Plasma synthesis of photocatalytic materials

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Development of efficient photocatalytic materials is a promising technology for sustainable and green energy production. Moreover, photocatalytic materials can be used in fabrication of self-cleaning surfaces and decomposition of CO_2 and toxic pollutants in air and water. Semiconductors with good photocatalytic activity are known since four decades ago and they are regarded as promising candidates for these new technologies. However, excellent semiconductor photocatalysts as pure TiO_2 uses only the small UV fraction of solar light energy and great efforts have been made to develop visible light photocatalysts by engineering semiconductor energy bandgap via doping. Low-pressure discharge plasma is known as one of the most versatile technology used for deposition of photocatalytic thin films. This lecture reviews the main results obtained by the author in using low-pressure plasma for synthesis of metal oxide thin films with applications in photocatalysis. Most of the work is devoted to synthesis and characterization of titanium dioxide thin films obtained by either radio frequency magnetron sputtering deposition (RFMSD); plasma enhanced chemical vapour deposition (PECVD) and high power impulse magnetron sputtering (HiPIMS) deposition. In the case of RFMSD, efforts have been made to investigate the effects of plasma parameters, film thickness and substrate on the film properties. The TiO_x thin films obtained by PECVD contained a large amount of hydroxyl groups, which enhances their photocatalytic activity and electric conductivity. Recent results obtained by short-pulse and multi-pulse reactive HiPIMS depositions of TiO_x thin films are also described. It is shown that design of pulsing scheme of short-pulse HiPIMS in Ar/ O_2 gas mixture can be easily used to tailor the structure and properties of the deposited films.

1. Introduction

Discovery of photocatalytic hydrolysis of water on the UV light irradiated titanium dioxide (TiO_2) four decades ago [1] has led to development of semiconductor photocatalysis as a distinct research topic in the modern science and technology. Since then, titanium dioxide is regarded as an important environmental material with applications in photocatalytic air and water purification, hydrogen energy, and fabrication of self-cleaning and antibacterial surfaces [2]. The capacity of TiO_2 surface to degrade organic macromolecules and decompose water is own to the strong oxidation potential of the holes generated by the UV light in the valence band and strong reduction potential of electrons generated by UV radiation in the conduction band [3]. The long life time of these photogenerated charge carriers and their availability for surface reactions are key factors for the good photocatalytic property of this material [4]. In the case of plasma syntheses of theTiO_2 thin films, both factors are affected by the film structure, film thickness and substrate [5].

As an effect of the photocatalytic activity, the UV light irradiated TiO_2 surface becomes super hydrophilic because of the photocatalytic decomposition of either water or hydrophobic adsorbate molecules at Ti^{4+} photoreduced to Ti^{3+} sites, which typically are situated at the oxygen bridges on the surface. The UV induced hydrophilicity is reversible, the surface turning hydrophobic during storage in dark, in visible light [6], or by wet rubbing [7]. Recent studies revealed the role that charge carrier production and transport in the TiO_2 film have on the UV light induced surface reactions [4]. Formation of OH groups on the UV light irradiated TiO_2 surface was proved by ESR measurements [8] and it is believed that this hydroxyl groups contribute to the photocatalytic activity and UV light induced super hydrophilicity of the TiO_2 surface [9]. Hence, the light irradiation induced hydrophilicity can be used as an indicator of the film surface photocatalytic activity. Moreover, changes of surface hydrophilicty induced by light irradiation can be probed at nanoscopic level by atomic force microscopy (AFM) measurements of friction and adhesion forces in air between a hydrophilic AFM tip and film surfaces. Thus, it is possible to probe differences in photocatalytic activity of film surfaces at nanoscopic level.

