Transmission of Low Energy (<10 eV) O^+ Ions through Several Monolayer Thick Rare Gas Films

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(Received 24 February 1994)

We present the first systematic study of the transmission of low energy oxygen ions (<10 eV) through ultrathin films of Ar, Kr, and Xe. For rare gas films adsorbed on an oxidized W(100) surface, we find that a small fraction of O^+ can penetrate more than 5 ML thick films of Kr and Xe. The attenuation of O^+ is strongest for Ar overlayers. We attribute the attenuation mainly to elastic scattering of the ions with the rare gas atoms. We suggest that structural characteristics of rare gas films adsorbed on this surface are the cause for low attenuation in the first 1–2 monolayers.

PACS numbers: 34.40.+n, 34.70.+e, 79.20.Hx, 79.60.Dp

The interaction of electrons or photons with surfaces can lead to DIET processes, desorption induced by electronic transitions [1,2]. The desorbing species can be neutral or charged, and can either be in the ground state or in an excited state (metastable). It is usually assumed that most of the desorbing species originate from the top one or two surface layers, since elastic and inelastic scattering processes of ions produced beneath the surface inhibit their escape through top layers into vacuum [3–7]. Although ions are in most cases the minority species among the desorption products, we focus in the following on ions due to their ease of detection as compared to neutrals.

The question of the depth of origin of secondary ions can be seen from a different viewpoint: What are the various interaction mechanisms of low energy ions (<10 eV) with ultrathin solid films? It is commonly assumed that both elastic scattering and neutralization are the dominant types of interaction in this range of collision energies [8,9]. Although there exists a wealth of information on the interaction of keV and MeV ions with rare gas solids [10], molecular solids [11,12], and other insulators [13], only little is known about the ion-solid interaction in the collision energy regime less than 10 eV [8,14]. In order to gain insight into this subject we are currently performing a series of experimental investigations on the transmission of low energy ions through ultrathin films of various atomic and molecular solids. We have started with the most weakly interacting solids, rare gas films.

We use a novel experimental approach [15]: The ions are generated by electron stimulated desorption (ESD) from various compound surfaces, such as oxides, hydroxides, or fluorides. This results in a low energy ion beam with a well defined energy and angular distribution. The thin solid films (thickness ranging from fractional monolayer to several monolayers) are condensed onto the compound surface, so that the ions desorbed from the compound surface by the nearly unattenuated electron beam have to travel through the thin film to be detected. We measure the yield, energy, and angle of the ions with and without overlayer.

Here we summarize results of the study of transmission of 7 eV oxygen ions desorbed from an oxidized W(100) crystal, through ultrathin films of argon, krypton, and xenon. Surprisingly, we find that a small fraction of the oxygen ions can penetrate more than 5 monolayers (ML) of Kr or Xe, whereas less than 3 monolayers of Ar suppress the O^+ signal nearly completely.

The experiments are carried out in an ultrahigh vacuum chamber (base pressure: $<10^{-8}$ Pa) that is equipped with instrumentation for surface analytical techniques, including AES (Auger electron spectroscopy), LEED (low energy electron diffraction), ESDIAD (electron stimulated desorption ion angular distribution) [15,16], and TDS (thermal desorption spectroscopy).

The W(100) crystal is mounted on a sample holder attached to a closed cycle helium refrigerator which permits cooling of the sample to 25 K. The crystal can be heated radiatively and by electron bombardment. It is heated to 860 K in an oxygen atmosphere (5×10^{-6} Pa) to form a thin oxide film [17,18]. The oxidized surface is clean as determined by means of AES and exhibits a (1×3) LEED pattern.

The rare gases are dosed onto the oxidized surface through a directed doser equipped with a capillary array plate. The purity of the gases is checked in the gas phase by mass spectrometry and after adsorption by AES. We estimate an upper limit of the contamination to be 0.5%. The thickness of the rare gas films is derived from TDS: We have performed a detailed investigation of the thermal desorption of Ar, Kr, and Xe from the oxidized W(100) surface which allows us to identify monolayer coverage. From this we can dose films of various thicknesses with a reproducibility of ±10%. The uncertainty is slightly larger for Ar (20%) due to some ambiguity of the peak identification. The TDS results are described elsewhere [19].

