# Study of high k dielectric material -Growth and Characterizations of Zirconium Oxide nanoparticles

M.Sc. Thesis By Tarun Indoriya



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# Study of high k dielectric material -Growth and Characterizations of Zirconium Oxide nanoparticles

## A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree

of

Master of science

By

**Tarun Indoriya** 

#### **INDIAN INSTITUTE OF TECHNOLOGY INDORE**



#### INDIAN INSTITUTE OF TECHNOLOGY INDORE

**CANDIDATE'S-DECLARATION** 

I hereby certify that the work which is being presented in the thesis entitled "study of high k dielectric material- Growth and characterizations of zirconium oxide nanoparticles". In the partial

fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DEPARTMENT OF PHYSICS, Indian Institute of Technology, is an authentic record of my work carried out during the period from August 2022 to June 2023 under the supervision of Prof. Sudeshna Chattopadhyay, Professor, Department of Physics IIT INDORE. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with the date

#### TARUN INDORIYA

This is to certify that the above statement made by the candidate is correct to the best of my /our knowledge.

Sune 7. 2023

Signature of the Supervisor of

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My Parents

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#### **Chapter 1**

## Introduction

#### **1.1 Motivation**

We live in a world filled with gadgets and we certainly can't imagine our lives without them. The invention of gadgets like computers, cellphones, Tabs, Televisions has become possible due to discovery of semiconductors and evolution of electronics. The innovation of mini circuit components like transistor, capacitor, Diode, resistor and inductor able us to fit all the complicated circuits on a tiny Silicon chip. Every single gadget mentioned above consist these chips and components of electronics.

Apart from Semiconductors, Another important type of materials needed in these components are **Dielectrics**. These are essentially insulating materials and are widely used in almost every type of electric component like capacitors, transformer, high voltage cables, solar cells and circuit boards due to their electric properties.

They can be also be used in energy storage by applying voltage across the material. This is usually done with capacitor. In capacitor, dielectrics are used as an insulating layer between the two conductive plates, which allows for the storage of charge. Another common application of dielectrics is in transformers, which are used to change the voltage of alternating current electricity. Dielectric are used as the insulating materials in transformers to prevent current from flowing between the coils, which could have cause a short circuit. They are used in in printed circuit boards, [1] here they are used as an insulating layer between conductive traces.

Apart from their electric properties, dielectrics are also have other useful characteristics like high thermal resistance and chemical stability. These properties make them perfect for use in tough surroundings like high temperature application or in contact with corrosive chemicals. Overall, dielectrics are essential materials in numerous electrical and electronic application, providing reliable and efficient insulation for a wide range of devices and systems. Its important to study and analyze these materials and enhancing their properties by experiments for advancing the electronic components and helping in the development of next generation of these devices. In most of devices, dielectric material basically acts like a capacitor. To store charge hence energy. Like in metal oxide field effect transistor or MOSFET, it is used as an insulating layer which prevent the leakage current and also act as charge storage. Due to the mechanism of MOSFET if we want to increase the performance of it, we need to increase the capacitance [2]. Increasing the dielectric constant of the material is one of the way to increase the capacitance. As we will further see, that is the only effective way to increase the capacitance. For that reason, it become important to study about materials with high dielectric constant. Before we goes into the details of their specific use and properties in electronics, we have to understand the physics of the dielectric materials.

#### **1.2 Working of Dielectric**

The dielectric behavior is related to the polarization of the material, which is the separation of electric centers of positive and negative charge. The reason of this separation is the presence of an external electric field. When this field is applied, it exert electric force on the both negative and positive center in opposite. Due to this, electrons are displaced from their equilibrium position. This displacement creates a dipole moment, which results in a polarization of the material. The degree of polarization depends on the strength of the electric field, the dielectric constant of the material, temperature of material, the polarization can be either permanent or temporary. We can see this in mathematic form below.

Dipole moment of a system with two equal and opposite charge with distance d.

$$\mathbf{P} = \mathbf{q}.\mathbf{d} \tag{1}$$

This dipole moment is proportional to the applied electric field

$$\mathbf{P}=\boldsymbol{\alpha}.\mathbf{E}$$

$$\mathbf{P}=\mathbf{E}_{0},\boldsymbol{\chi}.\mathbf{E}$$
(3)

Here  $e_0$  is the permittivity of free space.

 $\chi$  is the susceptibility of the material.

