CHAPTER II

EXPERIMENTAL TECHNIQUES
The thin film technology combination with the materials science has paved the way for significantly reduction in the size of the electronic components and devices for applications from console to portable and then to miniaturization. The miniaturized microelectronic circuit requires several thin film passive and active components for wide verity of applications. These thin film coatings are either elemental, compound, multicomponent or alloy and forming single layer or multilayer on substrates of different nature, shape and size. In the generation of such thin films a large variety of thin film deposition techniques has been developed. The physical principles of various thin film deposition techniques, their advantages and limitations are discussed at length in the literature [1 - 4]. The physical properties of the deposited films mainly depend on the method of deposition and the process parameters maintained at the time of preparation of the films. In most of the physical deposition methods one has to control the deposition conditions like residual gas pressure, substrate material, substrate temperature, source material, source temperature, source to substrate distance, partial pressure of reactive gases etc. The physical and chemical characterization of the deposited films is essential to determine the required physical properties for any device applications.

Numerous deposition techniques are available for the preparation of thin films with required material. The concern here is the appropriate deposition method for preparation of thin films in the thickness range of a few nanometers to about few tens of micrometers. The thin film characterization is also very important to determine the quality of the deposited films which strongly depend on the deposition parameters. The details of the preparation of Ta2O5 films by dc and rf reactive magnetron sputtering technique employed in the present investigation and the characterization techniques used to analyze the deposited films are presented.

In this chapter we briefly describe various thin film deposition techniques employed for preparation of Ta2O5 films. The characterization techniques used for analysis of the deposited Ta2O5 films were also presented.

2.1 Thin film deposition techniques

Various thin film deposition techniques such as anodic or thermal oxidation [5, 6], atomic layer deposition [7], ion-assisted deposition [8], liquid phase deposition [9], sol-gel [10, 11], chemical vapor deposition [12], low pressure chemical vapor
deposition [13, 14], plasma enhanced chemical vapor deposition [15, 16], metal organic chemical vapor deposition [17, 18], electron beam evaporation [19, 20], ion-beam sputter deposition [21], sputtering [22 - 32] and pulsed laser deposition [33] were effectively employed for preparation of Ta₂O₅ films. Among these techniques, reactive magnetron sputtering is one of the most industrially practiced techniques for preparation of uniform films on large area substrates. The main features of sputtering technique are: high uniformity thickness of the deposited films, good adhesion to the substrate, there is no direct heating of the material, no reaction between the evaporated and source materials since no source was used as in thermal evaporation, deposition of stoichiometric films as that of the original elemental compound or alloy target composition and better reproducibility of the films on large area substrates.

The details of the sputter deposition and various configurations of sputter deposition methods are given as follows.

2.1.1 Sputtering

Sputtering was discovered in 1852 by Grove [34] while investigating discharge tubes using a silver needle cathode. The ejection of atoms from the surface of a material (the target) by bombardment with energetic particles is called sputtering. If the ejection is due to positive-ion bombardment, it is referred to as cathode sputtering. The ejected or sputtered atoms can be condensed on a substrate to form a thin film. The sputtering process is given below:

2.1.1a Sputtering Process

The ejection of atom or molecule from the surface of the target due to bombardment of the energetic ion is called sputtering. Fig. 2.1 shows the schematic diagram of sputtering process. Sputtering occurs on the target when an energetic ion or atom makes a series of collisions with the target. The following are the typical possible reactions at the cathode due to ion bombardment [35]: the ion may be reflected, the impact of the ion may cause the target to eject an electron, the ion may get buried in the target, leading to the phenomenon of ion implantation, the ion impact may cause some structural rearrangements in the target material, the ion impact may set up a serious of collisions between the atoms of target (cascade
collision process), possibly leading to the ejection of one of the atoms, the process being called sputtering.

![Sputtering diagram](image)

Fig 2.1 Sputtering progress (Chapman 1980)

A few workers were formulated the theories of sputtering, the hot-spot evaporation theory was formulated by von Hippel [36] and by Townes [37], has yielded to the overwhelming experimental evidence, due largely to the work of Wehner [38, 39], that sputtering is not energy but rather a momentum-transfer process, as originally suggested by Stark [40]. The early momentum-transfer or collision theory of Kingdon and Langmuir [41] has seen numerous developments. Henschke's [42] has suggested billiard-ball model, which was valid at low energies, considers sputtering as the result of double or triple collisions of the ion with the lattice atoms followed by its back reflection by the lattice. More sophisticated theories, such as those of Keywell [43] and Pease [44], considered sputtering was essentially a radiation-damage phenomenon. Accordingly, the incident ion displaces a number of atoms (knock-on) during its passage through the material and thus loses its
energy, or cools. Some fraction of the knocked-on atoms will diffuse to the surface and emerge as sputtered atoms. The incident ion actually becomes a neutral atom because of auger neutralization before impact that is, it picks up an electron from the target [45], so that an energetic atom that shares its momentum with target atoms. A target atom that gains enough energy from the collision will be displaced from its normal lattice site. The ejection of number of atoms from the target surface per incident ion is called the sputtering yield. The sputtering yield is the most important parameter for characterizing the sputter process. The Sputtering yield depends on the bombarded material, its structure and composition, the energy of the incident ion and the experimental geometry of the sputter cathode. The sputtering yield as a function of the atomic number of the target displays an undulatory behavior, and the periodicity of the undulations corresponds to the groups of elements of the periodic chart of the elements. The yield increases strongly with decreasing heat of vaporization. The yield of a single-crystal target increases with decreasing transparency of the crystal in the direction of the ion beam. The exact details of the interaction of an ion with the target atom, the momentum transfer, and the collision mean free path mainly depend on its energy. With increasing energy (E), the interaction changes from billiard-ball to coulomb and then to a nucleonic model. Pease's [44] theory gives the following expression for the sputtering yield:

\[ Y = A n^{0.5} \left( \frac{E}{4E_d} \right)^{0.5} \left[ 1 + \frac{\ln(E/E_s)}{\ln 2} \right] \]  --- (1)

where \( A \) is the cross section for imparting energy greater than \( E_d \), the energy required to displace an atom from its lattice site, \( E \) the mean energy of the struck atom, \( E_s \) the sublimation energy and \( n \) the number of atoms per unit volume. Depending on the ion source, two techniques namely ion beam sputtering and glow discharge sputtering have been developed, among which glow discharge sputtering was found to be the most convenient because of the precise control on the chemical composition and physical properties of the deposited films using a large number of sputtering parameters.

2.1.2 Glow discharge sputtering

A brief account of glow discharge phenomena related to dc and rf sputtering are given below:
2.1.2a Dc sputtering

The simplest and most widely used one among the others is the glow discharge between two electrodes and is commonly referred to as a diode arrangement as shown in the Fig. 2.2. The substrate in such diode system is normally placed on the anode and kept at anode potential. It may be left floating, in which case it will acquire a negative. Fig 2.3 illustrates the manner in which a glow discharge form in a low pressure gas with a high impedance dc power supply. When a voltage is applied first a very small current flows. This is due to the presence of a small number of ions and electrons resulting from a variety of sources such as cosmic radiation. Initially the current is nearly constant, because all of the charge present is moving. As the voltage is increased sufficient energy is imparted to the charged particles, so that they produce more charged particles by collision with the electrodes (secondary electron emission) and with neutral gas atoms. As more charge is created the current increases steadily. But the voltage is limited by the output impedance of the power supply. This region is known as the Townsend discharge. Eventually an avalanche occurs. When ions strike the cathode the secondary electrons release which form more ions by collision with neutral gas atoms. These ions then return to the cathode produced more electrons that in turn produce more ions. When the number of electrons generated is just sufficient to produce enough ions to generate the same number of electrons, the discharge is self-sustaining. The gas begins to glow, the...
voltage drops and current rises abruptly. At this point the mode is called the normal glow. Since the secondary electron emission ratio of most materials is of about 0.1, more than one ion must strike a given area of the cathode to produce another secondary electron. The bombardment of the cathode in the normal glow region self adjusts in area to accomplish this. Initially the bombardment is not uniform, but is concentrated near the edges of the cathode or at other irregularities on the surface. As more power is supplied the bombardment increasingly covers the cathode surface.

