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Electron-stimulated conversion of chemisorbed O to Al_2O_3 on Al(111)

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The transformation of a chemisorbed O layer on the Al(111) surface into Al_2O_3 under electron impact has been monitored by high-resolution electron energy-loss and x-ray photoelectron spectroscopies. Electron irradiation (100 eV) of chemisorbed O was observed to cause spectroscopic changes in the surface layer indicative of oxide formation. The energy transfer from the electrons to the chemisorbed O atoms through electronic excitations, leading to vibrationally excited adsorbed particles, is proposed to be responsible for the observed conversion of chemisorbed oxygen to Al_2O_3. The cross section for this electron-induced process is estimated to be 2×10^{-19} cm^2 for 100 eV electrons. © *1999 American Institute of Physics.* [S0003-6951(99)02746-1]

Controllable electron-beam-aided growth of oxide films is an important technological goal, which has not been investigated extensively. The use of electronic excitation processes to induce nonthermal chemistry (i.e., oxidation reactions) could be of importance in the microelectronics industry for growing thin insulating layers (especially of SiO_2 and Al_2O_3).

Electron beams have already been used for inducing growth of various compound thin films from precursor molecules on surfaces.[1–3] Direct electronic or multiple vibrational excitation has been proposed to explain current and field-induced phenomena observed under scanning tunneling microscope tips.[4–6]

The mechanism of electron-stimulated desorption (ESD), the first among the electron-stimulated surface processes to be investigated, has been studied by Menzel and Gomer, Redhead, and later by Antoniewicz.[7,8] It was suggested that the electronic excitation of the adsorbate molecule opens up new nonthermal routes for driving surface chemical reactions, or in other words, accessing the final products, which require an activation energy for production.[7] For 100 eV electrons used here, both valence- and core-level excitations are possible.

According to these accepted theories, direct energy transfer to an adsorbed H atom is negligibly small for 100 eV electrons, and becomes even less for more massive adsorbate molecules.[7] Thus, energy exchange between the electrons and adsorbed particles has to be indirect, causing the formation of excited species (e.g., through electronic excitations). A number of repulsive (unbound) and ionic states are accessible upon Franck–Condon electronic transitions (step 1, Fig. 1), and these states may lead to electron-stimulated desorption[4–9] or to electron-stimulated migration (ESM).[10] A downward transition from these states (step 2, Fig. 1) may lead to the population of vibrationally excited surface species in the ground electronic state. These ''hot'' states can then lead to surface chemical reactions (such as oxide formation) where the product states are separated from reactant species by an activation barrier, as schematically shown on Fig. 1 (step 3).

An extensive review of the use of electrons for inducing surface chemical reactions is given in Ref. 3. Electron irradiation has been already employed for the efficient oxidation of Al(111) by water at 90 and 300 K.[1]

The thermal oxidation of Al(111) itself has been studied using a wide range of experimental methods.[11–19] For atomically smooth Al(111), the sticking coefficient for O_2 at 300 K is small, of the order of 10^{-3}–10^{-2}.[13,15] At 300 K, chemisorbed O is produced initially upon the dissociative adsorption of O_2. Later it transforms to Al_2O_3 slowly at 300 K and more rapidly at higher temperatures.[15,19] Both x-ray photoelectron spectroscopy (XPS) and high-resolution electron energy-loss spectroscopy (HREELS) measurements are effective in discriminating chemisorbed O from Al_2O_3,[22] with HREELS being more sensitive.

In this work, we report the observation of enhanced Al_2O_3 formation upon electron bombardment (100 eV energy) of the chemisorbed O/Al(111) layer, as monitored by both HREELS and XPS.

