Structural, morphological, and optical studies of Rutile-phase TiO$_2$ rods grown on F:SnO$_2$-coated glass substrate by hydrothermal chemical bath deposition


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Structural, morphological and optical studies of Rutile-phase TiO$_2$ rods grown on F:SnO$_2$-coated glass substrate by hydrothermal chemical bath deposition

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ABSTRACT

Structural, morphological and optical studies of rutile-phase TiO$_2$ rods, grown on F:SnO$_2$-coated glass substrates, using hydrothermal chemical bath deposition, are reported. The methods used to determine the optical properties of a semiconductor-on-substrate two-medium system have been successfully applied to the following three-medium structure: vertically well-aligned rods of TiO$_2$, an F:SnO$_2$ (FTO) conducting thin film and a glass substrate. Reflectance fringe measurements yielded the thickness of the TiO$_2$ layer to be $d = 4.2$ µm, which agreed well with the length of rods observed using scanning electron microscope (SEM). The F:SnO$_2$ thickness of 569 nm measured from reflectance fringe spacings also agreed with SEM measurements. A room temperature absorption edge of $E_g = 2.90$ eV was obtained for the top layer of TiO$_2$ rods, which is similar to other values reported for TiO$_2$. A room temperature absorption edge of $E_g = 3.56$ eV was determined for the conducting F:SnO$_2$ layer.

Keywords: three-medium structure thin film semiconductors, TiO$_2$ rods, band-gap determination methods.

1. INTRODUCTION

Titanium dioxide (TiO$_2$) is the most attractive photo-catalyst due to its good charge transfer properties and high stability [1]. Specifically, single crystal rods or nanowires offer direct electrical pathways for photogenerated electrons and could increase the electron transport rate, thus improving the performance of photovoltaic devices such as dye-sensitized solar cells and solar-to-hydrogen cells [1-5]. However, the TiO$_2$-related materials studied to date [6-8] provide low overall solar-to-hydrogen efficiencies, which have been attributed to material aspects like interfacial band edge mismatch (due to band bending), poor photo-response, poor electrical conductivity, unsuitable band gap and low chemical stability. The highest solar-to-hydrogen efficiency reported recently for InGaP/GaAs/Ge three-junction cells combined with concentrator photovoltaic modules is 24.4% [9]. The achievement of such efficiencies when concentrator photovoltaic modules are not used, remains a subject for research – specifically materials development and characterisation, and the improvement of characterisation methods.

Methods for determining the optical properties, such as the band gap, of two, three and four-medium thin film semiconductor structures, were successfully developed previously [10-17]. For instance, Hall et al. [12] successfully studied the optical properties of cadmium sulfide and zinc sulfide from 0.6 to 14 µm. Furthermore, Sreemany et al. [16] proposed a simple spectrophotometric method for the determination of optical constants and band gap energy of multiple layers of TiO$_2$ thin films. The application of the methods developed for two-medium structures to a three-medium thin film structure made of well-aligned TiO$_2$ rods, F:SnO$_2$ (thin layer), and a glass substrate, is worth investigating. The fact that the top layer in this case (i.e. well-aligned rods of TiO$_2$) cannot strictly be considered as a thin layer, makes the study even more interesting.

2. EXPERIMENTAL DETAILS

2.1. Hydrothermal synthesis

Titanium butoxide (97%, reagent grade) and concentrated hydrochloric acid (31% - 32% by weight) were used as precursors. FTO-coated glass substrates, purchased from Technistro, were successively degreased in hot trichloroethylene, acetone and methanol. Each step was repeated three times for 3 minutes each. Finally, the substrates were washed in de-ionised (DI) water at room temperature and blown dry with N$_2$. In a typical synthesis, 30 ml of DI water was mixed with 30 ml of concentrated hydrochloric acid in a Teflon-lined stainless steel autoclave at room temperature, using a
magnetic stirrer. The mixture was stirred under ambient conditions for 10 min before the addition of 1 ml titanium butoxide. After stirring for another 10 min, three pieces of FTO-coated glass substrate were placed at an angle of ~45° against the wall of the Teflon-liner with the conducting side facing down. The hydrothermal synthesis was conducted at 150 °C for 20 h in an electric oven. After synthesis, the autoclave was cooled to room temperature in water, which took approximately 30 min. A more detailed explanation of this method was reported by Liu et al. [2] The FTO-coated glass substrates were then removed, rinsed extensively in DI water and blown dry with N2.

