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## Visible-light photocatalytic activity of $\text{TiO}_x\text{N}_y$ thin films obtained by reactive multi-pulse High Power Impulse Magnetron Sputtering

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## ABSTRACT

Reactive High Power Impulse Magnetron Sputtering operated in multi-pulse mode (m-HiPIMS) of a pure Ti target in  $\text{Ar}/\text{N}_2/\text{O}_2$  gas mixture (mass flow rates of 50, 2 and 0.16 sccm, respectively) has been used for the deposition of titanium oxynitride ( $\text{TiO}_x\text{N}_y$ ) thin films with variable content of nitrogen (from 0.6 at.% to 24.2 at.%). Increase of the nitrogen content in the deposited  $\text{TiO}_x\text{N}_y$  thin films determined a decrease of the optical bandgap energy and a corresponding increase of visible light adsorption. The photocatalytic activity for water molecule splitting of the films deposited on metallic substrate, which were used as the photo-anode in an electrochemical cell, has been investigated by measurements of photoelectrochemical current intensity versus biasing voltage during on/off cycles of visible light irradiation (sun light simulated by a xenon lamp). The as-deposited films have a short range order corresponding to rutile and anatase structures and showed very weak photocatalytic activity and chemical instability in the electrolyte of the photoelectrochemical cell. However, a post-deposition annealing treatment of the film with low content of nitrogen (0.6 at.%) improved considerably the visible-light photocatalytic activity, the film crystalline order and chemical stability.

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### 1. Introduction

Since the discovery of photocatalytic water splitting by Honda and Fujishima [1], titanium dioxide has been intensively studied as an environmental material with applications in photocatalytic purification of air and water and hydrogen fuel production from photocatalytic splitting of water molecules [2]. Among other photocatalyst semiconductors,  $\text{TiO}_2$  has been the most investigated material because, on one hand, it is regarded as a theoretical material model of photocatalyst semiconductors [3] and, on the other hand, it has very attractive properties for photocatalysis applications as low cost, high chemical stability, long lifetime of electron/hole pairs and high oxidizing power of photogenerated holes [4]. However, the large bandgap of  $\text{TiO}_2$  (3.2 eV for anatase and 3 eV for rutile) [5] restricts its good photocatalytic activity to a small fraction of solar energy radiation (UV light). Therefore, a large number of studies have been dedicated to extension of the photocatalytic activity of  $\text{TiO}_2$  to visible light. A good photocatalyst semiconductor for water splitting under solar light should have the minimum energy of the conduction band (CBM) higher than the potential energy for hydrogen reduction ( $\text{H}^+/\text{H}_2$ ) and the maximum of the valence band (VBM) lower

than the potential energy of oxygen oxidation ( $\text{O}^-/\text{O}_2$ ), which is at  $-1.23$  eV (versus the NHE). For anatase  $\text{TiO}_2$  the CBM is just above the  $\text{H}^+/\text{H}_2$  reduction energy level (0.37 eV), while the VBM is located deeply at  $-2.83$  eV (versus NHE) [6]. Therefore, visible light photocatalysts developed from the  $\text{TiO}_2$  structure used doping with metal cations or acceptor anions for engineering the band energy structure of this material. Compared to cation doping, the anions doping is less likely to form charge recombination sites and is, therefore, considered a more effective approach used for enhancing the photocatalytic activity of  $\text{TiO}_2$ . However, Yan et al. [6] have found that  $\text{TiO}_2$  co-doping with Zr cations and N anions is more effective than doping with either cations or anions. Asahi et al. [7] have theoretically evaluated the effect on the band energy structure of substitutional doping with C, N, F, P and S anions for O in anatase  $\text{TiO}_2$  and found N as the best candidate for engineering the  $\text{TiO}_2$  energy band structure for visible light photocatalyst applications. In N-doped  $\text{TiO}_2$ , the p states of N mix with 2p of O, thus shifting the VBM upwards without notably changing the position of CBM. Since the pioneering work of Asahi et al. [7], many authors tried to synthesize good photocatalyst semiconductors based on nitrogen doped titanium dioxide or titanium oxynitride ( $\text{TiO}_x\text{N}_y$ ) [8]. However, the fact that the states introduced by dopant atoms act as recombination centers for electron–hole pairs as well as the thermal instability associated with doped materials hampered the photocatalytic performance of