Various deposition techniques have been developed to produce TiO_2 thin films with the goal of obtaining photocatalytic surfaces. Among these techniques, low-pressure plasma depositions are known to produce highly stable films with good substrate adhesion and hardness. This work reviews results obtained by the author in plasma assisted depositions of photocatalytic titanium dioxide thin films. Titanium dioxide thin films were obtained by

radio frequency magnetron sputtering deposition (RFMSD); plasma enhanced chemical vapour deposition (PECVD) and high power impulse magnetron sputtering (HiPIMS) deposition. In the case of RFMSD, effects of plasma parameters and bombardment by plasma particles of the surface of the growing film are investigated. In the case of PECVD, it is shown that incorporation of hydroxyl groups in the film enhances their photocatalytic activity and electric conductivity. Short-pulse and multi-pulse reactive HiPIMS is also used for deposition of TiO_x thin films in reactive gases (Ar/O_2), but the photocatalytic activity of these films is so far inferior to that of TiO_x thin films obtained by RFMSD and PECVD.

2. Titanium dioxide thin films obtained in low pressure plasma depositions

The RFMSDs have been performed by sputtering of a TiO_2 target (a sintered TiO_2 disk with the diameter of 10 cm, 99.99% purity) in a radio frequency discharge in Ar (6 sccm) and O_2 (0.6 sccm) at pressure values ranged between 0.13 and 1.3 Pa. A sketch of the experimental device used in RFMSD of TiO_x thin fims is given in Fig. 1 a). The substrate holder was positioned at 10 cm from the cathode and heated at 240°C during depositions. More details on the RFMSD system have been given in [10].

In RMSD, the structure and photocatalytic activity of the deposited TiO_x films are greatly affected by the working gas pressure [10]. It has been shown that the mesoscopic structure and photocatalytic activity of the TiO_x films obtained by RFMSDs are determined by the plasma particle bombardment of the film surface during deposition. Single Langmuir probe and optical emission spectroscopy diagnosis [11] of RFMSD plasma proved that the gas pressure value has a big impact on plasma parameters and plasma particle bombardment of the deposited films. At relatively high value of the gas pressure (1.3 Pa), the plasma particles (ions and electrons) have low energy, which favours deposition of amorphous TiO_x thin films with a short range order of anatase type, good UV-light-induced hydrophilicity, and microscopically smooth and homogeneous surfaces. At lower gas pressure values, the energy of plasma particles increases, which determines depositions of TiO_x films with mixed crystalline and amorphous structure and relatively rough and inhomogeneous surfaces.

Amorphous TiO_x thin films have been also obtained by PECVD using remote microwave plasma in H_2/O_2 mixture gas. Figure 1 b) shows schematically the setup used in PECVD. In this deposition technique, tetraisopropoxide (TTIP), $Ti(OC_3H_7)_4$, was decomposed by the O and OH radicals formed in a in H_2/O_2 (48 sccm/12 sccm) mixture gas plasma generated in a quartz tube by a microwave discharge (500 W) placed at a distance of 60 cm from the substrate. More details of this experimental setup and properties of TiO_x thin films deposited by this technique are given elsewhere [12]. The PECVD films contained a large amount of hydroxyl groups, which improved their electric conductivity and photocatalytic activity. Photocatalytic activity of the deposited films can be tested by measurements of water contact angle for films of which surfaces were intently contaminated with hydrophobic molecules (oleic acid) and then exposed to UV light [13]. Figure 2 shows comparatively the variation of water contact angle with the UV light irradiation time for films deposited by RFMSD (at 1.3 Pa), PECVD and short pulse HiPIMS. After surface contamination, the films showed a contact angle around 80°.

