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Conduction studies on tantalum-tantalum oxide-metal system

K C Kalra* & Parveen Katyal
Department of Chemistry, Maharshi Dayanand University, Rohtak 124 001

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Conduction data on tantalum-tantalum oxide-vacuum evaporated metal systems have been obtained. Current voltage plots show that at lower voltages charge transfer is through ohmic conduction. At higher voltages the slope of log I-log V plots are close to 3 indicating that the space charge limited conduction (SCLC) mechanism is operative. Similar gradual transitions from ohmic conductivity to SCLC are indicated irrespective of the nature of the metal, polarity of the electrode and the thickness of the oxide film. The gap-state density N(E) at the Fermi level, calculated by two different methods, are in close agreement for different metals, oxide thicknesses and polarity of the electrodes.

Recently Hukovic and Ceric[1] have put forward a space charge limited conduction mechanism (SCLC) in Ta (−)/Ta_2O_5—electrolyte system. SCLC mechanism has also been proposed in thin films of copper phthalocyanine by Gould[2]. Varying mechanisms such as theories of flaws[3], tunneling[4], hopping[5,6], p-n or p-i-n junction[6], bulk limited Poole-Frenkel[7,8] and electrode limited Schottky[9-11] have been suggested by different workers. In view of the conflicting mechanisms, in the present work investigations have been carried out on Ta-Ta_2O_5-metal system to understand the nature of conduction process. The results obtained have been utilised to calculate the density of states in the gap of Ta_2O_5 films.

Materials and Methods

Tantalum specimens (2×10^{-4} m^2 in area) with short tags were cut from 99.9% pure tantalum sheets and the edges of the specimens were abraded with fine emery paper to make them smooth. The specimens after dipping in KOH melt were washed with distilled water and chemically polished by treating with freshly prepared mixture of 98%. H_2SO_4 + 70% HNO_3 + 48% HF (5:2:2, v/v) for 3-5 sec. The tags of the specimens were covered with a thick anodic film formed in 100 mol m^{-3} aqueous citric acid at room temperature. The specimen thus prepared was placed in a glass cell and was surrounded by platinum gauze which served as a cathode. Anodic polarisation of the sample up to a desired formation voltage was carried out at a constant current density (50 Am^{-2}) in 100 mol m^{-3} aqueous citric acid using an electronically operated constant current generator. The anodized sample was mounted (Fig. 1) on a perspex piece with a suitable depression and the contact with bulk tantalum was made with a standard thermosetting silver preparation. The edges of the specimen were protected by epoxy resin to prevent conduction through them. Contact with an anodic film was made by evaporating different metals separately *in vacuo* (2-3 × 10^{-5} mm Hg) using vacuum coating unit (Hind Hivac model 12A4). A dc microvoltmeter and a standard resistance of 192 KΩ in series with the specimen were used for conduction studies. Citric acid used was from BDH (AR). The density and dielectric constant of tantalum oxide film were taken as 7930 Kg m^{-3} and 27.6 respectively as reported by Young[12]. The thickness of the film was determined using Faraday's law. All data refer to 298 K.

Results and Discussion

The dc currents were obtained for various Ta-Ta_2O_5-metal systems at 298 K using Ta_2O_5 film of thickness 81 nm. The plots between logarithm current (logI) and logarithm voltage (logV) when Ta was used as a positive electrode and Ag (or A1) was used as a negative electrode are shown in Fig. 2. Similar plots between log I and log V when polarities of the electrodes were reversed, i.e. when Ta was a negative electrode and Ag (or A1) was a positive electrode are shown in Fig. 3. The log I versus log V curves (Figs 2 and 3) appear to be divided in 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 voltages is the region of ohmic conduction. The slopes of steeply rising curves vary between 2.73 and 3.15 and thus in this region of higher voltages current is proportional to nth power of voltage. The values of n for these systems are given in Table 1 and are approximately close to 3. Since the current varies with voltage with

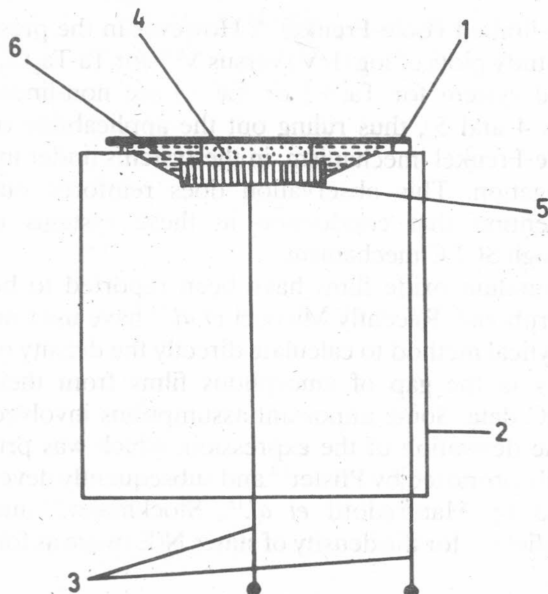

Fig. 1—Encapsulation of tantalum specimen [1, Metallic evaporated electrode; 2, perspex; 3, wire for metallic contact; 4, tantalum oxide layer; 5, tantalum specimen; and 6, epoxy resin

