CHAPTER 4
HIGH-K DIELECTRIC CHARACTERIZATION

The miniaturization of electronic devices viz., metal-insulator-semiconductor, RF (radio frequency) micro-electro-mechanical systems (MEMS) capacitive switch, RF MEMS phase shifter, dynamic random access memory, electro luminescent devices etc., along with improved performance (high speed, reduce size and low power consumption) have been demonstrated by replacing low-k dielectrics such as SiO$_2$, Si$_3$N$_4$ or its oxynitrides by high-k dielectrics [1-3]. Employing high-k dielectric in RF MEMS capacitive switch drastically improves RF performance in terms of large down state capacitance which results in better isolation, high capacitance ratio as well as reduction in size.

In this chapter, high-k dielectrics i.e. hafnium oxide and tantalum oxide have been characterized. The samples have been characterized using XRD, FTIR, EDAX, AFM and Laser Ellipsometer. The impact of annealing temperatures in O$_2$ and N$_2$ ambient on structural properties such as crystallite size, phase, orientation, stress have been studied using XRD. Annealing temperature as well as ambient condition has significant effects on stress, crystal size and thus the arrangement of atoms.

4.1 Hafnium Oxide

Hafnium oxide have been reported as potential contender among several other high-k dielectrics such as barium strontium titanate, zirconium titanate etc. The primary factors responsible for this are its outstanding electrical properties like wide band gap, high refractive index, high dielectric constant and better chemical stability i.e. excellent process compatibility with concurrent IC technology [1, 4].

The study conducted by Yi Zhang et al. [5], have demonstrated RF MEMS capacitive switch using hafnium oxide with isolation -40 dB in the frequency range 4-35 GHz. Hafnium oxide based RF MEMS capacitive switch with better isolation -60 dB at 35 GHz as well as capacitance ratio 43 was exhibited by X.J. He et al.[8].
Various research groups have reported characterization of hafnium oxide [5-7]. However, the detailed information of the microstructure and morphology of HfO$_2$ film have not been studied well for RF MEMS devices. Therefore, it is important to look into the structure of film.

Many deposition techniques such as chemical vapor deposition [9], ion-beam evaporation [10], RF sputtering [11-12], pulsed laser deposition [13] for HfO$_2$ thin film have been reported. In the present work, RF sputtering has been employed due to its low temperature processing, high deposition rate, good step coverage [1, 14-15]. Further the as-deposited samples have been separately annealed at 400 ºC, 600 ºC, 800 ºC and 1000 ºC in O$_2$ and N$_2$ ambient for 10 min. The deposition technique and post deposition annealing have significant impact on structural properties [3]. Hafnium Oxide exhibits three different phases: monoclinic, tetragonal and cubic, depending upon process parameters, though the most stable phase is monoclinic [4].

This section discusses, the effect of post deposition annealing in O$_2$ ambient, on structural and morphological properties. To obtain thin film with high dielectric constant, it is necessary to have a correct combination of various structural properties e.g. phase, texture and stress [16-18].

4.2 Experimental Details

A 2 inch low resistive p-type Si (100) substrate has been taken for the process. After standard cleaning treatment, substrate has been subjected to moisture bake at 120 ºC to prepare it for subsequent HfO$_2$ thin film deposition using MRC 8620J sputter system. Initially, vacuum chamber has been evacuated to base pressure 3e-6 Torr. HfO$_2$ target of 2 inch diameter and 99.95 % pure has been employed for sputtering process. The target has been kept at 8 cm distance from the substrate. Before deposition, HfO$_2$ target has been pre-sputtered for 10 mins using Ar alone with shutter above the gun closed. The deposition has been carried out for 35 mins with sputtering power 250 W to achieve 100 nm thin HfO$_2$. The chamber pressure has been maintained at 3 mTorr during sputtering. Further the samples have separately
been annealed in quartz tube furnace at temperatures 400 °C, 600 °C, 800 °C, 1000 °C respectively for 10 minutes each in O₂ and N₂ ambient.

The structural measurements have been characterized by X-ray diffraction using Bruker D8 Advance X-ray diffractometer system. The incident beam optics consists of a Cu Kα radiation source (λ=1.5406Å). The crystallite size of 100 nm HfO₂ thin film has been calculated using well known Scherrer’s Eq.4.1 [19-20].

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

4.1

where \(D\) is the crystallite size, \(k=0.9\) is the crystal constant, \(\lambda\) is the wavelength of X-ray used, \(\beta\) is the broadening of diffraction line measured at half of its maximum intensity and \(\theta\) is the angle of diffraction [19-20]. Bragg’s law has been used to calculate the interplanar spacing, \(d_{(hkl)}\), from \(2\theta_{(hkl)}\) as shown in Eq. 4.2.

\[
d = \frac{\lambda}{2 \sin \theta}
\]

4.2

A Bruker Tensor 37 type Fourier transform infrared (FTIR) spectrometer has been used to obtain bond information of the HfO₂ thin films. The samples have been studied in the range of 1200-400 cm\(^{-1}\) by FTIR spectroscopy.

The Elemental or Energy dispersive X-ray spectroscopy (EDAX) has been used to detect elements present in significant quantity (quantitative determination of bulk element composition). The EDAX analysis of HfO₂ film deposited on silicon substrate, has been carried out on JEOL SEM system operated at 16 kV accelerating voltage. Surface morphology of HfO₂ thin film has been studied by Nova Atomic Force Microscope (AFM). The refractive index and thickness have been measured by laser ellipsometer SENTECH SE500 using laser radiation of 632 nm wavelength.
4.3 HfO$_2$ Annealed in O$_2$ Ambient

In this section the effect of annealing in O$_2$ ambient on structural and morphological properties of HfO$_2$ thin film has been discussed.

4.3.1 Crystallographic analysis

The crystal structure and orientation of the HfO$_2$ samples have been studied using X-ray diffraction (XRD) patterns. Fig. 4.1(a) shows the typical XRD patterns of as-deposited and annealed HfO$_2$ thin films at 400 °C, 600 °C, 800 °C and 1000 °C in O$_2$ ambient which specify that, the HfO$_2$ is purely crystalline in nature. The XRD pattern of as-deposited HfO$_2$, contains peak at Bragg’s angle 2θ=28.45895, assigned to (-111) crystallographic plane which indicates the presence of small nano crystallites [33].

