

CHAPTER I

REVIEW OF ELECTRICAL CONDUCTION AND OPTICAL STUDIES IN
ELECTROCHROMIC AND PHOTOCROMIC THIN FILMS



1.1. Introduction

A large number of electrochromic and photochromic materials have been developed in the past two decades¹⁻¹⁰, as film-based energy efficient windows. It is possible to alter the transmission and reflection properties of such films electronically. The aperture of a film can be electrically, optically or thermally adjusted. Optical shutters are those windows whose transmission as well as reflectance can be controlled electrically and optically. This type of shutters are coloured by the application of DC voltage or photon irradiation. Those materials which show colour change due to the application of electricity are known as electrochromic materials, and those which produce colour change due to photon irradiation are called photochromic materials. Materials which produce colour change due to heating are called thermochromic materials.

The energy that flows through the window aperture can be adjusted by integration or attachment of the switching device. Electrochromic devices act as switching devices. Energy management of incident solar



radiation for heating and lighting can reduce net energy consumption. If an optical shutter has high infrared reflectance in one of its optical state, it can have adjustable heat-mirror characteristics. An ideal optical shutter is one that responds automatically to a changing ambient environment to provide comfort visual needs and energy savings. Such a device may be connected to a building energy management system that adjusts heating, cooling and even lighting to work space needs.

Electrochromism has been observed in oxides based on Tungsten, Molybdenum, Nickel, Cobalt, Iridium, Manganese, Chromium, Vanadium, Titanium, Neobium, Tantalum , several mixed oxides, and many organic materials. This thesis deals with Molybdenum trioxide (MoO_3), Vanadium pentoxide (V_2O_5) and Titanium dioxide (TiO_2) films. The spectral changes produced due to UV-irradiation of the above three electrochromic materials have been studied. Infrared and X-ray diffraction studies of these materials have been done as a part of optical studies. Micrographs of MoO_3 films



at different annealing temperatures have also been studied in this thesis. In the case of electrical studies the activation energy variation due to thickness and DC conductivity variation with time of ultraviolet (UV) irradiation have been investigated. Electrical studies of metal-insulator-metal (MIM) viz. Al-MoO₃-Al, Al-V₂O₅-Al, Al-TiO₂-Al have also been investigated. Thermogravimetric studies of thin films of MoO₃ have also been made. Windows made of MoO₃ and a combination of MoO₃ and V₂O₅ have been fabricated and investigations have been made.

Some important physical parameters of bulk form of MoO₃, V₂O₅, and TiO₂ are given in table 1.1. The bulk material of TiO₂ is known to have two main phases, rutile and anatase. The rutile is a high temperature stable phase while anatase is formed at lower temperature.



Table 1.1 Physical parameters of MoO_3 , V_2O_5 , and TiO_2 materials.

Physical parameters	MoO_3	V_2O_5	TiO_2	
			Anatase	Rutile
Atomic weight	143.94	181.88	79.88	79.88
Density ($\times 10^3$) kg m^{-3}	3.124	3.357	3.84	4.26
Structure	Ortho-rhombic	Ortho-rhombic	Tetra-gonal	Tetra-gonal
Lattice constants				
a_o	3.962	11.519	3.785	4.5937
b_o	13.858	4.373	3.785	4.5937
c_o	3.697	3.564	9.514	2.9618
Valence electrons of corresponding transition metals	$4d^5 5s^1$ (Mo)	$3d^3 4s^2$ (V)	$3d^2 4s^2$ (Ti)	$3d^2 4s^2$



1.2 Earlier work

Carl M. Lampert⁴ reviewed numerous inorganic and organic materials in the context of developing a film-based optical shutter for energy efficient windows. Extensive electrical and optical investigations of electrochromic materials have been made in the last decade¹¹⁻¹⁴.

Blanc and Stabler¹⁵ have studied the electro-colouration of transition metal doped strontium titanate (SrTiO_3). Optically and electrically coloured MoO_3 and WO_3 have been studied by Deb^{16,17} and Tubbs¹⁸, and the spectra have been found to be similar for both colouration techniques. The absorption shows a broad peak centred in the red region of the spectrum (300-1000 nm) with a minimum in the violet-blue region. Water of hydration incorporated in vacuum evaporated^{19,20} MoO_3 and tungsten trioxide (WO_3) facilitates photo decomposition during UV irradiation. The trapping of electron at oxygen vacancies²¹⁻²³ is proposed to be the cause of photochromism.



According to Rabalais²³ the sub-stoichiometric amorphous material MoO_{3-x} contains oxygen ion vacancies that act as positively charged defects. Electrical colouration promotes electrons from the valence band into these positively charged defects. The energy associated with these anion defects may be greater than $k_B T$ at ambient temperature (where k_B is Boltzmann's constant and T is the temperature) in order to trap the electron. The trapped electrons are responsible for the small band in the blue region.

