CHAPTER IV

4. Introduction

Nanometersized materials have recently gained a considerable amount of attention of their unique physical and chemical properties, because of their large surface to volume ratio and quantum size effect [1, 2]. Nanostructured TiO$_2$ is one of the most extensively studied oxides because of its remarkable optical and electrical properties along with its potential utilization in photocatalysis [3], photovoltaic cells [4], dye sensitized solar cells (DSSC’s) [5] and gas sensors [6] as low cost material.

Over the lifetime of the TiO$_2$ electrode; there are seven known polymorphs, observed six of which have distinct structures, such as anatase ($\beta$-TiO$_2$), rutile ($\alpha$-TiO$_2$), brookite type ($\gamma$- TiO$_2$), pyrite ($\alpha$-$\text{PbO}_2$), baddeleyite (ZrO$_2$) type, fluorite [7]. Among these crystalline phases, the anatase phase exhibits a high photocatalytic activity and thus has recently attracted much attention in the field of photocatalysts for decomposition of environmental pollutants and dye sensitized solar cells (DSSC’s) [8, 9].

Performance of TiO$_2$ for technical applications is strongly influenced by its morphology, crystallite size, crystalline phase and impurity type concentration. Porous, nanocrystalline TiO$_2$ is of great interest because; the function and performance of the material are strongly dependent on its morphology [5]. Porosity leads to a comparatively large internal surface area, which is advantageous for many applications where a good accessibility to the film surface becomes necessary. Porous materials as an electrode material exhibit good electrochemical performance because these materials possess both a high surface area and pores which are adapted to the size of ions [10].

In the present chapter, we have particularly successful in creating TiO$_2$ nanoparticles and nanoflakes. The strategy to design nanparticulate thin film is entirely based on a wet chemical, bottom up approach; such an approach does not require any template, membrane or surfactant.
4.A Synthesis of nanostructured TiO$_2$ thin films by SILAR method

Accordingly, the advance of synthetic methods, in which the crystalline phase, size and shape of the TiO$_2$ nanocrystals can be controlled, is of importance. In recent years, many studies related to the synthesis of nanostructured TiO$_2$ have been focused on the control of morphology as well as particle size. Many deposition methods such as thermal and anodic oxidation of titanium [11], electron beam evaporation [12], chemical vapor deposition [13], sol–gel [14], spray pyrolysis [15], chemical bath deposition (CBD) [16-18], SILAR [19-21], electrodeposition [4, 22] etc. have been reported to prepare nanocrystalline TiO$_2$ thin films. These processes have been used environmentally benign conditions. Therefore, the soft chemical processes (“bottom-up” approaches) are important for the preparation and fixation of TiO$_2$ particles. One of the recent soft chemical solution methods for the deposition of thin films is SILAR method. It is relatively a new and less investigated method and based on sequential reaction at the substrate surface, rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The features of the SILAR method include excellent material utilization efficiency, good control over the deposition process alongwith the film thickness, low cost and large-scale deposition capability on virtually any type of substrate [23].

In the present section, deposition of porous and nanograined TiO$_2$ films by using SILAR method is reported.

4.A.1 Experimental details

4.A.1.1 Substrate cleaning

The glass microslide and stainless steel substrates cleaned by employing the procedure as described in section 3.A.1.1.

4.A.1.2 Experimental setup for deposition of TiO$_2$ films by SILAR method

Fig. 4.1 shows the schematic of SILAR method for deposition of TiO$_2$ films. The deposition of TiO$_2$ thin film is carried out using four beakers
system at room temperature. The 0.1M Ti(III)Cl$_3$:15% HCl solution was used as a cationic and 0.01M NaOH solution was used as an anionic precursors. One SILAR cycle consists of four steps: (1) adsorption of titanium species for 20 s, (2) rinsing with distilled water for 5 s to remove excess adsorbed or loosely bounded titanium species, (3) reaction with NaOH precursor solution for 10 s to form stable TiO$_2$, and (4) rinsing with purified water for 5 s to remove excess or unreacted species or powdery TiO$_2$. The higher concentration of precursor solutions resulted in a higher growth rate but the quality of the film was poor due to powdery deposit. In order to remove hydroxide from deposited film and to improve the crystallinity, the films were heat treated at 673K for 2h. Preparative parameters are given in the table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1 Preparative parameters for the deposition of TiO$_2$ using SILAR method</th>
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<tbody>
<tr>
<td>Cationic precursor</td>
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<tr>
<td>Anionic precursor</td>
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<tr>
<td>Rinsing bath</td>
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<tr>
<td>Adsorption time</td>
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<tr>
<td>Reaction time</td>
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<td>Rinsing time</td>
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<tr>
<td>Substrates</td>
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</table>
4.A.1.3 Characterization techniques

The as-deposited and annealed (at 673 K) TiO$_2$ films were characterized for structural, surface morphological, electrical and optical properties using the techniques described in section 3.A.1.3.

