DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-77/20
November 1977

Oxidation of Al Single Crystal Surfaces by Exposure to O_2 and H_2O

by

W. Eberhardt
II. Institut für Experimentalphysik der Universität Hamburg

C. Kunz
Deutsches Elektronen-Synchrotron DESY, Hamburg

NOTKESTRASSE 85 · 2 HAMBURG 52

Oxidation of Al single crystal surfaces by exposure to O_2 and H_2O

W. Eberhardt[+] and C. Kunz[++]

[+] II. Institut für Experimentalphysik, Universität Hamburg,
Luruper Chaussee 149, D-2000 Hamburg 50

[++] Deutsches Elektronen-Synchroton DESY, Notkestraße 85, D-2000 Hamburg 52

The initial stages of oxidation of Al single crystals are studied by soft x-ray photoemission spectroscopy at photon energies hν = 30 eV and 111.3 eV using synchroton radiation. Both the valence band region and the substrate Al 2p core levels are measured with high resolution to clarify the differences between a) the geometrical effects at different surfaces, (100) and (110), and b) between the oxidation by pure O_2 and H_2O. There is a well established but not very dramatic difference in the O 2p induced band between the two crystal surfaces when oxidizing with O_2. The Al 2p spectra reveal an initial state of oxidation with less O atoms per Al atom than in Al_2O_3. This state disappears at higher exposures with O_2 while it is absent when oxidizing with H_2O. Only about 1/4 of the exposure with H_2O is needed to obtain the same coverage as with O_2.

1. Introduction

In order to clarify the mechanism of catalytic reactions on transition metal surfaces the separation of contributions from s, p and d states is one of the central problems. Attempts are being made to approach this problem from many different sides. One possible way is the investigation of chemisorption on simpler metals than transition metals e. g. Al, which has a free electron like valence band made up mainly of s and p symmetric states.

Most of the investigations dealing with the oxidation of Al are carried out at in situ evaporated polycrystalline films. There are measurements by Krueger and Pollack[1,2] showing the differences in the kinetics for adsorption of O_2 and H_2O by weight gain measurements. This was further investigated by Fuggle et al.[3] who looked for photoelectrons originating from the O 1s level of adsorbed H_2O and O_2 after excitation by Al K_α radiation concluding that after room temperature adsorption of H_2O more than 90 % of the hydrogen was released into the vacuum.

Yu et al.[4] have measured the valence band photoemission after exposure to oxygen and compared their measurements with theoretical calculations of Lang and Williams[5]. Flodström et al.[6] have investigated the initial oxidation of Al polycrystalline films using synchroton radiation with variable photon energy measuring EDC's from the valence band and the Al 2p core level simultaneously. They interpret their results in terms of an initial physisorbed phase of oxygen on Al, which only leads to oxidation at exposures above 200 L.

Until now there are only few experiments using clean Al single crystals with oriented surfaces[7,8]. These measurements clearly show differences in the oxidation on the 3 low index surfaces. Martinsson et al.[7] obtain EDC's of the valence band region by excitation with HeI radiation and perform sticking coefficient measurements using the oxygen Auger signal. Gartland[8] has published results of the work function change after oxidation on the (100) and (111) surfaces. These measurements lead to different adsorption models for these two surfaces. He concludes that there is a statistical adsorption on the (111) surface, whereas on the (100) surface only an island growth model gives good agreement between theory and experiment.

We here present the first photoemission measurements of both the valence band and Al 2p core states from the same Al single crystals with (100) and (110) surfaces after adsorption of O_2 and H_2O. These measurements are taken with the new FLIPPER monochromator at the DORIS storage ring[9]. Therefore both the valence band region and the Al 2p lines are accessible with high resolution.

Lang and Williams[5] calculate the electronic structure of adsorbed oxygen atoms on a jellium substrate. If this picture of the interaction between the electrons of the adsorbate and a free electron substrate was meaningful, then the results for Al should be quite close to the theoretically predicted ones. On the other hand, as measurements show[7,8] there are differences for different single crystal surfaces. Such a behaviour is not explainable by the jellium picture but could be brought forth by a theory which incorporates the arrangement of the atoms at the surface like e. g. the cluster calculations of Harris and Painter[10].