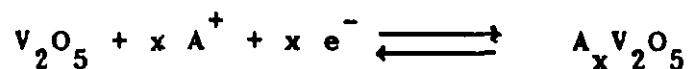
Jagadeesh and Damodara das²⁴ have reported that in evaporated MoO_3 films the predominant defects are oxygen vacancies. Gavrilyuk et al.²⁵ studied the photoinjection of hydrogen in transition metal oxide heterostructure like $\text{VO}_2\text{-WO}_3$. The usual method of hydrogen injection is the cathodic polarisation of transition metal oxide in solutions of protonic electrolytes. Electrons are injected into the oxide from the cathode. Double charge injection in the presence of an electrical field or current alters the light transmission of oxides²⁶. Photoinjection of



hydrogen is observed in several saturated oxides of transition metal with vacant d-orbitals.

Schirmer et al.²⁷ have reported that the absorption band produced during the colouration of WO_3 is due to the formation of small polarons. Also it was reported²⁸ that absorption band formed when amorphous WO_3 films undergo photochromism is the same as that formed in electrochromism. However the maximum concentration of optically induced colour centres is about two orders of magnitude less than in the electrochromic case.

Wruck et al.²⁹ and Cogan et al.³⁰ have described the electrochromic properties of V_2O_5 thin films. Hydrogen or lithium atoms can be added to or removed from the V_2O_5 superstructure through a reaction;

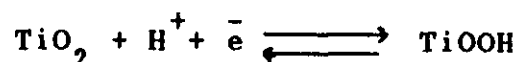


where A = H or Li. Goldner et al.³¹ have used V_2O_5 films as counter-electrode in WO_3 devices. Sputtered films of V_2O_5 have been studied extensively as optically



inactive or weakly colouring counter-electrode for electrochromic devices^{30,32-34}.

Amorphous TiO_2 undergoes an electrochromic reaction³⁵ as shown below



Narasimha Rao et al.³⁶ have investigated optical properties of electron beam evaporated TiO_2 films. Tetsuya Seike and Junichi Nagai³⁷ have studied electrochromism of 3d transition metal oxides which includes TiO_2 . Ozer³⁸ has found reproducibility of colouration cycle in the study of electrochromism in TiO_2 films.

Amorphous transition metal oxides show semiconducting properties³⁹. A general condition for semiconducting behaviour is that the transition metal ion could exhibit several valence state so that electron hopping from low to high valence state can take place⁴⁰. In the case of V_2O_5 the valence states are V^{4+} and V^{5+} . And MoO_3 shows valence states Mo^{5+} and Mo^{6+} .



Hashimoto and Matsuoka⁴¹ have studied the degeneration of electrochromism of amorphous WO_3 and $\text{WO}_3\text{-TiO}_2$ films prepared by electron beam gun and found that life-time of $\text{WO}_3\text{-TiO}_2$ films are five times longer than that of WO_3 films.

Detailed studies of ECDs have been reported with dielectric layers of magnesium fluoride (MgF_2)⁴²⁻⁴⁴, silicon oxide (SiO_x)^{45,46}, lithium fluoride (LiF)⁴²⁻⁴⁷ and chromium oxide (Cr_2O_3)⁴⁸⁻⁵⁰. ECDs with MgF_2 , SiO_x and LiF rely on ambient water, and become non-functional under dry conditions. However, designs with Cr_2O_3 can maintain their water and operate as ECDs even in vacuum⁴⁸.

The limitations inherent to such ECDs have led to the search in thin film designs with an ion storage layer operating in concert with the EC tungsten oxide. These devices with hydrated tantalum oxide ($\text{Ta}_2\text{O}_5\text{:H}_2\text{O}$) films for ion conduction and iridium oxide for ion storage are available⁵¹⁻⁵³. ECDs of the latter kind are used in proto-type sun-glasses capable of varying the transmittance between 70 and 10 %⁵³.



Work has also been reported with Li^+ as conducting film. Thus lithium aluminium fluoride (LiAlF_4) films⁵⁴, lithium doped MgF_2 films⁵⁵ and lithium tungsten oxide (LiWO_4) films⁵⁶ have been reported. Transparent ECDs have been given by Goldner et al.^{31,57}. For several of the devices with Li^+ conductors, dehydration is not assured and hence H^+ conduction contributes to the electrochromism.

Different types of ECDs and the material properties are reviewed here. The drawbacks of ECDs have been image drift and slow response. Light-emitting diodes and liquid crystal displays have been developed to overcome these disadvantages. The advantage of electrochromic displays are principally high contrast ratios, low-power memory and wide viewing angles. For energy efficient window shutters, the important characteristics are solar-matched spectral response, low power, wide operating temperatures and wide range of intensity response. Shutters can also be made programmable and manually controlled according to



heating and cooling needs. It should be stable to solar radiations, weather and cleaning.

1.3. Electrochromism

An electrochromic material is a material in which an optical absorption band can be introduced or an existing band altered by the passage of current through the material or by the application of an electrical field. The phenomenon is called electrochromism. These material are used in display devices^{58,59}. The simplest example of this process is the creation of F-centres in alkali halide crystals when a voltage is applied between two metal electrodes attached to two faces of the crystal at 700°C ²². The effect occurs because electron injected from the negative-pointed electrodes are trapped at anion vacancies thereby forming F-centres. Charge neutrality and current continuity are maintained by anion vacancy motion originating from the positive electrode. This indirectly signifies a net mass transport of anions to the positive electrode. If the electrode potential is reversed V-centres are produced accompanied by the release of alkali metal at the



negative electrode.