![Fig. 2.3 Formation of a dc glow discharge](image)

until nearly uniform current density is achieved. Further increases in power produce both increase in the voltage and current density in the discharge. This region is called abnormal glow; is the mode used in sputtering virtually all other glow discharge processes. If the cathode is not cooled, when the current density is reaches about 0.1 A/cm², thermionic electrons are emitted in addition to the secondary electrons, follow by a further avalanche. The output impedance of the power supply limits the voltage, and the low voltage high current arc discharge forms. Crucial to the formation an abnormal glow is the breakdown voltage $V_B$, this voltage is mainly depend on the mean free path of secondary electron and distance between the anode and cathode. Each secondary electron must produce about 10-20 ions for the original avalanche to occur. If the gas pressure too low or anode cathode separation is too small, the secondary electrons cannot undergo a sufficient number of ionizing
collisions before to strike the anode. If the pressure and separation are too large, ions generated in the gas are slowed by inelastic collisions so that they strike the cathode with insufficient energy to produce secondary electrons. This is a quantitative statement of Paschen’s law which relates the breakdown voltage to the product of gas pressure and electrode separation.

\[ V = \frac{a(Pd)}{\ln(Pd) + b} \]  

--- (2)

where \( V \) is the breakdown voltage, \( P \) the pressure, \( d \) the gap between the cathode and anode. The constants \( a \) and \( b \) depend upon the composition of the gas.

Fig 2.4 shows the luminous regions of a dc glow discharge, the voltage distribution and the net space charge as a function of distance from cathode to anode. Adjacent the cathode, there is a brilliant luminous layer known as cathode glow. This is the region in which incoming discharge ions and positive ions produced at the cathode are neutralized by a variety processes. This is also the region in which secondary electrons begins to accelerate away from cathode. The light emission is the characteristic of both the cathode material and the incident ion.

![Fig 2.4 Luminous regions, voltage and net space charge versus position in a dc glow discharge](image-url)
Secondary electrons are repelled at higher velocity from the cathode and start to make collisions with neutral gas atoms at a distance away from the cathode corresponding to their mean free path. This leaves a dark space which is well defined. The dark space is also the region in which positive ions are accelerated towards the cathode. Since the mobility of ions is very much less than that of electrons, the predominant species in the dark space are ions [47]. The Faraday dark space and positive column are nearly field free regions whose sole function is to connect electrically the negative glow to the anode. In most sputtering system the anode is located in the negative glow and these other regions do not exist. The length of the unobstructed negative glow is exactly equal to the range of electrons that have been accelerated from the cathode [48]. When the negative glow is truncated higher voltage must be applied to make up for the ions that would have been generated in the part of it that is blocked by the anode. In general for uniform cathode bombardment the cathode must be located at the 3 - 4 times the thickness of the dark space away from the cathode. This distance is inversely related to the gas pressure.

Though the dc sputtering is widely used in depositing thin films of various materials, it has certain inherent disadvantages. The basic disadvantage being that the sputtering target should be conducting; otherwise, a positive space charge is build up on the cathode preventing the sputtering. Also if voltage is applied not all the sputtered atoms will have this energy, but will have a wide energy distribution because of collision with the atoms. The low deposition rate posses a major problem in depositing thick films using this technique. Operating the sputtering process at higher pressure enhances the rate of sputtering but the rates of deposition will be poor. Increasing the cathode potentials at low pressure leads to a $1^4$ increase in the temperature of the target and a simultaneous increase in the substrate temperature, which plays a dominant role on the morphology and structure of the sputtered films.

2.1.2b Bias sputtering:

The deposition technique shown in Fig.2.5 employed by Maissel and Schaible [49] is called bias sputtering. The idea of sputter deposition with simultaneous sputter cleaning by bombardment was originally conceived by Fredrichs [50], and the arrangement in which is shown in Fig. 2.6. Here, an asymmetric alternating current rather than direct current is applied between cathode and substrate so that more
material is deposited on one half-cycle than is removed by reverse sputtering in the other half-cycle. Bombardment removes not only the adsorbed gases (yielding a purer film) but also the initial oxide layers which are responsible for good bonding of the film. Good bonding may be retained by precoating with a positive bias.

C: cathode, A: anode, S: substrate, HT: high tension, P: plasma, I: intermediate electrode, LT: low tension

Fig. 2.5 Schematic diagram of bias sputtering

C: cathode, A: anode, S: substrate, HT: high tension, P: plasma, I: intermediate electrode, LT: low tension

Fig. 2.6 Schematic representation of asymmetric sputtering
2.1.2c Ion plating:

The effect of sputter cleaning of an evaporated film is utilized in a system called ion plating [51]. The experimental arrangement of the technique is shown in Fig. 2.7. The films are obtained by evaporation from a filament and the deposit is simultaneously bombarded with accelerated gas ions. The electrons bombard the filament and partially sustain evaporation. This technique was effectively employed by Strauss et al [52] for deposition of Ta$_2$O$_5$ films.

2.1.2d Triode Sputtering:

Auxiliary electrons may be supplied thermionically from a filament. Both the total ionization and the ionization efficiency are increased by accelerating the electrons by means of a third electrode and injecting them into the plasma. This assisted sputtering process is called the triode sputtering. This is further enhanced by the presence of a magnetic field inclined to the lines of force between the cathode and the anode. Fig. 2.8 shows the experimental arrangement of the triode sputtering. The triode sputtering system, first employed by Ivanov et al [53] and has become, in a variety of forms and electrode configurations [54], a standard sputtering unit for most
laboratories. Such a system has been used by the author for sputtering noble metals at ~ 20 A/min at about 1 mbar. A significant advantage of the system is the fine control of current density and hence the sputtering rate can be controlled by applied magnetic field.

2.1.2e Rf sputtering

As the frequency of an applied ac signal is increased above 50 KHz two important effects occur. First, electrons oscillating in the glow discharge space acquire sufficient energy to cause ionizing collisions, thus reducing the dependence of the discharge on the secondary electrons and lowering the breakdown voltage. Second, the electrodes are no longer required to be electrical conductors, since rf voltages can be coupled through any kind of impedance. Therefore it is possible to sputter any type of material from metal to dielectrics. At typical rf frequencies used for sputtering are in the range 5-30 MHz, most ions are sufficiently immobile that one would expect negligible ion bombardment of the electrodes. In fact this is not the case. If one or both of the electrodes is coupled to the rf generator through a series capacitor, a pulsating, negative voltage will be developed on the electrode [55].
Owing to the difference in mobility between electrons and ions, the I-V characteristics of a glow discharge resemble those of a leaky rectifier as shown in Fig 2.9 (a). Upon application of an rf (frequency of 13.56 MHz) voltage through the capacitor, a high initial electron current flows to the electrode. On the second half of the cycle, only a relatively small ion current can flow. Since no charge can be transferred through the capacitor, the voltage on the electrode surface must self-bias negatively until the net current (averaged over each cycle) is zero. This results in the pulsating negative potential shown in Fig 2.9 (b) [56]. The average dc value of this potential \( V_s \) is nearly 0.56.

