Research Article

Doped Titanium Dioxide Films Prepared by Pulsed Laser Deposition Method

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TiO2 was intensively researched especially for photocatalytic applications. The nitrogen-doped TiO2 films prepared by pulsed laser deposition (PLD) method were reviewed, and some recent new experimental results were also presented in this paper. A new optical transmission method for evaluating the photocatalytic activity was presented. The main results are (1) PLD method is versatile for preparing oxide material or complex component films with excellent controllability and high reproducibility. (2) Anatase nitrogen-doped TiO2 films were prepared at room temperature, 200°C, and 400°C by PLD method using novel ceramic target of mixture of TiN and TiO2. UV/Vis spectra, AFM, Raman spectra, and photocatalytic activity for decomposition of methyl orange (MO) tests showed that visible light response was improved at higher temperature. (3) The automatic, continuous optical transmission autorecorder method is suitable for detecting the photodecomposition dynamic process of organic compound.

1. Introduction

1.1. General Description of Preparation of TiO2 Films. In recent years, the field of photocatalysis has become an extremely well-researched field due to wide application interest in self-cleaning surfaces, water or air purification, self-sterilizing surfaces, antifogging surfaces, optical or gas sensor [1–4], and so forth. TiO2 is a fascinating material that has been intensively researched by worldwide researchers. For photocatalytic applications, much attention has been paid to understand and alter the optical properties of titanium dioxide, especially for enhancing visible light absorption mainly by narrowing the band gap (3.2 eV) for using the economical and ecological sunlight. Theoretical calculations have been performed to clarify the effect of anion doping of TiO2 on band gap modifications [20–22].

Nitrogen-doped TiO2 materials were intensively researched since Asahi et al. proposed that it has narrow band gap and little recombination of electrons and holes [23]. However, Batzill et al. reported that no band gap narrowing is observed for N-doped TiO2 single crystals, but N-doping induces localized N 2p states within the band gap just above the valence band (VB). N is present in an N(III) valence state, which facilitates the formation of oxygen vacancies and Ti 3d band gap states at elevated temperatures. This thermal instability may degrade the catalyst during applications [24]. Socol et al. proposed that both substitutional N and O vacancies contribute to the visible light absorption [25]. The width of the TiO2 band gap was not affected by the presence of fluorine either, as reported by Todorova et al. [5]. The red shift of the absorption edge was attributed to the increased rutile content in the fluorine-doped TiO2 powers. The codoping effect between nitrogen and hydrogen is responsible for the
enhanced photoactivity of N-doped TiO₂ in the range of visible light [26].

Balek et al. prepared nitrogen and fluorine codoped titania photocatalyst samples for air purification by spray pyrolysis method [27]. A high photocatalytic activity in a visible light region of spectrum depended on the spray pyrolysis temperature and can be ascribed to a synergistic effect of nitrogen and fluorine doping. Synergetic effect also happened in Nd₃O₅ modified TiO₂ nanoparticles, formation of the surface anatase/rutile phase junction favors photoinduced charge separation and further improves its photocatalytic activity [28].

Qu et al. prepared Fe(3+) and Ce(3+) codoped nanostructure titanium dioxide films via the improved sol-gel process. The samples had smaller crystal size, larger surface area, and larger pore volume. They also found that codoped ions could obviously not only suppress the formation of brookite phase but also inhibit the transformation of anatase to rutile at high temperature. Fe(3+)/Ce(3+) codoped TiO₂ film showed excellent photocatalytic activity compared with pure TiO₂ film, Fe(3+) or Ce(3+) single doped TiO₂ film. They concluded that the surface microstructure of the films and improved sol-gel process ions doping methods are responsible for improving the photocatalytic activity [29].

Our group has reported works about hydrophilicity between titanium oxide coatings with and without addition of silica. Through the investigation of change of water contact angle on the surface after UV exposure and sunlight radiation, it can be concluded that hydrophilicity of mixed coatings with low-temperature heat treatment of titanium oxide and silica is much better than a pure titanium oxide coating. This effect makes for an improved self-cleaning coating under natural sunlight. The mechanism is that particles of titanium oxide separated by silica reduce the contact chance of recombination of electrons and holes, thereby increasing the photocatalytic action on organic compounds. The addition of silica increases water absorption in the coating. Water molecules absorbed by silica will be photocatalyzed to free hydroxyl groups under the illumination of UV light. These groups benefit the hydrophilicity of coating [30].