Minor peaks of other orientation are also present due to monoclinic crystallites. Therefore, anisotropy exists and (-111) crystallographic plane exhibits lowest strain energy [4, 21]. Crystallite size and preferred orientation along (-111) planes increase with increase in annealing temperatures. XRD pattern of annealed HfO$_2$ at 1000 °C indicates highly oriented nature. In the present case, increasing temperature favors
the preferred orientation along (-111) while minimizing the strain energy. For further analysis of growth process, crystallite size and lattice mismatch at nanoscale dimension, high resolution scans have been performed on (-111) plane as shown in Fig. 4.1(b). Due to the shift and broadening of diffraction peaks, significant change occurs in crystallite size and strain [21]. The diffraction peak shifts to higher angle (2θ) in as-deposit HfO₂ thin film compare to standard position at 28.347 [22]. This indicates to the fact that the contraction of the lattice occurs with 0.38 % compressive strain. At lower annealing temperature i.e. 400 ºC and 600 ºC, 2θ shifts to lower side of standard value which points to the expansion of the lattice with tensile strain of 0.58 % and 0.39 %, respectively. With further increase in annealing temperature at 800 ºC and 1000 ºC, peak again shifts to higher 2θ which attribute to lattice contraction with compressive strain 0.30 % and 0.19 %, respectively.

Most of the existing research work have studied the effect of stress on crystal arrangements and have significantly discussed only lattice expansion after annealing [21]. None of the prior works have observed both trends i.e. lattice expansion and lattice contraction at annealing temperature. However, we have observed both the two different trends i.e. lattice expansion at lower annealing temperature and lattice contraction at higher annealing temperature. It is anticipated that the lattice expansion has occurred due to dominant repulsive force between Hf⁴⁺-Hf⁴⁺ atoms. This signifies that there is deficiency of oxygen. However at high annealing temperature, lattice contraction exists due to strong attraction force between Hf⁴⁺-O²⁻ dipoles which in effect points to oxygen efficiency. The same is exhibited in results from FTIR and laser ellipsometry analysis which is discussed in further section. The crystallite size obtained for (-111) crystallographic plane of as-deposited HfO₂ thin film is ≈ 6.12 nm, which matches very well with previously reported article [21]. With increase of the annealing temperature, the crystallite size increases, nevertheless the d spacing decreases as shown in Fig. 4.2(a).
### 4.3.2 FTIR spectra of sputter deposited HfO\textsubscript{2} thin film

Fig. 4.2(b) shows Fourier Transform Infrared (FTIR) spectrum of HfO\textsubscript{2} thin film. The bonding structures of HfO\textsubscript{2} films have been identified in the 1200-400 cm\textsuperscript{-1} spectral region. FTIR spectrum of hafnium oxide film shows broad absorption band between 1100 and 1000 cm\textsuperscript{-1} which corresponds to transverse optical component of asymmetrical stretch of SiO\textsubscript{4} [3, 23-24].

![Figure 4.2](image)

#### Table 4.1

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>FWHM</th>
<th>2θ(deg)</th>
<th>D(nm)</th>
<th>d(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-deposited</td>
<td>1.33837</td>
<td>28.45895</td>
<td>6.12</td>
<td>0.3132</td>
</tr>
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<td>400 °C</td>
<td>1.272</td>
<td>28.17662</td>
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<td>0.3163</td>
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<td>600 °C</td>
<td>1.16311</td>
<td>28.23311</td>
<td>7.04</td>
<td>0.3157</td>
</tr>
<tr>
<td>800 °C</td>
<td>0.94207</td>
<td>28.43506</td>
<td>8.69</td>
<td>0.3135</td>
</tr>
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<td>1000 °C</td>
<td>0.62054</td>
<td>28.40323</td>
<td>13.2</td>
<td>0.3138</td>
</tr>
</tbody>
</table>

According to report Neumayer et al. [25], a wide absorption band between 1200 and 810 cm\textsuperscript{-1} indicated that it was due to three components viz., asymmetric stretch of SiO\textsubscript{4} between 1180 and 1080 cm\textsuperscript{-1} [26], absorption peak at \(\approx\)970 cm\textsuperscript{-1} was attributed to HfSiO, and at \(\approx\)880 cm\textsuperscript{-1} was assigned to Si-O. Absorption peak, indicated at \(\approx\)1105 cm\textsuperscript{-1} was assigned to interstitial oxygen in the Si bulk [2, 27].
However in this research work, peaks at ≈1105 cm\(^{-1}\), 970 cm\(^{-1}\) and 880 cm\(^{-1}\) have not been found. T.C. Chen et al. reported the presence of a peak lying between 934 cm\(^{-1}\) and 838 cm\(^{-1}\) corresponding to Si-O\(^-\) [28]. However in as-deposited film, a peak has been found at 921 cm\(^{-1}\) later which has disappeared after annealing treatment. It is apparent that when the annealing temperature increases, strength of absorption peak assigned to Si-O vibration becomes weak. The weak peak detected at 610 cm\(^{-1}\) for the film annealed at 800 and 1000 °C is related to absorption of a Si phonon [24]. Also, the wide peak lying at 748 cm\(^{-1}\) corresponds to HfO\(_2\) [2, 24]. The other main peaks around 512, 412 cm\(^{-1}\) are due to Hf-O chemical bonds [2, 23, 29-31]. With increase in annealing temperature, more oxygen is absorbed by thin film and therefore Hf-O bond peaks increase due to oxidation of HfO\(_2\) thin film. At 412, 512 cm\(^{-1}\), absorption of photon increases with increase in annealing temperature which reveals strengthening of Hf-O bonds as shown in Fig 4.2 (b). Using XRD analysis, the same dominant attraction force between Hf\(^{4+}\) - O\(^{2-}\) dipoles (which signifies more oxygen is absorbed by thin film) is observed at 800 °C and 1000 °C annealing temperature.

### 4.3.3 Elemental composition analysis of HfO\(_2\) film

EDAX spectrum (shown in Fig. 4.3) represents the different elements present in the thin film. The data in Fig. 4.3 is shown with no smoothing, filtering or processing of any kind. The EDAX spectrum shows clear peaks corresponding to the 72 Hf L (7.89 keV) line, 72 Hf M line (1.64 keV) and 8 O K line (0.52 keV). The 14 Si K line (1.74 keV) peak is observed in the EDAX spectrum is due to silicon substrate. No other peak is observed over the entire 0 keV to 20 keV detection window.
Figure 4.3: Chemical composition of HfO$_2$ is determined by EDAX.