The dielectric constant is

Thus, we see that the dielectric constant depends on the susceptibility of the material. Which is nothing but a constant which have the information of the dipole moment, orientation of bonds etc.

### **Chapter 2**

## **Theoretical and Experimental Background**

#### 2.1 Moore's law and problem stated

As the requirements for the more computational capability is rising by time, the circuits on the Silicon chips are becoming more and more complex to represent more advanced functions. Now, to fit those complex and integrated circuits into a smaller and smaller area, we need more and smaller electrical components year by year. In 1965, Gordon Moore made an observation that the number of transistors in a dense integrated circuit doubles about every two years. This is called Moore's law. [3]

Now, this contraction in size of electric components creates a problem for them. We can understand that by taking the example of **Metal oxide field effect Transistor** or MOSFET. In following figure, we can see the schematic diagram of MOSFET.



Fig. 1: Schematic diagram of MOSFET

Here we can see a thin layer of metal oxide between conductor and semiconductor. This layer has some very important functions like, preventing the leakage current due to its insulating properties and with that, it also works as a charge collector because we can see that the conductor, metal oxide and the semiconductor surface makes a capacitor altogether. This capacitor collects charge on its surface and block the way for electrons to flow from one terminal to other whenever the capacitor is given a voltage across itself. Hence the function of MOSFET as an electronic switch is carried by this capacitor. The metal oxide works as a dielectric between the plates of capacitor.

Now, as we discussed above, the shrinking size of these components creates a problem, that's because when the thickness of dielectric layer reaches to the order of angstrom, the quantum effects comes into consideration. As we seen, the dielectric layer works as an insulator to prevent the leakage current. But after a certain limit, due to the effect **Quantum Tunneling** the electrons can just pass through the insulating layer even though they doesn't have enough energy to cross the barrier.

In that situation, the insulating layer will no longer prevent the leakage current and the transistor will be ruined. This means that we can no longer reduce the size of the transistor or capacitor. Now, when we look at the capacitance of a parallel plate capacitor

$$C = (\mathcal{E}_r \cdot \mathcal{E}_0 A)/d \tag{5}$$

In order to make a better functioning transistor, we need to increase the capacitance to make it a better charge collector which will work as a better switch. To increase the capacitance, there are 3 ways. One, increase the area of capacitor. Two, increase the dielectric constant of the material. Three, decrease the layer thickness of dielectric material. [4]

Out of these three options, only second option of increasing the dielectric constant actually remains because we can't increase the area if we want smaller and smaller transistors, also we can't decrease the thickness too much due to pre explained quantum tunneling. So the only way we can get the job done is by increasing the dielectric constant.

Currently, Silicon dioxide is used mostly as a gate dielectric material due to its various properties. The high dielectric strength of SiO<sub>2</sub> ensures reliable operation even at high electric fields [5]. Furthermore, Silicon dioxide exhibits excellent thermal and chemical stability, which makes it resistant to degradation during device fabrication processes and device operation. These desirable properties have made Silicon dioxide the predominant choice for gate dielectric applications, enabling the advancement of numerous electronic devices and integrated circuits.

#### 2.2 The required conditions.

We need materials with high dielectric constant or say electric permittivity to fulfill the needs as described in chapter 2. But the high permittivity is not the only factor one need to consider, for there are serval important aspects which plays an integral role in this situation. For example, to act like an insulator to prevent the leakage current, the material must have a high energy band gap. In addition to that, we want our dielectric to be thermally stable. Thus there are various factor and qualities we need to discuss before we start looking our search for dielectric material.

Following are the basic requirements

#### 1. Permittivity and barrier height.

The most obvious requirement is the permittivity. It should be more than Silicon dioxide. The permittivity of a material depends on its polarizability which depends on the electronic and ionic dipole moment. Generally large ions exhibit more response to external electric field due to more number of electrons. The following figure shows the variation of the effect of both electronic and ionic dipole.



Fig. 2: The variation of polarizability with both electronic and ionic dipole [6]

Also, the band gap is actually decrease with the increasing size in a particular group of the periodic table. One explanation [7] of this phenomenon can be attributed to the band theory.in the following table, we can see the permittivity and band gap of the various metal oxides.

