CHAPTER VI
DC CONDUCTION STUDIES OF ANODIC OXIDE FILMS ON METAL
Conduction through valve metal-metal oxide-metal systems have engaged the attention of various workers because of their utility in capacitor technology as well as these systems possessing rectifying properties. Conduction in thin insulating films of metal oxide are ascribed to different mechanism. The earlier view was that charge flow was concentrated in localized defects through the dielectrics but the recent work suggest that charge flow is distributed throughout the film. Young made charge flow studies in tantalum oxide films prepared by r.f. sputtering and preferred bulk limited Poole-Frenkel conduction. Other authors suggested that charge flow is through electrode limited Schottky conduction. Gubanski and Hughes adduced evidence for the space charge limited conduction (SCLC) by investigating the transport of charge through thin anodic tantalum oxide with gold counter-electrodes. More recently Hukovic and Ceric have put forward a SCLC mechanism in Ta(-)-Ta$_2$O$_5$-electrolyte system. SCLC mechanism has also been proposed in thin films of copper phthalocyanine by Gould. It appears that the views regarding the conduction mechanism are at variance. Moreover, conduction studies on Ti-TiO$_2$-metal system and Nb-Nb$_2$O$_5$-metal system does not appear to have received much attention. In the present work, investigations have been carried out on both Ti-TiO$_2$-metal system as well as on Nb-Nb$_2$O$_5$-metal system to understand the nature of conduction process. The effects of nature of the metal,
thickness of TiO$_2$ or Nb$_2$O$_5$ film, polarity of electrode and temperature on conduction mechanism have also been studied.

**EXPERIMENTAL**

Titanium or niobium specimens (2x10$^{-4}$ m$^2$ area) with short tags were cut from sheets of titanium or niobium. The specimens were polished mechanically and chemically by usual methods described earlier (Chapter II). Contact with the bulk titanium or niobium from tag of sample was made using copper clip. Each specimen was mounted on a piece of cleaned glass slide using a suitable adhesive. Edges of the specimens were protected by epoxy resin to prevent conduction through edges. Another contact required for various oxide films was obtained by deposition of different materials Al or Sn or Sb. A sketch of an encapsulated specimen is shown in Fig. 1(a).

Anodization on encapsulated titanium or niobium specimen at constant current density 50 Am$^{-2}$ in mixed solution of 100 mol m$^{-3}$ disodium hydrogen phosphate with diethylene glycol (both 1:1 by volume) was carried out using constant current generator and the films formed were upto the formation voltage (20, 30, 50, 70 and 80V in case of titanium and of 20, 30, 50, 60 and 70 V in case of niobium). The thickness of the films were determined using Faraday's law and were found to be 33, 49, 81, 114 and 130 nm ($\pm$0.5%) respectively in case of titanium and 31, 46, 77, 92 and 107 nm ($\pm$0.5%) respectively in case of niobium. Contact with the oxide film was achieved by evaporating different metals (Al, Sn and Sb) under high vacuum (10$^{-5}$ torr at 298 K using a
Fig. 1(a) Encapsulation of titanium specimen:
(1) titanium specimen; (2) TiO$_2$ layer; (3) & 4 contact to titanium bulk & counter electrode; (5) evaporated metal electrode and (6) glass slide.

Fig. 1(b) Circuit diagram: (1) Power supply; (2) Specimen; (3) ammeter; and (4) voltmeter
VICO thin film unit (VC-12). The evaporated metal acts as a counter electrode for the system under investigation. Samples prepared as such were used for the study of I-V characteristics. The sample was mounted in a metallic cryostat for making measurements. Suitable bias provided an IC regulated dc power supply (Omega). Current measurements were made with the help of a multimeter (Philips PM 2718) with an accuracy of ±0.00002 A. The circuit diagram presented in Fig. 1(b) was employed in the present investigation. The density of TiO$_2$ films was taken as 3840 Kg m$^{-3}$ as reported by Mizushima$^{19}$ and that of Nb$_2$O$_5$ films was taken as 4360 Kg m$^{-3}$ as reported by Holtzberg$^{20}$. The dielectric constants of titanium or niobium oxide films were calculated from capacitance measurements and were found to be 48.1 for TiO$_2$ films and 42 for Nb$_2$O$_5$ films.
RESULTS AND DISCUSSION