4.A.2 Results and discussion

4.A.2.1 Growth mechanism

Thin TiO$_2$ films were obtained by immersing substrate into separately placed cationic and anionic precursors along with rinsing between every immersion with ion exchanged water. The growth kinetics of a thin film deposition process is ion-by-ion growth mechanism, which involves the ion-by-ion deposition at nucleation sites on the immersed surfaces [23, 24].

In TiO$_2$ deposition, a film deposit on a substrate through a controlled heterogeneous precipitation of TiCl$_3$. The proposed reaction mechanism is as follows: In the SILAR method, a thin layer of Ti(OH)$_3^+$ ions is adsorbed on the substrate by the immersion of the substrate into the cationic precursor solution kept at room temperature.

$$\text{Ti}^{3+} + \text{H}_2\text{O} \rightarrow \text{Ti} (\text{OH})_3^+$$

4.1
With further reaction is followed by the immersion of the wet substrate in NaOH anionic solution, where the chemical reaction between OH$^-$ and the adsorbed Ti(OH)$_3^+$ ions leads to the deposition of adherent nanometer sized TiO$_2$ layer.

$$\text{Ti(OH)}_3^+ + \text{OH}^- \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O}$$

The non-adherent particles were washed away into the water bath. The cycle of ion adsorption followed by chemical reaction is repeated several times to achieve terminal film thickness.

### 4.A.2.2 Thickness measurement

Fig. 4.2 (a) shows the film thickness variation with number of deposition cycles. The rate of increase in the thickness is nonlinear, which has been attributed to the growth by nucleation and coalescence process. More nucleation sites contribute to coagulation during the growing procedure. Furthermore, slight decrease in film thickness observed could be attributed to the formation of outer porous layer and/or the film which may develop stress to cause delamination, resulting in peeling off the film after the film reaches at maximum thickness [25]. The terminated thickness, at which the highest amount of TiO$_2$ is deposited on the substrate, is 0.82 mg.cm$^{-2}$ after 120 cycles. Fig. 4.2 (b) shows photograph of TiO$_2$ thin film over ~22 cm$^2$ area confirming the feasibility of SILAR method for large area deposition.
Fig. 4.2 (a) Variation of TiO$_2$ film thickness with immersion cycles (b) shows the photograph of the as-prepared and heat treated TiO$_2$ thin films.

4.A.2.3 Structural characterization

Fig. 4.3 (a) and (b) shows a typical X-ray diffraction patterns of as-deposited and heat-treated TiO$_2$ thin films on glass substrate. No distinct diffraction peak other than (110) [JCPDS card no. 21-1276] is observed in XRD pattern of as-deposited films, which probably means that the film consisted of hydrous TiO$_2$ colloidal particles with low crystallinity. Intensity of (110) peak is increased as an effect of heat treatment, which attributed to the improvement in crystallinity. Anatase phase was confirmed by the XRD pattern. Fig. 4.4 (a) and (b) shows the SAED patterns of respective films. The SAED pattern for as-deposited film showed fuzzy and broad rings, generally observed for amorphous materials whereas, heat-treated showed the spots instead set of rings due to the random orientation of crystallites, corresponding to the diffraction from different planes of nanocrystallites.
Fig. 4.3 The X-ray diffractograms of (a) as-deposited and (b) heat-treated at 673 K of TiO$_2$ thin films.

Fig. 4.4 shows SAED patterns of (a) as-deposited and (b) heat-treated TiO$_2$ films.

