The principal contributions of Nanostructured Oxides and Materials are exchanging information about the fundamental and applied research developments in the area of oxides and materials on national and international levels. Valorization of the competence in the oxides and materials research and activation the international cooperation links beside facilitation for scientists lead to access into recent achievements.

In fact, in recent years the materials science and engineering have successfully contributed too many interdisciplinary fields in nano structures. Therefore, transfer of ideas, methods and tools from traditional to a new scale should be a promising endeavor. An additional objective is to increase the understanding of the fundamental principles which underlies the problems of nano in the life realms. This is of great relevance to the society and science, in particular for economic endeavors. Objective assessment of risk and quantitative representations of information that support decisions has a vital role to play in many other areas. To encompass this broader perspective, the scientific aim of Nanostructured Oxides and Materials rested on different mutually interlocking working groups. The contributions have focused on nano research studies. Interactions between authors within their published chapters can be described as links between nodes. In addition to the topology of these works, which are for nano systems have to be revealed from data, also the link capacity plays a considerable role, for example in information transfer. These chapters address problems from various perspectives.
NANOSTRUCTURED
OXIDES AND MATERIALS
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The principal contributions of Nanostructured Oxides and Materials are exchanging the information about the fundamental and applied research developments in the area of oxides and materials on national and international levels. Valorization of the competence in the oxides and materials research and activation the international cooperation links beside facilitation for scientists lead to access into recent achievements. In fact, in recent years the materials science and engineering have successfully contributed too many interdisciplinary fields in nano structures. Therefore, transfer of ideas, methods and tools from traditional to a new scale should be a promising endeavor.

An additional objective is to increase the understanding of the fundamental principles which underlies the problems of nano in the life realms. This is of great relevance to the society and science, in particular for economic endeavors. Objective assessment of risk and quantitative representations of information that support decisions has a vital role to play in many other areas. To encompass this broader perspective, the scientific aim of Nanostructured Oxides and Materials rested on different mutually interlocking working groups. The contributions have focused on nano research studies.

The first chapter is devoted to the preparation of high quality transparent conductive SnO₂ nanostructures by post-oxidation of vacuum evaporated tin, on quartz and silicon substrates. The oxidation was achieved in a short time (90 sec) which is known as Rapid Thermal Oxidation (RTO). Many growth parameters have been considered to specify the optimum conditions, namely,
oxidation temperature and oxidation time. Optical, electrical and structural properties of SnO₂ nanostructures are investigated and analyzed extensively with respect to growth conditions. It has been used in manufacture of MIS devices and for comparison: two types of silicon substrates were used: (n-type and p-type). The optical properties of SnO₂ nanostructures have revealed that, the optical band gap is 3.54 eV at optimum condition. The transmission rate of SnO₂ nanostructures was high (95%) which was reduced with the reduction of oxidation time, while the electrical properties of undoped SnO₂ confirm that these films are n-type and highly conductive. The electrical resistivity was found to be very sensitive to the thickness and substrate temperature. Lowest resistivity of about (0.022 Ω.cm) was found for SnO₂ nanostructures prepared at (150nm). The XRD spectra have revealed a high oriented grain in the (101). The FTIR measurement shows that the formation ability of O-Sn-O band directly depended on oxidation temperature and oxidation time.

The second chapter focused on electrochromic materials that exhibit a reversible optical property change under the application of a small applied electric field. Transition Metal Oxides (TMO) are a class of materials that undergo a reversible optical and electrical property change due to their special structures and multiple oxidation states. These materials are capable of switching between different metastable states whose optical and electrical properties can be distinctly different. It is interactivity by way an electric field that makes these materials extremely attractive from the application stand point. By preparing these materials in thin film form one gets the further advantage of an even more precise control of the dynamic properties due to the ensuing size (thickness) effect. In addition to this,
one dimensional effect, by adjusting the nanostructure of these films, a wide range of switching properties can be induced in these films for various applications. In this chapter, the importance of nanostructuring of thin films in tailoring the optical, electro chromic and photonic properties is reviewed. The results on the periodic and non-periodic nanostructuring of two of the most important TMO thin films studied to date, Tungsten trioxide (WO$_3$) and Molybdenum trioxide (MoO$_3$) are discussed, as examples.

The microelectronic community has been forced to use alternate channel materials like high mobility III-V semiconductors in the mainstream digital electronics in order to continue scaling of MOSFET beyond sub 45 nm. In this third chapter, a review of III-V MOSFET structures and models has been done. Various challenges such as suitable low defect density dielectric deposition, integration with silicon, mobility issue with p-MOSFETs and their possible solutions along with the design issues have been discussed and reviewed while implementing the III-V technology for nanoscale MOSFETs.

The fourth chapter is to explain the process of Zirconium oxide (ZrO$_2$) thin films were deposited on glass by pulsed direct current reactive magnetron sputtering. Optical properties and surface morphology of these thin films were investigated and compared with previous studies. The properties of thin films depend on the deposition method used. In addition, our results show that the properties of these films highly depend on the deposition conditions (substrate nature, temperature, deposition rate and so on). Especially, in situ with ex situ heating processes performed on these films is compared. It is found that both ex situ and in situ heating treatments lead to the
formation of denser materials, and consequently, to a reduction of the thickness of the thin films as well as an increase of their refractive index. However, these results are more apparent in the case of in situ heating. Furthermore, when investigating the evolution of surface roughness in the case of in situ heating, a minimum temperature for a substrate is found close to 200 °C.

Other side, a review of metal oxides materials for nanowires growth purpose via sol-gel method is presented in chapter five. The materials are Titanium dioxide (TiO₂) or Titania. It was resumed with explanation of nanocrystal formation and followed by comparing the properties of two materials. The outlook and other unique properties of these two materials that suit for many applications will be discussed further below.

The last chapter submits combustion of citrate complex of a popular choice to synthesize nanocrystals of transition metal oxides in a single-step process. The amount of citric acid used for combustion is conventionally calculated based on the total valence of the oxidizing and reducing agents while keeping the equivalent ratio unity such that combustion energy is a maximum. This chapter demonstrates by employing quantum chemical calculations that the amount of citric acid could be reduced to nearly half if prepared for appreciable amounts. Transition metal oxides belong to quaternary double perovskites, with general formula \( \text{Ba}_2\text{RESbO}_6 \) (RE = Rare-earth), have been synthesized as nanocrystals as examples to validate the calculations.

Interactions between authors within their published chapters can be described as links between nodes. In addition to the topology of these works, which are for nano systems have to be revealed from data, also the link capacity plays a
considerable role, for example in information transfer. These chapters address problems from various perspectives. As the editor of this book, I hope that the current selection of chapters provides a good overview of the research activities within the nano structures. The results should also boast future research activities within the new actions and contributions.

I would like to acknowledge Prof. Datuk Dr. Kamarudin Hussin, the Vice-Chancellor of University Malaysia Perlis, for his support and encouragement during the preparation of this book. Also, I would like to thank Prof. Dato’ Dr. Zul Azhar Zahid Jamal, Deputy Vice-Chancellor for Academic and Internationalization; Prof. Dr. Abdul Hamid Adom, Deputy Vice-Chancellor for Research and Innovation and Prof. Dr. Uda Hashim, Director of Institute of Nano Electronic Engineering for their reinforcement and propping for preparing this book. I appreciate the amount of work that goes into writing papers when the authors are heavily burdened with other demands on their time. Finally, I present my special greetings to the UniMAP Press for giving us the opportunity to publish and distribute the Nanostructured Oxides and Materials.

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CHAPTER 1
Morphology, Structural, Optical and Electrical Properties of High Quality Tin Oxide Nanostructures

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ABSTRACT

In the present work, preparation of high quality transparent conductive SnO₂ nanostructure by post-oxidation of vacuum evaporated tin, on quartz and silicon substrates is presented. The oxidation was achieved in a short time (90 seconds) which is known as Rapid Thermal Oxidation (RTO). Many growth parameters have been considered to specify the optimum conditions, namely, oxidation temperature and oxidation time. Optical, electrical and structural properties of SnO₂ films are investigated and analyzed extensively with respect to growth conditions.

After obtaining the best results for the preparation of a film, it has been used in manufacture of MIS devices and for comparison: two types of silicon substrates were used: (n-type and p-type). The optical properties of SnO₂ films revealed that the optical band gap is 3.54 eV at optimum condition. The transmission rate of SnO₂ films was high (95%) which was reduced with the reduction of oxidation time, while the electrical properties of undoped SnO₂ films confirm that these films are n-type and highly conductive.

The electrical resistivity was found to be very sensitive to film thickness and substrate temperature. Lowest resistivity of about (0.022Ω.cm) was found for SnO₂ film prepared at (150nm). The XRD spectra revealed a high oriented grain in the (101). The FTIR measurement shows that the formation ability of O-Sn-O band directly depended on oxidation temperature and oxidation time. In order to characterize the prepared device the electrical properties were measured and indicated that the barrier height is greatly depended on interfacial layer thickness (SiO₂).

Keywords: Tin Oxide Nanostructures, Optical, Characterization, Analysis.
1.1 Introduction

Transparent Conducting Oxides (TCO) film is a material that is highly transparent in the range of visible light, and at the same time, electrically conductive [1]. The first semitransparent and electrically conductive films were reported as early as 1907. However, substantial technological advances were only made after the 1940s when interest in these materials was generated by their potential applications in industry [2]. This material has been used in a wide range of applications in science and technology, including solar cells, heat reflecting mirrors, antireflection coating and a variety of electro-optical devices such as flat panel display devices and many other different applications depending on the type of material; the most popular are ZnO, CdO, In$_2$O$_3$ and SnO$_2$ [3,4].

If these semiconductors are prepared intrinsically i.e. without intrinsic or extrinsic dopants, their resistivity is very high (of the order of $\geq 10^7 \, \Omega \, \text{cm}$). For many manufacturing companies of TCO films the aim is to achieve stable film properties for large area coating processes with low film resistance and high transmittance within the visible spectrum range. Adding oxygen or nitrogen gas into the coating chamber, make possible to produce oxydic or nitridic dielectric layers from metal targets [1] Tin oxide (SnO$_2$) a tetragonal rutile structure with lattice parameters $a = b = 4.737 \, \text Å$ and $c = 3.826 \, \text Å$ [5]. The unit cell contains two tin and four oxygen atoms. Each tin atom is bound to six oxygen atoms at the corners of a regular octahedron, and every oxygen atom is surrounded by three tin atoms the corners of an equilateral triangle [6]. The SnO$_2$ films are n-type semiconductors with a direct optical band gap of about 3.87-4.3 eV. However, in nanostructure form, depending on the deposition technique its structure can be polycrystalline or amorphous.

The grain size is typically 200-400 Å, which is highly dependant on deposition technique, temperature, doping level etc. SnO$_2$ film close to stoichiometric condition have low free carrier concentration and high resistivity, but non-stoichiometric SnO$_2$ films have high carrier concentration, conductivity and transparency. These films are used as window layers and heat reflectors in solar cells, various gas sensors, LCDs etc [5]. At last, the SnO$_2$ is chosen because of its high electrical
conductivity and its transparency in the visible and infrared light, the refractive index lies in between 1.9 and 2.0 [3].

1.2 Physical Properties of SiO$_2$

SnO$_2$ films with different orientation have been fabricated by various nanostructure growth technique such as chemical vapour deposition, electron beam evaporation, sputter deposition and Pulse Laser Deposition technique (PLD) [7]. The effect of deposition temperature on the structural properties of SnO$_2$ nanostructure has been studied by many workers. It has been found that, the film prepared by a vapour deposition at 575°C is better and showed a polycrystalline nature oriented along the (101), (211) and (301) planes at $2\theta = 34.281^\circ$, 52.156$^\circ$ and 66.285$^\circ$, respectively with single phase SnO$_2$ as shown in Figure 1.1a. Figure 1.1b shows the XRD patterns with d and (h k l) values of SnO$_2$ films prepared at 575°C substrate temperatures. The presence of other orientations such as (110), (200), (220), (310) was also detected with lower intensities.

The low intensity of the appeared planes at lower temperature indicates low crystalinity and tiny crystalline size [8]. For Nd-doped SnO$_2$ films deposited at same substrate temperature, the XRD showed no peaks corresponding to Nd or its compounds, but the intensity of SnO$_2$ peaks decreased. The decrease in peak intensities is basically due to the replacement of Sn$^{4+}$ ions with Nd$^{3+}$ ions in the lattice of SnO$_2$ film. This process leads to the shifting of Sn$^{4+}$ ions to the interstitial sites and also an increase in the amorphous phase.

![Figure 1.1:](image)

(a) X-ray Diffraction pattern for SnO$_2$ films at different substrate temperature (b) X-ray Diffraction pattern for SnO$_2$ films with d & (h k l) values at 575°C [8].
When the SnO$_2$ films prepared by the C.V.D technique using SnCl$_4$ and TMT precursors on borosilicate and soda-lime substrates, all films deposited at higher temperature with both types of precursors, the XRD data for samples showed the presence of single phase SnO$_2$ as in Figure 1.2. In comparison, the film deposited at low temperature using the SnCl$_4$ precursor results in a mixed phase of SnO and SnO$_2$ the presence of the SnO phase reduces the band gap to 3.62 eV, compared to the 3.92-4.0 eV range for the single-phase SnO$_2$ samples deposited at higher temperature [9].

![Figure 1.2: XRD data for SnO$_2$ deposited at low and high temperatures [9].](image)

The SnO$_2$ films were transparent in the visible region, the absorption coefficients ($\alpha$) were determined by measuring transmittance ($T_r$) and reflection ($R_r$) in these films it may be written as a function of the incident photon energy ($h\nu$) as: [10].

$$\alpha = (A/h\nu)[h\nu - E_g]^m$$

where, $A$ is a constant which is different transition indicated by different values of $m$ and $E_g$ is the separation between the bottom of the conduction band and the top of valence band [10]. Films have a good transparency in the visible and a high reflectivity in the IR spectral range, when use of tin oxide coatings as heat mirrors shown in Figure 1.3 [11].
The transmission ($T_r$ %) versus wavelength plots of pure SnO$_2$ thin layers deposited on glass substrate at different temperature shown in Figure 1.2 - 1.15. It was clearly seen that, in the visible region, the transmittance is about 90% which gives a very low absorption [12].

The parameters of these processes can be determined from the spectral dependence of the absorption coefficient $\alpha$. The dependence of $\alpha$ on the wavelength $\lambda$ can be well-known correlation between $T_r$, the reflection $R_r$ and $\alpha$

$$T_r = (1 - R_r)^2 \exp(-\alpha t)$$  \hspace{1cm} 1.1

which is correct for the condition $\exp(2\alpha t) >> R_r^2$  \hspace{1cm} 1.2

If the value of $T_r$ for two different thickness $t_1$ and $t_2$ are known then $\alpha$ can be obtained from equation (1) [13]

$$\alpha = \frac{1}{t_2 - t_1} \ln \left( \frac{T_r}{\ln \frac{T_{t_1}}{T_{t_2}}} \right)$$  \hspace{1cm} 1.3
The variation in $\alpha$ with photon energy (in electron volts) was found to obey a relation of the form: [14]

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2}$$

Which is valid for the allowed direct transitions between the sample parabolic bands as shown in Figure 1.5? Once the linear portions of the plots are extrapolated to zero, the direct energy gap is 3.76 eV for SnO$_2$. The FTIR spectrum exhibits a medium broad band from Sn-OH group and adsorbed water. The strong peak at 619 cm$^{-1}$ is assigned to vibration (Sn-O-Sn) of tin oxide framework. From this study it was found that, propylene oxide accelerated the gel formation as shown in Figure 1.6 [15].

![Figure 1.5: The dependence of the square of the optical absorption coefficient $\alpha^2$ on the photon energy for SnO$_2$.](image)

![Figure 1.6: FTIR spectra of prepared SnO$_2$ nanoparticle [48].](image)

Figure 1.7 displays the FTIR spectrum of SnO$_2$ powders, in this figure; the SnO$_2$ absorption band is located close to 500 cm$^{-1}$, while the others correspond to water and organic compounds. It can be observed that, while the band at 1000 cm$^{-1}$ disappears at 200 °C, the other at 3500 cm$^{-1}$ remains noticeable even at 300 °C [16].
Figure 1.7: FTIR for Sol-Gel SnO$_2$ solution (bottom curve) and calcinated at different temperatures [16].

Figure 1.8 shows the FTIR spectra of SnO$_2$ films as a function of the amount of added Si. The phonon mode of 580 cm$^{-1}$ and 680 cm$^{-1}$ correspond to Sn-O bands, and the phonon mode at 1090 cm$^{-1}$ and 1220 cm$^{-1}$ confirms the Si-O-Si stretching vibrations. As shown in last figure, the band at 1020 cm$^{-1}$ and 1220 cm$^{-1}$ increase with the amount of Si added, which indicates the increasing density of Si-O bands and corresponding of Si-O bands [17].

Figure 1.8: FTIR spectra of the SnO$_2$ films as a function of the amount of Si dopants [17].

The conductivity in nanostructures is generally related to the morphology. The surface morphology of SnO$_2$ films prepared by spray pyrolysis technique onto glass or quartz substrates was studied with atomic force microscopy using several samples with different thickness. SnO$_2$ films are highly conductive material with negative charged conductivity. It resistivity found to decrease rapidly through annealing in vacuum or air also by suitable doping with different dopant. Also this dopant material could be used to convert the conductivity to positive type, for example in case of Nd dopant the majority carrier convert from electron to holes and then the film are p-type semiconductor [5].
Figure 1.9 shows the electrical resistivity of SnO₂ nanostructure as a function of thickness. The variation in the resistivity for air-annealed samples was such that a decrease was always initially observed. The relatively high resistivity as well as the amorphous nature of the unannealed film may be attributed to the production of non-stoichiometric SnO₂ films which may be fine grained and are thus structureless. However, these effects may also be due to the generation of SnO-rich films. It is well known that SnO₂ is an oxygen-deficient semiconductor and that SnO is an insulator. Vacuum annealing may there for lead to the conversion of SnO to SnO₂ according to the reaction below.

\[ 2 \text{SnO} \rightarrow \text{SnO}_2 + \text{Sn} \]

Where tin is precipitated at interstices or grain boundaries, giving a film with reduced resistivity. The decrease in resistivity during air annealing may also due to the conversion of SnO to SnO₂ according to the reaction:

\[ \text{SnO} + \frac{1}{2} \text{O}_2 \rightarrow \text{SnO}_2 \]

So that, the SnO concentration is decreased, leading to an increased conductivity. The minimum resistivity of the SnO₂ films about \(3 \times 10^{-2} \ \Omega \text{cm}\) [13].

Figure 1.9: The dependence of the resistivity on the thickness for thin SnO₂ films [12].

The electrical properties of the SnO₂ films were performed by temperature-dependent Hall measurements in conjunction with resistivity measurements. Figure 1.10 shows that, the mobility of the samples deposited at 550°C and 600°C is constant at low temperatures. This may be the result of carrier scattering dominated by neutral-impurity scattering and grain-boundary scattering. At higher temperatures, the mobility of these samples
starts to decrease, possibly due to the contribution from lattice scattering. For the film deposited at 450 °C, the mobility decreases continuously from low to high temperatures. This may be the result of higher levels of impurities, the presence of mixed phase, and the smaller grain size of this sample [9].

![Figure 1.10: Hall Mobility versus temperature. Data for SnO₂ films deposited by TMT process at 600 °C [9].](image)

The variation of resistance of SnO₂ films with respect to the deposition parameters are given in Figure 1.11 (a, b). The resistivity of SnO₂ films changes from 9.19×10⁻⁴ (Ω cm) to 1.073×10⁻⁴ (Ω cm) as the substrate temperature varied 400-575 °C. The decrease in resistivity with temperature may be attributed to the growth of grain size and improvement of film homogeneity [8].

![Figure 1.11: Variation of resistance of SnO₂ films with (a) Substrate temperature (b) Time of vapour deposition [8].](image)

### 1.3 Experimental Process

Test quartz slides, each of 2×2 cm² area, were used as substrates. They were cleaned by alcohol with ultrasonic waves in order to remove the impurities and residuals from their surfaces. Beside that a Square-shaped n&p type silicon samples, each of 1×1 cm² area, of 1.5-4 Ω cm resistivities were prepared using a wire-cut machine. The samples
were etched with CP4 solution consisting of (HNO₃, CH₃COOH, HF) of ratios (3:3:5) to remove oxides. They were then cleaned using alcohol and ultrasonic machine (Cerry PUL 125 device) for 15 minutes then they were cleaned by water and ultrasonic waves for another 15 minutes.

A thermal evaporation system type (Edwards) was used to evaporate high purity (99.9 %) tin on quartz slides and (n-Type, p-type) Si substrate at room temperature under low pressure (\(10^{-6}\) torr). A Rapid thermal oxidation (RTO) of Sn film was employed to prepare SnO₂ films at different temperature and oxidation time. After being cleaned, the samples were fixed on the quartz tube irradiated by halogen lamp directly. Thermal oxidation process took place at temperatures between (373- 973 K), and at different oxidation times in order to obtain the best oxidation of tin nanostructures. Ohmic contacts were fabricated by evaporating 99.999 purity aluminum wires for back contact and 99.999 purity gold as front contact using Edwards coating system.

X-ray diffraction measurement was carried out according to the ASTM (American Society of Testing Materials) cards, using Philips pw 1050 X-ray diffractometer of 1.54 Å from Cu-kα. The grain size \(D_g\) of the crystalline material; which plays the important role in the material properties, can be estimated easily from the X-ray spectrum by means of Full Width at Half Maximum (FWHM) method that is often calculated by Scherrer relation [18].

\[
D_g = \frac{K \lambda}{\beta \cos \theta}
\]

Where K= 0.94 , λ is the wave length of incident X-ray radiation , \(\beta\) is the intrinsic full width at Half Maximum of the peak , and \(\theta\) is the Bragg’s diffraction angle of the respective XRD peak. Using this data, the dislocation density \((\delta)\), and the micro strain \((\varepsilon)\) can be calculated, which will elucidate the nature of the prepared SnO₂ films [19]. Optical transition measurement: A double-beam UIR-210A spectrophotometer from Shimadzu was used in order to record the optical transmission and absorption spectra of the prepared films at different preparation
conditions within the wavelength range (300-900 nm). All films were deposited on quartz substrate. The optical band gap was estimated graphically by applying the Tauc model [14]:

\[
\alpha h \nu = (h \nu - E_g)^{1/2}
\]

Where \( h \) is Plank constant and \( \nu \) is the frequency of the incident photon.

Fourier Transform-Infrared Spectroscopy (FTIR) probes the molecular vibrations of molecules. The (SHIMADZU- 8400S) Scan of the FTIR measurements are performed over the range between (400-4000) cm\(^{-1}\). The electrical resistance of the prepared films was determined as a function of the substrate temperature and its value (\( R \)) is given for a rectangular shaped sample by [20]:

\[
R = \rho \left( \frac{l}{b t_t} \right)
\]

where \( \rho \) is the electrical resistivity of the sample and \( l, b \) and \( t_t \) are the length, width and thickness of the sample, respectively. The conductivity is the inverse value of the resistivity. The activation energy (\( E_a \)) which can be calculated using the equation: [22].

\[
\sigma_{dc} = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)
\]

where \( \sigma_0 \) is the high temperature limit of conductivity, \( E_a \) is activation energy and \( kT \) is the thermal energy associated with temperature variation in the measurement where \( k \) is Boltzman constant and \( T \) is absolute temperature [21]. The thermoelectric power of nanostructures prepared at different conditions was measured Seeback coefficient (\( S \)) given by \( S = \Delta V/\Delta T \) [23]. To judge the performance of the transparent conducting film, the figure of merit is calculated which defined as:

\[
F.M. = -1/\rho \ln T_r
\]

Where \( \rho \) is the resistivity (\( \Omega \cdot cm \)) and \( T_r \) is the average fractional transmittance from 300 to 900 nm [24].
1.4 Results and Discussion

1.4.1 Morphology Study of SiO₂

We have studied the surface morphology of the produced TCO films. The following figures show the optical micrograph of SnO₂ nanostructures, those prepared at various growth conditions. These micrographs reveal that the film morphology can be easily recognized through the film homogeneity and color. Figure 1.12, gives the optical micrographs of the 250 nm films thickness deposited on quartz substrate and oxidized at different oxidation temperature and constant oxidation time.

The color of films tends to be dark (nearly black) which reflect the metallic nature of Sn, which typically has dark color as well as the high reflectivity of the obtained film. It can clearly be noticed that the film color is the same as the physical color of the thin metal, so, they look in dark black (a, b) and less darkness obtain at 473 K in Figure (c) where the transformation films to oxide films started.

The optical micrographs at an oxidation time of 60 sec and oxidation temperature of 573 and 673 K are shown in Figures 1.13 (a, b), also recognized changes in the prepared film and morphology changes to become more transparent and less darkness in relation to transmission of microscope light through the prepared film. In the last figure, the dark droplets and particles of submicron sizes are observed over the film surface and they are spread randomly.
as dark regions on the film surface which results from incomplete transformation of Sn film to its oxide.

