

Deep Oxidation of Aluminum by a DC Oxygen Plasma

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Resumen A novel way to obtain aluminum oxidation using a DC oxygen plasma is described. It is shown that the alumina layer is ~ 50 nm thick and the oxidation results in a stoichiometric formation of Al_2O_3 . The influence on the oxidation of the electrode distance and pressure are studied. By analysing the experimental data, we find that the kinematics of oxide growth can be described as having two main contributions coming from the plasma and the surrounding ionized gas.

Introduction

The aluminum oxide films have become important in many potential technological applications [1,2]. Metal oxides including ultra thin epitaxial oxide films play an important role in material research, displaying metal-, semiconductor-, and insulator-like properties [3].

In particular there has been an increasing interest to grow alumina films in magnetic tunnel junction devices [4], which have applications as magnetic sensors and non volatile memories. The magnetic tunnel resistance effect is extremely sensitive to the precise interface structure [5]. Specifically the Al_2O_3 acts as a barrier insulating material and the surface must be free from defects in order to avoid electrical conductivity. The usual way to prepare the films is to evaporate an aluminum layer and then to oxidize it. Developments of new oxidation techniques are then necessary to improve quality.

Oxidation of aluminum up to 2 nm is a straightforward approach [6], but deeper oxidations are difficult to produce because the initial layer shields further oxidation. We address the problem of deep oxidation by implementing a new technique which makes use of a continuous oxygen plasma. The first section gives the experimental set up and describes the oxidation. Then we present Auger measurements, and finally we investigate the kinematics of oxide growth.

Experimental setup and oxidation

The basic experimental setup is shown in Figure 1. Aluminum samples with sizes of $1.72 \text{ cm}^2 \times 0.13$ mm thick were cut from a larger piece of high purity Al foil. The sample is put in a chamber which is maintained in a oxygen atmosphere of about 0.1 bar. Prior to the oxygen exposure (99.8% pure oxygen, the main impurity is nitrogen) the chamber was outgassed several times for periods of some hours.

The untreated sample contained already a native oxide layer (OL) of about 2 nm, which is characteristic of aluminum surfaces exposed to atmospheric pressures for long times. The presence of this native oxide is not relevant to the present work, since the final OL thickness is several times larger.

Inside the chamber the sample touches perpendicularly the electrode maintained at higher potential (hereafter referred to as the positive electrode), and the distance to the electrode kept at lower potential (the negative electrode) varies from 0.4 to 1.6 cm. The electrodes are also made of high purity Al wire. The flowing current is less than 3 mA and remains approximately constant during the experiment. The voltage across the electrodes is about 500 V.

The plasma is formed by negative oxygen ions going from the negative to the positive electrode. The beam has a column shape and it slowly scans the sample surface contained within the cone delimited by the shadow lines as show in Figure 1. It will be seen that the region which suffers oxidation is mainly that impinged by the plasma.

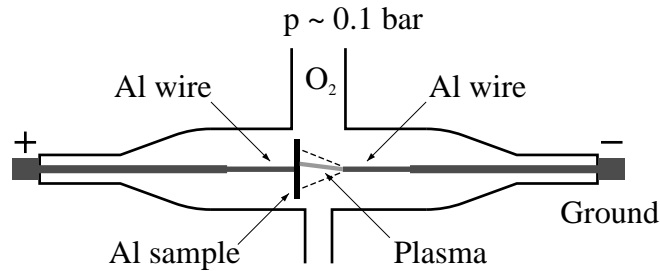


Figure 1. Experimental setup for sample oxidation.