4.3.4 Surface Morphology
Figure 4.4: 2-D and 3-D AFM images of HfO$_2$ thin films: (a) as-deposited (b) 400 ºC (c) 600 ºC (d) 800 ºC (e) 1000 ºC annealed in O$_2$ ambient

Table 4.2

ROUNness AND GRAIN PARAMETERS OF HfO$_2$ THIN FILMS

<table>
<thead>
<tr>
<th>HfO$_2$ thin film</th>
<th>RMS roughness (nm)</th>
<th>Average roughness (nm)</th>
<th>Mean grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-deposited</td>
<td>7.33</td>
<td>6.13</td>
<td>37.856</td>
</tr>
<tr>
<td>400 ºC</td>
<td>19.70</td>
<td>17.20</td>
<td>53.202</td>
</tr>
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<td>600 ºC</td>
<td>8.46</td>
<td>7.09</td>
<td>48.359</td>
</tr>
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<td>800 ºC</td>
<td>14.80</td>
<td>12.40</td>
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</tr>
<tr>
<td>1000 ºC</td>
<td>13.2</td>
<td>16.4</td>
<td>67.364</td>
</tr>
</tbody>
</table>
The surface morphology of as-deposited and annealed HfO$_2$ thin films have been analyzed using atomic force microscopy in tapping mode. The films are scanned over 1x1µm$^2$ at 3.656V, 1 Hz frequency. Fig. 4.4 shows 2-D and 3-D AFM images of as-deposited and annealed HfO$_2$ thin films. AFM images have been obtained at different locations of wafer which show that the film is homogeneous, free of cracks and pinholes. The root mean square (RMS) roughness, average roughness and mean grain size are shown in Table 2. Annealing temperature, ambient conditions and stress have significant impact on grain size as well as surface roughness [32]. Most of the research groups have studied a normal trend of increasing grain size after annealing [34]. Instead, we have analyzed different trends of grain size. AFM data shows that the film’s RMS roughness reduces maximum at 600 ºC annealing temperature. The reduction in the size of nanoparticles is observed at 600 ºC annealing temperature. However, with further increase in annealing temperature from 600 ºC to 800 ºC, the smaller nanoparticles start combining together in order to form a larger nanoparticle. It is clear that rearrangement of nanoparticles at annealing temperature is due to presence of stress in the film.

4.3.5 Laser Ellipsometry

Laser Ellipsometer is a high performance tool to measure refractive index and thickness of materials. It is widely known that the refractive index is closely related to the structural properties and optical density of the film [1].

Figure 4.5: (a) Dependence of refractive index (n) on annealing temperature in O$_2$ ambient, at wavelength 632 nm. (b) Real part of dielectric constant, $\varepsilon_r$, at wavelength 632 nm on annealing temperature in O$_2$ ambient.
The thickness of HfO$_2$ thin film is shown in Fig. 4.6. Fig. 4.5 shows refractive index and real part of dielectric constant of HfO$_2$ thin film as-deposited and annealed at various temperatures in O$_2$ ambient.

It is observed that refractive index decreases initially at 600 °C annealing temperature which signifies that the film is less optically dense. This could have occurred due to stress (i.e. lattice expansion), which implies dominant repulsive force between Hf$^{4+}$-Hf$^{4+}$ atoms and therefore reduction in oxygen atoms. Also reduction in the size of nanoparticles at 600 °C annealing temperature is confirmed from AFM data. At 800 °C and 1000 °C annealing temperature, refractive index increase which indicates that the film is denser (optically). It is considered to be caused by lattice contraction, resulting in increase in attraction force between Hf$^{4+}$-O$^{2-}$ dipoles. The same is concluded from XRD and FTIR analysis. The variation in grain size and thickness of HfO$_2$ thin film with increase in annealing temperature is confirmed from the AFM data and thickness plot (shown in Table 4.2 and Fig. 4.6). The annealing temperature as well as ambient has significant impact on thickness of thin film. At low annealing temperature, the variation in film thickness is due to the rearrangement of grains and then densification of thin film occurs which is also confirmed using AFM analysis. At high annealing temperature, film thickness increases due to oxygen diffusion in HfO$_2$ thin film. Thus oxidation of HfO$_2$ thin film has been occurred and at 1000 °C film is fully oxidized [35]. It is observed that the nature of polarization is different due to presence of stress in crystalline HfO$_2$ thin film [32].
Since the sputtered thin film is transparent at 632 nm, therefore, dielectric constant’s imaginary part goes to zero (no extinction coefficient) and the dielectric constant becomes equal to the square of refractive index ($\varepsilon = n^2$) [2]. Fig. 4.5(b) shows the dielectric constant’s real part ($\varepsilon_1$) of as-deposited HfO$_2$ and annealed HfO$_2$.

### 4.4 HfO$_2$ Annealed in N$_2$ Ambient

In previous section, the impact of annealing in O$_2$ ambient on structural and morphological properties has been discussed. For better electrical properties, annealing temperature above 600 °C is desired in O$_2$ ambient. In this section, the effect of annealing temperature in N$_2$ ambient on HfO$_2$ thin film is discussed. We have observed only expansion in lattice after annealing treatment. The samples annealed in N$_2$ ambient show close match of interplanar spacing to standard ICDD as compare to annealed data of O$_2$ ambient. It reveals that the structural, morphological of thin films are better in N$_2$ ambient than O$_2$ ambient and thus electrical properties.

#### 4.4.1 Crystallographic analysis

The XRD pattern peaks of as-deposited and annealed HfO$_2$ thin film at 400º, 600º, 800º and 1000º in N$_2$ ambient are assigned to monoclinic HfO$_2$ as shown in Fig. 4.7 (a). The diffraction pattern indicates that the thin film is crystalline in nature. The broad peak at $2\theta = 28.45895$, is assigned to (-111) crystallographic plane which explains the presence of small nanoparticles. The nanoparticle size and preferred orientation along (-111) planes increase with increase in annealing temperatures. However, minor peaks due to other orientation are also present. Anisotropy generally exists in crystalline film and also strain energy will be different in various crystallographic planes [4,21]. The growth will typically prefer those orientations with lowest strain energy density. In our case, (-111) crystallographic plane reveals lowest strain energy.
Figure 4.7: (a) XRD patterns of HfO$_2$ films as-deposited and annealed at various temperatures in N$_2$ ambient. (b) High resolution XRD scans of monolithic (-111) peaks of HfO$_2$ films.