As for photo-induced hydrophilicity effect, Fujishima et al. have reached the conclusion that there is an aspect of this effect that does not involve simply the cleaning of the surface. The precise nature of the effect has not been elucidated even now, but researchers proposed that the surface species are basically the same ones involved with conventional photocatalysis [2]. Henderson presented recent research highlights of the significant insights obtained from molecular-level studies of TiO₂ photocatalysis. This comprehensive review has illustrated how a surface science perspective on TiO₂ photocatalysis can provide unique insights and motivate more fundamental research in photocatalysis [3].

1.2. TiO₂ Films Prepared by PLD Method. PLD technique is a versatile tool for preparing thin-films, because it is capable of preparing films with various properties by simply adjusting the deposition conditions, like the type of target, type of substrate and its temperature, distance between the target and substrate, type and pressure of ambient air, and laser wavelength, and so forth. Its advantages for the film growth of oxides and other multicomponent materials include stoichiometric transfer, growth from an energetic plasma plume, reactive deposition, good adherence to the substrate surface, excellent controllability, and high reproducibility. PLD has played a significant role in advancing our understanding of the physics of the thin-film structures, the material science of a new system, and so forth [31].

With the use of PLD, TiO₂ films doped with metal, transition metal, or nonmetallic elements have been prepared, and their properties were controlled by varying the preparing parameters [25]. Socol et al. have grown crystalline anatase phase TiO₂ thin films by PLD technique in oxygen, nitrogen, and methane and nitrogen with oxygen mixture. Their studies proved the positive influence of anion doping on the photoreduction activity under visible light exposure. The best photoactivity under visible light exposure was obtained for films deposited in pure nitrogen, which was correlated with the highest red-shift (480 nm) of the absorption edge and the largest nitrogen incorporation characteristic to these films. Quite different evolutions were observed in case of UV light irradiation. Significant results were obtained in this case for the films deposited in pure oxygen or methane, while the photoactivity (quantum yield) of the films deposited in nitrogen was lower as compared with the blank.

Sato et al. prepared N-doped TiO₂ films by the atmospheric controlled PLD (AC-PLD) method to generate visible light active photocatalytic films [32]. For nitrogen doping, the use of CH(3)CN gas was found to be more effective than the use of NH(3). The visible light absorption properties of the films were very sensitive to the CH(3)CN partial pressure during ablation. When using CH(3)CN, nitrogen and an equal quantity of carbon was uniformly doped into the TiO₂ films. The resultant films showed better catalytic performance than those which were either undoped or doped using NH(3). It is also suggested that stronger reducing agents such as carbon are required for doping nitrogen into TiO₂ films.

Metal nanoparticles can act as electron traps due to the formation of a Schottky barrier at the metal-semiconductor contact. Holes can decompose organic substances more efficiently, because it has strong oxidative power. Sauthier et al. used PLD technique to prepare Ag-TiO₂ nanocomposites to improve photocatalytic activity and compared with that of bare TiO₂ [33]. It was proposed that two distinct mechanisms can contribute to the enhanced photoreactivity under near-UV irradiation. The first is Ag NPs retard electron-hole recombination by photogenerated electron transfer from TiO₂. And the second one is localized surface plasma resonance absorption of Ag NPs, which can have positive effect on the photocatalytic activity.

The films with more clusters exhibited higher photocatalytic performances than the films with less clusters [34]. The author pointed out that the specific surface area of the films was increased by the deposition of clusters. The larger contact area induces high decomposition rate [35]. It is interesting that the clusters formed in PLD method are not desirable in other semiconductor industrial fields, like
The photocatalytic activity of the N-doped TiO$_2$ films with surface area of about 18 cm$^2$ was studied by decomposing organic methyl orange (MO) dye in aqueous solution. The initial concentration of MO solution is 2 mg/L, and the total solution is about 80 mL. A tungsten halogen lamp was used as visible light source with 180 mW/cm$^2$ power density on the surface of the MO solution. During the photodegradation experiments, the absorbance of the solution was measured at 460 nm wavelength, which corresponds to the peak absorbance of MO. The intensity of the transmitted detecting light was recorded by a data recorder, whose data sampling interval was set as 2 minutes. This photocatalytic activity evaluating experimental method has not been used before to our knowledge.

