SUMMARY
The thesis has been divided into seven chapters and the summary of the work presented in various chapters is outlined below:

CHAPTER I

The first chapter contains a comprehensive review of literature on anodic oxide film formation on metals and theories for high field ionic conduction. Guntherschulze-Betz empirical relation, Cabrera-Mott theory, Dignam's theory of cooperative ion migration through anodic film, Dewald's theory of dual-barrier control with space charge and theories related with breakdown voltage studies have been presented along with their present status.

CHAPTER II

The second chapter concerns itself with the study of kinetics of growth of anodic oxide films on tantalum (The valve metal used throughout these studies is pure tantalum). Ionic conduction through oxide films on tantalum in various aqueous electrolytes at different current densities at varying temperatures have been studied and the steady state kinetic data have been analysed in light of various theories of ionic conduction. Guntherschulze-Betz empirical relation, Cabrera-Mott approach and Dignam's theory have been discussed. Guntherschulze-Betz constant \( A \) is found to increase with temperature while constant \( B \) is temperature-independent. Both the constants are observed to be dependent on the nature of the electrolyte. The Tafel slope (derivative of field strength with logarithm of current density) has been found to depend on current density but is independent of temperature.
Since the Tafel slope is temperature-independent, the applicability of single barrier Cabrera-Mott theory for anodic growth of film is ruled out. Dignam's parameters have been evaluated and their dependence on temperature, nature of electrolyte and current density examined. Though there is an appreciable contribution to the quadratic term yet the parameters, the zero-field activation dipole ($A^*$), the Morse-function parameter ($J$) and current density ($i_0$) are found to be temperature-dependent which were assumed temperature independent by Dignam. Hence Dignam's approach does not explain our data satisfactorily.

CHAPTER III

As discussed in Chapter II, the single barrier theory of Cabrera and Mott is not applicable and Dignam's approach is inadequate to explain our data. Therefore, Dewald's double barrier theory which takes into account the space charge effect has been examined in this chapter. Various parameters of anodic oxidation have been evaluated using Dewald's theory. The entrance barrier energy has been found greater than the corresponding diffusion barrier energy and this suggests that the rate-controlling step in the kinetics of growth of anodic film is the ionic movement across the film and not at the metal/oxide interface. The value of net activation energy calculated using Dewald's theory agrees well with the value calculated using Dignam's approach. The data suggest that Dewald's theory which takes into account the space charge effect is better than other theories of film growth kinetics.
CHAPTER IV

The anodic oxide film on a valve metal can be formed up to a certain maximum value of voltage designated as breakdown voltage. Breakdown voltage of anodic oxide film formed on tantalum in aqueous electrolytes has been studied in this chapter. Of the various methods of identifying breakdown voltage, the appearance of sparking is found to be a superior method. The breakdown voltage is found to be independent of current density used for film formation, field strength, topography of the specimen and pH of the electrolyte solution. However, it depends upon the nature of the electrolyte, concentration of the solution and temperature employed. It has been found that only the anions of the electrolyte influence the breakdown voltage. It appears that during anodic polarization the electrons from the anions of the electrolyte get injected into the conduction bands of the film. Due to high field strength the electrons acquire very high energy and cause release of secondary electrons, resulting in the multiplication of avalanches and hence breaking the film.

CHAPTER V

To get more insight into the breakdown phenomenon, steady electronic current data through films in contact with aqueous electrolytes have been obtained and are discussed in this chapter. The effect of field strength, temperature of the bath, composition, concentration and resistivity of the
contacting electrolyte have been studied. The data show that
the same relation between electronic current and field holds
irrespective of the film thickness. The data also indicate
a direct relation between electronic current and breakdown
voltage. The effect of electrolyte concentration on breakdown
voltage can be explained in terms of Ikonopisov's electron
injecting avalanche model. The major factor contributing to
a decrease of breakdown voltage with an increase in the con-
centration of the electrolyte has been found to be due to the
increase in primary electronic current.