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>FWHM</th>
<th>2θ(deg)</th>
<th>D(nm)</th>
<th>d(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>1.33837</td>
<td>28.45895</td>
<td>6.12</td>
<td>0.31326</td>
</tr>
<tr>
<td>400 °C</td>
<td>1.28629</td>
<td>28.142</td>
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</tr>
<tr>
<td>600 °C</td>
<td>1.1997</td>
<td>28.33579</td>
<td>6.827</td>
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<tr>
<td>800 °C</td>
<td>0.94529</td>
<td>28.29876</td>
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<td>0.59745</td>
<td>28.30891</td>
<td>13.7</td>
<td>0.31488</td>
</tr>
</tbody>
</table>

In order to analyze annealing process and its effect on crystallite size, lattice mismatch at nanoscale dimension, high resolution scan is performed on (-111) plane as shown in Fig. 4.7 (b). The shift and sharpening of diffraction peak is the significance of change occurred in strain and size, respectively [21]. The XRD peak shifts to higher angle (2θ) in as-deposit HfO$_2$ thin film compare to standard position at 28.347 [22]. This suggests the occurrence of lattice contraction with 0.38% compressive strain. After annealing, diffraction peak shifts to lower side which indicates lattice expansion. Though, the 2θ of 600 °C annealed film is comparable with standard value of 2θ. The annealed films (400 °C, 600 °C, 800 °C, and 1000 °C) attribute to tensile strain i.e. 0.70%, 0.03%, 0.16%, 0.13% respectively. Lattice contraction in as-deposited film could be occurred due to nucleation of atoms during sputtering process. Lattice expansion after post deposition annealing has been appeared due to stretching or rearrangement of bond energy which results in reshuffling of atoms. **More closely matching of interplanar spacing offers more exact electrical properties.** The crystallographic properties are shown in Table 4.3. The crystallite size obtained for (-111) crystallographic plane of as-
deposited HfO$_2$ thin film matches well with previously reported article [21]. With increasing annealing temperature, crystallite size increases, nevertheless d spacing tends to become stable after 600 °C and matches closely with standard interplanar spacing ($d=0.31447\text{nm}$) [22] as shown in Fig. 4.8 (a).

4.4.2 FTIR spectra of sputter deposited HfO$_2$ thin film

![Figure 4.8: (a) Variation of FWHM, D (crystallite size) and $d$(-111) spacing with annealing temperature. (b) Infrared absorption spectra for HfO$_2$ thin film as-deposited and annealed at various temperatures in N$_2$ ambient.](image)

Fourier transform infrared (FTIR) spectrum of as-deposited and annealed (in N$_2$ ambient) HfO$_2$ thin films are shown Fig. 2(b). The chemical bonds have been detected in the 1300-400 cm$^{-1}$ spectral region. The wide absorption between 1100 and 1000 cm$^{-1}$ range has been shown in FTIR spectrum of HfO$_2$ film. This indicates due to the presence of asymmetrical stretch of SiO$_4$ [3, 23-24]. Neumayer et al. [25] has reported, a broad absorption band between 1200 and 810 cm$^{-1}$ which was due to three components viz., absorption range from 1180 to 1080 cm$^{-1}$ indicated asymmetric stretch of SiO$_4$ [26], absorption peak at ≈970 cm$^{-1}$ absorption peak was assigned to HfSiO, and at ≈880 cm$^{-1}$ was attributed to Si-O$^-$. Absorption peak, found at ≈1105 cm$^{-1}$ was due to the interstitial oxygen in the Si bulk [3, 27].

Nevertheless in this research work, peaks at ≈1105 cm$^{-1}$, 970 cm$^{-1}$ and 880 cm$^{-1}$ have not been observed. According to T.C. Chen et al. research work, the peaks lying at
934 cm\(^{-1}\) and 838 cm\(^{-1}\) were due to the presence of a Si-O\(^-\) chemical bond [28]. However in as-deposited film, a peak at 921 cm\(^{-1}\) has been detected. After annealing treatment, the peak has been disappeared. With increase in annealing temperature, vibration of Si-O chemical bond becomes weak. The weak peak found in 800 °C annealed film at 610 cm\(^{-1}\) is due to the absorption of a Si phonon [24]. The small absorption peak lying at 748 cm\(^{-1}\) is due to HfO\(_2\) [3, 24]. The absorption peaks at 512 and 412 cm\(^{-1}\) corresponds to presence of Hf-O chemical bonds [3, 23, 29-31].

### 4.4.3 Elemental composition analysis of HfO\(_2\) film

![Figure 4.9: Chemical composition of HfO\(_2\) is determined by EDAX.](image)

The elements present in thin film without filtering, smoothing or processing of any kind have been confirmed using EDAX as shown in Fig. 4.9. The peaks at 72 Hf L (7.89 keV) line, 72 Hf M line (1.64 keV) and 8 O K line (0.52 keV) have been observed due to the HfO\(_2\) thin film. The peak at 14 Si K line (1.74 keV) is also detected in the EDAX spectrum which corresponds to silicon substrate.
### 4.4.4 Surface Morphology

#### Table 4.4

ROUGHNESS AND GRAIN PARAMETERS OF HfO$_2$ THIN FILMS.

<table>
<thead>
<tr>
<th>HfO$_2$ thin film</th>
<th>RMS roughness (nm)</th>
<th>Average roughness (nm)</th>
<th>Mean grain size (nm)</th>
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<tbody>
<tr>
<td>as-deposited</td>
<td>7.33</td>
<td>6.13</td>
<td>37.856</td>
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<tr>
<td>400 °C</td>
<td>3.37</td>
<td>2.43</td>
<td>41.705</td>
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<td>1000 °C</td>
<td>3.81</td>
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![Surface Morphology Images]
The surface morphology of HfO$_2$ thin films have been studied using atomic force microscopy in tapping mode. The scanning area of films is 1x1 µm$^2$ at 3.656 V, 1 Hz frequency. The 2-D and 3-D AFM images of as-deposited and annealed HfO$_2$ thin films are shown in Fig. 4.10. The scan has been performed on various positions on thin film. AFM images show that the film is homogeneous and crack free. The root mean square (RMS) roughness and average roughness are shown in Table 4.4. Ambient conditions and annealing temperature have considerable effect on surface roughness as well as arrangement of atoms [32]. With further increase in annealing temperature the smoothening of thin film has been occurred [34]. The film annealed in N$_2$ ambient shows better roughness compared to film annealed in O$_2$ ambient [46]. The formation of cluster is clearly visible at 800 ºC from 2 D AFM data with increase in annealing temperature. The increase of nanoparticle size with increase in annealing temperature is observed as shown in Table 4.4.
4.4.5 Laser Ellipsometry

For measurement of refractive index and thickness of materials: Laser Ellipsometer is high performance tool. It is usually known that the structural properties and density of thin film are closely related to refractive index [47]. Fig. 4.11 shows refractive index and real part of dielectric constant of HfO$_2$ thin film as-deposited and annealed at various temperatures in O$_2$ ambient. Initially refractive index increases with increase in annealing temperature and finds its maximum value at 600 °C.

Figure 4.11: (a) Dependence of refractive index (n) on annealing temperature in N$_2$ ambient, at wavelength 632nm. (b) Real part of dielectric constant, $\varepsilon$, at wavelength 632nm on annealing temperature in N$_2$ ambient.