Fig 2.9 Formation of a pulsating negative sheath on a capacitive coupled surface in rf glow discharge

equal to the peak voltage applied [57]. To obtain sputtering from only one electrode in an rf system, it has been shown [58] that the electrode which is to be the sputtering target must be an insulator or must be capacitive coupled to the rf generator and that the area of that electrode must be small compared to that of the directly coupled electrode. Also the ratio of the voltage between the glow space and the capacitive coupled electrode \( (V_c) \) to the voltage between the glow space and the large directly coupled electrode \( (V_d) \) is

\[
\frac{V_c}{V_d} = \left( \frac{A_d}{A_c} \right)^{1/4} \quad (3)
\]

where \( A_d \) and \( A_c \) are the areas of the directly and capacitive by coupled electrodes respectively. In practice, the directly coupled electrode is the system grounded,
including base plates, walls, etc., and is quite large with respect to \( A \). In triode sputtering, due to the presence of an additional electron source, the ionization in the discharge can be increased. The increased ionization in the discharge led to an increase in the rate of sputtering and hence the deposition rate.

A significant development employing rf excited discharge to sputter insulators was announced by Anderson et al [59]. Direct current sputtering of insulators is not possible because of the buildup of positive surface charges which would repel the energetic ions. Methods to neutralize this surface charge by injecting electrons [60] from a gun, or by placing a metal screen [61] over the cathode surface, thus producing a conductive sputtered metal film, have been devised. These techniques obviously are not clean. A high-frequency alternating potential may be used to neutralize the insulator surface periodically with plasma electrons, which must be switched in a period that is short compared with the time positive ions require to travel from the edge of the ion sheath to the surface of the insulator. The fast electrons can still respond to the alternating field. The surface potential changes at a rate of \( \frac{dV}{dt} = \frac{I}{C} \), where \( I \) is the ion current and \( C \) the capacitance of the insulator. Radio-frequency sputtering is shown in the Fig. 2.10. It is a versatile technique and has several other useful applications.

- The high rf sputtering rates of metals and insulators at relatively low pressures can be further enhanced by employing simultaneous dc (1 to 5 kV) and rf (1 kW) sputtering. The superimposed rf and dc method further allows a flexibility of operation with conduction and insulating materials over a large range of the inert-gas pressure.

- Reactive sputtering in a diode arrangement is limited to making films at low rates. This is limited by the fact that a small amount of the reactive gas must be used so that the reaction at the cathode does not decrease sputtering rate because of the formation of an insulating layer or poisoning of the cathode. Since insulators can be rf-sputtered, rf sputtering is ideally suited for high rate reactive sputtering.

If the deposited substrates are placed on the cathode, rf sputtering may be used to etch metals, semiconductors, and insulators. If certain patterns are required, they may be generated by photoresist materials. Thereafter, the bare film material and the photoresist material of the pattern can etched away simultaneously by rf sputtering.
The universality and the absence of undercutting (in contrast to chemical etching) are the chief advantages of rf sputtering. This technique has been successfully used for etching of resistor patterns in cermet films with a definition significantly better than that obtained by conventional chemical-etching techniques. This technique is effectively used for deposition of tantalum oxide films either by using metallic tantalum target or insulating tantalum oxide target [30].

2.1.2f Ion-beam Sputtering

By producing ions in a high-pressure chamber and then extracting them into a differentially pumped vacuum chamber through suitable apertures with the help of suitable electron and ion optics, a beam of ions may be obtained for sputtering in vacuum. Such an arrangement is called a duoplasmatron, and is as shown in Fig.2.11. Principle of extraction is attributed to von Ardenne [62]. Although the von Ardenne type of ion source [63] is theoretically very efficient, in practice many complicated ion-optical problems limit the total beam current density. Current densities of 50 mA/cm² for H₂ ions with potentials exceeding to 10 kV have been obtained for beam sizes of a fraction of a millimeter. Such sources have found a wide variety of applications but are not well suited for deposition of films by sputtering which would require a high-current beam spread over a large area. Some sources have, however, been used in measuring sputtering yield of materials. Cevro et al [21] prepared Ta₂O₅
films on quartz substrates using ion-beam and dual ion beam sputter deposition techniques.

(1) ion source (2) sputter target (3) electron emitter for charge neutralization (4) substrate and (5) ion source to deliver ions to the substrate

Fig. 2.11 Schematic of ion beam sputtering system.

2.1.3 Magnetron sputtering

The ionizing efficiency may be increased very conveniently by increasing the path of the ionizing electrons, for example a transverse magnetic field normal to the electrical field. The magnetron target is based on the work carried out by Penning [64] in 1936. The concept was subsequently developed by other workers resulting in the sputter gun [65, 66] and cylindrical magnetron cathode [67] on the other hand, the planar magnetron which is perhaps the most widely used target assembly was not introduced until the early 1970's by Chapin [68], although the basic configuration was demonstrated by Keasaer and Pashkova [69]. The ions of course, experience the same Lorentz force as the electrons; however, due to the much higher mass, their motion is not as restricted. The Larmor radius of an electron in a magnetic field typical of a magnetron cathode is 1 - 3 mm, whereas that of the ions is at least an order of magnitude higher. Where the field lines are parallel to the cathode surface the motion of the ions is perpendicular to the target surface. Ions extracted from the plasma sheath, are accelerated across the cathode dark space (typically 3mm) and
strike the target resulting in removal or sputtering of the target material. In sputtering discharges, the sputtering rate depends directly on the ion flux, and this in turn depends on the density of ions in the plasma. The use of magnetic field is primarily to trap electrons close to the sputtering target, so as both to prevent them from escaping to the walls where they will cause ion loss by recombination but also to create ions by electron impact close to the sputtering target.

The interaction between the magnetic field $B$ and an electron with vector velocity, $V$ is given by

$$ F = eV \times B $$

where $F$ is the force which is in a direction orthogonal to both the magnetic field and electron velocity vectors as shown in Fig. 2.12. As a result, there is a strong tendency for the electron to travel in helical motion close to the target surface where both the magnetic field strength and the electron velocity are large. By this means of magnetic enhancement, ion flux can be increased to several tens of milliamps per square centimeter, with corresponding increase in deposition rates. This led to an increase in the electron path hence an increase in ionization efficiency. The radius of gyration is given by

$$ r = \frac{m_e v}{Be} $$

![Fig. 2.12 The influence of a magnetic field on electron motion (Chapman 1980)](image)

On the other hand, permanent magnets like barium and strontium ferrites, AlNiCo (aluminum, nickel and cobalt alloy) and rare earth samarium cobalt magnets have been widely used. The basic condition in choosing the magnets is that the transverse component of the magnetic field in front of the target is typically in the...
range of 200 - 500 Gauss, though the threshold magnetic field for achieving magnetron discharge is as low as 90 Gauss [70]. Higher magnetic field will result in lowering of the operating pressure. The high discharge current density is possible in a magnetron cathode leads to excessive heating of the target and hence a cooling system is necessary. The surface temperature of the target of 1 cm thickness would be 993 K if the power density was 10 W/cm² [71]. This provides an additional source of substrate heating and could have deleterious effects on the target. Limited water cooling of the target will eventually limit the power that can be dissipated and thus the sputtering rate can be obtained. Most of the ion energy that reaches the target is dissipated there as heat. Hence sufficient water cooling of the target is necessary to maintain the target at low temperatures. Otherwise, the possible adverse effects such as the target may be damage and a hot target will also cause the substrate heating through thermal radiation and out gassing will occur.

