CHAPTER 4

Nanocrystalline TiO$_2$ Thin Films

Reactive sputtering is widely investigated for the formation of compound films of nitrides, oxides, carbides and their combinations as well as nanocomposite films [1–5]. The direct current reactive magnetron sputtering of TiO$_2$ films is of great scientific and technological importance as it permits desirable properties of the films with high deposition rate as well as good adhesion at low substrate temperature. Moreover, it enables the growth of nanocrystalline TiO$_2$, because part of the energy required for the formation of crystalline phases is supplied by the plasma. Anatase and rutile phases of TiO$_2$ are well distinguishable in terms of their structural and physical properties. The ion bombardment of a growing surface during sputter deposition has received considerable interest as it influences the microstructure and physical properties of the deposited films [6–8]. The energy and inertia of the bombarding species generally determine the balance between implantation, densification, and sputtering effects.

The ion bombardment during sputtering can be effectively utilized for the
densification and crystallization of the growing film at ambient deposition temperature. The interaction of low-energy ions with a growing surface is of particular interest for the formation of thin films of controlled structure with low defect densities which is required for semiconductor and optical purposes. Nanocrystalline systems are interesting from the fundamental point of view due to the changes in the basic electronic and vibrational properties with respect to the bulk. Nucleation and growth stages of thin solid films depend on the deposition conditions, for example, gas pressure has a considerable effect on the microstructure of TiO$_2$ films deposited via reactive magnetron sputtering [1,9]. The evolution of nanocrystalline phases is governed by the deposition conditions and post-deposition heat treatment. The microstructure, associated defect structure, and film stress depend on the local conditions at the nucleation stage either in plasma environment or during post-deposition process. Thin films may be amorphous or lacking in completely ordered crystalline structure. If polycrystalline, the film is organized as many small, crystalline grains packed together as a solid. X-ray diffraction being sensitive to the local arrangement of atoms is frequently used to study deviations from the perfectly crystalline order [10]. This is of particular interest in the study of nanocrystalline materials where the line profile analysis can provide information on the shape and size distribution of crystalline domains and lattice defects like dislocations etc. Size and strain are the predominant sources of x-ray line broadening, especially in nanomaterials [10–12]. When microstrain can be neglected, the coherently diffracted domain size can simply be evaluated by the Debye–Scherrer equation. While the basics of size broadening are well established, analysis of strain broadening is currently a field of strong activity. It is also possible to consider the strain anisotropy arising from the anisotropy of the elastic medium and of the specific defect considered [13,14]. The elastic properties are intrinsic characteristics of solids and their anisotropic nature will help to understand properties of materials. This is useful in materials technology for optimising the mechanical performance of nanomaterials to meet specific needs of applications.
4.1 Role of Radio Frequency Substrate Bias

In this experiment, TiO$_2$ films are deposited on floating and RF biased substrates at a fixed sputtering power density of 0.35 W/cm$^3$ and RF power is varied while keeping the O$_2$ partial pressure fixed at 20% of total gas (Ar+O$_2$) pressure.

4.1.1 Plasma characteristics

For Ar/O$_2$ glow discharge, electron temperature, electron density and plasma potentials are calculated from the current-voltage (I–V) characteristics of the Langmuir probe. Plasma potentials corresponding to the depositions at different substrate bias are evaluated from the electron current saturation point [15]. Even in the absence of RF bias, the substrate is negatively biased to the floating potential, $V_a$ with respect to the plasma potential, $V_p$. So, the positive ions are extracted from the plasma to the floating substrate and the difference, ($V_p - V_a$) determines the ion energy acquired in a collisionless sheath in front of the substrate. Assuming the Maxwellian electron energy distribution function with electron temperature, $T_e$ and collisionless sheath, the energy, $E_i$ of singly charged ions can be expressed by the relation [16],

$$E_i = e(V_p - V_a) = \frac{kT_e}{2} \ln \left( \frac{m_i}{2.3m_e} \right)$$

(4.1)

where $k$ and $e$ are the Boltzmann constant and electronic charge, respectively. $m_e$ and $m_i$ are the mass of electron and ion, respectively. A rough estimation of ion energies of singly charged positive ions arriving at the substrate due to the RF bias is made from the differences, ($V_p - V_{sb}$), where $V_{sb}$ is the DC component of self-bias developed at the substrate due to applied RF bias. The total energy delivered to the growing surface by all the bombarding ions is the product of energy, $E_i$ and the total flux of bombarding ions [1]. The plasma parameters are summarized in Table 4.1. At optimum self-bias of −40 V, the electron temperature and the electron density are respectively 3.97 eV and 1.2 × 10$^{10}$ cm$^{-3}$. It is observed that, ion energy increases considerably with substrate bias. Thus, higher self-bias increases the energy of the impinging ions on the growing surface which leads to the significant changes in the properties of the growing films.
### Table 4.1: Plasma conditions for depositions of TiO₂ films with RF substrate bias

<table>
<thead>
<tr>
<th>Parameters</th>
<th>DC self-bias due to applied RF voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-35</td>
</tr>
<tr>
<td>$P_{\text{DC}}$ (W/cm³)</td>
<td></td>
</tr>
<tr>
<td>$p_{\text{Ar},O₂}$ (Pa)</td>
<td></td>
</tr>
<tr>
<td>$p_{\text{O₂}}$ (Pa)</td>
<td></td>
</tr>
<tr>
<td>$d_{\text{TS}}$ (mm)</td>
<td></td>
</tr>
<tr>
<td>$V_p$ (V)</td>
<td>-12.57</td>
</tr>
<tr>
<td>$T_e$ (eV)</td>
<td>5.53</td>
</tr>
<tr>
<td>$n_e$ (cm⁻³)</td>
<td>$4.9 \times 10^9$</td>
</tr>
<tr>
<td>$E_i$ (eV)</td>
<td>22.4</td>
</tr>
<tr>
<td>$r$ (nm/min)</td>
<td>9.45</td>
</tr>
</tbody>
</table>

($P_{\text{DC}}$, max. DC power density at the substrate; $p_{\text{Ar},O₂}$, working pressure; $p_{\text{O₂}}$, oxygen partial pressure; $d_{\text{TS}}$, target-to-substrate distance; $V_p$, plasma potential w. r. t. ground; $T_e$, electron temperature; $n_e$, electron density; $E_i$, ion energy; $r$, deposition rate)

#### 4.1.2 Structural characterizations

The structures of TiO₂ films are examined by XRD measurements. Figure 4.1 shows the XRD patterns of the films deposited on quartz substrates at $V_\alpha$ and different $V_{\text{sb}}$ in the -40 to -100 V range. The films deposited at the floating potential (-35 V) of the substrate do not show any peak, indicating amorphous structure. At a low $V_{\text{sb}}$ of -40 V, the diffraction peaks corresponding to (110), (210), (211), (220) and (301) planes of rutile TiO₂ are observed. On further increase of $V_{\text{sb}}$ to -100 V, the peak corresponding to the (210) plane almost disappears and the intensity of the peak corresponding to the (110) plane decreases. All peaks with low intensity are broad, indicating small crystallite size and/or random lattice strain. This phenomenon suggests the possible coexistence of amorphous titania along with crystalline rutile phase for the films deposited at different $V_{\text{sb}}$.  

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Figure 4.1: XRD pattern of TiO$_2$ films deposited with substrate bias.

From the broadening of the XRD peak, the average crystallite size is estimated from the Debye-Scherrer equation [11]:

$$ t = \frac{K \lambda}{B \cos \theta} $$

(4.2)

