

PHOTOELECTRON STUDY OF PLANAR ALUMINA GROWTH ON POLYCRYSTALLINE ALUMINUM

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We have followed by XPS the oxidation of aluminum foils at 500 °C and various oxygen exposures. It is shown that the oxide growth depends strongly on the surface preparation step prior to the exposure, leading to various core-level shifts with respect to the metal. Differences between the various oxides are attributed to the formation of native defects in the oxide layer. This influences the physical properties of the layer as well as its growth kinetics.

1. Introduction

Heterogeneous catalysis is one of the main fields of application of surface science. Besides adsorption and reaction studies on monocrystalline faces, one approach to this subject is the use of “model catalysts” formed by dispersion of a metal on a support. The criteria required for such models are:

- to simulate realistically a classical catalyst (aggregates of metal, oxide type of the support);
- to have built in clean conditions;
- to be suitable for surface as well as chemical studies.

Some of these criteria are conflicting such as the necessity to have a conducting support for surface studies and the generally highly insulating supports of classical catalysts. One possibility to solve such a conflict is to grow a homogeneous oxide layer on a metal so that the deposit “sees” this layer only, but which is thin enough to avoid charging of the sample. One advantage of this technique is that the sample can be resistively heated.

In a recent article, Cocke et al. [1] reviewed the knowledge we have on the growth of alumina on aluminum. It is reported that by exposure of Al to oxygen at room temperature an amorphous layer of Al_2O_3 is obtained which crystallizes at about 350 °C in the γ form if the layer is not thicker than a few tenth of an Å. Several facts show that the growth of a three-dimensional oxide on Al is far from clear. By XPS, core-level shifts of the Al 2s and Al 2p peaks of about 2.6 eV are generally reported [2,3] but a value as high as 3.6 eV was

also published [4]. Recently Ocal et al. [5] obtained various values from 2.6 to 3.7 eV. Using ion scattering, they distinguished between stoichiometric and non-stoichiometric oxides depending on the growing process of the oxide. We will show here that it is possible to monitor the XPS core-level shift depending on the preparation of the surface before the exposure and that this influences the growth kinetics of the oxide layer. Moreover comparison with an α -Al₂O₃ sample will shed some light on the structure of the oxide.

2. Experimental

The experiments were conducted in a VG-ESCA III system using an Al K α photon source. The analyser was adjusted to obtain a constant resolution of 0.75 eV.

The polycrystalline samples were of high purity grade from Goodfellow. They were cleaned using an Ar ion gun with an energy of 3 keV and a current of 10 up to 50 μ A. The α -Al₂O₃ single crystal with a surface plane of the (0001) orientation was cleaned by ion bombardment at 3 keV and then heated under vacuum at 700 °C for 15 min.

3. Results

Fig. 1 shows the Al 2p peaks of four samples oxidized up to atmospheric pressure at a temperature of 500 °C. All of these samples were submitted to a total oxygen exposure of 3×10^8 L. The samples are labelled A, B, C, D and correspond respectively to spectrum a, b, c and d. When visible, the metal peak appears at a binding energy of 72.65 eV from the Al Fermi level. We outline two striking features on this figure:

- The binding energy of the oxide peak is different for the four samples and spread from 74.70 eV for sample D to 75.55 eV for sample A. This corresponds to a shift varying from 2.05 to 2.90 eV.
- The intensity ratio between the peak of the metal and the peak of the oxide is each time different, that is the growth kinetics seems different. The higher the binding energy the lower the oxide growth rate.

Let us recall that the various samples were all part of the same Al foil and that the exposure conditions were each time the same. The only difference between the samples was the dosing of the ion bombardment in the cleaning procedure of the sample. Spectrum d corresponds to the lower dosing (10 μ A, 15 min) and from d to a the dosing becomes progressively higher up to 50 μ A, 60 min.