Most magnetron source operates in the pressure range from 1x10⁻³ mbar to 20 mbar and a cathode potential of 300 - 700 V. The sputtering rates are primarily determined by the ion current density at the target. The depositing rates are affected by the factors such as applied power, source to substrate distance, target material, partial pressure, sputtering pressure, substrate temperature etc. In magnetron sputtering, the following parameters influence the film properties by carefully adjusting these parameter, good quality films will be deposited. The parameters are the sputtering current, ultimate vacuum, gas mixture, substrate temperature and substrate bias voltage. The sputter current determines mainly the deposition process and hence the time which remains for the arriving particles during the growth process for either surface diffusion and agglomeration on existing growth centers or nucleation with other adatoms. The applied voltage determines the maximum energy, with which sputtered particles can escape from the target (reduced by the binding energy). Energies of the sputtered particles show a broad distribution with a maximum of the distribution between 1 - 10 eV. The applied voltage determines also the sputter yield.

The pressure in the sputter chamber determines the mean free path $\lambda$ of the sputtered material, which is inversely proportional to the pressure. Together with the target to substrate distance, the pressure controls the number of collision occurs for the particles on their way from target to substrate. This can influence the porosity of
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the films, which in turn influence the crystallinity and texture. Using a desirable gas mixture of oxygen / nitrogen and argon can control the stoichiometry of the deposited oxide / nitride films. The substrate temperature can have a strong impact on the growth behavior with respect to crystallinity or density of the films. It can be adjusted between room temperature and 773 K (for glass substrate). But even during sputtering without external heating the substrate temperature may rise considerably, especially during long sputtering times for the deposition of thick films.

Substrate bias voltage can be applied up to ±100V and even more negative bias voltage, which has the effect of accelerating electrons or ions towards the substrate or keeping them away. Usually substrate and target surface are parallel to each other. A variation of the deposition angle (that is the sputtering under oblique incidence) can be achieved by tilting the substrate. Thereby a new preferential direction for the film growth and potentially anisotropic films can be produced. The main features of magnetron sputtering are the high rate of sputtering due to the confinement of the plasma close to the target surface, sputtering can takes place at a low gas pressure due to the increased path length of electrons within the plasma and prevention of their escape, high rate of material removal from the target occurs when the magnetic field lines are parallel to the cathode surface and the target utilization in most of the magnetron targets is about 30%.

The planar magnetron cathode has many advantages over other target assemblies, particularly its simplicity and its suitability for ion line production systems and coating of large area planar substrates. A number of cathode geometries are shown in Fig 2.13. Some of the problems mentioned above could be solved when the sputtering is associated with a transverse magnetic field. It produces several modifications in the basic process. The required magnetic field can be provided with either the permanent magnets or electromagnets. The magnets are well matched with the target with proper design. This is because of the influence of the magnetic field on the target-generated secondary electrons. The generated secondary electrons are trapped in the magnetic field geometry and they do not bombard the substrate and tend to move in a cycloid path near the target obeying the Lorentz force relation and thus do not contribute to the substrate temperature and radiation damage. Such a process is called dc magnetron sputtering, which is advantageous in the deposition of thin films from metallic target (electrically conducting target) at low temperature substrates like
plastic and surface sensitive MOS devices. In dc magnetron sputtering, the ionization efficiency increases and it enhances the deposition rate. It is a potential process for industrial applications. Different types of magnetron sources like planar magnetron, cylindrical magnetron and conical magnetrons are developed depending on the need in specific applications.

2.1.4 Cathode geometry and electron / ion motion

The planar target in its simplest form is shown schematically in Fig. 2.14. It consists of the target material backed by permanent magnets that provide a toroidal confinement field with the field lines forming a closed tunnel on the target surface. The field strength is chosen to provide effective confinement for electrons while allowing heavier ions considerable freedom. The transverse field component is typically >100 Gauss. Secondary electrons emitted from the target during the sputtering process are accelerated across the cathode dark space towards the highly charged plasma sheath. Their path is modified by the E x B Lorentz force. One
component of their motion is a helical path about the magnetic field lines. The electrons traveling along these helical lines towards the centre of the target are reflected due to the higher density of field lines in this region and the repulsive electric field encountered. After reflection the electrons eventually reach the perimeter of the target where the field lines again intersect the surface. An anode

![Diagram of magnetron cathode](image)

Fig. 2.14 Two variations of the planar magnetron cathode. The confinement field is indicated by the curved lines

placed in this region effectively collects these electrons and prevents them from reaching the substrate. A second component of their motion is a drift from one field line to another resulting in a race track effect about the toroidal tunnel on the target surface. The combined motion gives an extended path length resulting in a large number of collisions of the electrons with gas atoms. Ideally, their energy is dissipated by these ionizing collisions before reaching the anode ring. Since not all field lines terminate on the cathode surface or the anode ring, some electrons may escape from the trap. These electrons can reach the substrate; however in general, their density is low. The net effect of this trap is an increase in plasma density close to the target, which in turn leads to higher deposition rates. The low density of electrons reaching the substrate also results in lower substrate temperatures.

2.2 Reactive sputtering

Reactive sputtering is a combination of the physical sputtering process and chemical reaction in a plasma environment. Reactive sputtering was developed in the 1950s by Westwood [72]. Reactive sputtering is commonly used for the deposition of oxide, nitride and carbide thin films. Reactive sputtering has proliferated, particularly
over the past few decades. It is used extensively by manufacturers of coated 
architectural glass roll or web coatings, coated cutting tools, optical coatings, 
decorative and functional coatings for plumbing and hardware items, microelectronic 
devices, surface acoustic wave devices and transparent conducting oxides etc.

In one sense all sputtering is reactive because there are always residual gases 
in the chamber that will react with the sputtered species. However in reality, reactive 
sputtering occurs when a gas is purposely added to the sputtering chamber to react 
with the sputtered material. Reactive gases like oxygen or nitrogen are introduced 
into the system along with the inert gas to deposit oxides or nitrides. In reactive 
sputtering, one important problem is that the metallic sputtering target may become 
oxidized by the reactive gas. The oxidation of the metallic sputtering target during 
reactive sputtering may occur by collision of oxygen species from the plasma with the 
target or by chemisorptions of oxygen followed by oxidation.

When a metal is sputtered in the presence of a reactive gas, the three possible 
locations at which reaction between sputtered atoms and reactive gas takes place at 
any or all of three locations, which are at the target, in the gas phase and on the 
substrate surface. When the reaction takes place at the target surface, an insulating 
film formed on the target would terminate the process of a dc discharge was 
employed, or would often slow it down in an rf discharge. Reaction in the gas phase 
often will lead to the further agglomeration or nucleation of the resulting molecules 
so that the material arrives at the substrate in large particles or powder, producing a 
finaile coating of limited utility. Normally the way of reaction is on the substrate 
surface. In order to accomplish this effectively, the process must be well controlled. 
The reaction during transport may not be possible due to momentum and energy 
conservation effects and as such the most probable location is near the substrate or the 
target. The phase of the compound film formed depends on both the percentage of the 
reactive gas in the sputtering environment and the reduce field $E^*$ defined as

$$E^* = \frac{\text{Cathode voltage}}{(\text{Target to substrate spacing} \times \text{Pressure})} \quad \text{(6)}$$

The significance of $E^*$ is that the energy of the negative ions originating at the 
cathode is supposed to be proportional to it and thereby strongly influence the re-
emission coefficient [73]. Therefore, $E^*$ is important in controlling the particular phase grown.

