

Heat Treatment, Ion Mobility Studies of Aluminium Oxide Films

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ABSTRACT

Heat treatment, ion mobility and effect of heat treatment on variously formed oxide thin films on aluminium in different aqueous electrolytes have been studied. The capacitance of aluminium oxide films depends on concentration and nature of the aqueous electrolyte. It has been observed that aluminium ions are mobile during the growth of aluminium oxide films in various electrolytes. On heat treatment in air the oxide film becomes more conducting. The conductivity depends on the time period and temperature of heat treatment but it is independent of film thickness and nature of the electrolyte. Two different types of patterns of conductivity were observed before and after heating of anodic aluminium oxide films. One is associated with high conductance and low rate of change of capacitance with increase in temperature and second is associated with low conductance and high rate of change of capacitance with increase in temperature.

I. INTRODUCTION

Kinetics of growth on tantalum in various aqueous electrolytes and their breakdown voltage characteristics has already been reported by the author^{1-4,24}. The present work is an extension of earlier investigations on aluminium oxide films. Ion mobility and heat treatment studies on aluminium oxide films have been made in various electrolytes and it has been found that the conductivity patterns before and after heating show similar trends and are of two types, one is associated with high conductance and low rate of change of capacitance with increase in temperature and the other is associated with low conductance and changes capacitance more rapidly with increase in temperature.

II. MATERIALS AND METHODS

For ion mobility measurements 0.25 mm thick aluminium specimens were anodized upto identical formation voltage in 0.1M aqueous potassium nitrate at a current density of 5mA/cm². After anodization these aluminium specimens were paired together to form aluminium/aluminiumoxide/aluminium sandwich geometry. In this manner perfect sealing of the specimen I and II was done except on the outer surface of the specimen II. The effective surface area for experimental purpose after sealing was 1 x 10⁻⁴ m². For heat treatment of aluminium oxide films, aluminium specimens with small tags were cut from 99.9 % pure aluminium sheets and the edges of the specimens were abraded with fine emery paper to make them smooth. The specimens were then dipped in dilute solution of sodium hydroxide for 2-3 sec to clean the surface and finally washed with distilled water. The chemical polishing of these specimens were done by dipping in a freshly prepared etching mixture of O-phosphoric acid, sulphuric acid and nitric acid in the ratio of 70:25:5 at a temperature of 350-360K for 2-4 sec and then washed with distilled water and drying in a current of hot air .The final etching was done just before the anodization. The tag of the specimen was covered with a thick anodic film in an electrolyte in which further anodization on square portion of the specimen was to be carried out. The specimen thus prepared was placed in a glass cell and was connected with a platinum electrode which served as cathode during the growth of oxide film. Anodization of the specimen was carried out at constant current and the supply of the current was cut off by an electronic control after the desired voltage of formation was reached. The heating of the samples in air was done in a pre- calibrated silica tube furnace. The density of the aluminium oxide film was taken as 3565 Kg/m³ as reported by Tazima²⁵. All data refer to 298+-0.5K unless otherwise stated.

III. RESULTS AND DISCUSSION

Aluminium specimens I and II were anodized at film formation voltages of 60, 80 and 100V in 0.05 M potassium chloride at a current density of 10mA/cm² and their capacitances before sealing were measured and found to be 3.17, 2.36, 1.65for sample1 and1.87,1.35and1.13 F x 10⁻⁶ for sample II at the above film formation voltages respectively. In the combined assembly the capacitance of both samples I and II are same (1.19,0.82and 0.67x 10⁻⁶ F at 60,80 and 100 V respectively) and the values are in proportion to their reduced