Figure 1.13: Surface morphology of (SnO) samples prepared at oxidation time 60 sec (a) oxidation.

At higher oxidation temperature around 773 and 873 K, Figures 1.14 (a, b) shows that oxides film begins to demonstrate over the metal atoms that are still available in the film structure which reflects the incident light, so they appear as black dots in the microscope picture. While the oxides appear as brown particles for tin oxide molecules respectively. This result is inconsistent with XRD result which will be given later. The obtained films at oxidation temperature of 973 K for Sn film Figure 1.14 (c) displays smooth uniform grain size and void-free film.

Figure 1.14: Surface morphology of (SnO₂) samples prepared at oxidation time 60 sec (a) Oxidation temperature (773 K), (b) Oxidation temperature (873 K) and (c) Oxidation temperature (873 K)

The best surface morphology of produced films which represent the optimum case was obtained at 873 K oxidation temperature and oxidation time of 90 sec in Figure 1.15 where Sn metal film totally transform to its SnO₂ film.
1.4.2 Structural Properties of SiO2

The crystalinity of the produced material was characterized using X-Ray Diffraction (XRD). This technique was also employed by other group which gives an indication about the grain size and formation material type of the prepared nanostructure. The following figures show the XRD patterns for samples grown at different oxidation temperature and oxidation time. For Sn films depositing on quartz substrate. One peak could be recognized in Figure 1.16, the film is single crystalline with a tetragonal structure according to the ASTM standards where (200) Sn, with lattice constant of (a=5.8285 Å) respectively could be recognized. This is related to the formation of tin nanostructure and such result indicates that no formation of the oxide film occurs on quartz substrate.
Figure 1.17 (a, b) represent the sample prepared at 373 and 473 K oxidation temperatures and constant oxidation time. There is one sharp peak in this pattern at $2\theta = 30.6402^\circ$ for Sn film correspond to diffraction from (200) plane. Where no formation of the oxide film and all the lines correspond to a single crystalline tetragonal Sn phase.

Figure 1.17: XRD pattern of Sn nanostructure deposited at (a) T=373 K and (b) T=473 K, oxidation time 60 sec.
At farther increase in oxidation temperature up to 573 and 673 K, as in Figure 1.18 (a, b), the XRD pattern consists of two sharp peaks at $2\theta = 30.1340^\circ$ and $2\theta = 30.7633^\circ$ which are related to the formation of SnO film with orthorhombic structure. The intensities of the (101) peaks show the formation of SnO oxide and a polycrystalline in nature. Figure 1.19 (a, b) gives the XRD results for a sample prepared at 773 and 873 K, where four peak are recognized. In this diffraction pattern, the peaks at $2\theta = 33.8436^\circ$ and $2\theta = 34.0896^\circ$ are corresponding to the diffraction from (101) planes which are related to the formation of SnO$_2$ films.

Figure 1.18: XRD pattern of Sn nanostructure oxidation at (a) T=573 K and (b) T=673 K, oxidation time 60 sec.

Figure 1.19: XRD pattern of Sn nanostructure oxidation at (a) T=773 K and (b) T=873 K, oxidation time 60 sec.
The XRD pattern at the oxidation time of 60 sec and increasing temperature up to 973 K are shown in Figure 1.20. It shows that, the peaks appeared at $2\theta=26.7397^\circ$ and $2\theta=34.0658^\circ$ in the spectra of the SnO$_2$ are corresponding to the reflection from the planes (110) and (101). The intensities of the peaks are increasing with the increases of oxidation temperature and can be attributed to the improvement in the crystallinity at higher temperature.

This improvement in the structural order can also be attributed to the increase in the SnO$_2$ film density, which results in demonstrated of (101) SnO$_2$ peak rather than other peak. Figure 1.21 (a, b, c) shows the diffraction pattern for samples prepared at different oxidation time. At 90 sec oxidation time Figure 1.21 (a) shows that the structures of films are clearly improved where a significant increase in peak intensity at (101) plane. This indicates the formation of nearly stoichiometry SnO$_2$ films. The intensities of these peaks reduce with the increasing of oxidation time up to (120 sec) as shown in Figure 1.21 (b, c).

The results below ensure that, the optimum value of oxidation temperature is 873 K and oxidation time is 90 sec. The deviation in XRD peak of the film with respect to the standard ASTM data is attributed to the mechanical micro stress produced by different sources like impurities,
defects and vacancies reside in the film structure. Results at higher oxidation time (140 sec) and at the same oxidation temperature are shown in Figure 1.21 (c), which recognizes the peaks at $\theta = 33.9813^\circ$ in the spectra of SnO$_2$ film corresponding to the reflection from (101) plane.

The presence of sharp peaks (in all deprogram) indicate that all films are polycrystalline in nature and in accordance with data reported in literature. These results are similar to that obtained by other workers [25, 26, 5, and 27]. The corresponding lattice constants for each diffraction peak are shown in Table 1.1 and 1.2. These tables also describe the different diffraction planes, their relative intensities, Bragg’s angle and miller indices. Table 1.3 shows the FWHM of the XRD and exhibits the value of the estimated grain size for the prepared films at different growth conditions. It appears clearly from the results that these are an enhancement in the film morphology and smoothness with increasing the oxidation time up to (90 sec, 873 K).

![Figure 1.21: XRD pattern of Sn nanostructure oxidation at T = 873 K and oxidation time (a) 90 sec (b) 120 sec (c) 140 sec](image)
Here, it is recognized that the reduction in the FWHM, reflected in the grain size. The dislocation density and the micro strain increased with the increase of oxidation temperature at oxidation time 60 sec. It was observed that the dislocation density and the micro strain decrease at optimum condition (90 sec, 873 K)

<table>
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<th>DEPOSITION CONDITION</th>
<th>(2θ)°</th>
<th>l/l_1</th>
<th>d (Å)</th>
<th>(h k l)</th>
<th>l/l_1</th>
<th>d (Å)</th>
<th>TYPE</th>
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<td>30.6529</td>
<td>100</td>
<td>2.91429</td>
<td>200</td>
<td>100</td>
<td>2.91</td>
<td>Sn</td>
</tr>
<tr>
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<td>30.6402</td>
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<td>2.91547</td>
<td>200</td>
<td>100</td>
<td>2.91</td>
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</tr>
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<td>2.91682</td>
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<td>100</td>
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<td>T=573K</td>
<td>30.1340</td>
<td>100</td>
<td>2.96328</td>
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<td>100</td>
<td>2.97</td>
<td>SnO</td>
</tr>
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<td>2.90</td>
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<td></td>
<td>31.0598</td>
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<td>64</td>
<td>2.89</td>
<td>SnO</td>
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<tr>
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<td>100</td>
<td>2.91964</td>
<td>50</td>
<td>50</td>
<td>2.93</td>
<td>SnO</td>
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<td></td>
<td>31.9622</td>
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<td>33.8436</td>
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<td>2.64648</td>
<td>101</td>
<td>81</td>
<td>2.644</td>
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<td>T=873K</td>
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<td>100</td>
<td>2.89626</td>
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<td>33.1044</td>
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<td>50</td>
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<td>34.0896</td>
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<td>T=973K</td>
<td>26.7397</td>
<td>4</td>
<td>3.33123</td>
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<td>80</td>
<td>3.33</td>
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<td>30.8386</td>
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<td>2.89</td>
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</tr>
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<td>50</td>
<td>2.62972</td>
<td>101</td>
<td>80</td>
<td>2.63</td>
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### Table 1.2: XRD results for nanostructures prepared at $T = 873\,^\circ\text{K}$

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<th>$d_3$</th>
<th>$d_4$</th>
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<td></td>
<td>32.7901</td>
<td>2.72906</td>
<td>030</td>
<td>30</td>
<td>2.715</td>
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<td>33.0188</td>
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<td></td>
<td>34.0027</td>
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<td>80</td>
<td>2.63</td>
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<td>t=120 sec</td>
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<td>2.89151</td>
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<td>2.89</td>
<td>SnO</td>
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<tr>
<td></td>
<td>32.3045</td>
<td>2.76896</td>
<td>50</td>
<td>2.768</td>
<td>Sn$_3$O$_4$</td>
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<td></td>
<td>33.1776</td>
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<td>2.711</td>
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<td></td>
<td>34.1664</td>
<td>2.62221</td>
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<td>63</td>
<td>2.64</td>
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### Table 1.3: FWHM for SnO$_2$ Samples at different condition.

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<tr>
<th>DEPOSITION CONDITIONS</th>
<th>HKL</th>
<th>FWHM DEGREE (SnO$_2$)</th>
<th>GRAIN SIZE (NM)</th>
<th>DISLOCATION DENSITY($\Delta$) $10^{15}$LINES/CM$^2$</th>
<th>MICRO STRAIN ($E$) $10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=773K t=60 sec</td>
<td>(101)</td>
<td>0.1682</td>
<td>51.94</td>
<td>3.7</td>
<td>4.19</td>
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<tr>
<td>T=873K t=60 sec</td>
<td>(101)</td>
<td>0.1712</td>
<td>51.03</td>
<td>3.84</td>
<td>4.45</td>
</tr>
<tr>
<td>T=973K t=60 sec</td>
<td>(110)</td>
<td>0.2</td>
<td>42.78</td>
<td>5.46</td>
<td>4.3</td>
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<tr>
<td></td>
<td>(101)</td>
<td>0.1948</td>
<td>44.85</td>
<td>4.97</td>
<td>4.72</td>
</tr>
<tr>
<td>T=873K t=90 sec</td>
<td>(101)</td>
<td>0.1544</td>
<td>56.58</td>
<td>3.12</td>
<td>3.21</td>
</tr>
<tr>
<td>T=873K t=120 sec</td>
<td>(101)</td>
<td>0.1945</td>
<td>44.92</td>
<td>4.95</td>
<td>4.9</td>
</tr>
<tr>
<td>T=873K t=140 sec</td>
<td>(101)</td>
<td>0.1557</td>
<td>56.11</td>
<td>3.17</td>
<td>3.46</td>
</tr>
</tbody>
</table>
1.4.3 Optical Properties of SiO2

The influence of growth conditions on the optical properties of the prepared films was studied extensively. The transmission of the deposited films on quartz substrates was measured and recorded at the ultraviolet and visible regions for the films growth at different oxidation temperatures and oxidation time.

Figure 1.22 (a) shows films without any treatment which represents purely metal film that has high reflectivities in the visible and near infrared regions. The effect of oxidation temperature on the optical properties of the film can be observed in Figure 1.22 (b). The results show an increase in the transmission with oxidation temperature and constant oxidation time at a given wavelength, the increase in $T_r$ % is attributed to the well adherent and crystalline nature of the film throughout the coated area, which is obtained due to uniform oxidation and improvement in lattice arrangement, resulting in better optical properties. It is found that the transmission obtained was (~ 80%) and this agrees with the result in a similar work [28]. The improved transmission in the short wavelength region and the peak transmission was in excess of 94% at thicknesses of 50 nm is due to the phase transformation from polycrystalline SnO to SnO$_2$ as shown in Figure 1.22 (c).

A steep fall is observed at the wavelength of 350 nm for SnO$_2$ respectively, which itself denoted as cut off wavelength, and this fall is a characteristic of high quality crystal films. SnO$_2$ films have a good transparency in the visible region. It is known that the sharp decrease in transparency of tin oxide films in UV and IR regions is caused by fundamental light absorption and by free-carrier absorption respectively. Figure 1.22 (d) shows the optical transmission (200-1000) nm as a function of the wavelength for SnO$_2$ film prepared at different oxidation time and constant oxidation temperature, high transmission (>90%) was exhibited by films prepared at (120 and 140) sec oxidation time, may be due to the increase in the oxidation leads to large molecular symmetry (stoichiometry) where (101) SnO$_2$ films are demonstrated over all other oxide film peaks.
In general, it has been found that, the transmission of the films was increased when the oxidation temperature was increased due to film transformation from metal to transparent oxide. The optical band gap was calculated for films prepared at optimum oxidation time and temperature. The plots of $(\alpha h \nu)^2$ against $h \nu$ for SnO$_2$ film prepared at (873 K) and (90 sec) is shown in Figure 1.23. The nature of the plot suggests a direct inter-band transition. The extrapolation of the straight-line portion to zero absorption coefficient ($\alpha=0$) leads to the estimation of band gap energy, this band gap found to be about (3.54) eV. This result is conditional with many other workers [29].

Figure 1.22: Optical Transmission as a function of wavelength for Sn nanostructures prepared on quartz substrate (a) At room temperature (b) Different temperatures (c) Different thickness (d) Different oxidation time.

Figure 1.23: Energy band gap of the SnO$_2$ at oxidation temperature (873 K) and oxidation time (90 sec).
The dependencies of absorption coefficients $\alpha$ on photon energy are represented in Figure 1.24 for film grown at different oxidation time. The direct optical band gap increases to give a blue shift. This shift is due to the increase in carrier concentration which results in filling the bottom of the conduction band and this filling prevents the transition of the photogenerated carriers into the filled levels according to quantum rules and hence leads to far transitions with larger photon energy. This shift is called Burstein - Moss effect. It is found the $E_g$ about 3.5-3.7 eV at $T=873$ K and different oxidation time has been represented in Figure 1.25. These results are agreed with published literatures [30].

Fourier transformation-Infrared spectroscopic results provide information about phase composition and the way in which oxygen is bound to metal ions. The following figures show the FTIR spectra of both Sn films deposited on quartz substrate and SnO$_2$ films prepared at different oxidation temperature and time. Figure 1.26 shows that, the absorption peak is around (216.01-3980.80) cm$^{-1}$ broken spectra which is related to the Sn metal atoms. These insure the deposition of pure metal nanostructure on quartz substrate.
Figure 1.27 (a, b) describe the FTIR results for film prepared at oxidation temperature 373 and 573 K, it is recognized that all the absorption peaks which related to the Sn metal atoms. It is observed that, the absorption spectra at (725.18, 671.18, 401.17, and 277.73) cm\(^{-1}\) is related to the formation of tin oxide molecules. Beside that, the presence of the absorption peaks are related to Sn atom that still un oxidized. Figure 1.27 (c) gives the FTIR results for films prepared at oxidation temperature of 873 K, it could be recognized absorption spectra related to Sn atom is clearly disappeared while that found at (879.48, 686.61, 370.31, 308.59, 300.87, 208.30) cm\(^{-1}\) are related to the formation of tin oxide molecules.

For the case of the tin oxide formation, the mean kinetic energy of the Sn atoms decreases through collision with oxygen, formation of (O\(^{2-}\)) ions (through energetic change reaction of Sn with O\(_2\) molecules). At oxidation (973 K) Figure 1.27 (g) absorption spectra related to Sn atom is clearly disappeared while that found at (879.48, 686.61, 370.31, 308.59, 300.87, and 208.30) cm\(^{-1}\) is related to the formation of tin oxide molecules. For the case of the tin oxide formation, the mean kinetic energy of the Sn atoms decreases through collision with oxygen, formation of (O\(^{2-}\)) ions (through energetic change reaction of Sn with O\(_2\) molecules). So, chemical bonding like (Sn-O) vibrational and (O-Sn-O) stretching modes are formed respectively. This could be recognized by the FTIR obtain result shown in the given figure. By increasing the oxidation time up to 90 sec Figure 1.28 the peak at (686.61 and 316.30) cm\(^{-1}\) are related to the formation of tin oxide molecule.

In all the above results, it is recognized that peak at (331.73, 408.88, 432.03, 486.03, 609.46, 648.04, 740.61, 810.05, 864.05, 887.19, 941.20, 972.06, 1010.63, 1110.92, 1172.64, 1211.21, 1311.50, 1350.08, 1419.51, 1720.39, 1735.81, 1905.54, 1951.83, 12005.83) cm\(^{-1}\) are related to quartz substrate.
Figure 1.26: FTIR spectrum of Sn nanostructure deposited on quartz substrate.

Figure 1.27: FTIR spectrum of Sn nanostructure prepared at a- T= 373, b-573, c-873 K and constant oxidation time.
1.4.4 Electrical Properties of SiO2

The logarithmic conductivity as a function of temperature for SnO$_2$ oxide samples prepared at the optimum condition and different film thickness are given in Figure 1.29. It is clear that, the values of conductivity increases with temperature, such as the general characteristics of the semiconductor with increasing temperature lead to an increase in the number of electron-holes pairs resulting on increased conductivity. The linear proportionality in the curve is related to the increase in the number of ionized carriers from the valance band to the conduction band as the substrate is heated.
The value of the activation energy has been estimated using Equation 1.10. Figure 1.30 shows the activation energy as a function of film thickness. It has been found that the conductivity of SnO$_2$ material increase with film thickness which is related to reduction in film resistance.

The variation in the resistivity with thickness for SnO$_2$ film is shown in Figure 1.31. The decrease in resistivity may be due to the conversion of SnO to SnO$_2$ so that the SnO concentration is decreased, leading to an increased conductivity due to the filling of the oxygen vacancies in SnO$_2$ and hence the oxygen-deficient SnO$_2$ would become nearly stoichiometric and insulating. The minimum resistivity of the SnO$_2$ films obtained in this work about $2 \times 10^{-2}$ $\Omega$ cm, and this agrees with the result in similar work [31,32].
Figure 1.32 shows the resistivity of the SnO\textsubscript{2} films versus heating substrate. While the resistivity of films decreases with higher substrate temperature may be attributed to the growth of grain size and improvement of film homogeneity.

![Figure 1.32: Resistivity versus Temperature for SnO\textsubscript{2} film.](image)

The conductivity type of the prepared semiconducting films are introduced by measuring Seeback coefficient and Figure 1.33 displays the relation between thermoelectric power and the heating temperature for samples prepared at optimum oxidation temperature and time. The results indicate that the materials under study are n-type semiconductor possibly due to the donor formation by O\textsubscript{2} vacancies, these results correspond to the published literatures [32].

![Figure 1.33: Thermoelectric power as a function of heating temperature for SnO\textsubscript{2} sample, and value of Seebeck coefficient is for the sample, respectively.](image)

An optimization between the resistivity and optical transmission could be obtained from the value of figure of merit (F.M.) shown in Figure 1.34 as a function of thickness. At low thickness, the films have very high transmission and very high resistivity. As a result, low F.M. value could be achieved with further increase in film transmission and decrease resistivity. Further increase in thickness (200-250 nm), the value of F.M decreases due to the increase in the
film resistivity. So, it is concluded that the thickness of 150 nm give the optimum photovoltaic characteristic for samples respectively.

![Graph showing Figure 1.34: Figure of Merit versus Thickness for SnO₂ samples.]

**1.5 Conclusions**

The summarized results from this work are the following:

a) This work explains the trends to the formation of high purity oxide from their high purity metal by Rapid Thermal Oxidation.

b) Several preparation conditions controlling the properties of the prepared oxide film were optimum oxidation temperature are (873 K) and optimum oxidation time (90 sec).

c) The optical properties results show the cut off wave length to appear at (350 nm) for SnO₂ films respectively for band gap of (3.54 eV) at optimum conditions while lowest resistivity of about (0.022 Ω·cm) was found for SnO₂ film prepared at (150 nm).

d) The X-ray diffraction result shows the SnO₂ films at optimum conditions (873K, 90sec) is stronger and corresponding to the reflection from (101) plane.

The FTIR result shows the SnO₂ films at optimum condition (oxidation temperature 873K and oxidation time 90 sec) is clearly at (686.61 and 316.30 cm⁻¹) and related to the formation O-Sn-O molecule.
References


ABSTRACT

Electrochromic materials are those that exhibit a reversible optical property change under the application of a small applied electric field. Transition Metal Oxides (TMO) are one such class of materials that undergo such a reversible optical and electrical property change due to their special structures and multiple oxidation states. These materials are capable of switching between different metastable states whose optical and electrical properties can be distinctly different. It is this interactivity by way an electric field that makes these materials extremely attractive from the application standpoint.

By preparing these materials in thin film form one gets the further advantage of an even more precise control of the dynamic properties due to the ensuing size (thickness) effect. In addition to this one dimensional effect, by adjusting the nanostructure of these films, a wide range of switching properties can be induced in these films for various applications. In this chapter, the importance of nanostructuring of thin films in tailoring the optical, electrochromic and photonic properties is reviewed. The results on the periodic and non-periodic nanostructuring of two of the most important TMO thin films studied to date, Tungsten Trioxide (WO₃) and Molybdenum Trioxide (MoO₃) are discussed, as examples.

Keywords: Electrochromics, Molybdenum Trioxide, Nanostructure, Optical Switching, Photonic Crystals, Thin Films, Transition Metal Oxides, Tungsten Trioxide.
2.1 Introduction

Materials and systems that change their properties as a function of their environment have always interested humanity since ages. Such changes give the user a control over the properties for various applications. If these changes are reversible or cyclic as a function of the cyclic change of a controllable environment, such interactive materials become even more interesting. The class materials that exhibit a reversible change in optical properties as a function of their environment or an applied external force are called the chromogenic materials. The earliest form of chromogenics practiced was in architecture in the Middle Eastern and tropical countries with hot climates. Trees with large leaves were deliberately grown along the side of the sun facing walls of buildings.

During the summer season, under the shade of the trees, the walls would receive less sunlight thus maintaining a relatively cooler temperature. In winter, however, with the disappearance of the leaves, much more light would fall on the walls providing a warmer interior in these buildings. Hence, the solar radiation received by walls would vary cyclically with the season. In recent years, chromogenics [1], refers to the area of the study of materials that exhibit a reversible change in optical properties (color) with the application of an external force such as heat, light, pressure, electric field and others.

A reversible change in the optical properties produced as a result of the influence of light has come to be known as photochromic change [2]. Photochromic glasses which darken in the sunlight are the most well known example. Similarly, if the reversible change is produced as a result of an applied electric field, it is termed as electrochromic change [3]. In the last few decades, there has been an enormous amount of research carried out in this field. One of the best known examples of this kind is the Liquid Crystal Displays (LCDs) which have found application in an innumerable number of fields.

Upon the application of a small electric field a change in the orientation of the molecules dispersed in the medium occurs thus changing the optical properties of the system. Display devices working
on the basis of a reversible electrodeposition of a metal are also an interesting form of electrochromics. If the reversible change occurs as a result of the heat applied to the system, these types of materials are called thermochromic materials [4]. A vast number of materials exhibit a change in their properties as a function of temperature. However, from the application point of view, the materials that exhibit such changes around the room temperature are more interesting.

The materials that exhibit drastic optical property change around room temperature are rare. In addition, there are also materials that exhibit a change in their optical properties under a gas pressure, termed as gasochromics [5]. Although, other possibilities exist to induce a reversible change in optical properties of materials, the above said forms are the ones that are better known and convenient from the application point of view. Amongst these various forms of chromogenic materials, the electrochromic materials are the ones that have attracted a lot of research and application attention due to the facile and direct control they provide via a small electric field of the dynamic change in optical properties.

This chapter is dedicated to the electrochromic properties displayed by two of the well known Transition Metal Oxides (TMO), Tungsten Trioxide (WO₃) and Molybdenum Trioxide (MoO₃), in their thin films form with an emphasis on the effect of the film nanostructure. Recent advancements in research and application in this area are discussed.

2.2 Transition Metal Oxides

Transition Metal Oxides (TMO), formed by the bonding between the transition metal and the oxygen, constitute one of the most interesting categories of materials exhibiting a wide variety of properties from metallic to semiconductor to insulating ones [6]. Transition metals, by general definition, are the elements that have at least one simple ion with an incomplete outer set of d-electrons. This general definition and the special chemistry of some of these elements restrict this category to the group IV to group XI of the periodic table.
The special properties of TMO stem, on the one hand, from the unfilled d-orbitals of these core transition metals and, on the other hand, from the p-orbital of the oxygen. The extent of the overlap of these orbitals dictates the wide range of electronic properties exhibited by these TMOs [7]. In addition, they also exhibit reversible switching properties under special conditions. The multiple oxidation states of many of these transition metals are the contributing factor to their switching ability and their metastable existence in these states.

Transition metal oxides exhibit a wide range of structures too which contribute to some extent their special properties. In this chapter we would be particularly interested in those TMOs which exhibit electrochromic switching ability under a small electric field. These oxides such as Tungsten Trioxide (WO₃) and Molybdenum Trioxide (MoO₃) are two of the most widely studied TMOs which exhibit reversible optical and electrical property change under the application of an electric field.

### 2.3 Thin Films and Nanostructure

Thin film is often referred to as the bi-dimensional state of matter and is achieved by reducing one of the three dimensions of the naturally occurring bulk materials to a level where a significant change in the physical properties of the materials occurs due to the size (thickness) effect [8]. This bi-dimensional state is often characterized by an enormous surface to volume ratio i.e. is a small amount of material is spread over a large surface. For transparent insulating materials (no free electrons), this is achieved when the thickness is of the order of the optical wavelength of interest.