Material	Dielectric Constant ( $\kappa$ )	Band Gap $E_G$ (eV)	$\Delta E_C$ (eV) to Si	Crystal Structure(s)
SiO <sub>2</sub>	3.9	8.9	3.2	Amorphous
$Si_3N_4$	7	5.1	2	Amorphous
$Al_2O_3$	9	8.7	$2.1^{a}$	Amorphous
$Y_2O_3$	15	5.6	$2.3^{b}$	Cubic
$ZrO_2$	25	5.8	$1.2^{a}$	Mono., tetrag., cubic
$HfO_2$	25	5.7	$1.5^{b}$	Mono., tetrag., cubic
$La_2O_3$	30	4.3	$2.3^{b}$	Hexagonal, cubic
$Ta_2O_5$	26	4.5	$0.5^{a}$	Orthorhombic
TiO <sub>2</sub>	80	3.5	1.2	Tetrag. (rutile, anatase)

Table 1: dielectric constants and band gap of various metal oxides [8] Comparison of Relevant Properties for Some High- $\kappa$  Candidates

This Table shows, that ZrO2, HfO2 and La2O3 offer relatively high values for both  $\kappa$  and *EG*. Most of the high- $\kappa$  metal oxides listed above crystallize at relatively low temperature (T ~ 500 – 600°C). An exception is Al2O3 where crystallization in thin films is observed at T ~ 800°C [9]. in various new dielectric metal oxides, the polarizability of metal oxygen bond which is ionic, cause increment of permittivity. Bonds which are much polarized are weak relative to the less polarizable Si O bonds inside SiO2. When we talk about mobility, it is found that due to a scattering mechanism due to polarization frequency, pure metal-oxide systems, like ZrO2 and HfO2, suffer degradation [10], and materials that deals in Si O bonds, like silicates have better mobility. It is also observed that the presence of a thin SiO2 interfacial layer between the Si substrate and the high- $\kappa$  dielectric can increase the resultant mobility by reducing this effect, although the maximum attainable effective mobility is still less that for the ideal SiO2/Si system.

#### 2. Thermodynamic stability

The most important factor in choosing the right material is the thermodynamic stability of its interface with Silicon. Most of the metal oxides reacts with Silicon and makes an unwanted layer. This layer works as a separate capacitor connected in series with the dielectric material. As we know, if two capacitors are connected in series then the overall capacitance reduces. That's why we need to select materials which have minimum reaction with Silicon and we have to use some reaction barriers which help in preventing the formation of interfacial layer.

It is proved that [11] under equilibrium conditions, Zirconium dioxide remains stable under contact with Silicon up to the temperature of 950 degree Celsius. This stability can be understand by the phase diagrams of these materials. Overall it is an important aspect to look when we are selecting the material for these kind of application.

Apart from these two major factors, there are some other factors also like **interface quality**, **film morphology**, **process compatibility** and **reliability** which should one consider while considering any material.

#### 2.3 Alternate dielectric materials

As per the factors discussed above, there are some very good alternate dielectric materials to consider. **Zirconium dioxide**, **Hafnium dioxide**, **Aluminum oxide**, **Titanium oxide** [12] are the frontrunners for this selection. These all materials have very high dielectric constant, high band gap in comparison to the Silicon dioxide. They have more or less stable interface or in some way treatable interface with the Silicon substrate. These materials can be deposited by various technics like spin coating, atomic layer deposition, magnetron sputtering etc. we used Zirconia due to it slight advantage of mobility and high band gap. We made nanoparticles of Zirconium dioxide by sol gel method because nanoparticles tends to have more band gap then bulk and as we have discussed, this is a huge aspect to consider.

#### **Chapter 3**

## **Properties and methodology**

## 3.1 properties of Zirconium dioxide

Zirconium dioxide, commonly known as Zirconia, is a versatile ceramic material that has gained significant attention in various scientific application. It exhibits exceptional physical and chemical properties, making it a highly desirable material in many fields. It possesses high melting and boiling points, excellent thermal stability, and remarkable resistance to corrosion, which make it suitable for application requiring extreme conditions. Additionally, Zirconia exhibits a unique combination of high mechanical strength and toughness, making it an ideal candidate for structural and load bearing applications. [13]

Zirconium dioxide finds widespread applications across multiple industries. In the field of materials science, Zirconia is extensively used as a ceramic material in manufacturing cutting tools, engine components, and wear- resistance coating. Moreover, Zirconia plays a crucial role in the field of solid oxide fuel cells and in the application as high dielectrics in the electronics.

