CHAPTER V

MECHANISM OF ELECTRONIC CONDUCTION THROUGH Nb-Nb_2O_5-METAL SYSTEMS

Introduction

Although the subject of electronic conduction through thin film insulators dates back a number of years, but the interest in this field was developed later on when applied to solid state devices. In the previous Chapters it has been established that continuous and apparently homogeneous oxide film can be grown on niobium under high electric field. It was concluded that the electric field during the growth of the film at constant current density is independent of film thickness. The existence of space charge in the oxide films on niobium has also been proved.
Such films on valve metals show asymmetric conduction or rectification when the contact with the oxide film was taken either by some electrolyte or by some evaporated metal film. The easy direction of flow of current is with base metal as negative. This property has recently been exploited industrially to fabricate rectifiers.

Lamb\(^3\) discussed the theoretical and experimental aspects of the five basic possible conduction mechanisms in thin films known as (i) ionic conduction (ii) space-charge-limited conduction (iii) tunnelling and internal field emission (iv) field assisted thermal emission (v) impurity conduction. Pitt\(^4\) reviewed the techniques for preparing metal/insulator/metal structure and discussed the mechanisms of current injection at the contact. Jonscher\(^5\) has discussed the effect of amorphous structure of films on their electrical characteristics and has considered the field-assisted, thermal emission, conduction mechanisms in such materials. Electronic conduction mechanisms are also reviewed by Simmons\(^6\), Harrop-Campbell\(^7\) and Chopra\(^8\). Various mechanisms such as theories of flaws\(^9\), hopping\(^10,11\), p-n or p-i-n junction\(^11\), field-assisted hopping\(^12-15\) (such as the Poole-Frenkel or Schottky mechanisms) have also been reported by various workers depending upon the nature of oxide film, field strength and the range of temperature, to explain the rectification characteristic of
oxide films, but none of them has proved to be satisfactory to explain all aspects of the phenomenon.

Charlesby\textsuperscript{16} postulated that the anodic current (in particular with Zr) obeyed a 'sinh' law and was, therefore, controlled by some activation energy barrier. Vermilyea\textsuperscript{17} offered an objection to Charlesby's interpretation of his data for Zr on the grounds that the postulated barrier of height 0.375 eV and width 7.2 Å would be penetrated by the wave-mechanical tunnel effect. Extensive work by Vermilyea\textsuperscript{18,19} on bulk Ta showed that flaw conduction was dominant in thicker oxide (> 1000 Å). He postulated two flaw conduction mechanisms, one being an actual opening of a hole in the oxide and the other involving some type of an electronic junction. Vermilyea\textsuperscript{20} found that flaws were generally thin spots in the Ta\textsubscript{2}O\textsubscript{5} with a conical topography which were marked by different interference colours and can be caused by particles of grease, oxide, carbide and by surface roughness. Young\textsuperscript{21} has discussed the low cathodic resistance in terms of weak spots in the oxide, which were thought to be fissures in the oxide. These weak spots were also responsible for most of the observed leakage current during polarization. This was, of course, not to say that in the absence of flaws there would no rectification. Van Geel\textsuperscript{22,23} proposed a p-n junction theory and this was further confirmed by Taylor and Haring\textsuperscript{24}. Rectification was attributed in
this paper to the contact between a p-type layer close to
the solution and the rest of the oxide which was supposed
to be n-type. It was not shown in detail how a p-n
junction could account for the observed behaviour. Sasaki\textsuperscript{25}
concluded that the Ta\textsubscript{2}O\textsubscript{5} constituted a p-i-n junction, the
p and n regions were localized near the contacts so that
no extensive space charges existed in the bulk of the film.
Mead\textsuperscript{12} studied the conduction through thick oxide (upto
870 Å) films in Ta-Ta\textsubscript{2}O\textsubscript{5}-Au structures. The result was
interpreted in term of Poole-Frenkel equation. Simmon\textsuperscript{13}
found that Schottky emission fits to these films.

Our present study is limited to dry contacts, i.e.,
the contact with the oxide film on niobium is taken by
evaporating metals (Ag, Al, Bi and Sn). The aim of present
work is to study
i) rectifying action of niobium oxide layers; and
ii) to know the exact mechanism of electrical conduction
in these films.
Experimental

To study the electrical properties of oxide films, various workers have employed different techniques for preparation of specimens in the sandwich geometry. In most of the techniques the leakage current is the main problem. In order to avoid this completely, Hansen's technique of encapsulation of silicon surface barrier was employed for the study of electronic properties through anodic niobium oxide films. This avoided cumbersome experimentation and ensured a complete edge protection, so that there was no leakage of current around the edges.

