Chapter 5

UV-VISIBLE AND MICRO-RAMAN SPECTROSCOPY
INVESTIGATION OF NANOSTRUCTURED TITANIUM
DIOXIDE FILMS
Chapter 5
UV-Visible and Micro-Raman Spectroscopy Investigation of Nanostructured Titanium Dioxide Films

5.1. Introduction

The optical and vibrational properties of low-dimensional semiconductors have attracted much interest, because they differ significantly from those of corresponding bulk materials and offer a great variety of attractive applications in electronic, optoelectronic and optical devices, solar cells, sensors etc (1-4). In order to get information regarding these properties, a number of techniques developed and applied for characterization of bulk materials, as new theoretical considerations have been carried out taking into account the reduced dimensionality of nanosized materials (5, 6). Raman scattering technique, based on inelastic light scattering and UV-visible spectroscopy, based on the illumination induced fundamental electronic excitations are well established procedures as the fast and non-destructive tools to explore the quantum mechanical properties of semiconductor nanostructures.

UV-visible spectroscopy is based on the transitions of electrons from the ground state to an excited state by receiving energy from the excitation source. The main mechanism of light absorption in pure semiconductors is direct interband electron transitions. Considerable enhancement of the absorption is expected in porous and microcrystalline semiconductors, when the share of the interface atoms is sufficiently large. A rapid increase in the absorption takes place at low ($h\nu < E_g + W_c$, where $W_c$ is the width of the conduction band) photon energies. Electron transitions to the conduction band become possible when $h\nu = E_g + W_c$. Further enhancement of the absorption occurs due to an increase of the electron density of states in only the valence band (7).

In many cases, the origin of the visible light absorption in TiO$_2$ has been connected with the formation of new energy levels within the forbidden energy gap of the semiconductor material (8). Particle size has a significant effect, called quantum-size effect, on the electronic, magnetic, and optical properties of semiconducting solids when their size, in at least one
dimension, becomes comparable with the Bohr exciton radius (1-10 nm) (9). A number of semiconductors such as CdS (10), ZnS (11) and ZnO (12) have been shown to exhibit spectral blue shifts in the absorption band edge as a consequence of exciton confinement with decreasing particle size as expressed by Brus equation (13).

\[ E = E_g + \left( \frac{\hbar^2}{8R^2} \right) \left[ 1/m_e^* + 1/m_h^* \right] - \left( 1.8 \frac{e^2}{4\pi\epsilon_0\epsilon_a R} - 0.124 \frac{e^2}{\hbar^2 (4\pi\epsilon_0\epsilon_a)^2} \right) \left[ 1/m_e^* + 1/m_h^* \right] \]

where \( E \) is the onset of absorption of the sample, \( E_g \) is the bulk band gap, \( R \) is the radius of the particle, \( m_e^* \) and \( m_h^* \) are the reduced masses of the conduction band electron and valence band hole in units of the electron mass, \( \epsilon_0 \) is the vacuum permittivity and \( \epsilon_a \) is the high frequency dielectric constant.

Until a few years ago, Raman spectroscopy was mostly applied in chemical studies as a complementary technique to infrared spectroscopy, giving information on the chemical composition and crystallinity of the sample. In particular micro-Raman spectroscopy, where a spatial resolution of less than 1 \( \mu \)m can be obtained, is very useful for local stress studies. Micro-Raman spectroscopy turned out to be a very interesting tool for the study of local stress in nanostructures (14).

Figure 5.1. Feynman diagram and related energy levels for a first order Stokes scattering process

The vibrations of a crystal are described not in terms of the vibrations of individual atoms but in terms of collective motions in the form of waves, called lattice vibrations. Each possible vibration \( j \) of the lattice is characterized by a wave vector \( q_j \) and a frequency \( \omega_j \). The vibration amplitude, at position \( r \), is given by
\[ Q_j = A_j \exp \left[ \pm i (q_j \cdot r - \omega_j t) \right] \]

where \( Q_j \) is the normal coordinate of the vibration (15) and \( A_j \) is a constant. Such a quantized lattice vibration is called a normal mode or a phonon. These lattice vibrations may cause a variation in the electrical susceptibility of the crystal, which can give rise to 'Raman scattering'. A classical way to explain Raman scattering is the following. When monochromatic light of frequency \( \omega_0 \) is incident on a crystal in a direction \( k_i \), the associated electric field \( E \) will induce at position \( r \) an electric moment \( P \), which is related to \( E \) through

