CHAPTER V

THERMAL STUDIES IN MOLYBDENUM TRIOXIDE AND VANADIUM PENTOXIDE FILMS

5.1 Introduction.

Thermogravimetry (TG) and differential thermal analysis (DTA) are carried out in MoO_3 films. From TG studies activation energy has been found out.

V_2O_5 films show thermoelectric power (TEP) in couple with aluminium films. Earlier workers[1,2] have also reported thin film thermocouples.

5.2. Experiment

TG and DTA studies are carried out using a Shimadzu thermal analyzer. Amorphous MoO_3 thin film is removed from the glass substrate and used for the study. The sample, weighing about 10mg, is taken in a small platinum sample holder and placed in the furnace of the analyzer. The heating rate was adjusted to $10^{o}C$ /min. The heat released by the hot source flows to the cold source (α Alumina) through a detection system that gives a signal proportional to the temperature difference between both sources. The area under the curve is proportional to the heat exchanged.

V_2O_5 film is deposited on glass substrate at a vacuum of about 10^{-5} mbar using electron beam gun. An aluminium film is coated on the same substrate so as to get a junction as shown in figure 5.1. By varying the temperature of the junction, the voltage developed at the n terminals A and V are measured using the electrometer. The other junction is at room temperature. Temperature of hot and cold ends are measured by copper constantan thermocouple Th1 and Th2 respectively.

5.3. Results and discussion.

5.3.1. TG-DTA studies.

Figure 5.2 gives the TG and DTA curves of MoO_3 film. The figure shows that the *dehydration process takes place in the first stage* and decomposition in the *second stage* of MoO_3. The film has begun to lose water molecule at $40^{o}C$ and dehydration has been completed at $120^{o}C$ by losing 80% of water. In this stage 12% of its weight has been lost. Seventy four percent of its weight has been lost by decomposition in the second

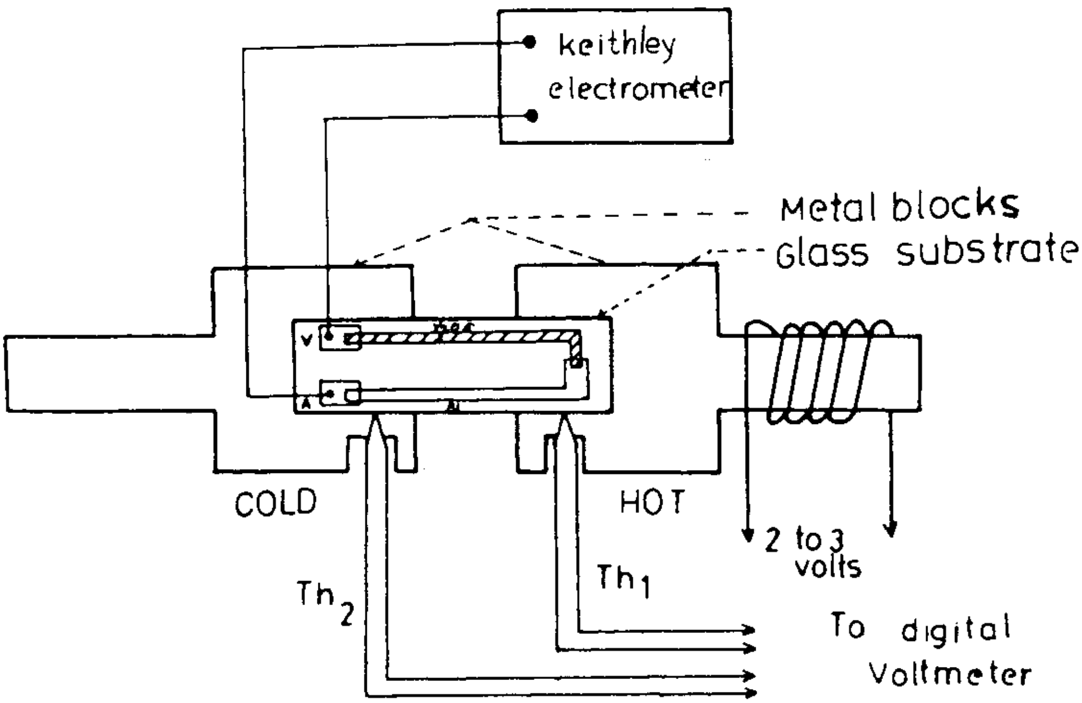

Fig.5 1. $Al-V_2O_5$ thermo-emf study set-up.

stage. The temperature during this stage is varied from 680 to 840^{o}C. These stages have been confirmed from DTG curve along with TG.