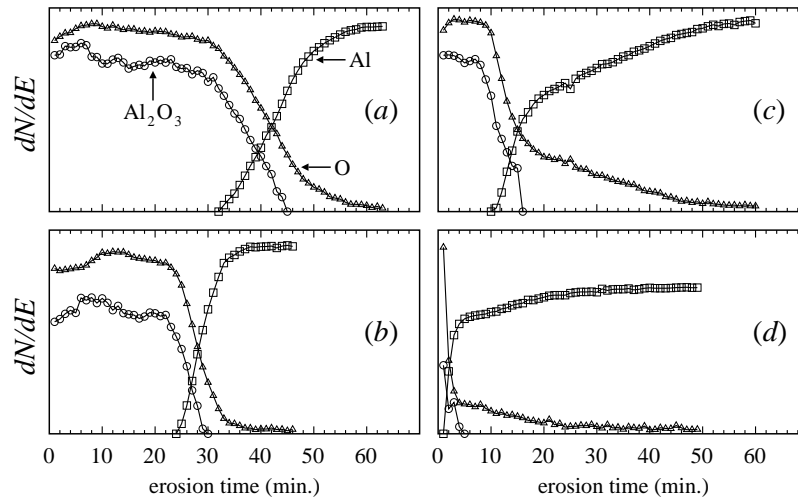


Figure 2. AES Profile of the oxidized sample at the regions (a) **I** = at the center, (b) **I** = displaced from the center, (c) **II**, and (d) a sample not oxidized in chamber.

Once a thick enough OL is formed by the plasma over a point at the surface, negative ions start to accumulate because the Al_2O_3 is a highly ionic material with a low electrical conductivity. The plasma is then deviated by the electric field generated by the accumulated negative charge, so that it impinges at a new location. The typical movement of the plasma over the surface is spiral like, starting at the center where the electric field between the sample and the electrode is higher at the beginning.

Not only ions inside the plasma contribute to the oxidation. There are some ions generated outside the plasma which are constantly impinging over the sample surface and slowly grow an OL. This builds at later stages a thick OL which also accumulates negative charges and hinders the plasma to reach the surface as explained previously. The plasma then bypasses the sample and is deviated to the positive electrode. At this point the oxidation process stops. We note that even for similar experimental conditions the total oxidation time may show significant variations.

There are 2 main characteristic regions in the sample after oxidation. We label with **I** the region affected directly by the plasma flux, whereas with **II** the region impinged only by ions coming from outside the plasma. The region **I** is shaped in a circle and increases with time as the plasma scans the surface.

Cross section profiles

In order to get concrete proof of the existence of alumina, AES profiles were performed (Figure 2). In all cases an Auger characteristic peak of Al_2O_3 appears at the beginning, since all samples contained at least the native OL. Within the OL a stoichiometric formation of Al_2O_3 appears and no traces of metallic aluminum are observed. The plasma covered region **I** (the thicker one) and the ionized gas falls over **I** and **II**. The largest OL thickness occurs in the center of the circle and decreases as we move away.

Tabla 1. Total charge q for different electrode separations D at constant pressure of 70 Torr. The charge q_D is calculated using (1). For that purpose σ_p and i_g have been fitted by least square deviation and the resulting percentual deviation of the calculated values is given in parentheses.

D (cm)	S_I (cm ²)	t (min)	q (C)	q_D (C)	
0.4	0.414	22	3.60	3.62	(+0.6%)
0.6	0.375	21	3.39	3.42	(+0.9%)
0.8	0.637	48	7.66	7.44	(-2.9%)
1.0	0.641	47	7.28	7.31	(+0.4%)
1.2	0.871	42	7.12	7.04	(-1.1%)
1.4	0.641	36	5.77	5.86	(+1.6%)
1.6	0.992	72	11.11	11.22	(+1.0%)

We have included the spectra of an aluminum sample not oxidized in the chamber (Figure 2-d). It contains only the native OL and displays the thinnest thickness. From this graph we can estimate the correlation of depth with the erosion time. The width at half height is 2 minutes and this should correspond to a layer thickness of about 2 nm. We may conclude that 1 minute of erosion digs approximately 1 nm in the alumina. The largest oxidation depth shown in Figure 2 is then ~ 50 nm, and it is more than 20 times larger than the native OL.

Charge measurements

We measured the total charge q which flows during the experiment, since the charge is proportional to the number of oxygen ions which strike the surface, and therefore the amount of Al_2O_3 is expected to increase with the charge.

