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Evaluation of Take-off-angle-dependent XPS for Determining the Thickness of Passivation Layers on Aluminium and Silicon

P. L. J. Gunter, A. M. de Jong and J. W. Niemantsverdriet*

Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, NL-5600 MB Eindhoven, Netherlands

H. J. H. Rheiter

Océ Netherlands B.V., NL-5900 MA Venlo, Netherlands

Investigating the effect of a cleaner (used to remove lubrication oil residues) on the surface composition of rolled aluminium foils, we applied angle-dependent XPS to determine the thickness of the passivation layer on these foils. We found the simple uniform overlayer model, which has frequently been applied to translate XPS intensity ratios into a value for the overlayer thickness, to be inapplicable on these aluminium foils. However, data obtained from an Si(100) single-crystal surface were in rather good agreement with the model. SEM images from the aluminium foils show that their surface is rough on the (sub)micron scale. We believe this roughness to be the reason for the inapplicability of the uniform overlayer model. Simulations of XPS intensity ratios for model rough surfaces support this point of view. Both experiment and simulations make it clear that one should not base XPS thickness determinations on one measurement only, because in that case the applicability of the uniform overlayer model cannot be checked.

INTRODUCTION

XPS thickness determination of passivation layers has been part of our research on technical aluminium foils which are used as a substrate for various types of organic overlayers. To remove hydrocarbon oil residues originating from the rolling stage in the fabrication, the foils are cleaned in an aqueous solution of sodium phosphate, sodium carbonate and surfactants. The cleaning improves the adhesive properties of the surface. We used XPS, SIMS and SEM to investigate the effect that the cleaning procedure has on the morphology, composition and thickness of the passivation layer on the aluminium. This forms essential information in choosing the contact time of foil and cleaner that results in optimum adhesive properties. In this paper we only present our findings in relation to the XPS thickness determination of passivation layers; the more general results are presented elsewhere.¹

XPS is frequently used for determining the thickness of passivation layers on metals. Several authors reported^{2–6} on the successful application of the following simple equation:

$$\frac{I_o}{I_s} = \frac{n_o \lambda_o}{n_s \lambda_s} \left[\exp\left(\frac{d}{\lambda_o \cos \theta}\right) - 1 \right] \quad (1)$$

Here I_o is the intensity (i.e. peak area) of the overlayer peak (e.g. the oxidic peak of the Al 2p or Al 2s signal) and I_s is the intensity of the corresponding substrate (metallic) peak. The symbol n denotes the volume density of electron-emitting atoms in the overlayer (n_o)

and substrate (n_s), λ is the inelastic mean free path of the appropriate photoelectrons in the overlayer (λ_o) and substrate (λ_s), θ is the electron off-axis angle with respect to the surface normal and d is the thickness of the overlayer.

One can use Eqn (1) to evaluate d from only one XPS spectrum. However, as Fadley has pointed out,⁷ several assumptions have to be made to derive Eqn (1). The most important of these are (1) that the overlayer is homogeneously composed and thus has a sharply defined border with the substrate, (2) that the resulting sharply defined local thickness d is in fact the same at every point of the surface and (3) that this surface is flat on the microscopic as well as on the macroscopic scale.

We measured Al 2p overlayer/substrate intensity ratios as a function of off-axis angle and could not fit these angle-dependent profiles with Eqn (1). For comparison we did the same with the Si 2p peaks from a silicon single crystal. The agreement with Eqn (1) was much better in this case. We conclude that the passivation layers on the aluminium foils deviate significantly from the ideal ones assumed in the derivation of Eqn (1). In this paper we present these experimental results. We further present some simulations of angle-dependent intensity ratios that one could expect to obtain from non-ideal passivation layers. These simulations further support our conclusion that one should not base an XPS thickness determination on a single measurement.

EXPERIMENTAL

The silicon sample used is a commercially available single Si(100) crystal. The aluminium samples were

* Author to whom correspondence should be addressed.

taken from rolled technical aluminium foils. These foils were cleaned for different periods of time in an aqueous solution of about 50% sodium phosphates, 30% sodium carbonate and 20% surfactants. The pH of the solution was 10, the temperature about 50 °C. Cleaning durations ranged from 30 s to 10 min.

The XPS experiments were performed in a VG Scientific Escalab 200 photoelectron spectrometer equipped with a monochromated Al K α source, operating at 15 kV and 34 mA, and a VGS 5250 Data System. The analyser is a 150 mm radius, 150°, spherical sector system which has a 3 $\times$ magnifying input lens of a nominal $\pm 12^\circ$ cone acceptance angle. This lens focuses the electrons from the sample onto a 6 $\times$ 10 mm² slit plate in front of the analyser. The detector consists of five channeltrons. All spectra were acquired in the Constant Analyser Energy (CAE) mode. The base pressure in the vacuum chamber during measurements was lower than 5×10^{-9} mbar. No cleaning procedures were applied before inserting the samples in the spectrometer, nor were any special precautions taken other than normal ultrahigh-vacuum (UHV) sample-handling procedures. All experiments were done at room temperature. No charging was observed during analysis as judged by the C 1s binding energy of 284.6 eV.

