Structural and optical properties of thin TiO$_2$:C films – influence of the substrate-erosion zone radial distance

Orlin Angelov
Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria
E-mail: orlinsolar@gmail.com

Abstract. The structural and optical properties were studied of thin TiO$_2$:C films deposited on glass substrates by r.f. magnetron co-sputtering of a TiO$_2$ target and carbon plates placed on its erosion zone in an atmosphere of Ar (0.5 Pa) + air(0.6 Pa). The total area of the carbon plates was 830 mm$^2$, and the radial distance between the center of the glass substrates $(15 \times 25 \times 1$ mm) and the circle of the erosion zone with a maximum sputtering rate was 2 cm and 4 cm. The as-deposited and annealed (air, 400 °C, 1 h) thin films with a thickness of about 150 nm were studied via reflectance and transmittance measurements, X-ray photoelectron spectroscopy (XPS), grazing incidence X-ray diffractometry (GI XRD) and Raman spectroscopy. The optical spectra of the thin films deposited at the higher radial distance from the erosion zone maximum demonstrated absorption in the visible range. The XRD patterns revealed a mix of amorphous and nano-crystalline anatase and rutile TiO$_2$ phases in all thin films. The reflections of the experimental XRD patterns indicated the presence of tensile stress in the grains. The Raman spectra confirmed the nano-crystalline structure of the anatase and rutile phases of the films. The incorporation is discussed of C atoms in the TiO$_2$ films.

1. Introduction

The activation of the most widely used phases of TiO$_2$, anatase (optical band gap, $E_g \sim 3.2$ eV) and rutile ($E_g \sim 3.02$ eV) to generate electron-hole pairs when used in various photo processes necessitates extending their absorption in the visible spectrum. Doping with metal atoms or metal oxides leads to a thermal instability of the thin film and formation of metal centers acting as electron traps, which reduces the photocatalytic efficiency [1]. The amorphousness of the structure influences the carrier’s migration in dependence on the long-range disorder of the catalytic materials’ internal structure.

Among the non-metal atoms for doping TiO$_2$, as N, S, F and C, the most commonly used are N and C. The anatase and rutile phases can be described by distorted TiO$_6$ octahedra including Ti$^{4+}$ ions surrounded by six O$^{2-}$ ions. The rutile phase has a slight orthorhombic distortion, while the anatase octahedron is more distorted. The valence zone of titanium dioxide is composed of 2p orbitals of oxygen atoms; and the conduction zone, of 3d orbitals of titanium atoms. The structural and optical properties of the TiO$_2$:C phases have been studied by DFT [2]. At low C concentrations, the O atoms are substituted by C atoms and oxygen vacancies are created. When the deposition of TiO$_2$ takes place in an oxygen-rich atmosphere, the C atoms predominate in the lattice sites where they replace the Ti atoms. The valence state of C dopants changes from -4 in carbides (Ti-C bonds) to +4 in carbonates groups with C-O bonds. The different bond types appear depending on the method and technological conditions of the films/nanoparticles preparation. In [3], the authors have demonstrated preparation at...
low temperature (60 °C) of micro-mesoporous TiO₂:C powders with anatase crystalline walls. The carbon substituted the O atoms in the lattice sites and the carbonate species with interstitial C atoms were bonded to oxygen. The effect of carbon is as a sensitizer for absorption in the visible spectrum and the creation of defects as interstitial or substitution sites in the titanium dioxide lattice, whereby interface states are formed leading to a reduction in the width of the forbidden zone (\(E_g\)) of titanium dioxide. Irie, et al. [4] have studied TiO₂:C thin films deposited by r.f. magnetron sputtering of a Ti target in Ar+CO₂ gas mixtures with different dopant concentrations. Many authors have studied the carbon doping of TiO₂ from gaseous phase containing CO₂; however, it is necessary to study the various possibilities for this doping, e.g. from a solid-state phase of carbon, and the effect of the different sputtering conditions in obtaining new materials.

The study presented addresses the influence of the substrate-erosion zone radial distance on the optical and structural properties of thin TiO₂:C films prepared by r.f. magnetron co-sputtering of a TiO₂ target with carbon plates placed on the erosion zone maximum in a gas mixture of Ar+air.

