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Adsorption of Chlorine on Clean and on Oxygen  
Pre-Exposed Al(111)

by

V.M. Bermudez and A.S. Glass

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ADSORPTION OF CHLORINE ON CLEAN AND ON OXYGEN PRE-EXPOSED Al(111)

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ABSTRACT

The adsorption of Cl<sub>2</sub> on clean and on O<sub>2</sub> pre-exposed Al(111) has been studied using Auger and electron energy loss spectroscopies, low energy electron diffraction, temperature programmed desorption and work function measurement. Near room temperature chlorine forms a disordered layer in a two-step process consisting of adsorption at surface sites, dominating at low exposure, followed by population of subsurface sites at higher exposure. Surface adsorption is characterized by a sticking coefficient of about 0.1, an increase in work function of about 1 eV and a desorption peak at about 200°C. The subsurface phase exhibits a smaller sticking coefficient and work function change and no distinct desorption peak. Pre-adsorbed O blocks formation of subsurface species but not those formed in the initial adsorption step. Cl<sub>2</sub> does not displace pre-adsorbed O, but O<sub>2</sub> displaces some subsurface Cl. Chlorination is found to occur inhomogeneously rather than uniformly in a layer-by-layer mode.

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## INTRODUCTION

The oxidation of Al (by O<sub>2</sub> or H<sub>2</sub>O) is one of the more thoroughly studied reactions in contemporary surface science<sup>1</sup>. The full range of available techniques has been applied to the O<sub>2</sub>/Al system, and a detailed mechanism for at least the initial stages of the oxidation process has been formulated<sup>2,3</sup>. However, little work has been done on the reaction of Al with other oxidizers such as halogens. In particular, the reaction of Cl<sub>2</sub> with Al is important as a basis for "dry processing" in the fabrication of integrated circuit interconnections. Because of the reactivity of Al with O<sub>2</sub> and H<sub>2</sub>O and the nearly unavoidable presence of such contaminants in realistic processing environments, it is also necessary to understand the effects of adsorbed O on the Al-Cl<sub>2</sub> reaction.

Early work for Cl<sub>2</sub> on polycrystalline Al<sup>4</sup>, using Auger electron spectroscopy (AES), measurement of the work function change ( $\delta\Phi$ ) and ellipsometry, suggested adsorption in a molecular precursor state which then dissociates to give chemisorbed Cl. Most recent work<sup>5-12</sup> has been done in the context of plasma etching of Al in Cl-containing media. Etching of clean (i.e., oxide-free) Al by Cl<sub>2</sub> occurs spontaneously at room temperature and above<sup>6,8-11</sup> and is not significantly enhanced by either gas-phase predissociation<sup>11</sup> of the Cl<sub>2</sub> or simultaneous ion bombardment<sup>6,8</sup>. The room-temperature etch rate, roughly proportional to Cl<sub>2</sub> pressure in the 10<sup>-7</sup> to 10<sup>-5</sup> torr range, is about 1 Å/min at 10<sup>-7</sup> torr<sup>8</sup>; the rate for HCl is much slower<sup>6</sup>. The desorbing species<sup>9</sup> is mainly Al<sub>2</sub>Cl<sub>6</sub> near 25°C and AlCl<sub>3</sub> at about 200°C. Chemisorption of Cl occurs<sup>9,10</sup> prior to the onset of rapid etching, and under steady-state conditions a surface chlorinated layer remains. In one of the few investigations of this layer, Park et al.<sup>8</sup> reported Al 2p photoemission data showing satellites at about 2 and 3 eV higher binding energy than the substrate peak, suggesting two distinct AlCl<sub>x</sub> surface species.

The goal of the present work is an understanding of the adsorption of  $\text{Cl}_2$  on  $\text{Al}(111)$  and the effects of pre-adsorbed oxygen on the  $\text{Al-Cl}$  interaction. AES, temperature programmed desorption (TPD) and  $\delta\Phi$  measurements were used as the principal experimental techniques. Low energy electron diffraction (LEED) and electron energy loss spectroscopy (ELS) results will also be reported.

#### EXPERIMENTAL DETAILS

Details concerning the apparatus and sample preparation have been given previously<sup>13</sup> in connection with infrared spectroscopic studies of  $\text{O}_2/\text{Al}(111)$ . The sample used was the well-polished 2.5-cm diameter specimen<sup>13</sup>; after  $\text{Ar}^+$ -ion bombardment and annealing the total impurity level (C, O and Cl) was  $< 0.005$  monolayers, based on tabulated AES sensitivity factors<sup>14</sup>. All experiments (except TPD) were done at a sample temperature of 32-42°C. ELS data (0.5 eV resolution) were obtained with a 0.1  $\mu\text{A}$ , 50 eV primary beam ( $\delta E = 0.25$  eV modulation,  $d[\text{EN}(E)]/dE$  mode). For AES a 0.5  $\mu\text{A}$ , 3 keV beam ( $\delta E = 2$  eV) was used, and scans were done quickly (5 eV/sec, 0.1 sec time constant) to minimize electron dose. The beam from the coaxial electron gun was incident normal to the surface. The data were frequently checked for electron beam effects (stimulated desorption or adsorption of Cl<sup>15</sup>, C or O<sup>16</sup>). Where observed, such effects will be noted. TPD was performed using a computer-interfaced quadrupole mass spectrometer (QMS), with channel multiplier, fitted with a quartz-glass enclosure<sup>17</sup> around the ionizer (removed for residual gas analysis, RGA). The heating rate was not constant, varying from 0.8 to 2.4 °C/sec.  $\delta\Phi$  data were obtained, to within  $\pm 20$  meV, using the retarding potential method and a 40 eV, 0.5  $\mu\text{A}$  beam from the Auger gun. The sample current,  $I$ , vs bias,  $V$ , was measured, and the shift of the peak in  $dI/dV$  vs  $V$  with  $\text{Cl}_2$  exposure gave  $\delta\Phi$  directly. The Cl coverage on (and, therefore, the work function change of) the hot tungsten gun filament is expected to be very low<sup>18</sup>.

