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Onset of oxidation of Al(111) at low temperatures: A study by electron-energy-loss spectroscopy and Auger electron spectroscopy

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The early stages of oxygen adsorption and oxide formation on Al(111) have been studied at 135 K using a combination of electron-energy-loss spectroscopy and Auger electron spectroscopy. Both surface and subsurface binding sites are occupied at 135 K, even at an oxygen exposure as low as 1.8×10^{15} molecules/cm^2. Further oxygen exposure preferentially increases the population of subsurface sites. When a sufficient number of oxygen atoms occupy surface and subsurface sites in close proximity, clustering occurs, resulting in Al_2O_3 formation. Aluminum oxide is characterized by a three-peak vibrational spectrum with a characteristic loss feature at 325–425 cm^{-1} and a distinct Auger transition at 54 eV. Surface spectroscopic studies of Al(111) oxidation are facilitated at low temperatures where kinetic retardation permits separation of the processes of chemisorption, penetration, and oxide formation.

The interaction of oxygen with aluminum has been extensively studied using several different surface-sensitive techniques in the temperature range of 300–500 K.[1–7] Auger electron spectroscopy (AES) studies[1,2] have revealed the oxygen-exposure dependence of Al(111) oxidation at 300–500 K. The general AES changes observed with increasing oxygen exposure are an increase in intensity of the oxygen *KLL* transition (510 eV) and the appearance of an Al AES transition (54 eV), due to oxidized Al. These changes in the Auger spectrum are accompanied by a decrease in intensity of the elemental Al $L_{23}VV$ transition (68 eV) as oxidation proceeds. For 300-K O_2 exposure, the reported absence of the oxide feature at 54 eV for oxygen exposures below 55 L (1 L = 1 langmuir = 1×10^{-6} Torr sec), as well as the distinct breaks in the plots of Auger intensities versus oxygen exposure suggest the existence of two distinct phases for this system; a chemisorbed phase followed by an oxidized phase.[1] The chemisorbed phase is described as only containing surface oxygen atoms, while the second phase is thought to be caused by the diffusion of oxygen atoms into the metallic subsurface.[1] Similar oxidation mechanisms for Al(111) were proposed based on low-energy electron diffraction observations,[1,3] and surface extended x-ray absorption fine-structure studies.[4]

Electron-energy-loss spectroscopy (EELS) studies and lattice-dynamics calculations for the interaction of oxygen with Al(111) were performed by Erskine, Strong, Firey, and deWette.[5–7] They observed loss features at nominally 645 and 845 cm^{-1}, which they assigned to modes involving surface and subsurface oxygen, respectively. The relative intensity of these modes changed with O_2 exposure, but they observed both features for any exposure at 300 K, suggesting that subsurface oxygen sites are always occupied for O_2/Al(111). There is, however, no clear indication in their study of the O_2 exposure required for Al_2O_3 formation to occur, or whether it, in fact, can occur at 300 K.

In this paper, we report studies on the early stages of oxygen adsorption and oxide formation on Al(111) using EELS and AES techniques. In order to retard kinetically oxide formation, we have worked at 135 instead of 300 K. Studies at low temperature can more easily separate the various stages of chemisorption, surface penetration, and oxidation. Our results show that at low oxygen exposures at 135 K, both surface and subsurface oxygen species are present. Higher exposures of oxygen give rise to oxide formation even at 135 K, characterized by distinct features both in AES and EELS. Sufficient clustering of surface and subsurface oxygen atoms to form Al_2O_3 only occurs at 135 K for exposures $\geqslant 2.1\times10^{16}$ (O_2 molecules)/cm^2.

Experiments reported here were performed in a stainless-steel ultrahigh-vacuum (UHV) chamber with facilities for crystal cooling and heating in the temperature range of 120–700 K. The chamber contains a single-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy, and a magnetically shielded high-resolution electron-energy-loss spectrometer for analysis of the vibrational spectra. *In situ* cleaning of the Al(111) crystal was accomplished by repeated cycles of argon-ion sputtering at 300 K and prolonged annealing at 700 K. The exposure of O_2 was carried out using a translatable molecular-beam doser, with a typical O_2 flux of 7.1×10^{13} (O_2 molecules) cm^{-2} sec^{-1}. A more detailed description of the apparatus, the preparation of the clean Al(111) crystal, and the crystal-mounting design are described elsewhere.[8]

EEL spectra were collected in a specular direction at an incident beam energy of 2–3 eV. Typical resolution from an oxygen-dosed Al(111) surface was 80–100 cm^{-1} at an elastic peak intensity of 10^5 counts/sec. Auger measurements were recorded in the $d[N(E)]/dE$ mode at a primary beam energy of 3.0 kV, a modulation voltage of 3.0 Vpp, and a total electron current at the crystal of 3.0 μA. The typical base pressure of the UHV chamber was less than 2×10^{-10} mbars.