3. Results and Discussion

3.1. Optical Spectra. The sample color is transparent prepared at RT or 200 °C, and light yellow at 400 °C. Figure 1 shows the transmission spectra of N-doped TiO$_2$ films prepared under different temperature. The absorption edges shift toward longer wavelengths from 300 nm to 350 nm with the increase of the substrate temperature, indicating a decrease in the band gap of the films, which may due to the N composition increase with the increasing temperature. This is different from the results suggested by Farkas et al. [47]. Another reason is the grain size increases with increasing temperature, resulting to weak quantum size effects causing the red-shift of the absorption edge [48]. X-ray photoelectron spectra measurement should be performed to detect the state and component of N element in the films. The N element is usually formed as TiO$_{2-x}$N$_x$ in films prepared by PLD method [42, 43, 47].

3.2. AFM Measurements. Figure 2 shows the AFM images of N-doped TiO$_2$ films prepared at room temperature, 200 °C, and 400 °C. The grain sizes are 18.5, 19.2, and 28.1 nm, and their root mean square (rms) of roughness is 3.32, 3.96, and 6.73 nm, respectively. This is in agreement with results obtained by Suda et al. [37]. With the temperature increasing, the grain size and roughness increase, which suggests an increase of crystallinity of the films, and inducing red-shift in absorption spectrum because of quantum size effect.

3.3. Raman Spectra. The micro-Raman spectra of TiO$_2$ films are shown in Figure 3. It can be seen that intense Raman peak does not occur until temperature reaches 400 °C, indicating the crystallization realized at that point. This is in accord with that in [48]. In our experiments, only anatase structures appearing as the typical Raman modes at 145, 198, 396, 517, and 640 cm$^{-1}$ are assigned to the $E_g$, $E_g$, $B_{1g}$, $A_{1g}$, and $E_g$ modes, respectively. The strongest mode at 145 cm$^{-1}$ indicates that the anatase phase with a long-range order has been obtained [49].

3.4. Photocatalytic Activity. Shinguu et al. proposed a reflectance method to evaluate the photodecomposition rate of TiO$_2$ films [41]. We have used the conductivity...
Table 1: Preparation of TiO₂ thin films by PLD method.