(A) D C conduction studies on titanium-titanium oxide-metal systems

Current and voltage were measured across titanium oxide films (33, 49, 81, 114 and 130 nm thick) using bulk Ti as positive (or negative) electrode and Al, Sn and Sb metals separately as positive (or negative) counter electrodes. The plots of current (I) vs. the applied dc voltage across titanium oxide films when bulk titanium was positive/negative with different counter electrodes (Al, Sn and Sb) are shown in Fig. 2. The flow of current is facile when Ti is negative. There is a sharp increase of current when applied voltage is between 3.55 and 4.27 V. This voltage is referred as critical voltage. Further increase in voltage increases the current sharply. The value of critical voltage with different metal counter electrodes such as Al, Sn and Sb are 4.27 V, 4.03 V and 3.55 V respectively and the corresponding electron work function of these metals are 6.81x10^{-19} J, 7.08x10^{-19} J and 7.53x10^{-19} J.

The plots of log I vs. $E^{1/2}$ with titanium as positive and negative and Al, Sn and Sb as counter electrodes are shown in Figs. 3 and 4. The log I vs. $E^{1/2}$ plots are linear when Ti is positive (Fig.3). However, these plots are non-linear when Ti is negative (Fig.4). This suggests that two different conduction mechanism are operating when Ti is positive and when Ti is negative electrode.
Fig. 2. Plot of current (I) vs. voltage (V) for Ti–TiO$_2$–metal systems when Ti is positive and negative: (1) Al–49 nm TiO$_2$; (2) Sn–49 nm TiO$_2$; (3) Sb–49 nm TiO$_2$; (4) Al–33 nm TiO$_2$; (5) Al–81 nm TiO$_2$; (6) Al–114 nm TiO$_2$; and (7) Al–130 nm TiO$_2$. 
Fig. 3. Plot of log I vs. \( \frac{E^{1/2}}{10^{-3} V^{1/2} m^{1/2}} \) for various Ti-TiO\(_2\)-metal systems when Ti is positive electrode. [(1) Al-49 nm TiO\(_2\) (2) Sn-49 nm TiO\(_2\) (3) Sb-49 nm TiO\(_2\) (4) Al-33 nm TiO\(_2\) (5) Al-81 nm TiO\(_2\) (6) Al-114 nm TiO\(_2\) and (7) Al-130 nm TiO\(_2\)].
Fig. 4. Plot of log I vs. $E^\frac{1}{2}$ for various Ti-TiO$_2$-metal systems when Ti is negative electrode. [(1) Al-49 nm TiO$_2$ (2) Sn-49 nm TiO$_2$ (3) Sb-49 nm TiO$_2$ (4) Al-33 nm TiO$_2$ (5) Al-81 nm TiO$_2$ (6) Al-114 nm TiO$_2$ and (7) Al-130 nm TiO$_2$.]
To get further insight into the problem, the plots between logarithm current (log I) and logarithm voltage (log V) are drawn for Ti (positive) and Ti (negative) and are shown in Figs. 5 and 6. When Ti is positive electrode, the log I vs. log V curves are linear, however when Ti is negative electrode, the log I vs. log V curves appear to be divided into two regions. (i) slowly rising curves and (ii) steeply rising curves. The slopes of slowly rising curves are close to unity i.e. in this region current (I) is proportional to voltage (V) and hence the region at lower voltage is the region of ohmic conduction. The slopes of steeply rising curves vary between 3.54 to 3.86 and thus in this region of higher voltages current is proportional to nth power of voltage for these systems. The values of n for these systems are given in Table I. Since the current varies with voltage with a power higher than 2; hence this region is the trap-limited space charge limited conduction (SCLC) region. The voltage which separates the ohmic conduction region from the SCLC region is known as transition voltage (V_t) and the values of V_t are also given in Table I.