Figure 1 shows corresponding EEL and Auger spectra recorded at three different oxygen exposures at 135 K. All the spectroscopic measurements were performed between 132 and 140 K. At very low O_2 exposure (3.5×10^{15} molecules/cm^2), the EEL spectrum is characterized by two loss features at 545 and 820 cm^{-1}. Similar frequencies were observed by Erskine and Strong[5] for O_2 adsorption at 300 K, and were assigned by use of lattice-dynamics calculations[6,7] to surface O-Al stretching motions and subsurface O-Al stretching motions, respectively. In addition, as an oxygen-exposed Al(111) surface is heated from 120 to 700 K, we observe a decrease in the loss feature at 545–675 cm^{-1} and a simultaneous increase in the 820–860-cm^{-1} loss feature,

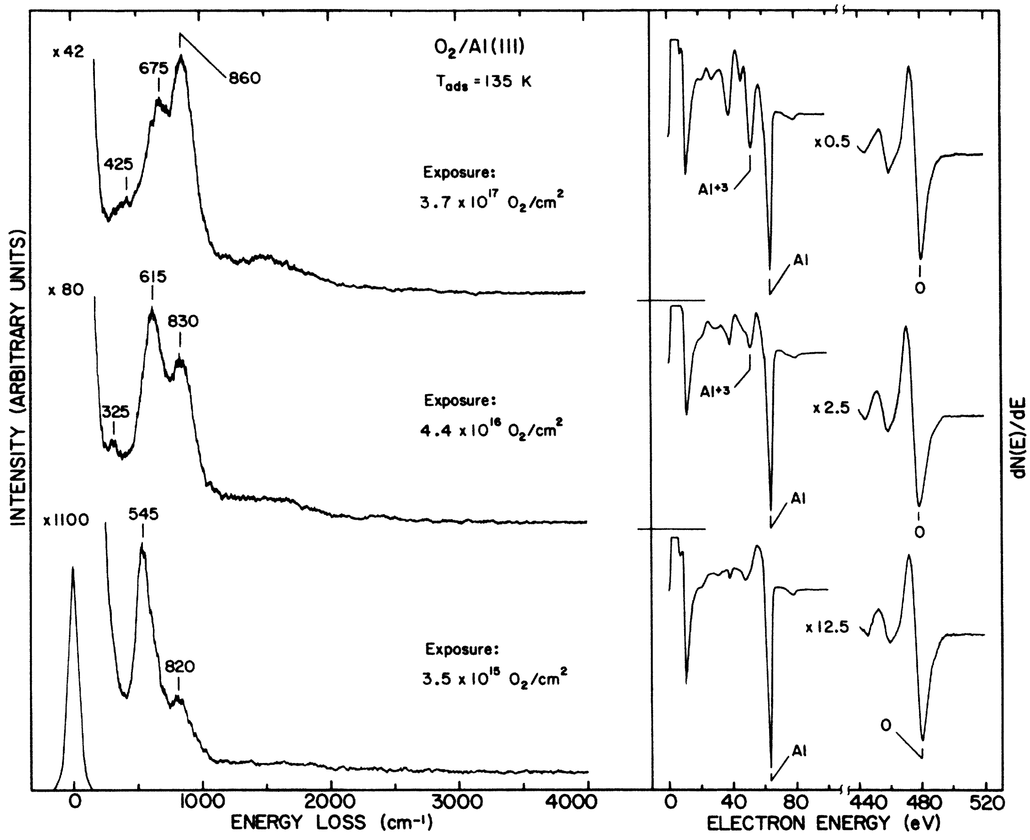

FIG. 1. EELS and the corresponding AES measurements for Al(111) exposed at 135 K to 3.5×10^{15}, 4.4×10^{16}, and 3.7×10^{17} (O_2 molecules)/cm^2. All spectra were recorded between 132 and 140 K.

