Study of optical transmittance of photocatalytic titanium dioxide films deposited by radiofrequency magnetron sputtering

Estudo da transmitância óptica dos filmes de dióxido de titânio fotocatalítico depositados por “magnetron sputtering” usando radiofrequência

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ABSTRACT

The optical transmittance of titanium oxide (TiO₂) films in the ultraviolet-visible region were studied in this work. Such films have possible application in photocatalysis at room temperature. Among many candidates for photocatalysts, TiO₂ is practically the only material suitable for industrial use at present. This is because TiO₂ has the most efficient photoacatalysis, the highest stability and the lowest cost. Photochemical reactions include the photoinduced redox reactions of adsorbed substances, or the photoinduced hydrophilic conversion of TiO₂ itself. Polyethylene terephthalate (PET) was chosen as the substrate because of its flexibility, high transmission in visible light and low cost. Glass blades were used as substrates for TiO₂ films for analysis by optical transmittance spectroscopy. The experimental results show that the TiO₂ films deposited on glass were associated with the anatase phase with a [0 0 4] preferred orientation. Ultraviolet near infrared spectroscopy revealed the high transmittance of the films in visible light and high absorption in the ultra-violet region under most deposition conditions.

Keywords: TiO₂, RF sputtering, Optical properties, Photocatalysis.

RESUMO

A transmitância óptica de filmes de dióxido de titânio (TiO₂) na região ultravioleta-visível foi estudada neste trabalho. Tais filmes têm possível aplicação em fotocatalise à temperatura ambiente. Entre muitos candidatos a fotocatalisadores, o TiO₂ é praticamente o único material adequado para uso industrial no momento. Isso ocorre porque o TiO₂ possui a foto catalise mais eficiente, a maior estabilidade e o menor custo. As reações fotoquímicas incluem as reações de oxirredução fotoinduzidas de substâncias adsorvidas ou a conversão hidrofílica fotoinduzida do TiO₂ em si. O teretaltato de polietileno (PET) foi escolhido como substrato devido à sua flexibilidade, alta transmissão na luz visível e baixo custo. Laminas de vidro foram utilizados como substratos para os filmes de TiO₂ para análise por espectroscopia de transmitância óptica. Os resultados experimentais mostram que os filmes de TiO₂ depositados no vidro foram associados à fase anatase com uma orientação preferencial em [0 0 4]. A espectroscopia de absorção no infravermelho revelou alta transmitância dos filmes sob luz visível e alta absorção na região ultravioleta sob a maioria das condições de deposição.

Palavras-chave: TiO₂, RF “sputtering”, Propriedades ópticas, fotocatalísse.
INTRODUCTION

Titanium dioxide (TiO₂) is an attractive material because of its outstanding physical and chemical properties. Various methods of TiO₂ film deposition have recently been investigated, including pulsed laser deposition (PLD), atmospheric dielectric barrier discharge, and plasma enhanced chemical vapor deposition (PECVD).

Although PECVD has many advantages, such as high purity and the easy control of reaction parameters, it is usually performed in high-vacuum environments or requires high temperatures for which the installation costs and the energy requirements are high. The optimal vacuum system parameters for obtaining titanium oxide thin films have been studied since 1972. The use of sputtering technique to deposit photocatalytic thin films has been reported. Among the various semiconductors employed, TiO₂ is the most preferred material for the photocatalytic process.

Recent studies reveal excellent TiO₂ photocatalytic stability. Another advantage is obtained when TiO₂ films present high crystallinity, which influences the charge carrier lifetime, and improves photocatalytic activity. The performance of these films in such technologies strongly depends on the TiO₂ polymorphic phase employed: rutile, anatase or brookite. Anatase exhibits advantages over rutile for catalysis, photocatalysis and solar cell applications. Some authors considered reactive magnetron sputtering as the technique to obtain TiO₂ anatase. It has been reported that the preferential growth in anatase is [001] based on Bragg-Brentano XRD analyses. Moreover, the ability to control texture and the crystallinity of the TiO₂ films allows increased catalytic processes. Other authors report that the modification of surface morphology of semiconductor photocatalysts can give rise to a more efficient form for photocatalytic applications.