In reactive sputtering, the target may become an insulating one when the rate of sputtering is less than the rate at which the reactive gas atoms reach the target. This is often termed as the target poisoning and it leads to undesirable effects like, drastic drop in deposition rate and extinction of the glow discharge itself. However, with the advent of magnetron sputtering the situation has become quite different. Due to high deposition rate, the critical pressure of the reactive gas at which the target poisoning takes place can be high. The immediate consequence of this is that the decomposition of the deposited film can be varied.

2.2.1 Reactive magnetron sputtering system

A reactive magnetron sputtering system was developed in the laboratory for the deposition of $\text{Ta}_2\text{O}_5$ films. The photograph of the sputtering system is shown in Fig.2.15. It consists of a vacuum chamber (both ends open) made up of stainless steel with 290 mm diameter and 350 mm height. The magnetron target assembly is mounted to the top plate (using Teflon as electric insulation) such that the sputtering can be performed in sputter down mode. The schematic of the planar magnetron target assembly designed and constructed in the laboratory is shown in Fig.2.16. The magnetron has been designed in such a way that two permanent ring magnets made of samarium cobalt, one of 10 mm diameter and the other of 54 mm diameter were kept concentrically under the target plate and are always water cooled. The samarium cobalt magnets are coated with a thin layer of lacquer prior to fixing them inside the planar target to prevent corrosion of the magnets due to water circulation inside the target. The vacuum chamber is pumped using a diffusion pump (300 lit/sec), which was backed by a direct drive rotary pump (200 lit/min).

A liquid nitrogen trap was incorporated between the chamber and the diffusion pump to minimize the oil vapor contamination in the chamber. The system gives an ultimate pressure of about $3\times10^{-6}$ mbar. Pure argon was used as sputter gas and oxygen as reactive gas. Pure oxygen gas was admitted into the chamber through the needle valve and the required oxygen partial pressure was set and allowed to stabilize. Argon gas was then introduced and the required sputtering pressure was maintained. The flow rates of both argon and oxygen gases were controlled.
EXPERIMENTAL TECHNIQUES

Fig. 2.15 Experimental set up of the magnetron sputtering system

Fig. 2.16 Schematic of planar magnetron target assembly
individually by Tylan mass flow controllers (Model FC-260). A continuously variable dc power supply of 750 V and 3 A was used as a power source for preparation of Ta2O5 films by dc magnetron sputtering method. An Advanced Energy rf power supply (model no. 3155021-000 N) with variable power sources of 600 watt was used a rf power source for the deposition of Ta2O5 films in rf magnetron sputtering method. Before deposition of each film, the target was sputtered in pure argon atmosphere for 15 min to remove oxide layers if any on the surface of the target. The substrates were kept parallel to the target at a distance of 75 mm. A chromel-aluminum thermocouple placed in contact with the substrate surface was used to monitor the substrate temperature with the help of the temperature controller the required temperature of the substrate was maintained with an accuracy of ± 5 °C.

2.3 Preparation of experimental Ta2O5 films
Thin films of Ta2O5 were deposited on silicon and quartz substrates by sputtering of tantalum target under various oxygen partial pressures, substrate temperatures and substrate bias voltages using the dc and rf power modes. The deposition conditions maintained during the preparation of Ta2O5 films were, the oxygen partial pressure in the range 3x10^-5 - 8x10^-4 mbar, substrate temperature in the range 303 - 973 K, substrate bias voltage in the range from 0 to -200 V in order to study their influence on the physical properties. The films formed at room temperature were annealed in air for an hour. In order to study the dielectric properties of the tantalum oxide films, the MOS capacitor with the configuration of metal/oxide/semiconductor (Si/Ta2O5/Al) was fabricated. The schematic MOS configuration of Si/Ta2O5/Al is shown in Fig. 2.17. The Ta2O5 films were deposited on p-type silicon substrate by dc/rf magnetron sputtering and the top electrode ‘Al’ was deposited using Hind High Vacuum coating unit by vacuum evaporation. The vacuum coating system used for deposition of ‘Al’ is shown in Fig. 2.18.

2.4 Substrate cleaning
Substrate cleaning requirements usually involve removing surface contamination such as greasy particles, dust, metals etc. The cleaning process usually varies with the substrate being cleaned. Also a meticulously cleaned substrate is a
Fig. 2.17 Schematic MOS configuration

Fig. 2.18 Photograph of the vacuum evaporation system
prerequisite for producing thin films with repeatable properties. Therefore, procedural
cleaning is mandatory to obtain porous free films with good adhesion of the deposited
films. In general, the contaminants present on the substrate surface can be classified
in to two groups which are organic and inorganic. Organic contaminants can be easily
removed by emulsifying the substrate surface with washing solutions. However, a
direct mechanical approach is required for the removal of inorganic contaminants
particularly when they are in particle form. A number of procedures [1, 23] are
available for the substrate cleaning such as immersing in solvents, ultrasonic
cleaning, cleaning with solvents, cleaning by heating and irradiation, spray cleaning,
electrical discharge etc. Amongst, ultrasonic cleaning is one of the best methods. In
this method, an ultrasonic wave with high accelerating force separates the
contaminating particles that are stick to the substrate surface. Quartz and silicon
substrates were used in the present study.

The systematic procedure adopted for the cleaning of quartz substrates was
outlined in the following steps: Initially, the substrates were wiped with acetone and
cotton wool to remove the visible contamination such as air dust, the glass substrates
were cleaned at first by mild soap solution, then washed thoroughly in deionized
water and also in boiling water, the substrates were cleaned ultrasonically for 15
minutes in the stainless steel tank of the ultrasonic agitator containing
trichloroethylene, the substrates were then washed with distilled water, the substrates
were mounted in a specially designed holder and kept over a beaker that contains
isopropyl alcohol, the alcohol is heated so that the substrates will be cleaned by the
vapor degreasing and the substrates were then subjected to ultrasonic agitation in
double distilled water.

The systematic procedure adopted for the cleaning of silicon substrates was
outlined in the following steps: contaminants present in the surface of the silicon
wafers at the start of processing or accumulated during processing have to be
removed at specific processing steps in order to obtain high performance and high
reliability semiconductor devices and to prevent contamination of process equipment,
especially the high temperature oxidation.

The Si wafers were placed in a Teflon container. Insoluble organic
contaminants in the wafer can be removed by immersing the wafers in the organic
clean solution, which is maintained at 75 °C (5:1:1, H₂O : H₂O₂ : NH₄OH) for 10
sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

Fourier Transform Infrared (FTIR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. In this investigation, the chemical binding configuration of the films was analyzed with Fourier transform infrared spectroscopy (FTIR) using Nicolet (model 5700 FTIR) spectrometer (in the wavenumber range 400 - 4000 cm\(^{-1}\)). The photograph of the FTIR used to analyze the films is shown in Fig. 2.19. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies "encoded" into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams "interfering" with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured; all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the
Fig. 2.19 Photograph of FTIR (Nicolet model 5700 FTIR)
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measured interferogram signal can not be interpreted directly. A means of decoding the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

2.5.3 Composition analysis

The chemical composition of the deposited $\text{Ta}_2\text{O}_5$ films is an important characteristic which has direct influence on the properties of the films such as structural, electrical and optical properties. A small change in chemical composition from the desired concentration of elements led to drastic variations in the physical properties of thin films. Various analytical techniques are available for analysis of the chemical composition of the films such as Auger electron spectroscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry, energy dispersive analysis of X-rays, Rutherford back scattering Spectroscopy and neutron activation analysis.