CHAPTER VI

The sixth and the seventh chapters deal with the related
aspects of anodic oxide films formed on tantalum. The various
aspects discussed in this chapter are as under:

A) Rectification studies: Rectification studies on $\text{Ta}_2\text{O}_5$
anodic oxide layers with vacuum-deposited Sb, Ni, Sn, Al,
Bi, Cu, Ag and Zn contacts have been made. The effects of
field strength, temperature, thickness of the oxide film
and the polarity of electrode on dc current have been studied.
In all these systems the conduction is asymmetric and these
systems act as rectifiers. There does not appear to be any
correlation between critical voltage and work function or
work function difference for the metal electrodes. It appears
that localized trap states in the band of oxide films are
responsible for conductivity through these films. Dominant
carrier transport in these systems is through Poole-Frenkel
conduction mechanism. The same conduction mechanism is operative irrespective of the polarity of the metal electrode.

B) Dielectric measurements:– The relation between capacitance and thickness has been established. A method for evaluating dielectric constant has been obtained. The effect of concentration and nature of the electrolyte on capacitance and dielectric constant have been studied.

C) Effect of added ions:– The addition of chloride ions has been found to inhibit film growth and the inhibiting effect becomes more pronounced with the increase in the concentration of chloride ions. It appears that during the growth of tantalum oxide film in the presence of chloride ions tantalum metal combines with chloride ions giving an adsorbed film of tantalum chloride (TaCl₅) which then undergoes partial dissolution providing Ta⁴⁺ ions in solution. The released tantalum ions can combine with the chloride ions in the solution giving rise to a stable chloro-complex of tantalum (of the type Ta₅Cl₅(a⁻⁵)⁻) which does not dissociate and thus prevents further participation of chloride ions in the anodic charge transfer. At higher concentration of chloride ions, the chloro-complex of tantalum is formed more efficiently, thereby inhibiting the growth of oxide film.

When a film is kept in concentrated hydrofluoric acid it dissolves and the dissolution rate depends on film thickness and concentration of hydrofluoric acid. It is most
likely that when Ta$_2$O$_5$ film is put in concentrated hydrofluoric acid, a surface layer of tantalum fluoride (TaF$_5$) is formed which dissolves completely in conc. HF and hence causes dissolution of the film.

D) **Current efficiency:** The current efficiency obtained using mass-gain method of such films are unity upto an electrolyte concentration of 100 mol m$^{-3}$. However, at higher electrolyte concentration, the experimental mass-gain of the tantalum sample during anodization is greater than that expected for the anodic formation of Ta$_2$O$_5$ on tantalum, implying that mass-gain is probably due to the incorporation of anions into the films.

**CHAPTER VII**

This chapter deals with the following aspects of the anodic oxide films.

A) **Ion-mobility studies:** These studies show that only tantalum ions are mobile during the growth of tantalum oxide films.

B) **Heat treatment:** Heat treatment of the oxide films in air makes these more conducting. This effect depends on the time period and temperature of heat treatment but is independent of film thickness and nature of the electrolyte. The conductivity patterns before and after heating show similar trends and are of two types: one is associated with high conductance and lower 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. The hypothetical break temperature is independent of the nature of electrolyte or treatment.

C) **Formation characteristics in presence of UV radiations:**

The data obtained during the growth of anodic oxide films on tantalum indicate higher values of, rates of growth, constant A (of Guntherschulze-Betz equation) and Tafel slopes in the presence of UV radiations than those in the absence of radiations. However, the values of constant B (of Guntherschultze-Betz equation), half-jump distances and breakdown voltages are lower in the presence of UV light. Faster rate in the presence of UV is probably due to increased number of mobile ions per unit volume and decreased width of potential energy barrier. Stimulation ionic movements due to UV radiations cause breakdown of films at lower voltages.