Niobium specimens (2 cm² in area) were cleaned and chemically polished by the method described in Chapter II. The experimental set up for anodic oxidation of niobium in 0.1N oxalic acid was also the same. The specimen was then mounted on a piece of perspex sheet which had a suitable depression and a small hole in the centre. Another hole was drilled at one corner of the perspex piece to have contact with the counter electrode. The edges of the niobium specimen were protected by an epoxy resin to prevent conduction around the edges. A sketch of an encapsulated specimen is shown in Fig.1.

The encapsulated niobium specimen was oxidized anodically in 0.1N oxalic acid electrolyte at a constant
current density of $1 \text{mAcm}^{-2}$ at $20^\circ\text{C}$. Five sets of specimens having 30, 50, 70, 90, 130 and 150 V films were prepared to study the behaviour of electrical conduction as a function of film thickness, temperature and applied electric field. Other specimens having 30V film were prepared to study the rectifying character of these anodic films. Contact with the oxide film was achieved by evaporating various metals (Ag, Al, Bi and Sn) under high vacuum (of the order of $10^{-6}$ Torr) using a vacuum coating unit (Model No.12A4 manufactured by Hind High Vacuum Co. (P) Ltd., Bangalore, India). The evaporated metal acts as a counterelectrode for the system under investigation. Study of electrical properties of the oxide films were carried out in two ways. At first, the rectifying action of the anodic oxide film of 30V thickness under different metal electrodes and of films of different thicknesses (30, 50, 70, 90, 130 and 150 V) under aluminium electrode have been studied. A dc microvoltmeter (Philips Model pp-9004) and a regulated power supply (0-30 V) which could read upto $\pm 0.01$ V were employed for these investigations. The second experiments includes the study of the effect of field strength, temperature and the nature of counterelectrode upon the electrical conduction mechanism through the oxide film. All electrical measurements were made with the help of dc microvoltmeter and megohm meter (Model RM 160 MK III, supplied by OSAW, Ambala Cantt).
Fig. 1. Encapsulation of niobium specimen.
1. Nb specimen; 2. Nb$_2$O$_5$ layer;
3. Contact wire; 4. Contact to bulk Nb;

Fig. 2. Circuit diagram
1. Nb–Nb$_2$O$_5$–metal structure; 2. One megaohm resistance; 3 and 4. D.C. microvoltmeter;
5. Power supply.
circuit diagram presented in Fig. 2 has been employed for present investigations. The temperature range of study was from 293.15 to 563.15K. The experimental set up while performing these studies were kept in an automatic air circulating thermostat. The accuracy of air thermostat was ± 0.05°C. A good reproducibility of results was obtained if the specimens were chosen carefully and processed in an identical way.
Results

The data for current-voltage characteristics through 30V thick niobium oxide films, when bulk niobium was positive/negative with different counterelectrodes (i.e., Ag, Al, Bi, and Sn) have been plotted in Fig. 3. The easy directions of flow of current is when Nb is negative. There is a sharp increase of current when applied voltage is between 1 to 3 volts. This voltage is generally referred as critical voltage. The ohmic behaviour of the system is observed upto 10-11 V when niobium is positive. Further increase of voltage increases the current sharply. The value of critical voltages for these metals (Ag, Al, Bi and Sn) along with their reported work functions are given in Table I. There does not appear to be any correlation between critical voltage and work function or work function difference of the metals. This is in contradiction to the observation of Mead\(^{27}\) for Ta-Ta\(_2\)O\(_5\) -metal devices. The data for effect of field strength (E) on the current (I) have been plotted as log I versus E\(^{5}\) for niobium positive as well as negative (Fig. 4-5) and are found to be linear. The values of slopes and intercepts of these plots were calculated by the method of least squares and are given in Table II.

The data for I-V characteristics are also obtained using different thicknesses of Nb\(_2\)O\(_5\) films for Nb-Nb\(_2\)O\(_5\)-Al
Fig. 3. Plots of current ($I$) vs voltage ($V$) when Nb is positive and negative.

Temp = 20°C
Nb-Nb$_2$O$_5$ Metal
Thickness of oxide = 707Å
O Ag, Δ Bi, • Sn, X Al

Fig. 3. Plots of current ($I$) vs voltage ($V$) when Nb is positive and negative.
TABLE I: Voltages at which conduction begins (critical voltage) through niobium-niobium oxide film for various metal counter-electrodes at room temperature. The predicted voltages are those based on the assumption that electrons will pass readily from the low work function to high work function electrode as soon as a voltage greater than the difference in work function has been applied. In the reverse direction, conduction should be observed at very low voltages (shown as zero in Table).

