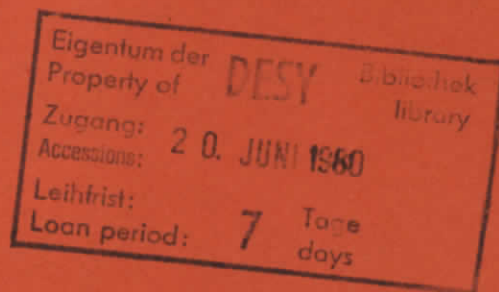


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INVESTIGATED BY SYNCHROTRON RADIATION INDUCED PHOTOEMISSION

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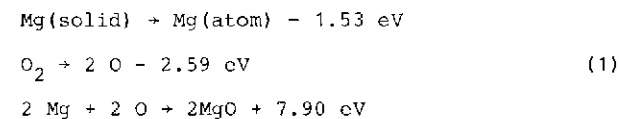
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The initial oxidation of aluminum and magnesium films is found to be a two-stage process. For aluminum, the first oxygen atoms adsorbed seem to form an ordered overlayer, this being followed by the formation of amorphous aluminum oxide. For magnesium, the first stage seems to involve oxygen atoms bound in a number of different bonding configurations followed by the formation of magnesium oxide. These transformation processes have been studied for both metals by monitoring changes in the shape of the oxygen 2p resonance and by investigating the metal 2p core level region with maximum surface sensitivity. The line-shapes of the metal 2p core levels for the oxides are very much broader than for the clean metal 2p core levels. This broadening is discussed in terms of phonon induced effects and changes in lifetime due to new Auger decay channels produced by oxidation. A comparison between scattering lengths in the metals as compared to the oxides is made.

INTRODUCTION

Different methods of electron spectroscopy have been extensively used to study the oxidation process in metals and semiconductors. In this paper we report on the specific advantages of using synchrotron radiation excited photoelectron spectroscopy.

The initial oxidation of 'polycrystalline' Mg and Al films has been investigated in the present study. Part of this work has been reported in a previous paper [1]. This report is an attempt to give a picture of the common chemical processes involved in the interaction of oxygen with polyvalent, free electron like metals. Characteristic of polyvalent free electron like metal oxide systems is the fact that metal-metal bond energies in the pure metals are much smaller than the metal-oxygen bond energies in their oxides, e.g., the Mg-Mg bond energy is 1.53 eV/bond as compared to the 3.95 eV/bond for the Mg-O bond. The reaction of oxygen with clean Mg is a strongly exothermal process,



Because of this, one expects the formation of an oxide layer on the metal surface without any intermediate steps (having life times long enough to be observed spectroscopically) in the metal-oxygen interaction. However, we must remember that in order to start reaction (1), an overlap of oxygen and metal orbitals is needed, which implies that reaction with impinging oxygen molecules will proceed more easily at certain sites on

the metal surface than at others. If ordinary crystallographic sites in the surface act as nucleation centres, different single crystal surfaces will show different oxidation behaviour [2,3]. The process of oxidation in polycrystalline films will depend critically on the type of crystallites making up the surface. If defect sites of different kinds are important in the nucleation process, the process of oxidation is expected to be about the same for all crystal surfaces, with the oxidation rates being determined to some extent by the quality of the surface.

Photoelectron spectroscopy is uniquely suited for studying surface processes. Due to the short scattering lengths in solids associated with electron kinetic energies of 20-1000 eV, the contrast between surface and bulk atoms is high. Both valence band and core levels can be studied with good energy resolution. When oxygen is being adsorbed on a clean metal surface, it is expected that three adsorbate induced structures will be seen in photoelectron spectroscopy. The O 1s and O 2s core levels are expected to appear as relatively sharp atomic-like structures at binding energies of  $\approx 530$  eV and  $\approx 25$  eV respectively. Unfortunately neither of these structures can easily be observed using synchrotron radiation excited photoelectron spectroscopy (SEPES). The characteristics of the beam line optics and monochromators currently available at different sources of radiation, e.g., SPEAR, Stanford and DESY, Hamburg, prohibit high resolution SEPES above  $\approx 300$  eV. It is then not possible to excite the O 1s level and the cross-section for exciting the O 2s level with these photon energies is low. The third structure induced in the spectra of oxygen will be