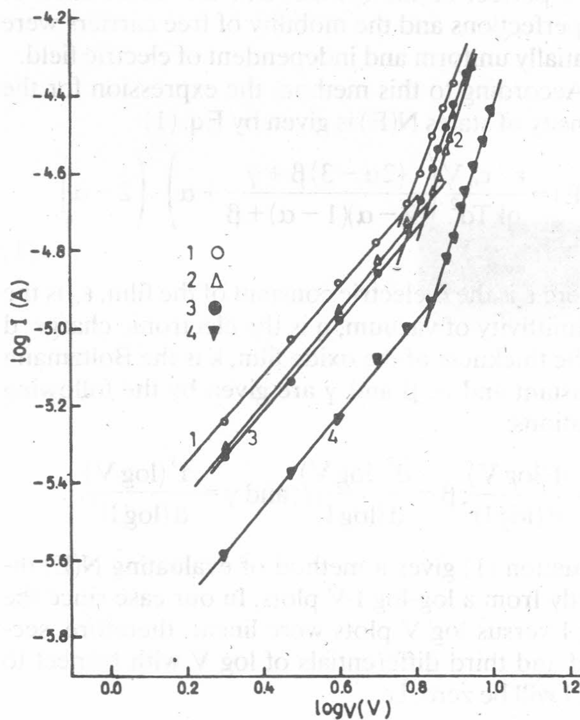

Fig. 2—Log I versus log V plots for various Ta-Ta_2O_5-metal systems when tantalum is positive electrode [Ag-81 nm Ta_2O_5 (○); Al-81 nm Ta_2O_5 (●); Sb-32 nm Ta_2O_5 (Δ); and Sb-324 nm Ta_2O_5 (▼)]

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 1.

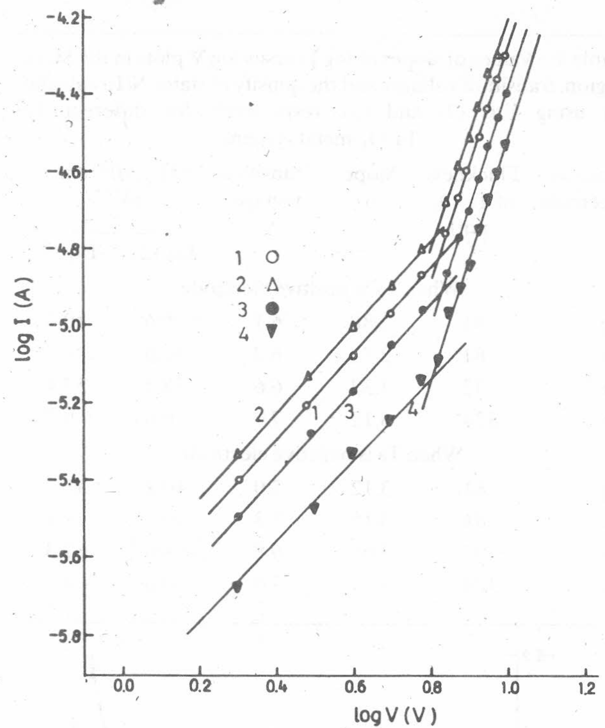

Fig. 3—log I versus log V plots for various Ta-Ta_2O_5-metal systems when tantalum is negative electrode [Ag-81 nm Ta_2O_5 (○); Al-81 nm Ta_2O_5 (●); Sb-32 nm Ta_2O_5 (Δ); and Sb-324 nm Ta_2O_5 (▼)]

