

EFFECT OF THE ALUMINIUM SURFACE MORPHOLOGY ON THE BARRIER TYPE ANODIC FILM GROWTH

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Abstract

Anodic alumina in both of its forms - a barrier type and a porous type - has received numerous studies and practical applications. Its potential could be further increased with the recent development of aluminium thin film sputter-deposition technologies. Most of the research has been performed towards Al foil anodizing; however in case of Al thin films the important knowledge is missing. In this study we have investigated the influence of the Al film structure and morphology on the electrochemical response during aluminium anodizing. Various Al thin films were prepared via an ion beam deposition, a magnetron sputter-deposition and a thermal evaporation. The films were then anodized in a barrier-type-giving electrolyte to various final potentials. The as prepared and anodized films were characterized by scanning electron microscopy and stylus profilometry to reveal the effect of the surface morphology on the anodizing behavior and dielectric breakdown in the anodic films. The breakdown potential was found to be typical for all the films tested, although being greatly dependent upon the initial film surface morphology. A model for explanation of the phenomena observed has been developed and justified experimentally.

Keywords: Anodizing, aluminium, anodic alumina, thin films, electric breakdown

1. INTRODUCTION

Anodic alumina can be prepared in two basic forms [1]: as a barrier (compact) oxide and as a porous oxide. The type of oxide grown by anodizing depends mainly on the electrolyte used [2]. Barrier type anodic oxide is composed of a compact alumina film, and its thickness is given by the potential value applied during anodizing [3]. Porous type alumina has complex structure composed of a barrier type film covered by a porous structure. The thickness of porous anodic alumina (PAA) depends on the current density and anodizing time [4]. The pores are typically in nanometer size [5] and therefore PAA has a great potential for nanotechnology. Recently many advanced applications of PAA have been reported [6,7]. Further, the importance of PAA could be extended by applying the anodizing technique to thin Al films [8]. Such an approach was recently demonstrated to be useful for preparation of nanowire arrays of several different metal oxides [9,10]. While many efforts have been made towards anodizing Al foils and most important aspects of such anodic processes are well studied, the understanding of processes of anodic alumina growth on thin Al films needs further clarification. Moreover, in case of Al thin films, their structure and morphology depend crucially on the film formation techniques and on the process conditions, which additionally complicates interpretation of the experimental results. Therefore, it is necessary to investigate the processes of Al thin film anodizing and their specificity, especially, the influence of aluminium structure and morphology on electrochemical responses during aluminium anodization.

In the present study, several Al thin films having various structures and morphologies were prepared and anodized in a barrier-type electrolyte in pursuit of studying the electrochemical responses and their dependence upon the technological, electrical and electrolytic conditions. The barrier-type anodizing was chosen for better understanding of the fundamental electrochemistry associated with anodic oxidation of aluminium thin films. The main attention was paid to investigation of the electric breakdown phenomena in the anodic films and the effect of the aluminium surface morphology on the breakdown development.

2. EXPERIMENTAL PART

2.1. Thin film preparation

Thin aluminium films were prepared by the following physical vapour deposition (PVD) techniques: an ion beam deposition (IBD), a magnetron sputtering (MS) and a thermal evaporation (TE). Three different IBD and MS films were prepared by varying the deposition conditions, while two different films were deposited by altering the TE regimes. Thus, the 8 variants of thin aluminium films having various structures and surface morphologies were prepared for anodizing experiments. For reference, a 100 micrometer thick as-rolled aluminium foil was also anodized under the same electrolytic conditions.

2.2. Anodizing

Anodizing experiments were performed in a potentiodynamic mode by sweeping the potential at a rate of 0.1 V/s from 0 to 200 V (exceptions are mentioned in later text). The current density was limited to 2.25 mA/cm². All anodizing experiments were carried out in a special flow-through anodizing cell at room temperature. Borate buffer (0.5 M H₃BO₃; 0.05 M Na₂B₄O₇) was used as the electrolyte [2]. The anodizing variables were controlled via a PC driven Keithley 2400 source meter.

2.3. Film characterization

Scanning electron microscopy (SEM) was used for characterization of the as-sputtered and anodized aluminium samples with the focus on the film structure and surface morphology, so as to estimate the quality of anodic alumina grown on the differently prepared thin aluminium films. SEM images were recorded without any sample pre-treatment in a Tescan Mira II scanning electron microscope. Stylus profilometry was used to investigate the surface roughness; each sample was measured at three different points using a Bruker Dektak XT instrument. The surface roughness was calculated as the average deviation from the real surface to a perfectly flat surface.

