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Take-off angle dependent x-ray photoelectron spectroscopy, secondary ion mass spectrometry, and scanning electron microscopy for determining the thickness and composition of passivation layers on technical aluminum foils

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Angle dependent x-ray photoelectron spectroscopy, static secondary ion mass spectrometry, and scanning electron microscopy have been used to investigate the effect of a cleaning procedure on the composition, morphology and thickness of passivation layers on technical aluminum foils. The results show that the cleaner, a solution of sodium carbonate, phosphate and surfactants, not only removes undesirable oil contaminations efficiently, but also etches the surface. Because magnesium-rich inclusions are etched at a faster rate than the surrounding aluminum, the foil acquires roughness on the scale of about 100 nm, whereas at the same time the surface composition changes. In particular, small amounts of phosphate are deposited on the surface. All these factors are considered favorable for improved adhesion.

I. INTRODUCTION

Rolled aluminum foils can be used as a substrate for various types of organic overlayers. However, oil residues from the rolling stage in the fabrication of the foils have to be removed to improve the adhesive properties of the aluminum surface. An aqueous solution of sodium phosphates, sodium carbonate, and surfactants can be applied as cleaning agent. We used x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and scanning electron microscopy (SEM) to investigate the effect of this cleaner on the morphology, composition, and thickness of passivation layers on the aluminum. This forms essential information in choosing the contact time of foil and cleaner that results in optimum adhesive properties.

XPS is frequently used for determining the thickness of passivation layers on metals¹ and in particular on aluminum.²⁻⁴ For an overlayer *o* of thickness *d* on a substrate *s*, the XPS intensity ratio is given by

$$\frac{I_o}{I_s} = \frac{n_o \sigma_o \lambda_o(E_o) [1 - \exp\{-d/[\lambda_o(E_o) \cos \theta]\}]}{n_s \sigma_s \lambda_s(E_s) \exp\{-d/[\lambda_o(E_s) \cos \theta]\}} \quad (1)$$

Here *I_o* and *I_s* are the areas of peaks in the XPS spectrum characteristic for the overlayer and substrate, respectively. The symbols *n_o* and *n_s* denote the corresponding atomic concentrations and *σ_o* and *σ_s* the XPS cross sections. *λ_{o(s)}* is the inelastic mean free path of electrons traveling through the overlayer (substrate); this parameter depends on the electron's kinetic energy: *E_o* for electrons emitted in the overlayer, and *E_s* for electrons emitted in the substrate. *θ* is the off-axis angle measured from the surface normal and *d* is the thickness of the overlayer.⁵ In case of passivation layers on aluminum, one can take the metallic part of an aluminum peak as the substrate peak and the oxidic

part as the overlayer peak. In that case *E_o* very nearly equals *E_s* and Eq. (1) reduces to

$$\frac{I_{Al^3}}{I_{Al}} = \frac{n_{Al^3} + \lambda_{Al^3}(E)}{n_{Al} \lambda_{Al}(E)} \times \{\exp[d/(\lambda_{Al^3} + (E) \cos \theta)] - 1\} \quad (2)$$

Strohmeier²⁻⁴ points out that a single measurement, i.e., with the detector at a fixed angle to the sample, is sufficient for determining the thickness of the aluminum oxide layer on aluminum foils. However, this is only safe if such layers are known to have a homogeneous composition and a uniform thickness. Non-uniform concentration profiles and, in particular, surface roughness cause serious deviations from Eqs. (1) and (2). In general, the intensity ratio varies less than predicted by these equations and the thickness *d* determined from Eq. (2) becomes an ill-defined quantity.^{5,6} In our work we used angle dependent XPS to check the applicability of Eqs. (1) and (2) for the samples under investigation.

II. EXPERIMENTAL

The aluminum foils contained 4.5% Mg in the form of inclusions of either Mg or Mg–Al alloy, as well as traces of Fe, V, Cr, and Mn. In their preparation, the foils were rolled in a Sendzimir rolling machine, a process in which aliphatic oil is used. The processing oil was removed by a commercially available cleaner, consisting of sodium phosphates (approximately 50 wt %), sodium carbonate (30 wt %) and surfactants (20 wt %)—the nature of which can not be disclosed for proprietary reasons—dissolved in water. The solution had a high pH of about 10.