4.A.2.4 FT-IR study

Fig. 4.5 shows FT-IR spectra of the (a) as-deposited and (b) heat-treated TiO$_2$ samples. From these spectra, it is observed that strong band ($\nu_1$) around at 620 cm$^{-1}$ is associated with the characteristic vibrational mode of anatase TiO$_2$ [26]. The absorption peak ($\nu_2$) at around 900 cm$^{-1}$ is assigned to characteristic stretching vibration of peroxo groups. The absorption peaks around at ($\nu_3$) 1370 and ($\nu_4$) 1638 cm$^{-1}$ may be due to the stretching and bending vibration of hydroxyl groups of molecular water [27]. The narrow band around ($\nu_5$) 2923 cm$^{-1}$ is due to organic residues originating from the
sample as a result of the impurities in preparation procedure [28]. The absorption at 3391 cm$^{-1}$ indicates that the presence of hydroxide group ($\nu_6$) [29], that can not be avoided in the SILAR method. As-deposited TiO$_2$ showed the higher depth at 3391 cm$^{-1}$ than heat-treated one, which attributed to removal of hydroxide after heat treatment. Hence results indicate the presence of Ti-O bonds, peroxo groups and OH groups for as-deposited film whereas after heat treatment the peaks attributed to the peroxo groups and OH groups were almost disappeared. Less intense hydroxide and hydroxyl groups from water found in the heat treated TiO$_2$ may be due to the fact that the spectrum was not recorded in situ and some adsorption of water from the ambient atmosphere might have occurred.

![FT-IR spectra of (a) as-deposited and (b) heat treated TiO$_2$ films](image)

**Fig. 4.5** FT-IR spectra of (a) as-deposited and (b) heat treated TiO$_2$ films

**4.A.2.5 Surface morphology**

Fig. 4.6 (a) and (b) shows the surface morphology of as-deposited and heat-treated TiO$_2$ films. From the micrographs, one can see the total coverage of the substrate with the clusters of TiO$_2$. The TiO$_2$ film shows the formation of nanosized smooth grains all over the surface containing some pits and meso sized pores. Such type of porous structure resulted due to the film formation is based on the nucleation and coalescence. While, Pathan et
al. [20] and Kale et al. [19] reported the compact structure, which might be due to the use of buffer solution and complexing agent. The improvement in the grain size is observed after heat treatment. Inset of fig. 4.6 (b) shows the spherical nanocrystalline grains from the shaded region. The nanocrystalline grains are formed by agglomeration of small particles having irregular shapes and sizes due to the low temperature deposition method. The evident size of agglomerated particles was in the range of 50 to 70 nm.

Fig. 4.6 SEM micrographs of (a) as-deposited and (b) heat-treated TiO$_2$ films. Inset of fig. (b) shows the micrograph revealed at X10,000 magnification.

Fig. 4.7 (a) and (b) show TEM images in (30 nm scale bar) of the TiO$_2$. The matrix consists of isotropic, nanometersized spherical grains. The circled region of TEM image of as-deposited TiO$_2$ clearly shows that the particles of TiO$_2$ come close to form the grain while, heat treated shows improvement in the structure, with spherical nanoparticles in the range of 5-10 nm. The large surface area with porous morphology is the key requirement for electrochemical electrode [23].
4.A.2.6 Optical absorption study

Optical absorption spectra of as-deposited and heat treated TiO$_2$ films are shown in inset of fig. 4.8, the absorption edge was found at 330 nm. These spectra reveal that TiO$_2$ film has low-absorbance in the visible region, which is a characteristic of TiO$_2$. The band gap of TiO$_2$ thin films was estimated from a plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$). The intercept of the tangent to the plot gave a good approximation to the band gap energy for this direct band gap material [30, 31]. Fig. 4.8 shows optical gap of the as-deposited film as 3.6 eV which is slightly greater than the heat-treated 3.4 eV. Due to the improved grain size of heat-treated, the absorption edge showed red-shift to some extent. The widened band gap of the TiO$_2$ films is attributed to the contribution of quantum size effect [32, 33].

Fig. 4.7 TEM Images of (a) as-deposited and (b) heat-treated TiO$_2$ films. (Circled region shows the improvement in crystallization in the range of 5-10nm after heat treatment).
Fig. 4.8 Plots of $(\alpha h\nu)^2$ vs energy $h\nu$ of (a) as-deposited and (b) heat-treated TiO$_2$ films. Inset shows variation of absorption $(\alpha t)$ with wavelength $(\lambda)$ of (a) as-deposited and (b) heat-treated TiO$_2$ films on glass substrate.