A strong dependence of the optical properties on the film thickness is seen due to the interference effect. In metals and semiconductors (with free or quasi-free electrons) this size reduction refers to film dimensions of the order of the free electron mean free path. A significant dependence of the optical and electrical properties of these materials as a function of thickness is achieved. The film conductivity and optical properties (transmittance, reflectance and absorbance) can be tailored by adjusting the film thickness within the ‘skin depth’ of the
metal. In addition to this size dependence, where it is assumed that the film maintains the same structure and density as the bulk material, one can also induce a nanostructure within the film. In this state, the film is formed from an assembly of the nanoparticles of the material. Further, this assembly of grains can be periodic or non-periodic. Shown in Figure 2.1 is a qualitative representation of these three types of films.

A normal thin film (also referred to as the coarse grain film) is characterized only by its size effect through thickness. The nanostructured [9] (also referred to as the mesoscopic) films, on the other hand, are made up of nanometer sized grains arranged irregularly (Figure 2.1b) or regularly (Figure 2.1c). Further, it is to be noted that the size of these particles arranged periodically or non-periodically can be adjusted for response in the wavelength region of interest. The large internal surface and porosity can lead to an even higher surface to volume ratio.

Hence, a totally new state of materials distinct from the bulk and thin films can be created by nanostructuring of the known materials [10-12]. The high density of pores and large internal surface lead to
many interesting properties such as an efficient transport of doped species (ions and atoms) and an efficient nanocomposite formation. Generally, the surface state, unlike the bulk state, is a non-equilibrium state due to the unbalanced inter-atomic forces. The adsorption of various molecules to which these surfaces are exposed re-establishes the equilibrium. Hence, the enormous internal surface formed by the nanostructuring is a highly active front with very high affinity towards surrounding molecules.

Both the physical and chemical aspects relating to nanostructuring of materials have important implications. With a precise control of dimensions (thickness) and the nanostructure via the preparation conditions one can implant totally new physical and chemical properties into hitherto well known materials. By general definition, films made up of grains of the size varying from a few nanometers to a few hundred nanometers are termed nanostructured or mesoscopic films. In addition, if these grains are arranged periodically on light wavelength scale, interesting photonic and optical properties can be induced in these films. The electrochromic properties of periodically and non-periodically nanostructured WO$_3$ and MoO$_3$ thin films is discussed below.

The nanostructuring of Titanium Dioxide (TiO$_2$) thin films are a well known example. The Coarse Grain (CG) or compact form of these films which hardly exhibited any electrochromic optical change was rendered highly efficiently coloring by their nanostructuring. This has been attributed to the significantly improved light harvesting (light-matter interaction) and interfacial (matter-matter) interaction [13]. Similarly, the technique of Glancing Angle Deposition (GLAD), which is one of the most efficient ways of periodic and non-periodic nanostructuring of materials, has been used to vary systematically the refractive index of various materials over a wide range.

The refractive index of silicon has been varied from its bulk value of 3.5 to that of ambient 1 by systematically varying the porosity (nanostructure) via the tilt angle [14]. Also, the systematic variation of the birefringence of silicon films has been achieved through the variation of the substrate tilt angle [15]. In our own laboratory, it has been demonstrated that through a systematic variation of the
sputtering pressure, the refractive index (n) of Tungsten oxide (WO₃) can be systematically varied between 2.15 and 1.87 [16]. These results are shown in Figure 2.2. Hence, the nanostructuring of materials and thin films have become an important tool in inducing new properties into the existing materials.

### 2.4 Electrochromic (EC) Materials

As pointed out above, these are materials that change their optical properties reversibly under the application of a small electric field [1]. In TMO based electrochromism, upon the application of the electric field, due to the insertion or extraction of certain charge species (electrons and ions), a reversible chemical reaction takes place. A new product with optical properties different from the original product is formed reversibly giving the coloration. Tungsten Trioxide (WO₃) is the best and the most studied TMO exhibiting this type of coloration. WO₃ is generally transparent in its normal state and reversibly colors to a deep blue state under the application of a small electric field. This coloration which occurs under the double insertion (electrons and ions) into the film and the reversible formation of the deep blue new product, the tungsten bronze, is termed the cathodic coloration. The ensuing reaction that occurs with the application of the electric field can be represented as follows:

\[
\text{WO}_3 + x e^- + xM^+ \leftrightarrow M_x\text{WO}_3 \text{ (cathodic coloration)}
\]

Figure 2.2: Effect of nanostructure on the refractive index (n) of sputter deposited Tungsten trioxide (WO₃) films under various deposition pressures.
Similarly, there are other TMOs that color under the double extraction i.e. in the normal state they are already colored and with the insertion of electrons and ions they become more transparent in the spectral region of interest. This type of coloration is termed anodic coloration. One of the most well known examples of this type is the Vanadium pentoxide ($V_2O_5$) which in its normal state is yellowish in color and upon the double insertion becomes more transparent in the visible region. The electrochromic coloration that takes place under the application of a small electric field can be represented as follows:

$$V_2O_5 + xe^- + xM^+ \rightarrow M_xV_2O_5 \text{ (anodic coloration)}$$

Yellow

Transparent

A commonly used approach in electrochromic devices is to combine a cathodically coloring TMO as the base layer, in which occurs the functional coloration, with an anodically coloring material as the ion storage layer. Generally, a five component structure, as shown in Figure 2.3, is necessary for a stable functioning of the EC device. This includes two Transparent Conductors (TC) used to apply the electric field, the Tungsten oxide base Electrochromic (EC) layer, an isolating Ion Conducting (IC) layer and an ion storage or Counter Electrode (CE) layer [3].

![Diagram of 5-layer electrochromic devices in the transparent (a) Normal States (b) Colored States.](image)
This entire stack is deposited on a transparent substrate such as glass. Under normal state (Figure 2.3a) the entire stack is comparatively transparent with the ions being stored in the counter electrode. Under the application of a small electric field and the double insertion of electrons (from the TC) and ions (from the CE) into the base EC layer, both the CE layer and the EC layer change color (Figure 2.3b). This complimentary behavior leads to a very effective coloration of the device. Many electrochromic devices have been fabricated based on this five layer approach [18-20].

The design of the EC devices commences from the base EC layer itself and the coloration efficiency it can undergo between the colored and bleached modes. Then the other layers are adjusted to accommodate the amount of charges required for this optical change [21]. Hence, the base EC layer plays the pivotal role in the overall optical performance of the EC device. Due to this reason a vast majority of the research work in the electrochromics field is dedicated to the study, understanding and improvement of this base layer. Tungsten trioxide (WO₃) and Molybdenum trioxide (MoO₃) are two of the most studied materials for this application. As outlined above, the nanostructure plays an important role in inducing certain new electrical, optical and electrochromic properties in these films.

2.4.1 Non-Periodically Nanostructured EC Thin Films

WO₃ is by far the most studied material in electrochromics work. This is owing to many reasons. The optical modulation occurring in WO₃ films is situated in the visible and solar spectral region which makes it interesting from the display device and energy efficiency application point of view. The optical modulation exhibited by these films can be absorption based or reflectance based, depending on whether the film is amorphous or polycrystalline [1], respectively. The WO₃ films exhibit a very high chemical and physical stability. The films also show a very high ionic charge storage capacity as well as high coloration efficiency. These films can be prepared by almost every thin film deposition technique known. In addition, most of these virtues of WO₃ films have been found to be nanostructure dependent which makes it an even more interesting and versatile material to work with.
WO$_3$ presents a perovskite-like structure with corner sharing WO$_6$ octahedra. The tungsten atom is present at the center of this octahedral with each of the corners occupied by the oxygen atom. It is the substantially open space in this octahedral that can accommodate the inserted ions which lead to the coloration. The inserted electrons, on the other hand, can be localized on the tungsten site or be free (non-localized), depending on the whether the WO$_3$ film is amorphous or crystalline [1]. The injection of electrons and ions in amorphous WO$_3$ films gradually leads to the development of the absorption band, generally, located in the visible and near infrared regions of the spectra.

This absorption band increases with increase in the amount of ions and electrons inserted. Visibly, this manifests as a deep blue coloration. Similar coloration is also found in oxygen deficient WO$_3$ thin films. In polycrystalline WO$_3$ films, however, the injected electrons become free electrons and contribute to the reflectance of the film as per the Drude model [3]. With increasing ions and electrons inserted into such a structure, with the shift of the plasma frequency towards lower wavelengths (higher energy), a wavelength selective reflectance increases. For the normal free electron density possible for such semiconductors, this increase in reflectance is effective, generally, in the near infrared region.

The plasma frequency and the reflectance change can manifest in the visible region only at very high concentration of doping of ions and electrons which is only possible in single crystals. These reasons make the two types of WO$_3$ films suitable for different applications. The amorphous films prone to absorption modulation are well suited for display device application, where as the polycrystalline WO$_3$ showing wavelength selectivity are more suitable for solar energy or heat management applications. In addition to the phase (amorphous and/or polycrystalline behavior) dependent electrochromic behavior is the nanostructure directed behavior. The high density of grain boundaries, the large internal surface and the porosity imposed in these structure play an important role.
In our laboratory, the effect of nanostructuring of the WO$_3$ films by various techniques on its properties has been studied. Using the thermal sublimation and condensation under various chamber pressures and treatment temperatures, Polycrystalline (PC), Coarse Grained (CG) and Nanostructured (NS) WO$_3$ films have been obtained with varying degree of morphology [22]. As can be seen from the Atomic Force Microscope (AFM) images of these films in Figure 2.4, the nanostructure changes quite profoundly with the deposition pressure and the ensuing thermal treatment.

Figure 2.4: Atomic force micrographs (AFM) of the WO$_3$ films: (a, b) Two-dimensional and three-dimensional view of amorphous (CG) film (c, d) Two-dimensional and three-dimensional view of Polycrystalline (PC) film (e, f) Two-dimensional and three-dimensional view of Nanostructured (NS) film.
For the actual characterization of these individual films an electrochemical method [3] or a dry method [17] of lithium insertion was used. The changing morphology had a profound effect both on the optical properties and the electrochromic properties of the films, as shown in Figure 2.5. While the normal (no lithium, curve A in Figure 2.5(a, b, c)) state transmission of the Coarse Grained (CG) and the Polycrystalline (PC) film are marred either by strong interference and/or absorption effects, the Nanostructured (NS) film was found to be extremely transparent due to the near total suppression of the interference effect.

The subsequent interference peaks in the transmission curve (Figure 2.5a) are suppressed due to the absorption emanating from an oxygen deficient film, as discussed above. This absorption is situated around 800 nm. Under the insertion of lithium, all the three types of films show an efficient coloration. However, there are distinct differences in the nature of this coloration.

Figure 2.5: Spectral transmission changes occurring in amorphous (a) Polycrystalline (b) Nanostructured (c) WO$_3$ films with the insertion of various amounts of lithium between 0 nm and 20 nm of lithium.
As can be seen from the Figure 2.5 (a), the absorption band in the amorphous band situated around 800 nm deepens and the coloration is more effective in the higher visible and lower NIR regions of the spectra. In the polycrystalline film, however, much more efficient coloration occurs spanning the entire spectral region studied. This is attributable to the polycrystals embedded in the WO3 amorphous matrix. Hence, such a film has contributions both to the absorption modulation and reflectance modulation which manifests as a broadband modulation in transmission (Figure 2.5b).

The nanostructured film (Figure 2.5c) starts out from a highly transparent state and exhibits a selective electrochromic modulation under lithium insertion which is mostly concentrated in the near infrared region. It was confirmed by independent reflectance measurements that the modulation was totally absorption based. The location of the absorption band and quasi-amorphous nature of the NS films presents an anomaly. The Coloration Efficiency (CE) of these films is shown in Figure 2.6. The PC films in this work show the most efficient coloration in the entire solar spectral range with peak efficiency in the NIR region (1200 nm). The CG or amorphous films show a less efficient coloration with peak value at lower wavelengths (800 nm). The NS-WO3 on the other hand shows the most selective coloration with a smaller change in the visible region and very efficient changes in the near infrared region (1200 nm).

Hence, each one of the films is suitable for different applications [21]. The amorphous and polycrystalline films with their coloration efficiency spanning both the visible and solar spectral ranges are suitable for display and energy efficiency applications. The nanostructured film with its wavelength selective coloration efficiency is more suitable for thermal management applications.
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Figure 2.6: Coloration efficiency (CE) of the Polycrystalline (curve A), Nanostructured (curve B) and Amorphous (curve C) WO$_3$ film as a function of wavelength for an insertion of 20 nm (approx. 12.5 mC/cm$^2$) of lithium.

Clara Santato et al. [23] have demonstrated the importance of nanostructuring of WO$_3$ films prepared using a novel sol-gel method with Poly (Ethylene Glycol) (PEG) as a structure directing agent. They have achieved highly transparent and high quality nanocrystalline WO$_3$ films with preferentially oriented monoclinic phase. The porosity of the film as well as the shape and sizes of the nanocrystals is found to be highly dependent on the preparation and thermal treatment parameters. The SEM images obtained on these films are shown in Figure 2.7 where the nanoparticles show a systematic evolution from a needle-like structure to a plate-like structure while undergoing a dimension transformation from a few nanometers to a 100 nm.

Figure 2.7: Scanning Electron Microscope (SEM) images of WO$_3$ films prepared by the deposition of a tungstic acid/PEG 300 colloidal solution and annealing (A) At 400°C for 30 min, (B) At 400°C for 10 h, (C) At 450°C for 30 min, (D) At 500°C for 30 min, (E) At 550°C for 30 min, (F) At 600°C for 30 min.
A direct correlation between the crystallinity and the photoresponse of these films has been established with the most crystalline samples showing the best photoresponse. The thinner forms of these mesoporous films are shown to have very good electrochromic properties. More recently, N.N.Dinh et al. [24] have used a simple and economical method to obtain nanostructured heterojunctions of TiO$_2$/WO$_3$. The work was undertaken with the aim of achieving chemically stable and efficient electrochromic devices. The approach proposed by these authors seems to be advantageous for large area deposition of these films.

C.M.White et al. have deposited WO$_3$ nanoparticles on an ITO coated polymer [25] using a hot-wire chemical vapour deposition method. The virtue of this method is the ability to tailor the particle size and morphology of the WO$_3$ nanoparticles as well as their high density production. In addition, the authors have demonstrated the uniform deposition of these films on flexible polymers without any damage. A simple hydrothermal method has been proposed to obtain WO$_3$ nanorods and nanowires on a large scale by Zhanjun Gu et al. [26]. These one-dimensional materials present unique properties interesting from both scientific points of view as well as for applications in electronics and optoelectronics.

Although, no electrochromic work is reported in this article, the work is interesting for the fabrication and control of nanostructures. By using the powerful technique of Glancing Angle Deposition (GLAD) [14], nanostructured WO$_3$ thin films with varying degree of grain sizes, film porosity and refractive index have been deposited in our laboratory [27]. These nanostructures, in addition to their high transparency in the normal state, show significant electrochromic coloration. The coloration efficiency is directly correlated to the quantity of WO$_3$ present in these nanostructures. Ultrathin WO$_3$ nanodisks of various dimensions and possessing single crystal characteristics have also been obtained using PEG as structure directing agent [28]. The flatness and the aspect ratio of these materials can be very useful for the different applications of WO$_3$ including the electrochromic devices. C.V.Ramana et al. [29] have deposited the nanostructured WO$_3$ thin films using the Pulsed Laser
Deposition (PLD) method. The confirmation of the structural and phase stability of films prepared by PLD even up to temperatures of 300°C is an interesting virtue from the electrochromic device fabrication point of view.

WO₃ nanorod assembly has also been carried out at room temperature without conventional surfactants or structure directing agents by the hydrothermal method by Jinmin Wang et al. [30]. The EC devices built from these assembled 1-D nanorods exhibit a high number of coloration/bleaching cycles and high efficiency coloration. The characteristics of these films are shown in Figure 2.8. However, the coloration response is very slow even in liquid electrolytes. Using a novel combination of ionic and polymeric surfactants. Deepa, M et al. [31] have successfully deposited thin film nanostructures by electrodeposition.

WO₃ films assembled of various nanoshaped structures and orientation have been deposited. The low temperature annealed films show a very good coloration efficiency as well as high cycling stability. The coloration efficiency drops briskly at higher temperatures. The poor response of the annealed films is attributed by the authors to the coarse grained nature of the framework inhibiting the passage of lithium. Novel electrochromic devices based on the combination of nanostructured WO₃ thin films as base electrochromic layer and dye-sensitized TiO₂ nanocrystalline thin films as counter electrode, have been built by P.Bonhôte et al. [32]. The device shows a very highly efficient EC coloration and very stable coloration/bleaching operation, with very slight degradation even after more than 14,000 cycles. The charge capacity of the nanostructured WO₃ was found to be higher than that of the derivatized TiO₂ nanocrystalline films. Hence, further improvement in efficiency is possible using thicker films.

Molybdenum Trioxide (WoO₃) is another well known candidate showing very rich cathodic electrochromic coloration as well as an efficient photochromic coloration. The crystal structure of WoO₃ is similar to that of WO₃ being perovskite-like. The thin films of WoO₃ have been studied quite a bit for their EC performance [33]. Despite their high EC coloration efficiency this material has received far less research
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Figure 2.8: Electrochromic coloration of the WO$_3$ nanorod film as function of the applied voltage in an electrochemical cell containing 1.0 M lithium perchlorate LiClO$_4$) in propylene carbonate (PC) as the electrolyte: (A) The as-prepared film, (B) Colored at -1.0 V, (C) Colored at -2.0 V, (D) Colored at -3.0 V, (E) Bleached at 3.0V, (F) Corresponding UV-vis spectra (G) Switching time characteristics between the colored and bleached states for the WO$_3$ nanorod film measured at 3.0 V at 632.8 nm wavelength.

and application attention than WO$_3$ thin films. Similar to the WO$_3$ thin films, new traits and improved performance of MoO$_3$ thin a film has been achieved by nanostructuring the films.

Dillon et al. [34] have used the Hot-Wire Chemical Vapour Deposition (HWCVD) to achieve MoO$_3$ thin films made up of nano-rods and nano-particles of dimensions between 10 and 50 nm. The incorporation of these nano-particles seems to have led to high performing EC devices, especially from the point of view of EC operation stability. The GLAD method has been used in our laboratory to achieve nanostructured MoO$_3$ thin films made up of 10 to 50 nm grain sizes [35]. A distinct evolution in the nanostructure was observed in these films upon annealing. These changes in structure were also reflected in the electrochromic performance of the films.

While the as-deposited samples showed a significant coloration in the visible region, typical of the MoO$_3$ films, the annealed samples showed a very pronounced EC coloration in the visible and the infrared region. Hence, from application point of view, the former type of films is suited for display devices and the latter for energy efficiency.
applications. The possibility of structure tailoring of electrochromic properties is demonstrated by Patil et al. [36] in their work on electrodeposited MoO$_3$ thin films with rod-like features. The films show a very good coloration in the visible region.

Sputter deposited nanostructured thin films of MoO$_3$ have been studied by Taj et al. [37]. The average grain size in these samples was found to be between 48 and 60 nm. The method of dry lithiation was used to follow the Electrochromic (EC) coloration. The EC coloration was found to be more centred in the visible region of the spectrum giving a darker appearance of the films. This is different than the typical bluish coloration often exhibited by the WO$_3$ films. An interesting feature reported in this article is the evolution of the nano/microstructure of the MoO$_3$ films as a function of the lithium inserted.

There seems to be a systematic inflation of the grains at the initial stages of the lithium insertion which eventually seems to distort the surface with continued insertion. McEvoy et al. [38] have studied the structural evolution and electrochromic properties of electrochemically deposited MoO$_3$ thin films. Post-deposition sintering seems to have a profound effect on the structure and EC performance of these films. The films sintered at low temperature seem to be amorphous, mixed valent and incorporate a lot of water in the structure. As a result these films show a good EC behavior in terms of reversibility. The films sintered at higher temperature were found to be more monovalent, dehydrated and mixed (amorphous and nanocrystalline) phased.

As a result and similar to the mixed phase polycrystalline films of WO$_3$ films discussed above [22], these films show a better optical modulation but with a reduced reversibility. These authors also have reported the structural distortion occurring in the MoO$_3$ polycrystalline films with the electrochemical insertion of lithium. Similarly, sol-gel prepared and sintered MoO$_3$ films have been studied by Hsu et al. [39]. The evolution of initially amorphous films towards well defined nanostructure with sintering is reported.
This structural evolution is shown in Figure 2.9. The work seems to indicate the existence of an optimum size of the nanocrystals dictated by an optimum treatment condition (350°C) in order to yield the best optical and electrochromic performance as shown in Figure 2.10. The work clearly indicates the role of crystal and/or grain size both on the optical and electrical properties of thin films. In this work films heated beyond 350°C films tend to have large grains leading to diffuse reflectance and lower transparency. The MoO$_3$ films heated to 350°C seem to show also the best EC performance due to the inter-particle space which is important for lithium diffusion. These films also show a good reversibility.

Figure 2.9: SEM micrographs of the sol-gel prepared MoO$_3$ thin films sintered to various temperatures.
2.4.2 Periodically Nanostructured EC Films

The aspect of periodically nanostructuring the same materials discussed above opens a whole new dimension of properties in photonics. When the grains or the nanocrystals of which the film is formed are of the dimensions of the wavelength of light and are periodically arranged, (Figure 2.1c), it leads to what are called as photonic crystals [40]. A beam of light incident upon this periodic structure experiences a periodic variation of dielectric constants. Bragg condition (for scattering) leads to the presence of a bandgap (called the Photonic Bandgap - PBG) for certain wavelengths.

These wavelengths are forbidden from entering the periodic structure. This effect is similar to the energy bandgap experienced by the electrons travelling in a crystal. The photonic bandgap depends strongly on the correspondence between the incident wavelength, scale of the periodicity (spacing) of the crystal and the contrast between the dielectric constants (grains and the interstices). The presence of the PBG has important consequences in the area of photonics. Photonic crystals of different dimensions (1-D, 2-D and 3-D) have been fabricated and studied for various applications.
However, if the photonic crystals are built out of switchable materials such as the Transition Metal Oxide (TMO) based chromogenic materials; the dielectric constants of the materials can be altered reversibly through various external influences. This can lead to a dynamic control of the photonic band gap. Such PBG tunable photonic crystals are of great importance in the area of communications and sensors [41]. Extensive work is being carried out in our laboratory on various ways of fabrication and operation of Transition Metal Oxide (TMO) based tunable photonic crystals. WO$_3$ inverse opals have been obtained by using polystyrene beads of 300 nm and 760 nm diameter. By dip-infiltrating and sintering the polystyrene templates with WO$_3$ by the sol-gel technique, WO$_3$ inverse opals were obtained. In Figure 2.11 are shown these WO$_3$ inverse opals. The hexagonally close packed pores (air) were surrounded by the WO$_3$ frame structure providing sufficient refractive index contrast.

![Figure 2.11: SEM surface images of the WO$_3$ inverse opals obtained with templates of 300 nm and 760 nm sizes.](image)

The reflectance spectra of these samples are shown in Figure 2.12. Each of the samples shows two bandgaps: the 300 nm template based sample shows the bandgaps at 344 and 532 nm wavelengths whereas the 760 nm template based sample shows the bandgaps at 700 and 1302 nm, respectively.

It was demonstrated that, these bandgaps can be continuously tuned electrochromically with the insertion of lithium. These results for dry lithium insertion are shown in Figure 2.13 for the WO$_3$ inverse opal...
based on the 300 nm template. The possibility of building continuously tunable photonic crystal devices based on chromogenic materials was also demonstrated [42]. Tunable one dimensional photonic crystal (periodic multilayers) based on the electrochromic coloration of porous and dense WO$_3$ films are proposed by Baloukas et al. [43]. Interference filters have been built out of these alternating quarter-wave stacks and the films are colored by the insertion of protons. These systems are proposed for energy efficiency application as smart windows.

Figure 2.12: Reflection spectra at near-normal-incidence of the samples in Figure 2.11: (a) 300nm template based WO$_3$ inverse opal and (b) 760 nm template based inverse opal.

Figure 2.13: (a) Reflection spectra at near-normal-incidence of the 300 nm WO$_3$ inverse opal as a function of inserted lithium (b) First reflection peak (c) Second reflection peak of this sample with insertion of lithium (d) First reflection peak (e) Second reflection peak mid-gap position as a function of inserted lithium.
2.5 Conclusion and Future Work

The importance of nanostructuring of thin films in general is reviewed in this chapter. Thin films offer the ability to alter greatly the optical, electrical and other size dependent properties of materials. The controlled variation of size of particles forming these films, the so-called nanostructured or mesoporous films, offer a wide variety of possibilities in tailoring the properties of materials. If this nanostructuring is applied to switchable materials such as the Transition Metal Oxides (TMO) which show a wide variety of chromogenic (electrochromic, thermochromic, photochromic) properties, the nanostructuring can lead to far reaching consequences.