2.2. Characterisation.

For structural and morphological analyses, a Bruker D8 Discover X-ray diffractometer (XRD) with a Cu-Kα X-ray source (λ=1.5405 Å) and a Jeol JSM-7001F field emission scanning electron microscope (SEM) were used. Reflectance and transmittance spectroscopic analysis was carried out using a Bruker Optics V80V FTIR spectrometer in order to determine the refractive index, band gap and layer thickness of the FTO film on the glass substrates, as well as the band gap of the TiO2 rods grown on the FTO film.

3. THEORETICAL CONSIDERATIONS: DETERMINATION OF REFRACTIVE INDEX n(λ), FILM THICKNESS AND BAND GAP ENERGY (Eg)

F:SnO2 and TiO2 are transparent semiconductors. Hence, in the form of a film on a substrate, they can be modelled as transparent homogeneous films of uniform thickness d and refractive index n (λ), bound on either side by two semi-infinite non-absorbing layers with refractive indices n0 and n2 [13, 16]. The reflectance (R) and transmittance (T) of the film, for a parallel beam of light of unit amplitude and wavelength λ at normal incidence, are given by [13, 16]:

\[
R = (r_1^2 + 2r_1r_2\cos2\delta_1 + r_2^2)/(1 + 2r_1r_2\cos2\delta_1 + r_1^2r_2^2) \quad (1)
\]

\[
T = (n_2/n_0) \left[ (t_1^2 + t_2^2)/(1 + 2r_1r_2\cos2\delta_1 + r_1^2r_2^2) \right] \quad (2)
\]

where

\[
\delta_1 = nd\frac{2\pi}{\lambda} \quad (3)
\]

\[
t_1 = (2n_0)/(n_0 + n) \quad (4)
\]

\[
t_2 = 2n/(n_2 + n) \quad (5)
\]

\[
r_1 = (n_0 - n)/(n_0 + n) \quad (6)
\]

\[
r_2 = (n - n_2)/(n_2 + n) \quad (7)
\]

At normal incidence, values of Rmin, Rmax, Tmin, and Tmax are derived from equations (1) and (2) as follows:

\[
R_{\text{min}} = ((n_0 - n_2)/(n_0 + n_2))^2 \quad (8)
\]

\[
R_{\text{max}} = ((n^2 - n_0n_2)/(n^2 + n_0n_2))^2 \quad (9)
\]

\[
T_{\text{min}} = (4n_0n^2n_2)/(n_0n_2 + n^2)^2 \quad (10)
\]

\[
T_{\text{max}} = (4n_0n_2^2)/(n_0 + n_2)^2 \quad (11)
\]

From equations (9) and (10), the refractive index as a function of wavelength can be determined. From two consecutive extrema (minima or maxima) of wavelengths \(\lambda_1\) and \(\lambda_2\), respectively, the thickness d of a transparent homogeneous film of uniform thickness can be determined [10]:

\[
d = (1/2)\left\{ (\lambda_1\lambda_2)/[(n_2\lambda_2) - (n_1\lambda_1)] \right\} \quad (12)
\]

where \(n_1\) and \(n_2\) are the refractive indexes of materials 1 and 2 at wavelength \(\lambda_1\) and \(\lambda_2\), respectively.

Near the absorption edge, the absorption coefficient \(\alpha\) is related to the energy \(hv\) of the incident photons by the following relation (from the Tauc-Lorentz model) [14]:

\[
\alpha = \frac{A(hv - E_g)^n}{hv} \quad (14)
\]
\[ \alpha = \left[ B \left( \nu - E_g \right) \right]^p / \nu \]

where \( B \) is a constant, \( E_g \) is the band gap and \( p \) is an index that characterises the optical absorption process. The exponent \( p \) is theoretically equal to 1/2, 2, 3/2 or 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively.

4. RESULTS AND DISCUSSION

Fig. 1 shows an (a) XRD pattern and (b) FTIR reflectance spectrum of FTO-coated glass substrate (as-received), far from the absorption edge of SnO\(_2\) (3.6 eV) [18]. The reflectance spectrum was measured from 400 to 1 000 nm. The calculated index of refraction \( n(\lambda) \) of F:SnO\(_2\) is given in Fig. 1(c). The insert in Fig. 1(a) is a typical low magnification cross-sectional SEM micrograph of the F:SnO\(_2\)-coated glass substrate.