Coats-Redfern[3] equation is given by

$$\ln [g(\alpha)/ T^{2}] = \ln \left[(A R / \phi E) (1 - \frac{2 R T}{E}) \right] - \frac{E}{R T} \qquad \text{—— 5.1}$$

where A is the pre-exponential factor,

$$A = \frac{k_B T_s}{h} e^{\Delta s/R}$$

E is the activation energy, ϕ is the rate of heating, k_B is the Boltzmann's constant, h is the Planck's constant, Δs is the entropy of activation and T_s decomposition temperature. From equation 5.1 $\ln [g(\alpha)/ T^{2}]$ vs $10^{3}/T$ gives straight line plot. E is calculated by least square method. The nine mechanisms based equations for the value $g(\alpha)$, proposed by Satava[4], is shown in the table 5.1

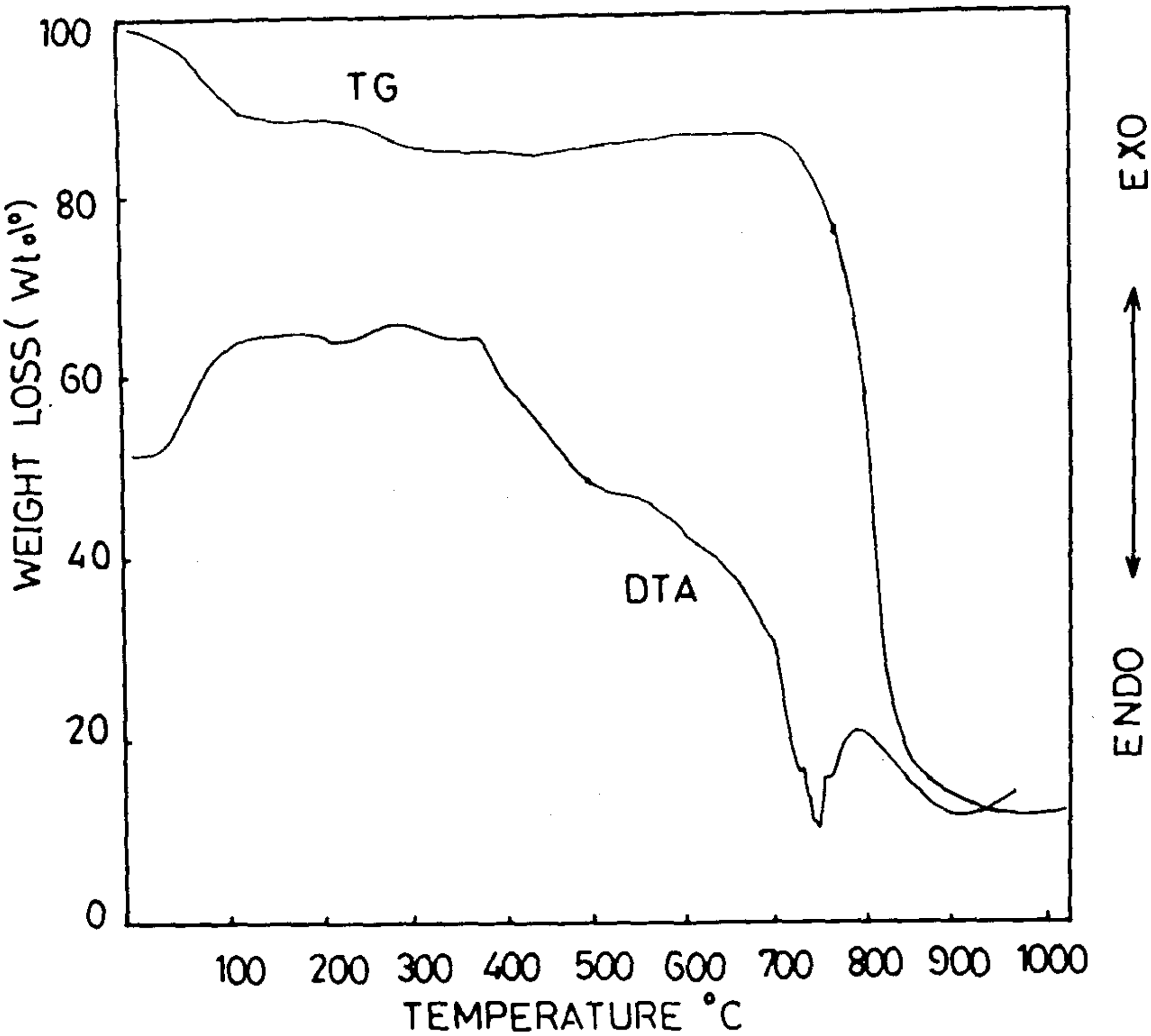

Fig.5.2. TG-DTA curve of MoO_3 film.

Table 5.1 Commonly used $g(\alpha)$ for solid state reactions

eqn.No.	Form of $g(\alpha)$	Rate of controlling process
1	α^2	One dimensional diffusion.
2	$\alpha + (1-\alpha) \ln (1-\alpha)$	Two dimensional diffusion.
3	$[1 + (1-\alpha)^{1/3}]^2$	Three dimensional diffusion spherical symmetry (Jander eqn)
4	$(1- \frac{2\alpha}{3}) - (1-\alpha)^{2/3}$	Three dimensional diffusion spherical symmetry (Ginstling Brounshtein eqn)
5	$- \ln (1-\alpha)$	Random nucleation - One nucleus on each particle (Mampel eqn.)