XPS spectra were measured with a VG Scientific ESCALAB 200 system, equipped with a monochromated

Al $K\alpha$ source, a hemispherical analyzer with a five channel detector and a manipulator which allows for rotation of the sample with respect to the analyzer. Electrons are focused onto the analyzer by a three times magnifying input lens of a nominal 12° cone acceptance angle. The pressure of the system while taking spectra was around 8×10^{-10} mbar. All spectra were analyzed by the software of the VGS 5250 Data System. Samples were mounted on the stainless steel sample stubs by using tantalum masks.

The SIMS spectra were recorded with a Leybold SSM 200 quadrupole mass spectrometer system. The pressure was in the 10^{-9} mbar range. The differentially pumped argon (99.999% pure, Messer Griesheim) ion gun (Leybold IQE 12-63) was operated at an energy of 5 keV and a current density of 50 nA/cm². The time to record both a positive and negative SIMS spectrum was 200 s, so that the total ion dose was 5×10^{13} ions/cm², which is about the static limit. The samples were mounted on the sample rod using tantalum masks; no tantalum signals were detected during the measurements.

Scanning electron images were obtained with a JEOL 840 electron microscope, with a primary electron energy of 5 keV, a beam current of 0.3 nA, a magnification of $3000\times$ and a base pressure of 10^{-6} mbar. Prior to measurement, the samples were covered with a layer of 10 nm Au from an evaporation source, in order to increase secondary electron emission.

III. RESULTS

A. XPS

Figure 1(a) shows three wide scans, taken from foil samples which differed only in the duration of the cleaning treatment undergone. The Ta peaks in the spectra originate from the sample holders and should be ignored. In addition to the expected carbon, oxygen, and magnesium, the untreated samples contain a significant amount of chlorine. As the spectra in Fig. 1(a) show, magnesium and chlorine are removed by the cleaner. The carbon intensity is reduced by a factor of 2, indicating that processing oil is removed by the cleaner. Note furthermore that the cleaning treatment of 4 min does not seem to have more effect on the foil composition than the 30 s treatment has.

Similar spectra as in Fig. 1(a) were obtained for other lengths of the cleaning time. We determined the peak areas of Mg 1s and C 1s, normalized them on the total Al 2p peak areas, and took the resulting ratios as a measure for the Mg and C content in the aluminum foils. The dependence of Mg and C content on the duration of cleaning treatment is shown in Fig. 1(b). From this figure one can conclude that the result of the cleaning procedure is effected in the first two minutes.

Figure 2 clearly shows the extra information one can get from angle dependent measurements. For the untreated aluminum foil, the carbon over aluminum intensity ratio increases as a function of off-axis angle. This means that the carbon forms a layer on top of the aluminum oxide. A rough estimate based on Eq. (1) indicates that the hydrocarbon layer has a thickness in the order of 3 nm. The

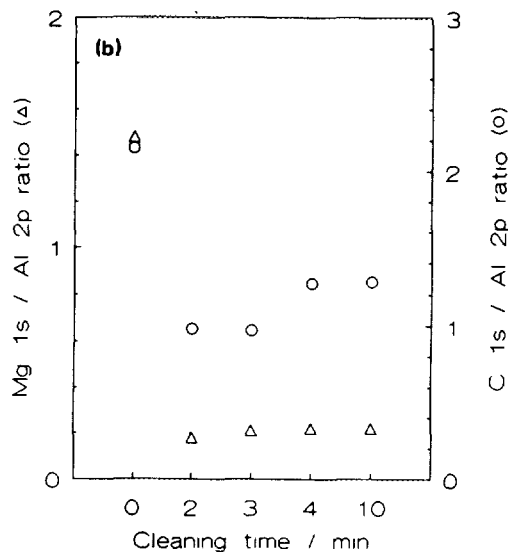
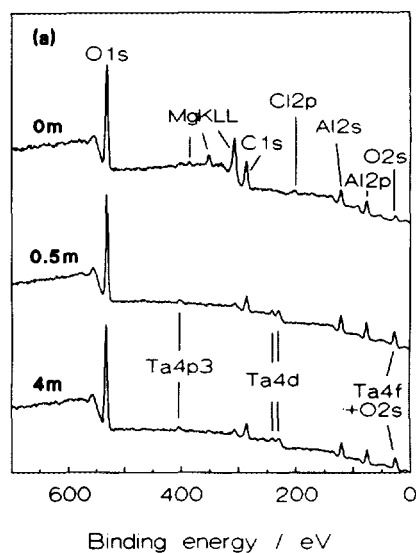