As of structure, Zirconium dioxide can exist in three distinct crystal structures; monoclinic, tetragonal, and cubic. At room temperature, pure Zirconia predominantly adopts the monoclinic phase, known as baddeleyite. In this form, the zirconium and oxygen atoms are arranged in three-dimensional lattice, with each zirconium atom surrounded by eight oxygen atoms. The arrangement of these atoms forms distorted octahedral coordination.

Temperature plays a crucial role in the structural stability of Zirconium dioxide. As the temperature increases, Zirconia undergoes phase transformation, resulting in changes to its crystal structure. At approximately 1170 degree Celsius, Zirconia transition from the monoclinic phase to the tetragonal phase, also known as the high temperature cubic phase or the fluorite structure, exhibits a highly symmetrical arrangement of zirconium and oxygen atoms.[14] The cubic phase of Zirconia is of particular interest due to its excellent mechanical and electrical properties, making it valuable for numerous application. In following figure, we can see the three crystal structures of Zirconia.



Fig. 3: Three different crystal phases of Zirconium dioxide [15]

Apart from that, if we look at thermal and mechanic properties of Zirconia, here are some key properties.

**Melting point:** the melting point of Zirconia is approximately 2715 degree Celsius. This high melting point indicates the materials exceptional thermal stability and resistance to high temperatures.

**Boiling point:** Zirconium dioxide has a relatively high boiling point of around 4300 degrees Celsius. This high boiling point further emphasizes its ability to withstand extreme heat conditions.

**Density:** the density of Zirconia is around 5.89 grams per cubic centimeter. This relativity high density contributes to its excellent mechanical strength and hardness. It is the hardest material after diamond.



Fig 4: Zirconia as a false tooth due to its incredible hardness

**Bandgap**: Zirconium dioxide in an insulating material, meaning it has a relatively large band gap. The band gap is the energy range in which electrons are not allowed to exist, leading to the insulating behavior. The band gap of Zirconia varies depending on its crystal structure. The monoclinic phase typically exhibits a band gap of around 5.6 to 6.0 electron volt (eV), while the tetragonal and cubic phases have slightly smaller band gaps of approximately 5.0 to 5.2 eV. [16]

**Electrical conductivity:** Zirconium dioxide is generally consider an insulator, as its band gap prevents the flow of electron in its pure form. However, when Zirconia is doped with certain electrons in its pure form. However, when Zirconia is doped with certain elements, such as yttrium, it can exhibit ionic conductivity at elevated temperature, especially in the cubic phase.

Due to these properties Zirconium dioxide is a near perfect material for proceeding as a gate dielectric.

## 3.2 Synthesis of Zirconium dioxide

The synthesis of Zirconium dioxide can be achieved through several methods, such as the precipitation, hydrothermal, sol-gel, and vapor deposition techniques. Each method offers different advantages in terms of purity, particle size control, and scalability. These synthesis routes enable the production of Zirconia in various forms, including powders, films, fibers, and bulk materials, tailored to specific applications.

The sol gel methods are generally used to prepare metal oxides and is efficient due to easy process and ability to control the purity, homogeneity and physical characteristics at low temperature [17].

We made Zirconium dioxide by sol gel method by using Zirconium (IV) proposide  $(Zr(OC_3H_7)_4)$  as a precursor and by drying in oven before hydrolysis [18].

Seventy weight percent of Zirconium (IV) proposide which is diluted by adding 1-propanol. 17.7g Zr-P mixed with 41.3g 1-propanol. And then hydrolyzed by drop by drop solution of aqueous ammonia under continuous stirring by a magnetic stirrer till one hour. Then the resulting gel was dried in an oven at  $110^{\circ}$  C till 12 hours then calcined at  $500^{\circ}$  C till 4 hours. We can understand the process by following figure.



Fig. 5: Flow chart of preparation method

As we can see, this process of making Zirconium dioxide nanoparticles is very simple and it produces Zirconia particles of the order of nanometers.

As of the chemical reactions of this process, we can see the following way in which these reactions.



#### **3.3** Characterization Technique

#### 3.3.1 X-Ray Diffraction Technique

The X-Ray diffraction technique was discovered in 1912 by Max von Laue and W. L. Bragg and his father W. H. Bragg. It is a powerful technique used to study the structure of crystalline materials. It is based on the principle that when X-rays pass through a crystal, they interact with the electrons in the atoms of the crystal lattice and are diffracted, or scattered, in different directions [19]. We can also get information like lattice parameters, crystallite size, spacing between two crystal planes and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects [20] etc. by using XRD.