derived from the O 2p level. The O 2p electrons are valence electrons, bonding the oxygen atoms to the metal surface. They hybridize with the metal valence orbitals and form chemical bonds which, for Al and Mg metals, are ionic. When oxidation is complete, they are part of the oxide valence band. The cross-section for the O 2p level is large for the photon energies available and the induced O 2p structure in the valence band can be studied with good accuracy. The shape of this structure and its binding energy can be compared with results from model calculations assuming different oxygen-metal atom configurations. So far, some progress in determining adsorption sites for the Al-O system has been made in this manner [4,5]. Because of its broad band character, the O 2p structure is not suited for monitoring the relative uptake of oxygen at different stages of oxidation. Uptake rates are best studied by monitoring a structure in the spectrum associated with an adsorbate core level. This cannot be done using SEPES, but the SEPES measurements can be complemented by either X-ray excited photoelectron spectroscopy (XPS) of the O 1s level or by Auger electron spectroscopy (AES) of the  $O_{KLL}$  transition. Both these types of measurements have been shown to yield accurate uptake curves for oxygen [2]. The metal substrate levels are also influenced by the oxidation process. As mentioned above, the metal valence levels participate and are modified by bonding to the oxygen atoms. However, for both Mg and Al, we can also study the 2p core levels with extreme surface sensitivity ( $\approx 5\text{\AA}$ ) and good energy resolution (0.3 eV) to obtain information about shifts in the binding energies of these levels for the substrate surface atoms. These 'chemical' shifts will tell us if

the chemical state of the surface atoms has been changed. For some time, it was believed that the only chemical states which could be studied by examining substrate core levels were the clean metal state and the fully oxidized state [6]. Intermediate states could only be determined by looking for shifts in the binding energies of the adsorbate core levels (O 1s). By excitation with synchrotron radiation, the contrast and resolution of the substrate surface atom binding energies are good enough to detect intermediate oxidation states, e.g., chemisorption phases. Effects in these surface atom core levels due to changes in the chemical state are easily detected, e.g., broadening and changes in loss (plasmon) structures. In addition, by changing the photon energy, the kinetic energies of the excited electrons change, i.e., the probe depth and thus the contrast between the surface and bulk electronic structures can be varied.

These advantages; high resolution, high surface sensitivity and continuously-tunable photon energy, make SEPES an excellent tool for oxidation studies. Its main limitation is that with the monochromators and beam optics available at present, the O 1s level cannot be studied.

#### EXPERIMENTAL

The measurements reported here were performed at two different storage ring radiation sources. The Al-O system was investigated at SSRL (Stanford Synchrotron Radiation Lab), Stanford and the Mg-O system at HASY (Hamburg Synchrotron Radiation Lab), Hamburg. The experimental set-ups were similar at both facilities. Monochromatized photons [7,8] in the energy range

10-300 eV were directed on to the samples. The kinetic energies of the excited electrons were analyzed in the angle-integrating mode by CMA's (cylindrical mirror analyzers, PHI 15-255G). The combined resolution of the radiation and electron kinetic energy was in the range 0.3-0.4 eV for all data reported. The Al and Mg films were evaporated in situ, the pressure rising from  $2 \times 10^{-10}$  Torr to  $1 \times 10^{-8}$  Torr during evaporations. Cleanliness was checked by monitoring the O 2p structure in valence bands. The O 2p intensities for clean films were always < 0.01 of the intensity at 'monolayer' coverage. The main difference in the set-ups was that at SSRL a p-polarized light configuration was used, compared to the s-polarized configuration used at HASY.

#### RESULTS AND DISCUSSIONS

##### Magnesium

The process of initial oxidation in Mg was followed by studying the Mg 2p core level ( $E_B^F = 50$  eV) and the valence band region for increasing amounts of oxygen exposure. The exposure range was chosen from the results of an AES study of the  $O_{KLL}$  peak produced in the oxidation of Mg. Fig. 1 shows the AES results: we have defined 'monolayer' coverage as the value at which the  $O_{KLL}$  peak reaches 90% of its final amplitude. This corresponds to an exposure of  $\approx 20$  L  $O_2$ . It should be recognized that the cessation in the growth of the  $O_{KLL}$  peak can have different causes; when the surface becomes covered with chemisorbed oxygen atoms or a thin oxide layer, oxidation proceeds at a much slower rate. If, on the other hand, diffusion of oxygen atoms into the metal takes place, the metal can

oxidize to a depth of several atomic layers. The change in the oxygen uptake curve is then related to the fact that the oxide layer becomes thicker than the spectroscopic probe depth. For  $O_{KLL}$  electrons, the probe depth can be estimated to be 10-15 Å [9].