4.4.2.7 Electrical resistivity

The electrical resistivity measurement using two point probe method was carried out within temperature range 300-650 K. The variation of log $\rho$ against 1000/T (shown in fig. 4.9), indicates the semiconducting nature of the film. The room temperature resistivity of as-deposited TiO$_2$ thin film was of the order of $10^7$ $\Omega$.cm which decreased to $10^5$ $\Omega$.cm after air annealing. The high resistivity is due to the nanocrystalline nature of the film. The electrical resistivity of nanocrystalline material is expected to be higher than that in the corresponding coarsely grained polycrystalline materials. The activation energies $(E_a)$ were estimated 0.82 and 0.25 eV for as-deposited and heat-treated samples, respectively.
Fig. 4.9 The variation of dark electrical resistivity (log $\rho$) with temperature (1000/T) of as-deposited and annealed TiO$_2$ films.

4.A.2.9 Contact angle measurement

Both super-hydrophilic and super-hydrophobic surfaces are important for practical applications. In the present case, the as-deposited and annealed TiO$_2$ films showed water contact angle 100$^\circ$ and 61$^\circ$, respectively. The water drop lies flat on the surface of as-prepared TiO$_2$ films in sheets instead of forming droplet, as seen in the fig. 4.10 (a). The superhydrophilic nature of the as prepared film due hydroxide residue present in the film. Whereas, fig. 4.10 (b) shows contact angle of heat treated films 61$^\circ$ i.e hydrophilic nature which attributed to the removal of hydroxide after heat treatment from the films [34].
4.A.3 Summary and conclusions

In summary, we have synthesized porous, nanograined, anatase TiO$_2$ material using a facile successive ionic layer and adsorption (SILAR) method. The XRD, SAED, SEM and TEM properties show the improvement in crystallization and grain size of the TiO$_2$ particles as an effect of heat treatment. Red shift was observed after heat treatment in the optical study. Hydrophilic nature of the TiO$_2$ films is observed attributed to the porous structure of the films. The porous microstructure revealed by SEM can accommodate the electroactive species in the solid bulk electrode material. The SILAR method is constructive for preparation of large area, porous and nanograined TiO$_2$ electrodes at the expense of small amount of initial ingredients.

Fig. 4.10 Measurements of water contact angle for (a) as-deposited and (b) heat treated TiO$_2$ thin films.
4.B Synthesis of nanostructured TiO$_2$ thin films by CBD method

Chemical bath deposition (CBD), one of the “Bottom-up” approach, has been well developed to fabricate large-area in view of its several advantages: it does not require sophisticated instruments; the starting chemicals are commonly available and cheap; the preparation parameters are easily controlled [32, 33]. However, little work has been done to prepare dense and adherent TiO$_2$ films by CBD method [16-18]. In order to improve the physical and chemical performance in the devices, designing the morphology of TiO$_2$ using CBD is a focus of current research.

4.B.1 Experimental details

4.B.1.1 Substrate cleaning

The glass microslide substrates cleaned by employing the procedure as described in section 3.A.1.1.

4.B.1.3 Experimental setup for deposition of TiO$_2$ films by CBD method

The TiO$_2$ thin films were synthesized by room temperature CBD method. In the typical synthesis, equimolar (0.1 M) titanium trichloride (TiCl$_3$:15% HCl) and ammonium chloride (NH$_4$Cl) in double distilled water. The ultrasonically cleaned glass and stainless steel substrates dipped vertically in the reaction bath. The depositions were carried out at predetermined time interval in between 15 - 35 h. In order to remove hydroxide from deposited film and to improve the crystallinity the films were heat treated at 673 K for 1 h. Fig. 4.11 shows the schematic representation of CBD method for TiO$_2$ films at room temperature. Preparative parameters are given in table 4.2.
Table 4.2 Preparative parameters for the deposition of TiO$_2$ using CBD method

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>0.1M TiCl$_3$, 15%HCl</td>
</tr>
<tr>
<td>Complexing agent</td>
<td>0.1M NH$_4$Cl</td>
</tr>
<tr>
<td>Deposition temperature</td>
<td>Room temperature (300 K)</td>
</tr>
<tr>
<td>Deposition time</td>
<td>15-35 h.</td>
</tr>
<tr>
<td>Substrates</td>
<td>Glass and stainless steel</td>
</tr>
</tbody>
</table>

Fig. 4.11 Schematic experimental set up for deposition of TiO$_2$ thin films

4.A.1.3 Characterization techniques

The as-deposited and annealed (673 K) TiO$_2$ films were characterized for structural, surface morphological, optical, electrical and wettability properties using the techniques described in section 3.A.1.3.