Figure 4.12: Thickness of HfO$_2$ thin film versus annealing temperature, at wavelength 632 nm.
It is noticed that refractive index increases at 600°C annealing temperature which indicates that the film is optically dense. This could also be anticipated from XRD analysis that interplanar spacing (d=0.31459 nm) at 600 °C matches closely with to the standard interplanar spacing (d=0.31447 nm) [22] and thus almost zero lattice expansion. At 800 °C annealing temperature, the refractive index decreases which shows that the film is less optically dense. It is considered to be caused by the less absorption of photon which results in weakening of Hf-O chemical bond. Due to presence of stress in thin film, the nature of polarization is quite different [32]. The HfO$_2$ thin film reveals transparent at 632 nm. Due to which, dielectric constant’s imaginary part tends to zero (no extinction coefficient) and thus dielectric constant becomes equal to the square of refractive index ($\varepsilon_1=n^2$) [3]. Fig. 4.11(b) shows the dielectric constant’s real part ($\varepsilon_1$) of as-deposited HfO$_2$ and annealed HfO$_2$ in N$_2$ ambient.

4.5 Tantalum oxide

The miniaturization of electronic devices with improved performance such as high speed, and low power consumption has been forced to replace low-k dielectrics such as SiO$_2$, Si$_3$N$_4$ or its oxynitrides by high k dielectrics [36]. Tantalum oxide has been reported as possible candidate among several other high-k dielectrics such as zirconium titanate, barium strontium titanate etc for metal-oxide-semiconductor, dynamic random access memory, RF MEMS capacitive switch, electro luminescent devices [17]. RF MEMS capacitive switches based on high-k dielectric, drastically improves RF losses in terms of high capacitance ratio with reduction in size as well.

In the present research work, among various deposition techniques such as chemical vapor deposition, e-beam evaporation, RF sputtering has been employed due to its better step coverage, low temperature processing etc. The samples have separately been annealed at 400, 600, 800 and 1000°C in O$_2$ and N$_2$ ambient for 10 mins. In order to achieve high dielectric constant, it is required to have a correct combination of various parameters for example texture, phase and stress [17]. In this work, the impact of post deposition annealing in O$_2$ ambient on morphological as well as
structural properties have been studied. We analyses that stress in the films can have a significant effect on the refractive index of Ta$_2$O$_5$ films on Si and thus dielectric constant.

4.6 Experimental Details

Ta$_2$O$_5$ thin film (100 nm) has been deposited on 2 inch low resistive p-type Si (100) substrate using radio-frequency sputtering. The vacuum chamber has been initially evacuated to base pressure $\sim 10^{-6}$ torr. Ta target of 4 in. diameter and 99.9999% pure has been employed for sputtering process. The highly pure sputtering gasses Ar and O$_2$ have been used for reactive growth to form Ta-oxide (TaO$_x$). A power of 500 W has been employed for reactive deposition with Ar to O$_2$ ratio of 60:40 (5.6 sccm Ar mixed with 3.6 sccm of O$_2$). The working gas pressure has been set to $7 \times 10^{-3}$ Torr.

Before deposition, Ta target has been pre-sputtered for 10mins using Ar alone with shutter above the gun closed. The deposition has been carried out for 40 mins to achieve thickness of 100 nm. Further samples have separately been annealed for 10 minutes each at temperatures 200ºC, 400ºC, 600ºC, 800ºC, 1000ºC in O$_2$ and N$_2$ ambient.

The structural measurements have been characterized by X-ray diffraction using Bruker D8 Advance x-ray diffractometer system. The incident beam optics consists of a Cu Kα radiation source ($\lambda = 1.5406$Å). A Bruker Equinox 55 type Fourier transform infrared (FTIR) spectrometer has been used to obtain information on both chemical composition and structure of the films. The bonding structure of the films was studied in the range of 4000-400 cm$^{-1}$ by FTIR spectroscopy.

The Elemental or Energy dispersive X-ray spectroscopy (EDAX) has been used to detect elements present in significant quantity (quantitative determination of bulk element composition) of sputtered Ta$_2$O$_5$ thin film. The EDAX analysis of Ta$_2$O$_5$ film deposited on silicon substrate, carried out on JEOL SEM system operated at 16 kV accelerating voltage. The refractive index and thickness have been measured by laser ellipsometer SENTECH SE500 using laser radiation of 632 nm wavelength.
4.7 Ta₂O₅ Annealed in O₂ Ambient

In this section the effect of annealing in O₂ ambient on structural and morphological properties of Ta₂O₅ thin film has been discussed.

4.7.1 Crystallographic analysis

The crystal structure and orientation of the Ta₂O₅ samples have been studied using X-ray diffraction (XRD) patterns. The typical XRD patterns of as-deposited (RT) and annealed Ta₂O₅ thin film at 400 °C, 600 °C, 800 °C and 1000 °C in O₂ ambient are shown in Fig. 4.13 (a). Initially as-deposited Ta₂O₅ thin film is amorphous in nature and starts crystalline after 800 °C annealing treatment. The XRD pattern contains various peaks, assigned to (0 1 0), (4 1 1)/(12 0 1), (11 0 2)/(12 1 1) and (24 1 0)/(12 2 1) which indicates the presence of nano crystallite size. The two different orientations at same 2 theta (2θ) could be because of growth of two different crystal structure. These peaks match with the peak positions listed for Ta₂O₅ in ICDD file No. 791375, confirming the films to be Ta₂O₅. The value of full width at half maximum (FWHM), 2theta, crystallite size and interplanar spacing corresponding to the most intense peak (010) at various annealed temperatures as shown in table 4.5. The average crystallite size of 100 nm Ta₂O₅ thin film is calculated using well known Scherrer’s equation [37]

![Figure 4.13: (a) XRD patterns of Ta₂O₅ films as-deposited and annealed at various temperatures in O₂ ambient. (b) Shift in the (010) peak of XRD pattern as compared to single crystal shown with sharp solid line.](image-url)
\[ D = \frac{k\lambda}{\beta \cos \theta}, \]

where \( D \) is the crystallite size, \( k(=0.9) \) is the crystal constant, \( \lambda(=1.5406\text{Å}) \) is the wavelength of X-ray used, \( \beta \) is the broadening of diffraction line measured at half of its maximum intensity and \( \theta \) is the angle of diffraction. Bragg’s law was used to calculate the interplanar spacing, \( d_{(hkl)} \), from \( 2\theta_{(hkl)} \) as shown in Eq. 4.4. The crystallite size depends on the broadening of the diffracted peak. From the calculations, the average crystallite size of 22.35 nm and 20.71 nm for 800 ºC and 1000 ºC annealed film in O\(_2\) ambient, respectively. The crystallite size matches closely with previously reported articles [38].

\[ d = \frac{\lambda}{2 \sin \theta} \]

The residual stress, strain in the sample could be determined from XRD profile. The shift in the most prominent peak position is also observed in our Ta\(_2\)O\(_5\) films as shown in Fig. 4.13 (b) for (010) plane. It indicates that micro strain has developed in the prepared thin films. In our case, Ta\(_2\)O\(_5\) (010) peaks are shifted towards lower angles of \( 2\theta \) as compared to the standard data (2\( \theta \)=22.819) from ICDD file No. 791375 which signifies to lattice expansion as shown in Fig 4.13 (b). The 800 ºC and 1000 ºC annealed films attribute to expansion in lattice with tensile strain 0.43 % and 0.20 %, respectively. Lattice expansion might be occurred due to strong repulsive force between Ta\(^{5+}\) - Ta\(^{5+}\) dipoles which implies oxygen deficiency.