Fig. 2 shows the Mg 2p peaks from a number of oxygen exposures, providing a coverage ( $\theta$ ) range from  $\theta = 0$  to  $\theta \geq 1$ . The clean metal Mg 2p peak is narrow (FWHM = 0.64 eV) and has an asymmetric line shape [10]. When interacting with oxygen, a new structure develops at higher binding energies: for oxygen exposures above 6 L  $O_2$ , this becomes a Gaussian peak (FWHM = 1.71 eV) shifted to higher binding energies by 1.3 eV. This new peak is due to Mg atoms which have reacted with oxygen. These bonds are ionic, but the magnitude of the chemical shift (1.3 eV) is such that there is not a complete transfer of Mg electrons to the oxygen atoms to obtain the formal valence of 2, but rather a less drastic redistribution of the electronic charge. The value of the shift, 1.3 eV, is identical to that observed in heavily-oxidized Mg and in bulk MgO [11,12].

It can be seen from Fig. 2 that for low coverages the oxygen-related structure is very broad and featureless. We interpret this as being due to the formation of a nucleation state, in which 'MgO' nuclei are produced at defect sites on the film surface. Further exposures make these oxide nuclei grow, forming islands of MgO and we can observe the oxide peak in the Mg 2p spectrum, shifted chemically by 1.3 eV. This interpretation is supported by spectra taken in the Mg valence band region (Fig. 3). At low coverages, a broad, undefined O 2p derived structured peaked - 6 eV below the Fermi level

observed as is an increased intensity of emission between the Fermi level and the O 2p peak at - 6 eV. We relate these observations to an oxide nucleation stage. At higher oxide coverages, the O 2p emission displays a two peak structure, the peak separation and shape being very similar to these of the MgO bulk oxide crystalline valence band [12].

Two comments about the Mg 2p peak in the clean and oxidized state are worth making:

First: the line shape. Why does the Mg 2p peak change from being narrow and asymmetric in the clean state to a broad Gaussian peak in the oxidized state?

Second: the Mg 2p emission intensity. In the oxide, the Mg 2p emission is about twice that from the clean metal at a photon energy of 120 eV ( $E_k = 70$  eV).

The narrow, asymmetric line shape for the 2p core level in Mg has been discussed extensively in the literature [10]. The broadening of the 2p levels upon oxidation was first suggested to be a lifetime effect [13]. The presence of the O 2p and O 2s levels in the oxide opens up new Auger decay channels for the Mg 2p core hole, e.g., interatomic Auger transitions of type  $L_{2,3} V_{O2p} V_{O2p}$ . Such transitions shorten the core-hole lifetime and broaden the photoelectron peak observed. This explanation could be ruled out when X-ray emission data showed that the Mg  $K\alpha_{1,2}$  line widths were essentially the same in the pure metal as in the oxide. Since  $K\alpha_{1,2}$  emission involves the Mg 2p level, one must conclude that the broadening of the Mg 2p photoelectron peak observed in the oxide cannot be due to shorter lifetime.

Citrin et al. [14] suggested a broadening mechanism specific for core levels in polar materials observed by XPS or by AES. Their idea is that after excitation the solid is left in different excited states, each consisting of the core hole and a number of excited phonons. The strong coupling of the core hole to the lattice is possible because in wide band gap insulators passive electrons are ineffective in screening the hole. Since both the creation and the adsorption of phonons are possible, the line shape will be Gaussian (symmetric). A model calculation for MgO [14] gives a value of the linewidth of 0.93 eV at 300 K for the Mg 2p level due to this mechanism. The observed linewidths is still broader. This was also stated in Citrins work, but no really satisfactory explanation has been given. However, we conclude that the main part of the broadening of the Mg 2p level in the oxide is due to the phonon mechanism.

The increase in emission intensity from the Mg 2p level in the oxide as compared to that in the clean metal is unexpected. The photoemission intensity from a core level can be written

$$I = \text{const.} \cdot \sigma \cdot \rho \cdot \lambda \quad (2)$$

$\sigma$  = cross-section for the core level at a given photon energy

$\rho$  = density of emitting atoms

$\lambda$  = excited electron scattering length.