We have examined here some of the work carried out on the nanostructuring of the most well known electrochromic thin films, WO$_3$ and MoO$_3$, to illustrate this point. Both the periodic and non-periodic nanostructuring of these materials is discussed. The wide range of properties a single material is capable of showing as a function of its nanostructure indicates that there is a tremendous potential of these materials to be explored. Although, only the electrochromic properties are discussed here, the nanostructuring of the WO$_3$ and MoO$_3$ films can also be used to tailor their other switching (photochromic and gasochromic) properties. The non-periodic nanostructuring of these materials can be achieved by applying a wide variety of deposition techniques, both chemical and physical.

However, the techniques available for their periodic nanostructuring are limited. A reliable method to obtain the periodic arrangement of particles and on a large scale is yet to be developed. Hence, the work related to the fabrication and study of 3D photonic crystals is in its infancy. The demonstration of the continuous tunability of the PBG in such photonic crystals is said to be an ‘exciting new development’ [41] that should of great interest to the photonic industry for designing novel optical devices. Remarkable research and application possibilities exist in the area of nanostructuring of transition metal oxide thin films.
For example, there is no work to date carried out on building photonic crystals based on the MoO$_3$ particles. This work will be interesting from the point of view of photochromics as well as electrochromics. If realised, such devices would provide the possibility to continuously tune the photonic bandgap through the influence of light as well as an applied electric field. Possibility also exists for coloring (writing) by laser and discoloring (erasing) by an electric field in many optical memory storage applications. Further, photonic crystals of various lattice constants can be built for applications in various wavelength regions of interest.

References


CHAPTER 3
III-V Semiconductors for Nanoscale CMOS Technology

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ABSTRACT

The microelectronic community has been forced to use alternate channel materials like high mobility III-V semiconductors in the mainstream digital electronics in order to continue scaling of a MOSFET beyond sub 45 nm. In this chapter, a review of III-V MOSFET structures and models has been done. Various challenges such as suitable low defect density dielectric deposition, integration with silicon, mobility issue with p-MOSFETs and their possible solutions along with the design issues have been discussed and reviewed while implementing the III-V technology for nanoscale MOSFETs.

Keywords: CMOS, MOSFET, Nanoscale, Design, Dielectric Interface.

3.1 Introduction

As per the Moore’s Law, the number of transistors per Integrated Circuit (IC) doubles every 18 months, and it has been the guiding principle for the semiconductor industry for more than last six decades [1]. The sustaining of Moore’s Law requires continual transistor miniaturization and performance improvement. This has resulted in the increase in power dissipation due to increase of transistor density and increased static leakage currents.

As the transistors are scaled down, the prime area of concern becomes of the drive current deterioration. This is because of the very high vertical and horizontal electrical field which reduces the carrier mobility and hence the drive current in scaled devices. At 90 nm logic node, the strained Si technology for mobility enhancement in the
MOSFETs by way of germanium incorporation into silicon lattice or by uniaxial compressive/tensile strain into the Si channel was introduced [2]. The vertical scaling (gate oxide scaling) also continued to sub angstrom levels of less than 30Å at 90 nm technology.

This lead to the increasingly high tunneling currents through the gate oxides and hence the increased static power dissipation in MOS devices [3]. The solution which came was the introduction of alternate dielectric with higher dielectric constant and larger physical thickness as SiO₂ was running out of atoms to scale [4]. To scale down further 45 nm logic node, the solution is either to reduce the transistor’s operating voltage or use a very high mobility material in the substrate to keep delays and power dissipation under the acceptable limits. With Si transistors, driving the voltage down while simultaneously enhancing transistor performance has become increasingly difficult, and the operating voltage for CMOS has reached sub 1 V for the last few generations of technology and the threshold voltage cannot be scaled down as it would increase the subthreshold currents.

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The technology scaling trend [5] shown in Figure 3.1 clearly indicates that, to take the scaling beyond 32 nm in 2010 to 11 nm in 2016, there has to be paradigm shift in the existing scaling approaches by replacing the conventional silicon planar MOSFETs to non conventional non planar MOSFETs made up of III-V materials. In this regard, ITRS Emerging Research Devices (ERD) and Emerging Research Materials (ERM) have also been considering for other technologically feasible solutions for scaling CMOS to and beyond the 16 nm technology generation by replacing silicon with other semiconductor channel materials and identifying new logic devices and architectures [6].

Figure 3.1: The technology roadmap for alternate channel materials [5].
The high mobility III-V devices are highly speedy and thus require lower supply voltage which will help in scaling down of the supply voltage further. Nevertheless, the possible introduction of III-V semiconductors into main stream digital microelectronic devices such as MOSFETs is full of challenges/issues like need of a suitable gate dielectric, integration with existing CMOS technology, it can still be a suitable choice to enable further scaling with deeper research initiatives in finding solutions in tackling challenges posed by this technology. Table 3.1 shows a comparison chart of possible III-V materials as replacements to silicon or germanium materials.

Table 3.1: Silicon, germanium and other compound semiconductors for microelectronic applications.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>Ge</th>
<th>Si</th>
<th>STRAINED SILICON</th>
<th>InP</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Effective Mass</td>
<td>0.082</td>
<td>0.19</td>
<td>-</td>
<td>0.08</td>
<td>0.063</td>
</tr>
<tr>
<td>Hole Effective Mass</td>
<td>0.33</td>
<td>0.15</td>
<td>-</td>
<td>0.6</td>
<td>0.076</td>
</tr>
<tr>
<td>Electron Mobility (cm²/Vs)</td>
<td>3900</td>
<td>1450</td>
<td>2900</td>
<td>5370</td>
<td>9200</td>
</tr>
<tr>
<td>Hole Mobility (cm²/Vs)</td>
<td>2270</td>
<td>500</td>
<td>2200</td>
<td>150</td>
<td>400</td>
</tr>
<tr>
<td>Bandgap (E₉) (eV)</td>
<td>0.67</td>
<td>1.12</td>
<td>1.08</td>
<td>1.34</td>
<td>1.42</td>
</tr>
<tr>
<td>Γ-L Separation(eV)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.59</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Source: The data has been taken from [7].

Table 3.1 clearly shows that, the compound semiconductors have higher electron mobility and velocity that the conventional materials like Si or Ge. However, the whole mobility does not show much improvement in III-V semiconductors.
3.2 Evolution of III-V MOSFETs

The last six decades saw a period of intense development and rapid progress in silicon MOSFET technology. Attempts during this period to develop a non silicon MOSFET technology (III-V semiconductors mainly) were not too successful for mainstream digital microelectronics. One of the prime reasons was the lack of production of suitable gate dielectric over the III-V semiconductors.

In this section a review of three types of the compound semiconductor based MOSFETs which have been evolved with time parallel with the development of the silicon technology has been done.

3.2.1 III-V MOSFET: (GaAs, InGaAs)

GaAs MOSFET was reported in 1997 by Parikh et al. [8] using Al2O3 as a dielectric. The drain current for this MOSFET was 330 mA/mm, breakdown voltage (Vbd) as 30V and transconductance (gm) as 110 mS/mm. Another dielectric Ga2O3 and Gd2O3 called as GGO is also used in the GaAs MOSFETs. In GGO based MOSFETs [9,10], trap charge density (Dit) is very low of the order of 2×1010 cm–2 eV–1 for a GaAs p-MOSFET. The reported gm was 0.3 mS/mm and Vbd of 3.6×106 V/cm [9, 10].

For In0.53Ga0.47As MOSFET with GGO, the gate leakage current is 10–9 A/cm2 and Vbd of 107 V/cm [11] which is higher than as reported in [9,10]. J.Y.Wu et al. [12] fabricated MOSFETs with GaAs immersed into Ga-ion containing nitric acid solution to make a stable oxide. This liquid phase oxide gate MOS has Vbd of 4.5 × 10⁶ V/cm and gate oxide leakage current as 10–8 A/cm². Yeong [13] reports the fabrication and characterization of the the liquid phase oxidation of the n-channel depletion-mode GaAs MOSFET.

Various other attempts have also been made to fabricate a MOSFET with the desired properties of low interface trap densities, higher drain currents. SiO2 on GaAs for a MOSFET reported higher Dit of 10¹⁶ cm⁻² eV⁻¹[14]. Thermal oxidation of InAlAs showed gm of 6 mS/
mm for gate length of 8 μm [15]. Ga₂O₃ on In₀.₂Ga₀.₈As p-MOSFET [16] showed interface charge density of 3×10¹¹ cm⁻²eV⁻¹. GGO on Be-doped n-type InGaAs n-channel MOS showed Dᵣ of the order of 10¹¹ cm⁻²eV⁻¹, maximum drain current of 30 mA/mm, gₘ of 1.7mS/mm and threshold voltage 1.8 V [17]. Lin et al. [18] reported Al₂O₃ on GGO on In₀.₂Ga₀.₈As channel giving a gₘ value of 48 mS/mm and maximum drain current of 135 mA/mm [18]. ZrO₂ on InGaAs grown on p-type InAlAs shows Dᵣ of 10¹³ cm⁻²eV⁻¹ [19]. InGaAs MOSFET [20] with ALD high-k Al₂O₃ dielectric has a gate oxide leakage current less than 10⁻⁴ Acm⁻² at 3V gate bias and Dᵣ of 1.4x10¹² cm⁻²eV⁻¹ has also been observed. Radosavljevic et al. [21] describe non-planar, multi-gate InGaAs quantum well field effect transistors (QWFETS) with high-k of thickness 20.5Å with low gate oxide leakage and high quality gate dielectric interface. Moran et al. [22] report the performance of 300 nm, 500 nm and 1μm metal gate, implant free, enhancement mode stacked AlGaAs/InGaAs/AlGaAs/GaAs MOSFETs with a dielectric Ga₂O₃/(GaₓGd₁₋ₓ)₂O₃.

The reduction in threshold voltage from 0.26 V to 0.08 V and an increase in gₘ as the gate dimension is reduced from 1 μm to 300 nm have been reported. Maximum drain current of 420 μA/μm and extrinsic gₘ 400 μS/μm are obtained from these devices. Gate leakage current of less than 100pA and subthreshold slope of 90 mV/decade were obtained for all gate lengths. Yanning et al. [23] demonstrate depletion-mode In₀.₇Ga₀.₃As buried-channel MOSFETs with HfO₂ gate dielectrics. The device reported good output and pinch-off characteristics, low leakage, and high Iₜ/₀ff of 10⁵.

Yanning et al. [24] report the long-channel GaAs MOSFETs and short-channel InGaAs MOSFETs with high current of 960 μA/μm and gₘ of 793 μS/μm with the results on 80 nm MOSFETs. Lina et al [25] report n- and p-type Al₂O₃/(GGO)/In₀.₂Ga₀.₈As/GaAs MOS capacitors using different metal gates. The In₀.₂Ga₀.₈As based MOS capacitors showed remarkably well-controlled threshold voltage. Zhao et al. [26] report the comparison of single dielectric HfO₂ based In₀.₅₃Ga₀.₄₇As MOSFETs and other stacked dielectrics based MOSFETs using the In₀.₅₃Ga₀.₄₇As MOSFET.
The results show that, the stacked dielectric case has lower subthreshold swing, higher drive currents and the $g_m$. This is due to the better interface quality in the stacked dielectric MOSFETs. Zhou et al. [27] report implant-free In$_{0.53}$Ga$_{0.47}$As channel MOSFETs grown on GaAs substrates by Metalorganic Chemical Vapor Deposition (MOCVD) and ALD Al$_2$O$_3$ was used as gate dielectric. The maximum drain current of 590 mA/mm and $g_m$ of 501 mS/mm was reported. The maximum gate leakage is 7.2nA/mm at the forward gate bias of 4V. Jon et al. [28] report a stacked layer GaAs substrate with Al$_2$O$_3$ as a dielectric.

Maximum drain current of 10.6 mA and $g_m$ of 11.25 mS/mm was achieved. Wu et al. [29] report inversion-mode InGaAs MOSFETs with gate lengths down to 150 nm with $g_m$ exceeding 1.1 mS/μm. The inversion-mode InGaAs FinFET with ALD Al$_2$O$_3$ as gate dielectric has also been reported. Ok et al. [30] report TaN/ZrO$_2$/In$_{0.2}$Ga$_{0.8}$As/In$_{0.53}$Ga$_{0.47}$As n-MOSFET with ALD ZrO$_2$. Improved drain current was reported. Lina et al. [31] report using UHV-deposited gate dielectric stack of Al$_2$O$_3$/GGO and TiN metal gate, the first self-aligned inversion-channel In$_{0.53}$Ga$_{0.47}$As MOSFETs of 1 μm gate length with a maximum drain current of more than 900mA/mm and a $g_m$ of 670mS/mm. Xu et al. [32] report ALD Al$_2$O$_3$ on GaAs on different crystal orientations.

The electrical measurements results obtained were different on different orientations. Passlack et al. [33] report electron mobilities exceeding 12,000 and 6000 cm$^2$/Vs have been measured on InP and GaAs based MOSFET structures respectively. INTEL has also shown keen interest in the production of III-V MOSFETs since the year 2005. In 2009, INTEL has reported a novel device of Schottky-gate InGaAs QWFETs and its performance is compared with strained Si MOSFET as reported by Dewey et al. [34]. QWFET has larger drive current over the strained Si MOSFET as also reported in Dewey et al. [34]. Intel is leading alternative technologies beyond silicon CMOS including germanium, III-Vs, carbon nanotubes and graphene.
3.2.2 **III-V MOSFET: (InP)**

Some of the research work to fabricate the InP MOSFETs has been described here. InP MOSFET with SiO$_2$ as dielectric has shown electron mobility in between 250–750 cm$^2$V$^{-1}$S$^{-1}$ as reported in [35]. Kawakami et al. [36] have also reported InP MOSFET with Al$_2$O$_3$ which showed $g_m$ of 10 mS (87 mS/mm of gate width). Wu et al. [37] have reported InP n-MOSFET with ALD grown Al$_2$O$_3$ with maximum drain current of 70 mA/mm and electron mobility as 650 cm$^2$V$^{-1}$S$^{-1}$. Akyol et al. [38] have reported ALD beryllium oxide on InP. BeO gate dielectric n-MOSFETs show excellent surface channel dc output characteristics, supporting high possibility of utilizing it in III-V CMOS technology.

3.2.3 **III-V MOSFET: (GaN)**

Gallium Nitride (GaN), a III-V semiconductor has been used in power electronic devices due to its wide bandgap properties. It can also be considered for the logic applications like GaAs and InP due to its high saturation current, high temperature stability and higher $V_{bd}$. Some of the research work to fabricate a GaN MOSFET has been described here. Using SiO$_2$ on GaN MOSFET maximum current and $g_m$ as 300 mA/mm and 60 mS/mm respectively [39] has been reported. GGO on GaN MOSFET showed leakage current of mA to nA as reported in [40]. SiO$_2$ deposited on GaN MOSFET showed $D_{it}$ as 3x10$^{11}$ cm$^{-2}$eV$^{-1}$ as reported in [41]. As reported in [42], SiO$_2$ on AlGaN/GaN MOSFET shows mobility of 1180 cm$^2$/Vs and maximum drain current as 600 mA/mm. Oh et al. [43] report NiO on AlGaN/GaN MOSFET has maximum drain current of 800 mA and $g_m$ as 105 mS/mm. Tsai et al. [44] have reported using a high-κ LaAlO$_3$/SiO$_2$ gate dielectric, the recessed-gate GaN MOSFET has a threshold voltage of 0.1 V, $V_{bd}$ of 385 V and $g_m$ of 136 mS/mm. As reported in [45], GaN MOSFET with SiO$_2$-Ga$_2$O$_3$ as oxide dielectric, low
leakage current in the order of pA and $D_{it}$ of $2 \times 10^{10} \text{cm}^{-2} \text{eV}^{-1}$ was obtained. S. Im et al. [46] report AlGaN/GaN MOSFET grown on Si and mobility was found as 120 cm$^2$/Vs and the drain current was 353 mA/mm, $g_m$ as 98 mS/mm and gate leakage current of $10^{-7}$ A/mm at gate voltage of 6 V. Ruan et al. [47] report mobility in GaN MOSFETs as 160 cm$^2$/Vs.

The review of the different channel material III-V MOSFETs above shows that a MOSFET is required to have a lower $D_{it}$, high drain current, high mobility and transconductance for any given technology even at the nanometer scale. In all the three categories of III-V MOSFETs, there are some architecture which have some desired properties and some undesirable properties. A trade off is required for a given structure to be used for a specific requirement or application.

### 3.3 III-V MOSFET Models

The compact models used in the industry include charge based models such as basic SPICE Level 1, Level 2, Level 3, BSIM models and the other advanced models such as BSIM 4 and 5 [48,49,50]. Secondly, the surface potential based models include the SP model, MOS Model 11, HiSIM model etc. [51, 52, and 53] and thirdly, the conductance based models like the EKV model [54]. But unfortunately, these models don’t include the III-V MOSFET models in the nanometer scales.

However, some attempts have been made to model the electrical parameters worldwide. Mori et al. [55] have used quantum Monte Carlo (MC) simulations to find the drain currents for long and ballistic channel III-V ultra thin body GaAs and InP MOSFETs. The results show a higher drain current for these MOSFETs as compared to the strain silicon or bulk silicon MOSFETs. The model proposed by Asenov et al. [56] for implant free III-V MOSFETs uses MC device simulations. Model developed by Oh and Wong [57] is a physics-based analytical compact model of InGaAs MOSFETs for digital logic applications.

The model includes SCE, trapezoidal-shape quantum-well energies, bias dependent ballistic ratios, and capacitances including 2-D potential profile information. Kalna et al. [58] propose for implantfree
III-V MOSFET based on InGaAs channel using MC device simulations. The gate lengths used were 30, 20 and 10 nm. The simulations were also carried out for variable In and Ga content in the III-V MOSFET structure. Tsuchiya et al. [59] evaluate performance limits of n-channel MOSFETs on the quantum-corrected MC simulation for high mobility III-V channel materials. The results indicate III-V materials are expected to perform better than the Si devices.

Islam and Haque [60] report a numerical model based on schroedinger-Poisson self consistent solutions for an InGaAs MOSFET to calculate the quantized energy levels. The Higher indium (In) content in the channel has a profound effect on the subband energies in the channel. As reported in [61] the ballistic drain current of III-V surface channel MOSFETs with ALD Al₂O₃ and InGaAs has been investigated using over-the-barrier transport model Numerical results show that the increase in ‘In’ composition in channel region results in increase in drain current.

Sharmin et al. [62] describe the characterisation and modeling of the interface trap density in In-rich In₀.₆₅Ga₀.₃₅As and In₀.₇₅Ga₀.₂₅As MOSFETs with ALD Al₂O₃ gate dielectric using the quantum mechanical CV analysis. The results show that donor-like traps dominate for In₀.₇₅Ga₀.₂₅As-channel compared to In₀.₆₅Ga₀.₃₅As-channel MOSFETs. Abdi et al. [63] describe the analytical model developed to study and model the electron mobility in wurtzite GaN MOSFETs. Ayubi-Moak et al. [64] describe the performance of implant-free n-type In₀.₇₅Ga₀.₂₅As MOSFET using a 2D finite-element MC device simulator with gate lengths of 30, 20 and 15 nm.

De Michielis et al. report the [65] analytical model for the ballistic current of n-MOSFETs as a function of the transport direction and of the properties of the channel material for GaAs. Yiming Li and Wei-Hsin Chen [66] describe electrical characteristics of MOSFET with silicon/gallium-arsenic (Si/GaAs) stacked film numerically. Several important device characteristics, such as the on-state current, the subthreshold swing, the drain induced barrier lowering, the threshold voltage, the threshold voltage roll-off, and the output resistance has been evaluated.
Compared with the results of pure Si MOSFET, Si/GaAs MOSFET shows promising characteristics after properly selecting the thickness of Si/GaAs film. Zhu et al. [67] report the modeling of the band structure of III–V material InSb MOSFETs calculated using Empirical Pseudopotential Method (EPM). Important electronic parameters such as effective mass, valley minima of InSb as a function of film thicknesses are calculated. The calculations reveal that the ‘effective mass’ of Γ valley electrons increases with the scaling down of film thickness. Kalna et al. [68] have simulated GaAs MOSFET with high-k gate insulator using ensemble MC simulations for 80 nm physical gate length.

The results show a 100–125% and 20–30% increase in the drive current compared to conventional Si MOSFETs and with strained Si channels on virtual SiGe substrates respectively can be achieved. Hisanao et al. [69] describe the electron transport phenomena in nanoscale InGaAs MOSFETs by using quantum corrected MC simulation for ballistic transport at gate length of 10 nm. Takahiro et al. [70] investigate the ability of the nano-scale III–V MOSFETs with InGaAs, GaAs or InP channels by using the quantum-corrected MC simulation. The results show a large average electron velocity because of the smallest electron effective mass in the Γ valley.

Rahman et al. [71] describe the performance limits of Si, Ge, GaAs and InAs MOSFETs using a semi-empirical atomistic tightbinding model and a top-of-the-barrier seminumerical ballistic transport model. Saeroonter et al. [72] have developed a physics-based compact model for III–V field-effect transistors for digital logic applications. Quantum effects, capacitance, gate tunneling leakage current and parasitic capacitance effects are included in this model. The III–V compact model also includes the gate leakage current and parasitic capacitance analytical models. Kalna et al. [73], examine the prospect of Implant Free (IF) III–VMOSFET for 22 nm technology using the MC device simulations.

The results show that, the indium content in InGaAs materials plays a significant role to deliver a high drive current because of the highly efficient injection of electrons into the channel. Chang-Hung et
al. [74] determine the Quantum Confinement (QC) in InGaAs on insulator n-MOSFET using Schrödinger equation. The simulations indicate that QC improves the subthreshold swing also. Donghyun et al. [75] examine the performance of uniaxial and biaxial strained In$_x$Ga$_{1-x}$As NMOS DGFET with (111) and (001) orientations under ballistic transport, taking into account nonparabolic full band structure, quantum effects, band-to-band tunneling and SCE.

The models described above are given by various research groups around the world. Some of these models are applicable for 22 nm technology which includes quantum effects, strain application etc. These models are basically numerical in approach and use MC simulations. These models need to be included in the current device simulators for the nanoscale applications for the successful implementation of III-V technology.

### 3.4 Challenges and Solutions of Using III-V Materials for MOSFETs

Various challenges posed by the III-V technology for the mainstream digital microelectronics have been briefly outlined in [76]. The main challenges in implementing III-V channels for manufacturing CMOS technology are many. First, III-V materials do not have an effective gate oxide. Despite some progress in recent years, the problem of forming a high-quality gate insulator remains a significant barrier to implementing III-V for CMOS applications. Second, III-V substrates are expensive, brittle and difficult to make in large sizes.

Third, the non-Si MOS technology needs to be compatible with the existing Si technology and they need to be scalable to nanoscale technology. Fourth, III-V materials do not have a higher hole mobility compared to Si as also shown in Table 3.1. However, III-Vs still have the net mobility advantage over Si for CMOS application due to their much higher electron mobility, and slightly lower or comparable hole mobility. All the above challenges are described in detail in the following sections.
3.4.1 High-k Dielectric Growth

In conventional III-V FET technology such as High Electron Mobility Transistor (HEMT), due to the lack of a stable gate dielectric stack, a direct schottky metal gate is used which results in a large gate leakage. So, to implement the III-V technology in mainstream digital electronics, a stable dielectric is required which is thermodynamically stable in contact with the III-V semiconductor. Besides, it should exhibit a small Dit, has sufficient band offsets with the channel material and a high dielectric constant (to avoid tunneling at nanoscale). The presence of the interface traps is undesirable for the III-V MOSFETs as it deteriorates the drain current as also reported in [77].

Interface passivation is required to reduce the defect density at the III-V semiconductor/dielectric interface. After several decades of research, a few interfaces of dielectric/III-V semiconductor have been developed. The dielectrics are GGO and Al₂O₃. The passivation required at the interfaces can be done using either an amorphous Si (a-Si) Interface Passivation Layer (IPL) or sulphur/hydrogen passivation. The passivation techniques and their relevance have been described below.

3.4.2 Passivation of III-V/Dielectric Interface

The passivation of the III-V semiconductor is necessary to gain full advantage of the III-V technology. The raw surfaces or unpassivated surfaces produce pinning of the fermi level at the interface and the fermi potential becomes independent of the doping concentration in the substrate [78]. So, all the electrical characteristics of the MOSFET get disturbed.