RESULTS

Aluminium

For the thickness determination of the aluminium passivation layers we used the metal/oxide Al 2p peak pair. Examples of the spectra obtained at different off-axis angles on a foil cleaned for 2 min are shown in Fig. 1(a). The peak at 75.5 eV is the oxidic Al 2p peak whereas the peak at 72.5 eV is the metallic Al 2p peak. To determine the peak intensities, we applied the fitting procedure of the VGS 5250 software, which uses a combination of Gaussian as well as Lorentzian components. Peak areas were taken as a measure of intensity. As an example the fitting curves for the upper

Figure 1. (a) XPS spectra obtained from an aluminium foil cleaned for 2 min. Both spectra were taken at a constant pass energy of 10 eV. In the upper spectrum the results of the fitting procedure are shown. (b) Plot of Al³⁺/Al 2p peak area ratios as a function of off-axis angle. The solid curves express the relationship described by Eqn (1) after substitution^{8,10} of $\lambda_o = 2.8$ nm, $\lambda_m = 2.6$ nm, $n_o = 72.6$ kmol m⁻³, $n_m = 100$ kmol m⁻³ and the values of d indicated.

spectrum in Fig. 1(a) have been drawn in. The Al³⁺/Al intensity ratios as a function of off-axis angle obtained in this way are presented in Fig. 1(b). From the figure it is clear that the simple relation expressed by Eqn (1) is not valid here. We found deviations from ideal behaviour for all aluminium samples, also for those that were not treated with a cleaner at all (see Fig. 2).

Silicon

For comparison we applied the thickness-determining procedure also on an Si(100) single crystal, from which we expected the passivation layer to be more like the ideally uniform one. Figure 3(a) shows spectra obtained from the silicon sample at different off-axis angles. The metallic and oxidic parts of the Si 2p peak are shown. We applied the same fitting procedures on the silicon spectra as on the aluminium spectra. In the upper spectrum in Fig. 3(a) the fitting curves are shown. By determining the Si⁴⁺/Si intensity ratios, we found the dependence on off-axis angle depicted in Fig. 3(b). The

Figure 2. Plot of Al³⁺/Al 2p peak area ratios as a function of off-axis angle, taken from foils differing in the duration of cleaning undergone. The solid curves express the relationship described by Eqn (1).

Figure 3. (a) XPS spectra obtained from an Si(100) single crystal. Both spectra were taken at a constant pass energy of 20 eV. In the upper spectrum the results of the fitting procedure are shown. (b) Plot of Si⁴⁺/Si 2p peak area ratios as a function of off-axis angle. The solid curve expresses the relationship described by Eqn (1) after substitution^{8,10} of $d = 2.0$ nm and $\lambda_o = 3.7$ nm, $\lambda_m = 3.2$ nm, $n_o = 36.5$ kmol m⁻³ and $n_m = 83.2$ kmol m⁻³.

Figure 4. Calculation of the angular dependence of the Al^{3+}/Al intensity ratio for passivation layer compositions as shown in the upper left corner. The layer thickness is taken to be equal to 4.0 nm; for λ a constant value of 2.7 nm is assumed. Note that the drawn curve corresponds to the uniform layer model.

(a)

(b)

Figure 5. SEM images of (a) an untreated aluminium foil and (b) an aluminium foil treated for 10 min. The images are taken in the secondary electron mode with the detector at the top right position of the pictures.

solid curve in this figure expresses the relationship given by Eqn (1) after substitution of $d = 2.0$ nm, $\lambda_o = 3.7$ nm, $\lambda_m = 3.2$ nm, $n_o = 36.5$ kmol m^{-3} and $n_m = 83.2$ kmol m^{-3} . For the inelastic photoelectron mean free paths we took the values as calculated recently by Tanuma *et al.*⁸ using the algorithm of Penn.⁹ These values have an estimated error of the order of $\pm 10\%$.⁸ We calculated the volume densities using data from Ref. 10.

DISCUSSION

Although the results obtained on the silicon samples show that it is possible to exploit Eqn (1) successfully for thickness determination, the aluminium experiments make it clear that this is not always the case. How can we explain the deviation from the behaviour predicted by Eqn (1)? In the Introduction we noted that in the derivation of Eqn (1) the passivation layer is assumed to have a homogeneous composition, a uniform thickness and a flat surface. Therefore one could expect the deviations seen to stem from a violation of one or more of these assumptions.