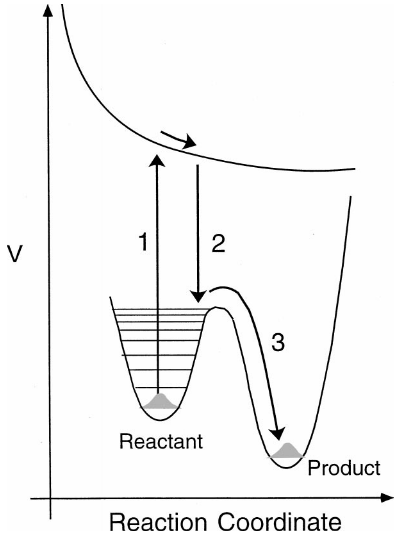

FIG. 1. Schematic stimulation of a surface chemical reaction by electronic excitation. Reactant species are excited by a Franck–Condon-type electronic transition (1) into the repulsive state, with a consequent downward transition back to the electronic ground state (2). The species formed in this process are vibrationally excited and are able to surmount the activation barrier and transform into product (3). Thus, previously inaccessible product species are formed as a result of electronic excitation.

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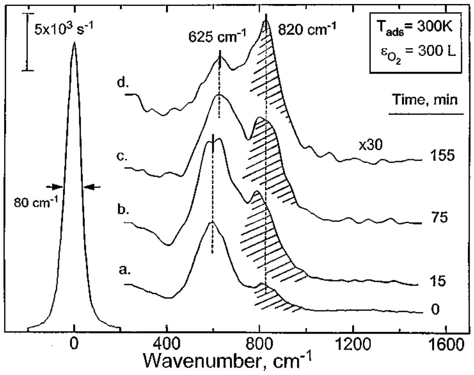

FIG. 2. Development of the HREEL spectra after electron irradiation of the chemisorbed O/Al(111) layer (300 L O_2 at 300 K) by 100 eV electrons (70 $\mu A/cm^2$, flood-type e-gun) at 300 K. (a) After adsorption of 300 L of O_2; (b) after 15 min electron irradiation; (c) after 75 min; and (d) after 155 min. The high-frequency mode at 820 cm^{-1} (crosshatched) is characteristic of Al_2O_3 and increases in intensity as it is formed on the surface under electron impact.

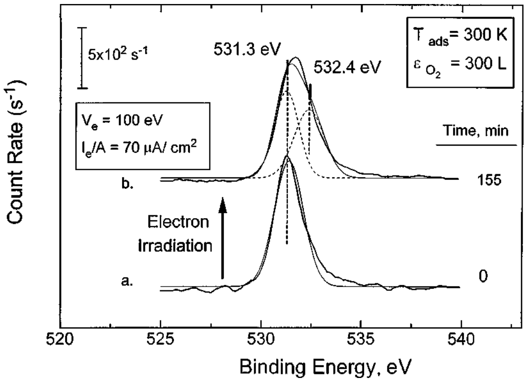

FIG. 3. XPS O(1s) peaks for (a) 300 L O_2 exposure carried out at 300 K; and (b) after irradiating the formed layer for 155 min by a 100 eV electron beam. Upon electron impact the O(1s) peak is broadened and shifted from 531.3 eV, with a component at 532.4 eV, indicating the transformation of the adsorbed species into oxide. Deconvolution into oxidic and chemisorbed O is shown.

Experiments were performed in a two-level UHV system equipped with HREELS, XPS, Auger electron spectroscopy, quadrupole mass spectrometry, and low-energy electron diffraction instrumentation. The base pressure was $2-3 \times 10^{-10}$ Torr. The experimental setup along with the crystal mounting are described in detail in Refs. 1 and 15. The Al(111) crystal (2-mm-thick disk of 12 mm diam) was purchased from MaTeck Co., Jülich, being oriented within 0.25° to the (111) crystallographic direction and polished to a mirror finish. It was extensively cleaned by Ar^+ sputtering (0.5–1 keV, 5×10^{-5} Torr Ar, 0.5–1.0 $\mu A/cm^2$ at 300 K) and annealing (723 K). (The importance of rigorous crystal preparation procedures is emphasized in Ref. 15). Oxygen exposures, given in langmuirs ($1 L = 1 \times 10^{-6}$ Torr s) were carried out by back filling the upper preparation chamber to 1×10^{-7} Torr pressure (not corrected for the ion-gauge sensitivity). Exposures were chosen so as to produce primarily chemisorbed O on Al(111) (Ref. 15). Electron irradiation of the adsorbed O/Al(111) layer was performed using an electron beam with 100 eV primary energy (70 $\mu A/cm^2$) from a flood-type electron gun. The electron dose was kept below 1 C/cm^2, determined by another research group as a critical value at which beam damage effects (formation of Al clusters) were observed for 1 keV electrons.[20] No detectable sample heating due to the irradiation was observed. The effect of electron impact on the conversion of the chemisorbed O to Al_2O_3 was monitored by HREELS (6 eV primary beam energy). Al(2p) and O(1s) peaks were also recorded to monitor oxide formation with XPS, using an Al $K\alpha$ x-ray source.[22]