The fermi level pinning is more in III-V interfaces with high k dielectrics due to the higher density of defects at the interface than the Si interfaces. The main issue is to estimate and control accurately the Dit. The fermi level can be unpinned by reducing the Dit. For that purpose, surface treatment of the III-V semiconductor becomes important. The surface treatment can be done by wet-chemical cleaning and sulfidization procedure, interface self-cleaning by ALD and
The issue of \( D_{it} \) of group III-V semiconductors and their interfaces with gate dielectrics has been addressed in the literature using two major approaches, namely: (1) by maintaining appropriate control of the interfacial bonds with oxygen, and (2) by using a-Si IPL and hydrogen anneal techniques.

The first approach was developed to form electrically inert bonds at the interface with gallium with oxygen rather than the arsenic with oxygen [79] for the GaAs based III-V MOSFETs. The second approach includes variety of techniques such as (1) pre-gate dielectric deposition treatment of the III-V surface with hydrogen or nitrogen plasma [80, 81] (2) wet chemical surface passivation with sulfur [82], and (3) deposition of a-Si [83] IPL. The second two techniques have been discussed below:

### 3.4.3 Hydrogen Passivation

Hydrogen passivation has been studied on the III-V materials by several researchers also. Pearton [84] reported that, the hydrogen anneal is quite effective in passivating deep levels of GaAs. Callegari et al. [80] reported that, \( D_{it} \) of GaAs/Ga\(_2\)O\(_3\) interface can be reduced to \( 10^{11} \) eV\(^{-1}\) cm\(^{-2}\) after the hydrogen plasma clean of GaAs surface prior to the e-beam deposition of Ga\(_2\)O\(_3\). Li et al. [85] showed that hydrogen plasma treatment improved \( D_{it} \) of GaAs/Si\(_3\)N\(_4\) interface. Passlack et al. [86] reported that, hydrogen anneal is very beneficial for improving GaAs/Ga\(_2\)O\(_3\) interfacial quality.

### 3.4.4 Amorphous Si (a-Si) IPL

The use of an ultra-thin a-Si layer demonstrated significant improvement of GaAs/SiO\(_x\), and GaAs/Si\(_3\)N\(_x\) interfaces with the reduced \( D_{it} \) to low \( 10^{11} \) eV\(^{-1}\) cm\(^{-2}\) [87]. Several research groups investigated GaAs based MOS devices with high-k oxides passivated with a-Si IPL demonstrated significant improved interface properties [88]. In addition to strong reduction of \( D_{it} \) resulting in un-pinning of fermi level, the Si IPL also benefited to decrease of the gate leakage current important for nanometer scale MOSFETs. The major disadvantage of the Si IPL is that it is oxidized along with the high-k oxide deposition, and thus
becomes a part of a gate stack contributing to oxide thickness thus degrading the electrical behavior of the device.

A review of several passivation techniques using silicon passivation for various III-V structures has also been done in [89]. In [90], long and short buried-channel In$_{0.7}$Ga$_{0.3}$As MOSFETs with and without a-Si passivation is experimentally fabricated. Devices with a-Si passivation show much higher $g_m$ and an effective peak mobility of 3810 cm$^2$/Vs. Short-channel MOSFETs with a gate length of 160 nm display a current of 825 μA/μm at gate overdrive voltage 1.6 V and peak $g_m$ of 715 μS/μm. These results indicate that, the high-performance In$_{0.7}$Ga$_{0.3}$ as channel MOSFETs passivated by an a-Si layer are promising candidates for advanced post-Si CMOS applications.

Oktyabrsky et al. [91] report enhancement mode n-MOSFETs with InGaAs and GaAs/InGaAs channels, ALD HfO$_2$ gate oxide and TaN gate. Good control of the drain current was achieved due to effective passivation of the III-V-high-k interface with ultra-thin MBE in-situ grown a-Si layer. High $g_m$ and high electron channel mobility were demonstrated.

### 3.4.5 III-V p-MOSFET

III-V semiconductors have very high electron mobility, making them ideal for n-channel devices. But CMOS needs p-channel transistors too and the hole mobility for III-V is too low as shown in Table 3.1, it is actually lower than silicon. One of the solutions of increasing mobility applicable in semiconductor industry is the application of strain on III-V semiconductors. Several efforts have been made to fabricate strained III-V p-type semiconductors and have resulted in high hole mobility. Hence, strain enhanced III-V p-MOS along with high mobility III-V nMOS show promise for being incorporated as MOSFET channels at the sub-22 nm technology node.

The application of strain causes reduction of carrier mass in the conduction valleys. Hole mobility is enhanced with strain which reduces the effective mass and splits the degeneracy between light hole and heavy hole bands reducing the number of states available for interband
scattering. Radosavljevic et al. [92] describe an III-V InSb p-channel QWFET using a compressive strain. The InSb p-channel QW device structure, grown using solid source MBE, demonstrates a high hole mobility of 1,230cm²/V-s. The shortest 40nm QWFET achieve peak $g_m$ of 510$\mu$S/µm at supply voltage of 0.5V.

Nainani et al. [93] describe a InGaSb III-V p-MOSFET due to its high bulk hole mobility that can be further enhanced with the use of strain. Both biaxial and uniaxial strains are applied. The hole mobility of 910cm²/Vs for surface channel MOSFET designs are obtained. Suthram et al. [94] examine the uniaxial strain application on III-V (100) GaAs p-MOSFETs. Ling et al. [95] describe the p-channel InGaAs QW-FET that incorporates uniaxial strain resulting in the enhancement in the transport characteristics of p-channel InGaAs QW-FET.

3.4.6 Integration with Existing Silicon Technology

For achieving complete advantage, III–V technology has to integrate with the low cost and proven and well-established Si technology for MOSFET applications. First, the integration would create more applications such as optoelectronics. Second, the advantages of silicon technology such as high thermal, electrical conductivity and mechanical hardness, which is better for microelectronic applications, would be beneficial for III–V technology also. The III–V materials have high speed, so combined devices would be speedier.

However, there are some challenges for the integration of III–V technology with the existing silicon technology. One of the challenges is the mismatch of lattice of two materials. The integration with silicon causes a high-density dislocation in III–V materials layer which can affect material quality. A technique called as lattice-matching epitaxy is used to minimize the lattice misfit. Second challenge is the thermal mismatch in integrated materials. It causes strain, defects, and mechanical cracks during device preparation and operation. Thirdly, Si diffusion into III–V layer when the layers are integrated. Kazior et al. also report the integration of [96] III–V devices and Si CMOS on a silicon substrate.
The challenges reported above are very critical and important for the successful implementation of the III-V MOSFETs. Of all the challenges, a suitable dielectric interface with low interface defect density, efficient application of strain on the III-V MOSFET structures, successful integration of the III-V materials with the IV materials with minimum mismatch and thermal stress. The other most important aspect of the outcome of the challenges is the impact on the electrical behavior of the devices made after meeting with the challenges.

### 3.5 Design Issues at Nanometer Scale

Upon fulfilling the requirements of suitable dielectric, integration with silicon or hole mobility enhancement for a III-V MOSFET, there are several design issues for this technology so that it becomes successful at the nanometer scale. One of the design issues is the delay \( \tau = \frac{C_g V_{dd}}{I_d} \) where \( C_g \) is the gate capacitance, \( V_{dd} \) is the supply voltage and \( I_d \) is the drain current. The delay determines the maximum speed achieved by the device [97]. The intrinsic gate delay of the device is defined as the time required for the input voltage to swing between zero and the supply voltage \( V_{dd} \).

The delay \( \tau \) is a metric for the switching frequency of the transistor which hence decides the clock speed of the chip designed from that device. The increase in the carrier mobility in III-V MOSFETs would lead to the decreased delays as the factor ‘\( I_d \)’ would increase and \( V_{dd} \) can hence decrease to provide margin for the reduced power dissipation in the CMOS circuits designed out of III-V MOSFETs. The power dissipated in a CMOS circuit is given by \( \alpha C V_{dd}^2 f \) where \( \alpha \) is the activity factor, \( C \) is the output capacitance and \( f \) is the clock speed (1/\( \tau \)). The power dissipation depends through a square law of supply voltage and hence the supply voltage needs to be reduced to reduce the power dissipation.

The FOM of a CMOS inverter designed out of the III-V MOSFET is:

\[
\text{FOM} = \text{power} \times \text{delay} = \alpha C V_{dd}^2 f \times \frac{1}{2f} = \alpha C V_{dd}^2 / 2
\]
The FOM gives a hint on how to decrease the power and delay. If the supply voltage is decreased, the speed would decrease and dynamic power dissipation would fall. If the supply voltage increases, it would be vice versa. However, after increasing the mobility of the charge carriers in an III-V MOSFETs, both delay and dynamic power dissipation can be effectively decreased.

The second parameter is the Drain Induced Barrier Lowering (DIBL). In short channel devices, the source-drain potential has a strong effect on the band bending over a significant portion of the device. Hence, the threshold voltages and the subthreshold currents of short channel devices vary with the drain bias. This effect is referred to as DIBL. The DIBL adds to the barrier lowering due to gate bias and enhances the electron injection from the source into the channel, leading to a noticeable increase of the channel current. When a high drain voltage is applied to a short-channel device, it lowers the barrier height, resulting in decreased threshold voltage. This would increase the subthreshold drain currents and hence the increased static power dissipation in a MOSFET. Finally, another parameter to consider is $I_{on}/I_{off}$ ratio. This ratio ultimately tells to maximize the ON current and minimize the OFF current of the MOSFET. Chau et al. [98] benchmarked the $I_{on}/I_{off}$ ratio for a number of nanoelectronic devices including Si CMOS. Table 3.2 also shows the $I_{on}/I_{off}$ ratio for various nanoscale topologies in III-V technology.

A review has been done in [99] to investigate the current scenario for 10 nm III-V MOS technology. The review suggests that the combination of higher injection velocity and scaled gate capacitance, for a 10 nm gate length and high-k dielectric III-V MOSFET with a thin InAs channel could be capable of reaching a drive current of about 1.5 mA/um. In [100], the scalability of GaAs double gate nano nMOSFETs has been investigated by the means of semi-analytical model of $I_{on}/I_{off}$ currents, accounting for quantum mechanical capacitance degradation, SCEs, band-to-band tunneling and source-to-drain tunnelling in arbitrary substrate and channel direction.
For devices with physical gate length below 13 nm (as required in the 22 and 16 nm nodes), this mechanism significantly penalises the $I_{on}/I_{off}$ trade off of small effective masses channel material like GaAs. In [101], a review of all the latest technologies has been done for sub 22 nm node and III-V technology has been also discussed as a front runner technology for the sub 22 nm node. In [102], a compact model of III-V HFETs is developed for digital logic circuit applications such as a six transistor SRAM cell at sub-22 nm technology with thin high-k dielectric for low gate tunneling current, and optimized extrinsic structure for minimum parasitic capacitance.

Lundstrom et al. [103] discuss the use of III-V technology for 65 nm technology to determine its electrical characteristics and intrinsic ballistic efficiency. Kwo et al. [104] describe the recent advances of III–V based MOSFET in MBE with ALD combined together for the growth of excellent high-k dielectrics with abrupt interfaces, critical for further CMOS scaling beyond the 45 nm nodes. Takagi et al. [105] discuss the III-V semiconductor channels on the Si CMOS platform with an emphasis on the combination of ultra-thin body and multi-gate structures. Table 3.2 shows some performance parameters of the III-V MOSFETs for the sub 100 nm scales. The table shows a relatively satisfactory performance of the compound semiconductors for use in sub 100 nm technology.

<table>
<thead>
<tr>
<th>PARAMETERS AT NANOSCALE</th>
<th>Si MOSFET [106]</th>
<th>InGaAs MOSFET [107]</th>
<th>InGaAs QWFET on Si [108]</th>
<th>InSb QWFET on Si [109]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gate Length (nm)</td>
<td>65</td>
<td>90</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>$I_{on}/I_{off}$</td>
<td>$&gt;10^4$</td>
<td>-</td>
<td>2150</td>
<td>370</td>
</tr>
<tr>
<td>Supply Voltage (V)</td>
<td>1.2</td>
<td>0.8</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>DIBL (mV/V)</td>
<td>80</td>
<td>-</td>
<td>90</td>
<td>82</td>
</tr>
</tbody>
</table>
3.6 Conclusion

Various types of III-V MOSFETs in terms of their structure, characteristics and performance for arsenide, phosphide and nitrides have been studied in this chapter. Various electrical parameters like threshold voltage, $D_{it}$, $g_m$ and types of gate oxide materials have been studied. The research on III-V MOSFETs for nanoscale implementation has been both carried out in literature theoretically and experimentally. The challenges to implement III-V materials to become mainstream such as good surface passivation, low gate oxide leakage, hole mobility enhancement and heterogeneous integration on Si platform have been discussed and must be overcome to implement this technology for the mainstream digital microelectronics. Other important parameters that need to be improved are the enhancement of $I_{on}/I_{off}$, reduced DIBL and the leakage currents.
References


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CHAPTER 4
The Role of Temperature on The Optical Properties and Surface Morphology of ZrO₂ Thin Films Deposited by Pulsed DC Reactive Magnetron Sputtering

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ABSTRACT

Zirconium Oxide (ZrO₂) thin films were deposited on glass by pulsed direct current reactive magnetron sputtering. Optical properties and surface morphology of these thin films were investigated and compared with previous studies. The properties of thin films depend on the deposition method used. In addition, our results show that the properties of these films highly depend on the deposition conditions (substrate nature, temperature, deposition rate and so on). Especially, we compare in situ with ex situ heating processes performed on these films. It is found that both ex situ and in situ heating treatments lead to the formation of denser materials, and consequently, to a reduction of the thickness of the thin films as well as an increase of their refractive index. However, these results are more apparent in the case of in situ heating. Furthermore, when investigating the evolution of surface roughness in the case of in situ heating, a minimum was found for a substrate temperature close to 200°C.

Keywords: Annealing Temperature, Interference Filters Magnetron Sputtering, Optical Properties, Oxides, Packing Fraction, Structural Properties, Surface Roughness, Thin Films, Zirconium Oxide.

4.1 Introduction

4.1.1 Interests for Zirconium Oxide

Since many decades, the tremendous amount of work devoted to the physics of thin films have made of this research field a subject matter on its own [1,2]. The interest toward the optical properties of thin films evolved into a research field of prime importance [3-5]. In the midst of the various optical materials available, dielectrics occupy a central position. The large number of publications on zirconium dioxide (ZrO₂; zirconia being the cubic crystalline form of ZrO₂) shows that the interest in regard to this material is very high.

1 Note to the reader: In order to give credit to pioneering works and so preserve the chronologic order in the cited contributions, The reference numbers are not systematically organised in numerical order.
2 Too numerous to be explicitly cited here.
CHAPTER 4 • The Role of Temperature on The Optical Properties and Surface Morphology of ZrO₂ Thin Films Deposited by Pulsed DC Reactive Magnetron Sputtering

This material is used in a variety of research fields such as in chemistry as catalysts [6,7], in electrochemistry as electrodes and electrochromic devices [8-11], in biology as bioactivators [12,13] and biosensors [14], in nuclear physics as scintillators [15] and for mirrors [16], in technology as waveguides [138], humidity sensors [17], windows and metal (protecting) coatings [18,19], lenses [20], membrane for micro fuel cells [21,22] and capacitors [23-25, 33]. Zirconium oxide also has thermoluminescent properties [26-28, 163]. Currently, interest is also oriented toward the fields of nanoparticles and nanostructured thin films [89, 78, 79,29,30, 100, 31-34]. Many physico-chemical properties are also under interest.

It has been shown that, oxygen can diffuse through ZrO₂ [35-38]. Finally, theoretical investigations also attract attention [39-41, 62, 65, 42-44]. Starting to grow significantly in the late 70s and early 80s [45-54], the interest toward the zirconium dioxide as thin films never declined since then and nonlinear optical properties are currently under investigation [55]. ZrO₂ is used in a wide range of applications. Due to its hardness (1 200 Hv, Vickers hardness test) and mechanical resistance to tension (700 MPa) and compression (2 GPA), ZrO₂ is widely used for its mechanical properties. In addition, ZrO₂ is an electrical insulator and because of its high dielectric constant and resistance to electric breakdown (high dielectric strength), is a suitable substitute for SiO₂ as very thin gates in electronic devices [56-58, 186, 59-62, 253, 63-68].

It is also used as a thermal barrier. In situation of high power lasers, a minute amount of light absorption can induce a rapid rise in local temperature that might be sufficient to induce morphological damage. In addition, a strong laser beam corresponds to a very high electric field that can induce dielectric breakdown of the materials, through ionization and the subsequent formation of localized microplasma. Due to its combination of transparency and dielectric strength, ZrO₂ appears as a good candidate for high threshold laser induced damage [102,69,70,81,71,172,177,72]. Due to the various crystalline forms that ZrO₂ can take [73, 102] and in order to inhibit possible morphological alteration in time, many studies have been devoted to stabilized ZrO₂ [74,75,76,256,77,179,21,78-84,175,85]. Composite and hybrid (inorganic-organic) materials [86-
and/or heterostructures [105, 60, 106, 107] are also of great interest.

However, because of its high refractive index and high transparency (for wavelength ranging from 340 nm to 7 μm) among other material [46, 47, 49, 108, 109], our own attention and contribution will be focused here on the optical and morphological properties of ZrO$_2$ in the form of thin films for optical applications [3-5].

### 4.2 Fabrication Techniques

Thin films devoted to optical applications are frequently made of dielectric (insulating) layers, often as metallic oxides as it is the case here for ZrO$_2$. The main way to produce such oxides thin films involves a reactive process, where the metal is sputtered in a residual atmosphere containing oxygen. Indeed, among the various fabrication techniques for ZrO$_2$ thin films devoted to various applications, including optical ones, it appears that vacuum depositions techniques (including reactive version for each one) are, by far, the most often adopted.

The sputtering [102, 74, 179, 110-118, 230, 119-126, 58, 127-132, 251, 23, 133-138] and electron beam [54, 139-142, 236, 143-145, 81, 146-149, 84] techniques attract considerable attention. Due to its ability to reduce arcing during the reactive process, pulsed direct current magnetron sputtering [50] is a valuable version of the sputtering technique devoted to reactive deposition of ZrO$_2$ [151-153, 256, 77, 154, 21, 105, 155-162, 268, 269].

It is important to mention that many other deposition techniques for ZrO$_2$ exist, such as (not limited to optical applications); sol-gels processes [163, 164, 89, 165-171, 71, 10, 172-178], atomic and molecular layer deposition and epitaxy [179, 275, 77, 180, 181, 236, 182-188, 80, 189-192], chemical vapour deposition [48, 74, 193-200, 33, 201], wet chemical and electrochemical methods [74, 202-207], electrical arcing [208-210, 86, 211, 13, 162, 244], laser ablation [212-215, 56, 216-218, 85], electrostatic and pirolytic spray [219-222, 8, 56, 223], liquid phase deposition such as dip, spin and blade casting coatings [74, 180, 224-
226, 176], photochemical processes [227-229] and resistively heated evaporation [230, 231]. For vacuum deposition, the glancing angle deposition is an interesting variant [232,233].

4.3 Fabrication Parameters

Many physical parameters may well affect the overall properties of ZrO₂, whether it is in the form of thin film or in the bulk form. The amount of energy brought into the material is a very important factor. Of course, among these parameters, heat is a key one. Certainly, heating a sample after its full formation or during its formation could lead to significant morphological differences. Indeed, for crystalline materials as well as for amorphous ones, the evolution of thermal agitation due to heating followed by proper cooling conditions allow atoms and molecules to locate themselves in sites where the sample Gibbs free energy would eventually be minimized (prior to heating).

This mechanism could lead to a denser material through the inhibition in the formation of voids. Accordingly, in case of thin films, this process should reduce their thickness and consequently, increase their refractive index. Thus, it seems reasonable that the refractive index depends on the density of the films [234]. However, because subsidiary effects such as surface roughness modifications might come out, it is important to take into account the surface morphology of the films, especially in the case of multilayer systems. Therefore, the actual heating process and its temporal evolution are both significant. For instance in situ (during sample formation) [21,235] versus ex situ (after sample formation) [102,236,237,238, 105, 239-241, 58, 71, 242, 243, 244] processes could give different outcomes. In both cases, heating favours a better oxidation. In this work, we compare in situ with ex situ heating processes for dielectric materials, taking ZrO₂ as a specific illustration and supporting example.

Other important parameters which it is worth mentioning are in situ and ex situ electromagnetic [245-248] and ionic bombardment [249, 92, 250-252]. Many other parameters are of course significant and have also been investigated. Among them, it is worth noting parameters
such as; the substrates\cite{102, 253} and interfaces \cite{254, 255}, the thickness \cite{105}, the sputtering power \cite{119} and deposition rate \cite{256, 235, 282, 257, 258}, the oxygen flow and-or pressure \cite{259, 86, 120, 260, 261, 258} and the target-substrate distance \cite{119}. In our opinion, the pulsed direct current reactive magnetron sputtering technique has not yet been fully studied. In this work, it is our aim to increase the amount of data on ZrO$_2$, compare our recent results with previous studies, in particular what concerns \textit{ex situ} and \textit{in situ} heating, and discuss the main convergences and divergences.

4.4 Experimental

4.4.1 Fabrication of Samples

ZrO$_2$ thin films of different thickness (typically, 100-300 nm thick) were deposited on standard glass substrates (Corning 2947 Micro Slides) from DC reactive magnetron sputtering. Because glass is transparent in the visible, is very smooth and easily available, we have focused our attention on this substrate. The glass substrates were thoroughly cleaned using methanol and dried with nitrogen gas flow. The films were made at room temperature as well as at various in situ temperatures. Sputtering deposition is a widely used technique which allows high deposition rates (Figure 4.1). It consists of the bombardment of a solid target made of the materiel to be deposited with energetic ions extracted from low pressure plasma.

![Figure 4.1: Schematic representation of the sputtering deposition method.](image)
Ions from the plasma are accelerated towards the target by a high electric field providing enough energy to eject atoms from the target which then migrate towards the substrate from uniformly randomized path. Reactive sputtering can also be used in the process when an appropriate reactive gas is introduced in the process chamber, like O₂ gas in our case. The advantages of the sputtering method are the following: the deposition process is relatively fast, produce dense defect-free oxide films and do not require high temperature; films have a composition close to that of the source material; high melting point materials are easily sputtered; sputtering usually lead to lest contamination than evaporation methods; sputtered films have a good adhesion on the substrate; it can also be performed top-down.

We have used the CMS-18 deposition system from Kurt J. Lesker Co. The targets were made of Zr, grade 702 purity, 3.0 inches in diameter, 0.25 inches in thickness. The sputtering was performed from ionization of an argon gas in the presence of oxygen (flow rate from 10% to 12% of the total flow rate). The total pressure of the gas mixture was set from 3.5 mTorr to 4.5 mTorr (467 – 600 mPa). However, in order to obtain well oxidized films and good stoechiometric conditions, we have used 10% oxygen and 4.0 mTorr as standard parameters for most samples. The plasma operating power was kept constant at 360 W. Target to substrate distance is approximately 10 cm, a distance roughly corresponding to the mean free path of the sputtered molecules which is an important parameter for the resulting properties of the films (see results section below). To obtain uniform layer deposition, the substrate rotates with a speed of 5 rpm. The thickness of samples was chosen by controlling the deposition time which was kept constant while studying the effect of a specific parameter.

4.4.2 Ex Situ Heating (Annealing)

To study the effect of heating the ZrO₂ thin films after deposition (ex situ heating), samples were put in a standard laboratory oven (KILN MFG inc. Colorado G series) running in ambient air at atmospheric pressure. We then compare the optical and morphological properties of the films before and after heating. In order to avoid ‘geometrical’ deformation of
the substrate and a concomitant alteration in the ellipsometric data, the annealing temperature is limited to 400°C. In addition the sample is sited flat on a thick glass plate in the oven during heating. However, most of the samples were exposed for one hour to a temperature of 300°C.

4.4.3 *In situ* Heating

To study the effect of the substrate temperature during the deposition process (*in situ* heating), we have used several *in situ* temperatures ranging from 100°C to 400°C. The desired temperature was obtained from a heater mounted above the substrate holder and fed by a power supply incorporated in the CMS-18 deposition system. For each sample, the temperature was kept constant for the whole deposition process. We also compare the optical and surface morphological properties of the ZrO\(_2\) thin films with the *ex situ* heated samples.

4.5 Characterisation

4.5.1 Optical Characterization

Optical properties of the films were characterized by ellipsometry and spectrophotometry. It is well known that, ellipsometry is a powerful tool in order to determine the refractive index of thin films [262-265] and was successfully applied to the case of ZrO\(_2\) thin films [231, 266, 93, 267-269]. The thickness, the refractive index and the extinction coefficient of our samples were obtained from ellipsometry. Most ellipsometers available for research operate only in the reflection mode which requires opaque substrates. The ellipsometer we have used for the characterisation of our samples is an in-house ellipsometer which operates in both reflection and transmission modes in the spectral range of 300 to 800 nm.

