The study on the thickness change of tantalum oxide as voltage drop in electrolyte

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Abstract— **Tantalum oxide (Ta_2O_5) films are of considerable interest for a range of application, including optical waveguide devices, high temperature resistors, and oxygen sensors. In this paper, we establish an anode oxidation process of tantalum thin film. The voltage drop in the electrolyte is affected not in voltage change but in current change. If the voltage drop in the electrolyte is same with cathode oxidation voltage, the current changes logarithmically in proportion to the voltage drop in interface of tantalum oxide and electrolyte. As a result of the measurement on the electrical property of tantalum oxide thin film, when the thickness of the insulator film is 1500Å, the breakdown voltage is 350volts and dielectric constant is 29.**

Index Terms— **tantalum oxide thin film, Anode oxidation, Electrolyte, Breakdown voltage, Dielectric constant etc.**

I. INTRODUCTION

The tantalum oxide thin film is most extensively used with dielectric material in devices. Because of their high dielectric constant, in recent years they have received increasing attention as a possible alternative dielectric to replace thin SiO_2 layers as capacitor insulators in high density dynamic random access memories, such as DRAM and in ultra large scale integrated (ULSI) devices

The thin film could be manufactured by the reactive sputtering method or the plasma oxidation method in the O_2 atmosphere. However, the insulation film manufactured in the cathode oxidation method is free from the pin-hole. It is more excellent on properties of the dielectric strength, the dissipation factor, chemical durability and etc. [1]-[3].

The research about the tantalum oxide thin film using the anode oxidation method was studied by Randall for the first time.

The space charge of the tantalum oxide thin film manufactured in the cathode oxidation method was combined among the insulation film growth.

The characteristic of the anodic tantalum oxide thin film depends on the concentration of electrolyte. The constant voltage oxidation process determines the characteristic of the insulating layer.

The characteristic enhancement on the thin film transistor of switching device in the TFT-LCD used as the display element is very important.

The Si_3N_4 thin film used gate insulator of TFT has low dielectric constant and many pin-holes, on the other hand the tantalum oxide thin film has high the dielectric constant. It can be applied to the gate insulator of the thin film transistor because it is free from pin-hole.

We use the anode oxidation process method in this paper. We experiment on influences of the anodizing voltage and anodizing current according to electrolyte concentration in Ta_2O_5 insulating layer [4]-[5].

II. ANODE OXIDATION OF TA THIN FILM

Each the anode oxidation is mainly used in forming the oxide layer of metals including Al, Ta, Nb, Ti and Zr, and etc.

The fundamental chemical formula expressing this kind of the process is

$M + nH_2O \rightarrow MOn + 2nH^{+} + 2ne$
On anode
$2ne + 2nH_2O \rightarrow nH_2\uparrow + 2nOH^{-}$
On cathode

The anode oxidation is mainly made in the aqueous electrolyte. However, the acid can be used as electrolyte according to the kind of various salt solutions.

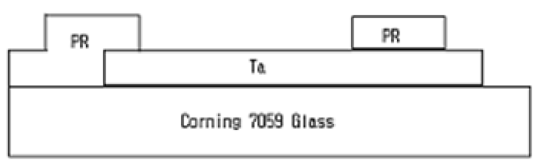

Fig.1. Cross-section of Ta thin film

Fig.1 shows cross-section of Ta thin film sample. According to the pH value of electrolyte, the mechanical and electrical properties of the oxide thin film are changed.

Moreover, the temperature of electrolyte and the anodizing voltage has an effect on the thickness of the oxide film.

As shown in figure 2, the anode oxidation is divided into 1) constant current oxidation process and 2) constant voltage oxidation process.

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The thickness of oxide thin film is proportional to the anodizing current and the final thickness is determined by the anodizing voltage.

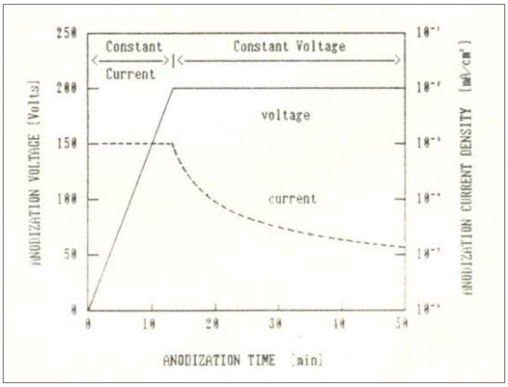

Fig. 2. Current-Voltage Anodizing Step for Ta_2O_5

After the anodizing voltage reaches the threshold level, the constant voltage oxidation process gets accomplished until the anodizing current reduces by 1~2% to the input value.

