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LOW TEMPERATURE XPS AND AES STUDIES OF O_2 ADSORPTION ON Al(100)

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Adsorption of O_2 on Al(100) at 80 K was studied by means of Auger and XP spectroscopies. At low surface coverages Al_xO_y oxides were formed with $x:y$ ratios from 3:1 to 1:1, depending on surface coverage. At higher coverages or heating to room temperature the oxide layer transformed to the familiar Al_2O_3.

The main purpose of the present work was the study of adsorption of O_2 on Al(100) at 80 K by means of Auger and XP spectroscopies. In the past this system has been studied extensively mainly at room and elevated temperatures. O_2 is known to adsorb dissociatively on aluminum at room and low temperatures [1]. From AES, XPS, UPS, and synchrotron measurements it seems that at low surface coverages intermediate aluminum oxides are formed and only at higher coverages the familiar oxide (Al_2O_3) is present. To our knowledge there is no AES and XPS work mentioned in the literature on the Al(100)/O_2 system at lower temperature. The XPS work of Carly and Roberts [2] was done on polycrystalline aluminum at 80 K.

In the present work the XPS measurements were carried out using Al Kα radiation. The pass energy was 50 eV. The uncertainty in the measured binding energies was ±0.2 eV. All the binding energies were calibrated with respect to the standard Cu(3p) (75.1 eV), Au(4f) (84.0 eV) and Cu(LMM) (568.0 eV) lines [3]. The temperature was monitored using a chromel–alumel thermocouple attached to the back of the sample.

In general, the AES lines recorded at 80 K are very similar in their energies and shapes to those obtained at room temperature [4]. In fig. 1 the intensities of the 47, 54, 67.7, 505 and 1386.5 eV lines are plotted as a function of oxygen exposure. It is seen that the intensity of the Al(LVV) (67.7 eV) line decreases for the lowest exposures measured (1 L) while the intensity of the O(KLL) (505 eV) line increases. Only after an exposure of 5–7 L the line at 54 eV (of Al_2O_3) appears. After heating to room temperature for 10 min and cooling to 80 K there is no change in the energies of the lines; the 67.7 eV line decreases

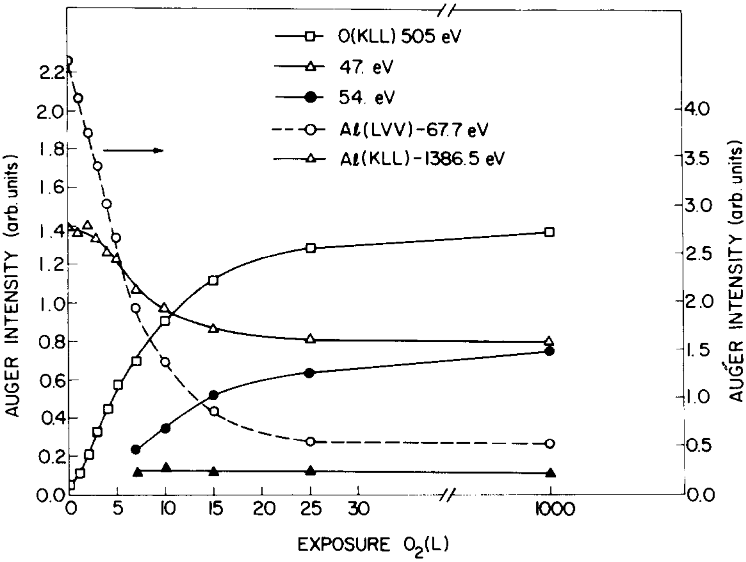


Fig. 1. Intensities of AES lines as a function of Al(100) exposures to O_2 at 80 K. The broken line refers to the right-hand scale.

slightly in intensity and the 505 eV line slightly increases. The intensity plot of the 54 eV line as a function of the 505 eV line (fig. 2) gives a straight line. Extrapolation of this line to zero intensity corresponds to an oxygen exposure of 3.5 ± 0.5 L. From these results we infer that for the initial amounts of the oxygen adsorbed, an intermediate form of oxide (Al_xO_y) with unknown