Electron stimulated desorption is performed using a focused 300 eV electron beam; the total electron fluence required for one measurement is $<2 \times 10^{13}$ cm^{-2}. The ESD ions can be detected either with a digital two dimensional ESDIAD detector operating in the TOF (time

0031-9007/94/73(6)/794(4)$06.00

of flight) mode [15], or the mass spectrometer with the ionizer turned off. The ESDIAD detector allows direct digital acquisition of 2D data, so that we obtain information on the total yield, the angular distribution and the mass/energy distribution of the desorbing ions. Application of a sample bias of +100 V allows detection of ions with polar desorption angles of up to ~70°. The mass spectrometer is mainly used for confirmation of results obtained with the ESDIAD detector and for high resolution mass analysis of the desorbing species.

It is known that electron bombardment of a W(100) surface oxidized as described above leads to the emission of oxygen ions [15,20,21]. Under our oxidation conditions we observe only O^+ ions leaving the surface on trajectories centered about the normal to the surface with a kinetic energy distribution that maximizes around 7 eV [15]. Their yield is $\sim 10^{-6}$ ions/e^-.

Adsorption of a rare gas on top of the oxidized surface leads to attenuation of the oxygen ions. Figure 1 shows the total angle integrated yield of the oxygen ions as a function of overlayer thickness for Ar, Kr, and Xe on a semilogarithmic plot. It can be seen that in all three cases the majority of the oxygen ions survives transmission through 1 ML of rare gas. The rare gas thickness at which the O^+ signal is decreased to 10% of the value from the clean oxidized surface is 1.6 ML for Ar, 2.9 ML for Kr, and 4.0 ML for Xe. The decrease is roughly exponential for the thicker films, and the slope is steepest for Ar (strongest attenuation) and least steep for Xe.

From Fig. 1 we can derive the attenuation cross section, σ_{exp}, for the exponential (thick film) regime, using an equation which is based on a continuum model of attenuation in a solid:

$$\sigma_{\mathrm{exp}} = -\frac{1}{N_{\mathrm{RG}}} \frac{\partial(\ln\Phi)}{\partial d}, \tag{1}$$

where d is the rare gas film thickness, N_{RG} the rare gas number density, and Φ the total O^+ flux reaching the detector. Using bulk values for N_{RG} of 2.66×10^{22} cm^{-3} for Ar, 2.17×10^{22} cm^{-3} for Kr, and 1.64×10^{22} cm^{-3} for Xe [22], we find the cross section to be largest for Ar and smallest for Xe: $(6.2 \pm 2) \times 10^{-15}$ cm^2 for Ar, $(2.2 \pm 0.3) \times 10^{-15}$ cm^2 for Kr, and $(1.4 \pm 0.2) \times 10^{-15}$ cm^2 for Xe. Furthermore, it can be seen that the oxygen ion attenuation is stronger for thicker films than for thin films: For Kr and Xe, there is a change in slope in Fig. 1 around 2 ML, for Ar around 1.3 ML. This is also reflected in the attenuation in the first layer compared to attenuation in a higher layer: In the first layer, the O^+ intensity decreases by about 40% of the clean surface value for all three rare gases. In the exponential regime, however, the signal decreases by 60% per layer for Xe, 85% for Kr, and by more than 99% per monolayer for Ar.

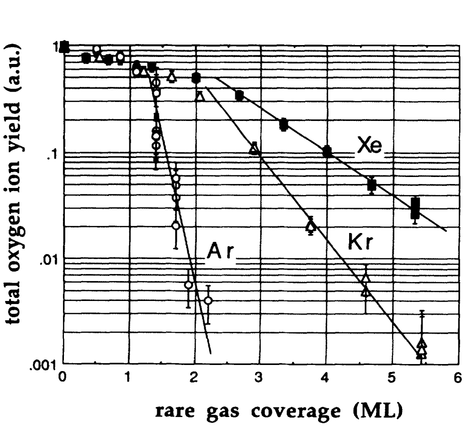

FIG. 1. Total O^+ yield as a function of rare gas coverage on a semilogarithmic plot. The lines are guides to the eye.

We have analyzed the angular and energy distribution of the oxygen ions as a function of rare gas film thickness of up to 3 ML for Kr and Xe. Up to 2 ML, neither the angular nor the energy distribution changes significantly. However, for films thicker than 2 ML we have found changes in the kinetic energy distribution and the angular distribution of O^+: We show in Fig. 2 the kinetic energy distribution of O^+, measured with a retarding field method, as a function of Xe thickness. It can be seen that for films thicker than 2 ML some O^+ have lost a significant amount of kinetic energy upon passage through the film. Moreover, we find that the ions which have lost kinetic energy leave the surface with larger polar angles which indicates that they have been scattered by large angles. We will report on the evidence for changes in the trajectory of the ions scattered by thicker (>2 ML) films shortly [19].