Fig. 6: Instrumentation of X-Ray Diffraction.[21]

In a cathode ray tube, X-rays are generated by heating a filament to produce electrons, applying voltage in such a way that accelerating electrons toward a target, and then bombards the target material. X-ray spectra are produced when accelerating electrons have enough energy to knock off the inner shell electrons of the target material. These spectra have a large number of components, the most common are K $\alpha$  and K $\beta$ , and are filtered for generating monochromatic radiation. This radiation is collimated and targeted to the sample. The atomic dimension of the sample is nearly equal to the X-Ray therefore radiation may interfere constructively or destructively producing a diffraction pattern in a particular direction. Bragg's law gives a simple model for explaining the condition required for diffraction. This law establishes a relation between the lattice spacing and diffraction angle in a crystalline sample and the wavelength of radiation.

where

 $n\lambda = 2d \sin \theta$ (6) n = integer(1, 2, 3, ....) $\lambda$  = wavelength d = spacing between plans  $\theta = Bragg's angle.$ Diffracted Incident  $n\lambda = 2d\sin\theta$ beam beam θ θ

d

Fig. 7: Bragg's Law reflection. The diffracted X-rays exhibit constructive interference when the path difference between first and second ray are integer number of wavelengths ( $\lambda$ ).

#### 3.3.2 Raman Spectroscopy

The Raman effect was discovered by Indian physicist sir Chandrasekhara Venkata Raman. Sir Raman used sunlight as the source, a telescope as a collector, and the detector as his eye. Raman Spectroscopy is a non-destructive chemical examination method that uses scattered light to measure a sample's vibrational energy modes. Raman spectroscopy gives detailed information on chemical structure, molecular interactions, crystallinity, strain, phase and polymorphy, and interatomic bond strength [22]. It is based on the interaction of electromagnetic radiation with chemical bonds in a material.

A commercially available Raman Spectrometer consists of three primary components which are the excitation source (which is a continuous wave laser), a sampling apparatus, and a detector.



Fig. 8: Instrumentation of Raman Spectroscopy

The Raman effect is based on the change in molecular polarizability. when the electric vector of EM radiation interacts with the sample, then electric dipole moment induces [23]. A molecule absorbs a photon with frequency (f), gets excited to a higher state and the excited molecule returns to the same state (emits light with the same frequency). this type of interaction is called elastic scattering or Rayleigh scattering, which is most probable. If the molecule does not return to the same basic state, then there will be an exchange of energy take palace between the molecule and scattered light. This type of interaction is called inelastic scattering or the Raman effect. Raman scattering is a very rare case (it happens once in million). After the interaction, if the frequency of the scattered photon is lower than the incident photon is called Anti Stokes line shown in the figure, change in photon frequency is called Raman shift [24]. Raman spectra are plotted between the radiation intensity and Raman shift, and by using group theory can determine the active Raman modes under the selection rule.



Fig. 9: Raman and Rayleigh scattering [25].

#### **3.3.3 UV visible spectroscopy**

UV-Visible spectroscopy is an analytical technique used to measure the number of distinct wavelengths of UV or visible light that are absorbed or transmitted by a sample relative to a reference or blank sample. The amount of energy required to promote electrons to higher energy states varies depending on the type of bonding environment in which they are present. Therefore, different substances absorb light at different wavelengths. By identifying the specific wavelengths that correspond to maximum absorbance, UV-Vis spectroscopy can be used to examine or identify various substances.

The spectrophotometer consists of a light source, a diffraction grating in a monochromator, and a detector. The light source comprises a deuterium arc lamp for the UV region and a tungsten lamp for the visible region. The monochromator scans through each wavelength so that its intensity can be measured as a function of wavelength. The spectrophotometer is a double-beam instrument that splits the light into two beams before it reaches the sample. One beam is used as a reference, while the other passes through the sample. The detector output is a plot of intensity versus wavelength that contains information about the sample. Photomultiplier tubes, photodiodes, or charged coupled devices are typically used as detectors. In following figure, we can see the schematic of UV visible spectroscopy [26].