6	$[-\ln (1-\alpha)]^{1/2}$	Random nucleation (Avirami eqn. I).
7	$[-\ln (1-\alpha)]^{1/3}$	Random nucleation (Avirami eqn II).
8	$1-(1-\alpha)^{1/2}$	Phase boundary reaction cylindrical symmetry.
9	$1-(1-\alpha)^{1/3}$	Phase boundary reaction spherical symmetry.

The value of $g(\alpha)$ is chosen from the table 5.1 for which the best fit straight line is obtained.

In the case of MoO_3 film two activation energies for different temperature regions are obtained. For low temperature, the activation energy is 0.50 eV and for high temperature range it is 1.77 eV. These values of activation energy is in agreement with that obtained by electrical studies in chapter III.

5.3.2 Thermo emf studies

Figure 5.3 shows the variation of thermo emf e_t with absolute temperature T of Al-V_2O_5 system of V_2O_5 thickness 105,152, and 162 nm respectively. All the curves show a peak near 400-410 K. After that it decreases. This may be due to the fact that the temperature of inversion is between 400-410 K.

From the computer-fit of the above curves, thermoelectric power[2] (TEP) at different temperatures is calculated using $S = \frac{d\, e_t}{d\, T}$, where e_t is the thermo-emf and T is the temperature.