where $B$, $\lambda$, $2\theta$, and $t$ are the full width at half maximum (FWHM) of the broadened diffraction line, wavelength of X-ray radiation, diffraction angle, and crystallite size, respectively. Here $K$ is the shape factor, 0.89 for perfect spheres. For films deposited at $V_{sb} = -40$, $-50$, $-70$, and $-100$ V, the crystallite size corresponding to the diffraction peak for the (110) plane are estimated to be 4.5, 3.4, 3.3, and 3.4 nm, respectively. Pawlewicz et al. [17] reported the influence of the RF substrate bias on the microstructure of TiO$_2$ and Ta$_2$O$_5$ films where the microstructure could be controlled.
from essentially glassy (grain size below 10 nm) to about 60 nm grain size by applying RF bias at the substrate. The crystalline nature of the films obtained by applying a bias could be attributed to the accelerated interaction of positive ions with the growing surface. Because the substrate bias provides the positive ions with additional kinetic energy, surface diffusion of adatoms is enhanced as a result of the collision of the accelerated positive ions in the sheath of plasma. Hence, thin films with fair amount of crystallinity are obtained with RF bias at the substrate. In general, substrate temperature and energy of the particles impinging on the growing surface are two key factors for the crystallization of sputtered films at fixed sputtering power and total pressure [8]. The composition, density, and energy of particles vary with self-bias, which facilitates the crystallization of TiO$_2$ films into anatase or rutile phase [8,18]. At ambient substrate temperature, nucleation of crystalline phase is probably due to the acceleration of energetic ions such as Ti$^+$, O$_2^+$, TiO$^+$, TiO$_2^+$, etc. impinging on the growing surface. It has been reported that the nucleation of rutile phase could be because of reactions of Ti$^+$ with O$_2^+$ [18]. More Ti$^+$ in combination with fewer TiO$^+$ and TiO$_2^+$ among the substrate incident ions favours the formation of nanocrystalline rutile TiO$_2$. The decrease in crystallinity for the films deposited at $V_{sb}$ of -50 and -70 V could be attributed to the inhibited lateral grain growth because of higher deposition rates at these conditions compared with the films deposited at $V_{sb}$ equal to -40 V. However, weakening of intensity of XRD peaks at a higher self-bias of -100 V may be interpreted by the antispattering phenomenon which is in agreement with the thickness reduction of the films. The film thicknesses are estimated from the UV-VIS-NIR transmittance spectra by using the Swanepoel technique [19]. The deposition rates are mentioned in Table 4.1. The deposition rate has the lowest value at the floating condition and increases till $V_{sb}$ increases to -70 V and finally decreases at -100 V. At -100 V, due to the antispattering of the growing surface by relatively high energetic ions, the deposition rate decreases appreciably. These variations in the deposition rates with self-bias are ascribed to the changes in the composition, density and energy of the particles arriving on the substrate surface. The bombardment of the growing surface with low energetic particles can create new nucleation sites [6]. Particles impinging on the growing film at the floating potential of the substrate may not have sufficient migration energy to
rearrange after adsorption which leads to the amorphous nature of the film. In order to rearrange adsorbed particles, the impinging particles need to have enough kinetic energy to exceed the specific potential energy barrier for crystallization. This corresponds to the crystallization nucleation energy [6]. Considering the same sputtering yield of Ti at a fixed $P_{DC}$ and $p_{Ar+O_2}$, the optimal arrival of particles and low-energy bombardment of ions at $V_{sb}$ of $-40$ V enhance crystalline nucleation and film growth rate as well as surface morphology (Figure 4.2). At higher $V_{sb}$ of $-50$ and $-70$ V, the increase in deposition rate could be due to the interaction of the growing surface with the plasma and the growth is dominated by chemical reactions rather than physical mechanisms. In the energy range of chemical reactions, ions are largely ineffective in influencing the physical properties and ions are only able to influence the atoms in the near vicinity of the impingement position [6]. Also they are not able to penetrate into the material and therefore do not generate secondary collisions. Hence, no sputtering occurs. This regime reaches up to several tens of eV [6]. At $V_{sb} = -100$ V, due to antispattering of the growing film surface by relatively high-energetic ions, the deposition rate decreases appreciably.

### 4.1.3 Morphology

The bombardment of a growing surface with energetic species enormously influences the microstructure. Figure 4.2 shows the $2.0 \times 2.0$ μm$^2$ three-dimensional AFM images of the TiO$_2$ surfaces and surface roughness distribution profile for the film deposited at $V_{sb}$ of $-40$ V. The film deposited at the floating potential shows a flat texture with the lowest value of RMS roughness ($R_q$) of 0.9 nm. No granular microstructure is observed in this film. At $V_{sb} = -40$ V, the film is composed of uniformly dispersed granular microstructure having $R_q$ of 1.1 nm. Moreover, the film is homogeneous within the resolution of the instrument. Further, with increasing substrate bias to $-50$ and $-70$ V, the RMS roughness increase appreciably to 2.6 and 2.5 nm, respectively. The value of $R_q$ for the film deposited at $V_{sb} = -100$ V is 2.1 nm. At this condition, the surface roughness is reduced as the morphology of the film becomes flattened and is eroded.
Figure 4.2: AFM images (2.0 μm × 2.0 μm area) of TiO₂ films deposited at different substrate bias, (a) –35, (b) –40, (c) –50, (d) –70 and (e) –100 V. (f) Surface roughness distribution profile for the film deposited at $V_{sb} = -40$ V. The RMS roughness is also noted in each case.
Figure 4.3: (a) UV-VIS-NIR transmittance spectra of TiO$_2$ films and quartz substrate, (b–c) spectral dependence of refractive index and extinction coefficient of films deposited at –35, –40 and –100 V substrate bias. Plots of (d) $(n^2 - 1)^{-1}$ vs $(hv)^2$, (e) $n^2$ vs $\lambda^2$, (f) $(n^2 - 1)^{-1}$ vs $\lambda^2$ of films deposited at $V_n$ and $V_{sb} = -40$ V.
4.1.4 Optical properties

Figure 4.3 shows the transmittance spectra of TiO₂ films deposited at different substrate bias in the -35 to -100 V range. The films are highly transparent in the visible region and ultraviolet light is effectively filtered. Moreover, the transmittance edge is red shifted when the substrate bias is applied during deposition. Hence, the optical band gaps decrease for the films deposited with RF substrate bias. The optical band gap $E_g$ is determined from the absorption coefficient calculated as a function of incident photon energy for indirect allowed transitions [20]. At incident energy close to the optical band gap, scattering losses are dominated by fundamental absorption and due to the weak strength of direct forbidden transitions; indirect allowed transition dominates the optical absorption just above the absorption edge. The band gap values are mentioned in Figure 4.3a. The value of $E_g$ for the film deposited at the floating potential of the substrate is estimated to be 3.33 eV, which is in agreement with the reported values for amorphous TiO₂ films [21,22]. The optical band gap decreases to 3.21 eV for the film deposited at $V_{sb} = -40$ V. The band gaps are larger than the bulk rutile (3.05 eV) for films deposited with RF bias. Such variations cannot be explained by the phase transition from amorphous to rutile. Satoh et al. [23] observed quantum-size effects in the optical band gap for both anatase and rutile TiO₂ particles. However, the study reveals that for a clear observation of band gap shift, the quantum-size effect requires sub-nanometer size control of particle size which is less than 2.0 nm. If the particle sizes are distributed over a larger range then an obvious blue shift in energy gap based on quantum-size effect is not possible [23,24]. The grain sizes of TiO₂ films deposited with RF substrate bias are larger than the critical size for quantum-size effects related to $E_g$ of TiO₂. Thus, the quantum-size effect is excluded as a reason behind the observed blue shift in the energy gap of the deposited TiO₂ films. It has been reported that TiO₂ films grown by sputtering at low temperature are characterized by the presence of an amorphous phase only or coexisting amorphous and anatase and/or rutile phases [25]. Possible reasons for the larger band gap for the films deposited with RF bias compared with bulk rutile are the electronic disorder (as the film states are expected to contain an amorphous component) which connects the degree of physical disorder or the strain effect (resulting from lattice distortion) that strongly affect the structure of the films. The spectral
dependence of refractive index, \( n \) and extinction coefficient, \( k \) are shown in Figure 4.3b–c. The optical constants, \( n \) and \( k \) follow normal dispersion in the selected spectral region which is a non-absorbing region. The lower values of \( n \) compared with bulk rutile could be due to the low packing density and oxygen deficiency. From optical properties and AFM characterizations, it is observed that the densification is dominant for \( V_{sb} \) in the range of -40 to -70 V. Above this, when \( V_{sb} \) is increased to -100 V, due to the antispattering effect, the densification is reduced. In the visible and near-IR region, light scattering might be the prime reason for the loss of light in non-absorbing TiO\(_2\) films [26]. The variations of extinction coefficient could be due to the surface imperfections such as surface roughness and density fluctuations. The dispersion plays crucial role in the design of optical devices. The dispersion parameters are obtained from the plots shown in Figure 4.3d–f by using the Eq.3.7–3.11 of Chapter 3. The estimated values of the dispersion parameters are summarized in Table 4.2. The more ordered the materials, the larger the dispersion energy. The values of \( n \) and \( k \) are considered at \( \lambda = 500 \) nm.