The apparent shift in diffraction patterns specifies the uniform stress originated in the film due to the lattice mismatch [39-40]. The crystallite size and strain could also be detected using W-H method approach. The finite crystallite size which varies as \( 1/\cos \theta \) (see Eq.(4.4)) and the other is the induced strain \( (\varepsilon) \), which is given by Wilson formula \( (\beta_{hkl} = 4\varepsilon \tan \theta) \) [37]. In Williamson-Hall approach the internal stress in the prepared films and the line due to finite size of coherent scattering
region are considered. The finite size is taken care by Scherres’s equation and stress by Wilson formula in Williamson-Hall equation as follow [37, 41]:

\[ \beta_{hkl} \cos \theta = \frac{k \lambda}{D} + 4 \varepsilon \sin \theta \quad 4.4 \]

where \( \varepsilon \) is the strain, which is usually assumed to be proportional to the square root of the density of dislocations, \( \beta_{hkl} \cos \theta / \lambda \) is the total integral breadth in reciprocal space and \( 2 \sin \theta / \lambda \) is the distance of reciprocal point from origin.

**Table 4.5**

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>FWHM</th>
<th>2( \theta )</th>
<th>D (nm)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800ºC</td>
<td>0.24459</td>
<td>22.71884</td>
<td>22.35</td>
<td>3.911</td>
</tr>
<tr>
<td>1000ºC</td>
<td>0.26384</td>
<td>22.77545</td>
<td>20.71</td>
<td>3.902</td>
</tr>
</tbody>
</table>

Figure 4.14: (a) Williamson-Hall plots 800ºC and 1000ºC annealed Ta₂O₅ film in O₂ ambient.

Fig 4.14 (a) and (b) shows the measured values of \( \beta_{hkl} \cos \theta \) as a function of \( 4 \sin \theta \) for 800 and 1000 ºC annealed Ta₂O₅ films. One can estimate the strain from the slope of the fitted line and crystallite size (D) from its intersection with the co-ordinate. Eq.(4.4) corresponds to uniform deformation model, which considers the isotropic nature of crystal.
In table 4.6, it is shown that the strain as well as the estimated crystallite size obtained for 800 °C annealed film is more than 1000 °C annealed film. It indicates that by increasing the annealing temperature, strain and crystallite size decreases.

### 4.7.2 FTIR spectra of sputtered Ta$_2$O$_5$ thin film

Fig 4.15 shows Fourier transform infrared (FTIR) spectrum of Ta$_2$O$_5$ thin film as-deposited and annealed at various temperatures in O$_2$ ambient. The bonding structures of HfO$_2$ films are detected in the 400-4000 cm$^{-1}$ spectral region; however the important features are seen in the ranges 400-1200 cm$^{-1}$ and 1400-3000 cm$^{-1}$.

![Figure 4.15: FTIR spectra of Ta$_2$O$_5$ thin films as-deposited and annealed at various temperatures in O$_2$ ambient](image-url)
TABLE 4.7
INFRARED ABSORPTION PEAKS IN AMORPHOUS AND CRYSTALLINE Ta2O5 THIN FILM

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Crystalline</th>
<th>Amorphous</th>
<th>Associated bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>640</td>
<td>Ta≡O stretching vibrations</td>
<td></td>
</tr>
<tr>
<td>810</td>
<td>≈900</td>
<td>Ta-O-Ta stretching vibrations</td>
<td></td>
</tr>
<tr>
<td>2343</td>
<td>2337</td>
<td>Ta=O stretching vibrations</td>
<td></td>
</tr>
</tbody>
</table>

Fourier-transfer infrared (FTIR) spectroscopy is a highly capable instrument for examining bonding structures since it can measure the vibrational modes due to atomic bonds in Ta₂O₅ thin films [42]. FTIR spectrum of Ta oxide film shows strong broad absorption band between 400 and 1000 cm⁻¹ which corresponds to vibration of oxygen atoms [42]. However, Haruhiko et al. observed Ta-O bond in broad absorption band between 200 and 1000 cm⁻¹ [42-44]. Haruhiko et al. and H.Ono et al. explains vibrational mode of Ta₂O₅ due to complex lattice structure using V₂O₅ which has same lattice structure. Clauws et al. [45] reports stretching vibrations due to V-O-V and O≡3V at absorption range between 600 and 1000 cm⁻¹. By comparing Ta₂O₅ data with V₂O₅, peak at ≈640 cm⁻¹ in amorphous film (=510cm⁻¹ for crystalline) attributes to vibrational mode of O≡3Ta bonds [42-44]. In crystalline films, small absorption peak at ≈810cm⁻¹ is attributed to stretching mode of Ta-O-Ta bonds, while in amorphous films, it is observed at ≈900 cm⁻¹ [42-44]. The samples annealed at 400, 600 ºC are amorphous which have same spectrum as that for an as-deposited. Annealed at 800 and 1000 ºC in O₂ ambient, crystallizes Ta₂O₅ which results in change in phonon absorption band. The two small peaks are also observed in the range 2330-2370 cm⁻¹ which signifies presence of Ta=O bonds in Ta₂O₅ structure, independent of whether they are amorphous or crystalline. In amorphous films, peaks are observed at 2337 cm⁻¹ and 2364 cm⁻¹ while in crystalline films, absorption peaks at 2343 cm⁻¹ and 2368 cm⁻¹. It is clear that when the annealing temperature increases, intensity of absorption peak attributed to Ta=O, which signifies the strengthening of oxygen bonds. Although, Haruhiko et al. indicated small sharp peak of double bond at 2335 cm⁻¹ in amorphous and after crystallization over 700 ºC, peaks shifted to 2340 cm⁻¹ absorption peak. The Infrared absorption peaks of Ta₂O₅ thin film is shown in Table 4.7.
4.7.3 Elemental composition analysis of Ta$_2$O$_5$ film

EDAX spectrum (shown in Figure 4.16) represents the different elements present in the Ta$_2$O$_5$ film. The EDAX spectrum shows a clear peaks corresponding to the 73 Ta L (8.14 keV) line, 73 Ta M line (1.70 keV) and 8 O K line (0.52 keV). The observed 14 Si K line (1.74 keV) peak in the EDAX spectrum is due to silicon substrate. No other peaks are observed over the entire 0 keV to 20 keV detection windows.