4.B.2 Results and discussion

4.B.2.1 Growth mechanism
CBD method is based on the formation of solid phase from a solution, which involves two steps as the nucleation and particle growth. The growth kinetics of a thin film deposition process is ion-by-ion growth mechanism, which involves the ion-by-ion deposition at nucleation sites on the immersed surfaces.

For deposition of TiO\textsubscript{2} films, TiCl\textsubscript{3}:15\% HCl was used as a source of titanium and ammonium chloride as a complexing agent. At the beginning of reaction,

\[ \text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^- \quad 4.3 \]
\[ \text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3\cdot\text{H}_2\text{O} \quad 4.4 \]

Ti\textsuperscript{3+} cations form amine complex of Ti(NH\textsubscript{3})\textsubscript{n}\textsuperscript{3+} (n = 1-4) with NH\textsubscript{3} (aq) in solution as:

\[ \text{Ti}^{3+} + n\text{NH}_3 \leftrightarrow \text{Ti(NH}_3)_n^{3+} \quad 4.5 \]

Here, initially the solution is acidic and the pH value is about 1 and then the pH of solution increases gradually and monotonically with time and the solution becomes alkalescent. On this alkalescent bath condition, the Ti(NH\textsubscript{3})\textsubscript{n}\textsuperscript{3+} is unstable and the following reactions occur:

\[ \text{Ti(NH}_3)_n^{3+} \leftrightarrow \text{Ti}^{3+} + n\text{NH}_3 \quad 4.6 \]
\[ \text{Ti}^{3+} + n\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_3^{+} \quad 4.7 \]
\[ \text{Ti(OH)}_3^{+} + \text{OH}^- \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O} \quad 4.8 \]

Further, pH value decreases again owing to the consumption of OH\textsuperscript{-} ions. In the processing, ammonium chloride is introduced as a complexing agent and exerts itself to control the release velocity of Ti\textsuperscript{3+} ions for deposition of TiO\textsubscript{2} thin film.

**4.B.2.2 Thickness measurement**

Fig. 4.12 (a) shows the graph of TiO\textsubscript{2} film thickness variation with deposition time. The film thickness was found to be increased with deposition time and remained constant after 30 h. The rate of increase in thickness was not constant through overall. Such behavior can be understood
by film formation and continuous precipitation in the bulk of solution. The formation of nucleation is necessary for a precipitate formation. The concept of nucleation in the solution is that the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film. Nonlinear rate of increase in the thickness attributed to the growth by nucleation and coalescence process.

Fig. 4.12 (a) Variation of TiO$_2$ film thickness with deposition time and fig. (b) shows photographs of the as-prepared and heat treated TiO$_2$ thin films.

4.B.2.3 Structural characterization

Fig. 4.13 (a) and (b) shows typical X-ray diffraction patterns of as-deposited and heat-treated TiO$_2$ thin films on glass substrate. The X-ray diffractogram of as-deposited film reveals the amorphous nature of the film, whereas improved crystallinity of the film after heat treatment reflects (110), (002) and (202) peaks in consistent with anatase phase [JCPDS card no. 21-1276].
Fig. 3.13 X-ray diffractograms of (a) as-deposited and (b) heat-treated TiO$_2$ thin films.

4.B.2.4 FT-IR study

The FT-IR absorption spectra of as-deposited and heat treated TiO$_2$ thin films in the range 4000–400 cm$^{-1}$ are shown in fig. 4.14. The five sharp absorption bands at $\nu_1$: 620, $\nu_2$: 950, $\nu_3$:1390, $\nu_4$:1631 and $\nu_5$: 3370 cm$^{-1}$ are attributed to the stretching vibration of TiO$_2$ in anatase, peroxy group, vibration of hydroxyl groups of molecular water and stretching vibrations of OH$^-$, respectively [27-29]. This result indicated that, as deposited film contains hydroxide and other bonds, which indicates that formation of hydroxide that cannot be avoided in the CBD method. After heat treatment, the peak corresponds to peroxy and OH$^-$ groups were almost disappeared. Less intense hydroxide and hydroxyl groups from water found in the heat treated TiO$_2$ may be due to the fact that the spectra were not recorded in situ and some adsorption of water from the ambient atmosphere has occurred.
Fig. 4.14 FTIR spectra of (a) as-deposited and (b) heat treated TiO$_2$ films.