FIG. 1. (a) XPS wide scan of the untreated aluminum foil, and of foils treated with cleaner for 0.5 and 4 min. The Ta signal is due to the sample holder. (b) XPS intensity ratios versus cleaning time for the different contaminants: Δ is Mg, and \circ is C.

angular dependence of the C 1s/Al 2p intensity ratio decreases dramatically for cleaned foils. As we discuss later, this decreased angular dependence can be largely attributed to increased surface roughness of the foils.

Applying a pass energy of 20 eV, it is possible to separate the oxidic and metallic part of the Al 2p peak clearly, see Fig. 3. We present the angle dependent intensity ratios of the Al³⁺ and Al⁰ peaks in Fig. 4, along with a number of theoretical curves based on Eq. (2). Apparently Eq. (2) does not apply. We come back on this in Sec. IV.

B. SIMS

The upper part of Fig. 5 shows the SIMS spectra of an untreated aluminum foil. The Al peak at mass 27 dominates the positive SIMS spectrum. Also the peaks at masses 43 (AlO⁺), 54 (Al₂⁺) and 70 (Al₂O⁺) are attributed to Al-containing ions. The contamination of the surface by

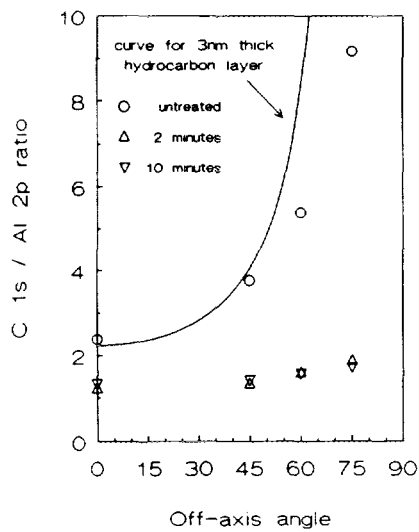


FIG. 2. XPS C 1s/Al 2p intensity ratios as a function of off-axis angle, \circ : untreated foil, Δ : foil treated with cleaner for 2 min, ∇ : treated for 10 min. The curve drawn corresponds to a 3 nm thick hydrocarbon layer; it is calculated using Eq. (1).

processing oil is visible in the carbon-containing cluster ions (C_xH_y) in the mass regions 12–15 and 24–26; these signals, however, appear most clearly in the negative SIMS spectra. Contaminants of the untreated Al foil are Na (23 amu), Mg (24), K (39), Ca (40), V (51), and Cr (52), where the intensities of sodium and potassium are strongly enhanced by the high ionization probabilities of these elements.

Negative SIMS is more sensitive to the presence of hydrocarbons at the surface than positive SIMS. Characteristic are the peaks at masses 12 (C^-), 13 (CH^-), 24 (C_2^-), and 25 (C_2H^-). The absence of hydrocarbon clusters of higher mass reflects that the processing oil is al-

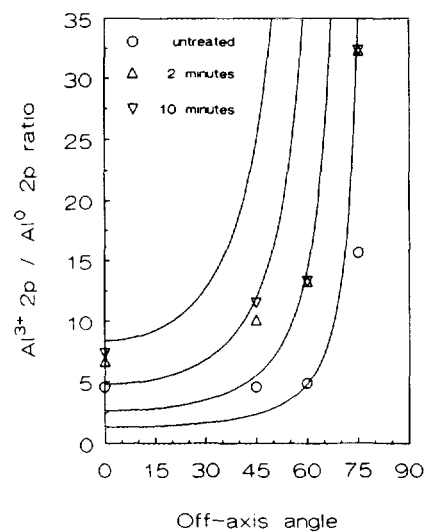


FIG. 4. XPS intensity ratios of the $Al^{3+} / Al^0 2p$ signals as a function of off-axis angle, \circ : untreated foil, Δ : foil treated with cleaner for 2 min, ∇ : treated for 10 min. Also shown are some curves calculated from Eq. (2). Going from top to bottom these curves correspond to oxide layer thicknesses of 7.0, 5.6, 4.2, and 2.8 nm.

phatic in nature. Furthermore, the negative SIMS spectrum shows a chlorine contamination; however, one should keep in mind that a low Cl concentration already gives a high SIMS intensity, due to its high electron affinity.