III. MODEL AND EXPERIMENTAL

The anode oxidation system used in this experiment can express as the Ta / Ta_2O_5 / Electrolyte System.

The relational expression between a experimentally obtained current and the electric field is I_a=A exp (B,E).

The current becomes the exponential function of the electric field.

The increment D of the oxide thickness is expressed in the Faraday's law as the amount of the current in which it passes the electrolyte cell for the anodizing Time t.

$$dD = K*dQ = K*I*dt$$

The total of the voltage drop sums voltage drop of the anodic oxide and electrolyte.

$$V = E*D + I*Re$$

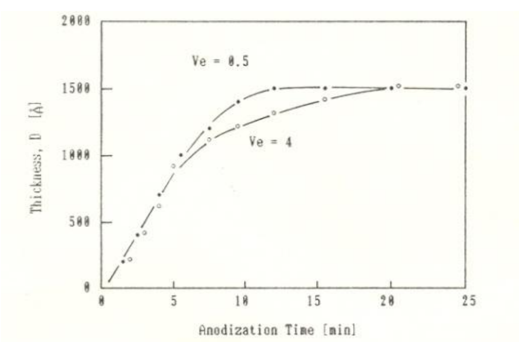

Fig.3. Thickness change of Ta_2O_5 film as time

Fig.3 shows thickness change of Ta_2O_5 film as time.

The oxide film elementarily depends on the kind of an electrolyte. The Ta_2O_5 insulating layer can nearly use all electrolytes of the hydrofloric acid. And it is influenced by the pH value. In this paper, the ammonium tartrate was used as an electrolyte for the Ta_2O_5 insulating layer production.

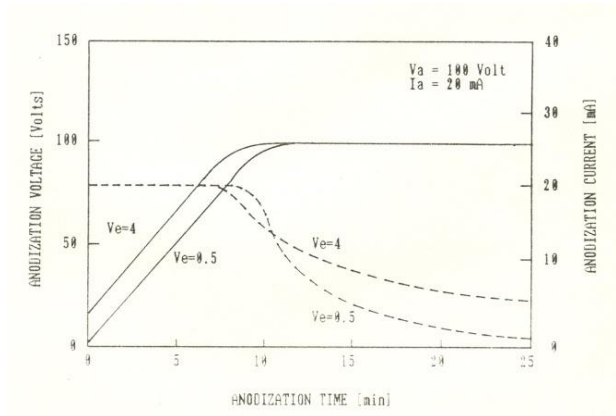

Fig.4. Change of current and voltage as time

TABLE.1
ELECTROLYTE CONDITION ON ANODE OXIDATION

Sample No.	Ammonium Tartrate		
	Concentration(%)	PH	Temperature(℃)
1	0.001	6.99	23
2	0.01	6.93	23
3	0.1	6.78	23
4	1	6.62	23

In Electrolyte, the Magnetic Stirrer for uniformly maintaining the concentration of electrolyte among the anode oxidation process was used. And we used a heater within the circumference of bath in order to experiment on the changing of characteristic of the Ta_2O_5 insulating layer according to the temperature of electrolyte. Fig.4 shows change of current and voltage as time. Table.1 shows electrolyte condition on anode oxidation.

The electrolyte cathode used the Pt electrode of 99.99% purity in order to prevent the corrosion.

We use Corning 7059 glass with substrate in this experiment. Fig.5 shows structure of electrolyte cell.

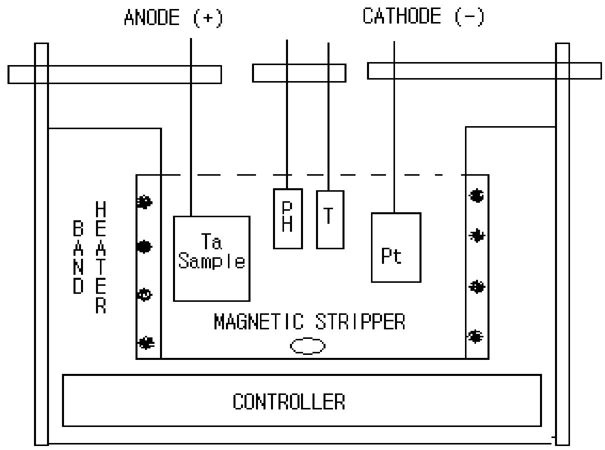

Fig.5. structure of electrolyte cell

The experiment sequence is as follows.

1. Glass cleaning: Firstly, the substrate boils for 30 minutes in the solution which mixes the NH_4OH: H_2O_2 : DI Water with 1:2:5 and cleans for 3 minutes in TCE, Acetone, and the Alcohol solution.