The cross-sections ( $\sigma$ ) for the Mg 2p levels in Mg and MgO are similar.  $\rho_{\text{MgO}}/\rho_{\text{Mg}}$  equals 1.23. The measured intensity ratio ( $I_{\text{MgO}}/I_{\text{Mg}}$ ) obtained from Fig. 2 is 2.1. This implies a

ratio ( $\lambda_{\text{MgO}}/\lambda_{\text{Mg}}$ ) of  $\approx 1.7$ . A calculation based on the electron density in the valence band and taking the possible influence of core levels into consideration [15] predicts  $\lambda_{\text{MgO}}/\lambda_{\text{Mg}} = 0.8$  for electrons having kinetic energies of 200 eV. In the present case, the kinetic energy of the excited electrons is only 70 eV, so that the calculation is not fully relevant. The results show that one has to be cautious in estimating scattering lengths in wide bandgap materials from calculations based on a free electron gas formalism, in which the electron density ( $n_e$ ) is the only parameter [16]. A source of error in our estimate of  $I_{\text{MgO}}/I_{\text{Mg}}$  is that we have not taken into account lost emission intensity from the main 2p peak because of intrinsic satellites [17]. This makes our measured value of the intensity ratio an upper limit. If we use the experimentally obtained  $\lambda_{\text{MgO}}/\lambda_{\text{Mg}}$  of 1.7 and calculate the  $\lambda_{\text{Mg}}$  from the free electron formalism, we obtain an lower limit on the oxide thickness at 'monolayer' coverage of 10 Å. The actual thickness is hard to estimate since it is difficult to calculate from the results in Fig. 2 actually how much clean metal 2p contribution is left in the 20 L O<sub>2</sub> curve.

#### Aluminum

Considerable experimental effort has been made to attempt to understand the oxidation of polycrystalline Al films [18-20] and AES data have shown that 'monolayer' coverage occurs for an oxygen exposure of  $\approx 150$  L O<sub>2</sub>. Compared to Mg, the rate of uptake is an order of magnitude smaller. Fig. 4 shows photoelectron spectra of the Al 2p ( $E_B^F = 73$  eV) region for an exposure range corresponding to coverages from  $\theta = 0$  up to  $\theta < 1$ .

As in Mg, the clean metal Al 2p peak is narrow and asymmetric (FWHM = 0.85 eV). However, at low coverage, oxidation proceeds in a different manner. Instead of a broad, undefined structure at higher binding energy, a new well-defined peak shifted towards higher binding energy by 1.3 eV appears. This new peak has not been observed in earlier XPS work on the oxidation of Al [21,22]. The shift observed is not characteristic of any known Al compound. For increasing exposures, this new peak gradually disappears and the high binding energy side of the 2p region becomes dominated by a Gaussian peak (FWHM = 1.64 eV) chemically shifted by 2.7 eV. This peak has been shown by XPS work to be characteristic of heavily oxidized Al or bulk  $\text{Al}_2\text{O}_3$  [12,21]. In view of the formal valencies for MgO (+2) and  $\text{Al}_2\text{O}_3$  (+3), the larger shift of the observed 2p peak in the latter is to be expected. This trend is continued for  $\text{SiO}_2$  (+4), the 2p peak shift being 3.9 eV compared to clean Si [23]. No attempts have been made to assign theoretically an observed chemical shift to a specific oxide structure. We are thus left with the possibility of comparing the observed shifts with experimental data from compounds of known structure. For structure determination, different types of absorption spectroscopies are much more powerful [24].

Fig. 5 shows the O 2p part of the Al valence band region for coverages above and below monolayer. Even for low coverages, the O 2p emission has a twopeak shape, a peak at - 7.0 eV and a shoulder at - 9.3 eV below  $E_F$  respectively. At high coverages, a significant broadening of the O 2p structure occurs. This broadening takes place very abruptly at  $\theta \approx 1$ . We interpret this broadening as being associated with a transition

between an intermediate oxidation (chemisorption) state and a state of amorphous oxide formation on the surface. It is puzzling that the Al 2p region shows a continuous transition between the intermediate and the bulk-like oxide states, whereas the change in O 2p emission has almost phase transition behaviour. Later work on single crystals [2,25] showed that the intermediate oxidation state was uniquely linked to the (111) crystal face. The conclusion which must be drawn is that our polycrystalline Al films are textured (111) crystallites. The main difference observed between the oxidation of Al films and Al (111) single crystals was in an abrupt O 2p broadening: for Al (111) single crystals, the O 2p peak broadened continuously up to  $\theta = 1$ . The cause for this difference is not clear.

If we compare the Mg 2p and Al 2p regions for coverages  $\theta \geq 1$ , we find that the oxide 2p peaks have similar shapes and linewidths, which means that phonon broadening is equally effective in both cases. Norman and Woodruff [26] have analyzed the difference in the 2p emission intensities of the oxides and for both Mg and Al. Their results on Mg agree with our Mg data and for Al they also find an increased 2p emission from the oxide. At monolayer coverage the intensity ratio  $I_{\text{AlO}}/I_{\text{Al}}$  is quite different for Mg than for Al. Qualitatively, one can say that the oxide layer is much thinner on Al.