2. Experimental

Thin films of TiO₂:C were prepared on glass substrates (15×25×1 mm) via r.f. magnetron co-sputtering of a TiO₂ target with carbon plates on its maximum erosion zone in gas atmosphere of Ar(0.5 Pa)+ air(0.6 Pa). The total area of the carbon plates was 830 mm². The glass substrates were fixed on a holder at a vertical distance of 5.5 cm from the TiO₂ target; the radial distance between the substrates centers and the circle of maximum sputtering rate of the TiO₂ target was 2 cm or 4 cm. The glass substrates were heated at 350 °C during deposition. The films were 150-nm thick. The samples were studied as-deposited and after annealing at 400 °C for 1 h in air. Their crystallographic structure was studied by grazing incidence X-ray diffractometry (GI XRD), Bruker D9 Advance XRD system. The XPS studies providing the binding energy (BE) of the atoms were performed on an ESALAB Mk II system (England) with Al Kα radiation (1486.6 eV) and a total instrumental resolution of ~1 eV. The vibrational properties of the films were studied by Raman spectroscopy (micro-Raman spectrometer HORIBA Jobin Yvon Labram HR 800 Visible with a He-Ne (\(\lambda=633\) nm) laser). The optical properties were studied by recording the transmittance and reflectance spectra by a Schimadzu 3600 UV-Vis spectrophotometer.

3. Results and discussion

The dependences of the optical absorption, \(\alpha\), and \(\ln \alpha\) on the photon energy, \(E\), of the as-deposited and annealed thin TiO₂:C films are presented in figure 1. The optical absorption, \(\alpha\), of the thin films in the range of fundamental absorption without scattering \((\alpha > 10^4 \text{ cm}^{-1})\) was determined through their reflectance (R) and transmittance (T) spectra using the approximation \(\alpha = (d^{-1})\ln((1-R)^2/T)\) [5], where \(d\) is the film thickness.

The band gap, \(E_g\), was determined using Tauc’s expression for indirect electron transitions \((\alpha h\nu)^{0.5} = A(h\nu-E_g)\) [6], where \(A\) is a constant. The Urbach energy, \(E_u\), of the thin films was determined through the reciprocal value of the slope in the dependence of \(\ln \alpha\) on \(E\) in the linear region below \(E_g - \alpha = \alpha_0 \exp(h\nu/E_u)\) [7], where \(\alpha_0\) is a constant. The \(E_g\) value was determined by the intersection point of the tangent line with the abscissa, \(E\), of the \((\alpha h\nu)^{0.5}\) dependence on the energy, \(E\). The values of \(E_g\) and \(E_u\) for the samples studied are presented in table 1. The as-deposited and annealed samples (figure 1) placed at the higher radial distance, RD, from the erosion zone maximum.

![Figure 1. Dependence of the optical absorption, \(\alpha\), multiplied by the energy, \(E\), \((\alpha E)^{0.5}\) on the photon energy for RD of 4 cm and 2 cm. The inset shows the energy dependence of the Urbach band tail.](image-url)
the weight fractions of the anatase and rutile phases and sizes decrease crystallographic plane are higher because rutile phases average grain size of the rutile phase are higher than phases, which indicates the existence of tensile stress in the films. The weight fractions of the anatase XRD spectra are 25.15 thin films. The most prominent anatase crystallographic planes (101) have peaks between on humps as spectra. The structure of the TiO\(_2\);C, 1 h increased absorption in the visible range. The lower band gap of the TiO\(_2\) demonstrates absorption transmission (not shown) and substrates more energy and possibility for rearrangement and improvement of the films than the atoms on the plates of graphite. When films on the substrates leave the plasma created by r.f. magnetron co-deposited and (101) anatase (RD 2 cm, the ratio is reversed for both the as-deposited and the annealed samples. The average grain sizes, \(D\), calculated by the Debye-Scherrer equation, are 20.8 nm and 12.9 nm for as deposited (101) anatase phases at RD of 4 cm and 2 cm, respectively; and for as-deposited (110) rutile phases, 11 nm and 4.4 nm at RD of 4 cm and 2 cm, respectively. The grains sizes for the (101) crystallographic plane are higher because of its lower formation energy. After annealing, the grains sizes decrease – 9.1 nm and 13.6 nm for (101) anatase phases at RD of 4 cm and 2 cm, respectively; and 4 nm and 7.5 nm for (110) rutile phases at RD of 4 cm and 2 cm, respectively. Our estimations of the weight fractions of the anatase and rutile phases demonstrated an increased anatase content and a