\[ P = \varepsilon_0 \chi \cdot E = \varepsilon_0 \chi \cdot E_0 \exp \left[ i (k_i \cdot r - \omega_0 t) \right] \]

where \( \chi \) is the susceptibility tensor, which describes the response of the crystal to the electric field. If the atoms of the sample are vibrating, the susceptibility may change as a function of these vibrations. This can be expressed by expanding \( \chi \) for each normal mode of vibration \( j \), in a Taylor series with respect to the normal coordinate of this vibration \( Q_j \) and neglect the third and higher-order terms:

\[ P = \varepsilon_0 \chi_0 \cdot E_0 \exp \left[ i (k_i \cdot r - \omega_0 t) \right] + \varepsilon_0 \frac{\partial \chi}{\partial Q_j} \left|_{Q_j=0} \right. A_j X \exp \left[ -i (Q_j + \omega_j) t \right] \exp \left[ (k_i + q_j) \cdot r \right] \]

From this it follows that the induced moment will re-radiate light which has three distinct frequency components: \( \omega_0 \), which is called Rayleigh scattering, and \( \omega_0 + \omega_j \) and \( \omega_0 - \omega_j \), which are called anti-Stokes and Stokes Raman scattering respectively.

From a quantum physical point of view, Raman scattering involves the destruction of a photon with frequency \( \omega_0 \), emitted by a light source, and the creation of a photon with frequency \( \omega_0 \) as shown in the typical Feynman diagram (figure 5.1) as described by Wolf et al. (15). The related energy levels for a first order Stokes scattering process is also shown in figure 5.1. An electron–hole pair is created through interaction of the incident photon (frequency \( \omega_0 \)), with an electron. By this interaction, the electron goes from the ground
state to an excited state. By electron–phonon interaction, where a phonon of frequency \( \omega_i \) is created (or annihilated in anti-Stokes). By recombination of the electron–hole pair, a photon with frequency \( \omega_s \) is emitted, where \( \omega_s = \omega_i - \omega_j \) (for anti-Stokes it would be \( \omega_i + \omega_j \)). Because conservation of momentum is required for each intermediate step whereas conservation of energy is required only for the overall process. Further, the three steps described above take place instantaneously, so the order in which they occur is not important.

Raman measurements provide detailed information about the structure and quality of low dimensional materials. The reason is that lattice vibrations are very sensitive to nearest neighbor interactions and therefore can effectively probe the crystal structure and quality at length scales of the order of lattice spacing. For example, studies of longitudinal optical phonons in semiconductors via Raman spectroscopy provide significant information about the strain, defects, and disorder in these materials (16-19). Specimens in the form of thin films have been extensively studied by Raman spectroscopy mainly to investigate the crystallinity, the effect of annealing in the structural properties and stress developed during these processes (20-28). As the grain size of nanomaterials decreases, the Raman scattering peaks become broader (29-41). It is proposed that size effect on Raman scattering in nanocrystalline TiO\(_2\) is interpreted as originating from phonon confinement (29-33, 41), nonstoichiometry (37,38) or internal stress/surface tension effects (36). From the above suggestions, the most convincing is the three-dimensional confinement of phonons in nanocrystals (29, 33, 40, 41).

In the present chapter, the analysis on the micro-Raman and UV-Visible spectroscopy investigations of nanostructured TiO\(_2\) film samples annealed at different temperatures are presented. The intensity and broadness characteristics of Raman band of anatase phase of TiO\(_2\) around 141 cm\(^{-1}\) is discussed in detail in this chapter. UV-Visible spectra of the samples as-deposited and annealed at different temperatures are discussed and the dependence of band gap energy on annealing temperature is analyzed.
5.2. Experimental details

Nanostructured TiO$_2$ films were prepared using a RF magnetron sputtering unit designed for upward sputtering configuration. Detailed experimental procedure regarding the preparation of the samples was discussed in chapter 4. The Raman measurements were performed using a LabRam HR 800 Micro-Raman instrument with 10 mW Ar (488 nm) laser as an excitation source focused into a ~1 µm diameter spot in a back scattering geometry, where the incident beam is linearly polarized. A Mplan 50× lens was used during all the measurements and a Peltier cooled CCD for spectral detection. The UV-visible transmission spectra of the films were recorded using JASCO V550 double beam spectrophotometer at room temperature.