#### CONCLUSIONS

The clean and oxidized states of Mg and Al show strong similarities. The metal 2p peaks in the clean state are narrow and asymmetric, with characteristic loss structures following the main peak. The oxide 2p peaks show broad chemically shifted



Gaussian peaks. For both metals, increased 2p core level emission is observed from the oxides as compared to the clean metals, which is interpreted as being due to a larger scattering lengths in the oxides for electrons of comparable kinetic energies. This difference in scattering lengths between the metals and their oxides disappear monotonically when the kinetic energies of the electrons increase (higher excitation energies) [27].

Oxide nucleation seems to be quite different for Mg and Al films. The Al films are to a large degree made up of (111) crystallites. On these crystallites, a unique chemisorption state exists. Nucleation proceeds first into this chemisorption phase and, with increasing oxygen exposures ( $\theta > 1$ ), the chemisorbed layer is transformed into an amorphous oxide. For Mg oxide nuclei are directly formed on the film surface. These nuclei grow by island formation and a complete oxide layer is formed at monolayer coverage.

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FIGURE CAPTIONS

- Fig. 1 Intensity change for the  $O_{KLL}$  and  $Mg_{LVV}$  peaks as a function of oxygen exposure. The oxygen exposures are given in langmuirs ( $IL = 10^{-6}$  Torr s).
- Figs. 2a and b Photoelectron spectra of the Mg 2p core region for clean and oxygen exposed magnesium films measured at an excitation energy of 120.3 eV.
- Fig. 3 The O 2p surface resonance in the valence band region for clean and oxygen exposed magnesium films at a photon excitation energy of 50.8 eV.
- Fig. 4 Photoelectron spectra of the Al 2p region for clean and oxygen exposed aluminum films measured at an excitation energy of 170 eV.
- Fig. 5 The O 2p surface resonance in the valence band region for clean and oxygen exposed aluminum films at a photon excitation energy of 50 eV.