The charge can be separated in two parts. One part q_p goes in the form of a plasma and the other q_g as a simply ionized gas or free electrons which are not bound to ions. We first assume that for fixed parameters (e.g. constant pressure and voltage) the plasma deposits an uniform amount of oxygen ions per unit area. Therefore it gives a constant charge density σ_p over region **I**, and setting S_I to be the corresponding area we have $q_p = \sigma_p S_I$.

We also suppose that the ionized gas falls uniformly over the sample increasing the amount of oxygen ions with the time t . If the current associated with the ionized gas is i_g then $q_g = i_g t$. The sum of the two charges gives the total charge

$$q = \sigma_p S_I + i_g t \quad (1)$$

The measurements are summarized in Tables 1 and 2. The distance between the electrodes was varied by a factor of 4 and the pressure by a factor of 2. It also gives the calculated values for the charge q_D (varying distance) and for q_P (varying pressure) based on (1). In the first case the fitted parameters are $\sigma_{pD} = 1.703$ C/cm², $i_{gD} = 0.1324$ C/min = 2.207 mA, and in the second case $\sigma_{pP} = 0.768$ C/cm², $i_{gP} = 0.1487$ C/min = 2.478 mA. The difference between σ_{pD} , i_{gD} and σ_{pP} , i_{gP} is significative and so we can not expect (1) to hold in this simple form both the distance and pressure dependence.

A careful numerical analysis shows that (1) holds for distance variations but not for pressure variations. One way to correct this deficiency is to let the parameters σ_p and i_g be functions of pressure. Since the relative variation in σ_p is much larger than i_g we assume the first to be pressure dependent and the second to be nearly constant. The value $i_g = i_{gD}$ obtained above represents about 80% of the total current.

Because σ_p is related to the charge or ions coming from the plasma, we arrive at the conclusion that the amount of oxygen deposited by the plasma over the region **I** is pressure dependent. This result could be expected since in a plasma the ions generated by the electric current depend on the pressure. Changing the pressure modifies the particle density and also the Debye length, which is an important characteristic of plasmas. A lower pressure or density produces a larger Debye length (inversely proportional to the square root of the particle density) and instead of a plasma it can become a simply ionized gas for very low pressures.

Tabla 2. Same as in Table 1 but now the oxygen pressure P changes and the electrode separation is kept constant at 1.0 cm. The charge q_P is calculated using the same equation but with new fitted parameters.

P (Torr)	S_I (cm ²)	t (min)	q (C)	q_P (C)	
50	0.609	29	4.53	4.78	(+5.5 %)
60	0.668	45	7.47	7.21	(-3.5 %)
70	0.641	47	7.28	7.48	(+2.7 %)
80	0.676	35	6.01	5.73	(-4.7 %)
90	0.625	21	3.57	3.60	(+0.8 %)
100	0.465	31	4.83	4.97	(+2.9 %)

The charge density deposited over the sample due to i_g is $\sigma_g = q_g/S_{I+II} = i_g t/S_{I+II}$. For the times listed in Table 1 the density σ_g varies between 1.62 C/cm² and 5.54 C/cm². A fraction of this quantity corresponds to oxygen ions and the rest to free electrons.

The total charge density in region **I** is $\sigma_I = \sigma_p + \sigma_g$ and in **II** it is $\sigma_{II} = \sigma_g$, so that σ_{II}/σ_I lies between 0.488 and 0.765. This should be equal to the OL thickness of **II** divided by that of **I** if the OL formed were simply proportional to the amount of oxygen striking the surface and there were no free electrons included in σ_g . Therefore the ratio between the OL thickness of **II** and **I** is less than σ_{II}/σ_I . From the Auger measurements in Figure 2 we can compare the thickness of two different points in region **I** with that of region **II** giving the ratios 0.33 and 0.50, in agreement with the previous discussion.

Acknowledgements

Fonds from MECESUP PUC0006 and FONDECYT 1000535 are greatly acknowledged.

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