areas of $1 \times 10^{-4} \text{ m}^2$, and the assembly acts as one unit. The tag of specimen I in each of the paired assembly was connected to the positive end of the constant current supply and the specimen II which was earlier anodized upto 60 , 80 and 100 V paired assemblies was further anodized upto 120, 160 and 200 V respectively. The capacitances of these paired systems were again measured taking specimen I and II in the circuit respectively and it was found that the capacitances of specimens I and II were almost same($1.16, 0.79$ and 0.64×10^{-6} F at 120,160 and 200V respectively and this ensured that complete sealing of specimen I and II and no possibility of electrolyte creeping into the oxide film. The magnitudes of the capacitances were further reduced due to further formation of oxide film. The assembly of specimens I and II was dismantled and then the capacitances of the separated specimen I and II were measured as also those of the outer and the inner surfaces of both the specimens after applying locomite to the other side. The capacitance of the specimen I after separation was found to be $3.16, 2.34$ and 1.62×10^{-6} F at 60, 80 and 100V respectively and before sealing were identical indicating that specimen I remain unaffected. The capacitances per m^2 for both the inner and outer surfaces of specimen I were found to be $1.14, 0.81$ and 0.60×10^{-2} F/ m^2 at film formation voltages of 60,80 and 100V respectively while the corresponding values for the inner surface of specimen II were $1.12, 0.83$ and 0.62×10^{-2} F/ m^2 . The magnitudes of the capacitance per m^2 for specimen I compare well with those of the inner surface of specimen II which concludes that the sandwiched oxide film is not affected. Further anodization of the separated specimen I increases the film formation voltage immediately and it attains the voltage of the film already present on it i.e. film formation voltage Fig.1. This implies that there is no possibility of oxygen ion moving through the electrolyte to specimen I to produce layers inside the existing oxide layers. The field strength of aluminium oxide film between specimen I and specimen II of this experiment remains unchanged and aluminium ions produced as specimen I are transported to specimen II through the aluminium oxide and then to solution to produce fresh layers on the outer surface of the sample II which shows that only aluminium ions are mobile during the growth of aluminium oxide film. The normal rate of anodization compare well with the anodization rate during this experiment.

(II) Heat treatment of aluminium oxide films in aqueous electrolytes.

Specimens of aluminium were anodized in 0.25M aqueous solutions of potassium nitrate, oxalic acid and potassium chloride at a current density of 10 mAcm^{-2} up to 50, 100, 150 and 200 V. These anodized specimens were Separately heated in a tube furnace in the presence of air at a constant temperature for different intervals of time. The specimens were allowed to cool and taken out & there capacitances measured in the respective aqueous solutions of potassium nitrate, oxalic acid & potassium chloride at room temperature ($298 \pm 0.5 \text{ K}$). from the plots of capacitance versus time of heating films formed up to different formation voltages (50, 100, 150 & 200 V in oxalic acid) at a fixed temperature, it is observed that while there is no appreciable change in the value of capacitance with time at room temperature, the capacitance of each of the film increases with the duration of heating which shows that on heating the films become more conducting. The change in capacitance is more for 50V film and decreases as the voltage film formation increases after heating for about 2.0 hours. However, after long time periods these differences disappear and films become equally conducting irrespective of voltage of film formation. Similar trends were shown by the films formed in other aqueous electrolytes. It is further observed that capacitances before and after heating for long hours in different electrolytes are affected by heat treatment to the same extent which concludes that effect of heat treatment on aluminium oxide films is independent of the nature of the electrolyte. Similarly on heating the oxide film formed at different temperatures for a fixed interval of time, It is observed that capacitances of the oxide film did not change when these were heated up to temperature of about 525K.(Table.1) and above this temperature, the capacitances increased almost linearly with rise in temperature of heating as shown in Fig.2. From the plots of capacitance versus temperature in various electrolyte it is observed that conductivity profile across the aluminium oxide film is of to types, one which is associated with high conductance and smaller rate of change of capacitance with temperature, and the other associated with low conductance and higher rate of change of capacitance with temperature. The conductivity patterns for both heated and unheated specimens of aluminium oxide films show similar trends. It appears that on heating of oxide films the conductivity results from the extraction of oxygen from aluminium oxide by aluminium and causing oxygen deficiency in the oxide film. In the presence of air, when oxygen deficiency reaches oxide – air interface it renders oxygen to

flow into the film. The flow of oxygen maintains the oxide composition both at the aluminium- aluminium oxide and aluminium oxide-air interfaces and is not affected by nature of the aqueous electrolyte.

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TABLE – 1

Capacitances of films formed at formation voltages of 50 and 100 V in various electrolytes before & after 5 hours of heating.