This procedure is useful for optical analysis carried out on thin films deposited on transparent substrates. In addition, the amount of information obtained from both transmission and a reflection measurement increases the accuracy in the determination of the optical constants. This method is also particularly interesting for films made of oxides because they can be themselves very transparent.
Figure 4.2: Schematic representation of the reflection-transmission ellipsometer.

Figure 4.2 shows the main features of reflection-transmission ellipsometry [270]. The incoming beam from the light-input system (monochromator, collimator, and filter) is quasi-monochromatic. Aligned on the optical path from the source are a reference detector, a polarizer, the sample, a reflection (or transmission) analyzer and a reflection (or transmission) detector. The reference detector eliminates possible problems of lamp-intensity variations. The positions of all these components are set by rotators and translators controlled by the data-acquisition program Winoptik. The apparatus allows for measurements of reflection and transmission coefficients for both \( p \) and \( s \) polarisation from different angles of incidence. Reflection and transmission spectrum are obtained from the spectral range of 300 nm to 800 nm. Finally, in-house software, Optikan, calculates from best fit the thickness (±1 nm), the refractive index (± 0.001) and the extinction coefficient (± 0.001) of the sample.

Of course, spectroscopy in the visible part of the electromagnetic spectrum is a very useful complementary tool in the study of ZrO\(_2\) [139, 151, 74, 140, 114, 117, 118, 213, 86, 87, 230, 246]. A spectrophotometer (CARY 5000 controlled by the Cary WinUV software) operating in the wavelength range 200–2500 nm was used to record the transmittance and reflectance...
spectra of the films. Figure 4.3 is a schematic representation of the apparatus for transmittance measurements. The beam coming out from the monochromator is split into two parts, one path used for light intensity measurements through the test sample and the other path used as a reference beam. The spectrophotometer can also be used to measure scattering or diffusing effects.

Figure 4.3: Schematic representation of the spectrophotometer.

4.5.2 Morphological Characterization

As mentioned earlier, ellipsometry was used to determine the thickness of the samples. However, ellipsometry is not the best tool to investigate the surface morphology of thin films. *A contrario*, tunnelling and atomic force microscopes (STM and AFM respectively) are figuring among the best tools and were used for ZrO$_2$ [271-273, 183, 80, 64, 229]. In this work, morphological properties of the films were analyzed using a Dimension 3100 Digital Instruments AFM. It operates using silicon tips with integrated cantilevers resonating at 270-340 kHz (Figure 4.4). Once the silicon tip scans the sample surface, forces on the tip, typically Van der Waals, lead to a deflection of the cantilever.

The deflection can be measured from a laser spot reflected from the top surface of the cantilever into an array of photodiodes. To obtain proper surface imaging, a motor controlling the mechanical tip motion is placed in a feedback loop as the tip is scanned across the surface. Analytical studies of roughness are provided in terms of parameters such as arithmetic average or root mean squared values of the vertical deviations with respect to an ideal smooth surface. Other very useful tools to reveal morphological details about ZrO$_2$
are electron microscope and X-ray diffraction [102, 274, 275, 236, 80, 276, 64, 277] and also various spectroscopic methods involving electromagnetic [278, 279, 93, 187] and ionic [280] radiations.

Figure 4.4: Schematic representation of the atomic force microscope.

4.6 Results

4.6.1 General Results

The present study is based on a total number of samples close to 30. When the total pressure inside the deposition chamber is below 350 mPa (≈2.5 mTorr) and for contents in oxygen of 12%, the ZrO₂ thin films are opaque. However, as shown in Figure 4.5 for a total pressure above 450 mPa (≈3.5 mTorr), the refractive index (and the corresponding packing fraction, $p$, defined below) of the ZrO₂ film is strongly dependent on the pressure and weakly dependent on oxygen content.

According to the literature, this behaviour is usually explained in terms of mean free path and deposition rate [Reference 5, Chapter 12]. Indeed, at higher pressure the mean free path is shorter and the energy of condensed particles decreases due to the increase of scattering. Low-energy condensed particles have lower surface mobility and less ability to form large crystallites. Accordingly, the film porosity increases and the refractive index decreases. On the other hand, the film thickness was not much affected by this variation of pressure since while the increase of porosity could have changed the thickness there was a corresponding decrease in the deposition rate. In addition, increasing the deposition rate by mean of a higher plasma operating power also increases the refractive index.
Besides, it is worth noting that a major challenge in many reactive processes is the ‘poisoning of the target’. Indeed, an important issue linked to reactive processes associated to insulating thin films is the metallic condition of the target surface. A good metallic condition is required. Otherwise, due to the presence of oxygen, the target surface becomes partly insulating and a voltage drop appears across the target’s insulating layer. In turn, the voltage responsible for the plasma activation in the vacuum chamber decreases which causes the sputtering rate to reduce, and so the refractive index and the layer homogeneity. In such condition, the insulating layer on the target surface continues to grow up to the point that arcing becomes prevalent. On the other hand, a stable and rather high deposition rate is obtained when there is a balance between the oxygen flow rate and the voltage drop across the target’s insulating layer. Due to a voltage transition from ‘metallic’ deposition to ‘poisoning’ condition can occur spontaneously, a feedback loop providing regulation appears to be very useful.

The process helps to get homogeneous thin films by increasing the total oxygen content in the deposition chamber, an increase in pressure while keeping constant the relative oxygen content will favour a poisoning condition. However, as shown in Figure 4.5, the fact that a higher refractive index is obtained at 11% O₂ compared to 10% O₂ content indicates that the films were not prepared in poisoning conditions and a better zirconium oxidation is obtained.

Figure 4.5: Determination of the effect of the total pressure on the packing fraction, \( p \), through refractive index and equation 4.1. Legend; black filled diamonds (continuous line): 10% O₂ content, white filled triangles (dashed line): 11% O₂ content.
Also shown in Figure 4.5, the comparison of the actual refractive index of the thin film, \( n_f \), to its bulk value, \( n_b \), on the basis of the model of Bragg and Pippard, makes it possible to determine the ratio of the volume of the solid part of the film to the total volume of the film including voids, a ratio which is known as the packing fraction (or packing density), \( p \) [281]. Moreover, in the specific case of ZrO\(_2\) thin films, it was shown that the packing fraction is described by the following relationship [52].

\[
r = \left( \frac{\sqrt{p} - 1}{\sqrt{p} + 1} \right) \left( \frac{\sqrt{p} + 1}{\sqrt{p} - 1} \right)
\]

Of course, alternatively, it is possible to deduce \( n_f \) from \( p \), when \( p \) is known via a proper method.

As shown in Figure 4.6, it is found that no dependence of refractive index on the ZrO\(_2\) film thickness. This indicates that the ZrO\(_2\) films produced by pulsed direct current reactive magnetron sputtering, at least under the selected growth parameters, do not suffer much from gradual inhomogeneity from the substrate to the film-air interface. This is in agreement with results obtained for thin films of ZrO\(_2\) obtained with radio frequency magnetron sputtering technique [117]. When the refractive index, \( n_f \), is converted into the packing fraction, \( p \), through the above equation (using \( n_b = 2, 21 \), at 600 nm 230, www.refractiveindex.info), the same independence on the ZrO\(_2\) film thickness as in Figure 4.6 is observed.
4.7 EX SITU Heating

4.7.1 Optical Properties

As expected from the discussion in the introduction section about heating and as shown in Figure 4.7, ex situ heating at 300 °C induces a morphological change leading to an increase in the refractive index of ZrO₂ thin films. Over the 16 samples prepared for this study, only two samples were found to have a slightly opposite behaviour.

![Figure 4.7: Change of refractive index upon ex situ heating. Legend: black columns: Before heating, white columns: After heating.](image)

4.7.2 Morphological Properties

Also in accordance with the discussion in the introduction and as shown in Figure 4.8, ex situ heating at 300°C induced a morphological change leading to a decrease in thickness of ZrO₂ thin films. Over the 16 samples prepared for this study, only two samples were found to have a slightly opposite behaviour. In brief, as expected through the inhibition in the formation of voids, heating lead to a denser material.
As shown in Figure 4.9, *ex situ* heating appears to modify the surface roughness of the ZrO$_2$ thin films such that, for most of the samples, the overall surface roughness increases. In addition, as shown in Figure 4.10, the grain width increases considerably. It is important to underline that this behaviour is systematic, despite the fact that in some cases the surface roughness slightly decreases, as seen in Figure 4.10. The results are not quite the same in the case of *in situ* heating where a minimum in surface roughness was definitely found around 200°C.

Indeed, in the case of *ex situ* heating, the main dynamics under consideration is a chemical reaction involving the process of oxidation in ambient air. On the other hand, in the case of *in situ* heating, the main process under consideration is the crystalline growth at very low oxygen partial pressure.
Figure 4.9: Typical AFM images showing the change in roughness of ZrO$_2$ thin films upon ex situ heating. (a) Before heating ($R_a = 2.29$ nm) (b) After ex situ heating ($R_a = 3.23$ nm).

Figure 4.10: Typical AFM images showing the change in grain width of ZrO$_2$ thin films upon ex situ heating. (a) Before heating ($R_a = 3.94$ nm) (b) After ex situ heating ($R_a = 3.73$ nm). Notice the reduction in the roughness parameter, $R_a$.

A quantitative way to characterize the statistical behaviour of the surface roughness consists in determining the deviations of the surface profile from its mean value. This approach is basically statistical and most commonly the useful parameter is the arithmetic average of the deviations, $R_a$ (‘a’ stands for ‘arithmetic’). Of course, the data analysis is based on evenly separated points. Height is assumed to be positive in the up direction, away from the film. Formally, $h_i$ being the deviation at location $i$ from the profile mean value, $h_m$ (‘m’ stands for ‘mean’), and $N$ being the number of data points, $R_a$ is calculated from:

$$R_a = \frac{1}{N} \sum_{i=1}^{N} |h_i - h_m|$$  \hspace{1cm} (4.2)
The compilation of data from 16 samples is shown in Figure 4.11. It can be seen that, on average, the surface roughness increases upon heating (The error bars in Figure 4.11 represent ±1 standard error). Finally, as it is usually the case such as shown in Figure 4.12, the surface roughness increases with the film thickness. This tendency is the same for both unheated and annealed samples.

![Figure 4.11](image1.png)

**Figure 4.11:** Quantitative determination of the surface roughness change of ZrO₂ thin films upon ex situ heating. Legend; black column: before heating, white column: after heating. The error bars in represent ±1 standard error.

![Figure 4.12](image2.png)

**Figure 4.12:** Evolution of surface roughness versus film thickness. Legend; black filled circles: Before ex situ heating, white filled squares: After heating.
4.8 In Situ Heating

4.8.1 Optical Properties

An interesting result about in situ heating of ZrO₂ thin films is shown in Figure 4.13. Indeed, the graph shows clearly that, while keeping the same deposition rate and duration for each sample, as the substrate temperature is increased the material refractive index increases while the film thickness decreases. Accordingly, as discussed in the introduction, a higher deposition temperature produces denser ZrO₂ thin films.

Note that, at least on average, the same results were observed while studying the effects of ex situ heating, but these results are more apparent in the case of in situ heating. As the substrate temperature increased, more energy is available for the incoming sputtered particles, a factor that favors their surface mobility and their ability to form large crystallites and denser films.

![Figure 4.13: Demonstration that in situ heating produces denser ZrO₂ thin films. Legend; black filled circles: refractive index, black filled squares: thickness](image)

A useful parameter in view of applications is the optical path length, given by the product of the refractive index and the geometrical path length (here, the thickness of the film). As seen in Figure 4.14, the normalised³ optical path length of samples decreases with the substrate temperature. From this graph, we conclude that the deposition of thin films at room temperature would require an increase of the deposition time by as much as 30% to get a thin film

³ Relatively to the denser film, obtained at 400 °C.
having the same optical path length as the thin films produced at room temperature.

Figure 4.14: Determination of the normalized optical path length versus substrate temperature (the sample heated at 400°C chosen as reference).

4.8.2 Morphological Properties

A somewhat unexpected result about in situ heating of ZrO₂ thin films is shown in Figure 4.15. Indeed, as a function of substrate temperature, at first there is a decrease in surface roughness, followed by an increase. This behaviour is found reproducible. Actually, the numerical data for five additional samples are shown in Figure 4.16, where a minimum in surface roughness is clearly seen. We do not have yet a definitive understanding of this behaviour. Note that C-Y. Ma et al. [64] have found similar results as regards to minimum in surface roughness around 250 °C for ZrO₂ thin films deposited on Si (100) substrates by rf magnetron sputtering.

On the other hand, internal stresses during the deposition process may affect the morphology of the films. While studying ZrO₂ films prepared by electron beam evaporation, D. Zhang et al. [1] have reported that there is a proper deposition rate which allow for minimum internal stress during growth. Their results suggest that, there must be a link between substrate temperature and surface morphology via the deposition rate.
Phase transitions generally occur abruptly at a specific temperature. However, since we are in presence of amorphous materials, the mechanism here could have some similarities with glass transition which could take place over some tens of degrees. An illustration to that could be the Thornton diagram [283] which is a very useful tool to get an insight of the morphology of thin films (as seen with the electron microscope) prepared by sputtering under various deposition conditions of pressure and substrate temperature.
In relation to this diagram, when the temperature changes from 100°C to 400°C the reduced temperature, $T/T_m$ (assuming the melting point of ZrO$_2$ is 2,715 °C, or 2,988 °K) changes from 0.125 to 0.225. Thus at a constant pressure of 530 mPa (4.0 mTorr) the deposition conditions are in the margin between zone ‘1’ and zone ‘T’. Therefore, the temperature change might allow for the crossing from zone ‘1’ to zone ‘T’, where the film’s morphology changes from a porous structure made of tapered crystallites separated by voids to a structure made of densely packed fibrous grains.

In addition, generally when thin films are prepared on substrate via the condensation of particles on substrates at low temperature compared with the melting point of the deposited material, the resulting structure is thermally unstable. Thus, we could conceive that, the observed behaviour results from two competing mechanisms where the transition from one state to the other occurs around 200°C. The challenge here consists to find a combination of mechanisms that, above 200°C, increase simultaneously the surface roughness and the packing fraction. Perhaps some kind of ‘phase transition’ similar to a glass transition could occur around 200°C in pure ZrO$_2$ thin films. As a matter of fact, it is known that, pure zirconium oxide is unstable [51, 111, 39] and thin films are in a metastable phase at atmospheric pressure and room temperature [141]. Alternatively, we could imagine that an incomplete stoichiometry is responsible for the observed behaviour.

### 4.9 Conclusions and Perspectives

Optical properties of thin films constitute a research field of prime importance. Among the various optical materials available for applications, dielectrics occupy a central position. Zirconium oxide (ZrO$_2$) in the form of thin films for instance is widely used in the optical and electronic industries in regard to its highly attractive properties. In this work, our aim was first to get an insight into general properties of oxide thin films, taking zirconium oxide as an illustrative case. It was also our goal to increase the amount of data available on that material and to compare our recent results with previous studies, in particular what concerns ex situ and in situ heating.
For that purpose, several ZrO₂ thin films were deposited on glass by pulsed direct current reactive magnetron sputtering. We found that, both ex situ and in situ heating treatments lead to the formation of denser materials, and consequently, to a reduction of the thickness of the thin films as well as an increase of their refractive index. However, these results are more apparent in the case of in situ heating. Furthermore, when investigating the evolution of surface roughness in that case as a function of substrate temperature, a minimum was found around 200°C.

Heat treatment of ZrO₂ thin films, when it is not too high in temperature would be of great value. Besides, when a minimum in surface roughness is achieved, even though the thin films are not at their best possible values of refractive index, are of great interest in multilayer systems because losses due to light scattering from the numerous interfaces could also be minimized. Finally, it seems reasonable to expect that many dielectrics and other materials would present similar behaviour under ex situ or in situ heating treatments. For instance, to find the best deposition temperature could be of prime importance when synthesizing these materials in order to meet optimum optical properties.
CHAPTER 4 • The Role of Temperature on The Optical Properties and Surface Morphology of ZrO2 Thin Films Deposited by Pulsed DC Reactive Magnetron Sputtering

References


[64] C.-Y. Ma, Z. Li, Q.-Y. Zhang, J. Inorganic Mater. 22 (2007) 742, Note to the Reader: This Article is Written In Chinese and English for Abstract and Figure Captions.


CHAPTER 5
A Review Of One-Dimensional Metal Oxide Nanowires Properties

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ABSTRACT

This work presents a review of metal oxides materials for nanowires growth purpose via sol-gel method. The materials are Titanium dioxide (TiO₂) or Titania. We begin this paper with explanation of nanocrystal formation and followed by comparing the properties of both two materials. Finally, the outlook and other unique properties of these two materials that suit for many applications will be discussed further below.

Keywords: Nanowires, Titanium Dioxide, Physical Properties, Optical Properties.

5.1 Introduction

Nanocrystals are the important components for next generation nanoscale devices, and the successful operation of these devices will be easily accomplished by using Nanocrystals with distinct sizes and shapes. Four types nanostructures are nanocomposite (3-dimensional), quantum well (2-dimensional), nanowire and nanotubes (1-dimensional), also nanoparticles (0-dimensional) [1]. One-Dimension structures (1D) are including nanowires or nanorods, nanotubes, nanobelts and nanosprings. The word ‘nanowires’ is seem to be very familiar among nanotechnology industry in this new global instead it is the hottest property.

Nanowire is one of new class of quasi-one-dimensional materials that have been attracting a great research interest in the last few years with aspect ratios (length-to-width ratio) of 1000 or more. The ‘nano’ is referred to wires’ diameter or thickness in the range of tens of nanometers or less. One dimensional nanowire structure with the smallest dimension is able to improve the transportation of electron which is the critical to the function and integration of these nanoscale
devices. These special properties of one-dimensional structure are not the same with bulk wire.

Nanowires’ shape and size are the crucial parameters to determine their physical and chemical properties. By controlling the parameters, the basic and technological advantages of this nanoscale wire are able to maintain and usable. As the size changes, their colour, phase transition temperature and band-gap energy also changes [2]. Its special properties which has efficient transport of electrons allows electron to easily flow across it. Semiconductor nanowires have a good system to investigate their properties, especially the mechanical, electrical or chemical properties. To form nanowires, bottom-up and top-down approaches can be used; where both have their own advantages.

Top-down approach is involving lithography process which needs to etch away certain areas to form nanowires [3]. Therefore, size of nanowires fabricated is depending on the machine technologies. Thus, the physical limits of photolithography become a problem [3]. Moreover, cost of machines and clean room environment increase with newer technologies. However, bottom-up approach is opposite to the top-down process because this approach adds atoms to create structure [3]. Besides that, nanowires are naturally growth and self-aligned by chemistry and biology. Since this approach can provide smaller structures than top-down approach, besides more economical without wasting material to etch, also has simple formation of film and structures, we believed that semiconductor industry will be dominated with this bottom-up approach to form nanowires. Simple sol-gel method provides a lot of advantages towards synthesizing nanowires.

To form nanocrystal, two procedures are required - nucleation and crystal growth. The nucleation is form when sudden increase of monomer concentration over super-saturation levels. The steps taken to grow nanocrystal structure are shown in Figure 5.1 below.
During these processes, a lot of parameters should be controlled to get perfect geometry of nanocrystal and the most critical part to get nanocrystalline phase is at the nucleating stage. Once nanocrystal seeds are formed with a specific crystalline phase, other factors for controlling the subsequent growth processes will affect the final geometry of nanocrystals. However, environment plays a key to gain the most stable phase structure. The size of macro-scale samples is comparable with nanowires and therefore significant changes of electrical signal can be seen if any interaction between macro-molecules forms [4]. Semiconductor nanowires have gained large interest as building blocks for low-cost, highly sensitive biosensors [5],[6]. Such semiconductor materials are titanium dioxide (TiO2), zinc oxide (ZnO) also tin oxide (SnO). The purpose of this chapter is inclining more on the behavior study of TiO2 that suit for the formation of nanowires for biosensor application.

5.2 History

TiO₂ has been explored a long time ago for their specific purposes on that time. From that, scientists begin to explore and investigate each applications; so that those latest finding can give a lot of benefits especially towards our technologies.
The element of Titanium (Ti) has been discovered on 1971 by amateur geologist and Pastor William Gregor, then vicar of Creed parish in Cornwall. The black sand that he found by a stream, nearby parish of Manaccan was attracted by a magnet. From his analysis, there are two metal oxides that are iron oxide and 45.25% of a white metallic oxide he could not identify [7]. Then, at the same time, Franz-Joseph Müller von Reichenstein produced a similar substance[8] and unfortunately, he also does not know about the material. In 1975, German chemist Martin Heinrich Klaproth was independently rediscovered titanium dioxide in rutile form and he named it for the Titans of Greek mythology.

After hearing about Gregor’s earlier discovery, he obtained the sample and confirmed it contained titanium. Then TiO₂ has been commercialized in the early twentieth century; start with two companies, Fujishima and Honda, who are discovering the phenomenon of phototcatalytic application in 1972 [9].

### 5.3 Physical Properties

There are two ways to grow nanowires using sol-gel method that is with or without seed layers. Seed layers also known as thin film where the particles size should be in nanometer and from that, nanowires will be grown on it. The size of particles in seed layers plays an important role to gain wires in nano scale.

TiO₂ is one of semiconductor material consist of three polymorphic phases: rutile (tetragonal density = 4.25 g/cm³), anatase (tetragonal, 3.894 g/cm³) and brookite (orthorhombic, 4.12 g/cm³) [10] that has a lot of advantages. Figure 5.2 shows the crystal structure of rutile, anatase and brookite.
TiO$_2$ has the basic structure of octahedron with Ti atom is at the center and oxygen at each corner, where each Ti$^{4+}$ ion is surrounded by an octahedron of six O$^{2-}$ ions. Orthrombic structure is the shape of compounds where in six groups of atoms are symmetrically arranged around a central atom. In rutile, tetragonal structure with two edges of octahedron is shared while four edges of octahedron are shared in tetragonal anatase structure. The shared areas are shown with arrows. The most stable rutile TiO$_2$ surface is (110) [12].

The phase structure is usually considered to has higher-temperature and higher-pressure phase if compared to anatase [13]. That is why rutile TiO$_2$ nanowires are high chemical and thermal stability. However, to get rutile structure, very high temperature is required during annealing; as high as 800°C. The anatase form of TiO$_2$ is less stable than rutile but is easily produced in nanocrystalline form since it takes average temperature to synthesis [14], [12]. The physical properties of rutile, anatase and brookite TiO$_2$ are shown in Table 5.1.
### Table 5.1: The physical properties of rutile, anatase and brookite of TiO₂.

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>TiO₂ RUTILE</th>
<th>TiO₂ ANATASE</th>
<th>TiO₂ BROOKITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Black or reddish brown in large thick crystals</td>
<td>Brown to black, also yellow and blue</td>
<td>Dark brown to greenish black</td>
</tr>
<tr>
<td>Golden yellow or rusty yellow as inclusion in thin crystals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Luster</td>
<td>Adamantine to submetallic</td>
<td>Adamantine to submetallic</td>
<td>Adamantine to submetallic</td>
</tr>
<tr>
<td>Transparency</td>
<td>Crystals are transparent in rather thin crystals otherwise opaque</td>
<td>Crystals are opaque</td>
<td>Crystals are opaque</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Tetragonal; 4/m 2/m 2/m</td>
<td>Tetragonal; 4/m 2/m 2/m</td>
<td>Orthorhombic; 2/m 2/m 2/m</td>
</tr>
<tr>
<td>Crystal Habits</td>
<td>Include eight sided prisms and blocky crystals terminated by a blunt four sided or complex pyramid. The prisms are composed of two four sided prisms with one of the prisms being dominant. Crystals with some twins forming hexagonal or octahedral circles</td>
<td>Typical tetragonal dipyramids that come to sharp elongated terminations points. These crystals look like stretched out octahedrons</td>
<td>Include the typical tabular to platy crystals with a pseudohexagonal outline. Magnet Cove specimens tend to be more equant with complex facets</td>
</tr>
<tr>
<td>Cleavage</td>
<td>Good in two directions forming prisms, poor in a third (basal)</td>
<td>Perfect in the basal direction and in four directions, pyramidal</td>
<td>Poor prismatically and in the basal direction</td>
</tr>
<tr>
<td>Fracture</td>
<td>Conchoidal to uneven</td>
<td>Subconchoidal</td>
<td>Subconchoidal and uneven</td>
</tr>
<tr>
<td>Hardness</td>
<td>6.0 - 6.5</td>
<td>5.5 - 6</td>
<td>5.5 - 6</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>4.2*</td>
<td>3.8 - 3.9</td>
<td>3.9 - 4.1</td>
</tr>
<tr>
<td>Streak</td>
<td>Brown</td>
<td>White</td>
<td>Light brown to white</td>
</tr>
</tbody>
</table>
Due to the quasi-one-dimensional geometry of the nanowires and the large surface-to-volume ratio, surface-induced effects play a significant role on the electrical properties of nanowire-based devices. Even a single molecule attached to the nanowire surface is able to change the electrical properties of the nanowire considerably. Therefore, a fictionalization of the nanowire surface gives way to highly sensitive sensors that can be arranged in a very dense assembly, owing to their nanosized dimension. However, the surface modification, immobilization and hybridization on the nanowire device arrangement have to be taken care in order to prepare a complete nanowire-based DNA sensor [15].