The effect of thickness of dc electronic current was studied by measuring I-V characteristics for different thickness of TiO_2 film (33, 81, 114 and 130 nm) for Ti-TiO_2-Al system. The magnitude of current decreases with thickness. The log I-log V plots (Fig.6) show a similar
Fig. 5. Log I vs. log V plots for various Ti-TiO₂-metal systems when titanium is positive electrode [(1) Al-49 nm TiO₂ (2) Sn-49 nm TiO₂ (3) Sb-49 nm TiO₂ (4) Al-33 nm TiO₂ (5) Al-81 nm TiO₂ (6) Al-114 nm TiO₂ and (7) Al-130 nm TiO₂].
Log I vs. log V plots for various Ti-TiO$_2$-metal systems when Ti is negative electrode. [(1) Al-49 nm TiO$_2$ (2) Sn-49 nm TiO$_2$ (3) Sb-49 nm TiO$_2$ (4) Al-33 nm TiO$_2$ (5) Al-81 nm TiO$_2$ (6) Al-114 nm TiO$_2$ and (7) Al-130 nm TiO$_2$].
TABLE-I

Values of slopes of log I vs. log V in the SCLC region, transition voltage and the density of states N(E) calculated using Eqns. (5) and (6) for different Ti-TiO$_2$-metal systems at 298 K.

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<th>Counter-electrode</th>
<th>Thickness of titanium oxide film (nm)</th>
<th>Slope of log I vs. log V in the SCLC region (n)</th>
<th>Transition voltage (V$_t$)</th>
<th>$N(E) \times 10^{-19}$ (eV$^{-1}$ cm$^{-3}$)</th>
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gradual transition from an ohmic conduction region at lower voltages to SCLC region at higher voltage when Ti is negative. However log I-log V plots are linear and consist of one region only when Ti is positive electrode (Fig. 5).

It is well known that if log I vs. \( E^\frac{1}{2} \) plots are linear then the conduction mechanism is either bulk-limited Poole-Frenkel or electrode-limited Schottky. However, in the present study log I-E^\( \frac{1}{2} \) plots are non-linear when Ti is negative electrode (Fig. 4), thus ruling out the applicability of Poole-Frenkel or Schottky mechanism in the Ti(-)-TiO_2-metall systems. This observation does reinforce our conclusion that conduction in these systems is through SCLC mechanism. Since log I-E^\( \frac{1}{2} \) plots are linear when Ti is positive, therefore, either conduction is through Poole-Frenkel or Schottky mechanism. The relation between current and field for both Poole-Frenkel and Schottky effects is of the same type and is given by Eq. (1).

\[
I = \alpha \exp \beta E^{\frac{1}{2}}
\]

where \( \alpha \) is pre-exponential factor and \( \beta \) is another constant. The value of \( \beta = (e^3/\pi \epsilon \epsilon_o)^{\frac{1}{2}}/kT \) when Poole-Frenkel effect is operative (where \( \epsilon \) is dielectric constant of the film and \( \epsilon_o \) is the permittivity of the free space). Again for Schottky effect, value of \( \beta \) is given by the relation, \( \beta = (e^3/4\pi \epsilon \epsilon_o)^{\frac{1}{2}}/kT \). The value of \( \beta \) for TiO_2 film was determined from capacitance measurements (and was found to be 48.1). The calculated value of \( \beta \) for Poole-
Frenkel and Schottky conduction mechanism are $4.2419 \times 10^{-4} V^{-\frac{1}{2}} m^{-\frac{1}{2}}$ and $2.1210 \times 10^{-4} V^{-\frac{1}{2}} m^{-\frac{1}{2}}$ respectively. The experimental values of (slope of plot of log I vs. $E^{2}$) for different counter electrodes using 49 nm thick films are $5.13 \times 10^{-4}$, $5.15 \times 10^{-4}$ and $5.29 \times 10^{-4} V^{-\frac{1}{2}} m^{-\frac{1}{2}}$ for Al, Sn and Sb metals respectively. Similarly using 33 nm, 81 nm, 114 nm and 130 nm thick TiO$_2$ films and Al counter-electrode, the values of slopes are $5.13 \times 10^{-4}$, $5.26 \times 10^{-4}$, $5.52 \times 10^{-4}$ and $5.38 \times 10^{-4} V^{-\frac{1}{2}} m^{-\frac{1}{2}}$ respectively. All these values of slopes indicate that Poole-Frenkel mechanism is operative. One of the more decisive ways to distinguish between the two mechanisms that have been proposed for conduction through these oxide films comes from the temperature dependence of the phenomenon. The behaviour of current with temperature at constant voltage (1.5V) for Ti(+)-TiO$_2$-Al is shown in Fig.7. The data have been plotted as log (I/T$^2$) vs. 1/T and the plot is found to be non-linear indicating that Richardson Schottky expression