The Cl<sub>2</sub> (>99.5% pure) was used without further purification. The Cu gasket assembly of the leak valve (Varian 951-5106) was electroplated with Au to retard corrosion. Exposures are given in Langmuirs (L), where 1 L = 10<sup>-6</sup> torr-sec = 2.41x10<sup>14</sup> Cl<sub>2</sub>/cm<sup>2</sup>, and were performed under computer control<sup>13</sup> by dynamic backfilling to 1-3x10<sup>-7</sup> torr (turbopump valved off and ion pump left open to the chamber). The Cl<sub>2</sub> was evacuated to ≤8x10<sup>-10</sup> torr before turning on any electron beam. Pressure was measured with either a nude hot-filament ionization gauge or a cold-cathode gauge; readings in both cases were the N<sub>2</sub>-calibration values. The Cl<sub>2</sub> sensitivity relative to that for N<sub>2</sub> is estimated<sup>19</sup> to be 1.9.

RGA (based on uncorrected parent-ion relative intensities) showed small amounts of CH<sub>4</sub>, CO and CO<sub>2</sub>. CO and CO<sub>2</sub> (and, presumably, CH<sub>4</sub>) are known<sup>20</sup> not to react at low pressure with Al at 25°C in the absence of electron irradiation, and no C accumulation was seen during these experiments. The small quantity of H<sub>2</sub> detected was shown to have no effect on adsorbed Cl, unlike the case<sup>21</sup> for Cl on Pt(111) and (110); no loss in Cl Auger signal was observed when the sample was first exposed to 10 or 50 L of Cl<sub>2</sub> and then to 10 L H<sub>2</sub>. H<sub>2</sub>O and O<sub>2</sub> were found at a level of (H<sub>2</sub>O+O<sub>2</sub>)/Σ(Cl<sub>2</sub>) ≈ 1.2% (where "Σ" indicates the sum of all isotopic species), and, following exposure of a clean Al surface to 80 L Cl<sub>2</sub>, the resulting O atomic fraction was about 0.05. However, later experiments using higher purity Cl<sub>2</sub> (total H<sub>2</sub>O and O<sub>2</sub> level ≤0.4%) showed the same degree of O contamination, suggesting that the source may, in part, be reaction of H<sub>2</sub>O in the UHV background with adsorbed Cl. For O<sub>2</sub> pre-exposed surfaces the additional O accumulated during Cl<sub>2</sub> exposure was negligible.

The major contaminant<sup>22</sup> was HCl (probably formed by reaction of Cl<sub>2</sub> with H-containing species on internal surfaces of the chamber). Initially (i.e., for the first of a series of exposures) Σ(HCl)/Σ(Cl<sub>2</sub>) was about 50% and decreased quickly to about 15% with successive exposures. These are

upper limits since experiments with different pumping rates and ionizer emissions show that a large part of the HCl seen in RGA is produced in the QMS ionizer. To assess the effect of HCl, a clean surface was exposed to a 1:1 mixture of HCl and DCl (a supply of pure HCl was not available). Based on 15% as an upper limit to the HCl concentration, 80 L of Cl<sub>2</sub> would involve 12 L of HCl. Exposure to 12 L of the HCl/DCl mix gave a Cl Auger peak smaller than that for 2 L Cl<sub>2</sub>, indicating that HCl is much less reactive with clean Al than is Cl<sub>2</sub>, as previously reported<sup>6</sup>. HCl is somewhat more reactive with an O pre-exposed Al surface, as reported<sup>23</sup> for Pb(110). Following a 5 L O<sub>2</sub> exposure, 12 L of HCl/DCl gave a Cl peak equivalent to about 5 L Cl<sub>2</sub> on the clean surface.

## RESULTS and DISCUSSION

### (a) Auger

Fig. 1 summarizes the AES data. The results (for a clean Al surface) were independent of whether Cl<sub>2</sub> pressure was measured with a hot-filament or cold-cathode ionization gauge, indicating that excitation or dissociation of Cl<sub>2</sub> by the hot filament is not a major factor in adsorption. There was no significant difference in Cl uptake for a clean unannealed Ar<sup>+</sup>-ion bombarded sample, indicating that surface disorder is not an important factor. A decrease in the rate of change of the Cl and Al peak-to-peak heights (PPH's) occurs at about 10-15 and 20-30 L, respectively. The shape of the main Al L<sub>2,3</sub>VV peak (68 eV) does not change appreciably with Cl<sub>2</sub> exposure. Hence, the coverage ( $\theta$ ) can be estimated, assuming a partial monolayer adsorbed on top of the substrate, using  $I(\theta)/I(0) = 1 - \theta[1 - \exp(-d/\lambda \cos\phi)]$ , where  $I(0)$  is the clean-surface Al PPH and  $\phi = 42^\circ$  the electron collection angle. For  $d = 2.17 \text{ \AA}$  (sum of Al and Cl covalent radii) and  $\lambda = 3.5 \text{ \AA}$  (as for clean Al<sup>24</sup>),  $\theta \sim 0.61$  monolayers is obtained at 20 L. In the present discussion a monolayer is defined as a continuous layer of close-packed Cl atoms. Using the Cl<sub>2</sub> ion gauge correction given above and a value of  $9.82 \times 10^{14}$  Cl/cm<sup>2</sup> at

$\theta = 1$  (based on a Cl van der Waals diameter<sup>21</sup> of 3.6 Å), one estimates an initial Cl<sub>2</sub> sticking coefficient of  $S \approx 0.12$ , vs 0.01 as reported by Smith<sup>4</sup> for Al films. The difference arises mainly from the fact that Smith<sup>4</sup> (using ellipsometry) determined that  $\theta = 1$  was achieved at about 200 L. Other S values, measured under etching conditions<sup>8,9,11</sup>, may not be directly comparable with the initial S.