In addition, photocatalysis with titanium dioxide (TiO₂) using natural solar radiation is one of the most efficient processes for inactivation of bacteria including E. coli, E. faecalis, Legionella, etc. and some specific fungi (Fusarium sp.) in water. Titanium dioxide is still useful as an active material in various applications such as dye-sensitized solar cells, fuel cells and optical coatings to produce antireflection layers on low-emissivity coatings and protective layers.

Titanium dioxide has gained attention owing to its nontoxic, chemical and environmental consistency and interesting optical properties, including its brightness and refractive index in visible region. In addition, TiO₂ of high transparency has been deposited in Ar/O₂ plasmas. Recent studies have reported the radiofrequency (RF) sputter deposition of TiO₂ using Ar/O₂ plasmas.

MATERIAL AND METHODS

Preparation of TiO₂ film

The TiO₂ thin films were deposited on both glass (dimensions of 75 × 25 × 1 mm) and polyethylene terephthalate (PET) substrates of 0.05 × 25 × 15 mm, in the direct current (DC) magnetron sputtering system schematized in Fig. 1. The target was titanium of 99.9% purity and total surface area (TA) of 7854 mm². The distance between target and substrate was 60 mm.

Figure 1: Schematic of the reactive magnetron sputtering film deposition system.
After the chamber was evacuated to a base pressure lower than 1 × 10⁻³ Pa, 50 SCCM of pure argon sputtering gas was fed to the chamber, and the discharge begun at a constant current of 0.45 A. After the discharge voltage has stabilized, 99.95% pure oxygen gas was introduced into the chamber at a constant flow rate of 10 SCCM for a deposition time of 3600 s. Working at a constant argon flow rate and discharge current, the discharge voltage increased from zero up to the threshold (applying three values of oxygen flow rate: 20, 25 or 30%), indicating that the effective reduction in the area of the metal being sputtered caused the formation of oxide. After that, the target voltage decreased to a stable value corresponding to the compound sputtering mode in which transparent TiO₂ films were deposited on the substrates. Low temperature growth of anatase has been reported by a few groups using metallic Ti as a sputtering target³⁴.

Photocatalytic activity

Photocatalytic efficiency of TiO₂ is expected to be low under visible light irradiation because UV light is about < 10% of the overall solar intensity. Thus, increasing the visible light absorption of TiO₂ materials may improve the photocatalytic activity by decreasing the energy bandgap or preventing (e⁻ / h⁺) pair recombination by electron-hole tapping. In this study, the effects of argon and oxygen in the gas feed for TiO₂ growth on the microstructure, light absorption and photocatalytic properties of TiO₂ thin films were examined.

According to the literature, a satisfactory catalytic activity is seen when the films have the two phases, with the concomitant increase in the ionic radius of the grains that form the anatase phase. However, in 1995, Linsebigler et al. reported anatase TiO₂ crystals with a gap ~ 3.2 eV at λ = 387 nm³⁵. The same value of bandgap for anatase TiO₂ (3.2 eV) was reported in previous studies³⁶,³⁷. Most proteins can absorb radiation of λ near 280 nm because of the presence of tyrosine phenylalanine, aromatic compounds and conjugated double bonds in benzene ring. These absorptions are observed in the presence of double bonds (π) with transitions π → π⁺, since n → π⁺ transitions are prohibited by the selection rules. It is believed that the degree of unsaturation given by bonds of the π type correspond to reduced transmittance compared to π type connections. The influence of unsaturation on the formation of biofilms is difficult to predict³⁸.

The electrical current and voltage parameters were also varied to seek the best deposition condition and, it can be controlled by the treatment time (deposition). Chemical reactions observed in this process were caused by the photoexcitation mechanism involving the formation of electron-hole pairs and valences. Those reactions can be seen in Fig. 2.