**Table 4.2: Dispersion parameters of TiO\(_2\) films at different substrate bias**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>DC self-bias due to applied RF bias (V)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>-35</td>
</tr>
<tr>
<td>( n )</td>
<td>2.42</td>
</tr>
<tr>
<td>( k )</td>
<td>( 2.5 \times 10^{-3} )</td>
</tr>
<tr>
<td>( \varepsilon_1 )</td>
<td>5.86</td>
</tr>
<tr>
<td>( \varepsilon_2 )</td>
<td>( 1.2 \times 10^{-2} )</td>
</tr>
<tr>
<td>( E_0 ) (eV)</td>
<td>5.64</td>
</tr>
<tr>
<td>( E_d ) (eV)</td>
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</tr>
<tr>
<td>( \varepsilon_L )</td>
<td>5.31</td>
</tr>
<tr>
<td>( S_0 ) (( \times 10^{13} ) m(^{-2} ))</td>
<td>6.49</td>
</tr>
<tr>
<td>( \lambda_0 ) (nm)</td>
<td>238.96</td>
</tr>
<tr>
<td>( N/m^* ) (m(^{-3})kg(^{-1}))</td>
<td>( 1.6 \times 10^{16} )</td>
</tr>
<tr>
<td>( \omega_p ) (Hz)</td>
<td>( 6.9 \times 10^{14} )</td>
</tr>
</tbody>
</table>

\( (n, \text{refractive index}; \ k, \text{extinction coefficient}; \ \varepsilon_1, \text{real part of dielectric constant}; \ \varepsilon_2, \text{imaginary part of dielectric constant}; \ \varepsilon_L, \text{lattice dielectric constant}; \ E_0, \text{single oscillator energy}; \ E_d, \text{dispersion energy}; \ \omega_p, \text{plasma frequency}; \ N, \text{free charge carrier concentration}; \ m^*, \text{effective mass of charge carrier}; \ \lambda_0, \text{average oscillator wavelength}; \ S_0, \text{average oscillator strength})\)
4.1.5 Dielectric properties

The dielectric and alternating current (AC) conductivity studies of TiO\textsubscript{2} films are performed in the frequency range $10^2$–$10^5$ Hz for 300–373 K temperature range. The dielectric constant ($\varepsilon$) is calculated from the measured value of capacitance ($C$), film thickness ($d$), and area of the capacitor ($A$) by the relation [27]:

$$\varepsilon = \frac{Cd}{\varepsilon_0 A}$$

(4.3)

where $\varepsilon_0$ is the permittivity of free space. The AC conductivity is [27]:

$$\sigma_{AC} = \omega \varepsilon_0 \varepsilon \tan \delta$$

(4.4)

where $\omega = 2\pi f$, $f$ being the frequency of the applied signal. Figure 4.4a shows the dielectric constant of TiO\textsubscript{2} films deposited at $V_{sb} = -40$ V as a function of frequency of the applied signal. It is observed that the dielectric constant decreases with frequency and attains almost a constant value at higher frequencies. The polarization effect at lower frequencies indicates the existence of Schottky barriers at the metal-insulator interfaces in agreement with the Simmons theory [28] of MIM structures. At lower frequencies, the blockage of charge carriers at the electrode–dielectric interface may result in the formation of space-charge layers which lead to a substantial increase in capacitance and hence to a higher dielectric constant. The dielectric constant remains almost constant at high frequencies as the charge carriers do not have sufficient time for long-range hopping before the field reversal. With increasing temperature, the dielectric constant increases which suggests that the relaxation frequency of the dispersion increases with temperature. This appears as an apparent increase in the dielectric constant at a fixed frequency. The dielectric constants at 313 K of the films deposited at $V_{al} = -35$ V and $V_{sb}$ of -40 and -50 V are shown in Figure 4.4b. The increase in dielectric constant with applied RF bias at the substrate during deposition could be attributed to the phase transition from the amorphous to the glassy rutile phase. The values of dielectric constant compared with bulk rutile are low possibly due to the coexistence of amorphous and rutile phases.
Figure 4.4: Dielectric constant vs frequency of TiO$_2$ films deposited at (a) $V_{sb}$ of -40 V, (b) $V_n$ and $V_{sb}$ of -40 and -50 V at 313 K. AC conductivity vs frequency of TiO$_2$ films deposited at (c) $V_{sb}$ of -40 V, (d) $V_n$ and $V_{sb}$ of -40 and -50 V at 313 K.
Figure 4.4c shows the AC conductivity of TiO\textsubscript{2} films deposited at $V_{sb} = -40$ V as a function of frequency. The conductivity at 313 K for the films deposited at $V_a = -35$ V and $V_{sb}$ of $-40$ and $-50$ V are shown in Figure 4.4d. The conductivity is found to increase with frequency according to the empirical power law [29]:

$$\sigma_{AC} \propto \omega^n$$

(4.5)

where $n$ is a fractional exponent roughly treated as constant less than 1, and is often used to characterize the AC component contributing to the dispersive region. Such behaviour is observed in entirely different types of materials such as disordered semiconductors, polymers, conducting polymers, compound ceramics, ion conducting glasses, heavily doped ionic crystals, etc. [30,31]. The value of $n$ in the range of our study is close to unity. When thermally activated hopping of electrons between pairs of localized states plays an important role, $\sigma_{AC}$ is proportional to frequency. In the range $10^2$–$10^{12}$ Hz, the AC conductivity of dielectric films are usually electronic in nature and vary according to whether the conductivity is bulk-limited or electrode-limited [28]. This result may be interpreted in terms of an electronic hopping motion corresponding to thermally assist tunnelling between discrete sites. Figure 4.5a shows the temperature dependence of AC conductivity of TiO\textsubscript{2} films deposited at $V_{sb} = -40$ V. Conductivity increases with temperature and also with frequency. The activation energy $E_a$ is calculated from the slope of the Arrhenius plot:

$$\sigma_{AC} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

(4.6)

where $k$ is the Boltzmann constant and $T$ is the absolute temperature. The activation energy at 100 Hz is estimated to 0.095 eV and decreases with frequency to 0.055 eV at 100 kHz. This decrease suggests that the applied field frequency enhances the electronic jumps between the localized states. The AC conductivity dependence on temperature of the films deposited at various conditions is shown in Figure 4.5b. At 1 kHz, the conductivity of films deposited at $V_{sb} = -40$ and $-50$ V is of the same order, and higher than the conductivity of the film deposited at $V_a = -35$ V. Similar behaviour is observed at 10 kHz, with an increase for the film deposited at $V_{sb} = -40$ V. Low activation energy
and conductivity increase with frequency confirm hopping to be the dominant mechanism in the range of study.

![Graph showing temperature dependence of AC conductivity of TiO2 films deposited at different frequencies](image)

**Figure 4.5**: Temperature dependence of AC conductivity of TiO2 films deposited at (a) $V_{sb}$ of -40 V at four different frequencies 100 Hz, 1, 10, and 100 kHz, (b) $V_{h}$ and $V_{sb}$ of -40 and -50 V at 1 and 10 kHz.

### 4.2 Growth of nanocrystalline TiO2 and Crystal Anisotropy

TiO2 films are deposited on grounded substrates at a relatively high power density level of 1.25 W/cm$^3$ and total sputtering pressure is varied while keeping the O$_2$ partial pressure fixed at 30% total gas (Ar+O$_2$) pressure.

#### 4.2.1 Plasma characteristics

Gas pressure has a major effect on the discharge parameters. Table 4.3 summarizes the plasma conditions for the deposition of TiO2 films. The electron-atom inelastic collision rates are increased by the increase of gas pressure with a large effect on the plasma density, electron temperature, and deposition rate. By the increase of the gas pressure the electron mean energy decreases. At low gas pressure, the electrons lose little energy...
in inelastic collisions with the atoms and therefore electron temperature is high [32]. The deposition rate increases significantly when the total pressure increases from 0.4 to 1.0 Pa could be due to the increased ionization rate.