To understand the results, we first have to consider the interaction of the primary electron beam with the rare gas film. It is known that the gas phase ionization cross section for rare gas atoms by 300 eV electrons is between 2.2 and 4×10^{-16} cm^2 [23]. Furthermore, the cross section for O^+ desorption from the oxidized W(100) does not depend strongly on the electron energy around 300 eV,

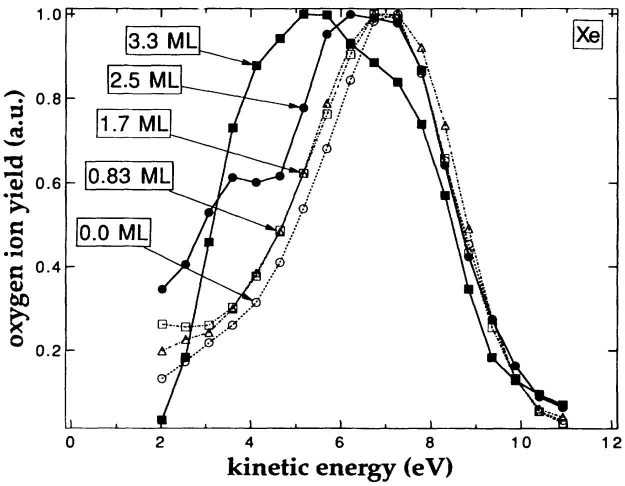

FIG. 2. Energy distribution of the O^+ from clean oxidized W(100) surface and of O^+ after passage through Xe films of various thickness (in monolayers), measured by a retarding-field method. Yields are normalized to unity at their maximum.

so that the energy loss of the primary electron beam in the rare gas film does not affect the ESD significantly. However, another issue is whether the same electron that causes the desorption of an O^+ also disturbs the rare gas film such that it could affect the O^+ transmission through the rare gas film. This could include rare gas desorption as well as formation of rare gas dimers or creation of excitons in the film [24]. The gas phase ionization cross sections for 300 eV electrons with rare gas atoms seem large enough for the electrons to interact with the rare gas film before O^+ ESD. However, not every ionization will lead to dimer or exciton formation, because the primary excitation can be quenched, especially on or near a surface [1,24]. In fact, Xe has been reported to have a total desorption cross section of only 3×10^{-19} cm^2 [25,26]. Hence we believe that these effects, although in principle possible, do not play a major role in the transmission of the O^+ through the rare gas film.

If the rare gas films were nonuniform in thickness, then there could be preferential escape of O^+ through holes in the films. We have performed detailed studies of the thermal desorption of rare gases from the oxidized W(100) crystal and have concluded that, at least for the first several monolayers, the rare gas solids grow in a layer by layer fashion [19] which suggests that islands are not the thermally favored structures. We have also studied the influence of annealing of the rare gas solids on the oxygen ion yield and have found no effect of annealing on the measured parameters [19]. Also, one could argue that the O^+ desorb primarily from edge or defect sites which might not be efficiently covered by the first or second monolayer of rare gas. However, desorption from edge and defect sites often leads to off-normal trajectories [27], which is not what we observe here. Hence we conclude that the observed attenuation of the oxygen ions is correlated to scattering processes between the oxygen ions and the rare gas atoms.

We suggest the following microscopic model: The passage of the oxygen ions through the rare gas film is determined by elastic and inelastic interactions of the ions with the rare gas atoms. Elastic scattering (ES) by large angles can prevent an oxygen ion from desorbing. Although many types of inelastic interactions are possible, we assume that charge transfer (CT) is the most likely inelastic interaction to influence the measured variables. Hence we write

$$\sigma_{\text{exp}} = \sigma_{\text{CT}} + \sigma_{\text{ES}} . \tag{2}$$

Elastic scattering changes the trajectory and the kinetic energy of the ions. It can lead to a deflection of an ion by an angle small enough so that the ion can still escape from the surface [28]. For larger angles, the path length of the ion in the rare gas film is increased, which leads to a higher interaction probability with the rare gas atoms; furthermore, the ion might not be able to leave the surface. If the ion backscatters, it will almost certainly not leave the surface as an ion, but be trapped in the film and neutralize. The energy loss of the oxygen ion after passage through a more than 2 ML thick xenon film, as depicted in Fig. 2, is an indication for elastic scattering of oxygen ions by the xenon atoms, especially since we observe that they desorb with large polar angles and must therefore have scattered. Based on the measurements of O^+ energy loss and wide angle scattering, we consider elastic scattering as an important attenuation mechanism.