5.3. Results and discussion

5.3.1. UV-Visible spectroscopy studies

Figure 5.2 & 5.3 show respectively the UV-visible transmittance and absorption spectra of the as deposited samples and the samples annealed at different temperatures. From figure 5.2, it is clear that there is no considerable difference between the transmission characteristics of the as-deposited sample and the samples annealed at 300 and 400°C. However, the samples annealed at 500 and 600°C show similar characteristics and which are totally different from those of the other samples. The transmittance of the samples annealed at 500 and 600°C was low (70%) at longer wavelengths and it gradually increased towards shorter wavelengths reaching a maximum value of about 96% around 450 nm. The transmittance decreases rather quickly on the higher energy side showing a shoulder near 370 nm. The sharp decrease of transmittance towards UV-region (below 370 nm) was due to the fundamental absorption of light caused by the excitation of electrons from the valance band to the conduction band of TiO$_2$ (42). Post deposition annealing in air of the as-deposited non-stoichiometric films leads to a complete oxidation of the films and strongly affected the UV-Visible spectra. The absorption above 400 nm in the samples annealed up to 400°C (figure 5.3) is attributed to a superposition of free carrier absorption, interband absorption and absorption by localized states. These localized states can arise from titanium atoms acting as electron traps at oxygen vacancies in the bulk of the semiconductor.
Imperfect crystallization leading to an amorphous zone near the surface of the colloidal particles could also lead to localized electronic states near the mobility edge of the semiconductor.

Figure 5.2. UV-Visible transmittance spectra of TiO$_2$ films as-deposited and that of annealed at different temperatures.

Figure 5.3. UV-Visible absorption spectra of TiO$_2$ films as-deposited and that of annealed at different temperatures.
Optical absorption coefficient ($\alpha$) as a function of wavelength is calculated using the formula (45), $\alpha(\lambda) = t^{-1} \ln(T_{\lambda}^{-1})$, where $t$ is the thickness of the film and $T_{\lambda}$ is the transmittance of the film at a particular wavelength $\lambda$. The value of $\alpha$ was found to be of the order of $10^5$ nm$^{-1}$ as shown in figure 5.4.

Figure 5.4. Absorption co-efficient ($\alpha$) versus photon energy ($h\nu$) of TiO$_2$ films as-deposited and that of films annealed at different temperatures.

Serpone et al. (9) established that both direct and indirect band-to-band transitions are operative in nanophase TiO$_2$. To determine the type of transition between the valance band and conduction band of the present samples, Tauc’s plots were used. Figure 5.5 shows the plot ($\alpha^2$) versus photon energy, $h\nu$, which was used to calculate the energy band gap, considering a direct allowed transition in different TiO$_2$ samples. The direct energy gap increased from 3.56 to 3.85 eV when the annealing temperature increased from 300 to
The indirect allowed transition for TiO$_2$ was taken into account by plotting $(\alpha hv)^{1/2}$ versus photon energy, $hv$, in figure 5.6. The indirect allowed band gap of the

![Graphs showing photon energy vs. $\alpha^2$](image)

**Figure 5.5**
Plots of $\alpha^2$ vs. Photon energy for (a) as-deposited TiO$_2$ film and that of films annealed at (b) 300$^\circ$C, (c) 400$^\circ$C, (d) 500$^\circ$C and (e) 600$^\circ$C.
Figure 5.6
Plots of \(\alpha^{1/2}\) versus Photon energy of (a) as-deposited TiO\(_2\) film and that of films annealed at (b) 300\(^\circ\)C, (c) 400\(^\circ\)C, (d) 500\(^\circ\)C and (e) 600\(^\circ\)C.
TiO₂ film samples increased from 3.24 to 3.65 eV as given in table 1. For the commercial anatase TiO₂ sample with a crystallite size of 39 nm, the band gap is about 3.2 eV (42). Reddy et al. (46) estimated a direct band gap of 3.36 eV for samples having a crystallite size of 6.8 nm and 3.32 eV for samples having crystallite size of 7.9 nm. The observed band gap values of the nanostructured TiO₂ film samples in the present study were in good agreement with the reported values of nanophase TiO₂ reported in the literature (46, 47). Compared to the band gap energy of bulk TiO₂, the observed blue shift in the value of E₈ of the film samples of the present study should be a result of quantum confinement of charge particles in the nano-sized crystalline grains of the samples. Amorphous TiO₂ has a band gap with extended band tailing. As a result of fine grain size and resultant quantum confinement effect, the band gap of the as-deposited samples was larger than bulk band gap. But due to the large volume fraction of the defective grain boundary regions, band tailing should make the effective band gap to be less than the case when band tailing was absent. Thermal treatment resulted in a more ordered grain boundary region of the grains, i.e., more crystalline grains causing a reduction in the extent of the band tailing and hence an increase in the measured band gap as if this collection of agglomerates behaved like a crystal plane as regards light absorption.