$$I = A T^2 \exp \left( \frac{\phi}{kT} \right) \exp \left( \frac{\left( e^2/4\pi\epsilon_0 \right)^{\frac{1}{2}}}{kT}\right)$$

is not applicable and thus ruling out Schottky mechanism.

According to Young$^4$, electrode-limited conduction predicts that with different work function counter-electrode the ratio of measured current $I_1$ and $I_2$ for metals $I_1$ and $I_2$ respectively is given by
Fig. 7. Plot of $\log \left( I/T^2 \right)$ vs. $1/T$ for Ti-TiO$_2$-Al metal system when Ti is positive electrode. Applied dc voltage is 1.5 V; Thickness of TiO$_2$ film = 81 nm.
where $\psi^1$ and $\psi^2$ are the potential barrier heights at the metal-insulator interface of different counter electrode metals. Simmons has shown that when two different counter-electrodes are used (with the same base electrode) $\psi^1 - \psi^2$ is equal to the difference in their work function i.e. $\phi_1 - \phi_2$:

$$\frac{I_1}{I_2} = \exp \left( - \frac{\phi_1 - \phi_2}{kT} \right)$$

(3)

This ratio of current of Al and Sb metals (i.e. $I_{Al}/I_{Sb}$) comes out to be approximately $0.4 \times 10^8$. On the other hand the measured ratio of the current is about 8. Similarly $I_{Sn}/I_{Sb}$ is about $0.6 \times 10^5$ and observed ratio is 0.53. This clearly shows the absence of electrode-limited Schottky conduction and thus emphasising that the dominant carrier transport in Ti(+)/TiO$_2$/metal systems is Poole-Frenkel conduction mechanism.

Anodic titanium oxide films have been reported to be amorphous$^{10-12}$. Recently Micocci$^{13}$ et al calculated directly the density of states in the gap of amorphous film from SCLC measurement using an analytical method. Some important assumptions involved in the derivation of the expression which was primarily proposed by Pfister$^{14}$ and subsequently developed by Manfredotti et al$^{15}$, Stockmann$^{16}$ and Weisfield$^{17}$, for the density of states $N(\epsilon)$ were as follows:
(i) The electrical length of the samples was assumed to be independent of applied voltage and current. The diffusion current was negligible.

(ii) It was assumed that only majority carriers (holes) were injected by a perfect ohmic contact and the distribution of imperfections and the mobility of free carrier were spatially uniform.

(iii) Quasi equilibrium conditions were reached at any injection rate, and the occupancy of space was determined by the position of quasi-Fermi level.

(iv) The density of free majority carriers was described by Boltzmann statistics.