3. RESULTS AND DISCUSSION

By altering the deposition conditions of the various PVD techniques we have prepared eight Al thin films with various structures and morphologies. The differences in the structure and morphology were confirmed by SEM and profilometry. Al thin film structure and morphology variations achieved by use of the different techniques are seen on SEM images in **Fig. 1**.

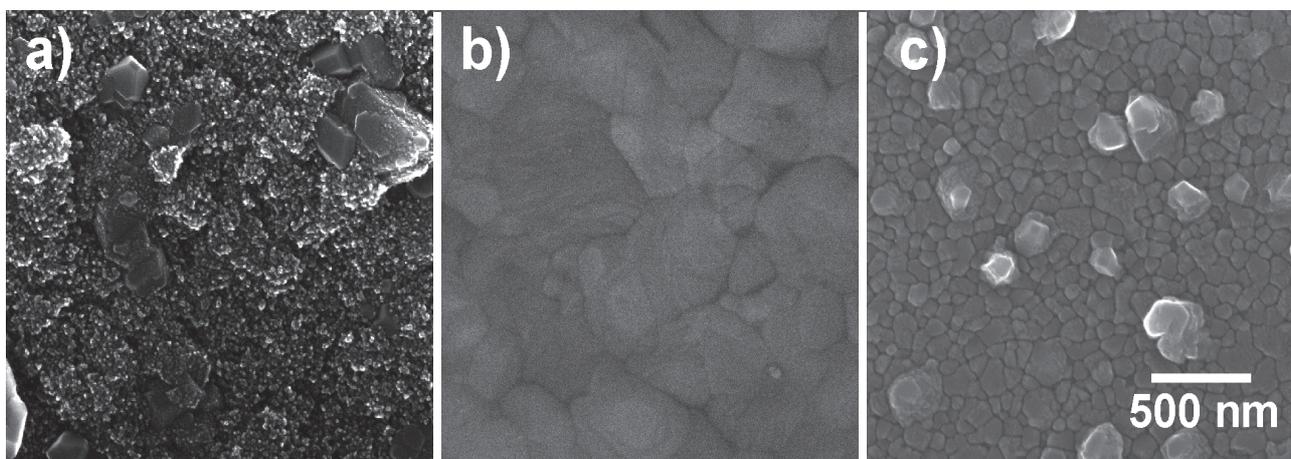


Fig. 1 SEM images of aluminium thin film deposited by (a) an ion beam assisted deposition (sample IBD 3), (b) a magnetron sputtering (sample MS 1) and (c) a thermal evaporation (sample TE 2). The variety of surface structure and morphology of the Al films deposited by various techniques is clearly visible. The scale bar is valid for all 3 images

The variations caused by controlling the deposition parameters were also observed (not shown). In order to perform a quantitative analysis of the films, the roughness of the samples was evaluated from the profilometry data. The calculated roughness as a single number is a very useful parameter to estimate the sample surface quality. The roughness values for all the samples are summarized in **Table 1**. The potentiodynamic anodization revealed a common feature in the breakdown behaviour of all Al thin films prepared here. Typically, the breakdown potential of all the films was below 200 V and happened reproducibly for each sample (data summarized in **Table 1**). It should be noted that the breakdown potential for an Al foil was much higher, and the current-time response of the potentiodynamically anodized foil till 200 V did not reveal a breakdown yet. The breakdown potential is known to depend on experimental conditions [11]. In case of the conditions used in our study, the breakdown potential during anodizing the Al foil was as high as 325 V. Typical anodizing responses for an Al film and an Al foil are shown in **Fig. 2**.

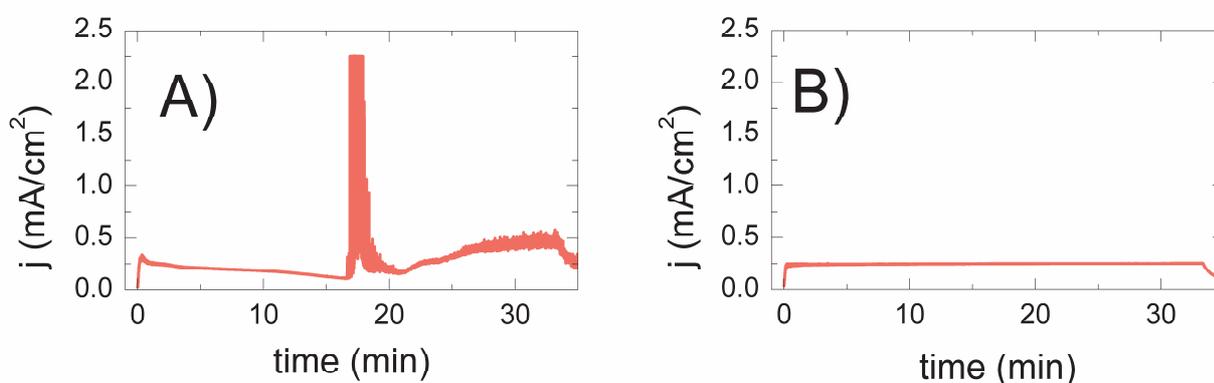


Fig. 2 Typical current-time responses during potentiodynamic anodizing of (a) an Al thin film prepared by ion beam deposition (sample IBD 1) and (b) an aluminium foil