The lower part of Fig. 5 gives the positive and negative SIMS spectra of an aluminum foil after a cleaning period of 2 min. The negative SIMS spectrum shows that indeed most of the hydrocarbons are removed from the surface by the treatment. Quantification of this reduction is possible by dividing the hydrocarbon intensity by a properly chosen reference characteristic for the substrate, e.g., $(C_2^- + C_2H^-) / AlO^-$. We thus estimate that at least 80% of the oil contamination is removed. As the foils were exposed to the air after cleaning, a fraction of the carbon results from air exposure. Hence the figure of 80% reduction probably underestimates the efficiency of the cleaning treatment for removing oil.

Another effect of the treatment is the removal of magnesium, potassium, calcium, and chlorine. Besides the removal of surface contaminants, also new species appear during the cleaning treatment. Clearly visible is the presence of phosphate, as evidenced by the peaks at masses 31 (P^+) and 47 (PO^+) in the positive spectrum and 31 (P^-), 47 (PO^-), 63 (PO_2^-), and 79 (PO_3^-) in the negative spectrum. Also the amount of chromium (52 amu), manganese (55 amu), and iron (56 amu) at the surface has increased. The evolution of a number of SIMS intensity ratios with cleaning time is given in Fig. 6.

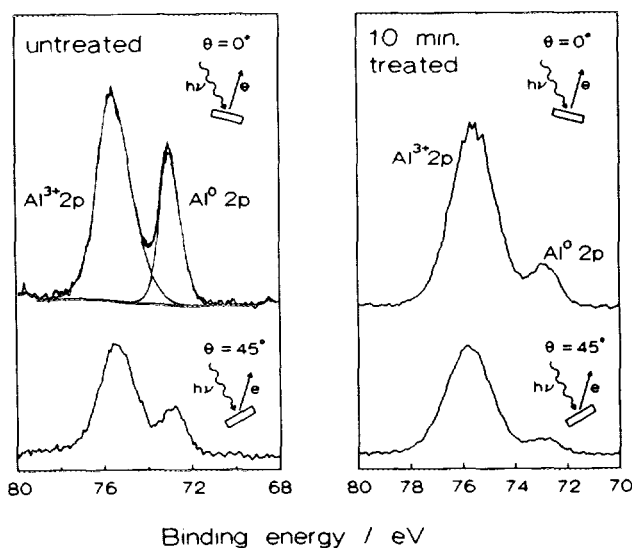


FIG. 3. Al 2p XPS spectra—taken at the indicated off-axis angles—of a foil before (left) and after cleaning for 10 min (right). These spectra were taken at constant pass energy of 20 eV.

C. Scanning electron microscopy

SEM pictures of Au-covered aluminum foils are given in Fig. 7. The images were taken in the secondary electron mode, with the detector at the top-right position of the picture. White, intense features correspond to elevated re-