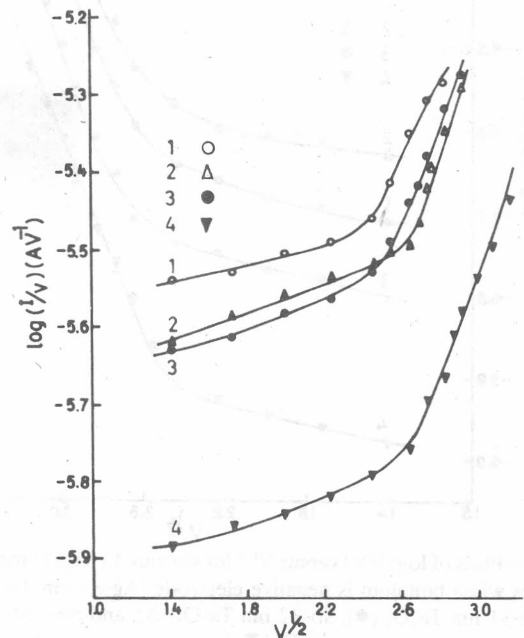

Fig. 4—Plots of log (I/V) versus $V^{1/2}$ for various Ta-Ta_2O_5-metal systems when tantalum is positive electrode [Ag-81 nm Ta_2O_5 (○); Al-81 nm Ta_2O_5 (●); Sb-32 nm Ta_2O_5 (Δ); and Sb-324 nm Ta_2O_5 (▼)]

The effect of thickness of dc electronic current was studied by measuring I-V characteristics for two different thicknesses of Ta_2O_5 film (32 and 324 nm) for Ta-Ta_2O_5-Sb system. The magnitude of current dec-

Table 1—Values of slopes of log I versus log V plots in the SCLC region, transition voltages and the density of states N(E) calculated using Eqs (2) and (3), respectively for different Ta-Ta_2O_5-metal systems

Counter-electrode	Thickness of Ta_2O_5 (nm)	Slope (n)	Transition voltage (V_t)	N(E) (10^{20} cm^{-1} eV^{-1}) Eq. (2)	Eq. (3)
When Ta is positive electrode					
Ag	81	2.80	6.1	9.6	10.2
Al	81	2.73	6.2	10.0	10.7
Sb	32	3.33	6.6	58.5	53.4
Sb	324	3.12	7.0	0.6	0.7
When Ta is negative electrode					
Ag	81	3.12	7.0	10.2	11.7
Al	81	3.15	7.3	10.5	11.5
Sb	32	3.06	6.8	64.6	67.3
Sb	324	3.21	7.0	0.6	0.7

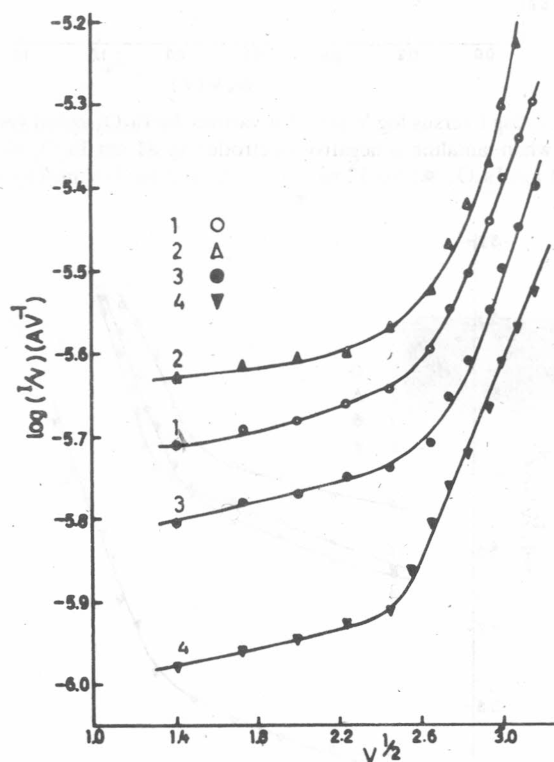

Fig. 5—Plots of log (I/V) versus $V^{1/2}$ for various Ta-Ta_2O_5-metal systems when tantalum is negative electrode [Ag-81 nm Ta_2O_5 (○); Al-81 nm Ta_2O_5 (●); Sb-32 nm Ta_2O_5 (Δ); and Sb-324 nm Ta_2O_5 (▼)]

reases with thickness. The log I-log V plots shown in Figs. 2 and 3 show a similar gradual transition from an ohmic conduction region at lower voltages to a SCLC region at higher voltages irrespective of the nature of the metal, polarity of the electrode and thickness of the oxide film.

It is well known that if the plots of log (I/V) versus $V^{1/2}$ are linear then the conduction mechanism is bulk-limited Poole-Frenkel[7,8]. However in the present study plots of log (I/V) versus $V^{1/2}$ for Ta-Ta_2O_5-metal system for Ta(+) or Ta(−) are non-linear (Figs 4 and 5), thus ruling out the applicability of Poole-Frenkel mechanism in the systems under investigation. This observation does reinforce our contention that conduction in these systems is through SCLC mechanism.

Tantalum oxide films have been reported to be amorphous[1]. Recently Micocci *et al.*[13] have used an analytical method to calculate directly the density of states in the gap of amorphous films from their SCLC data. 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(E) were as follows:

(i) Electrical length of the samples was independent of applied voltage and current.