![Figure 2: Chemical reactions stimulated by the interaction of a visible light photon with TiO₂ deposited on substrates.](image-url)

There are two types of photochemical reaction proceeding on the TiO₂ surface when irradiated with ultraviolet light. One is photoinduced redox reactions of the adsorbed substances through “electron-hole” pairs³⁹, and the other is hydrophilic photoinduced conversion of the film itself. Titanium dioxide is one of the most powerful oxidants because of the high oxidizing potential of holes in the valence band formed by photoexcitation⁴⁰,⁴².

In the absence of a catalytically active substance, the oxidation process of most hydrocarbons proceeds rather slowly. A photocatalyst should decrease the activation energy of a given reaction. A heterogeneous photocatalytic system consists of semiconductor particles (photocatalyst) which are in close contact with a liquid reaction medium. By exposing the catalyst to light, excited states are generated, which are able to initiate subsequent processes, such as redox reactions and molecular changes. Owing to their electronic structure, which is characterized by a filled valence band (VB) and an empty conduction band (CB), metal oxides, such as TiO₂, can act as sensitizers for light-induced redox processes. For example, UV light can excite pairs of electrons and holes; an electron (e⁻ | CB) is promoted to the conduction band while a positive hole (h⁺ | VB) is generated in the valence band. The photo-generated electrons then react with molecular...
oxygen (O₂) to produce super-oxide radical anions (O₂⁻), and the photo-generated holes react with water to produce hydroxyl (OH⁻) radicals. These two types of reactive radicals can work together to decompose organic compounds.

**Characterization and conditions**

A Shimadzu UV-310PC scanning spectrophotometer was used to measure the transmittance spectrum of TiO₂ films as a function in the wavelength range from 200 to 900 nm. This procedure is highly reproducible, and no error-bar was generated. Table 1 shows the parameters adopted for these series of depositions. The temperature determined by the plasma kinetics ranged from 40 and 45 °C.

| Experimental parameters | #A1 Ar = 20% (50 SCCM) O₂ = 25% (10 SCCM) | #A2 Ar = 20% (50 SCCM) O₂ = 25% (10 SCCM) | #A3 Ar = 20% (50 SCCM) O₂ = 30% (10 SCCM) | #A4 Ar = 35% (50 SCCM) O₂ = 20% (10 SCCM) | #A5 Ar = 35% (50 SCCM) O₂ = 20% (10 SCCM) | #A6 Ar = 45% (50 SCCM) O₂ = 20% (10 SCCM) |
|-------------------------|--------------------------------------------|--------------------------------------------|--------------------------------------------|--------------------------------------------|--------------------------------------------|--------------------------------------------|
| Electric current (A)    | 0.45                                       | 0.45                                       | 0.45                                       | 0.2                                       | 0.2                                       | 0.2                                       |
| Voltage (V)             | 519                                        | 517                                        | 507                                        | 437                                       | 437                                       | 416                                       |
| RF power (W)            | 233                                        | 232                                        | 228                                        | 87                                        | 87                                        | 83                                        |
| Deposition time (s)     | 3600                                       | 3600                                       | 3600                                       | 3600                                      | 3600                                      | 3600                                      |
| Background pressure (mbar) | 6.3 × 10⁻³                                | 6.4 × 10⁻³                                | 5.7 × 10⁻³                                | 9.2 × 10⁻³                               | 9.2 × 10⁻³                               | 1.26 × 10⁻³                               |

In addition, Table 2 shows the different sample positions on the electrode for the deposition of TiO₂ films.

| Code | Placement/assignment |
|------|----------------------|
| #B1  | Glass in the center of the electrode holder associated with the condition #A5 |
| #B2  | Glass in the electrode holder edge associated with the condition #A5 |
| #B3  | Glass in the center of the electrode holder associated with the condition #A6 |
| #B4  | Glass in the electrode holder edge associated with the condition #A6 |
| #B5  | PET in the electrode holder edge associated with the condition #A5 |
| #B6  | PET in the center of the electrode holder associated with the condition #A5 |