![Figure 4.16: Chemical composition of Ta$_2$O$_5$ is determined by EDAX.](image)

4.7.4 Laser Ellipsometry

Laser Ellipsometer is high performance tool to measure refractive index, thickness of materials. [46]. Figure 4.17 shows refractive index and real part of dielectric constant of Ta$_2$O$_5$ thin film as-deposited and annealed at various temperatures in O$_2$ ambient.

![Figure 4.17: (a) Dependence of refractive index, n, at wavelength 632 nm on annealing temperature in O$_2$ ambient. (b) Real part of dielectric constant, $\epsilon$, at wavelength 632 nm on annealing temperature in O$_2$ ambient.](image)
It is observed that refractive index decreases at annealing temperature which could be signified that the film is less optical dense [47]. This could have occurred due to stress (i.e. lattice expansion), which implies dominant repulsive force between Ta$^{5+}$-Ta$^{5+}$ atoms and therefore oxygen deficiency. Since the sputtered thin film is transparent at 632 nm, therefore, dielectric constant’s imaginary part goes to zero (no extinction coefficient), varies square of refractive index [48]. Fig 4.17 (b) shows the dielectric constant’s real part ($\varepsilon_1$) of as deposited Ta$_2$O$_5$ and annealed at 400,600,800 and 1000 °C in O$_2$ ambient. It is noticeable that the dielectric constant ($\varepsilon_1$) is found to be first increasing with annealing temperature after then at 600 °C it decreases. Thus suggesting nature of polarization is different in crystalline Ta$_2$O$_5$ thin film due to presence of stress as compared to amorphous.

### 4.8 Ta$_2$O$_5$ Annealed in N$_2$ Ambient

In this section the effect of annealing in N$_2$ ambient on structural and morphological properties of Ta$_2$O$_5$ thin film has been discussed.
4.8.1 Crystallographic analysis

The typical XRD patterns of as-deposited and annealed Ta$_2$O$_5$ thin film at 400 °C, 600 °C, 800 °C and 1000 °C in N$_2$ ambient are shown in Fig. 4.19 (a). The crystal structure and orientation of the Ta$_2$O$_5$ samples have been analyzed using X-ray diffraction (XRD) patterns. Initially as-deposited Ta$_2$O$_5$ thin film is amorphous in nature and starts crystalline after 800 °C annealing treatment. The XRD pattern contains various peaks, assigned to (0 1 0), (4 1 1) / (12 0 1), (11 0 2) / (12 1 1) and (24 1 0) / (12 2 1) which reveals the presence of nano crystallite size. The two different orientation at same 2 theta ($2\theta$) have been observed due to growth of two different crystal structure. These peaks match well with the peak positions listed for Ta$_2$O$_5$ in ICDD file No. 791375, confirming the films to be Ta$_2$O$_5$. The average crystallite size of 100 nm Ta$_2$O$_5$ thin film is calculated using well known Scherrer’s equation [37]

$$D = \frac{k\lambda}{\beta \cos \theta},$$

where D is the crystallite size, k(=0.9) is the crystal constant, $\lambda$(=1.5406Å) is the wavelength of X-ray used, $\beta$ is the broadening of diffraction line measured at half of its maximum intensity and $\theta$ is the angle of diffraction. The crystallite size could be determined by broadening of the diffracted peak. The average crystallite sizes are
22.66 nm and 18.65 nm for 800 °C and 1000 °C annealed film in N₂ ambient, respectively as shown in Table 4.8. The crystallite size matches closely with previously reported articles [38]. Bragg’s law was used to calculate the interplanar spacing, \( d_{(hkl)} \), from \( 2\theta_{(hkl)} \) as shown in Eq. 4.6.

\[
d = \frac{\lambda}{2\sin \theta}
\]

The strain in the sample could also be determined from XRD profile. The shift in the most prominent peak (010) position is also observed in our Ta₂O₅ films as shown in Fig. 4.19 (b) which specifies that micro strain has developed in thin films. In our case, Ta₂O₅ (010) peaks are shifted towards higher angles of 20 as compared to the standard data (20=22.819) from ICDD file No. 791375 which suggests to lattice contraction as shown in Fig 4.19 (b). The 800 °C and 1000 °C annealed films attribute to compressive in lattice with compressed strain 0.26 % and 0.13 %, respectively. Lattice contraction exists due to strong attraction force between Ta²⁺-O²⁻ dipoles.

The crystallite size and strain could also be detected using W-H method approach [37]. The apparent shift in diffraction patterns specifies the uniform stress originated in the film due to the lattice mismatch [39-40]. The finite crystallite size from Eq.(4.5) varies as \( 1/\cos \Theta \) and the other is the induced strain (\( \varepsilon \)), which is given by Wilson formula (\( \beta_{dl} = 4\varepsilon \tan \theta \)) [37]. In Williamson-Hall approach, the finite size is taken care by Scherres’s equation and stress by Wilson formula as shown in Eq. 4.7 [37,41].

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>FWHM</th>
<th>2θ</th>
<th>D (nm)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>0.27243</td>
<td>22.86538</td>
<td>22.66</td>
<td>3.884</td>
</tr>
<tr>
<td>1000°C</td>
<td>0.28279</td>
<td>22.83585</td>
<td>18.65</td>
<td>3.889</td>
</tr>
</tbody>
</table>
\[ \beta_{hkl} \cos \theta = \frac{k \lambda}{D} + 4 \varepsilon \sin \theta \]

where \( \varepsilon \) is the strain, which is usually assumed to be proportional to the square root of the density of dislocations, \( \beta_{hkl} \cos \theta / \lambda \) is the total integral breadth in reciprocal space and \( 2 \sin \theta / \lambda \) is the distance of reciprocal point from origin.

Fig 4.20 (a) and (b) shows the measured values of \( \beta_{hkl} \cos \theta \) as a function of \( 4 \sin \theta \) for 800 and 1000°C annealed \( \text{Ta}_2\text{O}_5 \) films. One can estimate the strain from the slope of the fitted line and crystallite size (D) from its intersection with the co-ordinate. Eq.(4.7) corresponds to uniform deformation model, which considers the isotropic nature of crystal. In table 4.9, it is shown that the strain as well as the estimated crystallite size obtained for 800 °C annealed film is more than 1000 °C annealed film.