In the present investigation the chemical composition of the experimental films was analyzed using X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy is also known as electron spectroscopy for chemical analysis is accomplished by irradiating a sample with monochromatic soft X-rays and analyzing the energy of the emitted electrons. XPS detects all elements with an atomic number ($Z$) between those of lithium ($Z = 3$) and lawrencium ($Z = 103$). This limitation means that it cannot detect hydrogen ($Z = 1$) and helium ($Z = 2$). Mg K$_\alpha$ X-rays (1253.6 eV) or Al K$_\alpha$ X-rays (1486.6 eV) are ordinarily used. The schematic representation of experimental setup of the XPS used to analyze the films in this investigation is shown in the Fig. 2.20. These photons have limited penetrating power in solid. They interact with atoms in the surface region causing electron emission as per the photoelectric effect. The emitted electrons have kinetic energies (KE) given by the relation [76]

$$KE = hv - BE - \phi_p$$  \hspace{1cm} (8)

where $hv$ is the energy of the incident X-ray photon, $BE$ the binding energy of the atomic orbital from which the electron originates, and $\phi_p$ the work function. The
Photo-Emitted Electrons (<1.5 kV) escape only from the very top surface (70 - 110Å) of the sample.

Focused Beam of X-rays (1.5 kV)

Samples are usually solid because XPS requires ultra-high vacuum (<10⁻⁷ torr)

Electron Energy Analyzer (0-1.5kV)
(measures kinetic energy of electrons)

Electron Detector (counts the electrons)

Fig. 2.20 Schematic representation XPS system
kinetic energy of the escaping photoelectron limits the depth from which it emerge, giving XPS as high surface sensitivity with sampling depth of a few nanometers. Photoelectrons are collected and analyzed by the instrument to produce a spectrum of emission intensity versus electron binding energy. Since each element has a unique set of binding energies, XPS can be used to identify the elements on the surface of the films. Also, peak areas at nominal binding energies can be used to quantify concentration of the elements. Small shifts in these binding energies (chemical shifts) provide powerful information about sample chemical states and short-range chemistry.

2.5.4 Structural analysis

The crystallographic properties of the thin films are extremely important and greatly influence the other physical properties such as atomic arrangement, electrical conductivity and carrier mobility and optical band gap etc. The structural studies of the experimental films were analyzed using X-ray diffraction. X-ray diffraction is the most widely used characterization technique for determination of crystallographic structure of the films. It gives information regarding the lattice parameters, crystal structure, orientation, defects, crystallite size and stresses if any present in the films. In this investigation, Siefert X-ray diffractometer (model 3003TT) with Cu K$_\alpha$ radiation source (wavelength, $\lambda = 0.15405$ nm) was used to study the crystallographic structure of the deposited films. The photograph of X-ray diffractometer is shown in Fig. 2.21. The X-ray source was scanned over the film in the $2\theta$ range of 10-80º. The X-ray generator was operated at 40 kV and 30 mA. From the XRD profiles the interplanar spacing ($d$), was calculated using the Bragg's relation [77],

$$2d \sin \theta = n\lambda$$

where $n$ is the order of the diffraction, $\lambda$ the wavelength of the X-ray source and $\theta$ the diffraction angle. The lattice planes (hkl) were identified (from the JCPDS data) and the lattice constants of the deposited films were determined using the relations [78],

For cubic structure,

$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \quad \text{[nm]}$$

66
Fig. 2.21 X-ray diffractometer (model Siefer 3003TT)
In the case of orthorhombic structure,

\[
d^2 = \frac{a^2b^2c^2}{h^2(b^2c^2)+k^2(a^2c^2)+l^2(a^2b^2)} \quad \text{[nm]} \quad \text{---(11)}
\]

For rhombohedral structure,

\[
d^2 = \frac{(h^2+k^2+l^2) \sin^2 \alpha + 2(hk+kl+lh)(\cos^2 \alpha - \cos \alpha)}{a^2(1-3\cos^2 \alpha + 2\cos^3 \alpha)} \quad \text{[nm]} \quad \text{---(12)}
\]

For hexagonal structure

\[
d^2 = \left[ \frac{4}{3} \right] \frac{(h^2 +hk + k^2)}{[a^2 + (l^2/c^2)]} \quad \text{[nm]} \quad \text{---(13)}
\]

The crystallite size (L) of the films was calculated from the X-ray diffraction peaks using the Debye - Scherrer's relation [76],

\[
L = \frac{k\lambda}{\beta \cos \theta} \quad \text{[nm]} \quad \text{---(14)}
\]

where k is a constant with a value about 0.89 for Cu target and \( \beta \) the full width at half maximum (FWHM) intensity of the peak measured in radians.

2.5.5 Surface morphology

The surface morphology and topography of the films was studied using atomic force microscopy. Atomic force microscope (AFM) is one of the powerful tool extensively used in industry and research laboratories for characterization of materials of any kind in connection with the study of surface morphology. Some of the applications of AFM include the high resolution examination of surface morphology, compositional mapping of heterogeneous samples and studies on the local mechanical, electrical, thermal and magnetic properties. The AFM provides true three dimensional surface profiles. Additionally, samples to be analyzed by an AFM do not require any special treatment which may destroy the sample. These measurements can be perform on scales from hundreds of microns down to nanometers using AFM hence of highly useful for the recent developments in nanoscience and technology.
In AFM, mechanical force interactions acting between a sharp probe and a sample are used for surface imaging. The probe, which represents a micromechanical cantilever with a sharp at one end, is brought into interaction with the sample surface. The interaction level between tip apex and the sample is determined through precise measurements of the cantilever displacements. An optical level detection, which had been originally suggested for gravimeters, has appeared for precise measurements of the cantilever deflections in most commercial AFM. A laser beam, which is deflected from the backside of the cantilever is directed to a four segment positional photo detector, which is divided into segments for measurements of normal and lateral deflections of the cantilever. To avoid parasitic interference at the cantilever, AFM based on a micro fabricated piezocantilever are used in which the cantilever itself provides not only the deflection sensing but also the actuation [79].

The surface imaging is realized by detecting the tip sample force in different locations while the probe is raster the sample surface with the help of a piezoelectric actuator. Main components of the atomic force microscopes are probes, optical detection system, piezoscanner and electronic for a management of scanning procedures and data acquisitions. In the microscope these components are assembled into a microscope stage, which must satisfy acoustic and electronic noise as well as small thermal scanners, which are applied for three dimensional movement of the sample are proved in AFM, are made of piezoelectric materials, which provide the precise positioning and ability to transport the objects on the micron range with subangstrom precision.

The experimental setup of atomic force microscope used in the present work is shown in Fig. 2.22. In the present investigation, Digital Instruments AFM Nanoscope III was used for obtaining the images of the grown films. The surface of the films is scanned over an area of 10 \( \mu m \times 10 \mu m \). The grain size and the surface root mean square roughness value of the samples are studied in order to get the morphological data.