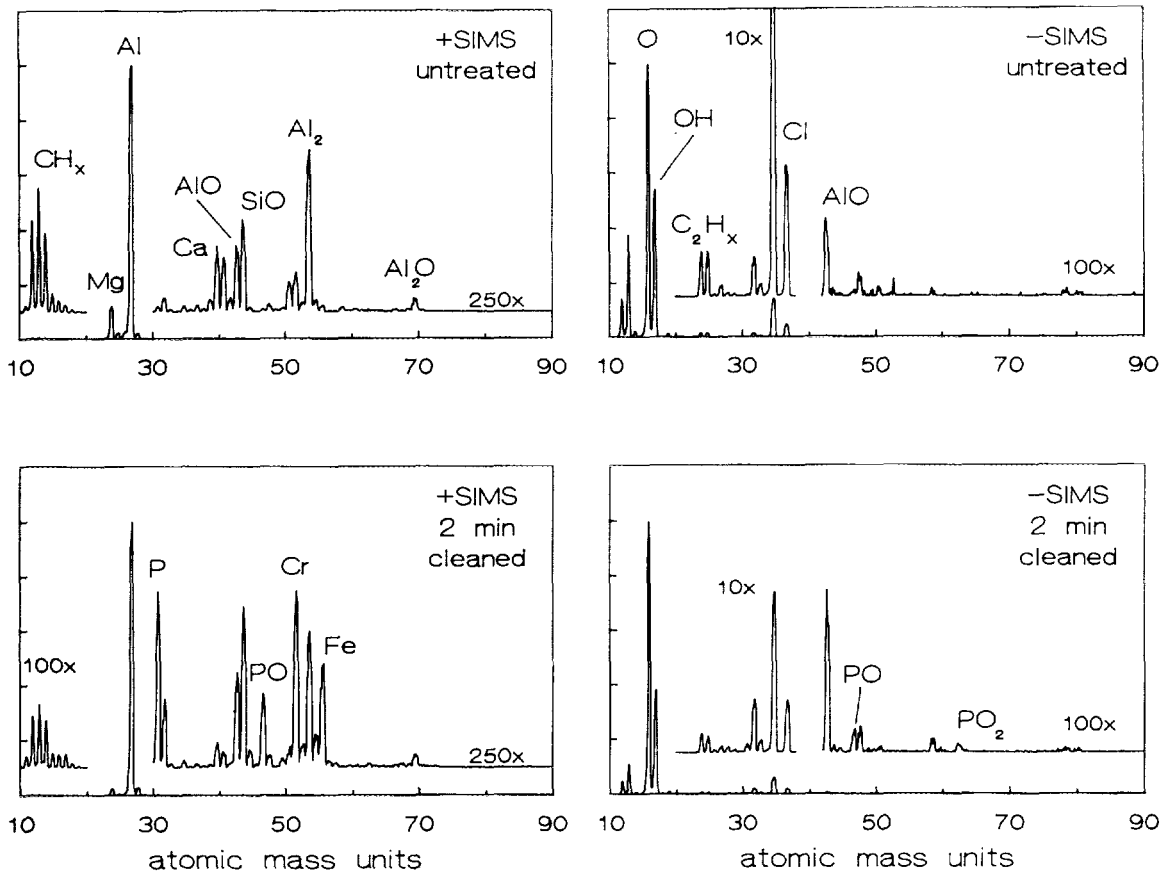


FIG. 5. Positive (left) and negative SIMS spectra (right) of an aluminum foil before (top) and after cleaning for 2 min (bottom).

gions of the sample, while dark features represent deeper regions from which secondary electrons cannot reach the detector.

The SEM picture of the untreated foil clearly exhibits deformations of the surface due to the rolling process. Measurement of the roughness by means of a stylus profile meter revealed that the tracks in Fig. 7(a) correspond to valleys of typically $5\ \mu\text{m}$ wide and $1\ \mu\text{m}$ deep. Apart from these parallel deformations, the surface appears flat, at least on the micrometer scale of these techniques.

Cleaning has a profound effect on the morphology of the foils, as Fig. 7(b) shows. The sharp edges due to the rolling stage have become much smoother and, in addition, a large number of holes has developed with diameters of typically $0.1\ \mu\text{m}$. The depth cannot be determined because the holes are inaccessible to the tip used in stylus profile measurements. The sharp holes correspond to regions which are etched at a faster rate than the surrounding medium. Because (i) we know that the Al foils contain inclusions rich in Mg, and (ii) both XPS and SIMS indicate that Mg is rapidly removed by the cleaner, we assign the holes in Fig. 7(b) to former Mg inclusions which are etched at a relatively high rate (with respect to aluminum) by the alkaline cleaner.

IV. DISCUSSION

The most important conclusions from this work, as drawn from Figs. 1(b), 6, and 7 are as follows.

(i) Rolled aluminum foils are covered by a deposit of oil residue; the surface region consists of a layer of aluminum oxide, which contains magnesium oxide and a chlorine contamination. The foils exhibit elongated deformations due to the rolling process. Apart from these features the surfaces are relatively smooth on the micrometer scale.

(ii) Cleaning with an aqueous solution of sodium carbonate, sodium phosphates, and surfactants with a pH of 10 removes most of the oil residue, increases the oxygen content and decreases the Mg content of the surface region; phosphate is deposited on the surface while at the same time the concentrations of the minor constituents, Fe, Cr, and Mn increase. The surface of the foils contains an abundance of small holes with typical dimensions on the order of $0.1\ \mu\text{m}$.