**Table 4.3: Plasma parameters for deposition at different gas pressure**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( P_{\text{Ar-O}_2} ) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>( P_{\text{DC}} ) (W/cm(^3))</td>
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</tr>
<tr>
<td>( d_{TS} ) (mm)</td>
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<tr>
<td>( t_d ) (min)</td>
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</tr>
<tr>
<td>( r ) (nm/min)</td>
<td>7.2</td>
</tr>
<tr>
<td>( T_e ) (eV)</td>
<td>3.8</td>
</tr>
<tr>
<td>( n_e ) (cm(^{-3}))</td>
<td>( 2.9 \times 10^9 )</td>
</tr>
</tbody>
</table>

\( p_{\text{Ar-O}_2} \), working pressure; \( P_{\text{DC}} \), max. DC power density at the substrate; \( d_{TS} \), target-to-substrate distance; \( t_d \), deposition time; \( r \), deposition rate; \( T_e \), electron temperature; \( n_e \), electron density

\[ \text{Figure 4.6: Raman spectra of TiO}_2 \text{ films deposited on silicon (Si) substrate at different gas pressure. The excitation source is Ar}^+ \text{ laser (488 nm). The sharp peak at 522 cm}^{-1} \text{ is due to Si substrate.} \]
4.2.2 Raman spectra

Anatase and rutile phases of TiO₂ have well distinct Raman active modes. The four modes $A_{1g}$ (612 cm⁻¹), $B_{1g}$ (143 cm⁻¹), $B_{2g}$ (826 cm⁻¹) and $E_g$ (447 cm⁻¹) of rutile TiO₂ are Raman active [33]. The anatase TiO₂ has six Raman active modes, $A_{1g}$ (515 cm⁻¹), $2B_{1g}$ (399, 519 cm⁻¹) and $3E_g$ (144, 197, 639 cm⁻¹) [33]. The ex situ Raman spectra of TiO₂ films are shown in Figure 4.6. At 0.4 Pa, the characteristic Raman bands of rutile TiO₂ appear at 151, 241, 434, 618 and 820 cm⁻¹ which are ascribed to $B_{1g}$, two phonon scattering, $E_g$, $A_{1g}$ and $B_{2g}$ modes, respectively. The Raman bands exhibit spectral modifications as $B_{1g}$ and $A_{1g}$ are blue shifted while $E_g$ is red shifted. Moreover, peaks are asymmetrically broadened. The grain size effect and oxygen non-stoichiometry might be the main factors which affect the frequency shift and peak broadening of Raman active modes [34]. At 1.0 Pa, the Raman bands appear at 157, 409, and 638 cm⁻¹ which are assigned to $E_g$, $B_{1g}$, and $E_g$ modes of anatase TiO₂ respectively. However, $E_g$ mode at 157 cm⁻¹ and $B_{1g}$ at 409 cm⁻¹ are blue shifted compared with bulk anatase [33]. The oxygen non-stoichiometry could be the main reason behind the frequency shift of $E_g$ mode. Also, in the case of nanocrystalline TiO₂, defects such as dislocations might induce the spectral modifications of the Raman bands. The degree of oxidation influences the shape and the position of Raman peaks. TiO₂ nanoparticles prepared by physical methods such as sputtering are most likely to contain sub-stoichiometric defects which affect the peak position in the similar way as the size confinement does [33,34]. At an intermediate pressure of 0.7 Pa, the Raman features resemble more to the Raman spectra of anatase TiO₂ although there is a possibility of superposition of $B_{1g}$ (409 cm⁻¹) and $E_g$ (434 cm⁻¹) mode of anatase and rutile, respectively and once again with spectral modifications.

4.2.3 Absorbance and photoluminescence spectra

Figure 4.7 shows the absorbance spectra of films deposited at 0.4, 0.7, and 1.0 Pa gas pressure. TiO₂ shows strong absorption in the UV region. The optical band gap decreases with increase of gas pressure. This variation is different from phase transition from rutile to anatase. At 0.4 Pa, the Raman spectra suggest nanocrystalline rutile TiO₂
and absorbance spectra indicate larger band gap compared with bulk rutile (3.05 eV). The crystallite size from XRD measurements is estimated to be 3.9 nm which is larger than the critical size of TiO$_2$ for the quantum size effect to be observed in the band gap of TiO$_2$ [23,24]. Hence, similar to TiO$_2$ films deposited with RF bias, coexistence of amorphous and rutile phases and/or the strain effect due to lattice distortion might be the reason behind the larger band gap of TiC$_{>2}$. Interestingly, at a higher pressure of 1.0 Pa, the optical band gap (3.0 eV) is smaller than the band gap of bulk anatase (3.20 eV). TiO$_2$ is likely to consist of many trap centres due to the oxygen vacancies from the non-stoichiometric defects. The electronic structure of non-stoichiometric TiO$_2$ is modified with the introduction of new energy levels in the mid gap due to the defect states which is responsible for the reduction of band gap and occurrence of photoluminescence in TiO$_2$ [35]. Semiconductors absorb light below a threshold wavelength, $\lambda_g$ called the fundamental absorption edge [36] which is related to the band gap energy via $\lambda_g$ (nm) $\approx$ 1240/$E_g$ (eV). Hence TiO$_2$ films can be photo excited by energy greater than or equal to band gap energy. Figure 4.8 shows the PL spectra of TiO$_2$ films deposited at 0.4, 0.7, and 1.0 Pa gas pressure. The defect states of TiO$_2$ are reflected by the intense visible photoluminescence originating from the surface oxygen deficiency. At 0.4 Pa, PL is due to the excitonic emission centred at 404 nm. At 0.7 Pa, excitonic emission occurs at ~408 and 436 nm. The latter could be attributed to the shallow trap emission [37]. At 1.0 Pa, the luminescence is dominated by near band edge luminescence and followed by shallow trap emission. The photoluminescence exhibits distinct peaks at 407 and 423 nm. The emission band centred at 407 nm could be related to band-to-band transition. The band centred at 423 nm is assigned to shallow trap emission. Of structural imperfections (as evident from Raman and absorbance spectra), oxygen vacancies are very common and might act as recombination centres of the photoinduced carriers. From band gap analyses, it is clear that oxygen vacancies form intermediate energy levels within the band gap introducing many recombination centres of photoinduced electrons and holes.
Figure 4.7: Absorbance spectra of TiO$_2$ films deposited at different gas pressure. Absorbance edge is red shifted with increase of gas pressure.

Figure 4.8: Photoluminescence spectra of TiO$_2$ films deposited at (a) 0.4, (b) 0.7, and (c) 1.0 Pa. The excitation wavelengths, $\lambda_{ex}$, are set at 300, 320, and 340 nm. (d) PL spectra of TiO$_2$ deposited at different gas pressure.
Figure 4.9: Three dimensional, 2.0 $\times$ 2.0 $\mu$m$^2$ area AFM images of TiO$_2$ films deposited at (a) 0.4, (b) 0.7, and (c) 1.0 Pa gas pressure. The values of RMS roughness are mentioned in each case. (d)-(f) FESEM images of TiO$_2$ films at 0.4, 0.7, and 1.0 Pa, respectively. Dense surfaces are obtained at higher gas pressure.
4.2.4 Morphology

Figure 4.9a–c represents the three dimensional AFM images of TiO\(_2\) in non-contact mode. Typical values of RMS roughness are 3.55, 7.29, and 10.75 nm for the films deposited at 0.4, 0.7, and 1.0 Pa gas pressure, respectively. AFM observations reveal smooth TiO\(_2\) surface deposited at a lower working pressure. At 1.0 Pa, TiO\(_2\) surface shows uniformly dispersed granular structure. Moreover, the surface is homogeneous within the resolution of the instrument. Figure 4.9d–f shows the FESEM images of TiO\(_2\) films. The size and size distribution of TiO\(_2\) nanocrystals strongly depend on the balance between nucleation and growth. TiO\(_2\) shows polycrystalline structure and the surface exhibits a lot of randomly distributed nano clusters. Compared with 0.4 and 0.7 Pa, TiO\(_2\) deposited at 1.0 Pa gas pressure represents a dense surface as smooth amorphous areas are hardly seen in the FESEM image. Moreover, majority clusters are non-spherical and closely connected to each other. The size of TiO\(_2\) clusters from AFM and FESEM observations is larger than the crystallite size from XRD measurements, \(d_{XRD}\) possibly due to the aggregation of crystallites.

![XRD patterns of TiO\(_2\) films deposited at 0.4, 0.7, and 1.0 Pa gas pressure. The crystallite sizes shown here are calculated from the Debye-Scherrer formula.](image)

**Figure 4.10:** XRD patterns of TiO\(_2\) films deposited at 0.4, 0.7, and 1.0 Pa gas pressure. The crystallite sizes shown here are calculated from the Debye-Scherrer formula.
4.2.5 X-ray diffraction and elastic anisotropy

The XRD patterns (Figure 4.10) reveal the evolution of crystalline TiO$_2$ phases from nanocrystalline rutile at 0.4 Pa to mix anatase/rutile at an intermediate 0.7 Pa and finally anatase at 1.0 Pa. At 0.4 Pa, the diffraction peaks corresponding to (110), (210), (211), (220), and (310) planes of rutile TiO$_2$ are observed. The peaks have been indexed according to the International Centre for Diffraction Data (ICDD) file 21-1276. At lower pressure, the nucleation of rutile is favoured by the higher kinetic energy of impinging particles on a growing surface as the ionized species undergo less frequent collisions with neutrals and hence the collisional energy loss is less significant [38]. The rutile crystallite size from the Debye-Scherrer formula [11] is estimated to be 3.9 nm. The mix phase of anatase and rutile occurs at intermediate pressure of 0.7 Pa. However, no brookite phase of TiO$_2$ is noticed. From the size analysis, it is clear that anatase grains seem to grow much faster than the rutile grains. At a moderate pressure of 1.0 Pa, the bombardment by relatively less energetic particles strongly promotes the growth of the anatase phase. The diffraction peaks are indexed according to (101), (004), (200), (105), (211), (204), (116), (220), and (215) planes of anatase phase. The diffraction pattern matches well to the ICDD file 21-1272 [37]. The value of $t_{\text{XRD}}$ is estimated to be 29.7 nm. The crystallization into the anatase phase is energetically favoured at medium temperature and energies which yet do not promote nucleation of the rutile phase [9]. Under such conditions, anatase grains grow much faster than the rutile grains. Above 2.0 Pa, thermalization of sputtered atoms and initially fast neutrals leads to amorphous phase.