According to this method, the expression for the density of states $N(E)$ is given by Eq. (4)

$$N(E) = \frac{\varepsilon \varepsilon_0 V}{qkTd^2} \left\{ \frac{(2\alpha - 3)\beta + \gamma + \alpha}{(2 - \alpha)(1 - \alpha)^2} \right\} (2 - \alpha)$$

where $\varepsilon$ is the dielectric constant of the film, $\varepsilon_0$ is the permittivity of vacuum, $q$ is the electronic charge, $d$ is the thickness of the oxide film, $k$ is the Boltzmann constant and $\alpha$, $\beta$ and $\gamma$ are given by the following relations.

$$\alpha = \frac{d(\log V)}{d(\log I)}; \quad \beta = \frac{d^2(\log V)}{d(\log I)^2};$$

and $$\gamma = \frac{d^3(\log V)}{d(\log I)^3}.$$
Eq. (4) gives a method of evaluating $N(E)$ directly from a log $I$-log $V$ plots. In our case since the log $I$ vs. log $V$ plots are linear. Therefore, second and third differentials of log $V$ with respect to log $I$ will be zero, i.e.

$$d^2(\log V)/d(\log I)^2 = \beta = 0; \text{ and } d^3(\log V)/d(\log I)^3 = \gamma = 0$$

substituting $\beta = 0$ and $\gamma = 0$ in Eq. (4) we get a modified expression for $N(E)$

$$N(E) = \frac{\epsilon_0}{q_kT} \frac{V}{d^2} \propto (2 - \alpha)$$

Equation (5) was used to calculate the density of gap state $N(E)$ in Ti(−)-TiO$_2$-metal system. The values of $\alpha = d(\log V)/d(\log I)$ were the reciprocal of the slopes of SCLC region of log $I$-log $V$ plots and $V$ was taken as equal to the transition voltage $V_t$. The calculated values of $N(E)$ for different metallic electrodes and different thickness of titanium oxide films are reportd in Table 1.

The Gap-state distribution in SCLC measurements may be represented by a model with constant density of traps around the Fermi-level. According to Lampert and Mark$^{18}$, the relation between current and voltage is given by Eq.(6).

$$I \propto V \exp \left(\frac{V}{V_0}\right)$$
where \( V_0 = qkTd^2 N(E)/\varepsilon \varepsilon_0 \). Equation (6) also provides a method of evaluating \( N(\varepsilon) \). If \( \log I/V vs. V \) is plotted, then the slope of linear plot will be \( I/V_0 \). Such plots for Ti(-)-TiO\(_2\)-metal systems are shown in Fig.8 and are linear in the SCLC region. Using the slopes of \( \log I/V vs. V \) plots, the values of the gap state density \( N(E) \) are calculated and reported in Table 1. The values of the gap-state density \( N(E) \) calculated by two different methods compare well. The value of \( N(E) \) decreases with increase in the thickness of the oxide film and varies approximately inversely with squared oxide thickness (Table 1).

The plot between electrical conductivity (\( \log \sigma \)) vs. reciprocal of temperature (I/T) for the ohmic region is shown in Fig.9 and is linear. This can be represented by the Eq.(7).

\[
\sigma = \sigma_0 \exp(-E_o/kT)
\]

The value of \( E_o \) was calculated from the slope and was found to be 0.0956 eV and the value of \( \sigma_0 \) was obtained 42.57(mA)\(^{-1}\) from the intercept.