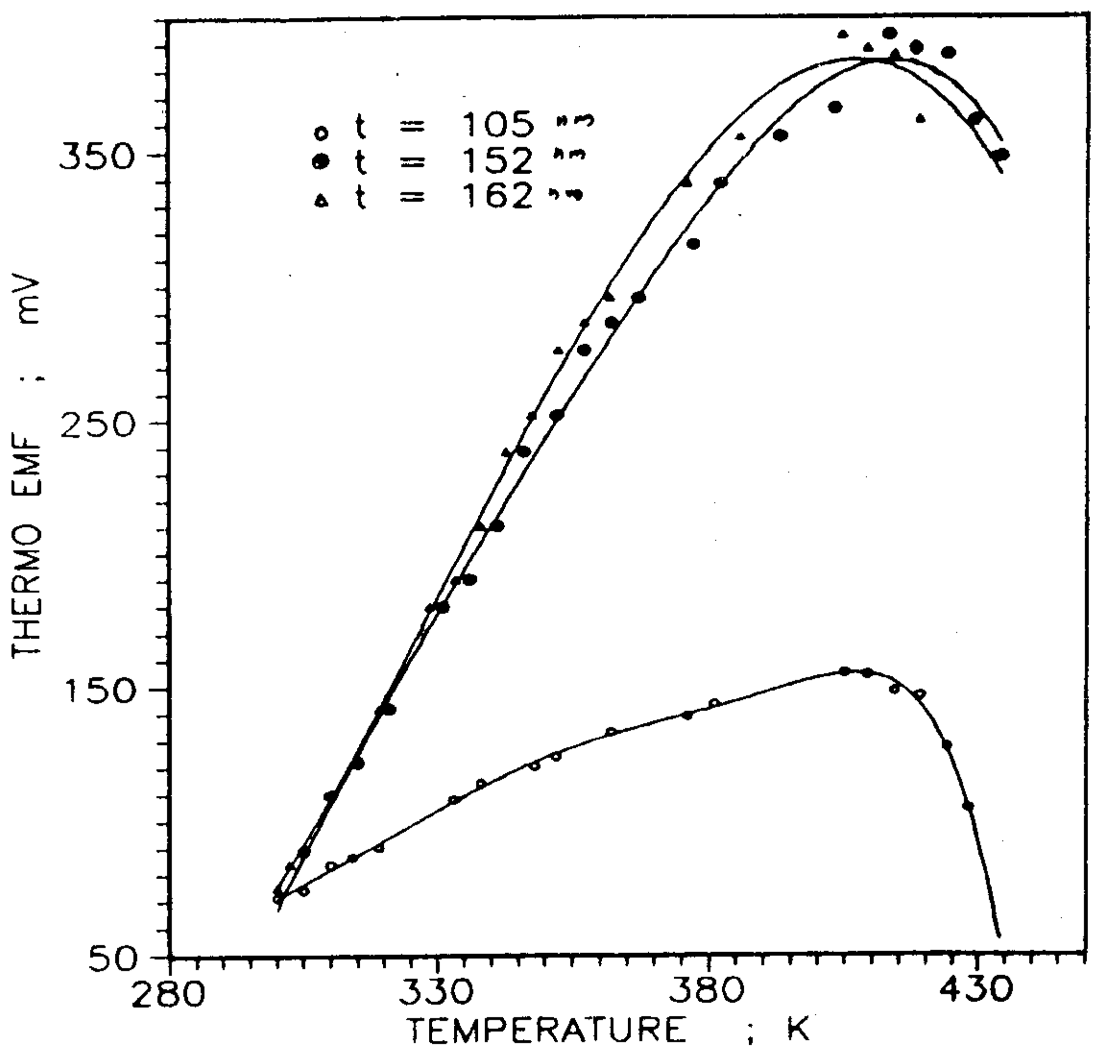

Fig.5.3. Plot of thermo-emf vs. absolute temperature for Al-V_2O_5 film for various thickness.

Figure 5.4 shows the variation of thermoelectric power with inverse of temperature as S vs $10^3/T$. These graphs are straight lines with positive slope which indicates that S decreases linearly with temperature. This is in agreement with the general expression for S in the case of amorphous semiconductors which is given by[1]

$$S = \pm \left(\frac{k_B}{e} \right) \left[(\Delta E_S / k T) + A \right] \qquad 5.2$$

where k_B is the Boltzmann's constant, e is the electronic charge and A is a small quantity which lies between 1 and 4[2,3] which represents the thermal energy transported by carriers. This type of variation of S with temperature has been reported in various chalcogenide glass systems[8-10]. The activation energy $\Delta E_S = E_C - E_F$, which means that the difference between the Fermi energy (E_F) and the energy level where charge transfer occurs (conduction band E_C). In a simple one band model with the Fermi energy pinned near the middle of the band gap, S is thermally activated with the activation energy of the carrier density activation energy.