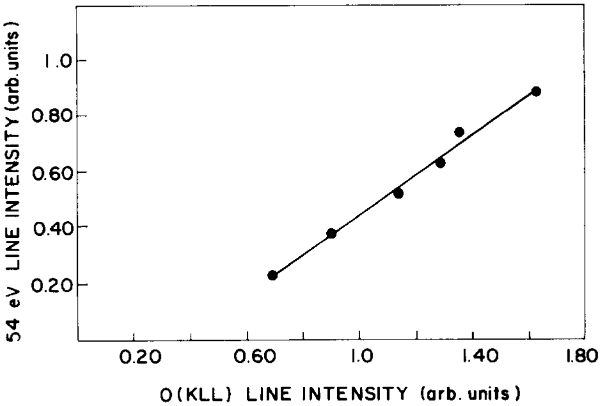


Fig. 2. Intensity of the oxide line (54 eV) as a function of the intensity of the O(KLL) oxygen line upon adsorption of O_2 on Al(100) at 80 K.

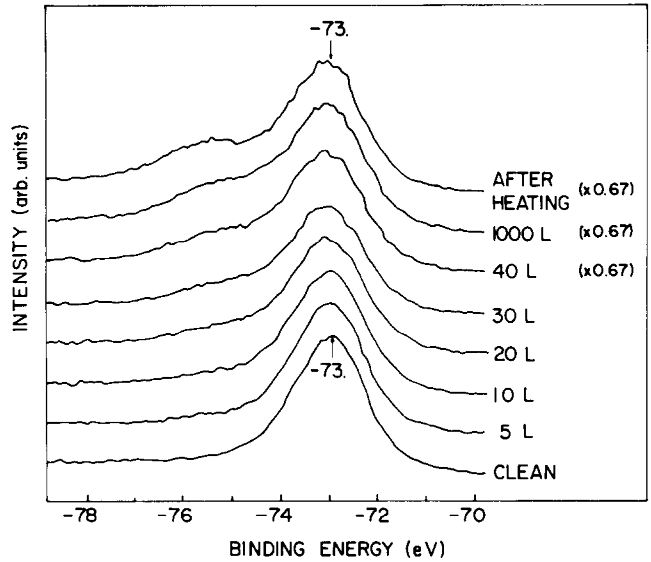


Fig. 3. Al(2p) spectra obtained upon adsorption of O_2 on Al(100) at different exposures of O_2 at 80 K.

stoichiometry is formed and only after an exposure of 3.5 L the familiar Al_2O_3 oxide is obtained.

The XP spectra of the Al(2p) and O(1s) lines of the clean Al and upon adsorption of different amounts of oxygen at 80 K are given in figs. 3 and 4. The numbers on each trace give the exposures in Langmuir units. The Al(2p) line is obtained at a BE of 73.0 eV (fig. 3), and its FWHM is 2.0 eV. On subsequent adsorption of oxygen, the lines assume an asymmetric shape and their intensities decrease. In parallel a broad line of aluminum oxide is developed at 74–77 eV. Curve fitting analysis [3] with Gaussian shape shows that the line FWHM is 3.2 eV and the maximum is shiftted by 1.2–1.9 eV with respect to the Al(2p) line of the clean metal. This oxide line consists of two lines as can be seen in fig. 5. The solid line refers to experimental results for Al(100) exposed to 30 L of O_2 at 80 K. The broken lines refer to the calculated spectra whose maxima are located at BE = 73.0 eV (pure Al), 74.5 eV (Al_xO_y) and 75.4 eV (Al_2O_3). The O(1s) line of atomic oxygen is obtained at 531.5 eV (fig. 4) and shifts to 532.0 eV at an exposure of 5–7 L. The line is symmetric in shape and its FWHM is 2.2 eV. After saturation exposure to O_2 (1000 L), heating to room temperature and recooling, the O(1s) line shifts to 532.3 eV. The oxide line shifts by 2.4 eV with respect to the clean metal and its FWHM decreases to 2.0 eV. The intensity plot of the 75.4 eV line (Al_2O_3) as a function of the O(1s) line (fig. 6) gives a straight line for O_2 exposures higher