Electrolyte	Film formation Voltage (V)	Capacitances (10^6 F)	
		Before heating	After Heating
Potassium nitrate	50	7.63	9.12
	100	3.98	4.65
Oxalic acid	50	8.39	9.02
	100	3.78	4.09
Potassium Chloride	50	10.72	12.47
	100	5.68	6.17

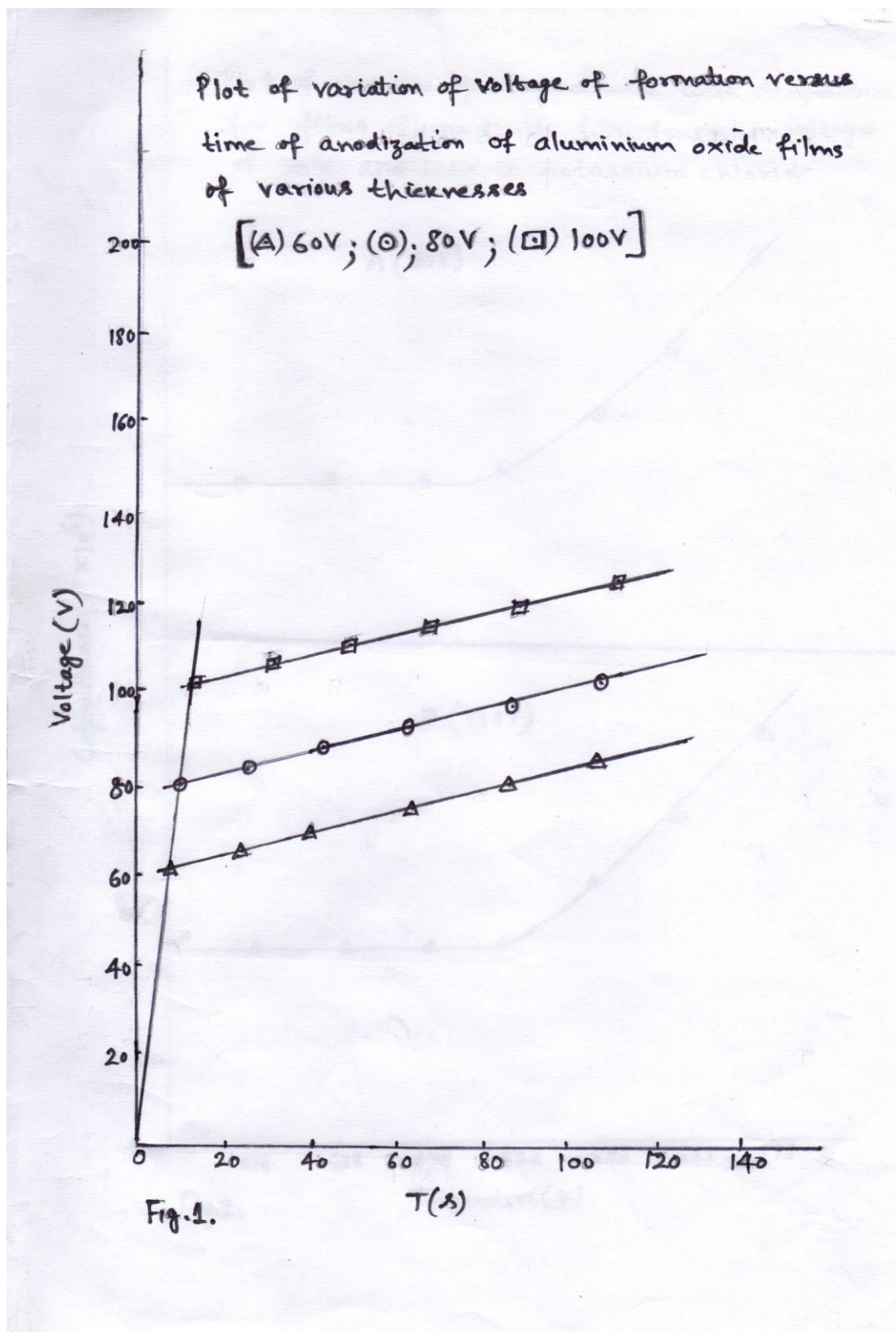


Fig. 1

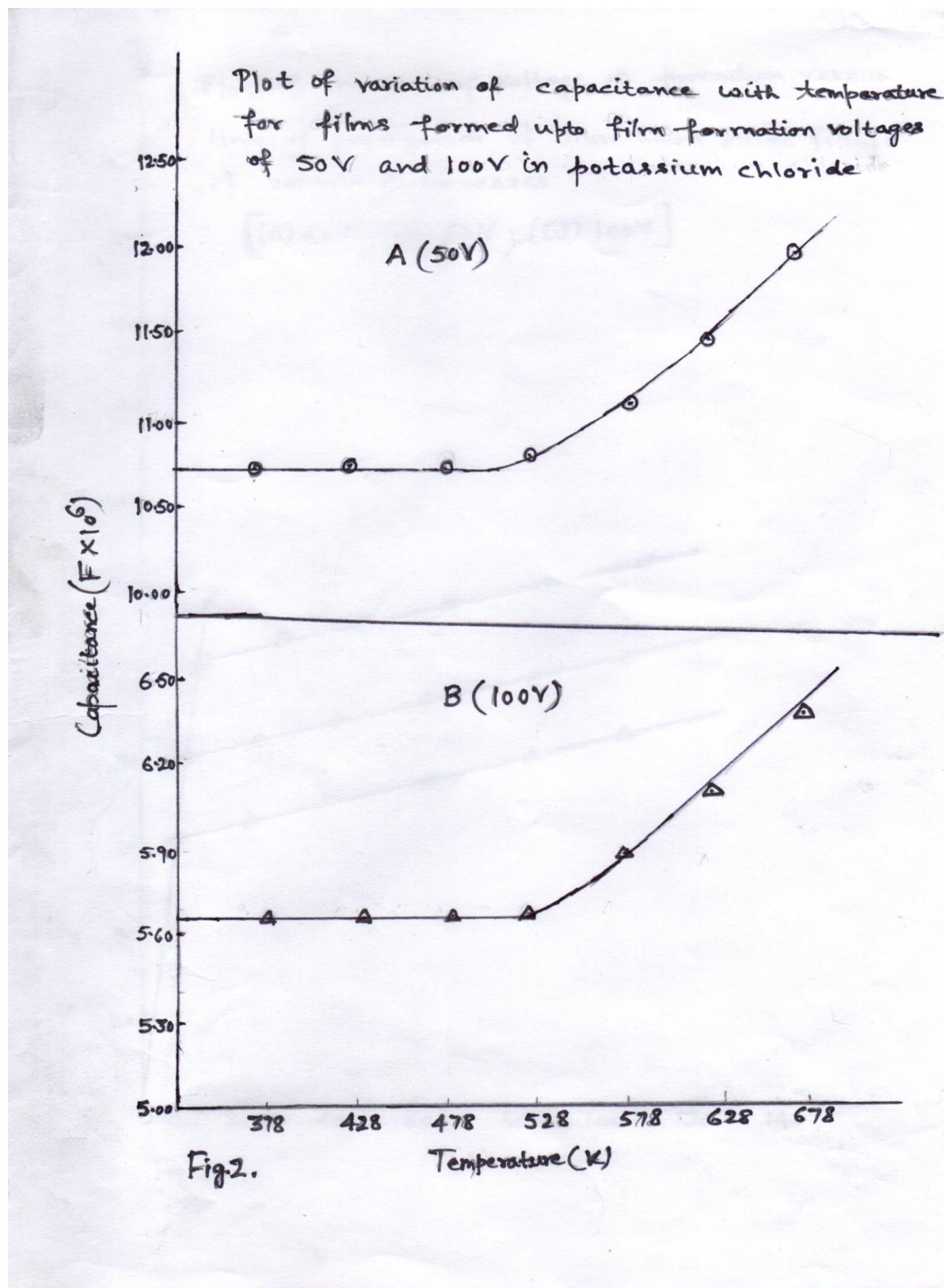


Fig. 2

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