We show on figs. 2 and 3 the evolution of samples B and C versus the exposure. It can be seen that if the 2p peak of the oxide is not clearly defined

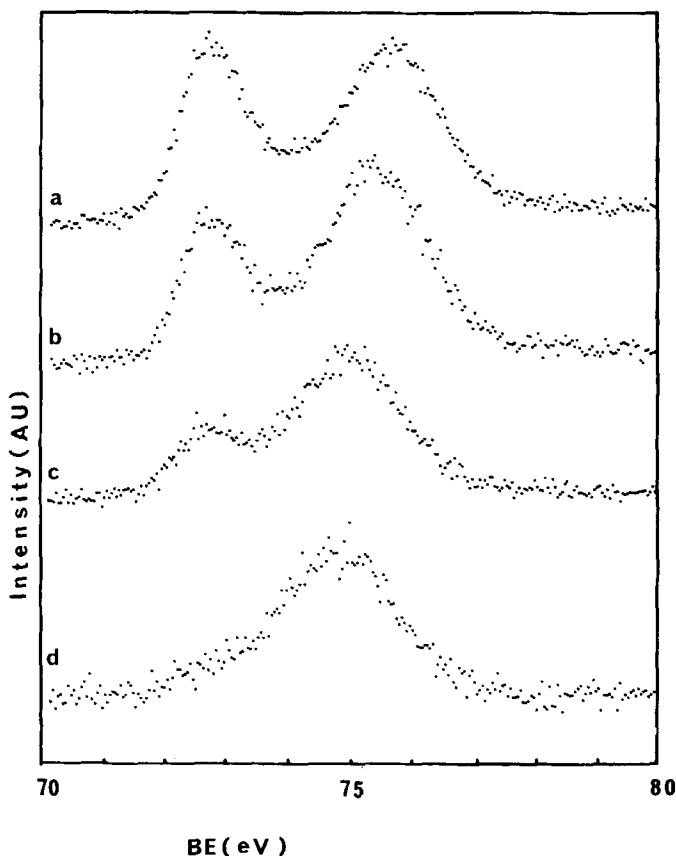


Fig. 1. Al 2p peak after oxidation (3×10^8 L, 500 °C) of (a) sample A, (b) sample B, (c) sample C and (d) sample D.

after the ion bombardment, it appears after annealing the sample at 74.9 and 75.25 eV, for sample C and B respectively. In the following evolution the intensity of the oxide peak increases but it remains at the same binding energy.

We show in table 1 the binding energy of the O 2s, Al 2p and O 1s peaks of the different samples. For comparison we report also the same features for the "as received" foil and for the α -Al₂O₃ sample. For the latter the values reported were calibrated from the Fermi level of a thin platinum film deposited on the sample at the end of the measurements. The binding energy of the O 2s or the Al 2s peak was then determined assuming them to be insensitive to the presence of platinum. We found this procedure satisfactory as the two measurements were in good agreement. Several features can be outlined from this table:

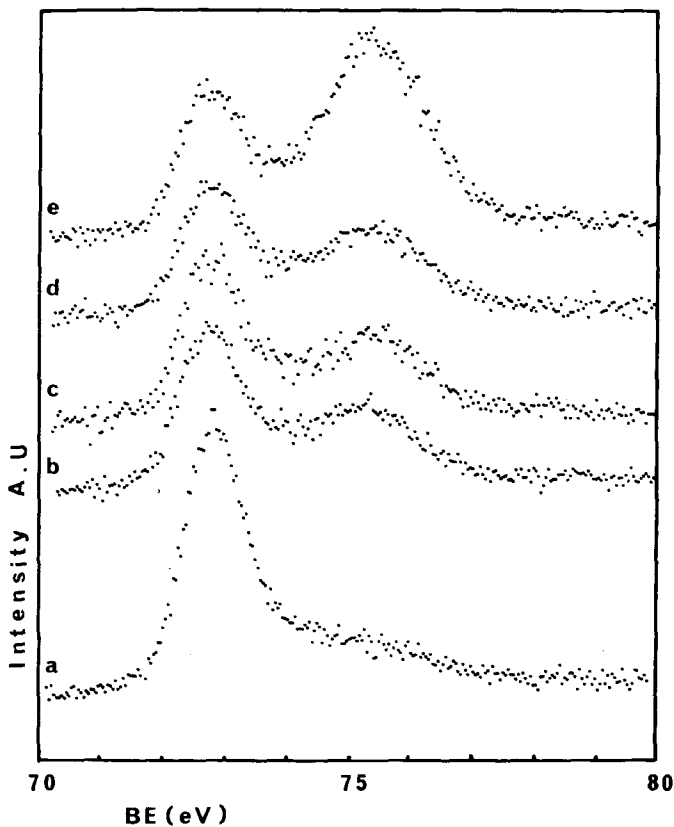


Fig. 2. Al 2p peak of sample B after successive treatments: (a) Ar bombardment; (b) annealing at 400 °C during 3 h; (c) 60 L oxygen exposure, 500 °C; (d) 4800 L oxygen exposure, 500 °C; (e) 3×10^8 L oxygen exposure, 500 °C.

Table 1

Valence and core-level binding energies (eV) obtained by XPS on the various samples

Sample	O 2p	O 2s	Al 2p	O 1s
A	9.55	24.30	75.55	532.55
B	10.15	23.90	75.25	532.10
C	10.4	23.50	74.90	531.95
D	10.24	23.25	74.70	
Native oxide			75.4	532.70
α -Al ₂ O ₃	9.65	23.55	74.65	531.55

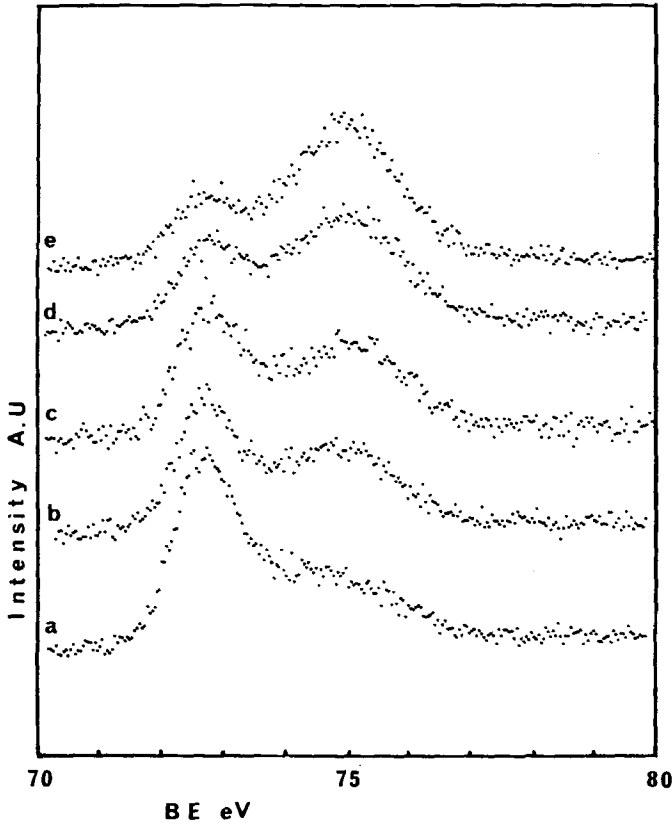


Fig. 3. Al 2p peak of sample C after successive treatments: (a) Ar bombardment; (b) annealing at 400 °C during 3 h; (c) 60 L oxygen exposure, 500 °C; (d) 4800 L oxygen exposure, 500 °C; (e) 3×10^8 L oxygen exposure, 500 °C.

- the difference in binding energy between the core levels is almost the same for each sample except for the native oxide;
- the binding energy of the core levels from α -Al₂O₃ seems close to the value obtained with sample D;
- the binding energy change of the valence-band feature does not follow the same trends as the core levels.