along with a decrease in the O(490 eV)/Al(68 eV) Auger peak-to-peak intensity ratio.[8] These AES spectral changes clearly indicate oxygen diffusion into the Al(111) crystal; hence the observed vibrational changes support the assignments by Strong *et al.*[6]

Important conclusions can be readily made from the lower spectra in Fig. 1 [3.5×10^{15} (O_2 molecules)/cm^2]. The observation of both surface and subsurface oxygen features in the EEL spectrum combined with the absence of an oxide feature (54 eV) in the Auger spectrum indicates that at very low oxygen exposure, oxygen dissociatively adsorbs to occupy both surface and subsurface binding sites without forming the oxide. It indicates that diffusion of oxygen atoms into the crystal lattice does not necessarily lead to formation of the oxide in this early stage of O-Al(111) interaction.

The middle set of EEL and Auger spectra was measured at an oxygen exposure of 4.4×10^{16} molecules/cm^2. The appearance of the well-documented[1] oxide feature at 54 eV in the Auger spectrum indicates the formation of aluminum oxide at this oxygen exposure. In addition, we always observe a new EELS loss feature in the energy range of 325–425 cm^{-1} whenever this 54-eV Auger transition is present. Hence this EELS feature is a characteristic of Al oxide formation. Strong *et al.*[6] believe this vibrational mode involves the relative movement of the surface oxygen and top Al layer with respect to a subsurface oxygen layer and the second Al layer. Our observations suggest that this mode not only requires surface and subsurface oxygen in close proximity, but clustering of sufficient oxygen atoms to have Al-O bonding similar to that found in Al_2O_3. Comparing this EELS spectrum with that observed at low oxygen exposure (the bottom spectrum), one can see the substantial increase in the intensity ratio of subsurface (820–860 cm^{-1}) to surface (545–675 cm^{-1}) peaks at the higher oxygen dose. A series of EEL spectra (not shown) recorded at low O_2 exposures (1.8×10^{15} to 2.0×10^{16} O_2 molecules/cm^2) are characterized by a progressive increase in the ratio of subsurface to surface peak intensities indicating the preferential occupancy of subsurface sites as the O_2 exposure increases at 135 K.

The top set of spectra in Fig. 1 was taken for a relatively high oxygen exposure at 135 K. This exposure led to significant oxide formation as clearly evident by the intense 54-eV Auger feature characteristic of Al_2O_3.[9] Similarly, the three-peak EEL spectrum observed at this exposure, in which the intensity of the higher frequency mode is greater than the mode(s) of lower frequency, is a characteristic of Al_2O_3.[5] Similar spectra are observed upon heating an oxygen-dosed layer to 690 K,[8] or upon prolonged exposure at 500 K.[5] The dominance of an 806-cm^{-1} mode is also observed[10] for single-crystal α-$Al_2O_3(0001)$.

A general trend we observe with increasing oxygen exposure, both prior to and after initial oxide formation, is a frequency shift to higher energy for all three vibrational transitions. A similar trend was observed at 300 K by Erskine and Strong[5-7] and modeled simply by increasing the number of subsurface oxygen atoms relative to surface oxygen atoms.[7]

Another change in the EEL spectra as a function of oxygen exposure is the progressive growth of the poorly resolved loss features in the energy range of 1280–1750 cm^{-1}. We attribute these features to multiple losses and combination frequencies of the more intense fundamental transitions.

A systematic look at the Auger spectroscopic changes occurring upon oxygen adsorption as well as the early stages of oxidation are shown in Fig. 2 in the form of AES intensities for both the oxygen *KLL* transition (480 eV) (Ref. 11) and the oxidized Al transition (54 eV). The inset in Fig. 2 gives a closer view of the Auger energy region between 35 and 75 eV. In these Auger spectra we can see the initial development of Al_2O_3. Though some changes occur in this region relative to the Auger spectrum of a clean surface (spectrum *a*), the oxide feature at 54 eV does not become discernible until the oxygen exposure reaches or exceeds 2.1×10^{16} molecules/cm^2 (spectrum *e*).