Fig. 10: Schematic of UV visible spectroscopy

UV-Vis spectroscopy is based on the Beer-Lambert law [27], which states that the light absorbance of a given material is directly related to the sample concentration and path length. A UV-Vis spectrophotometer records the degree of absorption and the absorption peak for each wavelength. The resulting spectrum is a graph of absorbance versus wavelength. UV-Vis spectroscopy is useful

in calculating the bandgap and size of nanoparticles. The absorption coefficient can be calculated from the Beer-Lambert law. The bandgap can be determined from the absorption spectra using the equation [28]

$$\alpha(\mathbf{v})\mathbf{h}\mathbf{v} = \mathbf{A}(\mathbf{h}\mathbf{v} - \mathbf{E} \mathbf{g})^{1/n}$$
(7)

Where,

 $\alpha$  - absorption coefficient

hv is the energy of photon

E<sub>e</sub> energy band gap and value of n depends on the nature of transition.

The intercept between the linear part of the fit and the x-axis gives the value of the bandgap energy of the material. UV-Visible spectroscopy is an analytical technique used to measure the number of distinct wavelengths of UV or visible light that are absorbed or transmitted by a sample relative to a reference or blank sample. The amount of energy required to promote electrons to higher energy states varies depending on the type of bonding environment in which they are present. Therefore, different substances absorb light at different wavelengths. By identifying the specific wavelengths that correspond to maximum absorbance, UV-Vis spectroscopy can be used to examine or identify various substances.

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#### **3.3.4 Impedance spectroscopy**

Impedance spectroscopy is a powerful analytical technique used to measure the impedance of a sample as a function of frequency. The technique has found applications in various fields, including material science, electrochemistry, and biomedicine. In impedance spectroscopy, a small AC voltage is applied to a sample, and the resulting current response is measured. The ratio of the voltage to the current gives the impedance of the sample. Impedance is a complex quantity that has both magnitude and phase components [29].

The impedance of a sample can be expressed as Z = R + jX, where R is the resistance, X is the reactance, and j is the imaginary unit. The reactance can further be divided into two components:  $X = X_L - X_C$ , where  $X_C$  is the capacitive reactance and  $X_L$  is the inductive reactance. The capacitive reactance arises from the sample's ability to store charge, while the inductive reactance arises from the sample's ability to store energy in a magnetic field.

The impedance of a sample can be measured using a variety of experimental setups, including a two-electrode cell, a three-electrode cell, or a four-electrode cell. In a two-electrode cell, the sample is sandwiched between two metal electrodes, and a small AC voltage is applied between the two electrodes. The resulting current response is measured, and the impedance is calculated. In a three-electrode cell, a reference electrode is used to measure the potential of the sample relative to a reference electrode. In a four-electrode cell, two electrodes are used to apply the AC voltage, and two electrodes are used to measure the resulting current response. The use of four electrodes helps to eliminate errors due to the resistance of the electrode-electrolyte interface.

The impedance of a sample can be analyzed using equivalent circuit models. Equivalent circuits are electrical networks that consist of resistors, capacitors, and inductors. The circuit elements represent different processes occurring in the sample, such as charge transfer, diffusion, and

capacitance. The equivalent circuit can be fitted to the experimental impedance data to extract information about the sample, such as its capacitance, resistance, and diffusion coefficient.

In summary, impedance spectroscopy is a powerful analytical technique used to measure the impedance of a sample as a function of frequency. The technique involves applying a small AC voltage to a sample and measuring the resulting current response. The impedance of the sample is calculated as the ratio of the voltage to the current and has both magnitude and phase components. The impedance can be analyzed using equivalent circuit models, which can provide information about the sample's capacitance, resistance, and diffusion coefficient.

### **Chapter 4**

## **Results and discussions**

### 4.1 X Ray Diffraction

To analyze the crystal structure and crystalline size, XRD studies were performed on the Zirconium dioxide sample. In the figure, we can see the XRD peaks.

These sharp peaks show the formation of crystal phase.



Fig. 11: XRD pattern of Zirconium dioxide nanoparticle

The pattern shows the angels corresponding to the peaks at  $2\theta$  at  $30.49^{\circ}$ ,  $35.03^{\circ}$ ,  $35.58^{\circ}$ ,  $50.56^{\circ}$ ,  $59.74^{\circ}$ ,  $60.41^{\circ}$ ,  $63.24^{\circ}$ ,  $64.50^{\circ}$ ,  $73.26^{\circ}$  and  $74.26^{\circ}$  which are confirmed by **JCPDF card no. 79-1769.** 

We also find the crystalline size by using **Deby Scherrer** formula [30].

$$\mathbf{D} = \mathbf{k}^* \lambda / \beta \cos \theta \tag{8}$$

Where, D = average size of the crystallites,

K= shape factor (K = 0.94),

 $\lambda = X$ -ray wavelength,

 $\beta$  = FWHM of the highest intensity reflection at diffraction angle  $\theta$ .