4.B.2.5 Surface morphology

Fig. 4.15 (a) and (b) shows the surface morphology (at X10,000 magnification) of as-deposited and heat-treated TiO$_2$ films. From the micrographs, one can see the total coverage of the substrate with the of TiO$_2$ nanoflowers. For as-deposited, small nanoflowers growth is favored on the substrate surface. Conversely, as an effect of heat treatment the diffusion rate of the constituent atoms is high resulting in a high rate of formation of TiO$_2$ larger nanoflowers. Fig. 4.15 (c) shows the SEM image of heat treated TiO$_2$ sample with X50,000 magnification, which reveals that the flower-shaped TiO$_2$ is not a simple aggregation of small crystallites, but is composed by nanoflakes growing homocentrically. The flakes are typically of few nanometres in thickness and tens of nanometres in dimension. The TiO$_2$ flakes lie on but do not grow on the substrates.
Fig. 4.15 The SEM micrographs (X10,000) of (a) as-deposited and (b) heat treated TiO$_2$ film. (c) High magnification (X50,000) SEM micrograph of heat treated TiO$_2$ film.

4.B.2.6 Optical absorption study

Inset of fig. 4.16 shows the variation of optical absorbance ($\alpha t$) for as-deposited and heat-treated TiO$_2$ thin films with wavelength ($\lambda$). A quick inclining trend at 300-400 nm in the spectrum was observed. The absorption spectrum of the nanocrystalline TiO$_2$ show shift towards the higher energy after heat treatment (red shift) attributed to quantum size effect [20].

Fig. 4.16 presents the plot of ($\alpha \nu$)$^2$ against $\nu$ for both TiO$_2$ films. The good relation between ($\alpha \nu$)$^2$ versus $\nu$ implies the direct transition nature for TiO$_2$ films. For as deposited and heat treated TiO$_2$ films, a band gaps 3.54 and 3.26 eV, respectively were obtained. Decrease in band gap energy after heat treatment is attributed to increase in flower size with flake
size. This opens up the possibility of the constructing thin film devices from these nanoflakes with tunable optical properties.

![Graph](attachment:image.png)

**Fig. 4.16** Plot of \((\alpha h\nu)^2\) vs. energy \(h\nu\) of (a) as-deposited and (b) heat-treated TiO\(_2\) films. Inset shows variation of absorption \((\alpha t)\) with wavelength \((\lambda)\) of (a) as-deposited and (b) heat-treated TiO\(_2\) films on glass substrate.

**4.B.2.7 Electrical resistivity**

From fig. 4.17, it is clearly seen that both as-deposited and annealed TiO\(_2\) films show negative temperature coefficient of resistance. After annealing, the electrical resistivity was decreased from \(10^6\) to \(10^4\) \(\Omega\).cm. This decrease in electrical resistivity of annealed film is may be due to the crystallinity improvement without any structural change.
Fig. 4.17 The variation of dark electrical resistivity (log $\rho$) with temperature ($1000/T$) of as-deposited and annealed TiO$_2$ films.

4.B.2.8 Contact angle measurement

The contact angle is expected to depend upon local in homogeneity, chemical composition and the surface morphology of the semiconducting electrodes. Fig. 4.18 (a) and (b) shows contact angles of as deposited and heat-treated TiO$_2$ thin films and were $34^\circ$ and $46^\circ$, respectively. Both as-deposited and heat treated TiO$_2$ film show hydrophilic nature. Slight increase in contact angle after heat treatment is attributed to removal of surface hydroxile bonds [27, 33].

Fig. 4.18 Measurements of water contact angle for (a) as-deposited and (b) heat treated TiO$_2$ thin films.
4.B.3 Summary and conclusion

In summary, TiO$_2$ nanoflakes with flowerlike morphology have been controllably synthesized by the CBD method using NH$_4$Cl as capping molecules. The XRD and FT-IR studies confirm the formation of anatase TiO$_2$ thin film. The SEM images reveal the improvement in flower size of TiO$_2$ as an effect of heat treatment. Hydrophilic nature of TiO$_2$ confirmed by wettability test, is a prime requirement in the electrochemical properties. The CBD method is constructive for preparation of large area nanoflake TiO$_2$ electrodes at the expense of small amount of initial ingredients.
References