Preparation of nanostructured Bi-modified TiO\textsubscript{2} thin films by crossed-beam laser ablation plasmas

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Abstract. The preparation and characterization of titanium dioxide thin films modified with different amounts of bismuth using a two laser ablation plasmas configuration is reported. The plasmas were produced ablating simultaneously two different targets, one of bismuth and other of titanium dioxide, using a Nd:YAG laser with emission in the fundamental line. The elemental composition, together with the vibrational and optical properties of the deposited films were investigated as a function of the parameters of the bismuth plasma. The composition of the thin films was determined from measurements of X-ray photoelectron spectroscopy (XPS) as well as by Rutherford backscattering spectroscopy (RBS). The structural modification of the deposited material, due to the incorporation of Bi, was characterized by Raman spectroscopy. The optical properties were determined from UV-Vis spectroscopy measurements. It is found that bismuth incorporation has an important effect on the optical properties of TiO\textsubscript{2} narrowing the band gap from 3.2 to 2.5 eV.

1. Introduction
The treatment of water polluted with recalcitrant organic molecules, has become an issue of current interest in which different areas of knowledge have converged in the search for possible solutions. In particular, the development of new nanostructured materials, powders and thin films, to be used as photocatalysts in the degradation of organic contaminants has shown outstanding results [1].

It is worth mentioning that most of these photocatalysts are only active with ultraviolet light, which limits them to use only a fraction, about 5\%, of the solar radiation. This has increased research in the development of active photocatalysts with wavelengths in the visible region of the electromagnetic spectrum, taking advantage up to 45\% of the total solar radiation reaching the Earth's surface.

In recent years, titanium dioxide (TiO\textsubscript{2}) thin films have been used as photocatalysts, for the degradation of different organic pollutants present in wastewaters, owing to its high stability in aqueous solution and its high oxidizing power [2]. However, one of the major disadvantages of TiO\textsubscript{2} is its relatively high band gap value (E\textsubscript{g} = 3.2 eV for the anatase phase) which impedes its activation with wavelengths greater than 387 nm, this is a drawback if sunlight is used to activate its photocatalytic response. The modification of TiO\textsubscript{2} with transition metals, is a technique frequently used to reduce its
band gap [3], allowing to use visible light for its activation and consequently take advantage of sunlight for this purpose.

In order to prepare TiO$_2$ thin films modified with metals, various deposition techniques, resulting in materials with promising photocatalytic properties, have been used. However, there is still much work to improve the characteristics of the deposits; specifically, the control of the composition is essential since the properties of the obtained materials depend strongly on the concentration of the modifying element.

This work reports on the use of a variant of the laser ablation technique, the so-called Crossed Beam Pulsed Laser Deposition (CBPLD) which has been successfully used to prepare thin films of TiAlN [5], allowing the incorporation of Al in the TiN lattice in a controlled way. It should be noted that the features of the employed configuration could result in nanomaterials with novel or improved properties.

2. Experimental Procedure

The thin films were deposited on glass substrates using the CBPLD technique [4], in which two different laser ablation plasmas are produced ablating simultaneously a TiO$_2$ and a Bi high purity (99.99%) targets. A Nd: YAG laser with emission in the fundamental line (1064 nm, 5 ns pulse duration) was used to generate the plasmas.

In order to obtain films with different bismuth content, the ion mean kinetic energy of the Bi ions was calculated using the time of flight technique (TOF) from measurements performed with a Langmuir planar probe (6 mm diameter). The films were deposited at room temperature under the same experimental conditions as the diagnosed plasma.

The physical properties of the thin films were studied as follows: composition was determined by Rutherford backscattering spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS). RBS measurements were carried out in a Tandem Van de Graff accelerator using a beam of $^7$Li (4.0 MeV) and a detection angle of 165°, while XPS measurements were performed with a Jeol JS 9200 spectrometer, with an X-ray source (K$_\alpha$ of aluminum) acquiring spectra in the low and high resolution regimes. The microstructure of the films was studied by Raman spectroscopy, the spectra were obtained using a micro-Raman LabRam 800 system, equipped with a confocal microscope, Olympus BX40, using the second harmonic of a Nd: YAG laser (532 nm) focusing the laser beam with a 50X objective onto the sample surface. A cooled CCD camera was used to record the spectra, typically an average of 50 accumulations of 10 sec was done in order to improve the signal to noise ratio. All spectra were calibrated using the 521 cm$^{-1}$ line of monocrystalline silicon. Optical properties were determined from UV-Vis measurements carried out on a Perkin Elmer lambda 35 spectrophotometer.

3. Results and Discussion

3.1 Plasmas characterization

The ion mean kinetic energy of the Bi ions was calculated using the time of flight technique (TOF) from measurements made with a Langmuir planar probe placed at the substrate position. Figure 1, show the TOF curves corresponding to plasmas produced with different laser fluences. It is seen that as the laser fluence decreases, the maximum of the curves shifts to higher times and its intensity decreases, indicating that the Bi$^+$ kinetic energy and the plasma density decrease.