We attribute the changes in composition and morphology of the foils to the etching action of the alkaline cleaning solution. The picture that emerges is that an untreated foil has a passivation layer of aluminum oxide, which contains magnesium inclusions (oxidic in the surface region), and a hydrocarbon layer on top. The cleaning removes the oil residue on a time scale of tens of seconds and then starts to etch the surface. Magnesium is etched at a faster rate than the surrounding alumina and magnesium rich areas are converted to the holes that are visible in the SEM pictures of all cleaned foils. The reason that simultaneously minor constituents such as Fe, Mn, and Cr enrich at the

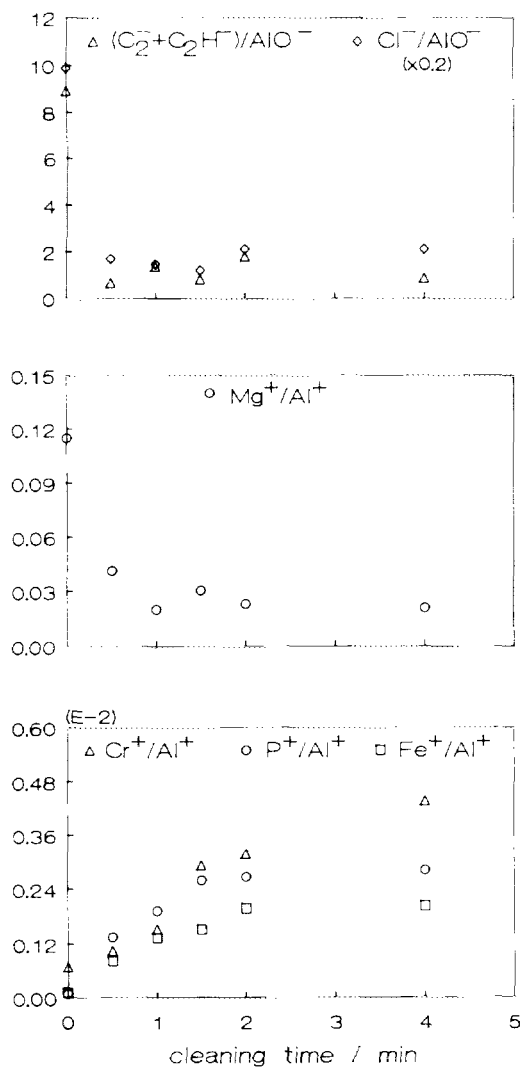


FIG. 6. The variation of characteristic secondary ion intensities with cleaning time (top: negative ions; middle and bottom: positive ions). All intensities are normalized to substrate signals.

surface of the foils, is probably that these elements are less sensitive to etching than Mg and Al.

The SIMS spectra, recorded under static conditions, refer to the outer layer composition and indicate that the processing oil is effectively removed from the surface after relatively short contact times of 30 s only. The XPS C 1s intensity drops by a factor of 2, but indicates a higher carbon concentration than the SIMS data do. As XPS probes a layer with a thickness of several nanometers, this technique also detects carbon that may be present below the surface. In this respect the angle dependent XPS data in Fig. 2 are of interest. The C 1s/Al 2p intensity ratio for the untreated foil increases strongly with increasing off-axis angle, indicating that the aluminum is covered by a hydrocarbon layer. The cleaned foils still contain a significant amount of carbon, however, with an off-axis angular dependence that resembles that of the aluminum. If the morphologies of the foils were the same before and after cleaning, the decreased angular dependence of the C/Al intensity ratio would imply that in the treated foils carbon