The chemical shift of core levels of the substrate atoms which are in contact with the adsorbate atom can serve as a sensitive indicator of the penetration depth of the electric field of the change aquired by the adsorbate atom. If chemisorption results in a binding similar to that of a heteropolar molecule a large chemical shift should occur. If we consider, on the other hand, binding to a metal with a high free electron density we expect the field to be screened at a distance from the surface which is small compared to the ionic radius of the substrate atoms. In this case no appreciable chemical shift will be observed.

For this type of investigation the availability of different photon energies is very helpful. To investigate photoemission from the valence band region, especially at coverages much less than a monolayer, one needs a photon energy between 20 eV and 40 eV because the cross section for the O 2p emission is decreasing rapidly with increasing photon energy. For the investigation of the 2p core levels of Al one needs at least 100 eV photon energy to get rid of the background of scattered electrons. Further, in order to obtain a high surface sensitivity of the signal, the detected electrons should have a kinetic energy around 50 eV in order to have a very short electron-electron scattering length (∿5Å) in the crystal. Again, the advantage of a tunable radiation source like synchroton radiation is obvious.

2. Experimental Details

The measurements were carried out with the FLIPPER monochromator at the DORIS storage ring. The resolution of the monochromator was about 60 meV at hν = 100 eV and 80 meV at hν = 30 eV. The photoelectrons were excited with s-polarized light and analyzed with a commercial double pass cylindrical mirror analyzer. Further details of the experimental setup will be described elsewhere[9].

We have investigated two single crystals[11] of Al having a (100) and a (110) surface. The crystals were electropolished[12] in order to obtain very smooth surfaces with only a very thin oxide layer of about 30 Å thickness. The crystals were cleaned *in situ* by ion bombardment and annealing at a temperature of about 450° C. The signal of the aluminum oxide being present at the surface was monitored looking at the O 2p emission with a photon energy of about 30 eV. For this photon energy the absorption coefficient of Al_2O_3 is about 20 times larger than that of pure Al. Thus the experiment was very sensitive to oxygen contamination. At the beginning of each run the oxygen signal was less than

0. 4 % of the signal we obtained after an exposure to 250 L of O_2, which corresponds approximately to a coverage of one monolayer.

During the exposures the ion gauge was switched off in order to avoid the presence of activated O_2 or H_2O. The pressure was controlled via the current of the ion getter pump. The gases we used contained less than 0.1 % of impurities, which was veryfied with a quadrupole residual gas analyzer. The pressure during exposure was kept at 2×10^{-7} Torr to be well above the residual gas pressure, which was in the low 10^{-10} Torr range.

3. Results on the valence bands

Fig. 1 shows EDC's of the valence band region of clean and oxygen covered surfaces taken at a photon energy of 32 eV with an overall instrumental resolution of 280 meV. On the (100) surface we observe an O 2p emission with a relatively sharp maximum centered at E_b = 7.5 eV (binding energy relative to the Fermi level) with a clearly detectable shoulder at E_b = 11 eV. The general shape of the O 2p emission does not change very much with exposure. On the (110) surface the maximum is broader and the shoulder at E_b = 11 eV may be distinguished clearly only at higher exposures.

In fig. 2 we compare the O 2p emission after adsorption of H_2O and O_2 for the different surfaces. The spectra for H_2O adsorption show practically no difference for the two crystal surfaces in the region from the Fermi level up to E_b = 12 eV. There is a third shoulder coming up at E_b = 14 eV especially clearly on the (110) surface. We have observed this extra feature with polycrystalline films also at high coverages of O_2. Thus we rule out that this extra structure is due to $(OH)^-$ radicals at the surface.

Additionally we show that the oxidation by H_2O vapour is much faster than by O_2 in agreement with ref. 3. The curve of the unoxidized Al can serve as a reference in each of the spectra in fig. 2.

4. Results on the Al 2p core levels

Fig. 3 shows the region of the Al 2p emission before and after adsorption of O_2 and H_2O. The spectra were taken with an overall instrumental resolution of 120 meV at a photon energy of 111.3 eV. The spin orbit splitting of the Al 2p level is clearly resolved. After adsorption of O_2 there appears additional structure in a region of up to 3 eV higher binding energies. For low exposures up to 100 L the intensity is nearly equally distributed in that region, whereas for higher exposures a broad single maximum appears at a distance of 2.6 eV to the center of the Al 2p doublet. There is a weak shoulder on the (110) surface at 1.4 eV higher binding energy, which is more pronounced for the (100) surface. After the adsorption of H_2O vapour only the broad structure at - 2.7 eV appears, which is the chemically shifted Al 2p level in Al_2O_3[14]. The direction of the shift to higher binding energy is explained by the higher electronegativity of O_2 compared to Al.