Pre-adsorbed O has a striking effect on Cl uptake. As discussed in refs. 1-3, 13 and works cited, the initial oxidation of Al proceeds in three (possibly overlapping) phases. The first, in order of increasing coverage, is the population of isolated surface and subsurface sites, followed by the clustering of sites to form rudimentary patches of oxide and, finally, the slow growth of an aluminum oxide film. The different stages can be distinguished by, for example, Auger PPH plots and changes in the Al L<sub>2,3</sub>VV line-shape<sup>2,3,13</sup>. Under the present conditions, the second (third) stage begins at about 5 (20) L of O<sub>2</sub>. For the O<sub>2</sub> pre-exposed surface the initial Cl uptake (up to about 15 L) is unaffected, but further adsorption is very slow (in comparison to the clean surface) beyond 20 L. Several experiments were done for lower (10 or 20 L) O<sub>2</sub> pre-exposures. The results are consistent with those in Fig. 1; namely, the Cl uptake at lower exposures is unaffected, while that at higher values is slowed. However, because of the significant electron beam effect on the Cl layer (as shown by points labelled "A" in Fig. 1) and the accumulation of small amounts of O during exposure of the unoxidized surface to Cl<sub>2</sub>, the most meaningful comparison is between samples with and without a large (50 L) O<sub>2</sub> pre-exposure.

The question of desorption of one species by the other has been considered. Fig. 1 shows that Cl<sub>2</sub> exposure does not produce a significant desorption of pre-adsorbed O. In addition, only a small (<10%) loss in Cl signal was observed when surfaces pre-exposed to 10 L of Cl<sub>2</sub> were subsequently exposed to 100 L of O<sub>2</sub>. However, a similar O<sub>2</sub> exposure reduced by

about 20% the Cl AES signal for clean Al pre-exposed to 80 L Cl<sub>2</sub>, suggesting that the Cl species formed at high coverage are more readily displaced by O<sub>2</sub> than are those present at low coverage. These results may be compared with those for other metals. For Ag(331)<sup>25</sup>, O<sub>2</sub> pre-exposure does not greatly inhibit Cl uptake, but O<sub>2</sub> does displace previously adsorbed Cl. For Ag(110), chlorination is found<sup>26,27</sup> to inhibit subsequent uptake of oxygen. Clean Pb(110) is found<sup>23</sup> to be much less reactive with HCl than with Cl<sub>2</sub> unless pre-exposed to O<sub>2</sub>, in which case HCl reacts with surface oxide to form a chlorinated layer with desorption of H<sub>2</sub>O. O<sub>2</sub> does not displace Cl from Pb(110) pre-exposed to Cl<sub>2</sub>.

We have considered (and dismissed) one possible explanation for the decrease in the rate of Cl uptake above 20-30 L; namely, the onset of spontaneous etching<sup>8-10</sup> (i.e., desorption of AlCl<sub>3</sub> or Al<sub>2</sub>Cl<sub>6</sub>). Two observations argue against this. First, previous work<sup>9,10</sup> using a quartz crystal microbalance to measure etch rate indicates that near 25°C etching does not begin before Cl<sub>2</sub> exposures in excess of 10<sup>3</sup> L. Second, with the sample in front of the QMS in a background of 2x10<sup>-7</sup> torr Cl<sub>2</sub>, no etch products were detected. For an etch rate<sup>8</sup> of 1 Å/min the product flux rate would be about 1x10<sup>13</sup>/cm<sup>2</sup>-sec which would have been readily detectable.

#### (b) Work Function

Fig. 2 shows the  $\delta\Phi$  results. In the first stage of adsorption  $\delta\Phi$  increases to a maximum of +1.08 eV, suggesting that negatively charged species (e.g., Cl<sup>-</sup> or Cl<sub>2</sub><sup>-</sup>) are formed "above" the surface. For a coverage of  $\theta \approx 0.61$  and  $\delta\Phi = +0.90$  at 20 L, one estimates  $\mu \approx 0.40$  D (Debyes) for the surface-normal dipole. This value is comparable to those for Cl on the (111) surface of other face-centered cubic metals (0.14 D<sup>21</sup> for Ni and 0.25 D<sup>21</sup> or 0.56 D<sup>28</sup> for Pd), suggesting that the present estimate of Cl coverage on Al is reasonable. In the second stage,  $\delta\Phi$  remains approximately constant, with some indication of a turn in the negative direction at higher exposure. The

nearly constant  $\delta\Phi$ , with a large increase in Cl coverage, indicates that either uncharged species are being formed or else ions are being distributed so as to produce only a small net contribution to the surface-normal dipole field (i.e., adsorption at surface and subsurface sites). Because of the high electronegativity of Cl, the latter explanation is considered more reasonable. Subsurface Cl adsorption may be accompanied by rearrangement of surface Al atoms to accommodate the large halogen species. Recently, concurrent surface and subsurface Cl adsorption has also been proposed for Cl<sub>2</sub> on Pb(110)<sup>23</sup> and on polycrystalline Mg<sup>29</sup> on the basis of angle-resolved core-level photoemission data. With pre-adsorbed O, a large positive  $\delta\Phi$  is seen for a small Cl<sub>2</sub> exposure, followed by saturation of  $\delta\Phi$  at a level well below that for the clean surface. The saturation value of  $\delta\Phi$  was found to vary considerably from run to run for O<sub>2</sub> pre-exposed surfaces (unlike for clean Al), suggesting that  $\delta\Phi$  is very sensitive to the distribution of Cl and O between surface and subsurface sites.