<table>
<thead>
<tr>
<th>Counter-electrode</th>
<th>Negative electrode</th>
<th>Predicted (volts)</th>
<th>Observed (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Nb</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>0.23</td>
<td>11</td>
</tr>
<tr>
<td>Sn</td>
<td>Nb</td>
<td>0.45</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Ag</td>
<td>Nb</td>
<td>0.68</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Bi</td>
<td>Nb</td>
<td>0.68</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Bi</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>
Fig. 4. Plots of log I vs $E^{1/2}$

Fig. 5. Plots of log I vs $E^{1/2}$
TABLE II: Values of slopes and intercepts of plots of log I vs $E^2$ (Fig. 4 and Fig. 5).

<table>
<thead>
<tr>
<th>Counter-electrode</th>
<th>Slope x $10^3\text{(V/cm)}^{-\frac{1}{2}}$</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Nb}^\text{+ve}$</td>
<td>$\text{Nb}^\text{-ve}$</td>
</tr>
<tr>
<td>Al</td>
<td>0.99</td>
<td>2.85</td>
</tr>
<tr>
<td>Sn</td>
<td>0.95</td>
<td>5.00</td>
</tr>
<tr>
<td>Ag</td>
<td>1.57</td>
<td>2.35</td>
</tr>
<tr>
<td>Bi</td>
<td>1.24</td>
<td>6.40</td>
</tr>
</tbody>
</table>
Fig. 6  Plots of current (I) vs voltage (V) when niobium is positive and negative.
systems and are plotted in Fig. 6. It has been found from the plots of current versus voltage (Fig. 6) that there is a little effect of thickness of oxide film on the critical voltage when niobium is negative. There is a slight decrease of current with increase of thickness when niobium is positive. The critical voltage value for 30V and 50V films are between 10 to 15 V. But for thicker films ohmic behaviour of current is observed upto 25V. Then small sparks are observed on the film surface with further increase of voltage. Higher voltages are required to observe the sparking of thicker oxide films. The magnitude of current at different field strengths for Nb-Nb$_2$O$_5$-Al systems have been plotted as log I versus E$^2$ for film of different thicknesses taking Nb as positive and negative are presented in Fig. 7 and Fig. 8, respectively. The magnitude of current increases with increase in thickness irrespective of the polarity of niobium electrode.
Fig. 7 Plots of log I vs $E^{1/2}$

$E^{1/2} \times 10^{-3} \text{ (V/cm)}^{1/2}$

Temp = 20°C
Nb-Nb$_2$O$_5$-Al

When Nb is positive:
Δ 30, ○ 50, ○ 70 V
X 90, Δ 130, ○ 150 V
Fig. 8  Plots of log I vs $E^{1/2}$

Temp. 20°C
Nb-Nb$_2$O$_3$-Al
When Nb is -ve
△ 30, ○ 50, ○ 70 V
X 90, △ 130, ○ 150 V

Fig. 9  Plots of log [$I/T^2$] vs $T^{-1}$

Nb-Nb$_2$O$_3$-Al
Thickness of oxide 707Å
● Nb is negative
○ Nb is positive
$V = 1$ Volt
Discussion

Anodic barrier films have amorphous and macroscopic structures which are heterogeneous in nature. The flaws are voids and regions of different composition of crystal structure from the remainder of the film. Such flaws resulted from the film growth on surfaces which were geometrically irregular or which contained oxide or carbides. The flaws could also be produced by abrasion, chemical etching or a crack in pre-existing oxide films. A schematic diagram of such flaws has been shown below:

The presence of voids or flaws has also been reported by Stringer for the high temperature formation of Ta$_2$O$_5$ film in low oxygen pressure atmosphere. It has been shown that the flaws are thin spots in the film and these have a diameter about equal to the film thickness. At flaws the
two surfaces of the film had roughly conical indentations of considerable depth so that the minimum thickness was less than half the film thicknesses elsewhere on the specimen. When the particles were very small, the flaws were circular and symmetrical, while the larger particles did not produce symmetrical flaws and the centres were elongated or irregularly shaped instead of a point. There was probably a gap of some kind between the metal surface and the central portion of the flaws.