2.5.6 Electrical characterization

2.5.6a Capacitance - voltage measurements

In the present work, capacitance-voltage characteristics of the capacitors with MOS configuration were measured using an automated HP 4275A LCR meter along
Fig 2.22 Experimental set up of atomic force microscope
Fig. 2.23 Capacitance - Voltage measurements set up
with a voltage source is shown in Fig. 2.23. Measurements were carried out for the capacitors at both forward and reverse sweep. Dielectric constant, flat band capacitance and flat band voltage, interface trap density of the capacitor were measured. Flat band voltage is equal to the work function difference between the gate metal and the semiconductor. The flat band capacitance equals to insulator (oxide) capacitance. For an ideal MOS structured capacitor, at zero applied bias, energy difference between the metal work function ($\Phi_m$) and the semiconductor ($\Phi_{sc}$) is zero, i.e., the work function difference ($\Phi_{ms}$) is zero. Therefore [80],

$$\Phi_{ms} = \Phi_m - \Phi_{sc} \quad \text{--- (15)}$$

where $\Phi_m$ is the workfunction of metal and $\Phi_{sc}$ the workfunction of semiconductor which can be achieved from the relations

$$\Phi_{ms} = \Phi_m - (\chi + E_g/2q - \Psi_r) = 0 \quad \text{for n-type semiconductor} \quad \text{--- (16)}$$

$$\Phi_{ms} = \Phi_m - (\chi + E_g/2q + \Psi_d) = 0 \quad \text{for p-type semiconductor} \quad \text{--- (17)}$$

where $\chi$ is the electron affinity of semiconductor, $\Psi_r$ the potential difference between the Fermi level $E_F$ and the intrinsic Fermi level $E$, and $\Psi_d$ the potential barrier between the metal and insulator. One can define the flat band voltage practically as the voltage corresponding to the flatband capacitance. Hence,

$$V_{FB} = \text{Voltage corresponding to } C_{FB}$$

$$C_{FB} = 1/(1/C_{ox} + L_D/q\varepsilon_a) \quad \text{--- (18)}$$

Here,

$$L_D = \frac{\varepsilon_a V}{qN_a} \quad \text{or} \quad \frac{\varepsilon_a kT/q}{q N_a} \quad \text{--- (19)}$$

for p-type semiconductors, when the -ve voltage ($V<0$) is applied to the metal plate, the top of the valance band been upward and is closer to the Fermi level. For an ideal MOS structure, no current flows, so the Fermi level remains constant in the semiconductor. Since the carrier density depends exponentially on the energy difference ($E_F-E_V$), this band bending causes an accumulation of majority charge carriers (holes) near the semiconductor surface. When a small +ve voltage ($V>0$) is applied, the bands bend downwards and the majority charge carriers are depleted.
+ve voltage is applied, the bands evermore downwards so that the intrinsic level E\textsubscript{i} at the surface crosses over the Fermi level E\textsubscript{F}. At this point the number of electrons (minority charge carriers) at the surface is larger than that of the holes, thus the surface is inverted, and this is called inversion.

2.5.6b dielectric properties

An important property of a dielectric material is its dielectric permittivity. A through knowledge of this parameter is essential for solving many problems in semiconductor physics and particularly in the electric field stimulated emission studies. Apart from this it leads to the analysis of some fundamental physical properties of the system like the presence of impurities, voids, structural defects, polarization mechanisms, relaxation mechanisms, etc. Most of the dielectrics are characterized by four factors namely the relative permittivity, loss tangent, dielectric strength and dielectric breakdown.

2.5.6c dielectric constant

According to Coulomb, the force of attraction and repulsion between the two charge carriers kept at a distance (d) in a medium of permittivity (\(\varepsilon\)) is,

\[
F = \frac{q_1 q_2}{4 \pi \varepsilon_0 \varepsilon d^2}
\]

where \(q_1\) and \(q_2\) are the charges of the two carriers and \(\varepsilon_0\) is the permittivity of free space \(8.85 \times 10^{-12} \text{ F/m}\). Consider a parallel plate capacitor of area \(A\), separated by a distance \(d\) in a medium of permittivity \(\varepsilon\). Let a potential \(V\) be applied to it and the charge carried by it be \(Q\). The electric field strength is \(\frac{V}{d}\) (volts per meter) then the permittivity of the medium \(\varepsilon\) is given by,

\[
\varepsilon = \frac{(Q/A)}{(V/d)} = C \frac{(d/A)}
\]

where \(C\) is the capacitance of dielectric, which is ratio of charge accumulated by the applied voltage and \(A\) the area of capacitor. The dielectric constant of a substance is purely an intrinsic property of the constituent ions.

\[
C = \varepsilon \varepsilon_0 \frac{(A/d)}
\]
2.5.6d Dielectric loss

The amount of power loss in a dielectric under the action of the voltage applied to it is commonly known as dielectric loss. When an alternating electric field (E) is applied to a dielectric the displacement vector (D) varies periodically with time. However D lags behind in phase relative to the field E, so that for example if

\[ E = E_0 \cos \omega t \]  

One have

\[ D = D_0 \cos (\omega t - \delta) = D_1 \cos \omega t + D_2 \sin \omega t \]  

Where \( \delta \) is the phase angle and

\[ D_1 = D_0 \cos \delta \text{ and } D_2 = D_0 \sin \delta \]  

For most of the dielectrics, \( \varepsilon D_0 \) is proportional to \( E_0 \) that is the ratio of \( \frac{D_2}{E_0} \) which is depend on frequency. To understand this situation, two frequency dependent dielectric constants \( \varepsilon' \) and \( \varepsilon''(\omega) \) are introduced which are given by,

\[ \varepsilon'(\omega) = \frac{[D_1/E_0]}{[D_0/E_0]} \cos \delta \text{ and } \varepsilon''(\omega) = \frac{[D_2/E_0]}{[D_0/E_0]} \sin \delta \]  

It is convenient to combine these two constants into a complex dielectric constant

\[ \varepsilon^* = \varepsilon' - j\varepsilon'' \]  

The relation between D and E both expressed as complex quantities, is then simply

\[ D = \varepsilon^* E_0 \ e^{j\omega t} \]  

From equation (20), \( \tan \delta \) can be obtained as,

\[ \tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \]  

2.5.6e Frequency dependent behavior of dielectric constant and dielectric loss in thin films

The dielectric constant \( \varepsilon \) and loss factor \( \tan \delta \) mainly depends on temperature and the frequency. Usually the dielectric constant decreases with increasing frequency. At very low frequencies, the dipoles are not accompanied by any loss of energy and hence \( \tan \delta \) is very low. At very high frequencies the dipoles are not able to follow the variations of the field, whereas the normal agitation is still present. The
capacitor element was assumed to comprise (i) an inherent capacity element \( c \) unaffected by frequency and temperature, (ii) a discrete resistance element \( R \) due to the dielectric film parallel with \( C \) and (iii) a series resistance \( r \) due to the lead lengths etc. It was assumed that while \( R \) would be affected by temperature due to the exponential factor in the relation,

\[
R = R_0 \exp \left( \frac{\Delta E}{kT} \right)
\]

the lead resistance \( r \) would be more or less of constant value. In general, \( R \) would be very much greater than \( r \). The series capacitance and loss factor \( \tan \delta \) were obtained as

\[
C = 1 + \left[ \frac{\omega^2 R C^2}{\omega^2 R C^2} \right] = (1 + D^2) C
\]

and

\[
\tan \delta = \left( \frac{1}{\omega RC} \right) + \left( \frac{r}{\omega RC} \right) + \omega RC = D \left( 1 + \frac{r}{R} \right) + \omega RC
\]

where

\[
D = \frac{1}{\omega RC}
\]

The loss minimum would be observed at frequency given by

\[
\omega_{\text{min}} = \left( \frac{1}{r RC^2} \right)^{\frac{1}{2}}
\]

where \( \omega R C >> r \) or \( r / R << 1 \) is true for all cases equation (26) reduces to

\[
\tan \delta = \frac{1}{\omega RC + \omega RC}
\]

when \( \omega \) is small \( \left( \frac{1}{\omega RC} \right) >> \omega RC \), then \( \tan \delta = \left( \frac{1}{\omega RC} \right) = D \) and when \( \omega \) is large \( \left( \frac{1}{\omega RC} \right) \) is generally \( \ll \omega RC \) and hence \( \tan \delta = \omega RC \).