The functional properties of TiO$_2$ are strongly dependent on a particular phase and the microstructure plays the fundamental role. The crystallite size is critical for phase stability and the presence of micro/macro strain may affect the photo-induced properties [14,39]. Diffraction profiles of crystalline materials contain a wealth of microstructural information. Each profile, in particular, is the convolution of several terms carrying information on specific broadening sources [10,40]. Finite size of scattering domains and lattice microstrain are the predominant sources of x-ray line broadening especially in nanomaterials.
Figure 4.11: X-ray line profile fitting of TiO$_2$ films deposited at 1.0 Pa gas pressure. The profile of standard corundum sample for the instrumental broadening correction is shown in the inset. The coloured (dark cyan) is the difference curve of observed and fitted intensity.

The diffractometer generally brings about a significant intrinsic, instrumental broadening of the diffraction lines. The first step in the line broadening analysis is to remove the instrumental contribution by the deconvolution method. The deconvolution procedure becomes straightforward with the choice of appropriate profile function [12]. Figure 4.11 shows the X-ray line profile analysis (XPA) of TiO$_2$ films deposited at 1.0 Pa gas pressure and of the standard corundum sample using a Gaussian function. The integral breadth, defined as the ratio between integrated intensity and peak maximum is frequently considered as a measure of the peak width. Under this assumption the instrumental broadening corrected integral breadth:

$$\beta = (\beta^2_{\text{obs}} - \beta^2_{\text{inst}})^{1/2}$$

(4.7)

where $\beta_{\text{obs}}$ and $\beta_{\text{inst}}$ are the integral breadths of the observed diffraction line broadening and instrumental broadening respectively. A simple analysis of integral breadths may be appropriate for obtaining semi-quantitative estimates of crystallite size and microstrain. Two basic approaches for the separation of size and strain broadening on the basis of
integral breadths can be adopted. In single line method, a diffraction line is conceived as a convolution of a Gaussian and a Lorentzian profile (i.e. as a Voigt function), where the Gaussian component is due to microstrain and the Lorentzian component is due to finite crystallite size [10]. Determination of the crystallite size (volume-weighted domain size in the direction parallel to the diffraction vector) $t$ and of a measure for the width of a microstrain distribution, $\varepsilon$ is possible making use of the equations [10]:

$$\beta_L = \frac{\lambda}{t \cos \theta}$$

$$\beta_\sigma = 4 \varepsilon \tan \theta$$

(4.8)

where $2\theta$ is the diffraction angle and $\lambda$ is the X-ray wavelength. The inverse proportionality between integral breadth and domain size is valid whatever the crystal shape and symmetry of the lattice. For the case of Gaussian microstrain distribution, it is possible to calculate the local root mean square strain from $\varepsilon$,

$$\varepsilon_{\text{rms}} = \langle \varepsilon^2 \rangle^{1/2} = (2/\pi)^{1/2} \varepsilon$$

(4.9)

Integral breadths expressions for various sources of line broadening can be combined. This is the basis of the Williamson-Hall (WH) method [41]. Williamson and Hall related the dependence of the full width at half maximum (FWHM) or integral breadth as a function of the diffraction vector to the volume weighted average size and mean square strain. The profile due to lattice microstrain tends to be Gaussian but not necessarily symmetric [12]. Assuming that the size and strain profile components are Gaussian profiles, the squares of the corresponding integral breadths are linearly additive to obtain the total integral breadth in reciprocal space,

$$(\beta^*)^2 = \frac{1}{<t>^2} + 4\varepsilon^2.(d^*)^2$$

(4.10)

Here $\beta^*$ and $d^*$ are given by

$$\beta^* = (\beta \cos \theta) / \lambda$$
\[ d^* = \frac{(2\sin \theta)}{\lambda} \]  

(4.11)

Hence a plot of \((\beta^*)^2\) vs \((d^*)^2\) as shown in Figure 4.12a should result in a straight line and the values of size and strain can then be obtained directly from the intercept and the slope of the straight line respectively. Equation 4.10 presents one specific expression for a ubiquitously adopted assumption that size broadening does not depend on the length of the diffraction vector whereas strain broadening does. However, this is the situation where WH method does not take into account the anisotropic nature of the crystal. Here, the lattice microstrain is assumed to be uniform in all crystallographic directions. This is known as the uniform deformation model (UDM). The peculiar effect of X-ray diffraction is that the line widths and shape depend on the anisotropic nature of the dislocation strain field and elastic medium [40]. The uniform stress deformation model (USDM) and uniform deformation energy density model (UDEDM) take into account the anisotropic behaviour of the Young’s modulus of crystals and hence could be more realistic [42]. Strain is defined as the deformation of an object from its ideal shape. The uniform strain (macro-strains) causes the unit cell to expand or contract, thus leading to a change in unit cell parameters and a shift in the peaks. There is no broadening associated with this type of strain. On the other hand, the non-uniform strain (micro-strains) leads to systematic shift of atoms, i.e., distortions of the crystal structure [14]. Strain anisotropy in a polycrystalline sample could have various causes. It can be introduced into the sample already during its processing or during further treatment. However, the most common reason is the elastic anisotropy of the crystal itself. For its evaluation, single crystal elastic constants are required. For small stresses and strains, the relationship between them is linear and follows the Hooke’s Law. In the generalized form, the strain \(\varepsilon\) is related to stress \(\sigma\) [43]:

\[ \varepsilon_{ij} = S_{ijkl} \sigma_{kl} \]  

(4.12)

where \(S_{ijkl}\) are the compliances of the crystal. Alternately,

\[ \sigma_{ij} = C_{ijkl} e_{kl} \]  

(4.13)
where \( C_{ijkl} \) are the elastic stiffness. Equations 4.12 or 4.13 stand for 9 equations. There are 81 \( S_{ijkl} \) (\( C_{ijkl} \)) coefficients. Also, \( S_{ijkl} \) or \( C_{ijkl} \) form fourth rank tensors. Anatase and rutile phases are tetragonal and for these crystal classes, crystal symmetry allows reduction into only six non-zero elastic constants \( C_{11}, C_{12}, C_{13}, C_{33}, C_{44} \) and \( C_{66} \) \[44\]. Because of non-availability of experimental values of single crystal \( C_{ij} \)s for anatase TiO\(_2\), the theoretical values based on generalized gradient approximation (GGA) have been considered \[45\]. The corresponding elastic compliances are calculated by using the relations \[44\]:

\[
\begin{align*}
S_{11} &= S_{22} = \frac{(C_{11}C_{33} - C_{13}^2)}{[(C_{11} - C_{12})C']} \\
S_{12} &= \frac{(C_{13}^2 - C_{12}C_{33})}{[(C_{11} - C_{12})C']} \\
S_{13} &= S_{23} = -\frac{C_{13}}{C'} \\
S_{33} &= \frac{(C_{11} + C_{12})}{C'} \\
S_{44} &= S_{55} = 1/C_{44} \\
S_{66} &= \frac{1}{C_{66}}, \quad C' = (C_{11} + C_{12})C_{33} - 2C_{13}^2
\end{align*}
\]

We may consider that a polycrystalline aggregate is a set of simple mono-crystals with a random orientation, the determination of stress-strain function can be established in two extreme cases: by equating any uniform strain in the polycrystalline aggregate to the external strain value or by equating the uniform stress to the external stress. The first scheme is called the Voigt approximation and the latter is the Reuss approximation \[43,46\]. A combination of Reuss and Voigt models gives a good description of X-ray elastic constants (stiffness and compliances). It is possible to experimentally verify the anisotropy of anatase and rutile by calculating the elastic modulus along different crystallographic planes. Within the Reuss approximation, the diffraction average compliances in the tetragonal system are \[14\]:

96
\[ \langle S_{11} \rangle = \frac{(H^4 + K^4)S_{11} + L^4S_{33} + (H^2L^2 + K^2L^2)(2S_{33} + S_{44}) + H^2K^2(2S_{13} + S_{66}) + 2(H^3K - HK^3)S_{16}}{(H^2 + K^2 + L^2)^2} \]

\[ \langle S_{13} \rangle = \frac{(K^2L^2 + H^2L^2 + 2H^2K^2)S_{11} + (K^2L^2 + H^2L^2)(S_{33} - S_{44}) + (H^4 + K^4 + H^2L^2 + K^2L^2)S_{12} + (H^4 + K^4 + 2L^4 + K^2L^2 + H^2L^2 + 2H^2K^2)S_{13} - 2(H^3K + HK^3)S_{16} - H^2K^2S_{66}}{2(H^2 + K^2 + L^2)^2} \]

(4.15)

where \( H = h/a, K = k/l, L = l/c \); \( a \) and \( c \) are the lattice parameters. Using the calculated X-ray elastic constants, the Young’s modulus, \( E_{\text{ijkl}} \) along the different [hkl] directions are obtained from the relation:

\[ \frac{(1 + \nu)}{E} = \frac{\langle S_{11} \rangle_{hkl} - \langle S_{13} \rangle_{hkl}}{\langle S_{13} \rangle_{hkl}} \]

\[ \frac{-\nu}{E} = \langle S_{13} \rangle_{hkl}, \nu \text{ being the Poisson’s ratio.} \]

(4.16)

**Figure 4.12:** (a) Williamson-Hall (WH) plot for TiO\(_2\) deposited at 1.0 Pa gas pressure. Volume weighted domain size \( t \) is calculated from the intercept and microstrain \( \varepsilon \) from the slope, (b) Modified WH plot under USDM. Isotropic stress \( \sigma \) is estimated from the slope, (c) Modified WH plot under UDEDM. Uniform deformation energy density \( u \) is estimated from the slope.
Table 4.4: Elastic constants, bulk modulus, shear modulus, anisotropy constants of anatase TiO$_2$

<table>
<thead>
<tr>
<th>$C_{ij}$ (GPa)</th>
<th>Bulk</th>
<th>Shear</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>320</td>
<td></td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>$C_{33}$</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>$C_{55}$</td>
<td>151</td>
<td></td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>$C_{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{23}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculated elastic compliances $S_{ij}$ (GPa$^{-1}$)

<table>
<thead>
<tr>
<th>$S_{11}$</th>
<th>$S_{22}$</th>
<th>$S_{33}$</th>
<th>$S_{44}$</th>
<th>$S_{55}$</th>
<th>$S_{66}$</th>
<th>$S_{12}$</th>
<th>$S_{13}$</th>
<th>$S_{23}$</th>
<th>Bulk</th>
<th>Shear</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0049</td>
<td>0.0049</td>
<td>0.0097</td>
<td>0.0185</td>
<td>0.0185</td>
<td>0.0167</td>
<td>-0.001</td>
<td>-0.0029</td>
<td>-0.0029</td>
<td>0.042</td>
<td>0.031</td>
</tr>
</tbody>
</table>

*aThe elastic stiffness of single crystal anatase TiO$_2$ (Shojaei et al. J. Phys.:Condens. Matter. 22 (2010) 015401.)

*bThe calculated bulk and shear modulus as the arithmetic average of Reuss and Voigt.

Table 4.5: Lattice parameter, unit cell volume, microstrain, rms strain, Young’s modulus of anatase TiO$_2$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit cell vol. (Å$^3$)</th>
<th>Micro-strain</th>
<th>rms strain</th>
<th>Young’s modulus $E_{hkl}$ (GPa) along [hkl] directions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$c$</td>
<td>$a/c$</td>
<td>$\varepsilon$</td>
<td>$\varepsilon_{rms}$</td>
</tr>
<tr>
<td>3.784</td>
<td>9.477</td>
<td>135.7</td>
<td>0.007</td>
<td>0.006</td>
</tr>
</tbody>
</table>
Chapter 4: Nanocrystalline TiO₂ Thin Films

The calculated values of elastic compliances, Young's modulus along different crystallographic directions and other crystal parameters are summarized in Table 4.4 and Table 4.5. Young's modulus along the [101] direction is \(E_{101} = 187\) GPa while along [004] direction it is \(E_{004} = 103\) GPa which shows strong anisotropy. In USDm, the anisotropic microstrain \(\varepsilon_{hkl}\) is caused by a uniform deformation stress \(\sigma\). In this approach, the Eq. 4.10 takes the form,

\[
(\beta^*)^2 = \frac{1}{<t>^2_y} + 4\sigma^2 \left(\frac{d^*}{E_{hkl}}\right)^2
\]

where the isotropic microstrain \(\varepsilon\) of UDM is replaced by \(\varepsilon_{hkl} = \sigma/E_{hkl}\), \(E_{hkl}\) being the Young’s modulus along different \([hkl]\) directions. Figure 4.12b shows the plot of \((\beta^*)^2\) vs \((d^*/E_{hkl})^2\). From the intercept and slope, the crystallite size and isotropic stress can be estimated. In UDEDM, the cause of lattice microstrain is assumed to be a density of deformation energy, \(u\). Thus assuming the density to be uniform, according to Hooke's law:

\[
u = \frac{1}{2} \varepsilon^2_{hkl} \frac{E_{hkl}}{E_{hkl}}
\]

The Eq. 4.10 modifies into

\[
(\beta^*)^2 = \frac{1}{<t>^2_y} + 8u \left(\frac{d^*}{E_{hkl}}\right)^2
\]

The plot between \((\beta^*)^2\) vs \((d^*/E_{hkl})^2\) is shown in Figure 4.12c. From the slope of the plot the uniform deformation energy density can be estimated.

Figure 4.13 shows the microstrain distribution along different crystallographic planes. It represents the anisotropic nature of the microstrain arising from the elastic anisotropy under USDm and UDEDM. With UDM, nature of lattice microstrain is uniform along all the crystallographic directions. As compared with USDm, the UDEDM estimates lower microstrain along most of the crystallographic directions. Although Eq. 4.17 and 4.19 both consider elastic anisotropy into account, still they have
differences. In Eq. 4.17, it is assumed that the deformation stress, $\sigma$ is isotropic, allowing $u$ to be anisotropic (as $u$ and $\sigma$ are related by $u = \sigma^2 / 2E_{hk}$), while Eq. 4.19 is developed assuming the deformation energy density, $u$ to be uniform in different crystallographic directions, treating the deformation stress $\sigma$ to be anisotropic. Assuming that the broadening is caused by elastic anisotropy of the crystal; the modified W-H plot somewhat improves the estimation of domain size and stress/strain present in the sample. For TiO$_2$ film deposited at 1.0 Pa gas pressure, USDM might be considered as the one which represents the best fit of the experimental data.

![Microstrain distribution of anatase TiO$_2$ along crystallographic directions under USDM and UDEDM. The dotted line represents isotropic microstrain, $\varepsilon$ estimated from UDM. The solid line is for the rms microstrain $\varepsilon_{rms}$.](image)

Table 4.4 presents the bulk modulus, shear modulus and anisotropy constants estimated based on the Voigt-Reuss-Hill averaging scheme for polycrystalline material. The Voigt model assumes that all grains have the same state of strain, which violates
the mechanical equilibrium. The calculated X-ray elastic constants are independent of $hkl$. The Reuss model assumes that all grains have same state of stress, which introduces discontinuities at the grain boundaries. The calculated X-ray elastic constants are $hkl$ dependent. Hence, neither the Voigt nor the Reuss average is quite right as there are variations of stress and strain throughout the sample, especially near grain boundaries where mismatched orientations occur. Also, the deformation of one grain is not independent of the deformation of its neighbour. The Voigt-Reuss-Hill model is based on the proof that the Voigt and Reuss models are the theoretical limits and is simply the arithmetic average of the two models, where anisotropy constants are [14]

\[
 A^*_{\text{compression}} = \frac{K_V - K_R}{K_V + K_R} \tag{4.20}
\]

\[
 A^*_{\text{shear}} = \frac{G_V - G_R}{G_V + G_R} \tag{4.21}
\]

where $V$ stands for the Voigt, $R$ for Reuss and

\[
 K_V = \frac{(2C_{11} + C_{33})}{9} + \frac{2(C_{12} + 2C_{13})}{9}
\]

\[
 G_V = \frac{(2C_{11} + C_{33})}{15} + \frac{(2C_{14} + C_{66})}{5} - \frac{(C_{12} + 2C_{13})}{15} \tag{4.22}
\]

\[
 K_R = [2S_{11} + S_{33} + 2(S_{12} + 2S_{13})]^{-1}
\]

\[
 G_R = 15[4(2S_{11} + S_{33}) - 4(S_{12} + 2S_{13}) + 3(2S_{14} + S_{66})]^{-1}
\]

The anisotropic constants $A^* > 0$ for an anisotropic crystal and $A^* = 0$ for isotropic crystal. It is a measure of the relative magnitude of the elastic anisotropy.
4.3 Effect of Post-deposition Annealing

TiO$_2$ films are initially deposited on grounded quartz substrates at a moderate power density level of 0.45 W/cm$^2$ and then heat treated at temperatures in 350–850 °C range in air for 60 min. The O$_2$ partial pressures during deposition are set at 30 and 70%, respectively for two sets of depositions at 0.3 and 0.5 Pa total gas (Ar+O$_2$) pressure. These thin films deposited at 0.3 and 0.5 Pa and subsequently annealed may be referred to as “Series A” and “Series B”, respectively. Due to plasma heating the substrate temperature during deposition is ~250 °C.