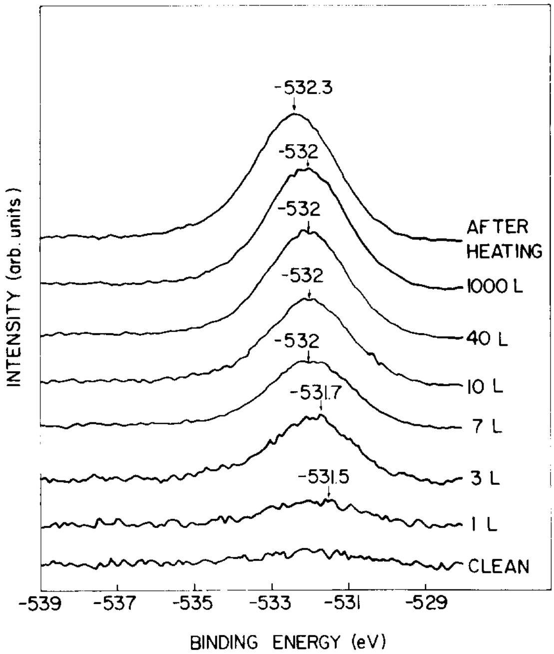


Fig. 4. O(1s) spectra obtained upon adsorption of O_2 on Al(100) at different exposures of O_2 at 80 K.

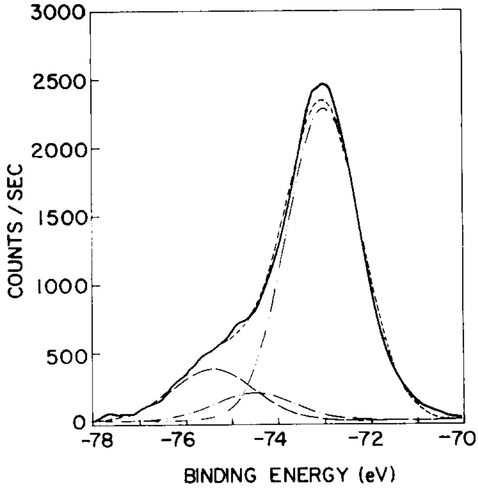


Fig. 5. Curve fitting analysis of the Al(2p) line after exposure of Al(100) to O_2 (30 L) at 80 K. The solid line refers to the experimental results, (------) calculated superposition line, (– · · · –) calculated pure Al(2p) line (73.0 eV), (– · – · –) calculated Al_xO_y line (74.5 eV), (– – –) calculated Al_2O_3 line (75.4 eV).

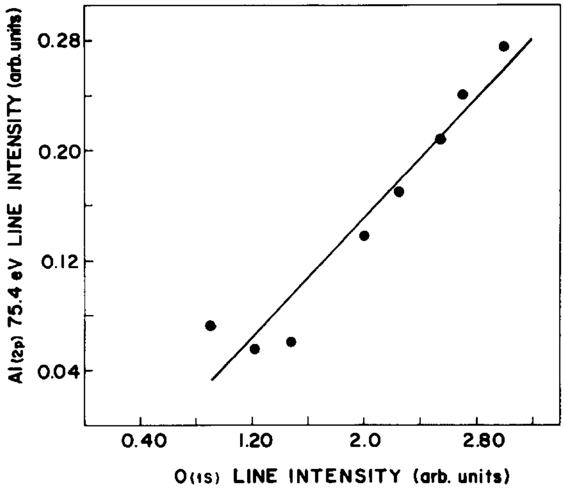


Fig. 6. Intensity of the oxide line (75.4 eV) as a function of the intensity of the O(1s) oxygen line upon adsorption of O_2 on Al(100) at 80 K.

than 10 L. For smaller exposures the intensity of the 75.4 eV line is too low to be taken into account. The estimated uncertainty in calculating the 75.4 eV line intensity is approximately ±25%. Extrapolation of this line to zero intensity corresponds to an oxygen exposure of 6 ± 4 L.