In contradiction to ref. 6 we do not observe an asymmetric broadening of the original Al 2p core levels in photoemission. This discrepancy with the spectra of ref. 6 is explained due to the fact that the Al 2p peaks merge with the subsequent shoulder due to the poorer resolution in the results of ref. 6.

5. Discussion

We note that the main peak at 2.6 eV chemical shift which dominates all the spectra at not too low coverages shows the same chemical shift as a thick layer of Al_2O_3. In the latter case the chemical shift is determined by the transfer of electronic charge from Al to O, due to the formation of the Al_2O_3 molecule. From the fact that the chemical shift after adsorption is equal to the one in the Al_2O_3 molecule we conclude that the positive screening charge in the Al is concentrated at those atoms which are in contact with the adsorbed O atom.

Unfortunately there are no calculations available which deal with the chemical shift of the Al 2p core level. However, we feel that such a result could be obtained by calculating the potential change at the position of the Al core from the change in the charge distribution after adsorption both in the jellium model[5] and the cluster model[10]. This comparison would allow to check how realistic the charge distributionsobtained from these calculations are.

If we compare the width and the local density of states of the O 2p level and the separation between the O 2p and 2s levels (fig. 4), we find a very good agreement of both the jellium[5] and the cluster calculation[10] with the experiment. Even though the absolute position relative to the Fermi level is not correctly reproduced. The structures at low exposures with O_2 in the Al 2p spectra at binding energy shifts smaller than the ones for Al_2O_3 may be interpreted as due to oxygen atoms which have penetrated into the bulk. Because more Al atoms share in the local interaction with the O-atom, the chemical shift for each Al atom is not as large as on the surface or when finally stoechiometric Al_2O_3 is formed. The (100) surface is the more open one and there one should expect more oxygen penetrating into the bulk which is in good agreement with the experimental result showing that the structures with intermediate shifts are more pronounced there.

For very low exposures up to 30 L we observe in the valence band region a peak coming up at a binding energy of E_b = 2 eV together with the usually observed structure around E_b = 7.5 eV. This extra peak (see fig. 5) increases in intensity with coverage and appears to be stronger on the (100) surface than on the (110) surface. Since we have taken spectra collecting electrons with all polar angles

between 0° and 90°, this structure may not be attributed to the surface state which has been observed in angular resolved spectra at the (100) surface.[14] This surface state shows a very strong dispersion which would result in a complete blurring in our angle integrated spectra. Messmer and Salahub[15] have carried out a cluster calculation for one O atom on an Al cluster of 25 atoms and in these calculations they have varied the distance of the O atom relative to the surface. For the case when the O atom aligns with the topmost Al surface layer (Z = 0) they calculated a density of states which has two peaks equally in strength at - 2.3 eV and at -6.5 eV relative to the Fermi level. This extra structure at E_b = 2 eV may no longer be resolved after larger exposures because the tail of the "normal" O 2p resonance extends up to the Fermi level. Thus these calculations support the assumption that some of the O atoms penetrate into the bulk. Work function measurements[8] give additional support for this assumption, since the work function decreases rapidly with coverage for the (100) surface. For the (110) surface there is a much smaller decrease observed in agreement with our interpretation of the Al 2p core level spectra. Since we attribute the shoulder at -1.4 eV in these spectra to be due to oxygen that has penetrated into the bulk.

The valence band emission after O_2 adsorption onto the (100) surface always shows the same spectral shape with the narrow peak and the shoulder. With increasing coverage there is only an increase in signal strength. This behaviour is in agreement with the island growth model predicted for this surface[8].

On the other hand due to the statistical adsorption on the (110) surface[8] the spectral shape of the O 2p emission is broader and more smeared out and shows no shoulder at E_b = 11 eV at low coverages. With higher coverage the spectrum changes towards that on the (100) surface.