Table 1. Calculated direct and indirect band gap values of anatase TiO₂ films annealed at different temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Calculated values of band gap (eV)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Direct</td>
</tr>
<tr>
<td>As-deposited</td>
<td>3.56</td>
</tr>
<tr>
<td>300°C</td>
<td>3.59</td>
</tr>
<tr>
<td>400°C</td>
<td>3.61</td>
</tr>
<tr>
<td>500°C</td>
<td>3.79</td>
</tr>
<tr>
<td>600°C</td>
<td>3.85</td>
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</tbody>
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121
A few reports (48-53) have claimed exciton confinement and thus Q-size effects in very small TiO₂ colloidal particles in the size range 1-12 nm. Anpo and co-workers (54) reported optical properties of particles of anatase and rutile titania with size in the range 3.8-53 nm and 5.5-200 nm respectively. Apparently, these crystallites displayed distinct size quantization effects even at such relatively large sizes. For a 12 nm rutile particle the bandgap increased by ~ 0.067 eV relative to the bulk bandgap (3.03 eV); for anatase particles the bandgap increased by about 0.156 eV relative to the bulk value of 3.18 eV.

We can infer that the band gap energy is partially dependent on the crystallinity of the film, as the band gap energies of highly crystalline thin films are similar to those of crystalline bulk materials, whereas amorphous or poorly crystallized films show band gap energies higher than those of the corresponding bulk materials (55, 56). We conclude from the present observations that our thin layers show much more pronounced size effects than a regular TiO₂ quantum well of the same thickness. This is presumably due to the fact that our layers are composed of distinct (partly cross-linked) nanocrystalline particles, whose size is smaller than the layer thickness. The size effects of individual quantum dots are therefore dominant in controlling the spectroscopic and photo-electrochemical properties of the layer as a whole. It should be noted that small particles in a solid layer should exhibit the full size-quantization effects only if mutual electronic interactions of particles are greatly diminished, e.g. by covering their surface with an insulating matrix (57, 58).

Figure 5.7 shows the transmission spectra of TiO₂ films deposited with an RF power 200 W and annealed at 600°C for 10 hrs. The spectra are characterized by interference fringes for photon energies above 365 nm (3.4 eV), which are due to the multiple reflections at the substrate/ TiO₂ interface. At approximately 376 nm (3.3 eV) the onset of the fundamental absorption can be seen. The refractive index of the prepared nanostructured TiO₂ thin films was calculated from the measured UV–Vis transmittance spectrum. The evaluation method used in this work is based on the analysis of the UV–Vis transmittance spectrum of a weakly absorbing film deposited on a non-absorbing substrate (59).
Figure 5.7. Transmittance spectra of as-deposited TiO$_2$ films deposited at an RF power of 200 W and that of film annealed at 600°C for 10 hrs.

Figure 5.8. Envelope method used for the calculation of refractive index of the TiO$_2$ film deposited at an RF power of 200 W and annealed at 600°C for 10 hrs.
Figure 5.9. Plot of refractive index (n) versus photon energy (hv) of the TiO$_2$ film deposited at an RF power of 200 W calculated by envelope method from the transmittance spectra shown in figure (7).