<table>
<thead>
<tr>
<th>Laser</th>
<th>Substrate</th>
<th>Target</th>
<th>Dopant</th>
<th>Crystalline phase</th>
<th>Ambient air</th>
<th>Photocatalytic activity *</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd:YAG, 532 nm</td>
<td>glass</td>
<td>TiO₂</td>
<td>—</td>
<td>rutile</td>
<td>O₂</td>
<td>—</td>
<td>1999</td>
<td>[38]</td>
</tr>
<tr>
<td>ArF 193 nm</td>
<td>Mica, quartz, Si</td>
<td>TiO₂</td>
<td>—</td>
<td>Rutile, anatase</td>
<td>Ar</td>
<td>—</td>
<td>2002</td>
<td>[39]</td>
</tr>
<tr>
<td>ArF 193 nm</td>
<td>α-Al₂O₃</td>
<td>Ti</td>
<td>—</td>
<td>Rutile, anatase</td>
<td>O₂</td>
<td>—</td>
<td>2004</td>
<td>[40]</td>
</tr>
<tr>
<td>Nd:YAG, 266 nm</td>
<td>Si</td>
<td>TiO₂</td>
<td>—</td>
<td>rutile, anatase</td>
<td>O₂</td>
<td>MB, anatase with clusters</td>
<td>2005</td>
<td>[34]</td>
</tr>
<tr>
<td>Nd:YAG, 532 nm</td>
<td>SiO₂(corning 7059)</td>
<td>TiO₂, TiO, TiN</td>
<td>N</td>
<td>anatase</td>
<td>O₂, N₂</td>
<td>MB, TiN target</td>
<td>2005</td>
<td>[37]</td>
</tr>
<tr>
<td>Nd:YAG, 532 nm</td>
<td>Glass</td>
<td>Ti</td>
<td>N</td>
<td>anatase</td>
<td>NH₃/N₂/O₂</td>
<td>—</td>
<td>2006</td>
<td>[26]</td>
</tr>
<tr>
<td>KrF 248 nm</td>
<td>Si or quartz glass</td>
<td>TiO₂, WO₃</td>
<td>multilayer</td>
<td>—</td>
<td>O₂</td>
<td>MB, WO₃, 5%</td>
<td>2006</td>
<td>[41]</td>
</tr>
<tr>
<td>Nd:YAG, 1064 nm</td>
<td>quartz glass</td>
<td>TiO₂</td>
<td>N</td>
<td>anatase</td>
<td>O₂, N₂</td>
<td>MB, MO, Eg = 1.0 eV, 2.5 eV</td>
<td>2008</td>
<td>[42]</td>
</tr>
<tr>
<td>KrF 248 nm</td>
<td>LSAT</td>
<td>TiO₂, TiN</td>
<td>N</td>
<td>anatase</td>
<td>O₂</td>
<td>—</td>
<td>2008</td>
<td>[43]</td>
</tr>
<tr>
<td>Nd:YAG, 266 nm</td>
<td>quartz</td>
<td>TiO₂, La₂O₃</td>
<td>La</td>
<td>Rutile</td>
<td>N₂</td>
<td>MB, 900°C postannealing</td>
<td>2009</td>
<td>[44]</td>
</tr>
<tr>
<td>KrF 248 nm</td>
<td>glass</td>
<td>TiO₂</td>
<td>C, N</td>
<td>anatase</td>
<td>O₂, N₂, CH₄</td>
<td>Cr(II), N doped</td>
<td>2010</td>
<td>[25]</td>
</tr>
<tr>
<td>KrF 248 nm</td>
<td>SiO₂ quartz</td>
<td>TiO₂</td>
<td>N</td>
<td>anatase</td>
<td>O₂, N₂</td>
<td>—</td>
<td>2010</td>
<td>[45]</td>
</tr>
<tr>
<td>KrF 248 nm</td>
<td>SiO₂ quartz</td>
<td>Ag, TiO₂</td>
<td>—</td>
<td>anatase</td>
<td>O₂</td>
<td>MB</td>
<td>2011</td>
<td>[33]</td>
</tr>
</tbody>
</table>

*Organic compound for decomposition and optimal conditions obtained. MO: methyl orange, MB: methylene blue, Cr(II): toxic Chromium ion, it can be photoreduced to Cr(III) state.

Figure 1: Transmission spectra of N-doped TiO₂ films prepared at different temperature, (a) RT, (b) 200°C, (c) 400°C.

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method to check the rate [35, 50]. Recently, we developed a transmittance method to detect the concentration of the MO to evaluate the photocatalytic activity of the N-doped TiO₂ films. The setup is shown in Figure 4. The light source can be visible or UV light as demand. The LED light is 460 nm or 650 nm wavelength, which corresponds to the peak absorbance of MO or MB. The relationship between the transmittance and concentration was calibrated. This method has the advantages of continuous, automatic check without disturbing the reaction process, and avoiding danger to operator when use UV light source, and so forth.

Figure 5 shows the decomposition rate with time of MO using N-doped TiO₂ films prepared at different temperatures under visible light irradiation. It is clearly shown that photocatalytic activity of N-doped TiO₂ films strongly depends on the preparation temperature. MO was almost decomposed completely after 4 hours for sample prepared at 400°C. This is due to band gap narrowing by nitrogen atom, larger surface area, and better crystallization at higher temperature.