The above example illustrates most of the requirement of an electrochromic material. First of all it must have a colour centre or optical absorption. Second feature is the presence of mixed conduction. This is necessary for electrochromism, which depends on injected charge to produce the altered states, since charge neutrality must be preserved. These two requirements restricts the range of available materials. In the above example the crystal must be heated to 700°C to raise the ionic conductivity of the alkali halides sufficiently to produce a measurable current and hence optical density change. The requirement of high temperature is the reason that it is not useful for most device applications.

If good electrochromic (EC) performance is desired in a solid at room temperatures, the activation energy for the slowest carrier must be quite low, say 0.4 eV or below. The slowest carrier is usually, but not always, the ionic carrier. This places the search



for good electrochromic material within the class of fast ion (superionic) conductors⁶⁰.

Deb¹⁶ reported that electrical colouration of electrochromic materials occurred in air but not in vacuum. He suggested that water vapour might facilitate electrical colouration and amorphous oxygen-deficient films coloured more. Colouration is caused by electron injection and filling of colour centres. In the case of oxide materials this may be due to the trapping of electrons in the oxygen vacancies present as a result of deposition. Chang et al.⁶¹ and Crandall et al.⁶² found out colouration of WO_3 and other materials in electrochemical cells employing a liquid or gelled electrolyte such as sulphuric acid. Hurditch⁶³ demonstrated the dependence of colouration time and voltage on the water content of hydrated $WO_3 \cdot H_2O$ films postulating the dissociation of H_2O and formation of blue hydrogen-tungsten bronze at the cathode. Arnoldussen⁶⁴ reported that electrical colouration in MoO_3 occurs by means of an electrochemical reaction with absorbed water vapor^u as the electrolyte. Gavrilyuk



et al have reported²⁸ that considerable structural changes produced in WO_3 films during the electrochromic process. If an electric field is applied in such a way as to bend the levels sufficiently, electrons from an external source can fill the band which results the phenomenon of electrochromism.

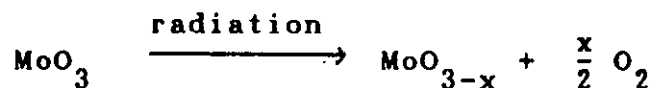
Using the Hubbard-Mott model, Donnadiou et al⁶⁵ have proposed an interpretation of the electrochromic effect. Following this model the colouration is explained by the electronic transition between the two Hubbard bands separated by the pseudo gap $u = \langle e^2 / \epsilon.r \rangle$, where e is the electron charge, ϵ is the effective dielectric constant, r is inter-electron distance and brackets represent the mean value.

1.4. Photochromism

A material whose colouring properties can be changed as a result of photon irradiation is called photochromic material and the phenomenon is called photochromism. This optically induced colouration can be produced in air or in vacuum. In the case of optical (UV) colouration, it is believed that energy radiation



actually results in the photo decomposition such as



where x is a small fraction contains number of oxygen ion vacancies. Ambient water vapour does not seem to be an essential factor since photochromism can occur even in vacuum though it is enhanced in humid atmosphere¹⁶. In MoO_3 optical absorption transitions from the valence band (O_{2p}) to the defect band can result from the photon irradiation⁶⁶. Population of the defect band in this way causes the formation of defect centres which results the phenomenon of photochromism.

Photochromism is due to the splitting of atomic hydrogen from the molecules of a hydrogenous compounds such as methanol which interacts with the photo excited semiconductor surface when the photon energy exceeds optical gap width of the material²⁸. Yao et al.⁶⁷ have studied photochromism in an electrically pretreated MoO_3 thin film by visible light. According to him when a thin film of MoO_3 is irradiated by ultraviolet light, electrons and holes are formed,



thereby allowing the photo generated holes to react with surface-absorbed species, causing the film to be negatively charged. The broad absorption band in the visible region of MoO_3 spectrum is due to the charge transfer transition from Mo^{5+} to the oxide ligands, producing Mo^{6+} 68,69. Structural changes produced due to photochromism have been illustrated in WO_3 by Gavriilyuk et al.²⁸.

1.5. Thermochromism

The colouration produced due to heat treatment is called thermochromism. Anwar and Hogarth⁶⁶ have suggested that the thermal colouration of MoO_3 is perhaps due to the filling up of doubly charged oxygen vacancies (v_o'' centres) by electrons associated with the acceptor level and also to the ionizing of the uncharged oxygen vacancies (v_o centres), which increases singly charged oxygen vacancies (v_o' centres).

1.6. Electrochromic devices

An electrochromic device (ECD) is one which changes its optical property in a reversible and



persistent way under the action of a voltage pulse. The electrochromic effect is mainly used for electronic display devices. Display device when operated is either bleached or coloured. For optical shutters, intermediate colouration is important. An advantage of ECD over other switching process is that they exhibit open circuit memory in either the bleached or coloured state. In some cases of ECDs, a metallic product is formed upon switching which enhances heat mirror benefits. These devices are also used in their absorptive form, as in photochromic glasses. The speed of switching for a display and its power requirements determine whether it is viable or not. For a window shutter even very slow reactions of the order of minutes, are acceptable. Also power requirement are much more stringent than for a battery-operated display devices. Life-time and operating temperatures are probably more demanding for a window shutter than for the display.

