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GROWTH OF THIN ALUMINA FILM ON ALUMINIUM AT ROOM TEMPERATURE : A KINETIC AND SPECTROSCOPIC STUDY BY SURFACE PLASMON EXCITATION

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Résumé : Les paramètres cinétiques, ainsi que l'épaisseur limite de l'alumine formée par oxydation de l'aluminium, à température et à pression ambiantes, ont été déterminées par la technique de réflexion totale atténuée. Le film d'oxyde croît rapidement et atteint une épaisseur limite de 32 Å après 10 minutes d'exposition à l'air. Des temps d'exposition ultérieurs n'entraînent qu'une faible augmentation de l'épaisseur de l'alumine (environ 40 Å après trois mois d'exposition). Une étude par spectroscopie Raman révèle la présence d'entités OH à la surface de l'alumine, dont les fréquences de vibration sont identiques à celles enregistrées pour des OH adsorbés sur de l'alumine γ . Par contre, aucun signal Raman pouvant être attribué à l'alumine n'a été observé.

Abstract : The kinetic parameters and the limiting thickness of alumina formed on an aluminium film, at room temperature, under ambient pressure, can be determined by using an attenuated total reflection experimental set-up. An oxide layer grows rapidly and reaches a limiting thickness of about 32 Å after 10 minutes of exposure. Longer exposure time leads to a slow increase (about 40 Å after three months). Raman spectroscopic investigation reveals the presence of OH surface groups at the same frequency position as those observed on γ -alumina. No vibrational bands of the aluminium oxide was detected.

INTRODUCTION

The kinetic of the low temperature oxidation of aluminium has been studied by a variety of techniques such as scanning high energy electron diffraction /1/, work function measurements /2/, infrared reflectance spectroscopy /3/, ellipsometric measurements /4/... It seems to be accepted that the kinetic of formation of the oxide layer follows a logarithmic law /5/. The model of the growing process suggests that oxygen ions rapidly exchange place with aluminium atoms at the surface during the initial stage of the reaction. After monolayer coverage, the sticking coefficient of oxygen drops rapidly, and then normal chemisorption of oxygen on the stable amorphous oxide layer occurs. The oxide continues to grow by an ionic diffusion mechanism. As revealed by the literature data, the oxide reaches a limiting thickness of 15-50 Å. Because the surface plasma wave is a sensitive probe of metallic surfaces, its propagation is influenced by any modification occurring at the dielectric-metal interface. Furthermore, it was first pointed out by Chen et al. /6/ that the enhancement of the electric field at the metal surface, at the surface plasmon resonance, could be used to enhance the Raman signals from overlayers.

In this study, the oxidation of aluminium at room temperature, under ambient pressure, was investigated using an attenuated total reflection (ATR) experimental arrangement.

EXPERIMENTAL

Under high vacuum conditions, an aluminium film was deposited on a prism, with an evaporation rate of 5 Å/s⁻¹. The thickness of the film was monitored using a quartz microbalance.

For kinetic investigation, 190 Å of aluminium was deposited on a CaF₂ prism. This thickness was calculated to obtain optimum resonance conditions in the UV region. After the evaporation, the prism was rapidly exposed to air, and located at the center

of a rotating stage, connected to microcomputer monitors. The angular position of the reflectivity minimum (θ_{\min}), in p-polarization, (see insert in fig. 1) was recorded as a function of the time exposure. The first measurement was done about one minute after the introduction of air in the vacuum vessel. The incoming beam into the prism originated from a He-Ne laser.

For spectroscopic study, a 6328 Å line of an argon laser was used, together with a double monochromator spectrometer having holographic gratings (1200 lines/mn, Ramanor HG-2S, Jobin-Yvon). Spectra recordings were monitored by a computer system, allowing accumulations in order to increase the signal to noise ratio.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the angular position of the reflectivity minimum (θ_{\min}) with the exposure time to the air ($\lambda = 6328 \text{ \AA}$, $d_{\text{Al}} = 190 \text{ \AA}$, $n_{\text{CaF}_2} = 1.433$). After about ten minutes exposure, the value of θ_{\min} tends to stabilize, thus allowing the recording of the reflectivity curve over a wide angular range (Figure 2).