3.5. Discussions. TiO₂ film is a versatile material for use in many fields. For photocatalysis applications, the main problems are to narrow the band gap for visible light and to retard the recombination of electrons and holes. Anion or cation doping, or codoping, noble metal, and multilayer structure modification methods, and so forth have been proposed to improve TiO₂ photocatalytic activity till now. PLD technique is a widely used method to prepare oxide materials; it is easy to change the growth parameters to get various properties of doped films. Its controllability and reproducibility provide much convenience for base research of films materials with high melting point or multicomponent.

In our N-doped TiO₂ preparation experiments, laser pulses with intensity density about $1.0 \times 10^{12} \text{W/m}^2$ was irradiated onto the surface of N: TiO₂ ceramic target. Plasma plumes were produced. Energetic N ion, Ti ion, and O ion, as well as N containing TiO₂ micrograins are ejected from the target surface to the glass substrate. The TiO₂ crystal nucleus formed and became larger with the subsequent plasma plume until they combined with each other to form thin film. During this process, N element was easier to incorporate into the lattice of TiO₂ as oxygen substitutor or interstitial atoms than that using N₂ air as N source, due to it got energy from the laser irradiation directly [37, 43]. Higher substrate temperature, 400°C in our procedure, is beneficial to form crystallization, and larger grains as shown in the AFM image. Large grains and high rms of roughness provide large surface area resulting to big contact chance of organic compound. Mole ratio of TiN and TiO₂ in target is 1 : 3, but we can speculate that the corresponding ratio inside the film is smaller due to relative easier desorption of small mass atom
Figure 2: AFM images of the surface morphology of N-doped TiO$_2$ films under different temperature, (a) RT, (b) 200°C, and (c) 400°C.

Figure 3: Raman spectra of N-doped TiO$_2$ films prepared at different temperature, (a) RT, (b) 200°C, (c) 400°C.

Figure 4: The schematic diagram of experimental setup for automatic detecting the photodecomposition rate. The whole setup is put in an aluminum box. The data record interval can be set from 1 minute to 1 hour. MO solution: methyl orange solution.

from the film surface [31]. MO was almost photodegraded completely using visible light after 4 hours.

Tachikawa et al. concluded that the adsorption dynamics of substrates and organic compound, the electronic interaction between TiO$_2$ and adsorbents, and the band structure and morphology of TiO$_2$ nanomaterials are crucial factors for establishing efficient photocatalytic reaction systems. The morphology of TiO$_2$ affects the charge recombination dynamics, and anisotropic adsorption was found in recent research [51].

Photocatalysis is a complex process involving chemical and physical reactions. The researchers should combine
the concentration changing with time. The initial concentration of Methyl orange about 2 mg/L, L, and C is the concentration changing with time.

\[ C(t) = C_0 - C \]

(a) Blank  
(b) RT  
(c) 200°C  
(d) 400°C

Figure 5: Decomposition rate with time of MO using N-doped TiO\(_2\) films prepared at different temperatures under visible light irradiation. (a) without TiO\(_2\), (b) RT, (c) 200°C, (d) 400°C. \( C_0 \) is the initial concentration of Methyl orange about 2 mg/L, and C is the concentration changing with time.

chemical methods and physical methods to overcome problems from photocatalytic material modification to degrade organic compound. For example, Rimeh et al. prepared Ti/TiO\(_2\) electrode by PLD technique and obtained a degradation rate of almost 75% of chlortetracycline within 2 hours.

4. Conclusions

Fascinating TiO\(_2\) films were worldwide researched using various preparing method. PLD technique is a versatile method for preparing films of oxide materials. Its advantages of controllability and reproducibility are suitable for basis research for preparing various properties of TiO\(_2\) films. Some recent experimental results obtained in our group were presented. N-doped TiO\(_2\) anatase films were prepared at substrate temperature from RT to 400°C by PLD method using a novel ceramic target of mixture of TiN and TiO\(_2\) and were characterized by UV/Vis optical spectra, AFM, Raman spectra, and photocatalytic activity for decomposition of methyl orange. It was found that the film crystallinity, the visible light response, and decomposition rate were significantly improved at higher temperature. New method of continuous autodetecting the solution optical transmission for evaluating the photodecomposition dynamic process was developed.

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References