Adsorption of 300 L O_2 on Al(111) at 300 K leads primarily to the production of chemisorbed O atoms based on spectrum (a), Fig. 2. The domination of the HREELS mode around 590 cm^{-1} indicates preferential population of this phase on the surface. Only very little oxide is observed on the surface in this case, in agreement with the literature where oxide formation has been monitored by HREELS.[15] The loss mode at around 820 cm^{-1}, ascribed to the oxidic O species on Al(111),[15,17,18] exhibits a very small intensity in spectrum (a).

Significant changes in the HREELS spectrum were observed when the chemisorbed O/Al(111) layer was exposed to a 100 eV electron beam. The HREEL mode indicating oxide formation (820 cm^{-1}) grew in intensity after electron impact. This process is illustrated in Fig. 2, spectra (b), (c), and (d) (after a total of 15, 75, and 155 min of irradiation).

This transformation (chemisorbed to oxidic) is confirmed by XPS data, presented in Fig. 3. Here, the XPS O(1s) peak is shown after O_2 exposure at 300 K [spectrum (a)] and after 155 min of electron irradiation [spectrum (b)]. The narrow peak centered at 531.3 eV binding energy shifts and broadens, as chemisorbed oxygen species are transformed into oxide. Both deconvoluted chemisorbed and oxidic components of the O(1s) XPS peak are shown (at 531.3 and 532.4 eV binding energy).[21] Thus, XPS as well as HREELS detects conversion of the chemisorbed species on the surface into oxide upon electron bombardment.

In these experiments the O(1s) integrated peak area increased upon transformation of chemisorbed O on Al(111) to oxide.[22] We ascribe this effect to the forward scattering of the photoelectrons in the case of oxide species. Similar effects where first described by Egelhoff[23] for Ni/Cu(100) and were later found for a number of other systems.[24–26] The increase of the O(1s) peak area upon transformation of the chemisorbed O to oxide upon annealing is shown in Fig. 4. For the complete transformation upon annealing up to ~650 K an increase of $40\% \pm 10\%$ is observed.

Chemisorbed O species on Al(111) are regarded as metastable and transform into oxidic species slowly with time at 300 K in an activated process.[13,15] The time evolution of the chemisorbed O layer at 300 K in the absence of electronic excitation is shown in Fig. 5, where the HREELS oxidic mode at 820 cm^{-1} very slowly grows in intensity after 120 and 1080 min. An additional feature at 370 cm^{-1}, appearing after electron irradiation, is observed for O/Al(111) and signifies changes in the structural properties of the oxide layer, as discussed in the literature.[15,17,18] Thus, the thermally induced formation of the stable well-developed oxide layer on the Al(111) surface is a relatively slow process at 300 K, compared to the rate of oxidation observed upon electron irradiation, as shown in Figs. 2 and 3.

The cross section for the electron-stimulated conversion of chemisorbed oxygen to Al_2O_3 may be estimated from the

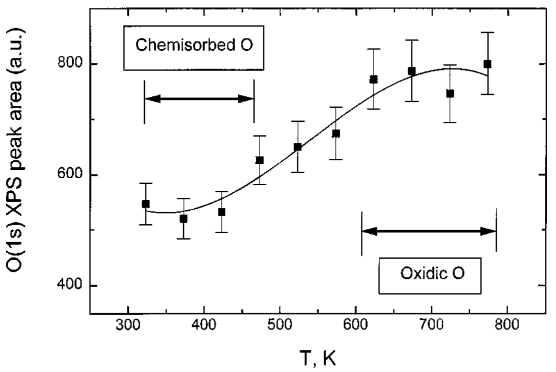

FIG. 4. XPS O(1*s*) integrated peak area changes upon annealing. An increase of approximately 40%±10% is observed.