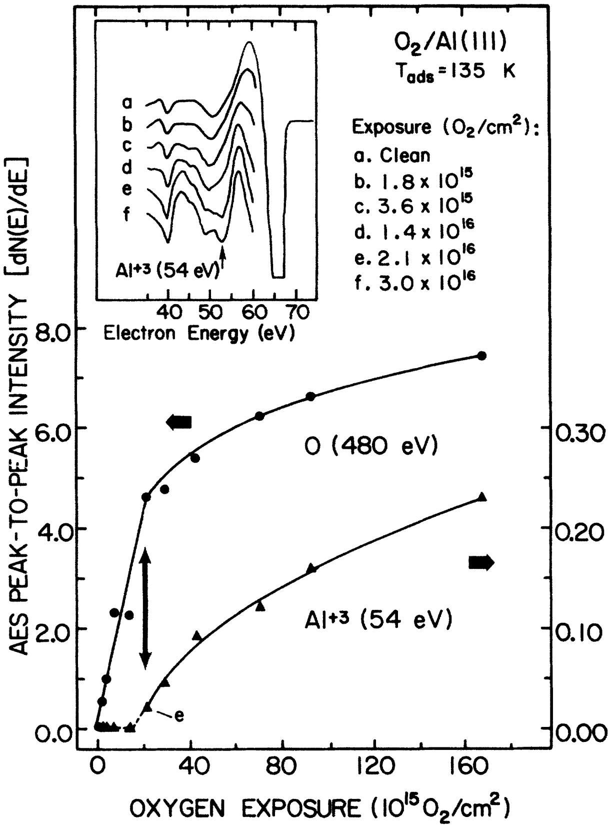

FIG. 2. AES intensities of the oxygen *KLL* transition (480 eV) and the oxidized Al transition (54 eV) as a function of oxygen exposure at 135 K. The inset shows Auger spectra in the energy range of 35–75 eV for the clean Al(111) surface and the very early stages of O_2 exposure. The O_2 exposures *b–f* correspond to the spectra shown in the inset.

The peak-to-peak intensity of the 54-eV feature is plotted at the bottom of Fig. 2 versus oxygen exposure. Five of the first six triangular points are measured from spectra *b–f* shown in the inset; several additional values measured at higher exposures are also given. This curve shows graphically that at 135 K, oxide formation first occurs near an exposure of 2.1×10^{16} (O_2 molecules)/cm^2 and increases nonlinearly with further exposure.

In the early stages of O_2 adsorption [$<2.1\times10^{16}$ (O_2 molecules)/cm^2], the top curve in Fig. 2 shows a linear relationship of the oxygen peak-to-peak intensity with oxygen exposure. The corresponding EEL spectra (not shown) show only two loss features indicating the presence of both surface and subsurface oxygen species. As the exposure reaches 2.1×10^{16} molecules/cm^2, the distinctive characteristics of the oxide, a loss feature in EELS in the range of 325–425-cm^{-1}, and a 54-eV feature in AES, are first observed. These observations indicate that a critical number of oxygen atoms in both surface and subsurface adsorption sites must cluster in order to form aluminum oxide. Simultaneous with the onset of the 54-eV oxide feature is a distinct break in the plot of oxygen AES intensity versus oxygen exposure. The abrupt change in slope in this curve indicates that the formation of Al_2O_3 on the Al(111) surface decreases the incorporation rate of oxygen. The simultaneous appearance of a 54-eV Auger transition, a 325–425 cm^{-1} vibrational transition, and a break in the oxygen *KLL* peak-to-peak intensity observed at this exposure provides strong evidence for measurable oxide formation. At the oxygen exposure where this occurs, the incorporation rate of oxygen slows down. This may be due to both a decrease in the O_2 sticking coefficient and/or a decrease in the rate of oxygen diffusion into the Al subsurface. The formation of Al_2O_3 at such a low temperature (135 K) is indicative of a low activation energy barrier for this process.

In summary, our results show that at 135 K, oxygen adsorption occurs in two stages. At oxygen exposures less than 2.1×10^{16} molecules/cm^2, oxygen atoms are chemisorbed on both surface and subsurface binding sites without formation of Al_2O_3. Upon further oxygen exposure, oxide formation occurs as an increasingly larger fraction of oxygen atoms occupy subsurface binding sites. The simultaneous and correlated occurrence of the 54-eV Auger transition and the 325–425-cm^{-1} vibrational transition indicates that this vibrational mode is a characteristic of Al_2O_3 formation. The combination of EELS and AES is complementary and extremely powerful in unraveling the progressive stages of O chemisorption, O penetration, and Al_2O_3 formation. The use of a low temperature for O_2 adsorption permits a clear separation of these processes.

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