According to Barr,³ passivated aluminium foils have been found to expose significant amounts of zero-valent aluminium on their surfaces, which are described as trapped Al atoms or clusters in the Al_2O_3 matrix. The effect of such inhomogeneities would be a less steep angular dependence of the intensity ratio. A simulation of the effect of an inhomogeneous oxide layer on a flat surface composition is presented in Fig. 4. The simulation is based on an evaluation of the integral⁷

$$\int n(z) \exp\left(-\frac{z}{\lambda \cos \theta}\right) dz \quad (2)$$

in which $n(z)$ is the concentration as a function of distance from the sample surface. For this $n(z)$ we substituted the overlayer (and complementary substrate) profiles shown in the upper left corner of Fig. 4. Note that we assumed a constant $\lambda = 2.7$ nm throughout the whole sample and a thickness d of 4.0 nm. As shown, non-ideal concentration profiles can cause significant deviations from Eqn (1). In principle, it is possible to reverse the process, i.e. to calculate the concentration profile by inverting this integral and substituting the measured angular-dependent intensities. Recently, progress has been made in developing stable algorithms to perform this task.¹¹⁻¹³ Of course, inversion only makes sense if the surface is really flat.

Fadley has described^{7,14} the effect of surface roughness on the angular dependence of overlayer/substrate intensity ratios. A surface, rough on a scale much bigger than the inelastic electron mean free path, causes deviations in the angular dependence of intensity ratios because of two reasons. First, some regions of the surface may not be effective in producing photoelectrons because they are shaded for electron exit by adjacent roughness contours. Secondly, the true electron exit angle at a given surface point will in general be different from the experimental value as defined with respect to the macroscopic surface plane.

From the SEM pictures in Fig. 5, showing the morphology of an untreated and a cleaned foil, we may conclude that the foil surfaces are rough on the

Figure 6. Calculation of the angular dependence of the Al^{3+}/Al intensity ratio for a material with a uniformly thick overlayer on (a) a triangular substrate surface and (b) a substrate surface with half-spherical holes. The roughness mean free path in the material, so that shading effects occur at higher off-axis angles. The layer thickness is taken to be equal to 4.0 nm; for λ a constant value of 2.7 nm is assumed.

submicrometre scale. The images were taken in the secondary electron mode with the detector at the top right position of the pictures. White, intense features correspond to elevated regions of the sample, while dark features represent deeper regions from which secondary electrons cannot reach the detector. The vertical deviations in these pictures are due to the rolling process. We believe that the sharp holes that are visible in the SEM picture of the cleaned foil correspond to etched surface regions that were relatively rich in Mg before cleaning. For details see Ref. 1.

We have calculated intensity ratios for two models of rough surfaces (see Fig. 6). The calculations are based on an adapted version of Eqn (1) as proposed by Fadley:^{7,14}

$$\frac{I_o}{I_s} = \frac{n_o \lambda_o \langle [1 - \exp(-d/\lambda_o \cos \theta^i)] \cos \theta^i \rangle}{n_s \lambda_s \langle \exp(-d/\lambda_o \cos \theta^i) \cos \theta^i \rangle} \quad (3)$$

where θ^i is the true off-axis angle, the subscript 'o' denotes the overlayer and the subscript 's' denotes the

substrate. The average is taken over the unshaded surface area. Note that we again assumed a constant $\lambda = 2.7$ nm and a layer thickness d of 4.0 nm. Of course, the exact nature of the deviations exhibited in Fig. 6 are strongly related to the shape of the surfaces, but the tendencies seen are quite general, which can be easily understood. For low values of θ , shading will not be of great importance and the main deviating effect is in θ^i , which on average will be higher than θ . Thus the overlayer/substrate intensity ratio will in general be high for low θ -values. In contrast, for high values of θ , shading will be important. The unshaded parts will have their normals more pointed to the detector than the shaded parts. Thus for high θ -values we expect a generally lower overlayer/substrate intensity ratio. Note that this implies that the least deviation from the ideal curves is to be expected for intermediate off-axis angles, for the simulations of Fig. 6, between 30° – 40° . We believe that surface roughness is the main cause of the deviation from ideal layer behaviour seen for the aluminium foils.

CONCLUSIONS

We have shown that the uniform overlayer model is not applicable on our technical aluminium foils for determining their passivation layer thickness accurately with XPS. This is due to surface roughness and/or inhomogeneities in the passivation layer, as the SEM pictures and our simulations strongly suggest. We therefore think that it is not appropriate to base the thickness determination of overlayers on technical samples on only one XPS measurement: one simply cannot check the applicability of the uniform layer model in that way.

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