4.3.1 Raman spectra

Figure 4.14 depicts the Raman spectra of the as-deposited and annealed films. Series A is characterized by mainly $B_{1g}$, two phonon scattering, $E_g$ and $A_{1g}$ Raman active modes of rutile TiO$_2$. These films may be treated as rutile rich films although weak intensity $E_g$ (157 cm$^{-1}$), $B_{1g}$ (402 cm$^{-1}$), and $A_{1g}$ (514 cm$^{-1}$) modes of anatase TiO$_2$ are observed. On the other hand for Series B, the Raman spectra are predominantly characterized by $3E_g$, $2B_{1g}$, and $A_{1g}$ modes of anatase TiO$_2$ till 650 °C and then the Raman bands of rutile TiO$_2$ appear due to the phase transition from anatase to rutile at 750 and 850 °C. Thus till 650 °C, series B represent anatase rich TiO$_2$ structure. However, in both cases, the Raman bands are asymmetrically broadened and exhibit frequency shift compared with bulk anatase and rutile TiO$_2$. For rutile TiO$_2$, two additional bands appear at ~112 and ~705 cm$^{-1}$. Swamy et al [47] reported that for mean crystallite size ~25 nm, the Raman spectrum of rutile TiO$_2$ nanocrystals displays an additional low frequency and possibly surface vibrational mode at ~105 cm$^{-1}$. Moreover, their results show that the Raman spectrum of rutile may have additional bands at ~700 cm$^{-1}$ when going from coarse grained to nanocrystalline form. Hence, the features at ~112 and ~705 cm$^{-1}$ may be assigned as additional modes for the nanocrystalline rutile TiO$_2$. The $E_g$ mode of rutile TiO$_2$ is red shifted and broadened with decreasing crystallite size, consistent with phonon confinement in rutile nanocrystals [47,48]. However, $A_{1g}$ mode experiences random shift with decreasing crystallite size. The $E_g$ (144 cm$^{-1}$) mode of anatase TiO$_2$ is red shifted with annealing temperature. At the nanoscale, the presence of oxygen vacancies too substantially affects the Raman features [33,48]. The evaluation of role of
stoichiometry is problematic, in particular, in nanocrystalline systems, due to the extreme difficulty in determining quantitatively the [O]/[Ti] ratio. Films of Series A are deposited at a reduced oxygen level compared with as-deposited films of Series B. The as-deposited films of Series A are likely to be non-stoichiometric. The thermal treatment in air reduces the possibility of deviations from [O]/[Ti] = 2. However, the presence of stoichiometric inhomogeneities cannot be excluded especially at small scales. Hence a general agreement about the origin of broadening and shifts of the Raman bands of nanocrystalline TiO₂ with respect to bulk is not clear from the above measurements.

Figure 4.14: Raman spectra of as-deposited and annealed TiO₂ films deposited at 0.3 (Series A) and 0.5 (Series B) Pa gas pressures. (*-contribution from the quartz substrate; **-additional surface vibrational mode at ~112 cm⁻¹ and #-additional band at ~705 cm⁻¹ characteristic of rutile TiO₂ nanocrystals).
Figure 4.15: FESEM images of as-deposited and annealed TiO$_2$ films.
4.3.2 Morphology

Figure 4.15 shows the FESEM images of TiO_2 films. At a higher gas pressure, the film represents a dense surface. The as-deposited films consist of nearly spherical particles which take irregular shape upon annealing. The films consist of particles of larger size than the mean crystallite size estimated from the XRD analyses and hence are polycrystalline having numerous randomly distributed grains. It is observed that anatase rich films with dense surface may be grown under the plasma environment where the impinging particles undergo more energy loss due to collisions before arrival to the growing surface at a higher pressure compared with rutile rich films deposited at a lower pressure. At elevated temperatures, rutile films show different morphology where B5 and B6 are obtained by phase transformation while A5 and A6 stand for the same phase.

4.3.3 X-ray diffraction

The XRD patterns are shown in Figure 4.16. At 0.3 Pa, the films are nanocrystalline rutile of mean crystallite size 2.9 nm. The annealing temperature has no significant effect on the crystallinity of rutile till 650 °C, apart from the evolution of anatase (101) peak. The crystallinity changes drastically at 750 °C and it completely transforms to rutile at 850 °C. At 0.5 Pa, nanocrystalline anatase with greater crystallinity and mean crystallite size 24.7 nm are obtained. The anatase phase crystallinity is improved with annealing temperature as new diffraction peaks appear in the XRD pattern. At 750 °C, the anatase transforms to rutile phase and complete conversion takes place at 850 °C. The mean crystallite size estimated from the broadening of (110) peak of rutile and (101) peak of anatase is shown in Figure 4.17a. The crystallite size changes marginally for anatase and rutile till the annealing temperature reaches 650 °C. At 750 and 850 °C, the crystallite size increases sharply. The change is more pronounced in the case of initially rutile rich films. However, rutile grains with larger size are obtained when the anatase transforms to the rutile phase. Moreover, transformation to rutile with greater crystallinity seems easier from initially anatase rich films. Figure 4.17b shows the rutile content of the films. The intensity ratio \( I_r/I_a \) of the strongest rutile reflection to the intensity of strongest anatase reflection is independent of the fluctuations in
diffractometer characteristics. This ratio therefore provides a useful index of sample composition. According to Spurr and Myers [49], the fractional ratio of anatase to rutile $f$ may be estimated from the relation:

$$ f = \frac{1}{1 + 1.26 \frac{I_{R110}}{I_{A101}}} $$

(4.23)

where $I_{R110}$ and $I_{A101}$ are the intensities of strongest reflections.

Figure 4.16: XRD patterns of TiO$_2$ films. Series A: deposited at 0.3 Pa and annealed at 350, 550, 650, 750 and 850 °C. Series B: deposited at 0.5 Pa and annealed at 350, 550, 650, 750 and 850 °C.
The as-deposited film of Series A contains 80.3% rutile. Due to the evolution of anatase phase, rutile proportion decreases till 550 °C. From 650 °C onwards, the rutile content increases again and complete transformation occurs at 850 °C. The rutile fraction increases gradually in the case of Series B, although a fall is noticed at 650 °C. However, the Eq. 4.23 predicts complete conversion to rutile at 750 °C. Larger crystallite size (which means fewer defects in the crystal structure) of anatase and phase stability of rutile at higher temperature could be the main reasons behind the faster transformation to rutile from the predominant anatase phase. The annealing temperature dependence of measured lattice parameters \( c \) and \( a \) as well as unit cell volume \( V \) is shown in Figure 4.18. The fluctuations of unit cell volume arise from the deviations of \( c \) and \( a \) values from the \( c_0 \) and \( a_0 \) values of bulk rutile and anatase. The existence of large amounts of grain boundaries in nanocrystalline materials results in the changes of the lattice parameters when compared with the coarse grained materials.
Figure 4.18: Lattice parameters $a$, $c$ and unit cell volume $V$ of rutile and anatase. Series A is for rutile and Series B is for anatase TiO$_2$. $a_0$ and $c_0$ are the theoretical values (ICDD 21-1272 and 21-1276) of lattice parameters. For tetragonal crystal, unit cell volume $V = a^2c$. 

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The rutile unit cell volume, however, remains almost constant and closely matched with the bulk values at higher annealing temperature. This could be attributed to the decreasing the microstructural defects with increasing the annealing temperature. The microstrain present in nanocrystalline rutile TiO₂ is estimated from the WH plot and the effect of the elastic anisotropy due to the anisotropic nature of the Young’s modulus is considered to predict the anisotropic behaviour of the lattice microstrain. Unlike anatase TiO₂, the experimental values of elastic constants of single crystal rutile TiO₂ are available [45,50]. Using the reported values of elastic stiffness, the elastic compliances are calculated by using the Eq. 4.14. The diffraction average compliances and Young’s modulus values along different crystallographic directions are calculated by using Eq. 4.15–4.16. Table 4.6 and 4.7 summarize the elastic compliances and Young’s modulus.