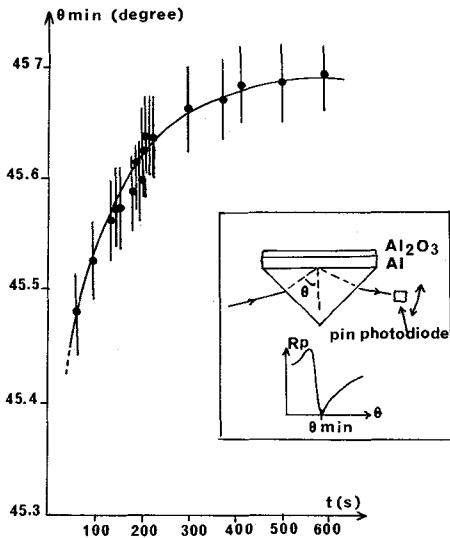


Fig. 1- Dependence of the angular position of the reflectivity minimum, θ_{\min} , versus the time exposure to air. ($\lambda = 6328 \text{ \AA}$, $n_{\text{CaF}_2} = 1.433$; thickness of the evaporated aluminium = 190 \AA)

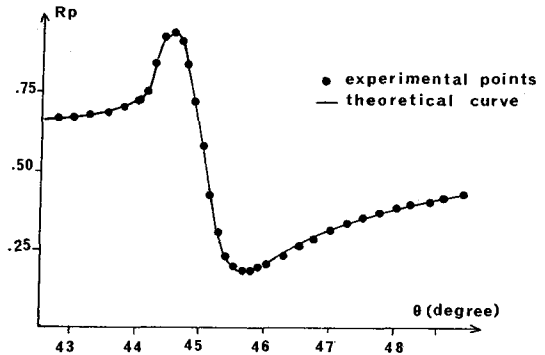


Fig. 2- Attenuated total reflectivity curve after 60 minutes exposure to air. Symbols are experimental points, and the solid line corresponds to the theoretical curve.

Note, on the reflectivity curve reported in figure 2, that the reflectivity R_p does not fall to zero because the thickness of the deposited aluminium was optimized for a minimum of R_p (R_{\min}) in the UV region. Nevertheless, the relative high value of R_{\min} may serve as a measurable parameter of the alumina growth [7].

The oxide grows rapidly during the initial stage of the reaction. So, even if theoretical predictions suggest a logarithmic growth law [5], it seems difficult to distinguish experimentally the logarithmic from the parabolic laws. So, we have reported on figure 3 the dependence of θ_{\min} versus $t^{1/2}$. The linear dependence observed up to about 7 minutes, permits the estimation of the θ_{\min} angular value at $t = 0$, i.e. for the pure aluminium film. Such an information cannot be obtained directly in our experimental conditions.

Because the θ_{\min} angular shift is due to the simultaneous increase of alumina $d_{\text{Al}_2\text{O}_3}$ and decrease of aluminium d_{Al} thicknesses, in the calculation of $d_{\text{Al}_2\text{O}_3}$, we

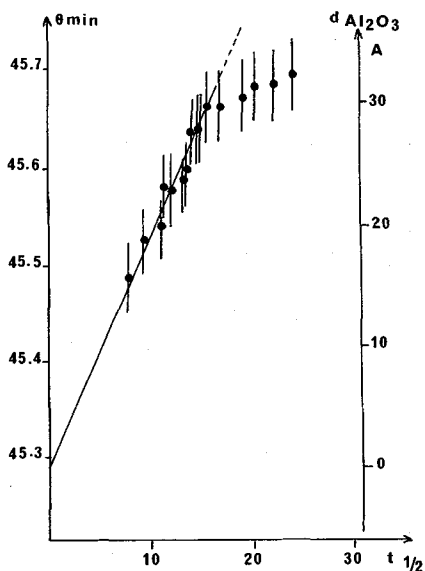


Fig. 3- Plot of θ_{\min} versus $t^{1/2}$. Note the fast increase of the alumina thickness during the first stage of the oxidation process, and the linear dependence of θ_{\min} with $t^{1/2}$ up to about 7 mn. The corresponding calculated values of $d_{\text{Al}_2\text{O}_3}$ are also reported (see text)

have estimated, from their relative density, that the ratio of alumina thickness over the loss of aluminium thickness was 1.6. We have shown /7/ that a good theoretical fit of the experimental reflectivity curve allows the determination of $d_{\text{Al}_2\text{O}_3}$ and ϵ_{Al} (ϵ = dielectric constant), if the refractive index of the alumina layer ($n_{\text{Al}_2\text{O}_3}$) is known. In this experiment, we have supposed that $n_{\text{Al}_2\text{O}_3} = 1.7$.