(B) DC conduction studies on niobium-niobium oxide-metal systems

Current and voltage were measured across niobium oxide films (31, 46, 77, 92 and 107 nm thick) using bulk Nb as positive (or negative) electrode and Al, Sn and Sb metals separately as positive (or negative) counter electrodes. The plots of current (I) vs. the applied dc voltage across niobium oxide films when bulk niobium was positive/negative with different counter electrodes (Al, Sn and Sb) are shown in Fig.10. The flow of current is facile when Nb is negative. There is a sharp increase of current when applied voltage is
Fig. 8. Plot of log I/V vs. voltage V for various Ti-TiO₂-metal systems when Ti is negative electrode [(1) Al-49 nm TiO₂ (2) Sn-49 nm TiO₂ (3) Sb-49 nm TiO₂ (4) Al-33 nm TiO₂ (5) Al-81 nm TiO₂ (6) Al-114 nm TiO₂ and (7) Al-130 nm TiO₂].
Fig. 9. Plot of logarithm of electrical conductivity vs. $1/T$ for Ti-TiO$_2$-Al metal system when titanium is negative electrode. Applied dc voltage is 1.5V; thickness of TiO$_2$ film = 81 nm.
Fig. 10 Plot of current I vs. voltage (V) for Nb-Nb$_2$O$_5$-metal systems when Nb is positive and negative [(1) Al-46 nm Nb$_2$O$_5$, (2) Sn-46 nm Nb$_2$O$_5$; (3) Sb-46 nm Nb$_2$O$_5$; (4) Al-31 nm Nb$_2$O$_5$ (5) Al-77 nm Nb$_2$O$_5$ (6) Al-92 nm Nb$_2$O$_5$ and (7) Al-107 nm Nb$_2$O$_5$].
between 2.47 and 2.81V. This voltage is referred as critical voltage (as described in section A). Further increase in voltage increases the current sharply. The value of critical voltage with different metal counter electrodes such as Al, Sn and Sb are 2.47V, 2.56V and 2.81V respectively and the corresponding electron work function of these metals are 6.81x10^{-19}J, 7.08x10^{-19}J and 7.53x10^{-19}J.

The plots of log I vs. $E^{\frac{1}{2}}$ with niobium as positive and negative and Al, Sn and Sb as counter electrodes are shown in Figs.11 and 12. The log I vs. $E^{\frac{1}{2}}$ plots are linear when Nb is positive (Fig. 11). However, these plots are non-linear when Nb is negative (Fig. 12). This suggests that like titanium in this case also, two different conduction mechanisms are operating when Nb is positive and when Nb is negative electrode.

To get further insight into the problem, the plots between logarithm current (log I) and logarithm voltage (log V) are shown for Nb (positive) or Nb (negative) in Fig. 13. When Nb is positive electrode, the log I vs. log V curves are linear, however, when Nb is negative electrode, the log I vs. log V curves appear to be divided into two regions (i) slowly rising curves and (ii) steeply rising curves. The slopes of slowly rising curves are close to unity i.e. in this region current (I) is proportional to voltage (V) and hence the
Fig. 11 Plot of log I vs. $E^{1/2}$ for various Nb-Nb$_2$O$_5$-metal systems when Nb is positive electrode. (1) Al-46 nm Nb$_2$O$_5$, (2) Sn-46 nm Nb$_2$O$_5$, (3) Sb-46 nm Nb$_2$O$_5$, (4) Al-31 nm Nb$_2$O$_5$, (5) Al-77 nm Nb$_2$O$_5$, (6) Al-92 nm Nb$_2$O$_5$ and (7) Al-107 nm Nb$_2$O$_5$. 
Fig. 12 Plot of log $I$ vs. $E^{1/2}$ for various Nb-Nb$_2$O$_5$-metal systems when Nb is negative electrode.

(1) Al-46 nm Nb$_2$O$_5$, (2) Sn-46 nm Nb$_2$O$_5$, (3) Sb-46 nm Nb$_2$O$_5$, (4) Al-31 nm Nb$_2$O$_5$,
(5) Al-77 nm Nb$_2$O$_5$, (6) Al-92 nm Nb$_2$O$_5$ and
(7) Al-107 nm Nb$_2$O$_5$. 
Fig. 13 Log I vs. log V for various Nb-Nb$_2$O$_5$-metal systems when Niobium is (A) positive electrode; (B) negative electrode. (1) Al-46 nm Nb$_2$O$_5$, (2) Sn-46 nm Nb$_2$O$_5$, (3) Sb-46 nm Nb$_2$O$_5$, (4) Al-31 nm Nb$_2$O$_5$, (5) Al-77 nm Nb$_2$O$_5$, (6) Al-92 nm Nb$_2$O$_5$, and (7) Al-107 nm Nb$_2$O$_5$. 
region at lower voltage is the region of ohmic conduction. The slopes of steeply rising curves between 2.95 to 3.09 and thus in this region of higher voltages current is proportional to \( n \)th power of voltage for these systems. The values of \( n \) for these systems are given in Table 2. Since the current varies with voltage with a power higher than 2; hence this region is the trap-limited space charge limited conduction (SCLC) region. As discussed in the earlier section, the voltage which separates the ohmic conduction region from the SCLC region is known as transition voltage \( (V_t) \) and the values of \( V_t \) are also given in Table 2.