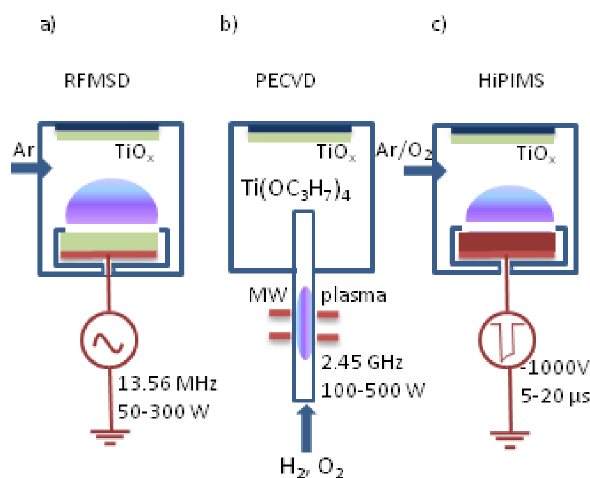

Fig. 1 Experimental setups used for deposition of photocatalytic TiO_x thin films. a) In RFMSD a ceramic target (TiO_2) is sputtered in Ar/O_2 (6 sccm/0.6 sccm) plasma. b) In PECVD the TiO_x thin film is deposited by decomposition of titanium tetraisopropoxide (TTIP) in the afterglow microwave plasma in H_2/O_2 (48 sccm/12 sccm) mixture gas. c) In reactive HiPIMS, TiO_x thin films are deposited in Ar/O_2 gas mixture by applying short negative voltage pulses to the magnetron cathode with titanium target.

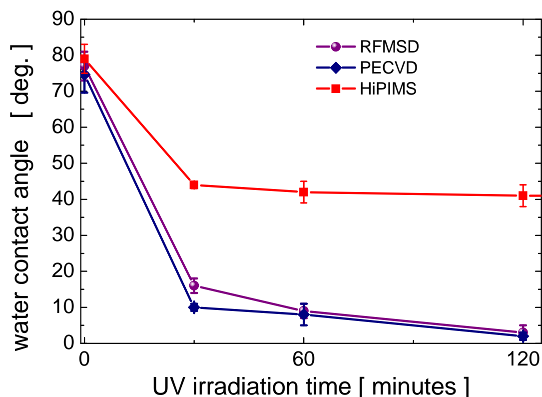

Fig. 2 Assessment of photocatalytic activity of amorphous TiO_x thin films obtained by RFMSD (1.3 Pa), PECVD and HiPIMS deposition, respectively. In these measurements the film surfaces were intently contaminated by adsorption of oleic acid. Then, water contact angle has been measured after various UV light irradiation time duration values.

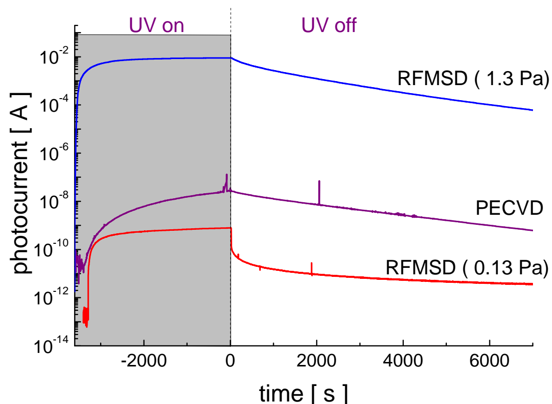

Fig. 3 Time variation of photocurrents measured on RFMSD and PECVD TiO_x thin films during an on-off UV light irradiation cycle

For RFMSD and PECVD films, the UV light irradiation for about an hour resulted in complete decomposition of hydrophobic molecules adsorbed on the film surfaces, as proved by the very low values of water contact angle (less than 10°) measured after irradiation. The TiO_x thin film obtained by HiPIMS deposition showed less photocatalytic activity, the water contact angle decreasing to only about 40° in these measurements. The experimental setup used in HiPIMS deposition is depicted schematically in Fig. 1c). In this deposition technique, a pure Ti target (diameter of 50 mm) was sputtered in pulsed high-density plasma generated in Ar and O_2 mixture gas (mass flow rates of 20 and 0.2 sccm, respectively) at a total pressure of 1.3 Pa. The plasma was generated by voltage (-1000V) pulses with 15 μs in width applied to the cathode target with a frequency of 1 kHz. The TiO_x films were deposited on substrates placed at a distance of 50 mm from the target surface.

Measurements of photocurrent during UV light irradiation on/off cycles revealed that the lifetime of photogenerated charge carriers in films with reduced photocatalytic activity is shorter (Fig. 3). The shorter lifetime of photogenerated charge carriers in the TiO_x thin film deposited by RFMSD at low pressure (0.13 Pa) is attributed to a higher density of charge recombination sites, this film having a mixed amorphous and crystalline structure.