DNA molecules are negatively charged and therefore applicable for the electrical detection with biofunctionalized nanowires. High chemical and thermal stability of this semiconducting nanowire allows it to be used for detecting biomolecules for cancer cells identification since this detection process dealing with biochemical compounds like protein, enzyme and DNA. Nanorods and nanowires of this material offer a significantly larger surface area in comparison to other forms such as films [16]. Different crystalline structures give different peak values. X-Ray Diffraction (XRD) is used to differentiate the phase structures form. Figure 5.3 shows the peak values of anatase and rutile structures of TiO$_2$ nanorods.

![Figure 5.3: X-Ray diffraction patterns of TiO$_2$ nanoparticles at (a) 1h annealing within 500°C growth of TiO$_2$ nanorods at 175°C within (b) 1h (c) 3h (d) 6h Rutile (R) and Anatase (A) are labeled [17].](image-url)
From Figure 5.3, there is a transformation of anatase to rutile phase once the reaction time increases. Besides that, it is obviously shows high crystalline structure of TiO$_2$ nanoparticles and nanorods. The most intense TiO$_2$ nanoparticles crystal peak is (101) while (101) peak is for TiO$_2$ nanorods. Atomic radius can influences the sensitivity level of material. Annealing temperature can play one of the important roles to control crystallite size besides method chooses to synthesis nanoparticles. Through Figure 5.4, it is obviously shows the relation between the temperatures required to anneal with the change in particles size.

As the temperature increase, the particles size also increase. This is happened because as the temperature is getting higher, it enhances the bonding between the crystallites sizes of Ti or Zn–and–O anatase. This also can be further proved through AFM result of J. Ben Naceur as shown in Figure 5.4. The author was studied the effect of different annealing temperature towards microstructural and optical properties of nanostructured TiO$_2$ thin films.

![Figure 5.4: X-Ray diffraction patterns of TiO$_2$ nanoparticles at (a) 1h annealing within 500°C growth of TiO$_2$ nanorods at 175°C within (b) 1h (c) 3h (d) 6h Rutile (R) and Anatase (A) are labeled [17].](image)

From the result in Figure 5.4, 600°C is an ideal annealing temperature to improve crystalline structure of TiO$_2$ film besides it creates high surface roughness. However, as the temperature is getting higher, the nanoparticles size is not suitable for the proceeding nanorods growth on it. This is because particles size may affect the diameter size of nanorods. Thus wider diameter nanorods will be grown which is not good for sensing applications as it requires small cross-sectional area. Besides that, Ti has high stability due to its high melting
and boiling point. That is why during TiO₂ nanowires growth purpose, the TiO₂ solution needs higher temperature [17], [18] to activate chemical reaction between precursor like titanium isopropoxide, titanium butoxide or titanium tetrachloride; solvent likes deionized water; and stabilizer likes hydrochloric acid. Otherwise, we may spend much time for this purpose.

Normally, nanowires will be grown on a seed layer. However, there is some journals proved that, nanowires can also grown without it. The most critical structure of TiO₂ nanoparticles and wires growth on SiO₂ substrate using sol-gel method can be seen via top view in Figure 5.5. Where FESEM is used to analyze both TiO₂ film and wires form in nanosize structure.

![FESEM image of TiO₂ thin film and nanorods (the inset picture) [18].](image)

Due to Akshay Kumar whose study ‘Growth of Aligned Single-Crystalline Rutile TiO₂ Nanowires on Arbitrary Substrates and Their Application in Dye-Sensitized Solar Cells’, the growth of nanowires on Si/SiO₂, Si (100), and Si (111) substrates were obtained dandelion shaped nanowire and the TiO₂ film with nanowires was relatively easier to peel-off from Si and Si/SiO₂ substrates. Table 5.2 shows the reading size of nanowires formed on different substrates.
CHAPTER 5 • A Review of One-Dimensional Metal Oxide Nanowires Properties

5.4 Optical Properties

The optical properties of TiO₂ are normally study by identifying its energy gap, refractive index also the absorption of photon. Index of refraction must be approximately 2.9, a value which can only be achieved by the rutile phase for titania [20].
Figure 5.6: 3D AFM images of TiO$_2$ nanoparticles at different annealing temperatures (a) 200 (b) 400 (c) 600 (d) 800 (e) 1000$^\circ$C [19].

Graph in Figure 5.7 was gained from Jinhong Yan who’s studied ‘Alcohol Induced Liquid-Phase Synthesis of Rutile Titania Nanotubes’. He was comparing the optical absorption edges for pure TiO$_2$ that is 398 nm and rutile TiO$_2$ is 414 nm. The absorbance values, shows a decrease in the energy band gap once it changes to rutile.

Figure 5.8: The optical absorption spectra of the TiO$_2$ nanowire arrays and TiO$_2$ thin film [21].

Due to this author, the shift of graph in Figure 5.8 towards decrement is mainly attributed to the quantum size effect. It reflects that, the TiO$_2$ nanowire arrays have wider energy gap with less possibility for the combination of electron-hole pairs, to give stronger redox ability and higher photodegradation efficiency than TiO$_2$ thin film.

Figure 5.9: Photoluminescence spectra of the (a) Precursor (b) Rutile TiO$_2$ nanotube [20].
Besides that, Jinhong Yana; people who discovered about ‘Alcohol Induced Liquid-Phase Synthesis of Rutile Titania Nanotubes’ has describes the PL spectra with an excitation wavelength of 260 nm and there is a difference between them in the range of 365–405 nm. Through Figure 5.9, the variation in the short wavelength must be related to the difference of the band structures between rutile and anatase phase. The intensity value is actually shows the intensity values of light emitted.

5.5 Application

Several modification and improvement have been made to ensure multiple applications of TiO$_2$ nanorods. Nanowires in molecular electronic devices are expected to be able in controlling electron transport which exploring the vast variety of molecular functions for electronic devices. Thus electronic device can operate even no current applied on it. Moreover, when biological materials are applied on it, the device turns to bioelectronic devices. The latest technology that applies nanowires is biosensor which benefits more on medical applications. The existence of nanowires may improve the performance of biosensor by accurate and fast biomolecules detection.

5.6 Summary

Metal oxide TiO$_2$ has it own unique properties where we believed is not fully covered yet especially when it turns into nanoscale. Nanotechnology is the latest issue in science and technology. However, the future of nanotechnology depends on the understanding and discovery of materials’ properties at the nanoscale, efficient manufacture of nanoscale materials and most importantly, device applications of nanoscale materials for real world applications. Further study need to be conducted continuously since there are still a lot of technologically unsolved problem.
REFERENCES


CHAPTER 6
Optimized Combustion Synthesis and Characterization of Nano-structured Ba$_2$RESbO$_6$ Perovskites

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ABSTRACT

Combustion of citrate complex has been a popular choice to synthesize nanocrystals of transition metal oxides in a single-step process. The amount of citric acid used for combustion is conventionally calculated based on the total valence of the oxidizing and reducing agents while keeping the equivalent ratio unity such that combustion energy is a maximum. This chapter demonstrates by employing quantum chemical calculations that the amount of citric acid could be reduced to nearly half if prepared for appreciable amounts. Transition metal oxides belong to quaternary double perovskites, with general formula Ba₂RESbO₆ (RE=Rare-earth), have been synthesized as nanocrystals as examples to validate the calculations.

Keywords: Perovskites, Synthesis, Characterization, Combustion.

6.1 Introduction

Perovskites-type oxides, routinely called Perovskites, have attracted considerable attention in many applied and fundamental areas of solid-state science and advanced materials research because of their technological potentials and academic interest. Traditionally, the perovskite oxides are prepared through solid state reaction of metal oxides and/or carbonates at elevated temperatures – a process called calcination. However, the resulting powder suffers from several drawbacks including:

a. Incomplete reaction of components because the starting chemicals are micron sized granules thereby resulting in inferior phase homogeneity.

b. Coarse grained powders of the final calcined ceramic due to prolonged high temperature processing which lead to poor sinterability.
The phase in homogeneity and powder coarsening adversely affect the physical properties of the final sintered ceramic. For example, ferromagnetic properties of Perovskites ceramics are severely affected by the coarse grains as the magnetic domains are of nanosize and the available properties results only from the surface of the grains. Therefore, in recent times, synthesis of advanced ceramics and specialty materials as nanometer sized grains gained increased attention owing to their huge surface-to-volume ratio as explained in the first chapter of this thesis. Using the high surface-to-volume ratio, the nanomaterials serve a given function with much lesser quantities than that required when bulk materials are used. Furthermore, properties of nanocrystals deviate from those of single crystals and coarse-grained polycrystals. This deviation results from reduced size of the nanocrystals and from numerous interfaces between adjacent grains [1]. In the case of ceramics, whose sinterability is a major issue, high surface to volume ratio of Nanocrystals offers increased surface energy thereby leading to enhanced sinterability? The faster reaction kinetics result in dense ceramic in shorter durations thereby the initial nanostructures in the sintered ceramic, which is the source of the superior mechanicals, electrical, dielectric, magnetic and optical properties of Nanocrystals [1-7].

The quaternary double Perovskites based on lanthanides (rare-earths), antimony, and barium with a general stoichiometry Ba\textsubscript{2}RESbO\textsubscript{6} have attracted considerable interest due to a number of fundamental and technological importances [8-11]. The Ba\textsubscript{2}L\textsubscript{n}SbO\textsubscript{6} Perovskites combine an alkali metal (Ba), a lanthanide (RE), a semi-metal (Sb), and a non-metal (O) – a combination of them would have interesting physical properties. There have been a number of analogues for these double Perovskites with general formula Ba\textsubscript{2}REMO\textsubscript{6}, where M represent Nb, Ta, Mo, Ir, Ru, and Bi characterized by a range of crystal structure and properties [12, 13].

The Ba\textsubscript{2}RESbO\textsubscript{6} has been known since 1965 when Blasse synthesized Ba\textsubscript{2}GdSbO\textsubscript{6} [14, 15]. Later, Casedo et al. synthesized nine other compounds of this group using rare-earths from Pr to Ho excluding Tb [16]. These authors pointed out that Ba\textsubscript{2}RESbO\textsubscript{6} have high melting points; therefore, they could be used as refractory materials. They have moderate dielectric constant (') and low loss tangent (tan )
making them attractive dielectrics in microwave electronic circuits [17]. In the year 1995, Koshy et al. showed that, $\text{Ba}_2\text{RESbO}_6$ Perovskites are chemically stable with functional ceramics such as superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) – thereby providing opportunities to build epitaxial films on $\text{Ba}_2\text{RESbO}_6$ substrates, active superconductor – insulator – superconductor interfaces, superconductor-insulator composites, and also could be used as crucibles for single crystal growth of YBCO [18]. Recently, Karunadasa et al. showed that, they are model system to study geometric frustration of magnetism in double perovskites [10].

The $\text{Ba}_2\text{RESbO}_6$ Perovskites powders has been calcined through solid state reaction of $\text{BaCO}_3$, $\text{Sb}_2\text{O}_5$, and $\text{RE}_2\text{O}_3$ at temperatures >1200 °C for durations > 36 hours with two or three intermediate grindings for the above studies [18-20]. To density the ceramic, the powder compacts were sintered up to 1600 °C. A number of $\text{Ba}_2\text{RESbO}_6$ Perovskites could not be sintered as single phase due to their high melting points; and therefore, such materials were sintered using a liquid-phase assisted sintering, i.e., adding small amounts of (< 1wt%) low-temperature melting oxides such CuO, which undoubtedly would destroy the chemical purity [19, 20]. Therefore, physical properties determined from those specimens would never been accurate.

To improve the characteristics of the $\text{Ba}_2\text{RESbO}_6$ powder and their sinterability, Wariar et al. has applied a combustion process [21-24] to synthesize them except when RE=La, Ho, Yb, and Tm as nanoparticles. The above combustion process, in which a solution containing a stoichiometric mixture of the ions forming the $\text{Ba}_2\text{RESbO}_6$ solid is allowed to undergo combustion in the presence of chelating and oxidizing agents, has been applied to synthesize a large number of ceramics. However, there is no attempt undertaken the process deeply. This chapter describes the analysis of the combustion process using quantum chemical computational methods. Furthermore, four new materials have been synthesized as nanocrystals and studied their powder characteristics.
6.2 Solution Combustion Synthesis

The solution combustion process involves rapid decomposition of a solution containing metal ions, an oxidizer, and a fuel. The solution combustion process was developed by Kingsley and Patil [25-28], in which an aqueous solution of metal nitrates (oxidizer) and urea (fuel) solution in a glass beaker were placed in a pre-heated furnace at 500°C, for synthesis of ceramic oxides [29-38]. However, this process can often lead to multiphase compounds, depending on the concentration gradient of the metal nitrates. This drawback has been overcome by taking advantage of coordination chemistry, i.e., by coordinating the metal ions in a chelating network thereby distributing the metal ions and controlled release of the ions during the formation of the solid. Using this approach, a number of ceramic oxides have been synthesized using chelating agents such as polyvinyl alcohol using urea as fuel and nitrates as oxidants.

However, these chelating agents are of higher molecular weight and the combustion energy is not always enough to remove all the carbonaceous materials from the final product. In other words, the combustion product has to be further subjected to heat treatment to remove the excess carbon or other carbonaceous materials. However, a survey of literature suggests that the above combustion processes are still under active use to synthesize metal oxide nanostructures. In another development, Jose et al. [21, 39-41] have developed a combustion process which uses low-molecular weight chelating agents such as citric acid and Ethylene Diamine Tetra Acetic acid (EDTA). This process is the only process currently available, to the best of our knowledge, to synthesize nanocrystalline materials in a single step processing.

The modified combustion processes is characterized by fast heating rate and short reaction times. These features make combustion synthesis an attractive method for synthesis of technologically useful
materials at lower costs compared to conventional ceramic processing. Other advantages of modified combustion synthesis include (i) use of relatively simple processing equipments – requires only a hot plate attached with a stirrer, and therefore, characterized by energy and cost saving advantages (ii) formation of ultrafine high-purity powders.

The modified combustion process involves formation of a precursor solution and refluxing in an open glass beaker to make coordinating complexes of the metal ions with the organic chelates while continuously remove the solvent. Upon removal of the solvent, a gel-like substance is formed which upon further heating undergoes deflation producing a form. The foam then gets ignited giving a voluminous and fluffy product of combustion. The salient features and advantages of combustion synthesis over the solid state reaction are outlined in Table 6.1.

**Table 6.1: Advantages of combustion method over solid state reaction.**

<table>
<thead>
<tr>
<th>COMBUSTION METHOD</th>
<th>SOLID STATE REACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion synthesis is a chemical method in which a homogeneous mixture of the metal ions is produced and hence the resulting powder is also homogeneous. Since no grinding is involved the material obtained is pure.</td>
<td>Solid state ceramic route is a physical method in which the metal oxides and carbonates were ground well in an agate mortar and the mixture is not homogeneous as that of chemical method. Due to multiple grinding possibility of impurity is more.</td>
</tr>
<tr>
<td>The precursor solution is just heated by a simple low temperature hot plate of the order of 300°C and hence sophisticated instrument is not required. Combustion synthesis is a unique single step process in which the phase pure powder is obtained during the combustion itself without requiring any calcinations step. Combustion synthesis is a bottom-up process and hence the grain sizes of the powder obtained through the combustion is in nano form. Require less time.</td>
<td>Mechanically grounded powder for a prolonged duration is heated in a furnace at very high temperature of the order of 1200°C for prolonged duration of 36 h to get the target compound. It involved multiple steps. OIN order to get the target material the powder has to be given intermediate grinding during the calcinations process.</td>
</tr>
<tr>
<td>Since the initial reactants of the powder are large, of the order of micron sized particle sand also high temperature calcinations is required, the resulting grain size of the powders are in micro meter. The process is time consuming.</td>
<td></td>
</tr>
</tbody>
</table>
6.2.1 Kinetics of the Solution Combustion

The combustion synthesis used in the present study employed citric acid to produce chelating complex and used nitrate ions as the oxidizer. The urea, which is the fuel used in the previous combustion process, has been replaced by ammonium hydroxide. However, the present combustion process is dramatically different from the previous combustion processes even in the presence of a chelating agent. The role of ammonium hydroxide is two fold:

a. To stabilize the metal ions in the citrate complex network.

b. To form trace amounts of ammonium nitrate, a well known explosive.

During the solution refluxing, the citrate complex is formed with trace amounts of ammonium nitrate. The trace amounts of ammonium nitrate initiate a small explosion which is fuelled by the citrate chelate. i.e, the present combustion process has a different chemistry compared to the previously adopted procedures.

The primary question to be addressed is the balance between the exothermic energy of combustion of the citrate complex and formation energy of the targeted compound. If the exothermic energy is higher than the formation energy of the complex, then the excess energy contributes to grain growth and formation of hard agglomerates. On the other hand, if the combustion energy is lower than the formation energy of the compound, then the final product is not expected to be single phase. To answer these questions, we have initiated the first principle quantum chemical simulations under the framework of Density Functional Theory (DFT). According to DFT, total energy of a material system can be expressed as a unique functional of electron density. In 25 years of its history, DFT has been a highly accepted predictive tool for determination of the structure and properties of molecules, clusters, and crystals in a number of environments such as high pressure and temperatures.
To determine the combustion energies, we considered a molecule with formula $\text{Ba}_2\text{LaSbO}_6$. Each cations, viz., Ba, La, and Sb should be anchored to citric acid network to produce a single molecule of $\text{Ba}_2\text{LaSbO}_6$. Total combustion energy of a citrate complex for a single $\text{Ba}_2\text{LaSbO}_6$ molecule can be determined from the total energy of the citrate complex holding its single formula unit. The DFT calculations were performed with the use of Beck’s three parameter hybrid method [42] with the Lee, Yang, and Parr (B3LYP) gradient corrected correlation functional [43] using Gaussian 03 programme packages [44].

Geometry optimizations were carried out using the standard double- quality Lanl2dz basis sets followed by harmonic frequency calculations and analysis of their IR spectra. No imaginary frequencies were observed in the IR spectra; hence indicating that the current calculations are realistic. Figure 6.1 shows the optimized structure of citric acid; the electronic distribution at the occupied (HOMO) and unoccupied (LUMO) molecular orbital are shown in Figures 6.2 and 6.3, respectively. The HOMO and LUMO of citric acid are located at the carboxyl groups opposite to the alcoholic group, respectively.

Figure 6.1: Optimized structure of the citric acid at the b3lyp/lanl2dz level of DFT.

Figure 6.2: Electronic surface structure of citric acid of the highest occupied molecular orbital.
The HOMO energy of the citric acid molecule occurs at 7.4595 eV and the LUMO occurs at 1.7023 eV. The calculated HOMO – LUMO energy gap of the molecule is 5.7572 eV. The adsorption energies of the Ba, La, and Sb atoms with citric acid individually as well as together for formation of a Ba$_2$LaSbO$_6$ molecule were determined by optimizing the geometries barium citrate, lanthanum citrate, antimony citrate, and barium lanthanum antimony citrate clusters. Hydrogen terminals were used to adjust valencies, which has been a common practice in computational chemistry. As hydrogen being the smallest atoms, its weight does not contribute appreciably in clusters of higher molecular weight. Figures 6.4 – 6.7 show the optimized geometries of each adsorption complex. Optimized bond lengths and bond angles of each citrate adsorption complex are in Table 6.2.

Figure 6.3: Electronic surface structure of citric acid of the lowest unoccupied molecular orbital.
Figure 6.5: Optimized structure of a lanthanum citrate complex. Atoms are scaled according to their relative sizes.

Figure 6.6: Optimized structure of antimony citrate complex. Atoms are scaled according to their relative sizes.

Figure 6.7: Optimized structure of a typical citrate chelating network. Atoms are scaled according to their relative sizes.

Table 6.2: Optimized bond lengths and angles of each adsorbed (X) atoms

<table>
<thead>
<tr>
<th>ADSORPTION COMPLEX</th>
<th>X – O BOND LENGTH (Å)</th>
<th>X – O – C BOND ANGLE (DEGREES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba – citrate</td>
<td>2.7893</td>
<td>89.7435</td>
</tr>
<tr>
<td>La – citrate</td>
<td>2.3508</td>
<td>136.5901</td>
</tr>
<tr>
<td>Sb – citrate</td>
<td>2.2025</td>
<td>120.2288</td>
</tr>
</tbody>
</table>
The Adsorption Energies Were Obtained From the Following Relation:

\[ E_{\text{Ads}} = E_{\text{Complex}} - E_{\text{citric acid}} \]

where \( E_{\text{Ads}} \) is the adsorption energy, \( E_{\text{Complex}} \) is the energy of the adsorbate complex, and \( E_{\text{citric acid}} \) is the energy of the citric acid. The adsorption energy of the complex is derived from the external heat source during refluxing the precursor solution. A single molecule of \( \text{Ba}_2\text{LaSbO}_6 \) is also modeled and shown in Figure 6.8. Table 6.3 shows the calculated adsorption energies of the complexes.

![Figure 6.8: Optimized structure a molecule of \( \text{Ba}_2\text{LaSbO}_6 \). Atoms are scaled according to their relative sizes. Symmetry of the molecule is adopted from the published bulk crystal structure. The bulk crystal structure of \( \text{Ba}_2\text{LaSbO}_6 \) is visualized as corner sharing \( \text{LaO}_6 \) and \( \text{SbO}_6 \) octahedra.]

<table>
<thead>
<tr>
<th>ADSORPTION COMPLEX</th>
<th>TOTAL ENERGY OF THE COMPLEX (eV)</th>
<th>ADSORPTION ENERGY OF THE X ATOM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Citric Acid</td>
<td>(-2.0674 \times 10^4)</td>
<td>--</td>
</tr>
<tr>
<td>Ba – Citrate</td>
<td>(-2.1363 \times 10^4)</td>
<td>(6.8823 \times 10^2)</td>
</tr>
<tr>
<td>Sb – Citrate</td>
<td>(-2.0868 \times 10^4)</td>
<td>(1.9341 \times 10^2)</td>
</tr>
<tr>
<td>La – Citrate</td>
<td>(-2.1542 \times 10^4)</td>
<td>(8.6750 \times 10^2)</td>
</tr>
<tr>
<td>(\text{Ba}_2\text{LaSb} – Citrate)</td>
<td>(-4.4822 \times 10^4)</td>
<td>(3.4235 \times 10^3)</td>
</tr>
</tbody>
</table>
The energy of a single molecule of Ba$_2$LaSbO$_6$ is found to be $1.4647 \times 10^4$ eV; i.e., formation energy of a molecule of the compound is higher than the adsorption energy of the ions required to form the complex; but ~75% less than the energy of the total complex. i.e., only one-fourth of the combustion energy is utilized for formation of the compound. Remaining three-fourth is either wasted as dissipation energy or contributed to the energy required for grain growth. Determination of the dissipation energy and that for grain growth is cumbersome due to the complexities of the processes; and therefore, no effort is devoted to evaluate them.

Thus, it turns out that reducing the combustion energy is the key to synthesize Nanocrystals of ceramic oxide with controlled particle size. Table 6.3 also shows that, energy of a complex is much lower when a chelating network is formed because it reduces the amount of citric acid required. Energy of a chelating network composing of a formula unit of Ba$_2$LaSbO$_6$ is ~50% less than that of the total energy of the citrate complex when considered individually. The current practice for an efficient combustion process for preparation of a ceramic compound is such that the amount of citric acid should be based on the relationship between the valence of all the cations in the compound and the number of coordinating sites available in citric acid [45, 46]. In the case of Ba$_2$LaSbO$_6$, valencies of all the cations are twelve and the number of coordinating sites available is three; which suggest use of four citric acid molecules to synthesize one molecule of Ba$_2$LaSbO$_6$.

However, the present calculation demonstrates that the amount of citric acid could be reduced to one-half than the currently adopted procedure. Therefore, this research work is aimed to synthesize the Ba$_2$RESbO$_6$ compounds using lower amounts of citric acids than currently adopted.

### 6.3 Combustion Synthesis of Nanoparticulate Ba$_2$RESbO$_6$ Perovskites

The flowchart of synthetic details of Ba$_2$RESbO$_6$ perovskite is summarized in Figure 6.9 below. One of the fundamental requirements for a wet-chemical synthesis of a ceramic oxide, including combustion
syntheses, is the availability of a soluble salt in a desired solvent. In this context, the antimony based complex Perovskites offers difficulties because a soluble salt in aqueous medium is not readily available. The most commonly available chemical for antimony is Sb$_2$O$_3$ which is insoluble in water or most commonly used mineral acids. After a number of trials using different mineral acids and basic media for dissolving Sb$_2$O$_3$, we have identified tartaric acid as its solvent. The Sb$_2$O$_5$ gave rise to a clear solution when it is refluxed in tartaric acid for ~2 h.

