

# GROWTH AND CHARACTERIZATION OF ANODIC ALUMINUM OXIDE

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## ABSTRACT

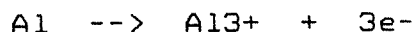
The growth of anodic aluminum films on silicon was investigated. The films were formed using an electrolytic cell with sulfuric acid and a lead cathode. The effects of electric potential, electrolyte concentration and anneal time were investigated with respect to film thickness, index of refraction and oxide quality with a three level-three factor Box-Behnken designed experiment. The results of the statistical analysis indicated poor repeatability in film qualities as evidenced in ellipsometric and C-V measurements.

## INTRODUCTION

The development of alternate methods of oxidation has been driven by interests in oxidizing III/V compounds such as In/P [1], multilevel metallization schemes where oxides cannot be thermally grown [2], and the need for low temperature oxidations due to the trend towards shallower junction depths. Anodic oxidation of aluminum is one method that has been investigated [3].

Anodic growth refers to the formation of an oxide by electrochemical reactions. It can be carried out in a simple inexpensive electrolytic cell with great accuracy and without costly and complicated equipment, such as chemical vapor deposition and sputtering systems used to deposit dielectrics [2][4]. The anodization apparatus consists simply of a voltage source, a multimeter for monitoring purposes, a lead cathode, a well for the electrolytic solution and a holder for the wafer which will also provide electrical contact to the backside of the wafer [5].

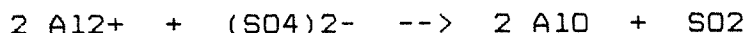
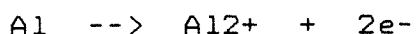
For the aluminum anodization process, the electrolytic solution used is sulfuric acid and the cathode is lead [6]. The reaction mechanisms are as shown below:



where  $\text{e}^{-}$  represents an electron. The aluminum is converted to

its oxidized state at the anode and the reaction is completed by the sulfate ion provide from the electrolyte to form the aluminum oxide [7]. The sulfuric solution was chosen due to immediate availability of materials.

Several parameters affect the formation and quality of anodic films. The parameters of concern in this experiment were the applied electric potential, the electrolytic concentration of the solution, and the annealing time in a 450C nitrogen/hydrogen ambient. A Box-Behnken, three level-three factor, style experiment was designed around these parameters. The electric potential was varied from 5 to 15 volts as selected from literature values. The concentration ranged from 2.5 to 15% by volume, again, selected from literature values. Annealing times of 0 to 30 minutes at 450C in a nitrogen/hydrogen ambient were chosen from standard RIT processes. The responses of interest were the film thickness, index of refraction and quality of the oxide as evaluated from C-V curves. Increasing solution strength tends to produce films that are more porous [6]. The porosity would degrade the oxide quality and be reflected in deviations in the index of refraction from the accepted value of 1.76 and in the electrical characteristics. The electric potential and electrolyte concentration both effect the growth rate in that as they increase so does the reaction rate [6][7]. If the rate is too high the reaction may not follow the one cited above and take the following [7]:



The resulting films would deviate in their indices of refraction and film thicknesses from run to run depending upon the stoichiometry and differences in the material properties between the two aluminum oxides. Annealing was seen to reduce the hysteresis of C-V voltage curves with increasing temperatures in an argon ambient by Matsui, et. al. [8]. It was desired to repeat this effect employing the standard RIT anneal process with varying times.

## **EXPERIMENTAL**

The anodization cell consisted of the apparatus described above and was arranged as shown in the schematic in Figure 1. The aluminum anode had an area of 5.5 cm<sup>2</sup> exposed to the electrolyte. The cathode had an area of 5.0 cm<sup>2</sup> of lead foil. The rubber o-ring formed a seal between the teflon plate and the wafer to contain the electrolyte.

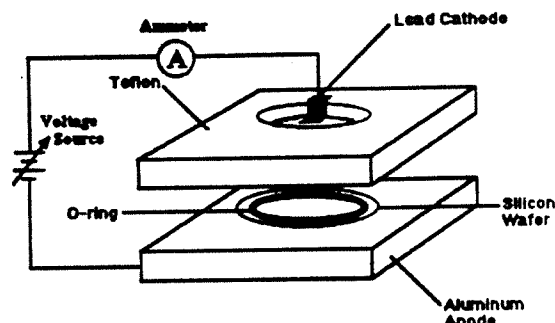


Figure 1: Anodization Apparatus

P-type <100> wafers were obtained with an average background doping of  $2.2 \times 10^{15}$  boron atoms/cm<sup>3</sup> as determined by four point probe measurements. They were scribed and cleaned via a standard RCA clean process. The back sides of the wafers were coated with aluminum using an evaporator with a tungsten filament. The film was annealed for 15 minutes at 450C in a nitrogen/hydrogen ambient. This was to provide ohmic electrical contact to the back side of the wafer as required for the anodization process. The front sides were next coated with 2000Å of aluminum. The aluminum films were anodized in ten milliliters of solution according to the concentration and voltage listed in the Box-Behnken experimental worksheet created in RS1 as shown in the Table 1.