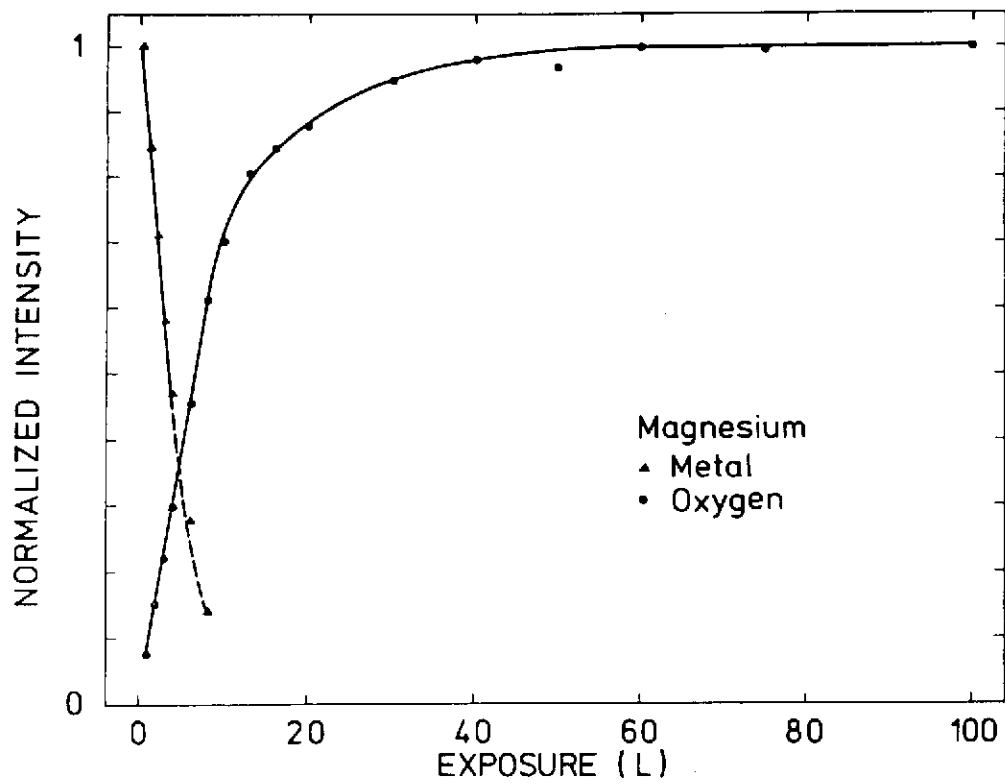


Fig. 1

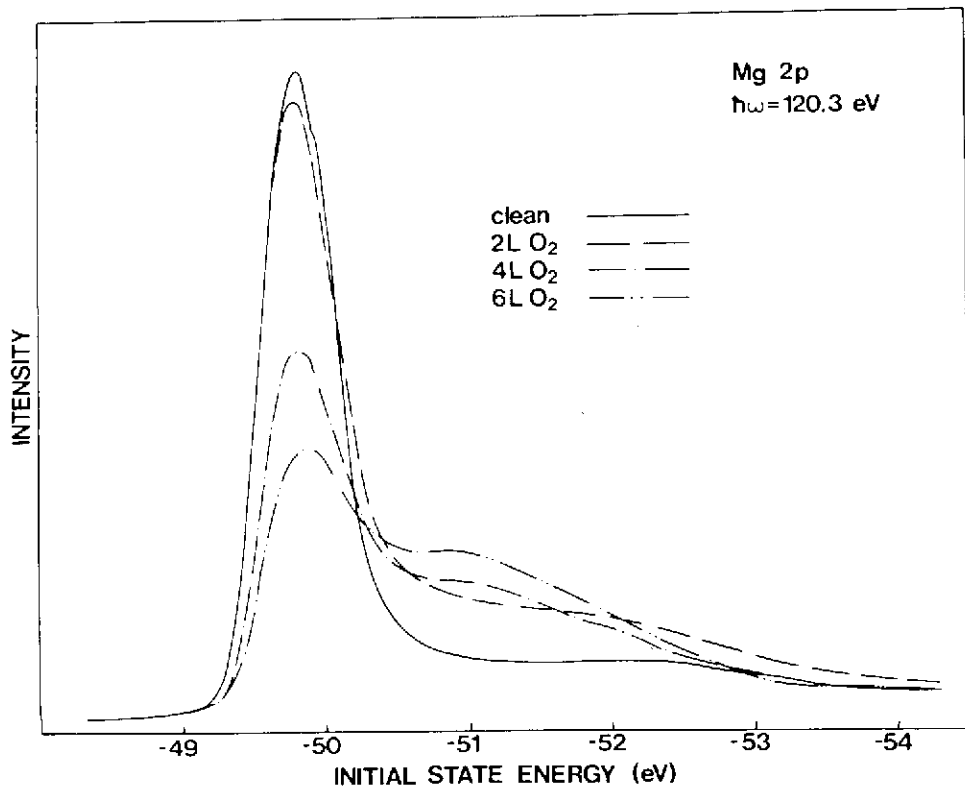


Fig. 2a