When the insulating film is sufficiently thin ($\approx 100 \, \Omega$), it is no longer opaque to electrons. Electrons that pass directly through the forbidden gap without surmounting the barrier are said to 'tunnel' through the forbidden gap. Therefore, tunneling would not be operative for thick $\text{Nb}_2\text{O}_5$ film at high field. Simple hopping conduction mechanism will also not possible at high field because at such field, the conduction electrons would be considerably modified from that of simple hopping conduction$^{29}$. Under these conditions, either electrons may be activated out of the trapping sites in the dielectric into the conduction band (Poole-Frenkel effect) or these may be introduced into the dielectrics by injection from the metal/dielectric interface and give rise to Schottky effect$^{29}$. All amorphous solids have been found to exhibit a non-linear behaviour of current-field dependence at high field ($\approx 10^5 \, \text{Vcm}^{-1}$ or more).
The relation between current (I) and field (E) is given by

\[ I = \alpha \exp. \beta E^\frac{1}{3} \] (1)

where \( \alpha \) is pre-exponential factor and \( \beta \) is another constant. When Poole-Frenkel effect is operative, the value of \( \beta \) is given by

\[ \beta = \left( \frac{e^3}{\pi \epsilon \epsilon_0} \right)^\frac{1}{3}/kT \]

Where \( \epsilon_0 \) is permittivity of free space and \( \epsilon \) is low frequency dielectric constant of the film. Again for the Schottky effect, the value of \( \beta \) is given by

\[ \beta = \left( \frac{e^3}{4\pi \epsilon \epsilon_0} \right)^\frac{1}{3}/kT \]

The value of low frequency dielectric constant (\( \epsilon \)) for Nb\(_2\)O\(_5\) has been taken as 42 as reported by Ikonopisov\(^{30}\). The experimental values of \( \beta \) for different counterelectrodes (i.e., slopes of lines in Fig.4 and Fig.5) lie between 0.95 to 1.57\times10^{-3} \text{ cm}^\frac{1}{3} \text{ V}^{-\frac{1}{3}} and 2.3 to 6.4\times10^{-3} \text{ cm}^\frac{1}{3} \text{ V}^{-\frac{1}{3}} for Nb (positive) and Nb (negative), respectively. The difference in calculated and experimentally determined values is probably due to the uncompensated high density ionizable centres under high
field or donor or acceptor like sites in the sample and it is proposed by Young that would be the same for both mechanisms for such a case and its value would depend upon the film thickness and space charge in which Schottky and Poole-Frenkel mechanism will be limiting characteristic. The values of constants ($\alpha$ and $\beta$) are dependent upon the nature of the counterelectrode and the polarity of the electrodes. One of the more decisive way to distinguish between both mechanisms that have been proposed for conduction through these oxide films is by a consideration of the temperature dependence of the phenomenon. The behaviour of current with temperature at constant voltage (IV) with the counterelectrode positive/negative for Nb-Nb$_2$O$_5$-Al is presented in Fig.9. The data have been plotted as log (I/T$^2$) versus 1/T and found to be linear. Thus Richardson-Schottky equation (Eq.(2)) is applicable to our systems.

$$I = AT^2 \exp(\frac{\varphi}{kT}) \exp \left[ \left( \frac{e^3}{4\pi \epsilon \epsilon_0} \right)^\frac{1}{2} \frac{kT}{E} \right] \left( \frac{e^3}{4\pi \epsilon \epsilon_0} \right)^\frac{1}{2} \frac{kT}{E} \right]$$

where $A$ is a Richardson constant and $\varphi$ is the electron work function. The value of $A$ and $\varphi$ are obtained from curves of Fig.9 and are given below:
The values of $\phi$ are low and nearly equal whether we take Nb positive or negative. This indicates that the Schottky barrier is independent of the ionic work function of the counterelectrode. The value of Richardson constant comes out to be very low as compared to its reported value of $120 \text{A/cm}^2\text{°C}$.

It can be concluded that our investigations show no correlation between critical voltage and work function or work function difference of the metals. Dominant carrier transport in Nb-Nb$_2$O$_5$-metal systems is through Schottky conduction mechanism. The same conduction mechanism is operative irrespective of the polarity of the metal electrode.

<table>
<thead>
<tr>
<th>$\phi$, eV</th>
<th>$A, (K \text{ cm})^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb (+ve)</td>
<td>0.032</td>
</tr>
<tr>
<td></td>
<td>$7.24 \times 10^{-11}$</td>
</tr>
<tr>
<td>Nb (-ve)</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>$4.12 \times 10^{-10}$</td>
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References