Coatings which are transparent in at least some part of the range 0.3-100 μm can be used as energy efficient windows. Properties of the window can be



divided into static properties and dynamic properties. In static case, the optical performance of the film remains the same irrespective of external conditions. This group can be subdivided into one for 'solar control' and the other for 'low thermal emittance'.

For 'solar control' coatings, it is to consider the case that in a hot climate solar energy enters through the windows cause overheating of rooms. Hence cooling is needed to obtain a comfortable indoor temperature. Conventional air-conditioning requires a lot of electrical energy, a part of which can be saved by the use of proper window coatings. The infrared part of solar radiation causes heating. Therefore a coating which is transparent only in the visible range while it is reflecting in the infrared range, can be used for lighting a space where heating is necessary.

Similarly the low thermal emittance in cold climate a window usually causes loss of energy. A large part of this loss is by thermal radiation to the ambients. Energy efficiency can be increased by use of coatings which are transparent in infrared region so



that the minimum use is made of the solar energy, while the emittance of thermal radiation is minimised. The required optical properties are hence high transmittance in infrared range and high reflectance in the visible range.

In the above two cases, types of coating are of great importance for energy efficient windows. It is clear that a "smart window" should exhibit properties which can be automatically tuned in such a way that a suitable amount of solar energy for visible light is allowed to pass through.

Several approaches exist for the coatings which are transparent at shorter wavelengths and reflecting at longer wavelengths. The best results are offered by very thin noble metal films. The thickness of the coating should have a certain threshold value. For thinner films there is an increase in shorter wavelength transmission, while the reflections of thermal radiations is not significantly affected. It is possible to improve transmittance by additional coatings which act so as to antireflect the metal⁷⁰⁻⁷³.



Windows, whose properties are dynamically changed can be illustrated with an example. Consider the window made by amorphous WO_3 films⁷⁴. WO_3 is deposited on a transparent conducting indium tin oxide (ITO) formed glass substrate in the presence of oxygen. Onto this magnesium fluoride (MgF_2) is evaporated in the presence of water vapour. A conducting semi-transparent gold (Au) film is evaporated over MgF_2 . As voltage V is applied between the ITO and Au films the transmittance is changed. This may be due to the dissociation of H_2O molecule and subsequent formation of tungsten trioxide bronze (H_xWO_3). Initial work on the above ECD type was reported by Deb⁷⁵ and its structure is shown in figure 1.1. In fully bleached state the transmission has a peak value of $\approx 50\%$, and the integrated solar transmittance is $\approx 25\%$.

From the above example it is clear that smart windows can be used to improve energy efficiency of buildings and vehicles by electrically controlling radiant energy transfer through them. The spectrally selective reflection modulation or tuning is desirable



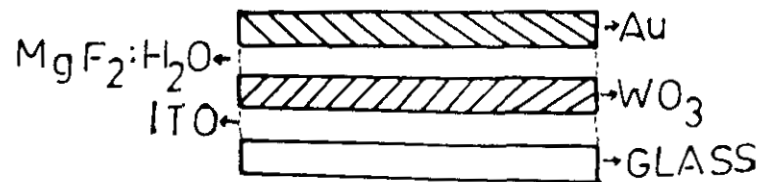


Fig 1.1. Structure of a typical arrangement of different layers in an electrochromic window

for at least three reasons: (i) to avoid excess strain and consequent degradation associated with heat (ii) to avoid decrease in thermal efficiency associated with the radiative emission and (iii) spectrally selective modulation (filtering) can be readily achieved compared to bound electron absorption modulation. Goldner et al.⁵⁷ have considered these factors to develop an electrochromic smart window.

The typical diagram of an electrochromic smart window is shown in figure 1.2. It consists of two transparent conducting (TC) layers sandwiching an electrochromic (EC) layer and a counter electrode (CE) layer which are separated by an ion-conducting (IC) layer. The three inside layers work as an electro-optically active battery. The EC layer is a mixed electron ion conductor.

1.7 Energy band structure

The electrochromic materials discussed above have an amorphous or polycrystalline structure in thin film state. The energy band consideration are usually



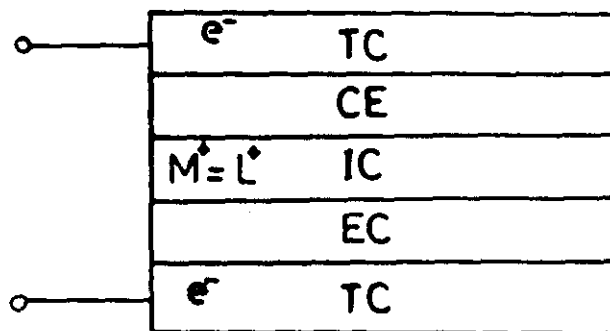


Fig.1.2. Arrangement of different layers in an electrochromic smart window:
 TC - transparent conducting layer,
 CE - counter electrode layer,
 IC - ion conducting layer,
 EC - electrochromic layer.

associated with periodicity of the crystal lattice. The lack of long range order in amorphous materials has been discussed^{76,77}. There is, however, short range order which is clear from the distribution function measurements or electron diffraction patterns⁷⁸. The broadening of discrete energy levels into bands occurs for two atoms as they approach one another.