Note that the magnitude of the energy loss in elastic scattering of O^+ from rare gas atoms is in the order Ar > Kr > Xe. However, from the ion-atom potentials as discussed in the following we expect the total elastic scattering cross section to be largest for Xe and smallest for Ar, which is opposite to the behavior of the experimental attenuation cross sections derived from our measurements. Guest *et al.* [29] investigated the interaction potential between O^+ and rare gases by experimental and theoretical methods. Their data show that the repulsive part of the potential surface of O^+Ar lies at a smaller distance than that of O^+Xe, with O^+Kr being in between. This suggests that the elastic scattering cross section is largest for Xe and smallest for Ar. However, in a subsequent paper [19] we present a microscopic model in which we show that the channels through which the oxygen ions can transmit the rare gas film, are largest for Xe and smallest for Ar, in agreement with the transmission data presented here.

We also consider the role of charge transfer on the attenuation of the oxygen ions:

$$O^+ + \text{RG} \rightarrow O + \text{RG}^+ + \Delta E . \tag{3}$$

Here, RG represents the rare gas and ΔE is the energy defect of the reaction, which for ground state species is the difference in ionization potential of O and RG.

Although there are models describing charge transfer cross sections [8,30], no model gives reliable estimates for collision energies below 10 eV. Most models relate the charge transfer cross section to the energy defect: The smaller ΔE, the larger the cross section. The energy defect for O^+/Ar (ion-atom collision) is larger than those for the other two rare gases and strongly endothermic; hence we would expect the smallest charge transfer cross section for Ar, compared to Kr or Xe. However, in the case of a collision of O^+ with a rare gas film supported on an oxide substrate and ranging in thickness from fractional monolayer to several monolayers, the energy defect may be slightly different from that derived above for the ion-atom collision. Hence we conclude that the charge transfer models do not allow accurate predictions for our system because of the low collision energy and because of electronic interactions between neighboring rare gas atoms and between a rare gas atom and the surface.

The data presented do not provide conclusive support that charge transfer is one of the ion attenuation mechanisms. However, it seems hard to explain the high attenuation cross section of 6.2×10^{-15} cm^2 for Ar with elastic scattering alone, suggesting that the attenuation could partly be caused by another mechanism, e.g., charge transfer.

It may seem remarkable that ions of such low kinetic energy can transmit a rare gas film several monolayers thick. It may be even more surprising that for Kr or Xe films less than 2 ML thick, those ions that transmit the film do so even without significant energy loss. We suggest that this and the low attenuation of the O^+ in the first two monolayers of rare gas film may be correlated to structural aspects of thin rare gas films. It has been shown that Ar on MgO grows in a commensurate structure for fractional monolayers, but forms a close packed layer with hexagonal symmetry as the coverage approaches one monolayer [31]. If the rare gases form a close packed first monolayer on our oxidized W(100) surface, then the phase of the first completed monolayer is hexagonal [the densest packing; this is the (111) plane of the fcc crystal] and the subsequent layers can grow in *A-B-C* fashion. There are still channels through the film after completion of 2 monolayers. Only upon completion of the third monolayer are these channels closed. We speculate that this growth may be the cause for our observation that a small percentage of the O^+ ions can transmit up to 2 monolayers of rare gas (seen for Kr and Xe) without having been elastically scattered in such way that they would have lost a measurable portion of their kinetic energy. The change in kinetic energy for films thicker than 2 ML corresponds to the filling of the third layer. Also the change in attenuation for Kr and Xe around 2.5 ML may be correlated to this growth. (If the structure were hcp instead of fcc, the channels would persist even beyond a thickness of 2 monolayers.)

In summary, we have found that 7 eV oxygen ions can penetrate several layers of a rare gas film. We have explained the results in a model which considers mainly elastic scattering and also charge transfer of the oxygen ions with the rare gas atoms. We conclude that, in certain cases, several monolayers of an overlayer are necessary to suppress completely a secondary ion signal from a surface. This shows that not all secondary ions desorbing under the impact of electrons, photons, or ions necessarily stem from the first or second layer of a compound surface. In the future, we will investigate molecular adsorbates and metals as overlayers in order to search for systematic trends about the correlation between the nature of the ion-atom collision and the suppression of secondary ions.