**RESULTS**

**Crystallographic directions, composition of TiO₂ films**

The TiO₂ films deposited under these conditions were studied using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). For some applications such as transparent conductors, the anatase phase with its larger crystallite size is preferable to obtain electrons mobilities. The average crystallite sizes for the TiO₂ films can be calculated from the broadening of the diffraction peak using Scherrer’s formula, D = 0.9k/B cosh, where k is the wavelength of Cu Kα radiation, B is the full width at half maximum (FWHM) of XRD peaks and h the Bragg diffraction angle of the line⁴³. At Tsubstrate ≥ 200 °C, the films tend to have random crystallite orientation and exhibit (0 0 4) and (2 0 0) reflections of the anatase phase, indicating that the growth temperature has a great impact on the structural properties of the prepared TiO₂ films⁴⁴.

The O1s XPS spectrum of TiO₂ films deposited in Ar-O plasmas was studied. The presence of an asymmetric component at the higher binding energy (BE) side with respect to the main peak (OI) indicates the existence of different chemical states of oxygen. The peak is deconvoluted into two components: the first at lower BE (530.64 eV) can be ascribed to the O1s core peak of O₂⁻ bound to Ti⁴⁺ in TiO₂⁴⁵, whereas the higher BE component located at 531.82 eV, may arise from the contribution of oxygen to Ti–OH bonds⁴⁶. The other component (OII) at the higher BE of 532.62 eV is associated with adsorbed molecular bonds such as C=O, O–C–O or O=C–O⁴⁷. Carbon probably was ejected from PET by sputtering and etching reactions, linking with oxygen introduced in vacuum chamber.

**Optical transmittance in the UV-visible region**

Titanium oxide films are transparent in the visible region and their transparency shows a sharp decrease in the UV region. For the initial studied samples, Fig. 3 shows the transmittance curves T (λ) as a function of wavelength for different proportions of argon and
oxygen gases, while Fig. 4 shows the results for different positions of the substrates on the upper electrode. The spectra were acquired immediately after removal of the samples from the reactor (also, immediately after deposition). Ultraviolet photons excite electrons from the valence band (vb) to conduction band (cb), leading to two types of charge carriers, electrons (ecb−) and holes (hvb+). These carriers are responsible for the activation of chemical reactions48,49.

Figure 3: Optical transmittance as a function of wavelength (λ) in the visible region, measured on the TiO2 deposited on glass by RF magnetron sputtering. The flow rates of argon and oxygen were 10 and 50 SCCM, respectively, for a deposition time of 3600 s.

A sharp decrease in the T(λ) curves in the visible region was seen for all gas proportions shown in Fig. 3 and, except under condition B3, also seen in Fig. 4. This implies that a polymer packing with this film in most of conditions, when exposed to ambient light may have on its surface an antimicrobial activity stimulated by photocatalysis caused by UV light through films, since absorption occurs in the visible region, including the blue ultraviolet radiation. Harmful bacteria may be destroyed when exposed to radiation of λ between 190 and 250 nm. The bactericide action of TiO2 arises from the existence of reactive groups, such as hydroxyl, on its surface. Reactive species, such as -OH and O2-, decompose organic compounds. This mechanism is responsible for the antibacterial action of irradiated TiO2 surfaces50. Ultraviolet irradiation of TiO2 promotes electrons (e−) from the valence band to the conduction band, which leaves positive charge carrier holes (h+) in the valence band. The e− and h+ charges migrate in random directions to the bulk or the surface. Those elementary charges that reach the surface of the catalyst can react with electron-donor and electron-acceptor species present at the semiconductor/electrolyte interface51. Moreover, the high absorption below 200 nm is associated with crystal-field splitting. It is known that Ti has octahedral coordination in anatase TiO2 causing a crystal-field splitting of the d-orbitals of titanium into two subbands: the
eg and the t2g orbitals, the eg orbitals (dz2 and dx2-y2) which point directly toward the oxygen ligands and form r-type orbitals; the t2g orbitals (dxy, dyz and dxz) point between the oxygen neighbors and form p-orbitals. The repulsive force between the dxy, dyz, dxz and oxygen ligands is weaker leading to a decreased energy for those orbitals. The Ti(3d4s4p) orbitals are then linearly combined with the O(2s2p) orbitals to form the molecular orbitals. Previous studies revealed that the upper t2g and eg are mainly of Ti3d character and form the conduction band, and the lower t2g and eg are mainly of O2p character and form the valence band.