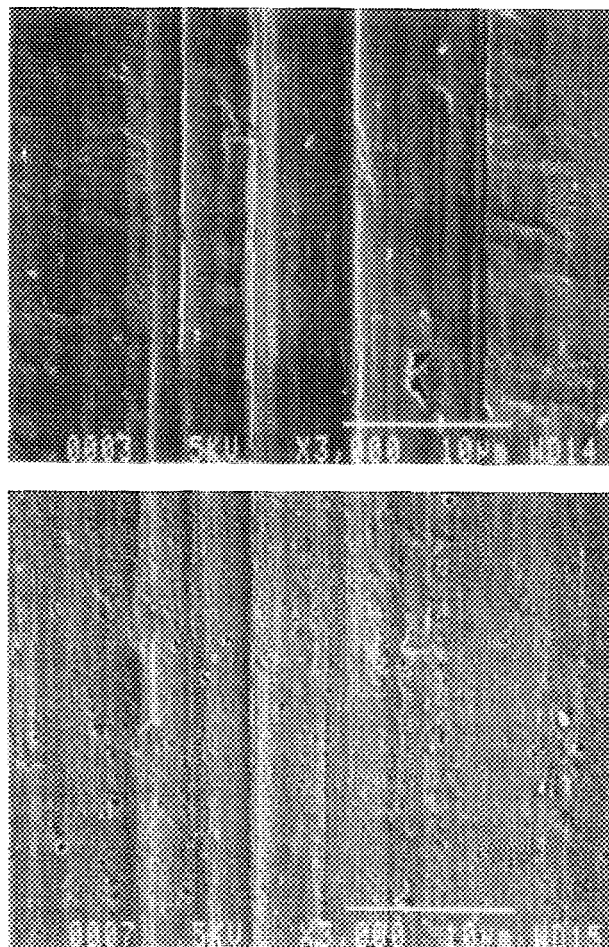


FIG. 7. Secondary electron images of an aluminum foil before (top) and after (bottom) cleaning, taken with the detector in the top right position of the picture.

is mixed with aluminum. However, cleaned Al foils become rougher on the submicron scale and this also causes the angular dependence to be less pronounced.^{5,6}

Qualitatively, the spectra suggest that cleaned aluminum foils have a thicker aluminum oxide passivation layer than the untreated foils. Apparently, the adsorbed processing oil inhibits further oxidation of the foils. The angular dependence of the Al³⁺/Al⁰ 2p XPS intensity ratio gives information about the distribution of oxide and metal. If the oxide forms a well-defined sharp uniform layer, the ratio is given by expression (2). However, Fig. 4 shows that the measured ratios as a function of angle cannot be described by Eq. (2). The deviation of the angular dependence from the ideal behavior expressed in Eqs. (1) and (2) can stem from inhomogeneous composition, a non-uniform thickness of the overlayer, or from surface roughness. In the latter case there is no unique orientation of the surface normal and the off-axis angle varies continuously over the surface. This is certainly an important factor in the angle dependent C 1s/Al 2p and Al³⁺/Al 2p XPS intensity ratios for the cleaned foils. With respect to the effect of inhomogeneous surface composition on the angular dependence of XPS intensity ratios it is interesting that,

according to Barr,¹ passivated aluminum foils have been found to expose significant amounts of zero-valent aluminum on their surfaces, which are described as trapped Al atoms or clusters in the Al₂O₃ matrix. The effect of this would indeed be that the Al³⁺/Al⁰ ratio increases less with increasing off-axis angle than Eq. (1) predicts.

Thus, several factors are present which cause the angle dependent Al³⁺/Al intensity ratio to deviate from the ideal expression in Eq. (2). Hence, its application on a single XPS measurement to determine the thickness of the aluminum oxide layer would yield a highly unreliable value. Thickness determinations with XPS should not be carried out without a check whether Eq. (2) is applicable.

The eventual goal of the cleaning procedure is to improve the adhesive properties of the foils for use as a substrate for organic layers. Removal of oil, and the development of surface roughness on the submicron scale will contribute to better adhesion. SIMS reveals that small amounts of phosphate (below the detection limits of XPS) remain on the surface. The deposition of phosphate increases with the time the foil is exposed to the detergent, and seems to stabilize after 2 min. The presence of phos-

phates is interesting, because phosphate is known to improve the adhesive properties of aluminum and steel surfaces towards protective coatings.⁷

As to optimizing the contact time between foil and cleaner, it is clear that 30 s is sufficient to remove the large part of the processing oil from the surface. However, the removal of Mg which as we believe is directly correlated to the development of surface roughness, and the phosphate content of the surface both stabilize after 1–2 min exposure to the cleaner. The results therefore indicate that the optimum contact time for cleaning should be on the order of a few minutes.

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