The effect of thickness of dc electronic current was studied by measuring I-V characteristics for different thickness of \( \text{Nb}_2\text{O}_5 \) film (31, 77, 92 and 107 nm) for \( \text{Nb-Nb}_2\text{O}_5\text{-Al} \) system. The magnitude of current decreases with thickness. The log I vs. log V plots (Fig. 13) show a similar gradual transition from an ohmic conduction region at lower voltages to SCLC region at higher voltages when Nb is negative. However log I vs. log V plots are linear and consist of one region only when Nb is positive electrode (Fig.13). A similar behaviour was observed in case of Ti-TiO\(_2\)-metal systems.

In the present study log I vs. \( E^{1/2} \) plot are non-linear when Nb is negative electrode (Fig.12), thus ruling out the applicability of Poole-Frenkel or Schottky mechanism in the \( \text{Nb}(-)-\text{Nb}_2\text{O}_5\)-metal systems. This observation does reinforce our conclusion that conduction in these systems is
Values of slopes of log I versus log V in the SCLC region, transition voltages and the density of states N(E) calculated using Eqns.(5) and (6) for different Nb-Nb$_2$O$_5$-metal systems at 298 K.

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<th>Counter-electrode</th>
<th>Thickness of niobium oxide films</th>
<th>Slope of log I vs log V in the SCLC region (n)</th>
<th>Transition voltage ($V_t$)</th>
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</tbody>
</table>
through SCLC mechanism. Since log I vs. $E^2$ plots are linear when Nb is positive, therefore, either conductin is through Poole-Frenkel or Schottky mechanism. The value of $B$ for Nb$_2$O$_5$ film was determined from capacitance measurements (and was found to be 42). The calculated value of $B$ for Poole-Frenkel and Schottky conduction mechanism are $4.56 \times 10^{-4} V^{-\frac{1}{2}} m^{-\frac{1}{2}}$ and $2.28 \times 10^{-4} V^{-\frac{1}{2}} m^{-\frac{1}{2}}$ respectively. The experimental values of $B$ (slope of plot of log I vs. $E^2$) for different counter electrodes using 46 nm thick films are $1.40 \times 10^{-4}$, $1.41 \times 10^{-4}$, and $1.64 \times 10^{-4} V^{-\frac{1}{2}} m^{-\frac{1}{2}}$ for Al, Sn and Sb metals respectively. Similarly using 31 nm, 77 nm, 92 nm and 107 nm Nb$_2$O$_5$ films and Al counter-electrode, the values of slopes are $1.33 \times 10^{-4}$, $1.51 \times 10^{-4}$, $1.55 \times 10^{-4}$ and $1.54 \times 10^{-4} V^{-\frac{1}{2}} m^{-\frac{1}{2}}$ respectively. The values of slopes do not clearly indicate whether Poole-Frenkel or Schottky is operative. However, behaviour of current with temperature at constant voltage (1.5V) for Nb(+)–Nb$_2$O$_5$–Al (in Fig. 14) reveals that Schottky mechanism is not operative. The data have been plotted as log (I/T$^2$) vs. I/T and the plot is found to be non-linear indicating that Richardson Schottky expression is not applicable and thus ruling out Schottky mechanism. Using Eq.(3), the ratio of current of Al and Sb metals (i.e. $I_{Al}/I_{Sb}$) comes out to be approximately $0.4 \times 10^8$. On the other hand the measured ratio of the current is about 1.5. Similarly $I_{Sn}/I_{Sb}$ is about $0.6 \times 10^5$ and observed ratio is 1.4. This also clearly shows the absence of electrode-limited Schottky conduction and thus emphasising that the dominant carrier transport in Nb(+)–Nb$_2$O$_5$/metal systems is Poole-
Fig. 14 Plot of log (1/T^2) vs. 1/T for Nb-Nb_2O_5-Al metal system when Nb is positive electrode. Applied dc voltage is 1.5 V; Thickness of Nb_2O_5 film = 77 nm.
Frenkel conduction mechanism.