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these new materials. The photo-catalytic process is also strongly affected by bulk material properties, such as crystallinity, a better crystallinity increasing the life time and mobility of charge carriers [9]. In general, the photocatalytic semiconductors with high defect density have a weak photocatalytic activity because of the formation of charge recombination centers. Recently, Yabi et al. [10] have predicted the  $\text{Ti}_3\text{O}_3\text{N}_2$  crystal as a new water-splitting photocatalytic material. The predicted value for instability energy,  $\Delta H = 31$  MeV/atom, indicates that this material can be synthesized. However, synthesis of this material has been not reported so far. The predicted band edge structure of  $\text{Ti}_3\text{O}_3\text{N}_2$  is interesting for visible light water-splitting photocatalysis because the CBM and VBM bracket the water redox levels and the energy bandgap is 2.37 eV. Due to this low value of the energy bandgap, the  $\text{Ti}_3\text{O}_3\text{N}_2$  crystal may exhibit better photocatalytic performance than TaON, the best known oxynitride photocatalyst so far [11].

In this work, we investigate the capability of the reactive High Power Impulse Magnetron Sputtering (HiPIMS) deposition technique to synthesize  $\text{TiO}_x\text{N}_y$  thin films with good visible light photocatalytic activity for water splitting. This deposition technique showed good reproducibility and process stability for synthesis of oxides, nitrides or oxynitrides thin films [12], which otherwise are difficult to achieve by more conventional magnetron sputtering techniques [13,14]. In a previous work [15], we have shown that reactive HiPIMS [16] working in multi-pulse mode (m-HiPIMS) [17] in Ar/O<sub>2</sub> gas mixture (0.2% O<sub>2</sub> of the total mass flow rate) can be easily manipulated for synthesis of substoichiometric  $\text{TiO}_x$  thin films with *x* values down to 1.63. The deficit of oxygen in the deposited  $\text{TiO}_x$  films was controlled by the HiPIMS pulse repetition frequency. Increase of this parameter determined a transition from oxidized towards metallic target sputtering with a noticeable increase of the sputtered Ti atoms in the gas phase. The limited amount of oxygen in the deposition chamber and the increased amount of sputtered Ti determined depositions of  $\text{TiO}_x$  thin films with a large deficit of oxygen at large values of the HiPIMS pulsing repetition rate. By adding nitrogen to the working gas, the excess of sputtered metal atoms and limited amount of oxygen content favour depositions of metal oxynitride films with larger content of nitrogen. Recently, we have proved this mechanism in the case of  $\text{ZnO}_x\text{N}_y$  thin films. Here, we use reactive m-HiPIMS depositions in Ar/O<sub>2</sub>/N<sub>2</sub> gas mixture for synthesis of  $\text{TiO}_x\text{N}_y$  with the content of N ranging from 0.6 at.% to 24.2 at.% (which is close to the N concentration in the predicted  $\text{Ti}_3\text{O}_3\text{N}_2$  material). Structure and composition of deposited films have been investigated by atomic force microscopy (AFM), X-ray diffraction (XRD), Rutherford Backscattering Spectroscopy (RBS), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The adsorption and photogeneration of electron–hole pairs under visible light irradiation were investigated by optical transmission spectroscopy measurements. The photocatalytic activity for water splitting under visible light illumination has been investigated by measurements of photoelectrochemical current intensity variations versus biasing voltage during on/off cycles of visible light irradiation (sun light simulated by a xenon lamp).