Forbidden band of an insulator with full allowed band is shown in figure 1.3. The Fermi level E_F indicated in the figure is a quantity defined by the Fermi - Dirac statistics⁷⁹.

$$n(E) dE = Z(E) F(E) dE \quad \text{--- 1.1}$$

where $n(E) dE$ is the number of electrons per unit volume occupying the states in the energy range between E and $E+dE$, $Z(E)$ represents the number of possible states per unit volume and

$$F(E) = \frac{1}{e^{(E - E_F)/k_B T} + 1} \quad \text{--- 1.2}$$



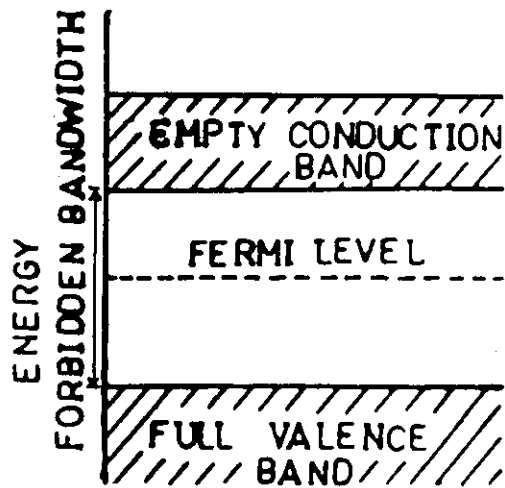


Fig.1.3. Energy band diagram for a typical insulator showing the valence band, conduction band and Fermi energy level.

where k_B is the Boltzmann's constant and T is the temperature.

If two solids are brought in contact, the Fermi levels equalize at the interface, the other energy levels moving to accommodate this. In pure insulators, the Fermi level bisects the forbidden band. If impurities are added, allowed levels move to the forbidden band, which in turn moves the Fermi level up or down. In the extreme, the impurity levels may cause the Fermi level to leave the forbidden band. The conduction then approaches that of a metal and is termed degenerate, which means the electrons are in different state at one energy level. The amorphous nature of insulating films results in a density of localized states situated within the so called 'forbidden' energy gap⁸⁰.

1.8. DC Conduction mechanism in Metal-Insulator-Metal (MIM) films.

Large current flows through thin insulator films than would be expected from bulk properties. The



two possible charge carriers are ions and electrons. The various mechanisms by which electrons are transported under the influence of an applied field is discussed. There are more than one transport mechanism for one particular applied voltage. But generally one mechanism dominates the observed current. Most insulators conduct ohmically below 10^7 V m^{-1} and non-ohmically above 10^8 V m^{-1} . Ohmic conduction is always extrinsic due to the presence of impurity, inhomogeneity etc. But non-ohmic conduction is intrinsic due to purity and homogeneity of the compound. This satisfies both ionic and electronic conduction. The two most important parameters which determine the ultimate transport mechanism are the interface barrier height and the thickness of the insulator. Depending upon the applied field conduction can be divided into high field, and low field conduction

1.8.1 High field Conduction.

This is further subdivided into electronic and ionic conduction.



1.8.1.1 Electronic Conduction

This is further classified into four and are illustrated in figures 1.4 and 1.5.

i) Conduction by means of the conduction band.

There are different ways by which electrons can be raised into the conduction band: thermally from the valence band if it has a small enough band width and the temperature is high enough (process 1.), by Schottky emission⁸¹ from the metal (process 2.), and by thermal excitation of electron into the conduction band from the trapping levels (process 3.) in the forbidden band of the insulator which is "Poole-Frenkel" effect.

ii) Tunneling processes

The tunneling can be from the metal into the conduction band (process 4), from the trapping levels in the insulator (process 5), directly between the valence band and conduction band (process 6), from the valence band directly into the metal electrode (process 7), or directly between the two metal electrode (process 8).