A good fit is obtained (figure 2) with : $d_{\text{Al}_2\text{O}_3} = 35 \text{ \AA}$; $d_{\text{Al}} = 166 \text{ \AA}$ and $\epsilon_{\text{Al}} = -42.3 + 21 i$ (at $\lambda = 6328 \text{ \AA}$).

The calculated value of ϵ_{Al} is in good agreement with those reported by Mathewson and Myers /8/. The so-calculated dielectric constant is of prime importance for the interpretation of the θ_{\min} angular shifts during the oxide growing process.

From our results, we can estimate that the θ_{\min} angular variation of 0.4 degree corresponds to the formation of 32 Å of alumina.

The recording of the reflectivity curve after three months exposure to air indicates that the alumina layer continues to grow and reaches a limiting thickness of about 40 Å.

The vibrational properties of the oxide film were tentatively investigated by Raman spectroscopy, with an exciting wavelength of 3638 Å. The diffuse Raman light was collected in a direction perpendicular to the surface (see insert figure 4). Due to the values of its dielectric constants, surface plasma waves of aluminium can be excited in the UV. This aspect is interesting in the case of spectroscopic study because of the ν^4 dependence of the Raman intensity (ν = frequency of the incident light).

The optimum incident angle for this study was chosen about 0.5 degree before θ_{\min} because the maximum amplitude of the surface plasma waves doesn't correspond with the minimum intensity of the reflected beam /9/.

All our attempts to observe Raman bands from the aluminium oxide were unsuccessful. Nevertheless, two bands located at 3697 cm^{-1} and 3795 cm^{-1} were observed, after 100 accumulations (figure 4). These bands disappear when rotating the polarization of the incident light, or after a small change of the incident angle.

We have assigned these Raman bands to OH groups bounded to alumina. Perri et al. /10/ have reported infrared absorption bands of OH-bounded γ -alumina, located at the same frequencies, but an additional band was observed at 3737 cm^{-1} on their spectrum. This band is not seen in our case, but it may be a shoulder of the 3697 cm^{-1} one. So, we suggest that the alumina films have a γ -alumina superficial structure.

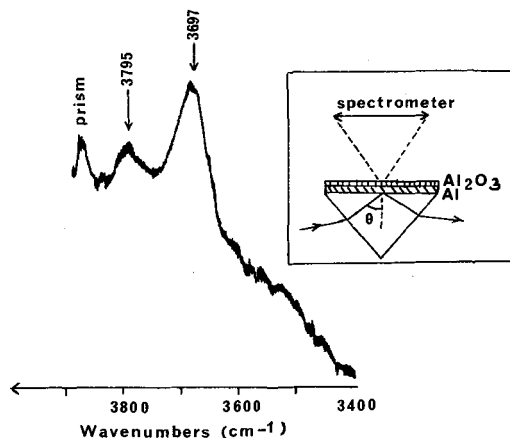


Fig. 4- Raman spectrum of OH groups bounded to alumina, after 100 accumulations, between 3400 and 3900 cm^{-1} . ($\lambda = 3638 \text{ \AA}$, 300 mW power, 6 cm^{-1} slit width, p-polarized light).

The observation of OH vibrational bands under excitation of surface plasmon by ATR is surprising, if one considers that attempts to obtain Raman spectrum from adsorbed molecules on silver films, by ATR techniques, were unsuccessful. An additional resonance contribution may be suggested in our case, because we were not able to detect any Raman signal of pyridine and formic acid adsorbed on the thin alumina film.

CONCLUSION

Attenuated total reflection is a useful technique to investigate the kinetic of formation of a thin alumina layer on an aluminium film. It may be applied to other relatively slowly evolving systems. For spectroscopic study of adsorbed molecules on alumina, further experiments are needed to clarify the possibilities of such an arrangement.

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