The adsorption of H_2O vapour is accompanied by an increase of H_2 in the residual gas[2]. This means that the H_2O molecule is dissociated and only oxygen stays at the surface whereas H_2 or H is set free[3]. Fuggle et al.[3] conclude from the chemical shift of the O 1s level that more than 90 % of the H_2O is dissociated. In the Al 2p region we only observe the peak at -2.6 eV so that we may conclude the dissociation only happens at the surface and no migration into the bulk is observed. After background subtraction the valence band spectra show no differences between the two Al surfaces (100) and (110) for H_2O adsorption.

6. Conclusions

We have demonstrated that it is necessary for the understanding of the nature of adsorption to look not only at the valence bands but also at the substrate core levels. From the Al 2p level emission we obtain the information that oxygen penetrates into the surface, especially for the (100) surface, whereas water vapour does not. Furthermore, we suggest that calculations of the core level chemical shifts should be included in both the cluster and jellium model calculations. This would allow for a valuable comparison with experiment.

Oxidation with vapour is preceeded by a nearly complete dissociation of the H_2O molecules. The oxidation with water vapour is about a factor of 4 faster than with O_2. There are no differences for the two single crystal faces for oxidation with water vapour whereas we find differences for oxidation with O_2 gas which are in agreement with the proposed oxidation models.[8]

7. Acknowledgment

We want to thank H.J. Fenzl (KFA Jülich) for generously providing the oriented and polished Al single crystals. Further, we thank W. Gudat, N. Lang and M. Pfuff for many fruitful discussions.

References

1. Wm.H. Krueger and S.R. Pollack, Surf.Sci. 30, (1972), 263
2. Wm.H. Krueger and S.R. Pollack, Surf.Sci. 30, (1972), 280
3. J.C. Fuggle, L.M. Watson, D.J. Fabian, and S. Affrossman, Surf.Sci. 49, (1975), 61
4. K.Y. Yu, J.N. Miller, P. Chye, W.E. Spicer, N.D. Lang, and A.R. Williams, Phys.Rev. B14, (1976), 1446
5. N.D. Lang and A.R. Williams, Phys.Rev.Lett. 34, (1975), 531
6. S.A. Flodstrom, R.Z. Bachrach, R.S. Bauer, and S.B.M. Hagström, Phys.Rev. Lett. 37 (1976), 1282
7. C.W.B. Martinson, L.G. Petersson, S.A. Flodstrom, and S.B.M. Hagström, ESA-Report SP 118, (1976), 177
8. P.O. Gartland, Surf.Sci. 62, (1977), 183
9. W. Eberhardt, G. Kalkoffen, and C. Kunz, to be published
10. J. Harris and G.S. Painter, Phys.Rev.Lett. 36, (1976), 151
11. High purity Al (>99.999 %) from VAW (Kryal R 5 NT)
12. R. Bischof, V. Sorajic, and U. Linke, KFA Jülich, internal report, March 1976
13. A. Barrie, Chem.Phys.Lett. 19 (1973), 109
14. P.O. Gartland and B.J. Slagsvold, submitted to Phys.Rev.Letters
15. R.P. Messmer and D.R. Salahub, in Computers in Chemical Research and Education, ed. by E.V. Ludena, N. Sabelli and A.C. Wahl, Plenum Press, New Nork.

Figure captions

Fig. 1 EDC´s of the valence band region after different exposures of oxygen for the (100) and (110) single crystal surface taken at a photon energy of hν = 32 eV.

Fig. 2 Photoelectron EDC´s of the valence band region after adsorption of oxygen and water vapour for the (100) and (110) single crystal surface. The spectra of the clean surfaces are dashed.

Fig. 3 Photoelectron EDC´s of the Al 2p emission region taken at a photon energy of hν = 111.3 eV before and after adsorption of oxygen and water vapour.

Fig. 4 Photoelectron EDC showing the valence band and the oxygen 2s emission after adsorption of 100 L of O_2 onto Al (100). The experimental curve is compared with calculations of Lang and Williams[5] (dashed) and Harris and Painter[10] (bars). The length of the bars indicates the charge within the oxygen muffin tin. The energy values of the calculations are normalized to the energy of the Al 2s level.