The dielectric studies on \( \text{Ta}_2\text{O}_5 \) films are characterized by forming metal-oxide-semiconductor (MOS) structure. The capacitance and the dissipation factor of the respective films in the frequency range 100 Hz to 10 MHz at room temperature were measured using an automated Hewlett Packard digital multi frequency LCR...
Area of the capacitor is measured using a traveling microscope. The dielectric constant has been calculated from the measured values of the capacitance, capacitor area \(A\) and the dielectric film thickness \(d\) using the relation

\[ \varepsilon' = \frac{C d}{\varepsilon_0 A} \]  

and the loss factor \(\tan \delta\) is given by

\[ \varepsilon'' = \varepsilon' \tan \delta \]

Current-Voltage characteristics studies have been made in the present work by depositing \(Ta_2O_5\) film on p-type silicon substrates. Aluminum metal has been deposited on \(Ta_2O_5\) films using a mask grid to provide top electrode metal contact and also by through the capacitor as a back contact for Si to form a \(Al/ Ta_2O_5/Si\) capacitor. The current through the capacitor as a function of applied voltage is measured using an automated I-V analyzer. The experimental set up used to measure current-voltage characteristics is shown in the Fig. 2.24. The dc electrical conduction through the MOS structure is a complicated process and involves different conduction mechanisms. These mechanisms are hopping conduction, Schottky emission, Poole-Frenkel emission, Space charge limited conduction process and tunnel emission. In this present investigation the conduction mechanisms is mainly Poole-Frenkel emission.

2.5.6f Poole-Frenkel effect

The physical basis for the occurrence of Poole-Frenkel effect is the lowering of the Coulombic potential barrier surrounding a localized charge under the influence of an external electric field [81]. This is otherwise, the bulk analogue of the Schottky effect at the interfacial barrier. If the Poole-Frenkel (PF) is assumed, the current through the dielectric is given by,

\[ J_c = C_t E \exp\left(-q\left[\frac{\Phi - (qE/\varepsilon_0 k_f)^{1/2})}{kT}\right]\right) \]  

where \(J_c\) is the current density, \(C_t\) the trap density related constant, \(E\) the electric field, \(q\) the charge of the electron, \(\Phi\) the barrier height, \(\varepsilon_0\) the permittivity of the free space, \(k_f\) the dynamic dielectric constant, \(k\) the Boltzmann constant and \(T\) the absolute temperature. The potential energy of the columnic field in Poole-Frenkel effect is four
Fig. 2.24 Measurement of I-V characteristics

Fig. 2.24a Jig used for the measurement of I-V and C-V characteristics
times that of due to image force and hence the Poole-Frenkel attenuation of a
coulombic barrier is twice that of due to the Schottky effect at neutral barrier.

2.5.6g Schottky emission

The leakage current governed by the Schottky mechanism is described by
Richard-Dushman equation,

\[
J = A T^2 \exp \left[ \frac{1}{kT} \left( \frac{q^2 E}{4 \pi \epsilon_0 k T} \right)^{1/2} \right]
\]

where \( A = C_{RD} \exp (-\Phi_b / kT) \)

The Schottky barrier height \( \Phi_b \) is extracted from the pre exponential constant in the
equation; Richardson constant \( C_{RD} = 120 \text{ Acm}^2 \text{K}^{-2} \) for free electron approximation.

Richardson-Schottky conductivity is electrode-limited. Although the functional
dependence of the conductivity upon field strength is the same for the Schottky and
the Poole-Frenkel mechanisms, one can differentiate quite readily between the two
types of conductivity from their different rates of change of conductivity with field
strength, viz., a plot of \( \ln \sigma \) versus \( E^{1/2}/kT \) results in a straight line of slope \( \beta_s \) or \( \beta_{PF} \).

These experimentally determined slopes can be compared with the theoretical \( \beta_s \) and
\( \beta_{PF} \), which can be calculated quite accurately provided that the high frequency
dielectric constant for the material is known. Alternatively, knowing that the
conductivity is either bulk-limited or electrode limited, one can calculate a value for
the high-frequency dielectric constant of the material by equating the experimentally
determined value for \( \beta \) to its appropriate theoretical equation.

2.6 Optical characterization

In order to determine the optical properties of \( \text{Ta}_2\text{O}_5 \) films such as optical
absorption coefficient, energy band gap, refractive index and extinction coefficient.
In the present investigation, the spectral transmittance of the experimental films was
recorded as a function of wavelength in the wavelength range of 300 - 2500 nm using
Hitachi U: 3400 UV-Vis-NIR double beam spectrophotometer. The photograph of
the spectrophotometer is shown in Fig.2.25. It is a computer controlled instrument
with an accuracy of wavelength \( \pm 0.2 \text{ nm} \) in UV-visible region and \( \pm 1 \text{ nm} \) in the near
infrared (NIR) region. Deuterium (D) and iodine tungsten (W) lamps were used as
the sources of light in the UV-Vis region and NIR region respectively. The block
Fig. 2.25 Photograph of the Hitachi U: 3400 spectrophotometer
diagram of the optical system of the Hitachi U: 3400 spectrophotometer is shown in Fig. 2.25. The light coming from two sources is reflected by mirrors and then passed through the monochromator and prism for the dispersion of light (spread into spectrum). Then a particular wavelength based on the requirement from the dispersed light was selected and passed it through the rotating mirrors, which directs the light beam alternatively through the sample and reference. These two light beams converge on the detector. The relative intensities of the two beams that strike the detector provide a measure of the amount of light absorbed or transmitted by the sample. The measured optical absorption and / or transmittance of the given sample is directly displayed on the monitor of the spectrophotometer as a function of wavelength.

This spectrum is recorded using a plotter, which is attached to the instrument. The Optical absorption coefficient ($\alpha$), which is the relative rate of decrease in light intensity along its path of propagation, was evaluated from the optical transmittance and near normal specular reflectance data using the relation,

$$\alpha = -(1/l) \ln \left[ T/(1-R)^2 \right]$$

[cm$^{-1}$] --- (39)

The optical transitions between the valance and conduction bands of a material can be understood by studying the dependence of $\alpha$ on photon energy (hv). For various types of optical transitions, the absorption coefficient obeys the relation [82],

$$\alpha hv = A (hv - Eg)^x$$

--- (40)

where $A$ is a constant, Eg the optical band gap and $x$ a constant. The value of $x$ depends upon the type of transition that occurs between the parabolic bands of the sample.

If

- $x = 1/2$ for direct allowed transition,
- $x = 3/2$ for direct forbidden transition,
- $x = 2$ for indirect allowed transition and
- $x = 4$ for indirect forbidden transition.

The optical band gap of the sample is determined by extrapolating the linear portion of the $(\alpha \, hv)^x$ versus photon energy (hv) plot onto the energy axis.
The refractive index $n(\lambda)$ of the films were calculated using the Swanepoel's envelope method [83] from the interference of optical transmittance spectra. The optical transmittance maxima $T_M(\lambda)$ and minima $T_m(\lambda)$ at various wavelengths were noted from the envelope to determine refractive index. The refractive index of the films was determined using the relation,

$$n(\lambda) = \left[ N + \left( N^2 - n_e^2 n_i^2 \right)^{1/2} \right]^{1/2} \quad ----(41)$$

where $N = (2n_e n_i) \left( \frac{T_m - T_M}{T_M T_m} \right) + \left( \frac{n_e^2 + n_i^2}{2} \right)$

The above experimental techniques were effectively employed for the preparation and characterization of $\text{Ta}_2\text{O}_5$ films.
References