The anodizing behaviour observed suggests a significant difference between the Al films and Al foils. In order to explain the low breakdown potential for the anodic films grown on the thin films, more experiments were carried out revealing eventually that one of the reasons of the observed abrupt voltage change during anodizing the Al thin films was the damage of the anodic oxide surface. This assumes that the surface damage will cause a rapid anodizing of the uncovered, non-anodized areas on the sample. All the anodized samples were therefore studied by profilometry in order to estimate the surface quality. The data obtained were evaluated and the surface roughness was calculated for all the samples. The surface roughnesses of the anodic oxide films were compared with the roughnesses of the corresponding initial Al thin films. The data are summarized in **Table 1**.

One may see that significant surface roughness change occurred for several samples, but in some cases there was no much change. Comparing the samples with and without the surface roughness change, we conclude that the surface roughness changes more obviously for the samples with the smaller roughness of the initial Al films. More studies of this phenomenon were done to a representative MS 1 sample showing a big surface roughness change. For comparison, a representative sample IBD 2, showing little surface roughness change, was also analyzed. SEM imaging of the MS 1 sample after the anodizing revealed a bubble-like structure of the damaged areas, often detaching from the sample surface (**Fig. 3a**). In case of IBD 2 sample, where the surface roughness did not change much during the anodizing, the SEM analysis confirmed that the anodic alumina film surface remained intact, i.e. without any visible damage (**Fig. 3b**).

Table 1 Summary of the roughness data measured on the as prepared Al films and on the corresponding anodic alumina films after anodizing, the ratio of the as prepared / anodic oxide surface roughness and the breakdown potential of the differently deposited aluminium films

Sample					
deposition technique	sample number	initial film roughness (μm)	anodic oxide film roughness (μm)	ratio after/before anodizing	brakedown voltage (V)
IBD	1	0.006	0.09	15.0	101
	2	0.03	0.03	1.0	136
	3	0.03	0.04	1.3	140
MS	1	0.01	0.16	16.0	142
	2	0.009	0.11	12.2	117
	3	0.06	0.07	1.2	112
TE	1	0.01	0.08	8.0	137
	2	0.01	0.02	2.0	150

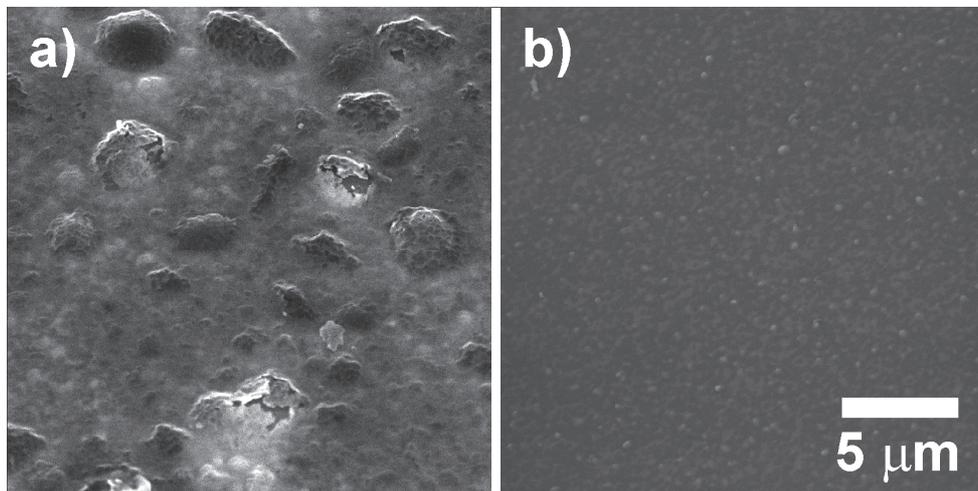


Fig. 3 (a) sample MS 1 after anodizing - a serious surface damage of the anodic film is clearly visible, (b) sample IBD 2 after anodizing - the surface of the anodic film remains relatively flat without visible damages. Both images were recorded at a 40° tilt to the substrate. The scale bar is for both images.