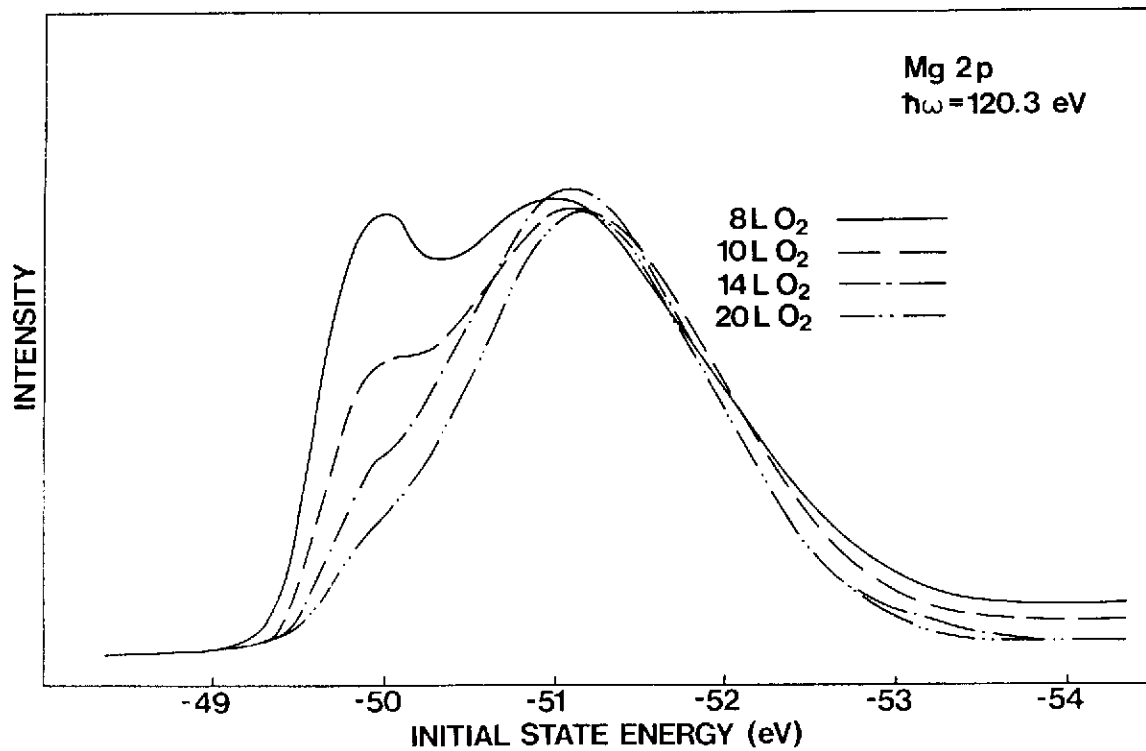


Fig. 2b

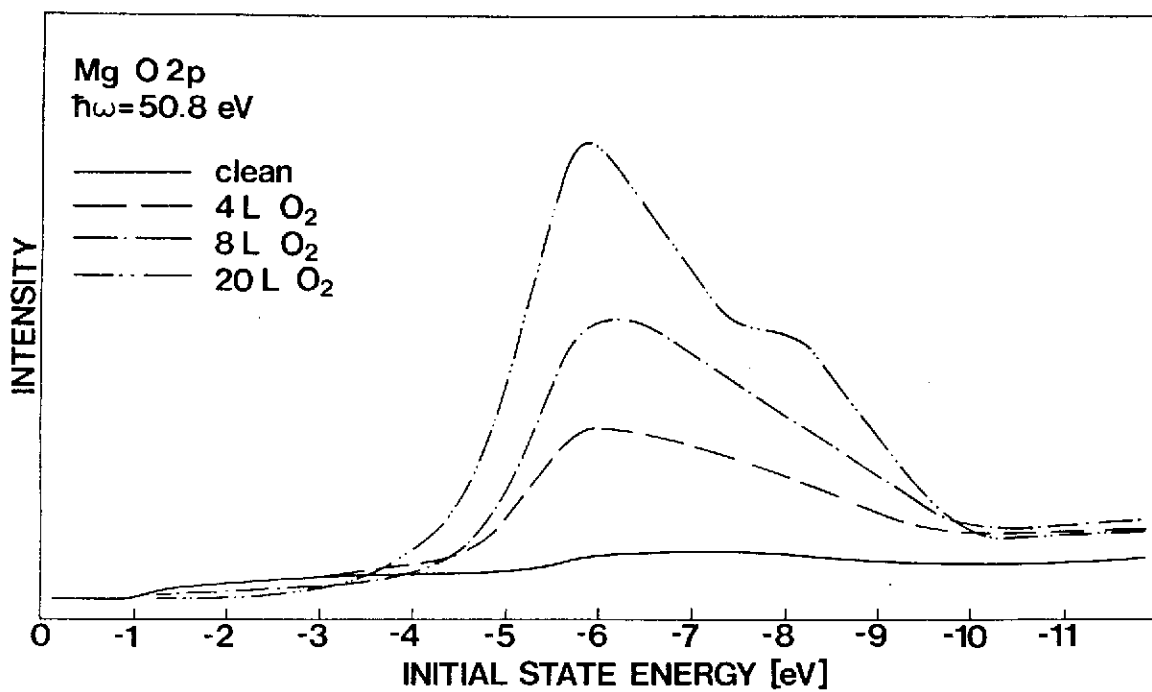


Fig. 3