The reflectance data used to determine the refractive index \( n(\lambda) \) of F:SnO\(_2\) on the glass substrate. Indices were calculated using equation (9). The absorption edge is close to the value of 3.6 eV reported for SnO\(_2\) epitaxial thin films [18].

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(a) XRD pattern and (b) FTIR reflectance and transmittance of FTO-coated glass substrate. Extrema numbering follows the method explained in Ref [12]. (c) Variation of refractive index \( n(\lambda) \) for the F:SnO\(_2\) on the glass substrate. Indices were calculated using equation (9). The absorption edge is close to the value of 3.6 eV reported for SnO\(_2\) epitaxial thin films [18].}
\end{figure}

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Fig. 1 shows an (a) XRD pattern and (b) FTIR reflectance spectrum of FTO-coated glass substrate (as-received), far from the absorption edge of SnO\(_2\) (3.6 eV) [18]. The reflectance spectrum was measured from 400 to 1 000 nm. The calculated index of refraction \( n(\lambda) \) of F:SnO\(_2\) is given in Fig. 1(c). The insert in Fig. 1(a) is a typical low magnification cross-sectional SEM micrograph of the F:SnO\(_2\)-coated glass substrate. The spectrum in Fig. 1(b) shows a series of reflectance maxima (and minima) of different orders \((m = 1, 2, 3 \ldots)\). The method used to label these extrema is explained in Refs. [16, 19]. Analysis of these extrema in the reflectance spectrum allowed for the determination of the thickness of the FTO layer, as discussed below. Note that in the wavelength range of interest (~600 to 1 000 nm), the attenuation caused by absorption of incident light by the conductive SnO\(_2\) can be neglected [19-20]. In fact, Pan et al. [15] reported that the extinction coefficients of SnO\(_2\) (or absorption index) are close to zero for the range of wavelengths between 350 nm and 1 000 nm. The reflectance data used to determine the refractive index \( n(\lambda) \) of the FTO on glass, were also taken from this region (~600 to 1 000 nm). Equation (9) was used to determine \( n(\lambda) \) from the wavelengths of the reflectance maxima shown in Fig. 1(b), using the refractive indices for air, \( n_0 = 1 \), and glass, \( n_2 = 1.515 \) [16, 20]. The refractive indices for FTO given in Fig. 1(c) range between ~1.7 and ~2.2. These values agree reasonably well with values between 2.0 and 2.1 reported by Atay et al. [21] in the same wavelength range. The calculated thickness of the SnO\(_2\) film is \( d \approx 569 \) nm.

Fig. 2 shows the (a) transmittance spectrum of an FTO-coated glass substrate near the band edge, and (b) the corresponding Tauc plot \( (\alpha \nu) ^{1/2} \) versus photon energy \( \nu \)). The straight line section in Fig. 2(b) follows the relation \( (\alpha \nu) ^{1/2} \approx (\nu - E_g) \). From an extrapolation to the energy axis, a room temperature band gap value of \( E_g = 3.56 \) eV was obtained. This absorption edge is close to the value of 3.6 eV reported for SnO\(_2\) epitaxial thin films [18].
Figure 2. (a) Transmittance spectrum of F:SnO$_2$-coated glass substrate near the band edge, and (b) Tauc plot $(\alpha h\gamma)^{1/2}$ versus energy $(h\nu)$ for FTO on glass.

Figure 3. XRD pattern (a) of as-grown rutile-phase TiO$_2$ and (b) reflectance of the sample. The XRD pattern of as-purchased FTO-coated glass substrate in Fig. 1(a) is inserted for comparison.
Fig. 3a displays an XRD pattern (a) of as-grown rutile-phase TiO$_2$ and (b) the reflectance of the sample. Fig. 3b was used for the determination of the thickness of the as-deposited material on FTO-coated glass substrate. All the diffraction peaks that appear in the XRD pattern of the TiO$_2$ film in Fig. 3(a) correspond to the tetragonal rutile-phase of TiO$_2$. The lattice parameters were estimated to be $a = b = 4.636$ Å and $c = 2.958$ Å, which are in close agreement with values reported by Liu et al. [2]. The narrow and pronounced (002) diffraction peak indicates that the material is of good crystalline quality and highly oriented with respect to the substrate surface. The preferred growth direction of TiO$_2$ is [001], with the growth axis parallel to the substrate surface normal.