The refractive index (n) over the spectral range is calculated by using the envelopes that are fitted to the measured transmittance as shown in figure 5.8 using the following equation (59):

$$n(\lambda) = \left[ S + \left( S^2 - n_0^2(\lambda) n_s^2(\lambda) \right) \right]^{1/2}$$

where $S$ is given by

$$S = 1/2 \left( n_0^2(\lambda) + n_s^2(\lambda) + 2 n_0(\lambda) n_s(\lambda) \right) \left[ \left( T_{\text{max}}(\lambda) - T_{\text{min}}(\lambda) \right) / \left( T_{\text{max}}(\lambda) \times T_{\text{min}}(\lambda) \right) \right]$$

where $n_0$ is the refractive index of air, $n_s$ is the refractive index of substrate, $T_{\text{max}}$ is the maximum envelope, and $T_{\text{min}}$ is the minimum envelope. It is noted that the refractive index of the thin films of titanium oxide decreases with photon energy as shown in figure 5.9.
The values of n are in accordance with the reported values of refractive index of nanostructured TiO$_2$ films available in the literature (60, 61).

5.3.2. Micro-Raman spectroscopy studies

![Micro-Raman spectra](image)

*Figure 5.10. Micro-Raman spectra of TiO$_2$ films as-deposited and that of films annealed at different temperatures.*
Micro-Raman spectra of TiO$_2$ samples as-deposited and annealed at different temperatures viz. 300, 400, 500 and 600$^\circ$C are shown in figure 5.10. The peaks in the spectrum of as-deposited film are not well developed and this spectrum is indicative of the amorphousness of the sample. Raman scattering as a non-destructive characterization probe, is very sensitive to the crystallinity and micro-nano structure of materials. Raman lines become weak and broad when the samples have local lattice imperfections. Weak bands on amorphous-like background indicate that the grains were not crystalline as observed from GIXRD and TEM analyses (section 3 of chapter 4 of this thesis). The Raman spectra of samples annealed at different temperatures show marked changes compared to the spectrum of the as-deposited sample. The sample annealed at 300$^\circ$C, showed distinct Raman modes around 141.3, 391.5, 513 and 633 cm$^{-1}$ corresponding to $E_g$, $B_{1g}$, $A_{1g}$ or $B_{1g}$ and $E_g$ phonon modes of anatase phase of TiO$_2$. It can be seen that the high frequency Raman lines became well resolved in the spectra of the samples annealed at 500$^\circ$C. In addition to this, intrinsically weak $E_g$ mode at 198 cm$^{-1}$ of the anatase phase became observable in the spectra of the samples annealed at higher temperatures (figure 5.11). These observations demonstrated the annealing dependent evolution of the anatase phase in the as-deposited amorphous TiO$_2$ films.

![Figure 5.11. Evolution of 198 cm$^{-1}$ Raman line of anatase TiO$_2$ on annealing in the present TiO$_2$ film samples](image)

126
The strongest mode at 141 cm\(^{-1}\) (E\(_g\)) arising from the vibrations of the anatase structure is well resolved (figure 5.12) which indicates that the anatase phase with a long range order developed in the annealed films. The characteristic Raman line of anatase phase of TiO\(_2\) (141 cm\(^{-1}\)) was reported to have tenfold greater intensity than that of any other phonons of either rutile or anatase phase (62). This result is almost satisfied in the case of the present samples as seen in figure 5.12 confirming the formation of anatase phase. The intensity of Raman modes observed in the spectra of sample annealed at 300°C increased in the case of samples annealed at 400, 500 and 600°C. No additional peaks were observed on annealing the samples. These observations indicate that the TiO\(_2\) polymorph present in all the samples was pure anatase phase and no trace of rutile or brookite phase was observed in the micro-Raman investigations.

![Raman spectra](image)