DISCUSSION
In recent decades, TiO2 semiconductors have attracted great interest due to their low cost and low toxicity, together with their high transparency, high refractive index, and good chemical stability. Nowadays, TiO2 thin films are used for a variety of applications, ranging from selective absorbing coatings to photovoltaic solar cells, gas sensors and photocatalysis. The literature reports the use of TiO2 films in advanced oxidative processes (POA), mainly in heterogeneous photocatalysis. The use of thin films of TiO2 in heterogeneous photocatalysis is possible because of its semiconducting characteristics, since it is active under irradiances for 300 nm < \lambda < 390 nm and remains stable after many catalytic cycles, owing to its large bandgap (3.2 eV). Semiconductor photocatalysis is one of the most promising processes for purification of water. Some studies point out that anatase TiO2 has more efficient photocatalytic properties. Moreover, some studies report that the addition of H2O2 as a photocatalytic activity accelerator has also been evaluated under natural sunlight. A weight relation of 1:2 of TiO2 to H2O2 was tested, using the TiO2 concentration that gave the fastest inactivation, i.e., 35 mg L\(^{-1}\) of TiO2. On the other hand, samples with only TiO2 were more efficient for the inactivation of Cryptosporidium parvum in water under simulated and natural solar radiation. A complete account of the mechanism of bacterial inactivation has been reported in some recent reviews. The preparation of TiO2 thin films by sputtering has prominent advantages such as clean process (without intermediate chemical products), high reproducibility and easy scale-up to produce uniform films on large area substrates. Different sputtering processes have been used for TiO2 deposition, in RF or DC modes. In the case of TiO2 solar radiation, the inhibition of the process may be caused by the effect of clogging the catalyst surface by organic molecules or microorganisms already present in this type of water. Therefore, competition occurs for the holes generated on the surface of the TiO2. When H2O2 is added to TiO2, an enhancement occurs because of the already described process of inhibition of electron/hole recombination is reduced and therefore generates more HO•. When a semiconductor is excited with sunlight, absorption of photons with energy higher than the band gap leads to the creation of electron-hole pairs. These photoexcited charge carriers react with the adsorbed oxygen molecules and water molecules leading to the formation of superoxide radicals (•O2–) and hydroxyl (•OH) radicals, respectively. These reactive oxygen species interact with the adsorbed toxic pollutants resulting in their degradation.

Thus, the authors of this work strongly recommend growing films under the conditions given by this work for photocatalysis, and the optical spectra confirm the suggested applications, since they presented high transmittance in the visible region, up to 350 nm, and high absorption near to and below 300 nm, which stimulates photocatalytic activity. About degradative processes on substrates: It is characteristic for UV degradative processes to occur under oxygen starvation and diminished UV beam penetration across the material thickness. Oxygen diffusion-limited reaction is caused when the oxygen from the atmosphere is consumed by rapid reaction near the illuminated surface before it can diffuse into the interior to react there. It is quite common in photooxidation of polymers. Oxygen starvation depends on the diffusion coefficient for oxygen in a particular polymer. It is, for example, two orders of magnitude smaller for PET than for polyethylene. The PET samples used in this work did not present any signal of degradation, due to UV radiation generated by the plasma deposition. Anyway, it is suggested to study the mechanisms of photodegradation of PET under UV for future studies, whose conditions can be found in Fechine et al.
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FUNDING
Conselho Nacional de Desenvolvimento Científico e Tecnológico [https://doi.org/10.13039/501100003593]
Fundação de Amparo à Pesquisa do Estado de São Paulo [https://doi.org/10.13039/501100001807]
#Project 2017/15853-0

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