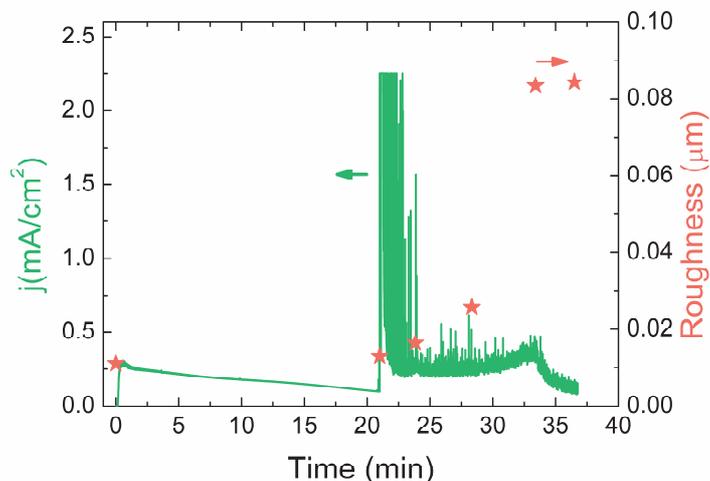


Fig. 4 The current density - time response during potentiodynamic anodizing (green curve, left axis) with notes for the surface roughness values measured for samples anodized to corresponding potentials (red stars, right axis)

Both sample types - with and without the anodic oxide surface damage - revealed similar current responses during anodization. Therefore, the breakdown observed during anodizing was assumed not to be caused by the surface damage. This assumption was confirmed by investigation of the surface roughness change during the anodizing. Sample TE1 was chosen as a representative of samples with significant roughness change after anodizing. Several pieces of sample TE 1 were processed. Each piece was anodized at the same voltage sweep rate but to a different potential. The results are summarized in **Fig. 4**.

The first piece of sample TE 1 was anodized to a potential close to, but below, the breakdown potential. The roughness of the anodic oxide was the same as that of the initial Al film. The second piece was anodized to a potential immediately following the breakdown potential value. A very low increase in the anodic alumina surface roughness was observed in this case. The minor roughness changes eventually proved that the serious surface damage did not occur during the breakdown event. Even in case of sample anodized to a potential of 170 V, which is more than 40 V higher than the breakdown potential, the anodic oxide surface roughness change was minor. The major change occurred between 170 and 200 V. Such a rapid increase of the surface roughness in such a small potential range could be related to the surface damage. Finally, the current decay following the potential limit of 200 V did not cause any change in the surface roughness. Interestingly, the serious surface damage was not accompanied by any further significant current density increase. The observed shift between the breakdown moment and the roughness change during the TE 1 thin film anodizing suggests that the breakdown mechanism could be the same in the case of the samples with smaller and bigger initial roughnesses. In other words, the breakdown potential is not associated with the film destruction. Furthermore, the profilometric observation of the shift of surface damage with respect to the breakdown potential allowed us to expect a similar behaviour also for the samples with the initially bigger roughness. As mentioned above, the breakdown potential does not depend on the initial roughness. Therefore, in case of samples with the initially bigger roughness, the shift between the breakdown and surface damage potential is bigger, too.

Taking into account all the findings of this work, a mechanism is proposed as follows. During the potentiodynamic anodizing, an electric breakdown occurs at a certain potential, the phenomenon being associated with an intensive and fast rise in the current density. According to the SEM observation of Al thin films with the initially bigger roughness and to the profilometric results, the roughness increases during the anodizing of samples with the initially smaller roughness, and the breakdown is not caused by a serious destruction of the anodic oxide film. Instead, the breakdown could be related to generation of defect sites in the anodic films. The occurrence of defect sites in an anodic film is known from earlier works done on anodizing Al foils [12]. The further potential increase causes, at least partially, the growth of the defects and/or gas evolution resulted from the higher conductivity of defect sites [13]. Finally, the processes lead to serious surface damage. The bigger initial surface roughness seems to provide more space for the defects expansion and stress dissipation. Therefore, the serious surface damage in case of samples with the initially bigger roughness takes place at relatively higher potentials.

4. SUMMARY AND CONCLUSION

The effect of surface roughness of the aluminium films on their electrochemical response during barrier type anodizing was investigated. Different aluminium films were prepared by means of various PVD techniques at circumstances of varying the deposition parameters. All the films revealed an electric breakdown at a potential lower than 200 V. The SEM analysis and profilometric measurement results allow us to conclude that the phenomenon is due to the defect sites in the anodic films. These defects grow in size, cause gas evolution and lead finally to seriously damaging the anodic films. A bigger surface roughness of the initial Al thin film does not influence the breakdown potential value although significantly increases the difference between the breakdown potential and the potential of film destruction. This effect could be due to a higher ability of the rough surface to host expanding defects and provide effective stress dissipation. The nature of such defects, their behaviour and their elimination will be the subject of a future work.

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