2. Dry: The glass is heated with the IR Lamp and the moisture is removed.

3. Ta deposition: Ta is deposited by 2,400Å thickness with the DC magnetron sputter machine. The deposition condition is P_b=3X10^{-7}Torr, P_o=3X10^{-3}Torr, Ar gas flow rate=15.0SCCM, I_{dc}=0.5A, V_{dc}=400volts, T_s=60.0min, and T=25℃.

4. Ta sample cleaning: it washes in TCE, acetone, and the alcohol solution for 3 minutes by ultrasonic wave. In the anode oxidation process, the photolithography process is facilitated for the ease control of the anodizing current density.

5. PR Coating: The AG 1,350 positive PR is coated 1.5μm thickness with the speed of 5,000RPM by spin coater.

6. Soft Baking: PR is baked for 20 minutes with 95℃.

7. PR Patterning: After exposure is made, the PR is developed and patterned.

8. Hard Baking: PR pattern is baked in 105℃ for 15 minutes.

IV. RESULTS AND DISCUSSION

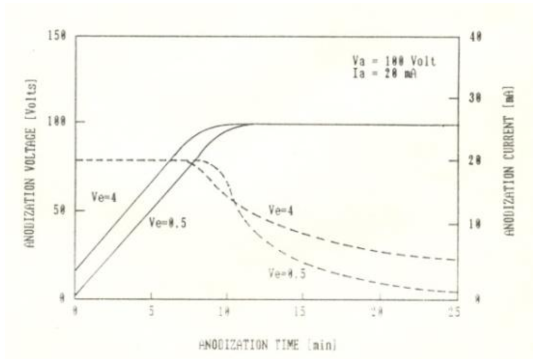

Fig.6. Change of I/V as time

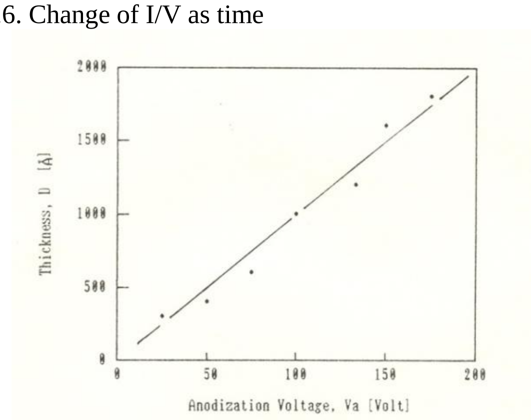

Fig.7. Thickness change of Ta_2O_5 film as voltage

The growth mechanism of the anodic oxide film according to the concentration of electrolyte was analyzed, and the change of the anodizing voltage and current was investigated on various other concentrations of electrolyte.

Fig.6 , 7 shows change of I/V as time and thickness change of Ta_2O_5 film as voltage separately.

As a result of the measurement on the electrical property of tantalum oxide thin film, when the thickness of the insulator film is 1500Å, the breakdown voltage is 350volts and dielectric constant is 29. Fig.8 shows capacitance of Ta_2O_5 film.

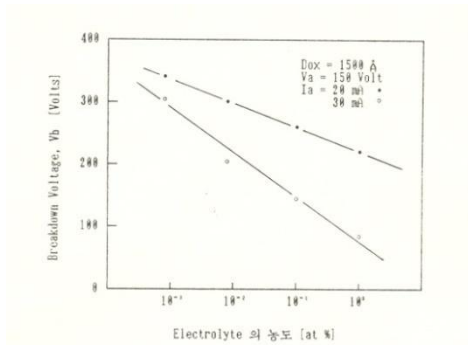

Fig.8. Capacitance of Ta_2O_5 film

V. CONCLUSIONS

The voltage (Ve) in electrolyte increases the initial value of anodizing voltage(Va) at constant current oxidation process, but has no effect on the change of Va property.

The final thickness of Ta_2O_5 thin films is determined by anodizing voltage(Va). The breakdown voltage of Ta_2O_5 thin films decreases as increasing of electrolyte concentration. Finally when the thickness of Ta_2O_5 thin films was 15,000 nm, the breakdown voltage of Ta_2O_5 thickness film was 350 volts and refractive index measured by spectrophotometer (= 400 800 nm) was 29. Fig.9 shows breakdown voltage change of Ta_2O_5

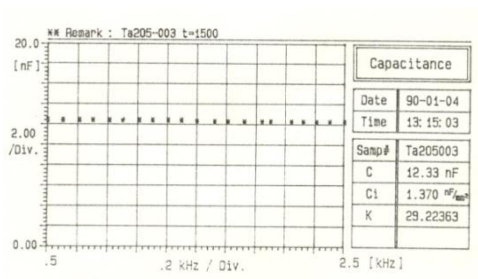

Fig.9. Breakdown voltage change of Ta_2O_5

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