(ii) Only majority carriers (holes) were injected by a perfect ohmic contact and the distribution of imperfections and the mobility of free carriers were spatially uniform and independent of electric field.

According to this method, the expression for the density of states N(E) is given by Eq. (1)

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

where ε is the dielectric constant of the film, ε_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 α, β and γ are given by the following relations:

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

Equation (1) gives a method of evaluating N(E) directly from a log-log I-V plots. In our case since the log I versus log V plots were linear, therefore, second and third differentials of log V with respect to log I will be zero, i.e.

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

Substituting $\beta=0$ and $\gamma=0$ in Eq. (1) we get a modified expression for N(E) (see Eq. 2).

$$N(E)=\frac{\varepsilon\,\varepsilon_0 V}{qkTd^2}\cdot\alpha(2-\alpha) \quad \ldots (2)$$

Equation (2) was used to calculate the density of gap state N(E) in Ta-Ta_2O_5-metal system. The values of

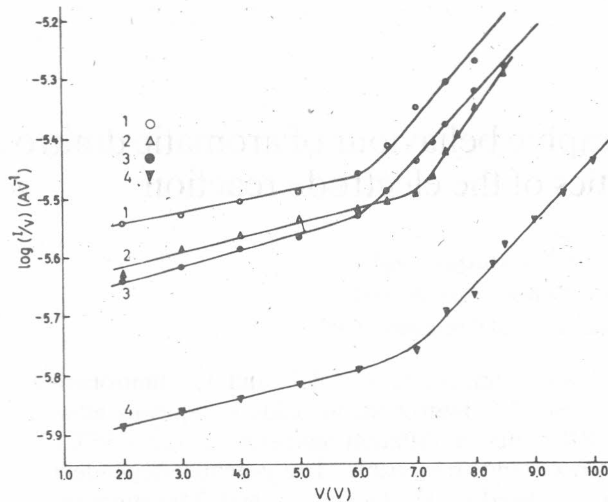

Fig. 6—Plots of log (I/V) versus V for various Ta-Ta_2O_5-metal systems when tantalum is positive electrode [Ag-81 nm Ta_2O_5 (○); Al-81 nm Ta_2O_5 (●); Sb-32 nm Ta_2O_5 (Δ); and Sb-324 nm Ta_2O_5 (▼)]

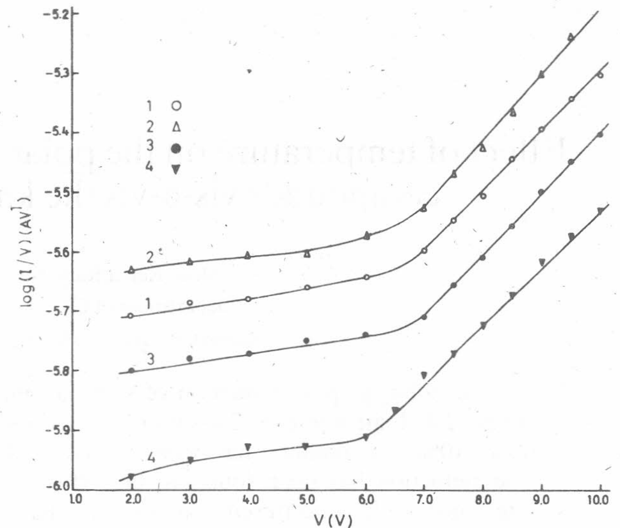

Fig. 7—Plots of log (I/V) versus V for various Ta-Ta_2O_5-metal systems when tantalum is negative electrode. [Ag-81 nm Ta_2O_5 (○); Al-81 nm Ta_2O_5 (●); Sb-32 nm Ta_2O_5 (Δ); and Sb-324 nm Ta_2O_5 (▼)]

$\alpha = d(\log V)/d(\log I)$ were 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 thicknesses of the tantalum oxide films are reported in Table 1.

The gap-state distribution in SCLC measurements may be representated 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. (3),

$$I \alpha V \exp(V/V_0) \quad \ldots (3)$$

where $V_0 = qkTd^2 N(E)/\varepsilon \cdot \varepsilon_0$. Equation (3) also provides a method for evaluating N(E). If log I/V versus V is plotted, then the slope of the linear plot will be $1/V_0$. Such plots for Ta-Ta_2O_5-metal systems for Ta(+) and Ta(−) are shown in Figs 6 and 7 and are linear in the SCLC region. Using the slopes of log I/V versus V plots, 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. For instance for about 10-fold increase in thickness of Ta_2O_5 film, N(E) approximately decreases by about a factor of 100, thus emphasizing that N(E) is inversely proportional to the squared oxide-thickness.

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