XPS data. We assume, based on our earlier findings,[15] that the initial exposure to O_2 (300 L, 300 K) leads to an initial coverage of $0.4\,\mathrm{ML} = 2\times10^{14}\,\mathrm{O/cm^2}$. Based on the deconvoluted XPS spectra,[22] in 155 min of bombardment, $7.2\times10^{13}\,\mathrm{O/cm^2}$ are converted into oxide (estimated from the relative areas of the deconvoluted chemisorbed and oxidic features after electron irradiation). The cross section for the electron-stimulated process may be estimated using

$$dN/dt = -(NQI_e)/(Ae), \tag{1}$$

$$\ln N/N_0 = -(QI_e t)/(Ae), \tag{2}$$

where Q = cross section and I_c/A = current density, e = electron charge, N/N_0 = fraction of the chemisorbed O atoms converted into Al_2O_3, and t is the time of electron irradiation. From Fig. 3, the cross section for 100 eV electron-stimulated conversion of chemisorbed O to Al_2O_3 is $2.4\times10^{-19}\,\mathrm{cm^2}$.

It has been reported that Al_2O_3 is slowly reduced by 1 keV electrons after a threshold electron fluence current value of 1 $\mathrm{C/cm^2}$.[20] Our measurements of the conversion of chemisorbed O to oxide are carried out at 100 eV below 0.7 $\mathrm{C/cm^2}$ and the described reduction process is not observed under our conditions.

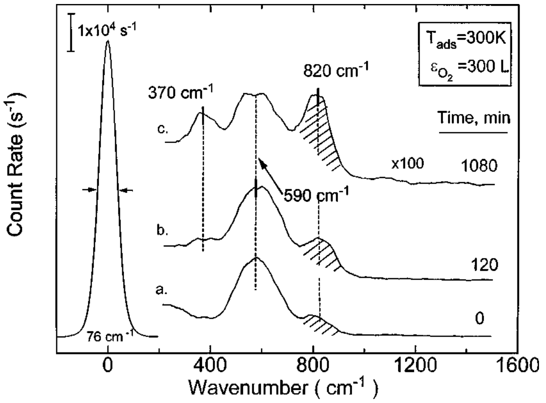

FIG. 5. Control experiment showing the development of the HREEL spectra with time at 300 K for the chemisorbed O/Al(111) layer, grown by oxygen adsorption at 300 K. (a) immediately after 300 L O_2 exposure; (b) after 120 min; and (c) after 1080 min. The high-frequency mode at 820 $\mathrm{cm^{-1}}$ increases in intensity as Al_2O_3 is slowly formed on the surface by a thermal process.

Summarizing, the electron stimulated conversion of chemisorbed O on Al(111) to Al_2O_3 has been investigated by two electron spectroscopies—HREELS and XPS. At an electron energy of 100 eV, a cross section for the conversion process of $2\times10^{-19}\,\mathrm{cm^2}$ has been measured. Although the details of the electronic excitation process have not been investigated, it is likely that such excitation leads to the production of vibrationally hot Al–O bonds, which induce the conversion of chemisorbed O to Al_2O_3. In addition, at 100 eV, other excitation processes, such as ionization, may play a role in the observed conversion process.

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[21] Deconvolution was carried using Microcal Origin software (version 3.5).
[22] It is known that chemical and structural changes in these films influence the angular distribution of the scattered core hole photoelectrons. Thus, the O(1*s*) XPS peak area increases due to forward scattering effects observed for the oxidic O species, dominating after annealing. To understand this effect we did an experiment where oxygen was dosed on the surface and subsequently annealed. The XPS O(1*s*) peak shape was monitored as a function of the annealing temperature (Fig. 4), and the integrated peak area was found to increase up to 40%±10% upon complete transformation of the chemisorbed O species into oxide. This dependence was later used as the correction function for coverage evaluation.
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