### (c) Temperature Programmed Desorption

Fig. 3 shows the TPD data. AES indicated that heating to about 440°C, following a total of 80 L Cl<sub>2</sub>, removed all near-surface Cl (through either desorption or subsurface diffusion) except for about 5% of the initial coverage. Cl was the only desorption product detected; Cl<sub>2</sub> and AlCl<sub>3</sub> were not observed, suggesting that Cl<sub>2</sub> adsorption is predominantly dissociative. Following Cl<sub>2</sub> exposure and recording of the TPD, another TPD scan was obtained as a "background". Subtraction from the original TPD then reduced the effect on the data of slow desorption of Cl from the sample holder, heater leads, etc. At sample temperatures above 300°C this "background" became significant, making TPD data difficult to obtain.

Following exposure of the clean surface to 10 L of Cl<sub>2</sub> a single broad peak was observed at about 200°C. The variation in temperature across the sample (observed using an infrared pyrometer) was much less than the width

of the TPD peak. "Calibration" vs the TPD of Ar implanted by 3 keV Ar<sup>+</sup> ion bombardment (see Appendix) shows that the integrated intensity of the Cl TPD peak is accounted for by desorption of roughly 50% of the surface Cl; whereas, AES after TPD indicates a reduction of >90% in the Cl PPH. No increase in the integrated TPD peak intensity is observed for 50 L Cl<sub>2</sub>; whereas, AES (Fig. 1) shows a large increase in the initial Cl coverage, and AES after TPD shows a reduction of about 75% in Cl PPH. This suggests that the 200°C peak is associated with Cl at surface sites, which saturate at lower exposures. For the subsurface Cl formed above 20 L, no distinct TPD peak was detected. It is unknown at present whether the subsurface Cl desorbs over a very broad temperature range, desorbs in a peak above 350°C, or diffuses into the bulk. Subsurface diffusion, which has been noted previously<sup>4,9,10</sup> for Cl on polycrystalline Al at room temperature, is considered the most likely explanation for the fact that not all the Cl at surface sites is accounted for by the 200°C TPD peak. Also unknown is the origin of the doublet structure in the Ar TPD and the significance of the fact that the Ar and Cl TPD peaks occur at nearly the same temperature.

#### (d) Model for Al Chlorination

The results are interpreted according to the following model. The Auger,  $\delta\Phi$  and TPD results clearly indicate that Cl<sub>2</sub> adsorption is a two-phase process. At low exposure, Cl<sub>2</sub> is adsorbed rapidly at surface sites, giving  $\delta\Phi > 0$  and a TPD peak at about 200°C. Above 20-30 L, Cl uptake occurs more slowly at subsurface sites (possibly accompanied by rearrangement of surface Al atoms), the occupation of which causes  $\delta\Phi$  gradually to reach a positive maximum and then turn toward negative values. O<sub>2</sub> exposure sufficient to reach the "oxide" phase ( $\geq 20$  L in this case) either depletes the subsurface sites or prevents their occupation by Cl, greatly slowing Cl uptake once the surface sites are filled. This mechanism then provides a basis for understanding how O inhibits the spontaneous etching of Al by Cl<sub>2</sub>,

since formation of the precursor Cl-saturated surface layer<sup>9,10</sup> is thus prevented. However, adsorbed O is also seen to have little or no effect on the initial chlorine uptake, suggesting that Cl and O occupy different surface sites. This is supported by the observation that O<sub>2</sub> does not significantly displace surface-site Cl, i.e., those species formed at low Cl<sub>2</sub> exposures.

On the basis of kinetic data (obtained at higher pressure, exposure and temperature than those used here), Smith<sup>4</sup> proposed a somewhat similar two-step mechanism involving Cl<sub>2</sub> adsorption in a molecular precursor state followed by dissociation and reaction with the substrate. Since we cannot be certain whether the initial (surface) species is Cl<sup>-</sup> or Cl<sub>2</sub><sup>-</sup>, the results and interpretation presented here are not inconsistent with those of Smith<sup>4</sup> if we identify the surface species with Smith's molecular precursor and the subsurface species with the dissociated phase.

(e) Other Results - AES Lineshapes, ELS and LEED

Some attention was paid to the Al L<sub>2,3</sub>VV lineshape (Fig. 4). For the O<sub>2</sub> pre-exposed surface, the "metal (Al<sup>0</sup>)" 68 eV peak, but not the 54 eV "oxide (Al<sup>+3</sup>)" peak<sup>3</sup>, is strongly attenuated by Cl<sub>2</sub> exposure, indicating that Cl preferentially occupies Al sites not multiply coordinated to O.

