Sack, M. Akbulut, and T. E. Madey, Phys. Rev. B **51**, 4585 (1995).

[7] M. L. Yu, Surf. Sci. **84**, L493 (1979).

[8] K. Prabhakaran, D. Purdie, R. Casanova, C. A. Muryn, P. J. Hardman, P. L. Wincott, and G. Thornton, Phys. Rev. B **45**, 6969 (1992).

[9] R. Heise and R. Courths, Surf. Rev. Lett. **2**, 147 (1995).

[10] V. N. Ageev, Y. A. Kuznetsov, B. Y. Yakshinskii, and T. E. Madey, Nucl. Instrum. Methods Phys. Res. B **101**, 69 (1995).

[11] V. N. Ageev, Surf. Sci. **336**, 321 (1995).

[12] P. Nordlander and N. G. Lang, Phys. Rev. B **44**, 13 681 (1991).

[13] J. B. Hasted and M. A. D. Phil, *Physics of Atomic Collisions* (Elsevier, New York, 1972).

[14] C. A. Papageorgopoulos and J. M. Chen, Surf. Sci. **39**, 313 (1973).

[15] M. L. Yu and N. D. Lang, Nucl. Instrum. Methods Phys. Res. B **14**, 403 (1986).

[16] R. Souda, W. Hayami, T. Aizawa, and Y. Ishizawa, Phys. Rev. Lett. **69**, 192 (1992).

[17] E. W. McDaniel, J. B. A. Mitchell, and M. E. Rudd, *Atomic Collisions: Heavy Particle Projectiles* (Wiley Interscience, New York, 1993).

[18] D. Rapp and W. E. Francis, J. Chem. Phys. **37**, 2631 (1962).