Anodic niobium oxide films have been reported to be amorphous\(^{21}\), Eq. (5) was used to calculate the density of gap state \(N(E)\) in Nb(\(-\))-\(\text{Nb}_2\text{O}_5\)-metal system. The values of \(\alpha = \frac{d\log V}{d \log I}\) were the reciprocal of the slopes of SCLC region of \(\log I\) vs. \(\log V\) plots and \(V\) was taken as equal to the transition voltage \(V_t\). The calculated values of \(N(E)\) for different metallic electrodes and different thickness of niobium oxide films are given in Table 2. As represented earlier Eq. (6) also provides a method of evaluating \(N(E)\). If \(\log I/V\) vs. \(V\) is plotted, then the slope of linear plot will be \(I/V_o\). Such plots for Nb(\(-\))-\(\text{Nb}_2\text{O}_5\)-metal systems are shown in Fig. 15 and are linear in the SCLC region. Using the slopes of \(\log I/V\) vs. \(V\) plots, the values of the gap state density \(N(E)\) are calculated and are given in Table 2. The values of the gap-state density \(N(E)\) calculated by two different methods compare well. The values of \(N(E)\) decreases with increase in the thickness of the oxide film and varies approximately inversely with squared oxide thickness (Table 2).

The plot between electrical conductivity \((\log \sigma)\) vs. reciprocal of temperature \((1/T)\) for the ohmic region is shown in Fig. 16 and is linear. This can be represented by the equation

\[
\sigma = \sigma_e \exp \left(-\frac{E_o}{kT}\right)
\]
Fig. 15 Plot of log I/V vs. voltage V for various Nb-Nb₂O₅-metal system when Nb is negative electrode [(1) Al-46 nm Nb₂O₅; (2) Sn-46 nm Nb₂O₅; (4) Al-31 nm Nb₂O₅; (5) Al-77 nm Nb₂O₅; (6) Al-92 nm Nb₂O₅].
Fig. 16 Plot of logarithm of electrical conductivity vs $\frac{1}{T}$ for Nb-Nb$_2$O$_5$-Al metal system when niobium is negative electrode. Applied dc voltage is 1.5V; thickness of Nb$_2$O$_5$ film = 77 nm.
The value of $E_0$ was calculated from the slope and was found to be 0.088 eV and the value of $\sigma_0$ was obtained from the intercept.

The effects of field strength, temperature, thickness of the oxide, the polarity of electrode and the nature of the metal on the DC conduction systems reveal that dominant carrier transport in Ti(+)/TiO$_2$/metal systems as well as in Nb(+)/Nb$_2$O$_5$/metal systems is through Poole-Frenkel conduction mechanism. In Ti(-)/TiO$_2$/metal systems as well as in Nb(-)/Nb$_2$O$_5$/metal systems, the current-voltage plots show that at lower voltages charge transfer is through ohmic conduction, however, at higher voltages the slopes of log I vs. log V plots are in the range of 3.54 to 3.86 in case of titanium and 2.95 to 3.09 in case of niobium indicating that the space charge limited conduction (SCLC) mechanism is operative. Similar gradual transitions from ohmic conductivity to SCLC are indicated irrespectively of the nature of metal and thickness of the oxide film. For Ti or Nb(negative electrode), the gap-state density $N(E)$, are calculated using approaches of Micocci et al and Lampert et al for different metals and oxide thicknesses. The values from the two methods compare well for all the systems. $N(E)$ varies approximately inversely with squared oxide thickness.
REFERENCES