Fig. 5 EDC's of the valence band region showing the fine structure after oxidation for small coverages. The "clean" spectrum obviously shows structure due to oxygen, but extrapolating from 250 L exposure, this spectrum is equivalent to an exposure of less than 1L. By the same extrapolation we get the exposure of the curve labelled 2L. The curves are normalized at the Fermi level.

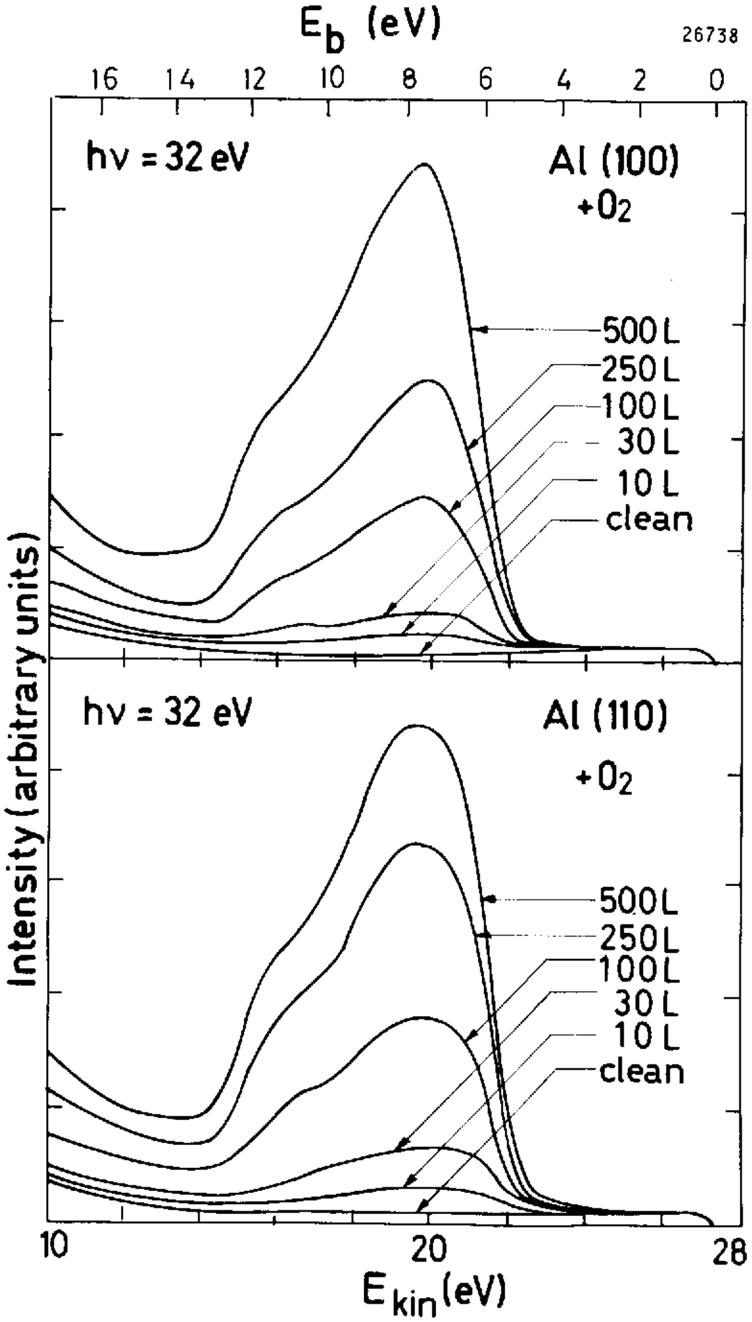

Fig. 1

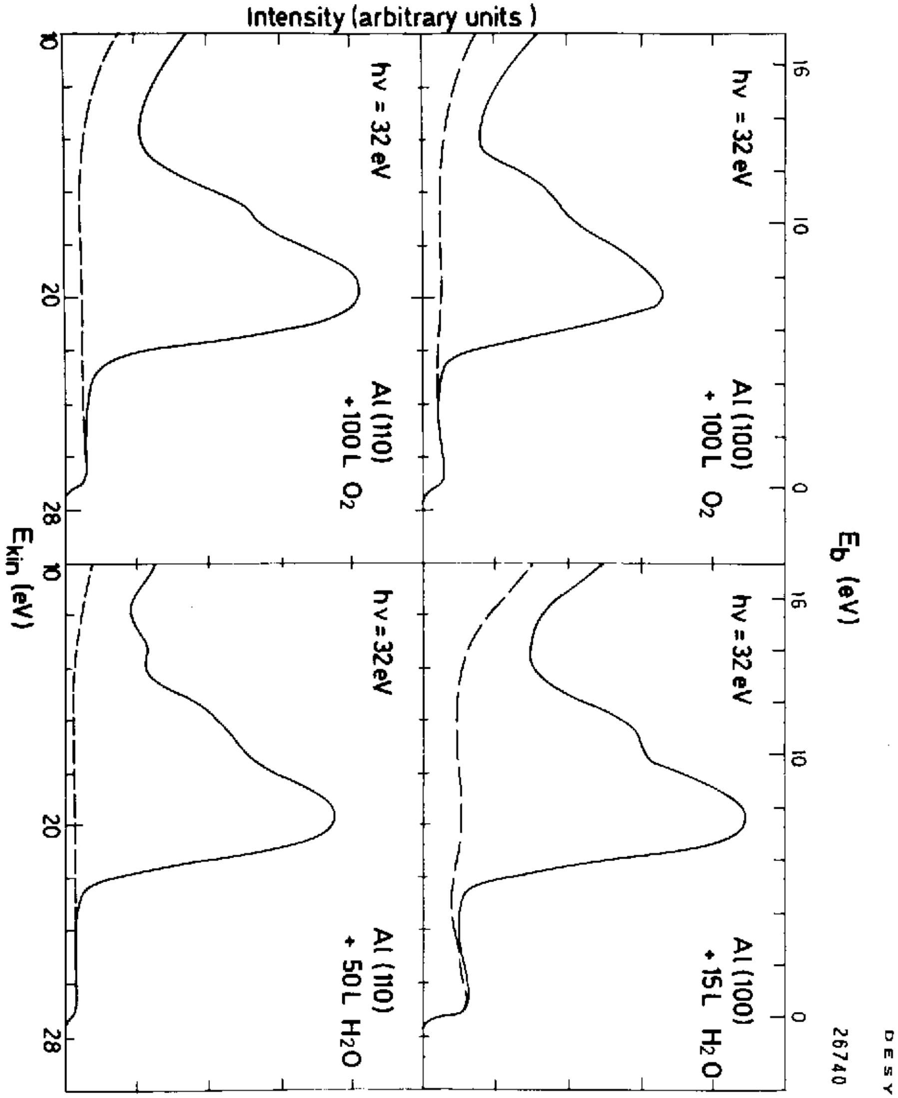
Intensity (arbitrary units)
hν = 32 eV
Al (100) + 100L O$_2$
hν = 32 eV
Al (110) + 100L O$_2$
hν = 32 eV
Al (100) + 15L H$_2$O
hν = 32 eV
Al (110) + 50L H$_2$O
E$_b$ (eV)
16
10
0
E$_{kin}$ (eV)
10
20
28
DESY
26740