ELS data for clean Al were in accord with previous results<sup>30</sup>. Cl<sub>2</sub> exposure caused a gradual decrease in intensity of the volume and surface plasmons, with nearly complete disappearance of the latter by 80 L. Cl-induced structure was seen at loss energies of  $\delta E = 6.5$  and  $19.5$  eV, the latter being very weak and tentatively assigned to the Cl 3s  $\rightarrow$  4p transition. Other, weaker losses<sup>30,31</sup>, possibly related to the small level of O contamination incurred during Cl<sub>2</sub> exposure, were found at  $\delta E = 3.5$ ,  $7.5$  and  $\sim 12$  eV. The data do not agree well with the ELS<sup>32</sup> of gas-phase Cl<sub>2</sub>, as might be expected for a high concentration of physisorbed Cl<sub>2</sub> weakly interacting with Al. Vibrational ELS would be necessary for investigating the presence of Cl<sub>2</sub> or Cl<sub>2</sub><sup>-</sup> (the latter having a Cl-Cl stretching mode<sup>33</sup> at  $265 \text{ cm}^{-1} = 32.8$

meV).

Cl<sub>2</sub> exposure caused a gradual degradation of the (111)-(1x1) clean-surface LEED pattern (observed at 40-80 eV primary beam energies) with nearly complete disappearance by 80 L. However, after 40 L of Cl<sub>2</sub>, for which the estimated average coverage (Fig. 1) is in excess of 1 monolayer, the LEED pattern is still clearly visible (and the Al surface plasmon is still present in ELS). These observations suggest chlorination in three-dimensional patches (rather than in a uniform film) and are consistent with the onset of subsurface Cl<sup>-</sup> adsorption as deduced from the  $\delta\Phi$  data. Annealing after a 40 or 80 L exposure caused a partial return of the pattern as the Cl coverage decreased; there was no indication of any ordered overlayer.

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#### APPENDIX

The Cl TPD was "calibrated" using Ar TPD observed under the same conditions. The implanted Ar and adsorbed Cl AES intensities are given by  $I_x = f_x N_x S_x$  ( $x \equiv \text{Ar, Cl}$ ) where  $S_x$  is the Auger sensitivity factor<sup>14</sup>,  $N_x$  the number of implanted Ar/cm<sup>2</sup> or adsorbed Cl/cm<sup>2</sup> and  $f_x$  the fraction of atoms detected in AES. As discussed in the text, the adsorbed Cl produced by a 10 L Cl<sub>2</sub> exposure is believed to occupy predominantly surface sites, giving  $f_{\text{Cl}} \approx 1$ .  $f_{\text{Ar}}$  is estimated using

$$f_{\text{Ar}} = \int_0^{\infty} n(z) \exp(-z/\lambda \cos\phi) dz / \int_0^{\infty} n(z) dz$$

where  $n(z)$  is the implanted-Ar distribution as a function of depth,  $z$ . Various functional forms for  $n(z)$ , e.g., symmetric Gaussian, joined half-Gaussian and Edgeworth functions, have been discussed by Gibbons et al.<sup>34</sup> The parameters needed to evaluate  $n(z)$  for implantation of 3 keV Ar<sup>+</sup> ions in Al have been calculated by Burenkov et al.<sup>35</sup> from which we obtain  $f_{\text{Ar}}$  in the range of 0.0067 to 0.010, depending on the expression used for  $n(z)$ . The ionizer of the gun used in these studies operates at a 200 eV electron ener-

gy, for which about 10% of the argon ions are  $\text{Ar}^{+2}$  (estimated using the energy dependence of the first- and second-ionization cross-sections<sup>36</sup>); this has been neglected in computing  $f_{\text{Ar}}$ . The possible channeling of some of the ions along the [111] axis has also been neglected since the  $\text{Ar}^+$  TPD data were obtained for samples already disordered by previous  $\text{Ar}^+$  bombardment, and Ar "desorption" occurs well below the Al annealing temperature. The Auger PPH ratio  $I_{\text{Cl}}/I_{\text{Ar}}$  then gives  $N_{\text{Cl}}/N_{\text{Ar}} \approx 0.09$ , i.e., for 10 L  $\text{Cl}_2$  the number of adsorbed  $\text{Cl}/\text{cm}^2$  is about 0.09 times the number of  $\text{Ar}^+/\text{cm}^2$  implanted at 3 keV. Comparison of the integrated intensities of the Cl and Ar TPD peaks (assuming equal QMS detection efficiency for Cl and Ar) then allows an estimate of the fraction of adsorbed Cl contributing to the Cl TPD peak.

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#### FIGURE CAPTIONS

1. AES first-derivative peak-to-peak heights (PPH's), vs Cl<sub>2</sub> exposure, for Al with 0 and 50 L O<sub>2</sub> pre-exposures. All plots are on the same scale. Points labelled "A" show the results for a new spot on the sample (not previously irradiated by the AES primary beam) following the last Cl<sub>2</sub> exposure. The clean-surface data show the small O uptake occurring during large Cl<sub>2</sub> exposures. The dashed line indicates the O detection limit under the rapid-scan conditions used to obtain these data. The relative sensitivities for the main Auger peaks are approximately Cl LMM (181 eV) : O KLL (510 eV) : Al LVV (68 eV) = 4 : 2 : 1 (ref. 14). All exposures are based on ion gauge readings uncorrected for the Cl<sub>2</sub>/N<sub>2</sub> relative sensitivity.
2.  $\delta\Phi$  vs Cl<sub>2</sub> exposure for Al with 0 and 51 L O<sub>2</sub> pre-exposures. The results for two separate clean-surface experiments are shown. For 51 L O<sub>2</sub>, the negative  $\delta\Phi$  at 0 L Cl<sub>2</sub> represents the effect of O<sub>2</sub> on the clean surface. Also shown are the results for O<sub>2</sub> exposure following exposure of the clean surface to 90 L Cl<sub>2</sub>. The uncertainty of  $\pm 0.02$  eV (same for each point) is indicated.