The mixed structure of this film has been observed as nanoscopic regions of high hydrophilicity mixed with regions of low hydrophilicity on the UV-light-irradiated film surface. These regions are discriminated by friction force microscopy measurements, the friction force being larger on highly hydrophilic regions than on less hydrophilic regions of the UV irradiated TiO_x thin films surface [14]. Figure 4 shows a comparison between friction force images (right side) obtained for RFMSD (0.13 Pa) and PECVD films, after they were irradiated by UV light. The PECVD film showed higher photocatalytic activity and more homogeneous and smooth surface as compared to the RFMSD film.

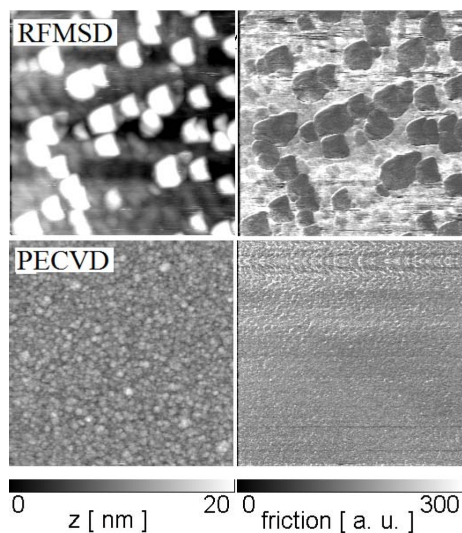

Fig. 4 Topography (left) and friction (right) images obtained by contact AFM scanning of RFMSD and PECVD TiO_x thin films after UV light irradiation.

In the case of RFMSDs of TiO_2 thin films on polymer substrates (Plexiglas and polycarbonate) it

has been found that the flux of plasma particle and radiation towards the film surface had a big impact not only on film properties, but also on the polymer substrate surfaces, which showed surface buckling instability. Use of a dummy substrate consisting of a thermal probe [15] determined the energy flux that is transported by plasma particles and plasma radiation towards TiO_x film surface during RFMSDs. It has been found that for the experimental conditions of RFMSD, the values of polymer surface temperature were much below the polymer melting temperature. This pointed towards the important role of argon ion bombardment and plasma UV radiation in driving of the polymer surface buckling instability. The instability was studied by AFM measurements, which revealed increase of the roughness of substrate surfaces by the increase of total energy transferred by plasma to the deposition substrate (Fig. 5).

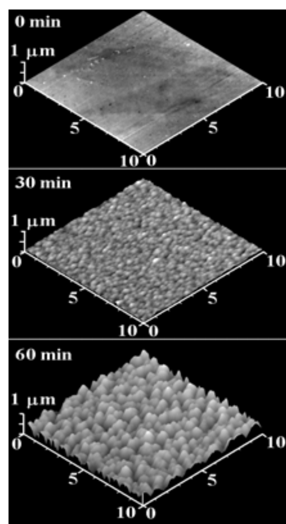

Fig. 5. Topography images of the surfaces of the Plexiglas substrate (0 min.) and TiO_2 films deposited on Plexiglas in 30 minutes and 60 minutes, respectively. RFMSD parameters were 40W and 1.3 Pa.

3. Summary

RFMSD, PECVD and reactive HiPIMS are very flexible low-pressure plasma techniques used for synthesis of photocatalytic semiconductor thin films. In the case of RFMSD of TiO_x thin films, the pressure of the working gas had a tremendous effect on the plasma parameters and plasma particle flux towards the growing film and, thus, had a big impact on the film structure and its photocatalytic activity. In this case, the plasma particle flux had also an impact on the polymer substrate causing the effect of surface buckling instability. This effect was not noticed for the case PECVD, which produced amorphous films containing a large amount of hydroxyl groups, which enhanced the electric conductivity and photocatalytic activity. Reactive HiPIMS was used also to deposit TiO_x thin films, but the photocatalytic activity of these films were not as good so far. In this latter deposition technique, the good flexibility of HiPIMS pulsing scheme is used to control the film structure and properties.

Acknowledgement

This work was supported by the Research Program of Romanian Research, Development and Integration National Plan II, Grant ID-JRP-2012-RO-FR-0161.

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