We acknowledge helpful discussions with H. Urbassek, M. Vicanek, V. Ageev, R.A. Baragiola, and R.E. Johnson. N.J.S. is a Feodor-Lynen Fellow of the Alexander-von-Humboldt Foundation.

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[1] T.E. Mådey, Science **234**, 316 (1986).
[2] R.D. Ramsier and J.T. Yates, Jr., Surf. Sci. Rep. **12**, 243 (1991).
[3] P. Sigmund, A. Oliva, and G. Falcone, Nucl. Instrum. Methods Phys. Res. **194**, 541 (1982).
[4] M. Vicanek, J.J. Jimenez Rodriguez, and P. Sigmund, Nucl. Instrum. Methods Phys. Res., Sect. B **36**, 124 (1989).
[5] P. Sigmund *et al.,* Nucl. Instrum. Methods Phys. Res., Sect. B **36**, 110 (1989).
[6] J.W. Burnett, J.P. Biersack, D.M. Gruen, B. Jørgensen, A.R. Kraus, M.J. Pellin, E.L. Schweitzer, J.T. Yates, and C.E. Young, J. Vac. Sci. Technol. A **6**, 2064 (1988).
[7] M.F. Dumke, T.A. Tombrello, R.A. Weller, R.M. Housley, and E.H. Cirlin, Surf. Sci. **124**, 407–422 (1983).
[8] H. Massey and H. Gilbody, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1974).
[9] U. Diebold and T.E. Madey, Phys. Rev. Lett. **72**, 1116 (1994).
[10] C.T. Reimann, W.L. Brown, and R.E. Johnson, Phys. Rev. B **37**, 1455 (1988).
[11] W.L. Brown, W.M. Augustyniak, L.J. Lanzerotti, R.E. Johnson, and R. Evatt, Phys. Rev. Lett. **45**, 1632 (1980).
[12] D.B. Chrisey, J.W. Boring, J.A. Phipps, R.E. Johnson, and W.L. Brown, Nucl. Instrum. Methods Phys. Res., Sect. B **13**, 360 (1986).
[13] W.L. Brown, Nucl. Instrum. Methods Phys. Res., Sect. B **32**, 1 (1988).
[14] R.E. Johnson, *Energetic Charged-Particle Interactions with Atmospheres and Surfaces* (Springer-Verlag, Berlin, 1990).
[15] N.J. Sack, M. Akbulut, and T.E. Madey, Nucl. Instrum. Methods Phys. Res., Sect. B **90**, 451 (1994).
[16] N.J. Sack, L. Nair, and T.E. Madey, Surf. Sci. **310**, 63 (1994).
[17] D.A. King, T.E. Madey, and J.T. Yates, Jr., J. Chem. Phys. **55**, 3236 (1971).
[18] D.A. King, T.E. Madey, and J.T. Yates, Jr., J. Chem. Phys. **55**, 3247 (1971).
[19] N.J. Sack, M. Akbulut, and T.E. Madey (to be published).
[20] T.E. Madey, J.J. Czyzewski, and J.T. Yates, Jr., Surf. Sci. **49**, 465 (1975).
[21] S. Prigge, H. Niehus, and E. Bauer, Surf. Sci. **75**, 635 (1978).
[22] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1986).
[23] L.J. Kieffer, At. Data **1**, 19 (1969).
[24] D. Menzel, Appl. Phys. A **51**, 163 (1990).
[25] Q.J. Zhang and R. Gomer, Surf. Sci. **109**, 567 (1981).
[26] Q.-J. Zhang, R. Gomer, and S.R. Bowman, Surf. Sci. **129**, 535 (1983).
[27] T.E. Madey, Surf. Sci. **94**, 483 (1980).
[28] Z. Miskovic, J. Vukanic, and T.E. Madey, Surf. Sci. **141**, 285 (1984); **169**, 405 (1986).
[29] M.F. Guest, A. Ding, J. Karlau, J. Weise, and I.H. Hillier, Mol. Phys. **38**, 1427 (1979).
[30] D. Rapp and W.E. Francis, J. Chem. Phys. **37**, 2631 (1962).
[31] J.M. Layet, M. Bienfait, C. Ramseyer, P.N.M. Hoang, C. Girardet, and G. Coddens, Phys. Rev. B **48**, 9045 (1993).