We show on fig. 4 the valence bands of samples A to D and α -Al₂O₃. We can distinguish two features in this latter: between 4 and 8 eV a low intensity region attributed mainly to O 2p non-bonding states, and a broad peak with its maximum at 9.65 eV attributed mainly to hybridisation between the Al 3p and O sp² orbitals [6]. This latter feature is designated as O 2p for simplicity in table 1. The valence band of sample D is broader and structureless. For

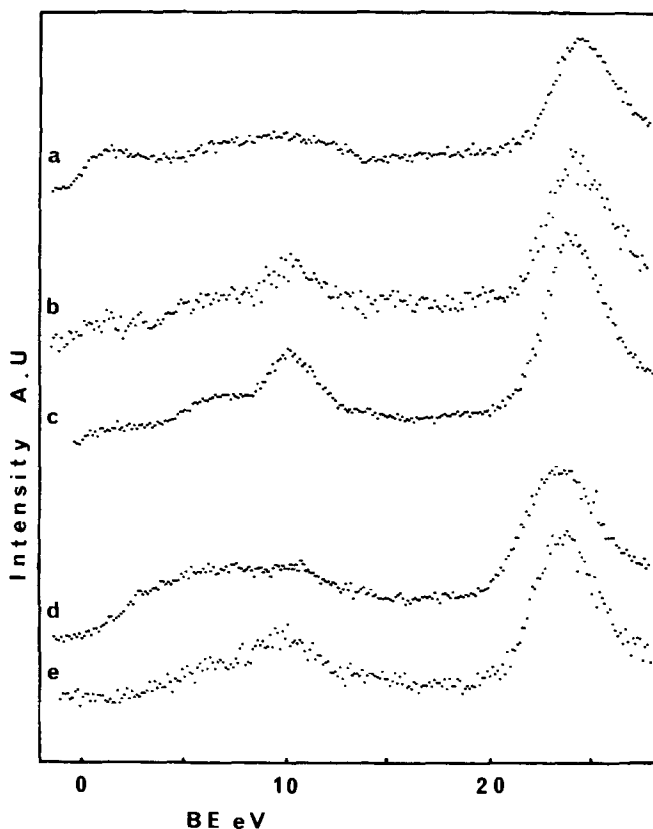


Fig. 4. XPS of the valence band of four Al samples after 3×10^8 L oxygen exposure: (a) sample A; (b) sample B; (c) sample C; (d) sample D; (e) valence band of $\alpha\text{-Al}_2\text{O}_3$.

samples B and C it looks similar to the valence band of $\alpha\text{-Al}_2\text{O}_3$ except for the binding energy of the O 2p states (see table 1) and the appearance of metallic states of Al. For sample A, the O 2p peak appears again very broad and centered around 9.75 eV.

4. Discussion

The results presented above seem to reveal several inconsistencies:

- on comparing the binding energies of the core levels, sample D seems to be close to $\alpha\text{-Al}_2\text{O}_3$;
- when comparing the valence bands, sample D appears clearly different of $\alpha\text{-Al}_2\text{O}_3$ but samples B and C look like $\alpha\text{-Al}_2\text{O}_3$.

In order to analyse these results and solve these apparent discrepancies, we will first try to discuss the most probable effects induced by the ion-bombardment process. Primary it (1) breaks the structure of the native oxide layer; (2) sputters the atoms resulting of action (1).

We can see in figs. 2 and 3 that this results in a badly defined oxide state, although annealing under ultra-high vacuum at 500  C seems to reconstruct the oxide. We can reasonably assume that the degree of order and the concentration of defects in the reconstructed layer will depend on the thickness of the layer itself and the degree of disorder before reconstruction, that is on the intensity of the ion bombardment. So, for a short ion treatment the picture could be as follows: the oxide layer is still thick and highly disorganised and when heated, it reconstructs in a high density of patches with a high density of defects between the patches and/or in the patches, so that it could be more or less amorphous after reconstruction. After a longer time of ion bombardment we can assume that only small patches of amorphous oxide remain on the sample. Heating results in small nuclei of reconstructed oxide dispersed on the surface of Al, in which the concentration of defects will be low. The nature of the defects induced by the preparation process of the surface remains questionable but probably consists of native defects such as misplaced atoms and oxygen or aluminum vacancies. What happens now during the oxide growth under oxygen exposure? This is illustrated by figs. 2 and 3 which show that during this step, the oxide develops itself with constant core-level binding energies. This leads us to assume that the surface state induced by the preparation process is not fundamentally modified by the oxide growth, that is the oxide nuclei start growing keeping their own degree of order. We will see now how this picture can help us to interpret the experimental facts.