The ion mean kinetic energy and plasma density calculations were performed assuming that the ions arriving to the Langmuir probe were predominantly Bi$^+$. The results indicate that Bi ions with kinetic energies from 56.5 to 195.2 eV are present. The plasma density was determined from the maximum values of current collected by the probe; it was found that it varies from $3.4 \times 10^{11}$ to $4.3 \times 10^{13}$ cm$^{-3}$. Figure 2 shows that these two parameters are related and follow an exponential tendency under the experimental conditions for the present experiments. Due to the fact that the plasma density and the kinetic energy of Bi$^+$ are correlated, each sample was deposited under the conditions defined by each pair of values, as shown in table 1.
Figure 1. Bi⁺ time of flight curves at different laser fluences

Figure 2. Plasma density as a function of the Bi⁺ mean kinetic energy

Table 1. Plasma parameters employed for thin film deposition

| Laser fluence (J/cm²) | Bi⁺ Kinetic energy (eV) | Plasma density (cm⁻³) |
|-----------------------|------------------------|-----------------------|
| 2.8                   | 56.5                   | 3.4 x 10¹¹            |
| 5.4                   | 89.8                   | 1.7 x 10¹²            |
| 7.5                   | 98.6                   | 2.7 x 10¹²            |
| 12.0                  | 110.3                  | 3.2 x 10¹²            |
| 14.0                  | 123.5                  | 6.4 x 10¹²            |
| 19.7                  | 139.0                  | 7.6 x 10¹²            |
| 24.8                  | 153.9                  | 1.1 x 10¹³            |
| 29.9                  | 195.2                  | 4.3 x 10¹³            |

3.2 Composition

RBS results showed that the atomic concentration of bismuth increases from 12 to 28 at. % in a monotonous way followed by a decrease from 28 to 18 at. % as shown in figure 3. In order to confirm the observed tendency, some samples were measured by XPS and the results revealed a good agreement with the RBS data. This figure shows two regions in which Bi content is incorporated in a different way. For kinetic energies lower than 140 eV, Bi is incorporated in an approximately linear way, whereas kinetic energies greater than 140 eV produce a decrease in the Bi content. According to data of table 1, the higher is the kinetic energy, the higher the plasma density, implying more species of bismuth arriving to the substrate that can be incorporated into the film. This is observed for kinetic energies lower than 140 eV, for greater energies a small amount of bismuth is incorporated, possibly because of re-sputtering processes or due to a decrease of the Bi sticking coefficient with energy.
Figure 3. Bismuth content as a function of the Bi\(^+\) mean kinetic energy

Figure 4 shows the Bi/Ti atomic ratio as a function of the Bi\(^+\) kinetic energy. It is clearly observed that at low kinetic energies the Ti atoms predominate, indicating that titanium dioxide is present as the main phase. As the Bi\(^+\) kinetic energy increases the Bi atoms begin to increase equalling the number of Ti atoms at an energy close to 140 eV, the bismuth oxide becoming the dominating phase as is shown in figure 4.

3.3 Microstructure

The Raman Spectroscopy results are shown in figure 5a. The spectra of films with Bi contents up to 19 at.% are characterized by peaks at 144, 395, 515 and 638 cm\(^{-1}\) assigned to the anatase phase of TiO\(_2\) [6]. It is observed that as the Bi content increases, the peaks become less intense and broader indicative of a decrease of the crystallinity degree attributed to distortions caused by the Bi incorporation into the TiO\(_2\) lattice. In fact, for Bi contents of 21 and 24 at.% the Raman spectra do not show any features suggesting amorphization of the material induced by the disorder introduced by the presence of Bi atoms. At the highest Bi content, 28 at.%, the obtained films are formed by bismuth oxide (Bi\(_2\)O\(_3\)) coexisting the \(\square\) and \(\square\) crystalline phases, as is shown in figure 5b [7]. When the films are deposited using higher Bi\(^+\) kinetic energies and plasma densities, the Bi contents diminish to values of 21 and 18 at.% and the Raman spectra show that, additionally to the peaks of Bi\(_2\)O\(_3\), Raman signals at 440 and 610 cm\(^{-1}\) associated with the rutile phase of TiO\(_2\) appear, suggesting that higher ionic bombardment favors the anatase-rutile phase transition.
3.3 Optical properties

UV-Vis transmittance spectra of deposited films are presented in figure 6. An important effect due to the Bi incorporation is observed: with increased content of Bi, the absorption edge shifts to higher wavelengths, indicative of a decrease in the gap band. This was calculated using the Tauc method [7]; the obtained results are presented in table 2. It is observed that the incorporation of Bi effectively narrows the band gap value from 3.2 to 2.5 eV. This is an interesting result because it suggests that these materials could be activated using visible light, such as the sunlight, in photocatalytic processes to degrade recalcitrant organic compounds. Further studies regarding this effect are underway.

4. Conclusions

Bismuth was incorporated into the TiO₂ lattice, from 12 to 28 at. % with important effects on the microstructural and optical properties of the resulting material. Raman investigations reveal a phase transition from the anatase phase of TiO₂ to a mixture of the and phases of Bi₂O₃. The incorporation of bismuth has an important effect on the optical properties of TiO₂; narrowing the band gap from 3.2 to 2.5 eV. This is an important result because these materials can be activated with wavelengths in the visible region of the electromagnetic spectrum. This can be useful to carry out reactions of degradation of organic compounds in aqueous solutions using solar light.
Table 2. Band gap energy as a function of the Bi content

| Bi content (at.%) | Band gap energy (eV) |
|-------------------|----------------------|
| 0                 | 3.2                  |
| 14                | 2.8                  |
| 17                | 2.9                  |
| 19                | 2.7                  |
| 21                | 3.1                  |
| 24                | 2.7                  |
| 28                | 2.4                  |
| 21                | 2.6                  |
| 18                | 2.5                  |

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6. References
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