After putting the values of K and other factors, the size of **ZrO2** crystalline turn out to be around **34 nm**.

#### 4.2 Raman spectroscopy

To analyze the vibrational phonon modes, disorder and size effect in the crystals of the order of nanometer, Raman spectroscopy was performed on the Zirconium dioxide sample. As we can see in following intensity vs Raman shift graph, before calcination there was a broad peak which signify random vibrations. After performing calcination we are getting some significant Raman peaks which shows the ordered vibration and further means the well arrangement of atoms.

The irreducible representation of optical phonon for tetragonal Zirconia

 $\Gamma = A_{1g} + 2B_{1g} + 3E_{g} + 2A_{2u} + B_{2u} + 3E_{u}$ Raman active  $\rightarrow A_{1g} + 2B_{1g} + 3E_{g}$  (6 peaks) IR active  $\rightarrow A_{2u} + 2E_{u}$  (3bands) Silent/Inactive  $\rightarrow B_{2u}$ 



Fig. 12: Raman spectra of Zirconium dioxide nanoparticles



Fig. 13: Different Modes of Lattice Vibration



Fig. 14: Different vibration modes of Zirconium dioxide [31]. Here, the big circle represent the Zirconium atom and smaller circle represent Oxygen atom.

In the following table and figures, we can see the different vibration modes of Zirconium dioxide and their illustrations.

Raman shift ( cm <sup>-1</sup> )	Type of vibration	Type of mode
144	Movements of Zr ion	B <sub>1g</sub>
256	Movements of Zr ion	Eg
302	Partially symmetric coupling	B <sub>1g</sub>
	of A <sub>1</sub> mode	
441	Due to partially symmetric	Eg
	coupling of both $B_1$ modes.	
629	Symmetric stretching of Zr-	A <sub>1g</sub>
	O-Zr bond	

Table 2: Different Raman peaks and modes of Zirconia nanoparticles

### 4.3 UV visible spectroscopy

10 milligram of the nanopowder was dissolved in 5 ml of isopropyl to analyze the optical properties of the material. Then the solution was ultrasonicate till 15-20 minutes to get a uniform suspension of nanopowder. Then the solution was put under the absorption spectroscopy and also, only isopropyl was also put their for calibration purposes. We can see the absorption spectra following.



Fig. 15 : The Absorption spectra of Zirconium dioxide nanoparticles.

The optical Bandgap energy  $(E_g)$  was calculated by using Tauc's relation [32] as given in equation (7)

$$(\alpha hv) = A(hv - E_g)^{1/n}$$

Where,

 $\boldsymbol{\alpha}$  - absorption coefficient

hv is the energy of photon

 $E_{a}$  energy band gap and value of n depends on the nature of transition.

The plot  $(\alpha hv)^2$  versus (hv) is obtained from it. Absorbance(A) is obtained from UV-Vis absorbtion. The absorbtion coefficient( $\alpha$ ) is calculated from Beer-Lambert law.

$$\mathbf{A} = \alpha \mathbf{cl} \tag{9}$$

Here, A is the absorbance

C is the concentration (mol/liter)

l is the length of the cuvette (1cm)

To measure the value of optical band gap, we extends the linear region of graph till x axis by making a straight line coinciding with the linear segment. The band gap of Zirconium dioxide nanoparticles was found to be 4.88 eV. We can see that in following graph.



Fig. 16: Calculation of Band gap

#### Urbach energy-

Materials with a smaller Urbach energy require less energy to excite their electrons and therefore absorb light more easily. Conversely, materials with a larger Urbach energy require more energy to excite their electrons and absorb light less easily. It is used to quantify the disorder in the band edges.

It is evaluated by fitting the absorption coefficient as a function of energy to an exponential function.

$$\alpha = \alpha_0 \exp((\mathbf{E} - \mathbf{E}_g)/\mathbf{E}_u) \tag{10}$$

here  $\alpha$ ,  $\alpha_0$ ,  $E_g$  and  $E_u$  are absorption coefficient, arbitrary constant, incidence energy, and Urbach energy respectively.