Fig. 2

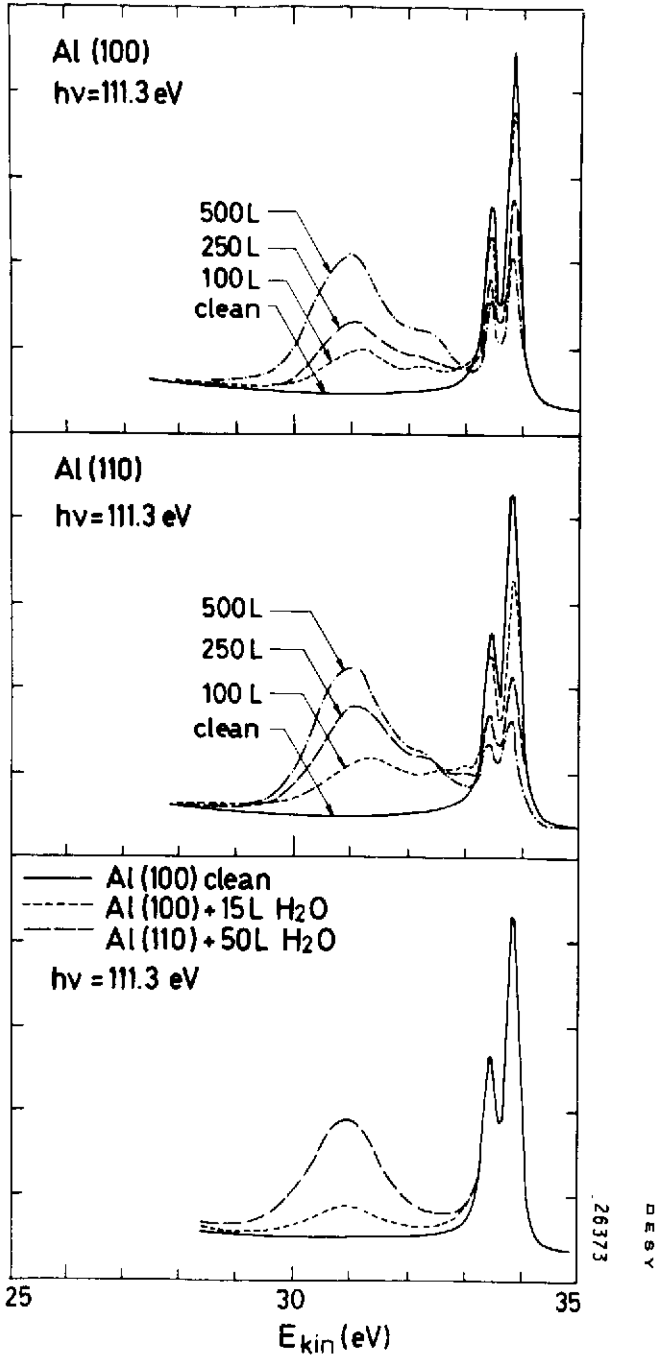
Al (100)
hν=111.3 eV
500 L
250 L
100 L
clean
Al (110)
hν=111.3 eV
500 L
250 L
100 L
clean
Al (100) clean
Al (100) + 15 L H$_2$O
Al (110) + 50 L H$_2$O
hν = 111.3 eV
25
30
35
E$_{kin}$ (eV)
DESY
26373

Fig. 3

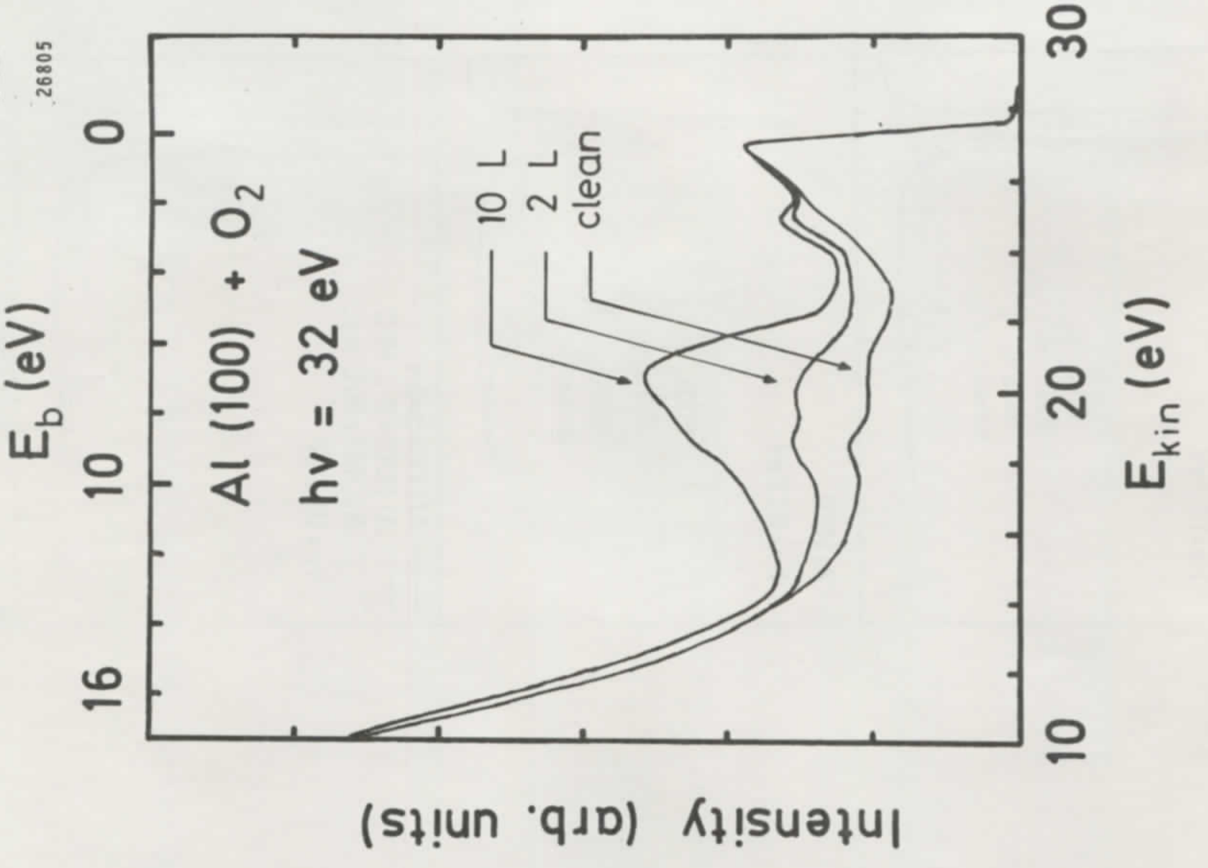
DESY
26805
E_b (eV)
16
10
0
Al (100) + O_2
hν = 32 eV
10 L
2 L
clean
Intensity (arb. units)
10
20
30
E_kin (eV)