(1) Valence band: if we take the valence band as largely determined by long-range order, it is clear that sample D does not correspond to a well-organised form of Al_2O_3 . The broad and structureless aspect of its valence band would rather confirm its amorphous nature as expected from the growing process. The similarities of the valence bands of samples B and C with that of $\alpha\text{-Al}_2\text{O}_3$ would confirm that long-range order is established in these samples. In the case of sample A, the contribution of metallic Al appears to be very high and it seems that the oxide nuclei are not yet big enough to reveal the characteristic valence band of Al_2O_3 .

(2) Core levels: aluminum is not known to take various oxidation states so that various binding energies cannot be attributed to such a phenomenon. On the contrary it seems that almost continuous binding energy shifts between 2.05 and 2.90 eV with respect to Al metal could be obtained. This could be encountered by changes in relaxation energy and would suggest a change of structure between the various samples. We have no evidence of such an evolution but on the contrary the valence-band shape suggests that at least

samples B and C have a similar structure. In order to check a possible change in relaxation energy we can use the Auger parameter introduced by Wagner [7]. In its modified form, it is defined as the Auger kinetic energy of a XYZ transition plus the binding energy of the core level labelled X , or the Auger kinetic energy minus the core-level peak kinetic energy plus the X-ray photon energy. It was shown that the change in Auger parameter is two times the change of extra-atomic relaxation energy ΔR [8]. The measurements were made using the main maximum of the O KVV Auger transition and the O 1s core level. It appears that samples A to D have the same modified Auger parameter (1039.6 eV) but the value obtained for the $\alpha\text{-Al}_2\text{O}_3$ is lower (1038.4 eV). First of all this means that the samples A to D have all the same relaxation energy so that the different binding energies cannot be explained this way. Another conclusion is that the structure of the oxide obtained by oxidation of Al is definitely different from the structure of $\alpha\text{-Al}_2\text{O}_3$. This could confirm that the oxide grown by oxidation of Al crystallizes in the γ form.

Another explanation of the observed shifts could be a change of the position of the Fermi level in the forbidden bandgap. Such an effect could be due to the appearance of localized states in the gap due to the existence of defects. This can explain why all the core-level peaks are shifted the same way. Several kinds of defects could be expected, for example donors states as O vacancies and acceptor states as Al vacancies. Each of these could influence the location of the Fermi level in the band gap which would depend on the degree or number of defects [9]. This interpretation seems most likely because it is in agreement with the preparation and growing process of the various samples. It would imply that all the features of the spectra from the oxide shifts with respect to the metal. However, it appears in table 1 that this is not the case for the valence-band features. The structure attributed to the O 2p states appears at 9.65 eV for $\alpha\text{-Al}_2\text{O}_3$ but always above 10 eV for samples B to D. The value reported for sample A at 9.75 eV is only the centre of the valence states of the oxide. We believe that besides the uncertainty in the measurements of the O 2p states, this discrepancy shows mainly that the structure is not completely similar between each sample (may be due to the various concentrations of defects) and is different from the structure of $\alpha\text{-Al}_2\text{O}_3$.

We will now discuss briefly the growth kinetics of the oxides. In fact the various samples cannot be strictly compared on this point as the initial state is always different: sample A is almost completely free of oxide after the preparation step (bombardment and subsequent annealing), whereas sample D is covered with several Å of oxide at the same step. However it appears clearly that the growth kinetics increases from A to D. This is not surprising when considering that to each sample corresponds a certain concentration of defects. Transport of oxygen through the oxide to the Al interface involves probably a vacancies migration mechanism so that the oxide with the lower concentration of defects has the lower growth kinetics.

5. Conclusion

We have shown that the degree of order of the Al_2O_3 layer grown by exposure of Al to oxygen at 500°C depends on the surface preparation. The defects induced by ion bombardment could lead to various binding energy shifts of the oxide core levels with respect to the metal. This is attributed to doping effects inducing a change in the Fermi level localization in the band gap. Besides this effect, it appears that the structure of the oxide is different from the structure of $\alpha\text{-Al}_2\text{O}_3$.

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