(4 cm) exhibit lower \(E_g\) values than those at the shorter RD of 2 cm. The atoms which build up the thin films on the substrates leave the plasma created by r.f. magnetron co-sputtering of the TiO\(_2\) target and plates of graphite. When reaching the substrates closer to the erosion zone maximum, these atoms have more energy and possibility for rearrangement and improvement of the films than the atoms on the substrates placed at a greater RD. The TiO\(_2\);C thin films deposited at a lower RD have a higher transmission (not shown) and a lower Urbach energy, \(E_u\), (table 1). TiO\(_2\) deposited at the higher RD demonstrates absorption extended to the visible spectrum \(E_u = 2.95\) eV after annealing. The optical absorption spectra of pure TiO\(_2\) thin films \(E_u \sim 3.2\) eV, not shown) deposited at different RD show no absorption in the visible range. The lower band gap of the TiO\(_2\);C films can be attributed to the structural defects near the band edge and the included C atoms, according to the XPS analysis.

The structure of the TiO\(_2\);C thin films was studied by XRD and Raman spectroscopy. The XRD spectra (figure 2a) of the films for RD of 4 cm and 2 cm demonstrate anatase and rutile phases for the as-deposited and the annealed samples. The reflections peaks from the crystallographic planes appear on humps that are due to an amorphous TiO\(_2\) phase, which is indicative of not fully crystallized TiO\(_2\);C thin films. The most prominent anatase crystallographic planes (101) have peaks between 25.15°-25.30°, while those of the rutile phase (110), between 27.2°-27.5°. The peaks positions in the XRD spectra are shifted to the smaller 2θ angles compared to the peaks positions in the not-disturbed phases, which indicates the existence of tensile stress in the films. The weight fractions of the anatase phase are higher than those of the rutile phase for the as-deposited and the annealed samples for RD of 4 cm; for RD of 2 cm, the ratio is reversed for both the as-deposited and the annealed samples. The average grain sizes, \(D\), calculated by the Debye-Scherrer equation, are 20.8 nm and 12.9 nm for as deposited (101) anatase phases at RD of 4 cm and 2 cm, respectively; and for as-deposited (110) rutile phases, 11 nm and 4.4 nm at RD of 4 cm and 2 cm, respectively. The grains sizes for the (101) crystallographic plane are higher because of its lower formation energy. After annealing, the grains sizes decrease – 9.1 nm and 13.6 nm for (101) anatase phases at RD of 4 cm and 2 cm, respectively; and 4 nm and 7.5 nm for (110) rutile phases at RD of 4 cm and 2 cm, respectively. Our estimations of the weight fractions of the anatase and rutile phases demonstrated an increased anatase content and a

| Band gap, \(E_g\), eV | Urbach energy, \(E_u\), eV |
|----------------------|--------------------------|
| As-deposited | Annealed, air, 400 °C, 1 h | As-deposited | Annealed, air, 400 °C, 1 h |
| RD 4 cm | 3.05 | 2.95 | 0.054 | 0.067 |
| RD 2 cm | 3.24 | 3.22 | 0.048 | 0.064 |