Experiment Worksheet

0	1 CONC (% by vol)	2 VOLTAGE (v)	3 ANNEAL (MIN)	4 HYSTERESIS (V)	5 CHARGE (μ/cm <sup>2</sup> )	6 THICKNESS (Angstroms)	7 INDEX
1	6.3	15	0	2.5	6.7e+23	1890	1.55
2	10.0	10	0	6.0	8.9e+23	2029	1.52
3	6.3	5	0	1.8	5.9e+23	1829	1.44
4	2.5	10	0	1.2	1.4e+23	1405	1.54
5	6.3	10	15	1.0	2.9e+24	1939	1.69
6	2.5	5	15	1.3	1.7e+24	1353	1.48
7	2.5	15	15	0.9	3e+24	1221	1.56
8	10.0	15	15	1.6	2.6e+24	2030	1.60
9	10.0	5	15	2.8	2.3e+24	2007	1.45
10	6.3	10	15	0.9	2.3e+24	1439	1.48
11	6.3	10	15	1.0	3.4e+24	1411	1.54
12	6.3	15	30	0.1	3.1e+24	1622	1.54
13	10.0	10	30	1.2	2.3e+23	1631	1.65
14	6.3	5	30	4.8	1.7e+24	1489	1.51
15	2.5	10	30	0.2	3.3e+24	1314	1.55

Table 1: RS1 Experiment Worksheet

The anodization end point was noted by stabilization of the current as monitored with the ammeter. Agitation was provided by a pipet. The film thickness and index of refraction were determined using the AME-500 ellipsometer at a wavelength of 6328Å. The C-V plots were obtained after evaporating aluminum

through a shadow mask with  $8.6 \times 10^{-3} \text{ cm}^2$  and  $31 \times 10^{-3} \text{ cm}^2$  holes and the appropriate anneals in a 450C nitrogen/hydrogen ambient as prescribed by the experimental worksheet.

## RESULTS/DISCUSSION

The films produced ranged in thickness from 1221 to 2087A with an average thickness of  $1646 \pm 296\text{A}$ . These are relative values due to possible misalignment of the system. True nulls were not obtained when determining the polarizer and analyzer angles. The confidence limits also varied for the thicknesses. Also imaginary portions of the indices were ignored. The colors varied from green to purple from wafer to wafer and some wafers were hazed. The haze is indicative of porosity caused by higher concentrations of electrolyte which is what the films were processed in. The uniformity across a wafer was noted by color gradients across the wafer as the ellipsometer had a large spot size and did not allow for exact values to be obtained. The color was very uniform across eight of the fifteen wafers. The other seven showed slight gradients across the wafer, slight meaning that it varied from a light blue to a dark blue from one side to the other. This nonuniformity can be accounted for by a nonuniform initial aluminum deposition. The variations among the wafers were far too great to be accounted for by differences in stoichiometry as suggested in the introduction. The statistical analysis with RS1 supported this view. The F-ratios indicated that the coefficients could all be zero with only an 80% confidence in the values it did calculate though there was no evidence of lack of fit for these coefficients.

The indices of refraction obtained varied from 1.44 to 1.54 with an average value of  $1.54 \pm 0.07$ , again, the inaccuracies in the ellipsometry measurements apply to these values. These were all lower than the value of 1.76 as listed in the CRC Handbook of Physics and Chemistry suggesting that the stoichiometry was not  $\text{Al}_2\text{O}_3$  and that the films were not of perfect quality as noted by haze on four of the wafers. Again no definite correlation was shown to the parameters investigated by the statistical analysis. The F-ratios indicated that all the coefficients could be zero with 60% confidence in the values it did calculate and with no evidence of lack of fit. This suggests that the range of concentration was too narrow to show a noticeable effect.

The C-V measurements obtained were evaluated for charge nonidealities such as mobile ionic, fixed, and trapped charge in the oxide as determined from shifts of the threshold voltage from the corrected ideal threshold (corrected in that the metal/semiconductor work function was included in the threshold determination). The amount of charge ranged from  $0.1 \times 10^{24}$  to  $3.4 \times 10^{24}$  ions with an average value of  $1.9 \times 10^{24}$  ions. The RS1 analysis could not be completed due to a divide by zero error that was encountered while analyzing it. The amount of charge was high. The amount of mobile ionic charge was expected to be very high due to the use of sodium in the formation of the

tungsten filaments used for the evaporations. The amount of interface traps was also very high as noted by the spreading of the C-V curves.

The hysteresis was measured by plotting the C-V curves with the capacitor biased at +10 volts for one minute and then replotting the curve after it had been biased at -10 volts for the same time and taking the voltage difference between the curves. The differences ranged from 0.1 to 6.0 volts. The average of the zero minute anneals was 2.8 volts, the 15 minute anneals was 1.4 volts and the 30 minute anneals was 1.6 volts. This demonstrated that annealing reduced the hysteresis with the 15 minute anneal showing the greatest reduction.

### SUMMARY

The anodic aluminum films were grown. The effects of electric potential, electrolyte concentration and anneal time were investigated with respect to film thickness, index of refraction and oxide quality with a three level-three factor Box-Behnken designed experiment. The results of the statistical analysis were inconclusive. It is suggested that a screening experiment be done to determine the factors that are of significant influence in the anodization process as performed at RIT. The films produced varied in thickness from 1221 to 2087A with an average value of 1646 +/- 296A and in the index of refraction from 1.44 to 1.54 with an average value of 1.54 +/- 0.07. The amount of mobile ionic and fixed charge in the films ranged from 0.1  $10E24$  to 3.4  $\times 10E24$ . The hysteresis was decreased by annealing with the smallest average shift of 1.4 volts for an anneal time of 15 minutes in a 450C nitrogen/hydrogen ambient.

### ACKNOWLEDGEMENTS

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