The following graph is drawn between  $ln(\alpha)$  and hv. We can see the liner section highlighted and the inverse of that slope will be Urbach energy. The Urbach energy for our sample is found to be 1.84 eV.



Fig.17: The calculation of Urbach energy.

#### 4.4 The impedance spectroscopy

To calculate the dielectric constant of the Zirconia nanopowder, we performed the impedance spectroscopy. In order to do this spectroscopy, we made a circular pallet of radius 5mm by applying pressure of 3 Ton by Hydrolic Press. The thickness of the pellet was found to be 1.75mm.

After the making of pallet, silver past was applied on both of its sides to make the contacts conductive. After applying the silver past, the pallet has now become essentially a parallel plate capacitor [33]. The impedance spectroscopy gave us the variation of capacitance with the frequency. As we know, the capacitance of a parallel plate capacitor is

$$C = (\mathcal{E}_{o}\mathcal{E}_{r}A)/d$$

Here,

 $\mathcal{E}_o$  is the permittivity of vacuum

 $\mathcal{E}_r$  is the relative permittivity of material or dielectric constant

A is the area of parallel plates

d is the thickness of capacitor

Now, if we want the dielectric constant of the material, we can rearrange the equation as

$$\mathcal{E}_{\rm r} = ({\rm C.d})/(\mathcal{E}_{\rm o.}{\rm A}) \tag{11}$$

We can see the variation of dielectric constant with the frequency in the following graph.



Fig. 18 : The variation of dielectric constant with frequency

As we can see, the dielectric constant decreases with the frequency and becomes saturated at very high frequencies. At 100 kHz, its value is around **53** Which is very high when compared to some other metal oxides like Silicon dioxide, aluminum oxide etc. [34]

The reason for this decreasing nature of graph can be easily understand. Every dielectric material responds to the external electric field by inducing an internal electric field in the opposite direction. This is due to the alignment of all the dipole moments. If the applied external electric field is altering its direction back and forth then the dielectric will also change its response accordingly. The dipoles will rotate according to the external field. The time which a dielectric takes to response after activation of external field is called relaxation time.

Now, At low frequencies, typically in the range of direct current (DC) or low-frequency alternating current (AC), the polarization process in dielectric materials has enough time to reach its maximum extent. This means that the charges within the material have enough time to rearrange themselves and align with the applied electric field. As a result, the dielectric constant remains relatively constant, and the material behaves as an effective insulator, storing a significant amount of electrical energy.

However, as the frequency of the electric field increases, the time available for polarization decreases. At higher frequencies, the oscillations of the electric field are faster, and the charges within the dielectric material do not have sufficient time to follow the rapid changes in the electric field. Consequently, the polarization process becomes less effective, and the material's ability to store electrical energy decreases.

At extremely high frequencies, such as those found in the microwave or radio frequency range, the charges within the dielectric material cannot react quickly enough to the rapidly changing electric field. The charges are unable to align with the field and cannot contribute significantly to the dielectric constant. As a result, the dielectric constant decreases with increasing frequency.

#### **Chapter 5**

### Conclusion

Nano crystalline tetragonal Zirconia was synthesized using sol gel method by doing hydrolysis of zirconium (IV) propoxide precursor. After calcination, the crystalline size was found out to be about 34 nm. All the vibrational modes were identified using Raman spectroscopy. The band gap of nanoparticles was calculated by using UV- Visible spectroscopy and by applying the Tauc's relation it was found to be 4.88 electron volt, which is much higher then conventional metal oxides. The Urbach energy was measured to evaluate the disorder of the nanostructures. It was found out to be 1.84 eV. Finally, the Impedance spectroscopy was performed on the sample to evaluate the dielectric properties of nanoparticles. The dielectric constant of the material was measured till the frequency of 100 kHz. The value of permittivity at 100 kHz was around 53, Which is much greater than the permittivity of Silicon dioxide, which is around 4. So we have grown the alternative efficient gate dielectric material, as ZrO<sub>2</sub> nanoparticles which have a large band gap and a high dielectric constant.

Following this work, the nanoparticles can be deposited on the Silicon substrate and the dielectric constant could be check for the different thickness of the layer. With that, by changing the pH value in the reaction, we can change the size of the nanoparticles and by changing the size, we can observe the change in dielectric constant and in band gap. Generally, the dielectric constant increase with size and band gap decrease with it. In order to keep these both values high, we need to find an optimum crystalline size on which, the gate dielectric will be most suitable for the uses in Nanoelectronics.

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