By analyzing the fringes (extrema) in the reflectance spectrum (Fig. 3(b)), the thickness of TiO$_2$ was determined as follows: the refractive indices of TiO$_2$ as estimated by Devore$^{11}$ were used to determine the layer thickness, since the theoretical model described earlier for a three-medium system (air-thin film-substrate) does not apply to a four-medium system (air-thin film-thin film-substrate). From the reflectance fringes, the thickness of the TiO$_2$ layer was estimated to be $d = 4.2$ µm.

![Figure 4](image-url)  
Figure 4. Low (a, b) and high (c) magnification top view SEM micrographs of rutile-phase TiO$_2$. (d) Low magnification cross-sectional view SEM micrographs of rutile-phase TiO$_2$.

Fig. 4 shows typical low (a, b) and high (c) magnification top view SEM micrographs of the TiO$_2$ film. The entire surface of the FTO-coated glass substrate is covered very uniformly with rutile-phase TiO$_2$ rod-like structures, as seen in Fig. 4. Moreover, the top surfaces of these rods appear to contain many step edges. It was debated that the growth of these rods may have proceeded by addition of titanium growth units at these step edges through the entire growth stage. The rods are tetragonal in shape (see Fig. 4(c)). Their average diameter was determined to be 175±7.5 nm. Fig. 4(d) shows a typical low magnification SEM micrograph of rutile-phase TiO$_2$ rods in cross-section. The FTO and TiO$_2$ layers can clearly be distinguished. The FTO has a thickness of ~600 nm, while the TiO$_2$ has a thickness of ~4.2 µm. These thicknesses are in agreement with the values determined earlier via reflectance spectroscopic analysis. Therefore, it is concluded that these rods definitely do not form a thin film.

Fig. 5 (a) shows transmittance spectrum of rutile-phase TiO$_2$ nanorods on F:SnO$_2$ glass substrate near the band edge, and (b) the corresponding $(\alpha h \nu)^{1/2}$ versus energy ($h \nu$) plot. The straight-line section in Fig. 5(b) follows the relation $(\alpha h \nu)^{1/2} \approx (h \nu - E_g)$. From an extrapolation to the energy axis a room temperature band gap value $E_g = 2.90$ eV was obtained for rutile-phase TiO$_2$ nanorods on F:SnO$_2$ glass substrate. This absorption edge is equal to the value of 2.90 eV previously reported for TiO$_2$ [15, 23]. It has to be pointed out that in cases where the influence of the second layer on the substrate contributed to the optical response, researchers could obtain the band gap values for both films [24]. In the

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present sample, the SnO$_2$ layer is an order of magnitude thinner than the TiO$_2$ layer, and it is expected that any contribution from the SnO$_2$ will be negligible compared to the much thicker TiO$_2$ layer, wherein most of the absorption during transmission of the radiation will occur.

![Figure 5](image.png)

Figure 5. (a) Transmittance spectrum of rutile-phase TiO$_2$ nanorods on F:SnO$_2$ glass substrate near the band edge, and (b) the corresponding $(abh)^{1/2}$ versus energy $(h\nu)$ plot.

3. CONCLUSION

The structural, morphological and optical properties of rutile-phase TiO$_2$ rods grown on F:SnO$_2$-coated glass substrates by hydrothermal chemical bath deposition have been studied. The methods used to determine the optical properties of two-medium thin film semiconductors structures were successfully applied to the following three-medium structure: vertically well-aligned rods of TiO$_2$ on F:SnO$_2$ conductive thin film (569 nm thick) on a glass substrate. The thickness of the TiO$_2$ layer was estimated, using reflectance fringes, to be $d = 4.2\ \mu$m, which agrees well with the length of rods observed using SEM. The room temperature absorption edge $E_g = 2.90\ eV$ was obtained for the top layer made of TiO$_2$ rods, which is the typical absorption edge value reported for TiO$_2$. The room temperature absorption edge of the conductive layer F:SnO$_2$ was also calculated and found to be $E_g = 3.56\ eV$. Therefore, the method for determining the optical properties, such as the band gap, of two, three and four-medium thin film semiconductor structures as summarised by Sreemany et al. [16] can be used on three-media structures where the top layer is made of semiconductor rods.

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REFERENCES