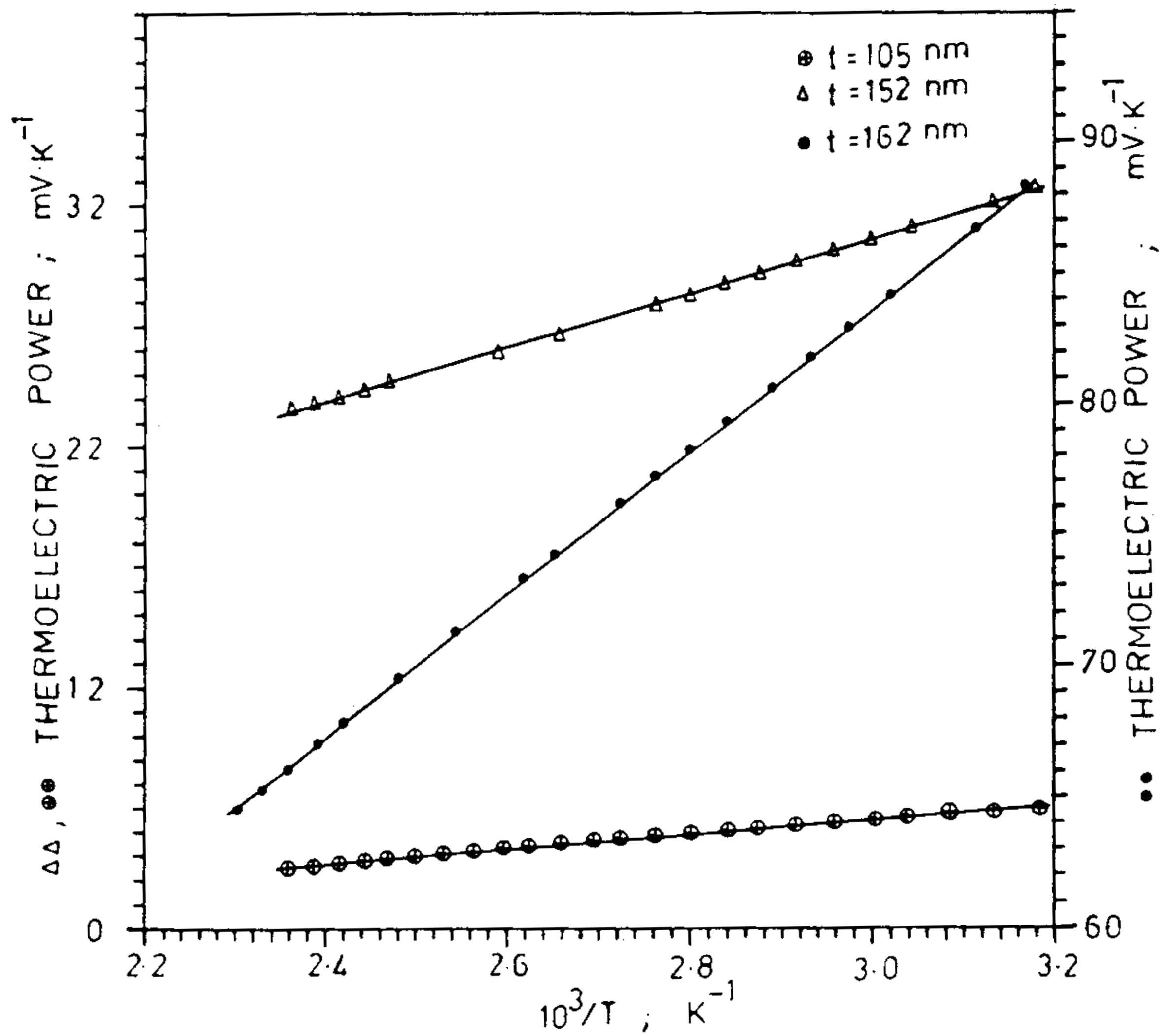

Fig.5.4. Plot of TEP vs. inverse of temperature for $Al-V_2O_5$.

5.4. Conclusion.

The thermal activation energy of MoO_3 films,determined by using TG studies, is different for lower and higher temperature ranges which is in agreement with that obtained by electrical studies using Arrhenius relation. The value of thermo emf of $Al-V_2O_5$ at different temperatures shows that there was an inversion temperature in between 400- 410 K. The thermoelectric power varies linearly with inverse of temperature.

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