Fig. 5

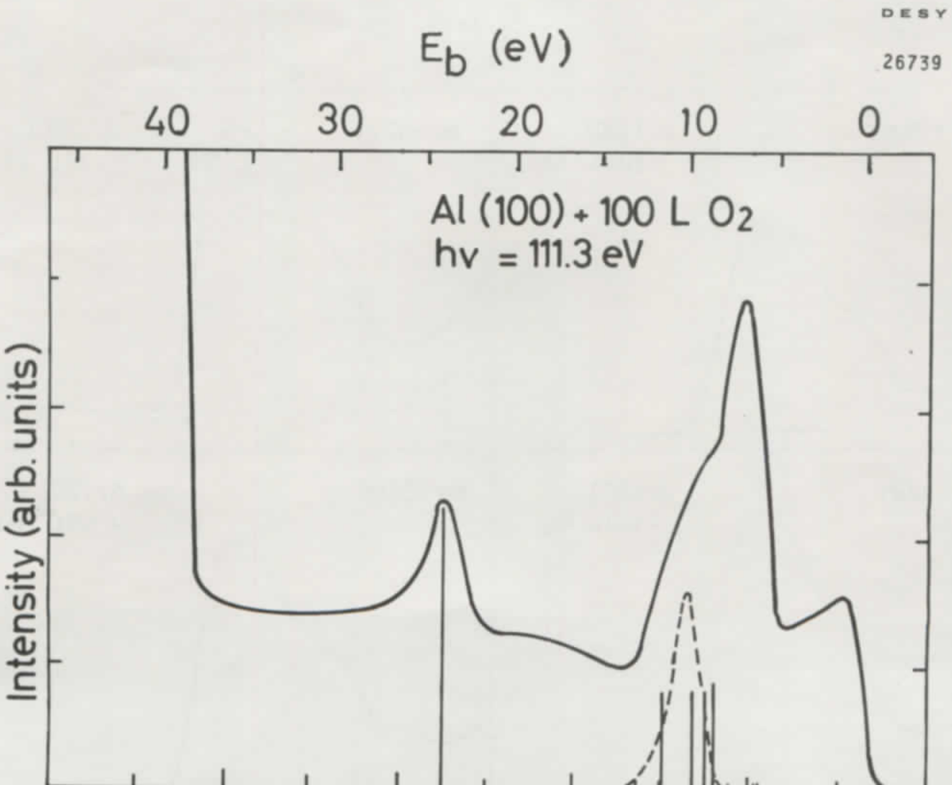
DESY
26739
E_b (eV)
40
30
20
10
0
Al (100) + 100 L O_2
hν = 111.3 eV
Intensity (arb. units)
60
70
80
90
100
110
E_kin (eV)

Fig. 4