Figure 6.9: Schematic diagram of experimental technique of combustion process.

Aqueous solutions containing ions of Ba, RE (RE = Tm, Ho, Yb, La) and Sb were prepared by dissolving stoichiometric amounts of high purity Ba(NO$_3$)$_2$ (99.9% CDH, India), RE$_2$O$_3$ (99.9% Alfa Aesar, India), and Sb$_2$O$_3$ (99.9%, Merck). The Ba(NO$_3$)$_2$ was dissolved in distilled water, RE$_2$O$_3$ in 0.1 N nitric acid, Sb$_2$O$_3$ in boiled tartaric acid in separate glass beakers and then mixed together in a 500 ml glass beaker. Citric acid was added to the above mixture. The amount of citric acid is determined based on the total valence of all the metal ions to be complexed such that the energy released is maximum based on the quantum chemical calculations described before. However, the ab-initio calculations are in highly ideal. When citric acid was added with the solution containing the RE$^{3+}$, Ba$^{2+}$ and Sb$^{3+}$ ions, the three – COOH groups accommodates the three RE$^{3+}$, Ba$^{2+}$ and Sb$^{3+}$ ions. The amount of citric acid used in this work is equal to;
The crucial step in the combustion process is the maintenance of oxidant and fuel in the solution which was controlled by addition of nitric acid and ammonium hydroxide. Addition of ammonium hydroxide triggered an exothermic reaction, which is assigned to the formation of citrate chelates as well as ammonium nitrate. Excess amounts of ammonia lead to the precipitation which could be further dissolved by the addition of nitric acid. The above solution containing the complex precursor mixture at a pH of ~10 is heated using a hot plate at ~ 250 °C in a ventilated fume hood. The solution boils on heating and undergoes dehydration and decomposition leading to a smooth deflation with enormous swelling thereby producing foam. The foam then ignites, which is triggered by the ammonium nitrate, by itself in ~10 s on persistent heating giving voluminous and fluffy product of combustion. The combustion product was flown off from the beaker to its surroundings because of the higher specific surface area of the nanopowder, which was collected by placing high purity butter papers in the combustion chamber. Table 6.4 summarizes the materials and quantities used during a successful combustion process.

Table 6.4 The amount of materials used in a typical synthesis to generate 5 g of the targeted material.

<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>$\text{Ba}_2\text{LaSbO}_6$</th>
<th>$\text{Ba}_2\text{HoSbO}_6$</th>
<th>$\text{Ba}_2\text{TmSbO}_6$</th>
<th>$\text{Ba}_2\text{YbSbO}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Nitrate</td>
<td>3.0241g</td>
<td>3.0482g</td>
<td>3.0340g</td>
<td>3.0199g</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>4.8213g</td>
<td>4.8713g</td>
<td>4.8418g</td>
<td>4.8119g</td>
</tr>
<tr>
<td>Nitric Acid (conc. HNO$_3$)</td>
<td>40 ml</td>
<td>40 ml</td>
<td>40 ml</td>
<td>40 ml</td>
</tr>
<tr>
<td>Ammonium Hydroxide</td>
<td>40 ml</td>
<td>40 ml</td>
<td>40 ml</td>
<td>40 ml</td>
</tr>
<tr>
<td>RE$_2$O$_3$ (RE=Ho, La, Tm, Yb)</td>
<td>1.1010g</td>
<td>1.1018g</td>
<td>1.1190g</td>
<td>1.1383g</td>
</tr>
<tr>
<td>Antimony Oxide</td>
<td>0.8430g</td>
<td>0.8500g</td>
<td>0.8460g</td>
<td>0.8420g</td>
</tr>
<tr>
<td>Tartaric Acid</td>
<td>6.0564g</td>
<td>6.0768g</td>
<td>6.0482g</td>
<td>6.0196g</td>
</tr>
<tr>
<td>Temperature</td>
<td>520 °C</td>
<td>530 °C</td>
<td>520 °C</td>
<td>540 °C</td>
</tr>
</tbody>
</table>
The temperature of ignition was determined by keeping a copper-constantan thermocouple in the combustion flame. The temperature of the reaction was determined using RTD MI-100 k–type temperature controller. Under optimal conditions, the ignition temperature was recorded to be ~500°C. The ignition temperature was found to depend on the amounts of nitric acid and ammonium hydroxide. Excessive addition of ammonium hydroxide and nitric acid has potential risks as it lead to formation of excess amounts of ammonium nitrate which in turn give rise to higher exothermicity. The temperature of combustion has been increased up to 800°C with double amounts of ammonium hydroxide and nitric acid. Because of this higher exothermicity, the combustion process reported here was suggested to have adverse role in its scalability in producing metal oxides on a commercial scale (Jose et al. Mater Res Bull 2007).

However, present experiment on the relationship between the combustion temperature and reaction components provide opportunities to further scale up the process to produce advanced ceramics and specialty materials on a commercial scale. Various stages during typical solution combustion are shown in Figure 6.10.

Figure 6.10: Various stages in a solution combustion process for synthesis of Ba₂RESbO₆. (A) Precursor solution (B) Solution foaming stage after the evaporation of water, excess volatile nitrates, and ammonium hydroxide (C) Solution getting auto-ignition on persistant heating (D) Completion of the combustion (E) The final ceramic powder, which is subse- quently characterized to be single phase.
6.4 Characterization of the Combustion Product

The powder obtained directly after combustion, the as-prepared powder, has been tested for:

a. The chemical stability - checking whether or not any reaction happens in the as-prepared solid phase.
b. The presence of carbonaceous materials.
c. Crystal structure.
d. Morphology.

Simultaneous Thermal Analyses (STA) involving differential thermal analysis and thermo gravimetric analysis were used to detect whether or not any solid state reaction or phase transition occur in the sample when the as-prepared powders were subjected to annealing. The presence of carbonaceous impurities was examined by combining STA and infrared spectroscopy. Crystal structure of the combustion product was examined by combining x-ray diffraction experiments and Rietveld analysis. Morphologies of the powders were determined by scanning (SEM) and Transmission Electron Microscopes (TEM).

6.4.1 Simultaneous Thermal Analysis

The TGA and DTA were carried out using Perkin-Elmer TG/DT thermal analyzer in the range 30–1100°C at a heating rate of 20°C/min in the nitrogen atmosphere. Figures 6.11 to 6.14 show the DTA and TGA curves of the as-prepared nanopowder of Ba$_2$RESbO$_6$ (RE = La, Tm, Yb and Ho) obtained directly after combustion. In all the cases, the TGA curves showed a weight loss <5% at temperatures ~150°C. This weight loss is attributed to the liberation of adsorbed moisture in the sample. Even though the materials are dried initially before recording the DTA and TGA curve, because of its ultrafine nature, moisture adsorption occurs immediately on the exposure to the atmosphere. No weight or enthalpy change occurred in the sample at higher temperatures i.e, in the 150–1100°C range.

The usual calcination temperature of these materials are above ~1200°C for a solid state reaction, which is further expected to be reduced due to the atomic level mixing of the reaction components during a wet chemical
synthesis. This observation implies that the combustion produced a single phase material, most likely the targeted compounds, i.e., Ba$_2$RESbO$_6$. Furthermore, a featureless STA confirms that combustion is complete with the used amount of citric acid and that no organic matter is present the sample.

Figure 6.11: DTA and TGA trace of the as-prepared Ba$_2$LaSbO$_6$.

Figure 6.12: DTA and TGA trace of the as-prepared Ba$_2$HoSbO$_6$.

Figure 6.13: DTA and TGA trace of the as-prepared Ba$_2$TmSbO$_6$. 
6.4.2 Infrared Spectroscopy

The Infrared (IR) spectra of the samples were recorded in the range 400-4000 cm$^{-1}$ on Thermo-Nicolet Avatar 370 Fourier Transform Infrared (FTIR) spectrometer using KBr pellet method. Figures 6.15 - 6.18 shows the FT-IR spectrum of as-prepared Ba$_2$RESbO$_6$ powder, which was recorded to further check the presence of organic impurities. The broad band centered at 1430 cm$^{-1}$ arises from adsorbed moisture as revealed in STA experiments. This corroborates the thermal analysis result that the combustion is complete and no organic matter is present in the sample. Symmetric and/or asymmetric bending and/stretching vibrations observed in the lower wave numbers, which are characteristics of inorganic phases.

Detailed descriptions on those vibrations are a subject of a complete crystal structure discussion of the title compounds and are reserved for the next chapter. No shift in the IR spectral bands was observed when samples annealed at temperatures above 1500°C was used for the measurements thereby confirming that the combustion is complete and that no organic matter present in the as-prepared sample.
6.4.3 Crystal Structure

To check whether the combustion product was single phase, crystal structure of the combustion product was studied using powder X-Ray Diffraction (XRD) technique using an X-ray Diffractometer (Model Bruker D-8) employing Nickel filtered CuKα radiation (\( \sim 1.5406 \, \text{Å} \)). Figures 6.19 - 6.22 show the XRD patterns of the combustion products of \( \text{Ba}_2\text{LaSbO}_6 \), \( \text{Ba}_2\text{HoSbO}_6 \), \( \text{Ba}_2\text{YbSbO}_6 \), and \( \text{Ba}_2\text{TmSbO}_6 \) for 2 between 20 and 70° respectively. Among them, \( \text{Ba}_2\text{LaSbO}_6 \) is reported to be monoclinic and the others have cubic...
crystal structure. Detailed crystal structure analyses of these compounds are in the next chapter.

All the peaks in the XRD patterns of the as-prepared powder were indexed to the structure assigned to the Ba$_2$RESbO$_6$ materials. No peaks corresponding to the secondary phases were observed in the XRD patterns. These observations clearly show that the Ba$_2$LaSbO$_6$, Ba$_2$TmSbO$_6$, Ba$_2$YbSbO$_6$, and Ba$_2$HoSbO$_6$ phase formations was complete during the combustion process itself without need for an additional heating stage. In many of the previous combustion processes that used chelating agents, a post annealing was necessary to remove the carbonaceous materials due to the involvement of high molecular weight organic compounds.

Furthermore, it should be pointed out that the single phase of Ba$_2$LaSbO$_6$, Ba$_2$TmSbO$_6$, Ba$_2$YbSbO$_6$, and Ba$_2$HoSbO$_6$ materials can be obtained through solid state reaction route only after calcining the reaction mixture at a temperature of 1200°C for 36 h with intermediate grindings. Thus, the citrate combustion process is a unique, straightforward and simple technique to get single phase Ba$_2$RESbO$_6$ (RE = La, Tm, Yb and Ho) materials.

![Figure 6.19: Rietveld refinement plot of as-prepared Ba$_2$LaSbO$_6$. The experimental and simulated intensity data (I$_e$ and I$_s$) are plotted as circles (o) and solid lines, respectively; and I = I$_e$ - I$_s$ below. The tick marks indicate the position of the all possible Bragg reflections of the monoclinic unit cell having space group P 2$_1$/c (No. 14). Detailed structural description is in the next chapter.](image)
Figure 6.20: Rietveld refinement plot of as-prepared Ba$_2$HoSbO$_6$. The experimental and simulated intensity data ($I_e$ and $I_s$) are plotted as circles (o) and solid lines, respectively; and $I = I_e - I_s$ below. The tick marks indicate the position of the all possible Bragg reflections of the cubic rocksalt unit cell having space group Fm3m (No. 225). Detailed structural description is in the next chapter.

Figure 6.21: Rietveld refinement plot of as-prepared Ba$_2$TmSbO$_6$. The experimental and simulated intensity data ($I_e$ and $I_s$) are plotted as circles (o) and solid lines, respectively; and $I = I_e - I_s$ below. The tick marks indicate the position of the all possible Bragg reflections of the cubic rock salt unit cell having space group Fm3m (No. 225). Detailed structural description is in the next chapter.

Figure 6.22: Rietveld refinement plot of as-prepared Ba$_2$YbSbO$_6$. The experimental and simulated intensity data ($I_e$ and $I_s$) are plotted as circles (o) and solid lines, respectively; and $I = I_e - I_s$ below. The tick marks indicate the position of the all possible Bragg reflections of the cubic rocksalt unit cell having space group Fm3m (No. 225). Detailed structural description is in the next chapter.
The particle size and strain of the as-prepared materials were studied by Williamson–Hall plot by fitting the XRD pattern of the as-prepared powder using the structure assigned to them. The method depends on the X-ray line broadening results from several sources including:

a. Instrumental Broadening.

b. Particle Size Broadening.

c. Strain Broadening.

d. Impurity Broadening.

The instrumental broadening was corrected by recording the XRD pattern of a silicon single crystal and the impurity broadening was ignored by taking advantage of the high level of purity of the chemicals used. The particle size depends on the full width at half maximum (fwhm) of the X-ray diffraction peak according to the Scherrer formula:

\[ t = \frac{0.94 \lambda}{\beta \cos \theta} \]

where \( t \) is the particle size in nm, \( \lambda \) is the wavelength of the first order X-ray (1.5406 Å), \( \beta \) is the FWHM and \( \theta \) is the diffraction peak angle. The calculated particle size by assuming uniform particles are given in Table 6.5. It shows that, the crystallite size of the as prepared Ba\(_2\)RESbO\(_6\) (RE = La, Tm, Yb and Ho) powder is ~30 nm on an average. Therefore, the as-prepared Ba\(_2\)RESbO\(_6\) powder prepared through the combustion method is of nanocrystalline nature.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>fwhm×10(^{-3}) (rad)</th>
<th>PARTICLE SIZE (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(_2)LaSbO(_6)</td>
<td>4.4483</td>
<td>32</td>
</tr>
<tr>
<td>Ba(_2)TmSbO(_6)</td>
<td>5.1286</td>
<td>22</td>
</tr>
<tr>
<td>Ba(_2)YbSbO(_6)</td>
<td>3.8726</td>
<td>25</td>
</tr>
<tr>
<td>Ba(_2)HoSbO(_6)</td>
<td>5.2752</td>
<td>27</td>
</tr>
</tbody>
</table>
6.4.3 Morphological Characterization

Shape and distribution of the particles composing the starting powder has profound influence on the final structure and properties of a sintered ceramic. Nanostructured materials have high surface-to-volume ratio; and therefore, have high surface energy. Particles tend to agglomerate to reduce the surface energy. In the present study, SEM was used to image the agglomerate and agglomerate size distribution and TEM was used to study the individual particle as well as study the internal structure of the materials.

6.4.3.1 Scanning Electron Microscopy

The agglomerate size distribution of the as-prepared samples was examined using SEM (Model–Hitachi S 2400 Japan). Samples for SEM was prepared by ultrasonically dispersing the combustion product on a metallic stud and the surface are evaporated to Figure 6.23 shows a typical agglomerate size distribution of a typical sample. The particles were observed to be uniform with an average agglomerate size of ~400 nm.

Figure 6.23: Typical SEM images of as-prepared Ba$_2$TmSbO$_6$. 
6.4.3.2 TEM Analysis of the Combustion Product

The TEM images were obtained by Model-JEOL 2010F transmission electron microscope operating at 200 kV. The samples for transmission electron microscope were prepared by ultrasonically dispersing the combustion product in methanol and allowing a drop of this suspension to dry on a carbon-coated copper grid. Figures 6.24 – 6.25 summarize the results of the TEM analysis of the combustion products, which shows that, the as-prepared Ba$_2$RESbO$_6$ powders are submicron sized aggregated nanocrystallites. To study the crystal structure and particle orientations. Selected Area Electron Diffraction (SAD) patterns were recorded at an accelerating voltage of 200 kV, which corresponds to an electron wavelength of 2.508 pm, and at a camera length of 915 mm.

The TEM studies on the powder morphology of the as-prepared Ba$_2$LaSbO$_6$ powder obtained by the combustion synthesis showed that the nanoparticles are of submicron size 20–40 nm with a mean size of 30 nm as shown in Figure 6.24 (left panel) is a typical TEM bright field image of the as-prepared powder and the right panel the corresponding Selected Area Electron Diffraction pattern (SAD). The ring nature of the electron diffraction pattern is indicative of the polycrystalline nature of the crystallites, but the spotty nature of the SAD pattern in Figure 6.24 (right panel) can be due to the fact that the fine crystallites having related orientations are agglomerated together resulting in a limited set of orientations.

Figure 6.24: Bright field TEM image (left panel) and (B) SAED pattern (right panel) of as-prepared Ba$_2$LaSbO$_6$. 
A typical lattice image of a powder particle is also imaged and shown in Figure 6.25. The lattice fringes correspond to the major (112) plane with lattice parameter ~2.99 Å. The grain boundary is sharp and no impurities or secondary phases could be located thereby indicating the phase purity of the as-prepared powder.

Figure 6.25: HRTEM lattice image of Ba$_2$LaSbO$_6$ showing sharp boundary.

Figure 6.26 shows the TEM image of Ba$_2$TmSbO$_6$ powder and its corresponding SAED pattern. Figure shows powder particles of aggregates in the size range ~100–200 nm. The aggregates in terms consists of finer nanocrystallites of size ~10–20 nm. The SAD pattern shows rings that can be indexed to cubic structure. The ring nature of the SAED is indicative of the polycrystalline nature of the crystallites. Figure 6.27 shows a high resolution lattice image showing a grain boundary; the grain boundary is sharp and free from any impurities. The sharp grain boundaries indicate the chemical purity of the samples developed by the combustion process.

Figure 6.26: Bright field image of as-prepared Ba$_2$TmSbO$_6$ powder (top panel) and its corresponding electron diffraction pattern (bottom panel).
Sintering is the most important step during ceramic processing because it is at this stage a powder compact is exposed to maximum temperature. During sintering process, mass transport occurs so as to minimize the surface energy. The as-prepared combustion product was sintered to high density ($\leq 97\%$ of the theoretical density). The as-prepared powders were mixed with a binder, in this case Polyvinyl Alcohol (PVA), in agate mortar for $\approx 1$ h and dried in an electrical oven. The dried powders were mechanically pressed in different shapes such as discs and parallelepipeds.

The pressed compacts were then sintered in a programmable furnace in the temperature range 1350–1400°C for 6 h and then furnace cooled to room temperature. The density of the sintered compacts was determined using the Archimedes’s method and the theoretical density was determined from the lattice parameters of the compounds. Table 6.6 shows the sintering temperatures, sintered and theoretical densities of each material considered in this thesis. The samples could be sliced into thin discs using a diamond cutter; well polished surfaces were obtained by mechanical polishing.
Table 6.6: Sintering temperature, theoretical and sintered density.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>SINTERING TEMPERATURE (°C)</th>
<th>THEORETICAL DENSITY (g/cm³)</th>
<th>SINTERED DENSITY (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₂LaSbO₆</td>
<td>1250</td>
<td>7.050</td>
<td>6.912</td>
</tr>
<tr>
<td>Ba₂HoSbO₆</td>
<td>1450</td>
<td>6.466</td>
<td>6.240</td>
</tr>
<tr>
<td>Ba₂TmSbO₆</td>
<td>1450</td>
<td>6.999</td>
<td>6.789</td>
</tr>
<tr>
<td>Ba₂YbSbO₆</td>
<td>1450</td>
<td>7.458</td>
<td>7.160</td>
</tr>
</tbody>
</table>

Microstructures of the sintered specimens were studied using SEM. Figures 6.28 – 6.30 shows the SEM images the sintered Ba₂RESbO₆ samples. The sintered specimen consisted of well crystallized sub-micron grains with sharp grain boundaries. No cracks or pores were observed on the surface. Sintering increased the grain size of the as-prepared Ba₂RESbO₆; average grain size determined from the SEM micrographs was ~700 nm.
The perovskite compounds are probably the most widely studied materials due to its wide application in the field of solid state science with regard to its physical properties, dielectric susceptibility, linear and nonlinear electro-optic effects. The general form of perovskite compound is $ABX_3$, where $A$ and $B$ are metallic cations and $X$ is a non-metallic anion. As the number of cations in $A$ and $B$ sites changes, the compounds become complex perovskites. Such compounds of the form $A_2BB'O_6$ are taken under study.

In the present work, the synthesis and characterization of quaternary double perovskites of the form $Ba_2RESbO_6$ has been studied. It is observed that, the nanocrystals of double perovskites show remarkable improvement in properties compared to its coarse grain structure. Earlier studies shows that, $Ba_2RESbO_6$ perovskites are chemically stable with functional ceramics such as superconducting YBCO, have high melting points, have moderate dielectric constant and low loss tangent. The normal solid state reaction method of synthesis was found unsuccessful as it destroys the physical properties of the compound during the liquid phase sintering process. Further the solution combustion synthesis using chelating agents to improve the characteristics and sinterability of $Ba_2RESbO_6$ powder has the drawback that the product has to be further subjected to heat treatment to remove excess carbon. This affects the properties of the product. It is also observed that, this method cannot be used to synthesis $Ba_2RESbO_6$ (RE=La, Ho, Yb and Tm).
The modified combustion process is used in the present study to synthesis the high purity nanocrystals of Ba\textsubscript{2}RE\textsubscript{2}SbO\textsubscript{6} (RE= La, Ho, Yb and Tm) perovskites. This process uses low molecular weight chelating agents such as citric acid and requires short reaction times and fast heating rate. This process overcomes the drawbacks of other synthesis methods. Advantage of using this method is that it requires simple equipment’s for the formation of ultrafine high-purity nanopowder.

The synthesis of nanoparticles of Ba\textsubscript{2}RE\textsubscript{2}SbO\textsubscript{6} perovskites using modified combustion process involves formation of a precursor solution and refluxing in an open glass beaker to make coordinate complexes of the metal ions with the organic chelates. The precursor solution is prepared by mixing solutions of Ba(NO\textsubscript{3})\textsubscript{2} in distilled water, RE\textsubscript{2}O\textsubscript{3} in nitric acid and Sb\textsubscript{2}O\textsubscript{3} in boiled tartaric acid. Citric acid taken as the chelating agent is added to this mixture. The amount of citric acid is such that the energy released during reaction is maximum according to Density Functional Theory (DFT). The addition of oxidant (nitric acid) and fuel (ammonium hydroxide) to this mixture enhances the exothermic reaction and leads to the formation of citrate chelates. This precursor solution on heating decomposes to produce foam. This foam then ignites on persistent heating and then gives the fluffy product. This product gets flown off from the beaker and is the required nanopowders. The powders are collected and its characteristics are studied.

The chemical stability and presence of carbonaceous materials of the as-prepared powder is tested using Simultaneous Thermal Analyses (STA) involving differential thermal analysis and thermo gravimetric analysis and infrared spectroscopy. The analysis of DTA and TGA curves shows no weight loss at higher temperatures~150–1100°C range. The calcination temperature is expected to be reduced. These facts confirm the chemical stability and absence of organic matter in the prepared sample. The FT-IR spectrum of the sample was recorded to prove the absence of organic matter. Absence of IR spectral band shifting in the case of samples annealed at temperatures above 1500°C confirms the same result as obtained in STA.

The crystal structure of the sample was analyzed by combining X-Ray Diffraction (XRD) experiments and Rietveld analysis. The crystal structure analysis shows that all compounds (Ba\textsubscript{2}TmSbO\textsubscript{6}, Ba\textsubscript{2}YbSbO\textsubscript{6},
and $\text{Ba}_2\text{HoSbO}_6$ have cubic structure except $\text{Ba}_2\text{LaSbO}_6$ which is monoclinic. The analysis of the peaks of the XRD patterns confirms that the prepared compounds are single phase nanocrystals. The average particle size of the as prepared $\text{Ba}_2\text{RESbO}_6$ (RE = La, Tm, Yb and Ho) powder calculated using Debye Scherrer formula is ~30 nm shows their nanocrystalline nature.

Morphologies of the powders were determined by Scanning Electron Microscope (SEM) and Transmission Electron Microscopes (TEM). The SEM image of the samples was recorded and the average agglomerate size of particles is observed to be ~400nm. The TEM image of the samples ($\text{Ba}_2\text{LaSbO}_6$, $\text{Ba}_2\text{TmSbO}_6$) was recorded. TEM analysis shows that, the nanoparticles are of submicron size of 30 nm on an average. It confirms the result obtained in XRD analysis. The SAED pattern of the samples is also recorded. The ring nature in SAED pattern indicates the polycrystalline nature of the samples and bright spots indicates the agglomeration of crystallites. The sharp grain boundary and phase purity of the samples are analyzed through the high resolution TEM (HRTEM) image. Furthermore, the prepared samples are sintered at different temperatures and sintering density of the samples was determined using Archimedes’ method and theoretical densities was also determined using lattice parameters and are tabulated. The observation of SEM image analysis concludes that the grain size of samples increases with sintering.
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