In fig. 7 the concentration of the atomic oxygen (σ_O), as calculated from [2]

$$Y_m/Y_s = \frac{\mu_m M_s \sigma}{\mu_s \lambda \cos\phi\, \rho N_A}, \tag{1}$$

is plotted as a function of exposure. Here Y_m is the integrated photoelectron intensity of the O(1s) line, Y_s is the intensity of the clean Al(2p) line of the pure aluminum, μ_m and μ_s are the photoionization cross sections of the O(1s) and Al(2p) levels ($\mu_{O(1s)} = 2.93$, $\mu_{Al(2p)} = 0.5371$ [5]), M_s is the atomic weight of Al, λ is the escape depth (2.7 nm) [2], ϕ is the angle of collection of the photoelectrons with respect to the sample normal ($\phi = 45°$), ρ is the density of the Al, and N_A is Avogadro's number. Adsorbate line intensites, normalized to the clean Al(2p) no-loss line, have been divided by two in order to take into account the intrinsic plasmon loss [2]. From the slope of the curve, the initial sticking probability (S_0) of O_2 on Al(100) was calculated and was found to be 0.28 at 80 K (as compared to 0.008 at 290 K [1]).

The stoichiometry of the formed Al_xO_y oxide, can be calculated by using

$$\sigma_{Al}/\sigma_O = \frac{Y_s(\text{oxide})\mu_m}{Y_m \mu_s}, \tag{2}$$

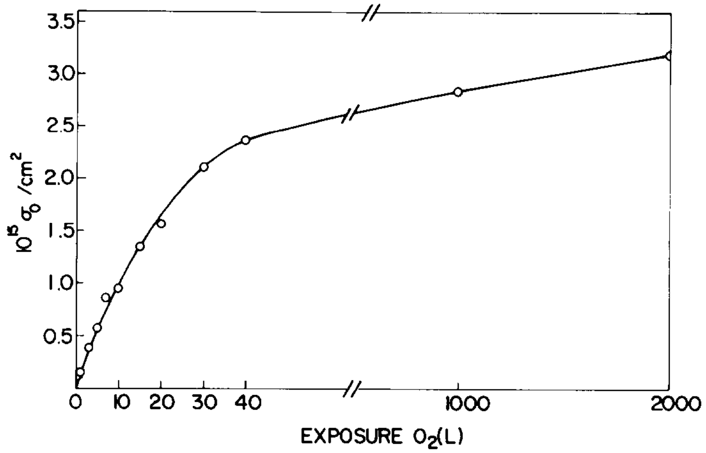
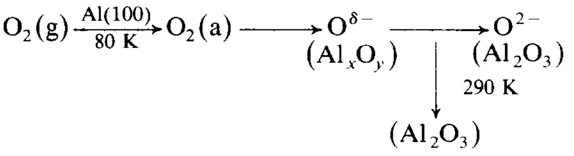


Fig. 7. Oxygen adatom concentrations (σ_O) as a function of Al(100) exposure to O_2 at 80 K.

which was derived from eq. (1). Here Y_s(oxide) is the intensity of the oxide component of the Al(2p) line. It was found that the ratio changed from a value of about 3 : 1 at low O_2 exposures to about 1 : 1 at saturation. After heating, this ratio decreased to 0.6(±0.2) : 1. In Al_2O_3 the expected value is 0.67 as confirmed by a separate experiment using polycrystalline aluminum foil covered with a 5 nm thick layer of Al_2O_3.

Relying on the described AES and XPS results we suggest that the mechanism of oxygen adsorption on Al(100) and of oxide formation is as follows:



$$\begin{tikzcd} O_2(g) \arrow[r, "Al(100)", "80\ K"'] & O_2(a) \arrow[r] & \underset{(Al_xO_y)}{O^{\delta-}} \arrow[r] \arrow[d, "290\ K"] & \underset{(Al_2O_3)}{O^{2-}} \\ & & (Al_2O_3) & \end{tikzcd}$$

At the beginning of the adsorption at 80 K the oxygen dissociates to atomic oxygen and forms a negatively charged $O^{\delta-}$ species leading to a number of Al_xO_y oxides where the $x : y$ ratio changes from 3 : 1 to 1 : 1. On further adsorption a fraction of the oxides transforms to Al_2O_3. On heating to room temperature Al_2O_3 is the only form present on the surface.

These conclusions are supported by recently published synchrotron results [6], where the behavior of the Al(2p) line in adsorption of O_2 on Al(111) at room temperature was investigated. Relying on the appearance of four Al(2p) new lines which were shifted from the clean Al(2p) line by 0.49, 0.97, 1.46 and 2.5–2.7 eV, four states of oxygen bonded to aluminum were identified.

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