Table 4.6: Elastic constants, bulk modulus, shear modulus, anisotropy constants of rutile TiO₂

<table>
<thead>
<tr>
<th>Elastic stiffness $C_{ij}$ (GPa)</th>
<th>Elastic modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$ $C_{22}$ $C_{33}$ $C_{44}$ $C_{55}$ $C_{66}$ $C_{12}$ $C_{13}$ $C_{23}$</td>
<td>Bulk</td>
</tr>
<tr>
<td>267</td>
<td>484</td>
</tr>
</tbody>
</table>

Calculated elastic compliances $S_{ij}$ (GPa⁻¹)

| $S_{11}$ $S_{22}$ $S_{33}$ $S_{44}$ $S_{55}$ $S_{66}$ $S_{12}$ $S_{13}$ $S_{23}$ | Bulk | Shear |
|---------------------------------|----------------|
| 0.0068 | 0.0068 | 0.0026 | 0.0081 | 0.0081 | 0.0053 | -0.0039 | -0.0009 | -0.0009 | 0.024 | 0.11 |


The calculated bulk and shear modulus as the arithmetic average of Reuss and Voigt.
### Table 4.7: Microstrain, rms strain, Young’s modulus, isotropic stress, uniform deformation energy density of rutile TiO$_2$

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$\varepsilon$</th>
<th>$\varepsilon_{\text{rms}}$</th>
<th>$E_{\text{[110]}}$ (GPa)</th>
<th>$E_{\text{[101]}}$ (GPa)</th>
<th>$E_{\text{[200]}}$ (GPa)</th>
<th>$E_{\text{[111]}}$ (GPa)</th>
<th>$E_{\text{[210]}}$ (GPa)</th>
<th>$E_{\text{[211]}}$ (GPa)</th>
<th>$E_{\text{[220]}}$ (GPa)</th>
<th>$E_{\text{[310]}}$ (GPa)</th>
<th>$E_{\text{[301]}}$ (GPa)</th>
<th>$\sigma$ (GPa)</th>
<th>$U_{\text{DED}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A5</td>
<td>0.0035</td>
<td>0.0028</td>
<td>364.0</td>
<td>313.2</td>
<td>146.9</td>
<td>344.1</td>
<td>237.6</td>
<td>279.8</td>
<td>364.0</td>
<td>187.1</td>
<td>185.2</td>
<td>0.876</td>
<td>0.0025</td>
</tr>
<tr>
<td>A6</td>
<td>0.0024</td>
<td>0.0019</td>
<td>364.0</td>
<td>146.9</td>
<td>344.2</td>
<td>237.6</td>
<td>280.0</td>
<td>364.0</td>
<td>187.0</td>
<td>185.4</td>
<td>0.654</td>
<td>0.0007</td>
<td></td>
</tr>
<tr>
<td>B5</td>
<td>0.0019</td>
<td>0.0015</td>
<td>364.0</td>
<td>313.3</td>
<td>344.1</td>
<td>237.6</td>
<td>279.8</td>
<td>364.0</td>
<td>187.0</td>
<td>185.3</td>
<td>0.412</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>B6</td>
<td>0.0018</td>
<td>0.0014</td>
<td>364.0</td>
<td>313.5</td>
<td>146.9</td>
<td>344.2</td>
<td>237.6</td>
<td>279.9</td>
<td>364.0</td>
<td>187.1</td>
<td>185.4</td>
<td>0.291</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

From Table 4.7 it is clear that rms microstrain decreases with annealing temperature. Also, rutile films obtained by thermal treatment of predominantly anatase phase have lower rms microstrain. The grain boundaries constitute the main contribution to the microstrain [51]. The higher the number of grain boundaries, the smaller the size of the crystallites. Annealing the films having larger crystallites (Series B), the microstructural defects tend to be reduced and grains tend to grow in order to reduce their surface energy. Young’s modulus, for example, for sample B6 along the [110] direction is $E_{\text{[110]}} = 364.0$ GPa while along [200] direction it is $E_{\text{[200]}} = 146.9$ GPa which shows strong anisotropy. Figure 4.19 shows the microstrain distribution of rutile TiO$_2$ along different crystallographic directions. The microstrain along [110] direction decreases with annealing temperature. Films annealed at 850 °C exhibit lower microstrain than the films annealed at 750 °C. Moreover, the rutile films produced by
annealing the films with higher content of larger crystallites exhibit lower microstrain. In the USDM when compared with UDEDM predicts lower microstrain for rutile TiO$_2$ along most of the crystallographic directions. This follows reverse trend when compared with anatase TiO$_2$ deposited at 1.0 Pa gas pressure.

![Figure 4.19: (a) Microstrain along [110] directions of rutile TiO$_2$, (b) Microstrain distribution of rutile TiO$_2$ (sample B6) along crystallographic directions under USDM and UDEDM. The dotted line represents isotropic microstrain, $\varepsilon$ estimated from UDM. The solid line is for the rms microstrain $\varepsilon_{\text{rms}}$.](image)

**Figure 4.19:** (a) Microstrain along [110] directions of rutile TiO$_2$, (b) Microstrain distribution of rutile TiO$_2$ (sample B6) along crystallographic directions under USDM and UDEDM. The dotted line represents isotropic microstrain, $\varepsilon$ estimated from UDM. The solid line is for the rms microstrain $\varepsilon_{\text{rms}}$.

### 4.4 Summary

TiO$_2$ films are deposited by DC reactive magnetron sputtering with ion assistance due to the DC self-bias developed at the substrate from the applied RF bias. The XRD pattern reveals that the films deposited without RF bias are amorphous. With RF bias, films are nanocrystalline with the formation of rutile phase of TiO$_2$. The DC negative self-bias developed at the substrate provides additional kinetic energy to the positive ions.
impinging on the growing surface which leads to the crystallization of TiO$_2$. Moreover, the crystallinity is retained over a range of ion energy. At $V_{sb}$ of $-100$ V, the deposition rate decreases which is attributed to the antisyputtering of the growing surface by energetic ions. The films are composed of small crystallite size and are smooth and highly transparent which make them useful as optical coatings. The larger values of the optical band gap for films deposited with RF bias could be due to either the electronic disorder from the possible coexistence of amorphous and rutile phases or to the strain effect resulting from the lattice distortion. The optical dispersion study using the Wemple-DiDomenico single oscillator model\cite{52} provides useful information on the dispersion parameters of reactively sputtered nano-rutile TiO$_2$ films with substrate bias. The dielectric constant decreases with frequency. The power-law dependence of AC conductivity together with low activation energy reveals the hopping of charge carriers as the dominant conduction process. It is observed that the microstructure of TiO$_2$ films may be controlled by the RF substrate bias where the plasma density and energy of the ions play significant role for the deposition and crystallization of optically promising thin films. TiO$_2$ films deposited at a higher sputtering power density are nanocrystalline even in the absence of RF substrate bias or substrate heating. The energetic ions of plasma are responsible for the crystallinity of reactively sputtered TiO$_2$ films without substrate heating, substrate bias or post-deposition annealing. Films deposited at a higher gas pressure reveal dense surfaces with greater crystallinity. Under these conditions, anatase grains grow rapidly than the rutile grains. XPA has been performed by using a Gaussian function and integral breadths expressions of line broadening for size and microstrain components are combined on the basis of the Williamson-Hall (WH) method. The elastic constants of materials are determined by the bonding between individual atoms. Within the Reuss approximation, the diffraction average of compliances and Young’s modulus ($E_{hkl}$) are calculated. Young’s modulus shows strong anisotropy. On taking into account of the anisotropic behaviour of Young’s modulus, the modified WH method could be a more realistic approach for the estimation of domain size and nature of the lattice microstrain. Isolated and spherical grains are observed on the surface of anatase and rutile rich films deposited at a moderate power density. Because atoms have a higher diffusion rate at higher annealing temperature, the
grain coalescent phenomenon leads to the irregular grain shape on annealed films. Since there is no equilibrium between the polymorphs of TiO$_2$, there is no specific temperature for the phase changes to occur. The temperature of anatase-to-rutile phase transition, in general, depends on various factors such as defects, impurities and grain sizes. The complete transformation from either predominant anatase or rutile phases to rutile phase also takes place at different annealing temperatures. The near bulk values of rutile unit cell volume at higher annealing temperature are consistent with the decrease of microstrain present in the sample. The properties of TiO$_2$ are closely related to its crystal structure that makes phase transformation one of the most important issues in the practical application of the material. The diffraction line profile analyses are extended to rutile TiO$_2$ with the consideration of strain anisotropy arising from the anisotropic nature of Young’s modulus of polycrystals. It is observed that the microstructure of TiO$_2$ films hugely depend on the deposition and post-deposition conditions.

4.5 References