Figure 2. XRD (a) and Raman (b) spectra of thin films TiO\(_2\);C deposited at, erosion zone-sample radial distances, RD, of 4 cm and 2 cm.
reduced rutile content after annealing for both RD. This trend results in smaller grains sizes of both phases and has been reported in the literature [8]. In nanoscale thin films, the anatase phase has a lower surface energy than the rutile phase, which is not valid for bulk materials [8]. During annealing, this stimulates an increase of the weight fraction of the anatase phase at the expense of the rutile phase. Elucidating this effect of annealing and formation of phases at different RD requires further studies. The Raman spectra (figure 2b) confirm the polycrystalline structure of the thin TiO$_2$:C films. The anatase phase has six Raman active modes, with the rutile phase having four Raman active modes [9]. The peaks of the bands in the Raman spectra of the TiO$_2$:C films corresponding to the anatase phase are at about 144 cm$^{-1}$ E$_g$ ($\nu_6$), 397 cm$^{-1}$ B$_{1g}$ ($\nu_4$) and 640 cm$^{-1}$ E$_g$ ($\nu_1$) [9]. The peaks corresponding to rutile phase are at about 143 cm$^{-1}$ B$_{1g}$, 447 cm$^{-1}$ E$_g$ and 611 cm$^{-1}$ A$_{1g}$ [9]. The mode E$_g$ ($\nu_1$) corresponds to Ti-O bonds with stretching vibrations and E$_g$ ($\nu_6$) and B$_{1g}$ ($\nu_4$) corresponds to O-Ti-O bonds with bending vibrations [9]. The other phases did not appear, which indicates possible inclusion of C atoms at the grains boundaries of the films. The XPS analysis demonstrates Ti$^{4+}$2p, O1s and C1s photoelectron bands in the spectra. The reference binding energy is 458.5 eV (Ti$^{4+}$2p). The C1s and O1s bands were deconvoluted to components through a fitting procedure using the XPSPEAK41 software. The accuracy of the measured BE was ~ 0.2 eV.

![Figure 3. XPS spectra of Ti$^{4+}$2p (a), O1s (b, c) and C1s (d, e) for TiO$_2$:C thin films deposited at different RD. The samples are as-deposited and annealed.](image)

The Ti2p photoelectron spectra (figure 3a) demonstrate splitting in two peaks – Ti$^{4+}$2p$_{1/2}$ at about 458.5 eV and Ti$^{4+}$2p$_{3/2}$ at about 464.4 eV for the as-deposited and the annealed thin films formed at both RD (4 cm and 2 cm). Comparison with the Ti2p splitting in the respective spectra of pure TiO$_2$ thin films (not shown) leads to the conclusion that there is no shift in the energy within the accuracy of measuring BE (0.2 eV). These positions are typical for normal states of Ti$^{4+}$2p in TiO$_2$. The O1s spectrum (figure 3 b, RD 4 cm, as-deposited) demonstrates two peaks. The one at about 529.8 eV corresponds to the lattice oxygen of TiO$_2$, the other at about 531.4 eV is assigned to mixed contributions from surface hydroxide and C-O bonds [10]. After annealing, the O1s spectrum (figure 3 c, RD 4 cm, annealed) exhibits a new peak at about 535.6 eV, which is assigned to C=O bonds [11]. The XPS spectra of the as-deposited and the annealed thin film obtained at RD of 2 cm (not shown) did not demonstrate a peak at about 535 eV. This can be due to the fewer defects in the films ($E_n$, table 1). The C1s photoelectron spectra obtained after deconvolution (figure 3 d and e, RD 4 cm, as-deposited and annealed) manifest C-C and carbon-oxygen types of bonds. The peak positions at about 285 eV, 286 eV and 288 eV are assigned to C-C (C atoms adsorbed at the surface), C-O and Ti-C-O bonds,
respectively [11]. This confirms the incorporation of carbon atoms in the TiO$_2$ films and their influence on the optical absorption in the visible region. Irie et al. [4] determined the carbon concentration by calculating the ratio of C/O atoms linked to Ti and excluded the carbon contained in the surface contaminant hydrocarbons from the carbon concentration in the thin films.

4. Conclusions
Thin TiO$_2$:C films deposited in Ar$_2$+air atmosphere by r.f. magnetron co-sputtering of TiO$_2$ target with carbon plates placed on the maximum erosion zone at different radial distances, RD, of the samples from the erosion zone demonstrate anatase and rutile phases in not fully crystallized TiO$_2$. The XRD spectra point to the existence of tensile stress in the films. Both as-deposited phases demonstrate higher grains sizes for the higher RD (4 cm), but after annealing both phases have a higher $D$ at the lower RD (2 cm). The weight fractions of the anatase phase increase after annealing at the expense of the rutile phase for both RD due to the lower surface energy of the nanoscale anatase phase. The Raman spectra confirm the polycrystalline structure of the films. The optical absorption spectra of the thin films deposited at the higher erosion zone-sample RD of 4 cm demonstrate absorption in the visible spectrum, which is due to the more disordered structures than those obtained at the lower RD of 2 cm and incorporation of C atoms, as demonstrated by the XPS analysis results. Further studies will be undertaken to elucidate the effect of annealing and formation of phases at different RD.

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