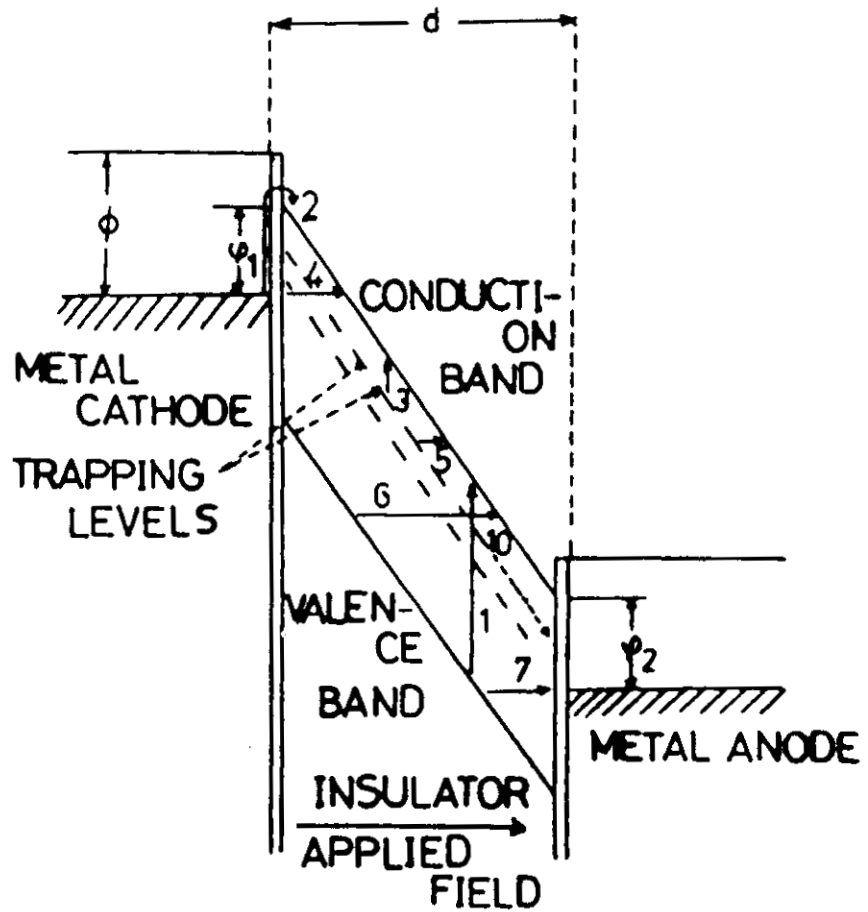


Fig.1.4. Energy band diagram of conduction processes in a thin film insulator in a high applied electric field.

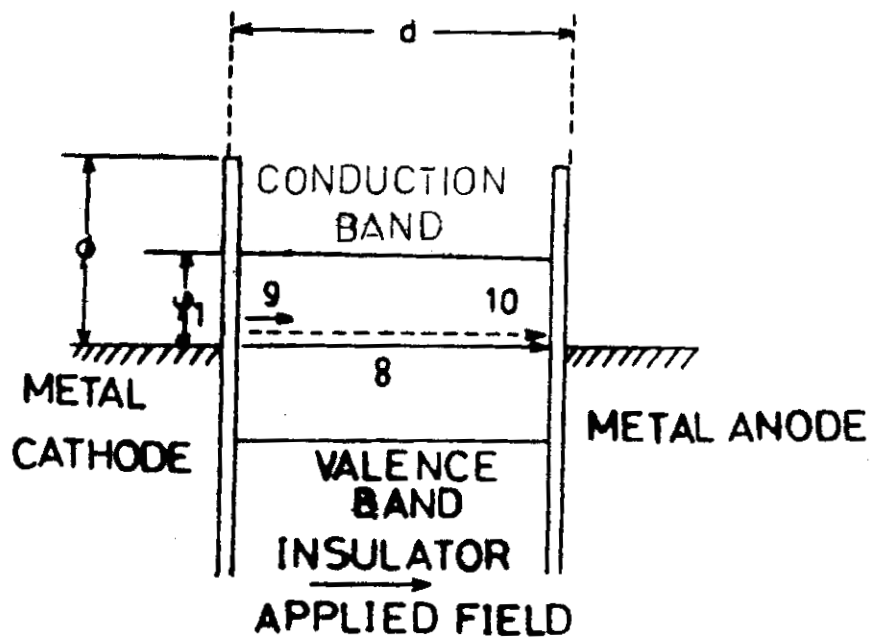


Fig.1.5. Energy band diagram of the conduction processes in a thin insulator film at a low applied electric field.

iii) Impurity conduction

It is used to refer electron hopping from one trapping (eg. impurity) centre to another without going up into the conduction band. This can give appreciable current flow if there are sufficient centres and is illustrated as process 9 in figure 1.5.

iv) Space-charge effect

If injection into the conduction band or impurity conduction or tunneling is not the rate-limiting process, it is possible for space-charge build up to be the major impedance. The charge build up from the electrons in the conduction band or in traps will in the limit balance out the applied voltage.

1.8.1.2 Ionic conduction

Ions in the form of impurities or defects move through the insulator under the influence of an electrical field and is similar to electron motion. Ionic conduction occurs under these circumstances and is shown as process 10 in figure 1.4.



1.8.2 Low field conduction

If an insulator which acts as dielectric, is thin enough, direct tunneling between the electrodes occurs at low fields. Such a method was considered in detail by Schnupp^{82,83} for film thickness less than 3 nm and is shown in figure 1.5 as process 8. Such thin continuous films are practically difficult to realise.

In general, the conduction bands of insulator bends near the metal-insulator interface. This simplest case of band bending is illustrated in figure 1.6(a). Here the band gap is small enough for the band bending to take place in a small region of film thickness. The Fermi level still bisects the forbidden band. The metal work function ϕ_m is greater than that of the insulator ϕ_i . Hence the bands usually bend upward as shown in figure 1.6(b).