## 2. Experimental devices, methods and techniques

In the m-HiPIMS, a single voltage pulse applied to the cathode (−700 V in peak value) with 15 μs in width was decomposed into a sequence of 3 individual micropulses with the width of 5 μs. By doing this, the sputtering rate has been noticeably improved due to diminished back attraction of sputtered and ionized atoms. The delay time between the micropulses within a sequence was kept constant (50 μs) in all the experiments. The value of 50 μs for the delay time between micropulses in m-HiPIMS has been chosen to optimize the m-HiPIMS deposition [17]. Typical time variations of the current intensity and discharge voltage during m-HiPIMS operation at sequence repetition frequency values of 400 and 1600 Hz are given in Fig. 1. Apart of a decrease of preionization voltage from −310 V to −20 V, the voltage waveform does not change noticeably with the increase of the sequence repetition

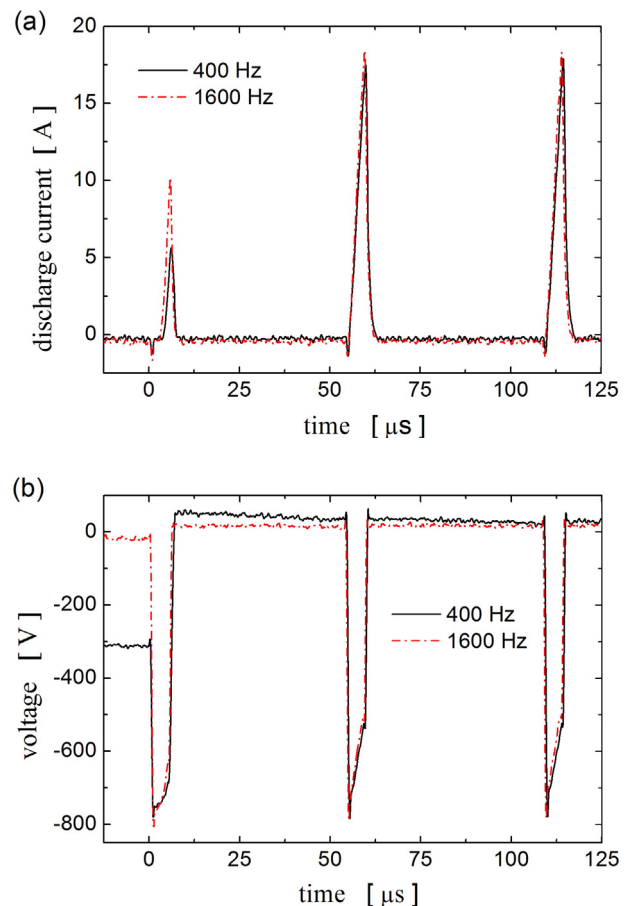


Fig. 1. Typical waveforms of the current intensity (a) and discharge voltage (b) for m-HiPIMS (sequence of three micropulses of 5 μs in width separated by time-off periods of 50 μs) at sequence repetition frequency values of 400 and 1600 Hz, respectively.

frequency from 400 Hz to 1600 Hz. The role of the pre-ionization is to provide between discharge pulses certain ionization degree of the working gas (very weak plasma), which prevents giant impedance jumps when switching from insulator to conductor (plasma) gas state. It is worth mentioning that, at high sequence repetition frequency the pre-ionization is no longer required, its role being played by the residual charged species surviving in the afterglow plasma. The peak value of the current intensity corresponding to the first micropulse from the multi-pulse sequence is sensitive to the repetition frequency due to a change of target surface condition during the long time between consecutive micropulse sequences. At low repetition frequency the discharge operates in compound mode, the target surface being covered with oxynitride compound, which determines a lower value of the peak discharge current intensity for the first micropulse. As the repetition frequency increase, the period between sequences becomes smaller and the target surface becomes less poisoned. The average power increases linearly from 20 to 80 W as the sequence repetition frequency increases from 400 to 1600 Hz. By increasing the m-HiPIMS pulsing repetition frequency, the amount of sputtered Ti increases and, due to the limited amount of oxygen in the deposition chamber, depositions of films with larger content of nitrogen is favoured.

All the experiments were performed in a high vacuum stainless steel chamber using a Ti target (99.995% purity, produced by Kurt J. Lesker Company) with a diameter of 50 mm and thickness of 5 mm. A low content in oxygen of the working gas was chosen to facilitate incorporation of nitrogen in the deposited  $\text{TiO}_x\text{N}_y$  thin films. Thus, the working gas was a mixture of Ar (mass flow rate of 50 sccm) and O<sub>2</sub> (mass flow rate of 0.16 sccm) and N<sub>2</sub> (mass flow rate of 2 sccm) at the total pressure

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