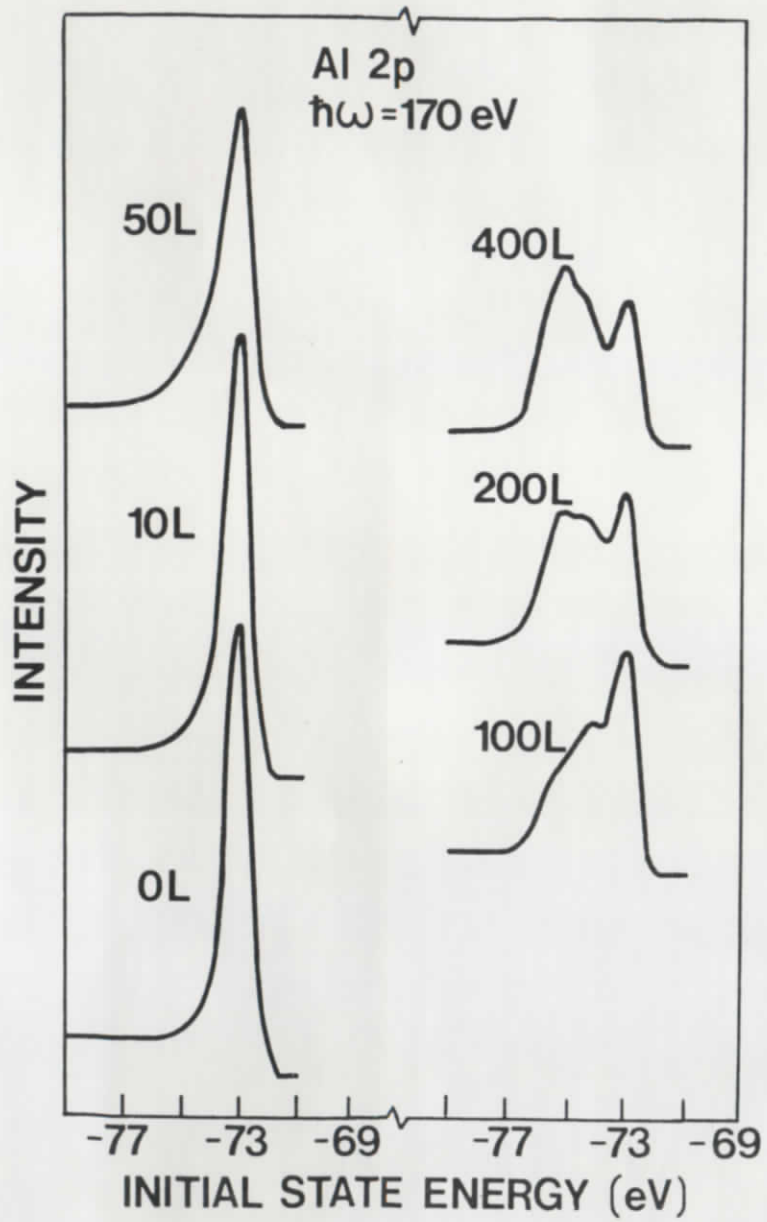


Fig. 4

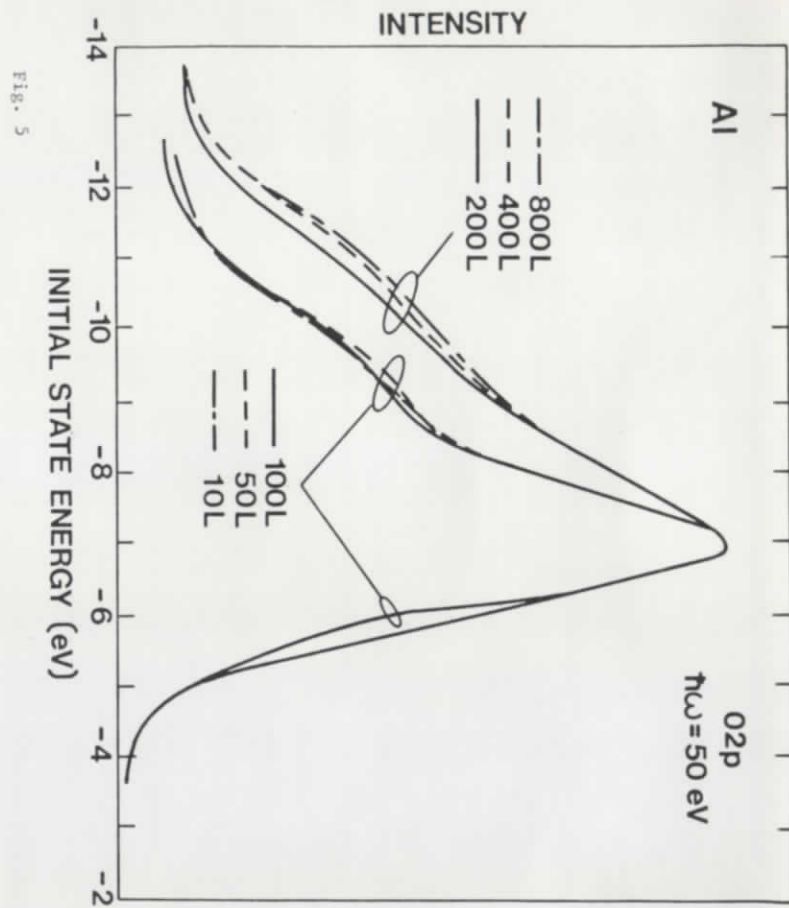


Fig. 5