Since thin films have a large value of ϕ , band bending will occur over a distance that will be large compared with film thickness. Under these conditions the observed bending will be small in magnitude and the



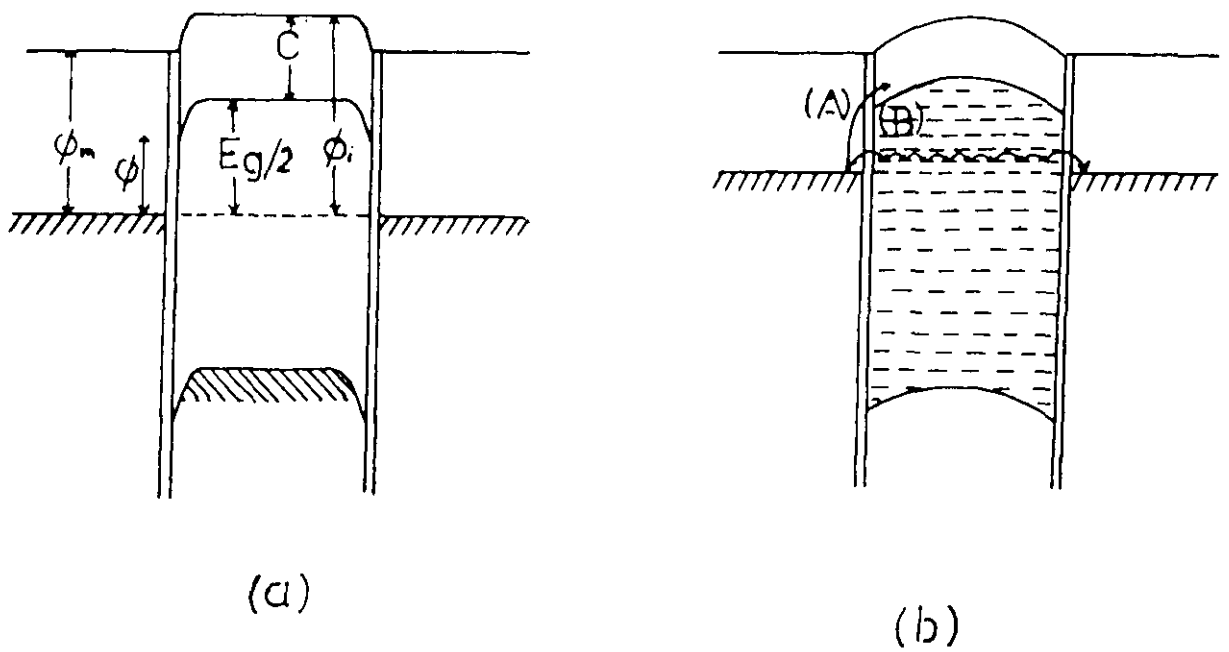


Fig.1.6. Energy band diagram showing band bending at insulator electrode interface. (a) diagram showing the energy gap. (b) diagram showing impurity conduction.

Fermi level will never be in the mid-band-gap position and is shown in figure 1.6(b). Al_2O_3 , MgO and SiO_2 have large forbidden band width, ie. $\geq 8 \text{ eV}$ ⁸⁴ and their conduction band width are of the order of 0.1 eV. By contrast typical metals have $2 < \phi_m < 6 \text{ eV}$. Aluminium ($\phi_m = 4.2 \text{ eV}$ ⁸⁴) is usually used as a contact for reasons of adhesion and breakdown. The barrier ϕ that an electron must jump (process A) in figure 1.6(b) to get into the conduction band is usually more than 1 eV. Since band-to-band conduction (process 1, in figure 1.4) is negligible, Schottky emission (process 2 in figure 1.4) is required to surmount this. Hill⁸⁵ reported that the magnitude of conductivity for Schottky emission over barriers $> 1 \text{ eV}$ is quite small to explain low field conduction. It is also noted that the one form of tunneling indicated for low field (process 8 in figure 1.4) occurs only with films of thickness $< 3 \text{ nm}$. Therefore the remaining two processes are electronic impurity conduction (process 9 in figure 1.5) and ionic conduction (process 10 in figure 1.5)

Materials usually obey Ohm's law at low field and can have conductivity independent of both thickness



and the nature of the electrode. Thus any electronic impurity conduction probably starts with a minimal, thermally assisted jump at the electrode interface. As the film is disordered, the localized levels will be relatively random. This impurity conduction is shown as process B in figure 1.6(b).

The conduction mechanism in amorphous insulating film at low fields is classified into electronic impurity conduction and ionic conduction.

1.8.2.1 Electronic impurity conduction

Electrons will move from one trap to another without going up into the conduction band (process 9) in impurity conduction. Presence of both donors and acceptors are the necessary condition for impurity conduction⁸⁶. The acceptors remove the electrons from some of the donors, and hence an electron can move from an occupied donor to an unoccupied one. An amorphous material will have structural traps. Hopping will still occur between these traps, just as normal impurity conduction. The hopping electrons have very low



mobility, and thus any effect of them is likely to be masked, if there are many electron in the conduction band. Insulators have very low thermally generated free carriers in the conduction band. But impurity conduction is more likely to be observable in an insulator than in a narrow-gap semiconductor. At low impurity level, electrons will either tunnel from site to site or jump the potential barrier between the site⁸¹. For silicon monoxide, impurity tunneling is the most predominant process.