**Figure 5.12.** The lowest-frequency E\(_g\) mode (141 cm\(^{-1}\)) of nanostructured anatase TiO\(_2\) films at various annealing temperatures.
In nanocrystalline anatase, the selection rule restricting first-order Raman scattering to optical phonons near the centre of the Brillouin zone \( (q=0) \) is relaxed and a range of \( q \) vectors \( \Delta q \sim 1/L \), where \( L \) is the crystalline domain size, becomes accessible (63). In the case of anatase TiO₂, the confinement effect can be observed with the change in the position and shape of the \( E_g \) mode at 144 cm⁻¹ (64). Raman spectrum of the sample annealed at 600°C for 10 hours gives an average full width at half maximum (FWHM) ~ 11 cm⁻¹ for the \( E_g \) Raman mode at 141 cm⁻¹ (figure 5.13). It is reported that the average FWHM for the \( E_g \) Raman mode of bulk anatase TiO₂ is ~ 7 cm⁻¹ (65). The increased broadness of the \( E_g \) Raman mode observed in the present study compared with the reported bulk values can be attributed to non-stoichiometry created by oxygen deficiencies and phonon confinement effect due to the breakdown of phonon momentum selection rule (66). Also, in the case of nanocrystals, it is worth noting that Raman intensity is related to interfacial vibrations in addition to bulk phonon modes, and the interfacial vibrations also make a contribution to the broadening of the Raman peaks (67). Choi et al. found a volume contraction effect in anatase TiO₂ nanoparticles due to increasing radial pressure as particle size decreases, and they suggested that the effects of decreasing particle size on the force constants and vibrational amplitudes of the nearest neighbor bonds contributed to both broadening and shifts of the Raman bands with decreasing particle diameter (68).

![Figure 5.13. Annealing temperature versus FWHM of the lowest-frequency \( E_g \) mode (141 cm⁻¹) of nanostructured anatase TiO₂ films annealed at various temperatures.](image-url)
Figure 5.14. Micro-Raman spectra of TiO\textsubscript{2} films annealed at 700°C and 800°C

Anatase to rutile transformation occurs in the bulk crystals in the temperature range from 750 to 850°C while for small particles this transformation was reported to occur at much reduced temperatures (69). Anatase to rutile transformation in ultrafine grained (~6 nm) agglomerates of chemically synthesized TiO\textsubscript{2} powders occurring in the 600 to 800°C range is reported by Edelson and Glaeser (70). In the case of RF sputtered TiO\textsubscript{2} films, Hunsche et al. (71) reported rutile crystallization above 500°C while anatase crystallization was suppressed in this temperature range (71). Report on the co-existence of anatase and rutile phase up to an annealing temperature of 600°C in magnetron sputtered TiO\textsubscript{2} films is also available in the literature (72). Further, from an investigation of the kinetics of anatase to rutile phase transition Hanley et al. (73) concluded that anatase crystallites must achieve a critical minimum size of 10-20 nm before transition to rutile can occur. In the present study the sample annealed at 600°C attained an average crystallite size ~10 nm as discussed in the section 3 of chapter 4 of this thesis. However neither the GIXRD pattern
nor the more sensitive micro-Raman measurements showed the presence of the rutile phase in the samples. Thus, the thermal energy supplied to the samples during annealing was consumed as the energy required for a structural rearrangement to assume the (004) preferred orientation rather than as the energy required for a phase transition to rutile phase. This argument is further confirmed from the micro-Raman spectra of the samples annealed at 700 and 800°C shown in figure 5.14. In this samples also, no trace of rutile phase appeared. It is reported that anatase-rutile transformation could be initiated from the rutile like elements created at the contacts between anatase particles (74). The lack of proper particle attachment would instead decrease the possibility of rutile transformation. The loosely packed particles might be one of the main factors responsible for the higher thermal stability of the anatase structure. Stable anatase phase nanostructured electrodes find a vital role in the solar energy conversion devices especially dye sensitized solar cells.

5.4. Conclusion

In the present chapter, analysis on the UV-Visible and micro-Raman spectroscopy investigations of nanostructured TiO$_2$ film samples annealed at different temperatures is presented. The band gap values estimated from UV-Visible spectra of the nanostructured TiO$_2$ film samples in the present study are in good agreement with the reported band gap values of nanophase TiO$_2$. Compared to the band gap energy of bulk TiO$_2$, the present samples exhibit a blue shift in the band gap value should be a result of quantum confinement effect in the nanosized crystalline grains of the samples. In the micro-Raman spectra of the samples the strongest mode at 141 cm$^{-1}$ ($E_g$) aroused from the vibrations of the anatase structure was well resolved which indicates that the anatase phase with a long range order developed in the annealed films. The increased broadness of the 141 cm$^{-1}$ ($E_g$) Raman mode observed in the present study compared with the reported bulk values can be attributed phonon confinement effect.

References


131

132
Chapter 6

UV-VISIBLE AND PHOTOLUMINESCENCE SPECTROSCOPY INVESTIGATION OF NANOSTRUCTURED TITANIUM DIOXIDE FILMS DOPED WITH ZnO