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>Scherrer’s method D (nm)</th>
<th>Strain (%)</th>
<th>Williamson-Hall method</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>22.66</td>
<td>0.26(compressive)</td>
<td>34.83</td>
</tr>
<tr>
<td>1000°C</td>
<td>18.65</td>
<td>0.13(compressive)</td>
<td>27.26</td>
</tr>
</tbody>
</table>

Table 4.9: Geometric parameters of \( \text{Ta}_2\text{O}_5 \) thin film of different annealing temperatures: (b) Scherrer’s method, (c) W-H analysis.

Figure 4.20: (a) Williamson-Hall plots 800°C and 1000°C annealed \( \text{Ta}_2\text{O}_5 \) film in \( \text{N}_2 \) ambient.
4.8.2 FTIR spectra of sputtered Ta$_2$O$_5$ thin film

Fig 4.21 (b) shows Fourier transform infrared (FTIR) spectrum of Ta$_2$O$_5$ thin film as-deposited and annealed at various temperatures in O$_2$ ambient. The bonding structures of HfO$_2$ films are detected in the 400-4000 cm$^{-1}$ spectral region; however the important features are seen in the ranges 400-1200 cm$^{-1}$ and 1400-3000 cm$^{-1}$.

![Figure 4.21: FTIR spectra of Ta$_2$O$_5$ thin films as-deposited and annealed at various temperatures in N$_2$ ambient](image)

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Associated bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline</td>
<td>Amorphous</td>
</tr>
<tr>
<td>510</td>
<td>640</td>
</tr>
<tr>
<td>810</td>
<td>≈900</td>
</tr>
<tr>
<td>2343</td>
<td>2337</td>
</tr>
</tbody>
</table>

Fourier-transfer infrared (FTIR) spectroscopy is a highly capable instrument for examining bonding structures since it can measure the vibrational modes due to atomic bonds in Ta$_2$O$_5$ thin films [42]. FTIR spectrum of Ta oxide film shows strong broad absorption band between 400 and 1000 cm$^{-1}$ which corresponds to vibration of
oxygen atoms [42]. However, Haruhiko et al. observed Ta-O bond in broad absorption band between 200 and 1000 cm\(^{-1}\) [42-44]. Haruhiko et al. and H.Ono et al. explains vibrational mode of Ta\(_2\)O\(_5\) due to complex lattice structure using V\(_2\)O\(_5\) which has same lattice structure. Clauws et al. [45] report stretching vibrations due to V-O-V and O≡3V at absorption range between 600 and 1000 cm\(^{-1}\). By comparing Ta\(_2\)O\(_5\) data with V\(_2\)O\(_5\), peak at \(\approx640\) cm\(^{-1}\) in amorphous film (\(\approx510\) cm\(^{-1}\) for crystalline) attributes to vibrational mode of O≡3Ta bonds [42-44]. In crystalline films, small absorption peak at \(\approx810\) cm\(^{-1}\) is attributed to stretching mode of Ta-O-Ta bonds, while in amorphous films, it is observed at \(\approx900\) cm\(^{-1}\) [42-44]. The samples annealed at 400, 600 °C are amorphous which have same spectrum as that for an as-deposited. Annealed at 800 and 1000 °C in O\(_2\) ambient, crystallizes Ta\(_2\)O\(_5\) which results in change in phonon absorption band. The two small peaks are also observed in the range 2330-2370 cm\(^{-1}\) which signifies presence of Ta=O bonds in Ta\(_2\)O\(_5\) structure, independent of whether they are amorphous or crystalline. In amorphous films, peaks are observed at 2337 cm\(^{-1}\) and 2364 cm\(^{-1}\) while in crystalline films, absorption peaks at 2343 cm\(^{-1}\) and 2368 cm\(^{-1}\). It is clear that when the annealing temperature increases, intensity of absorption peak attributed to Ta=O, which signifies the strengthening of oxygen bonds. Although, Haruhiko et al. indicated small sharp peak of double bond at 2335 cm\(^{-1}\) in amorphous and after crystallization over 700 °C, peaks shifted to 2340 cm\(^{-1}\) absorption peak. The Infrared absorption peaks of Ta\(_2\)O\(_5\) thin film is shown in Table 4.10.

4.8.3 Elemental composition analysis of Ta\(_2\)O\(_5\) film

![Figure 4.22: Chemical composition of Ta\(_2\)O\(_5\) is determined by EDAX.](image-url)
EDAX spectrum (shown in Fig 4.22) represents the different elements present in the Ta$_2$O$_5$ film. The EDAX spectrum shows a clear peaks corresponding to the 73 Ta L (8.14 keV) line, 73 Ta M line (1.70 keV) and 8 O K line (0.52 keV). The observed 14 Si K line (1.74 keV) peak in the EDAX spectrum is due to silicon substrate. No other peaks are observed over the entire 0 keV to 20 keV detection windows.

4.8.4 Laser Ellipsometry

Figure 4.23: (a) Dependence of refractive index, n, at wavelength 632nm on annealing temperature in O$_2$ ambient. (b) Real part of dielectric constant, ε, at wavelength 632nm on annealing temperature in O$_2$ ambient.

Figure 4.24: Thickness of Ta$_2$O$_5$ thin film versus annealing temperature, at wavelength 632 nm.
Laser Ellipsometer is high performance tool to measure refractive index, thickness of materials. [46]. Fig 4.23 shows refractive index and real part of dielectric constant of Ta$_2$O$_5$ thin film as-deposited and annealed at various temperatures in N$_2$ ambient.

It is observed that refractive index decreases at annealing temperature which might be signified that the film is less optical dense [47]. This might be occurred due to stress (i.e. lattice expansion), which implies dominant repulsive force between Ta$^{5+}$-Ta$^{5+}$ atoms and therefore oxygen deficiency. Since the sputtered thin film is transparent at 632 nm, therefore, dielectric constant’s imaginary part goes to zero (no extinction coefficient), varies square of refractive index [48]. Fig4.23 (b) shows the dielectric constant’s real part ($\varepsilon_1$) of as deposited Ta$_2$O$_5$ and annealed at 400,600,800 and 1000°C in N$_2$ ambient. It is noticeable that the dielectric constant ($\varepsilon_1$) is found to be first increasing with annealing temperature after then at 600°C it decreases. Thus suggesting nature of polarization is different in crystalline Ta$_2$O$_5$ thin film due to presence of stress as compared to amorphous.
4.9 References of Chapter 4


10 Thielsch, R., et al., “A comparative study of the UV optical and structural properties of SiO2, Al2O3, and HfO2 single layers deposited by reactive
evaporation, ion-assisted deposition and plasma ion-assisted deposition”, *Thin Solid Films*, Vol. 410, Issue 1-2, pp. 86-93, 2002