1.8.2.2 Ionic conduction

Ionic conduction results from the migration of actual impurity or defect in the film. The ions move by hopping over barriers of energy ϕ and separation l and the applied field E , and three types of behaviour occur as E is increased:⁸⁷

i) For $E < 10^7 \text{ V m}^{-1}$, $E_{el} \ll k_B T$ and Ohmic conduction

occurs as

$$J = \frac{C}{k_B T} \exp(-\phi/k_B T) \quad \text{-----} \quad 1.3$$



where C is a constant, J is the current density, and k_B is the Boltzmann's constant.

ii) For $E_{el} \simeq k_B T$, the barrier is appreciably distorted by the field so that,

$$J = \bar{C} \exp \left[- \left(\frac{\phi}{k_B T} - \frac{E_{el}}{2 k_B T} \right) \right] \quad \text{--- 1.4}$$

iii) For $E_{el} \gg k_B T$, the number of current carriers is increased by the field. Since multiple hops also occur in this region, the analysis is complex.

If the activation energy is large, it may not be easy to distinguish between ionic and electronic current. An activation energy of < 0.1 eV and high charge mobility are usually associated with electronic conduction, where as a value > 0.6 eV with a low mobility can be either ionic conduction or electronic conduction.



1.8.3 Temperature dependence

Temperature dependence of DC conduction is not easy to generalize whether the conduction is electronic or ionic. Tunneling (high field) conduction usually exhibits small temperature dependence. Ohmic (low field) conduction, whether ionic or electronic, usually obeys Arrhenius equation,

$$\sigma = \sigma_0 \exp \left(\frac{-\Delta E}{k_B T} \right) \quad \text{--- 1.5}$$

where σ_0 is a pre-exponential factor and ΔE is the activation energy, k_B is the Boltzmann's constant and T is the temperature. But

$$\sigma = N e \mu \quad \text{--- 1.6}$$

where N is the number of charge carriers, e is the charge and μ the mobility. With extrinsic electronic conduction the electron may move by hopping, i.e.

$$\Delta E = \Delta E_{\text{hop}} \quad \text{--- 1.7}$$



If the electronic conduction is by excitation into the conduction band, the production of free electrons n is activated. In this case band theory for semiconductors is applied.

Whatever the Ohmic mechanism, a $\ln \sigma$ vs $1/T$ plot ("Arrhenius plot") will usually exhibit increasing activation energy as T is increased, as shown in figure 1.7. At the highest temperature the intrinsic ionic or electronic conduction may finally appear, although the melting point may hide them.



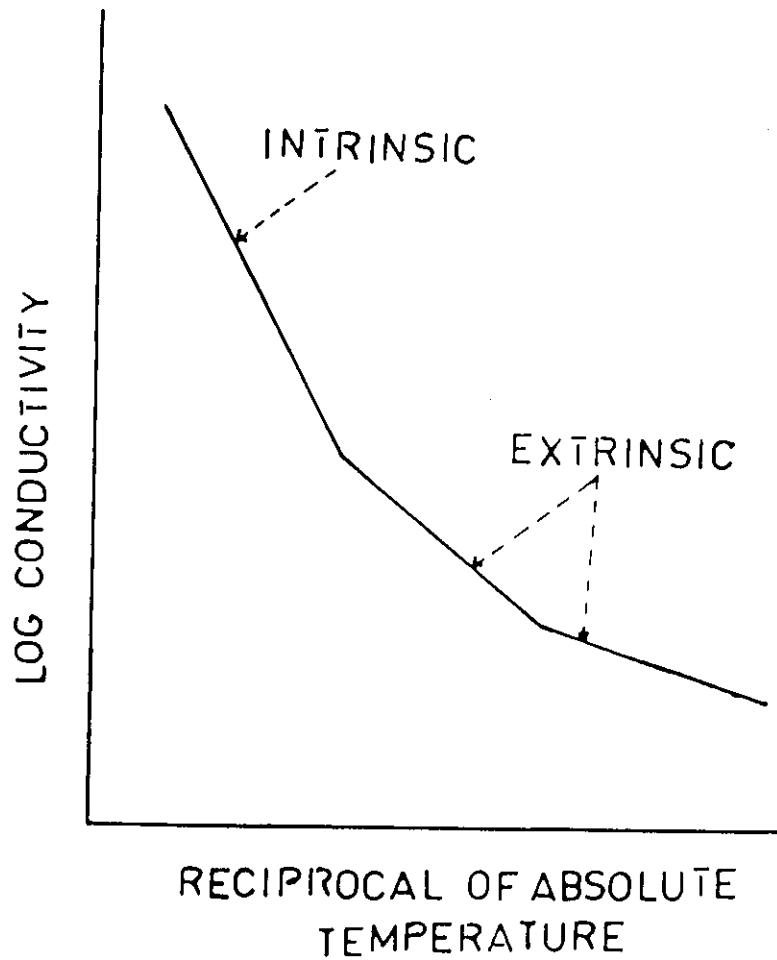


Fig.1.7. Arrhenius plot of conductivity of a typical insulator for low fields.

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