3. Temperature programmed desorption data (35 amu Cl) for clean and ordered Al(111) exposed to 10 Cl<sub>2</sub>. Also shown is the 40 amu Ar desorption following 10 min of Ar<sup>+</sup>-ion bombardment at 3 keV and about 6 μA/cm<sup>2</sup> at normal incidence.
4. Al L<sub>2,3</sub>VV lineshape (and other Auger features) for clean Al, after 50 L O<sub>2</sub> and after a subsequent 35 L Cl<sub>2</sub> exposure. The data show the attenuation of the Al<sup>0</sup> peak relative to the Al<sup>+3</sup> peak by Cl<sub>2</sub> and, incidentally, the small Cl uptake occurring during a large O<sub>2</sub> exposure.

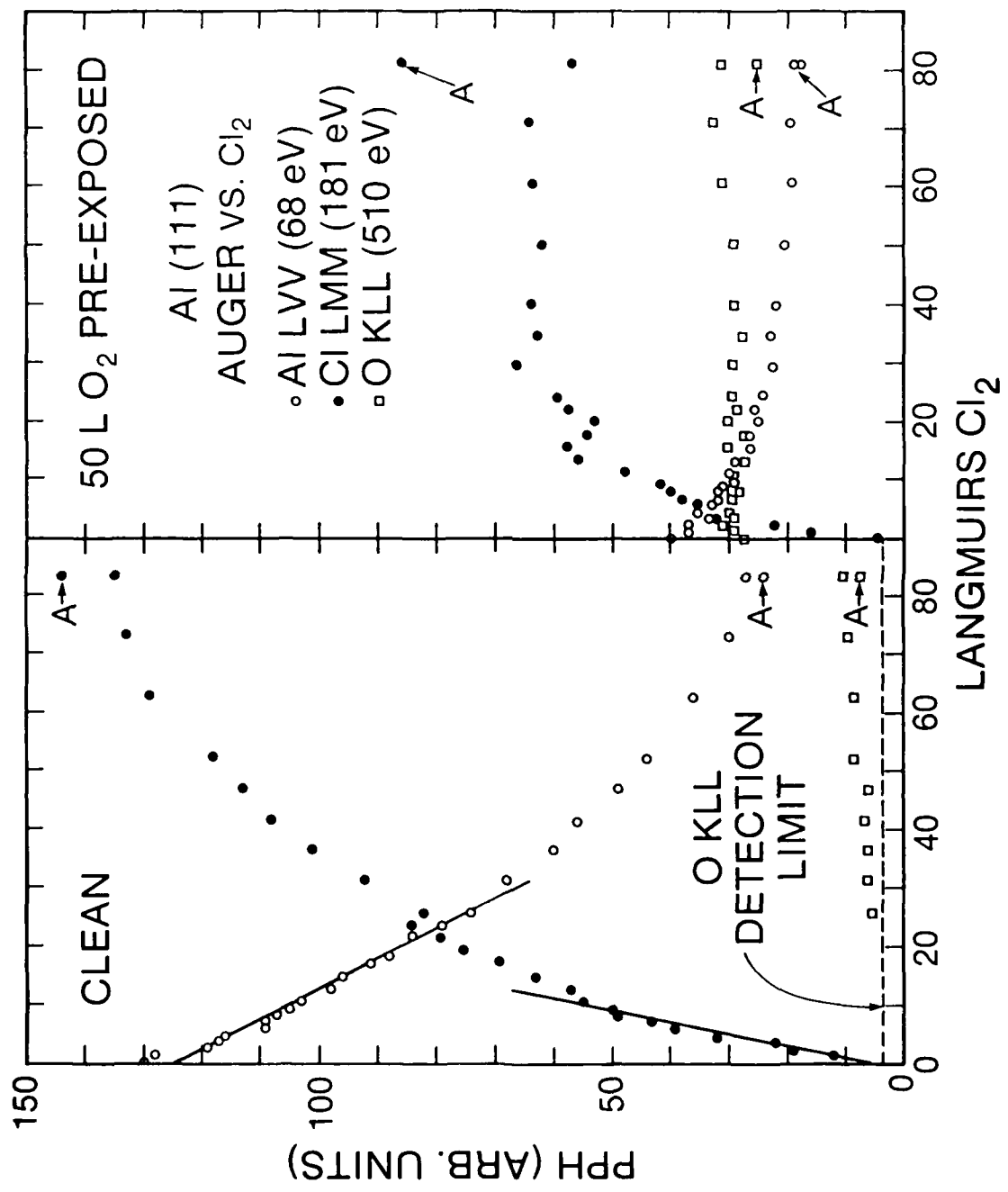


Fig. 1

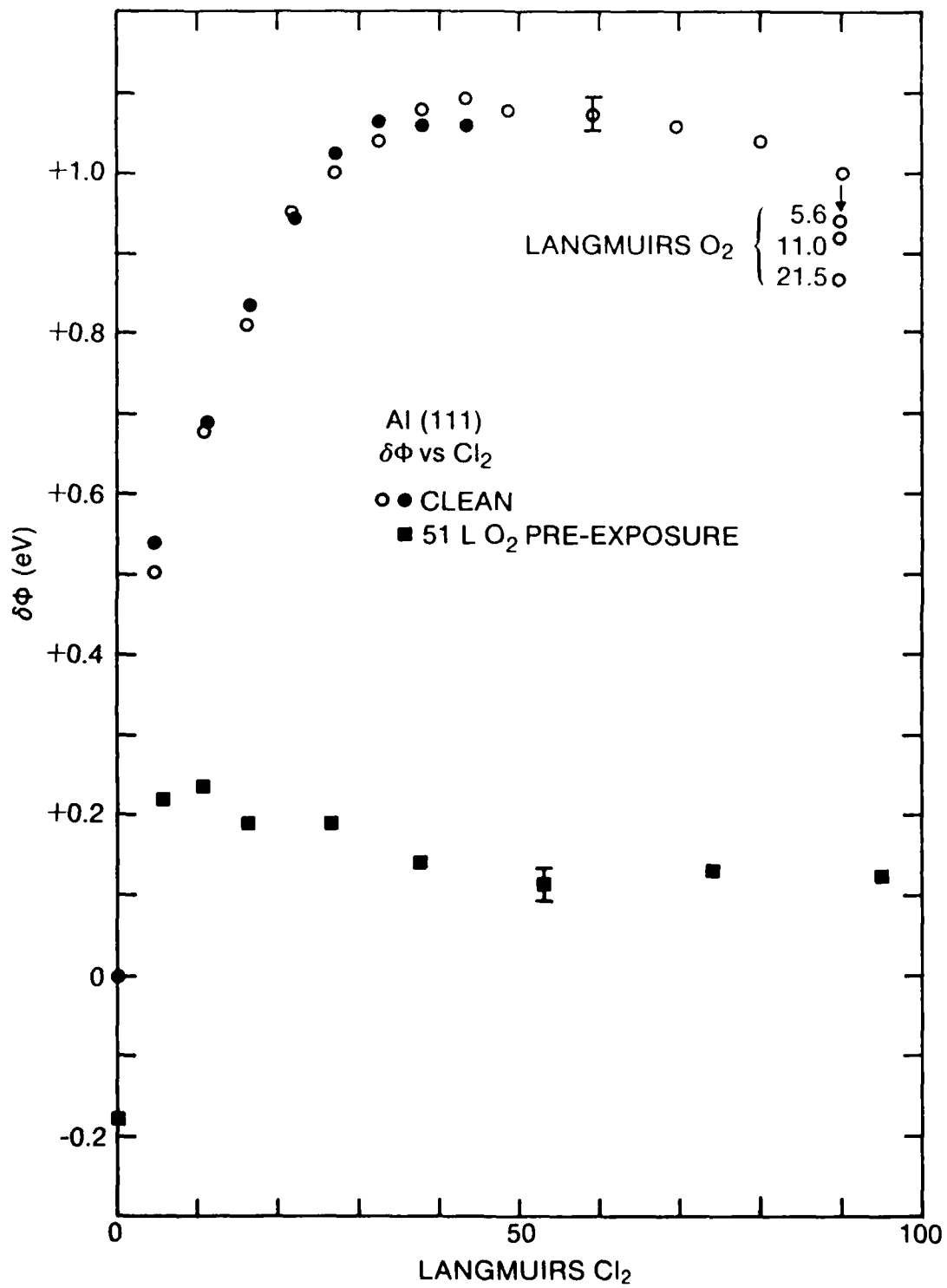


Fig. 2

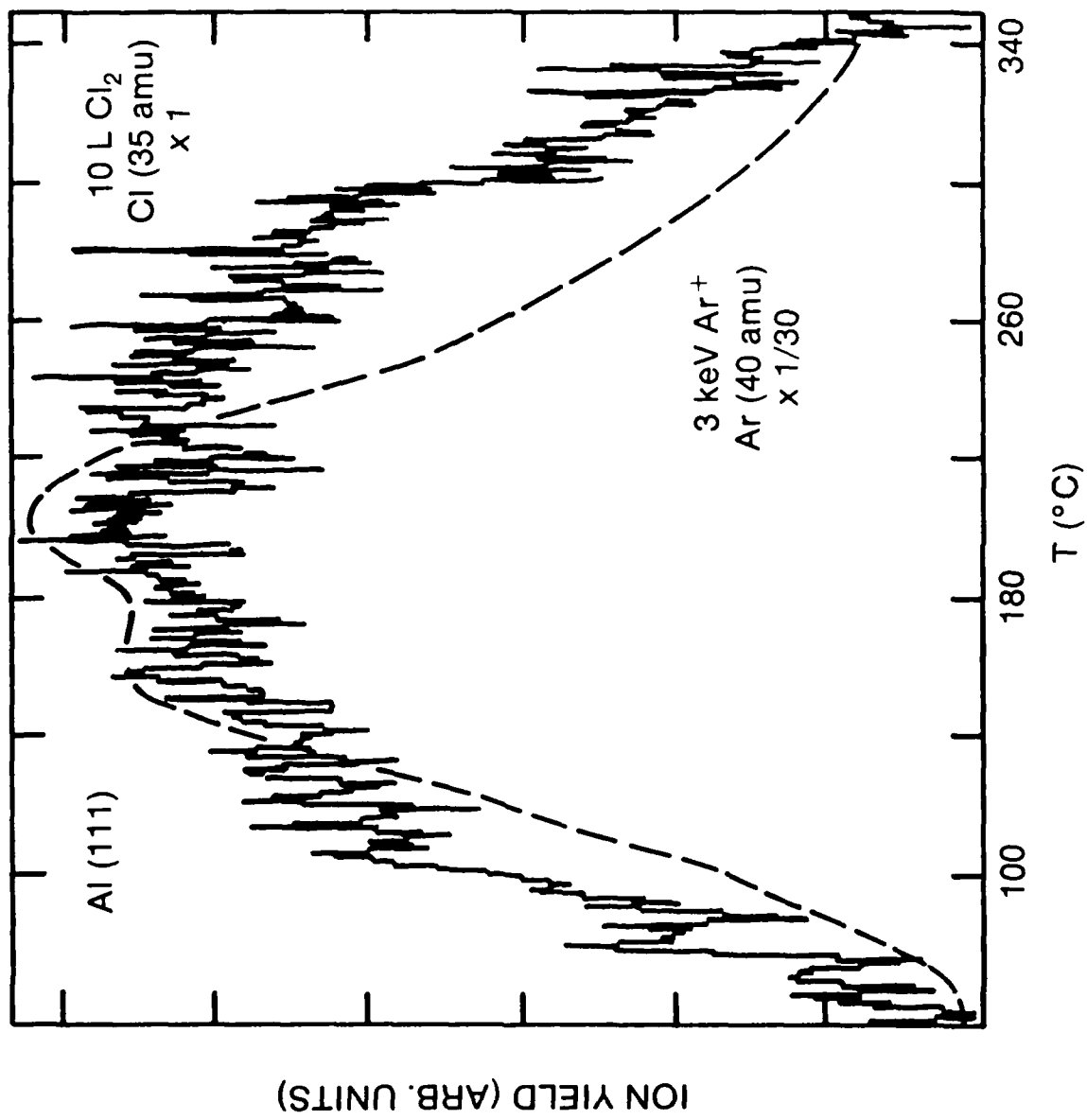


Fig. 3

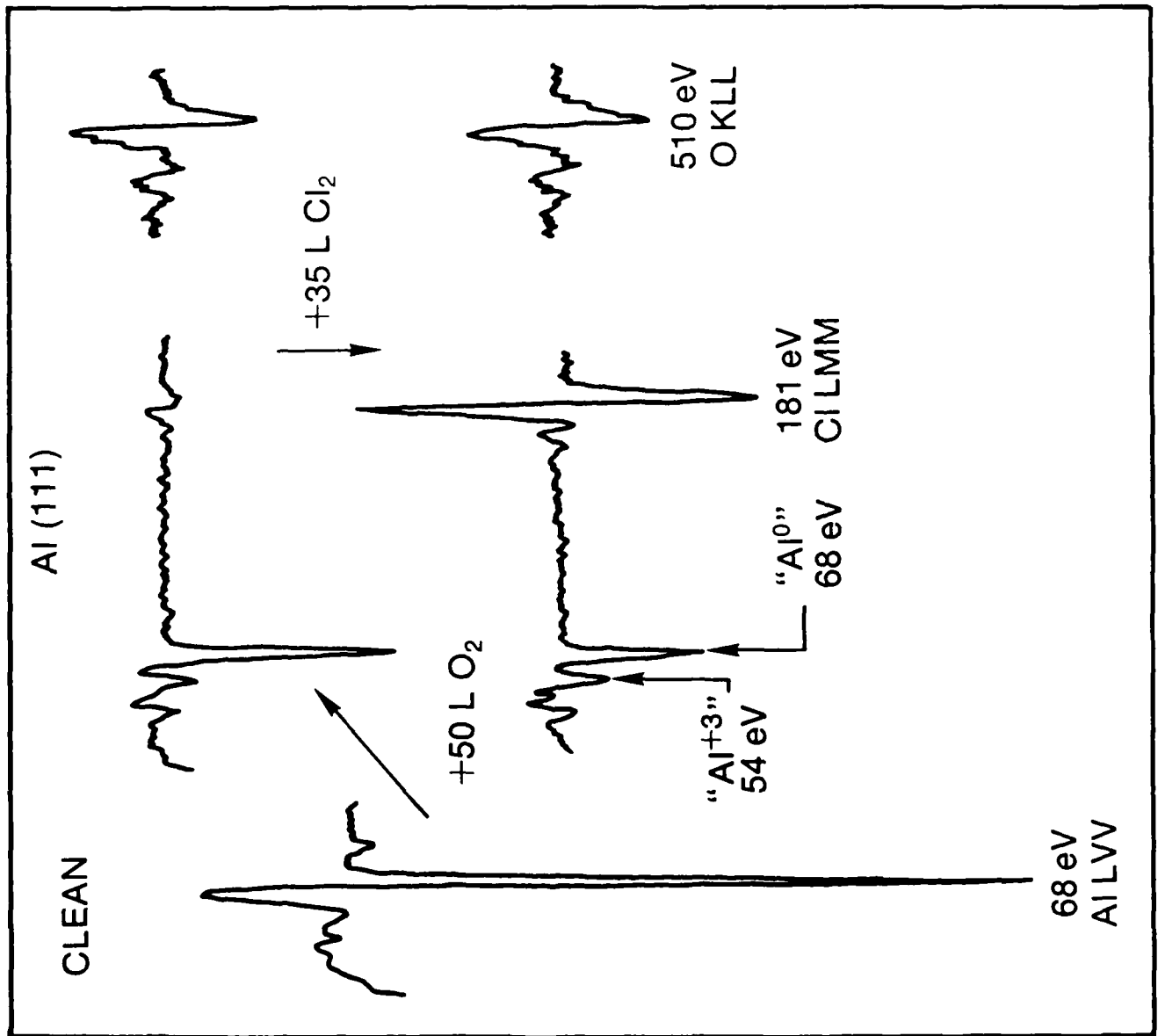


Fig. 4