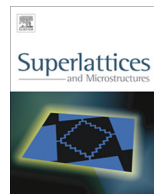




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# Direction-regulated electric field implanted in multilayer Mo–TiO<sub>2</sub> films and its contribution to photocatalytic property <sup>☆</sup>

Sheng-Yun Luo <sup>a,b</sup>, Bing-Xi Yan <sup>a</sup>, Jie Shen <sup>a,\*</sup>

<sup>a</sup> Department of Materials Science, Fudan University, Shanghai 200433, PR China

<sup>b</sup> College of Science, Guizhou University for Nationalities, Guizhou 550025, PR China

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## ABSTRACT

Multilayer Mo-doped TiO<sub>2</sub> thin films were prepared by In-situ RF magnetron co-sputtering. Surface morphology, crystallite parameters, valence states and absorption band were investigated with atomic force microscopy, X-ray diffraction spectroscopy, X-ray photoelectron spectroscopy and ultraviolet–visible spectroscopy. AC impedance spectroscopy and photocatalytic capability of different layer-assemble modes were examined on an electrochemical workstation under visible light. The result indicates the electric fields resulted from Fermi level drops could remarkably accelerate the separation of photogenerated carriers. The double-layer film, which was prepared by covering the uniformly Mo doped layer with an undoped surface layer, has the smallest impedance. The strongest catalytic capability is demonstrated by the three-layer film, which has an undoped surface layer, a uniformly doped middle layer and an ultra-thin, heavy doped bottom layer. Although different layer modes have little influence on absorption edge, our observations suggest that by manipulating doping content in each layer, we can implant upward electric field arrays, which has considerable potential to enhance the photocatalytic property, into multilayer Mo-doped TiO<sub>2</sub> films.

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\* Corresponding author.

E-mail address: [shenjie@fudan.edu.cn](mailto:shenjie@fudan.edu.cn) (J. Shen).

## 1. Introduction

Photocatalytic property of TiO<sub>2</sub> films is widely studied by researchers concerning self-cleaning coatings, environmental purifiers, and antifogging mirrors. To curtail the energy gap of TiO<sub>2</sub> films and enhance photocatalytic property under visible light, researchers have tried different dopant involving Mo, Ni, Ag, Fe, V, Nb, W, etc. [1–3]. Previous studies confirm that a small doping content is unable to improve film's absorption of visible light notably. If the doping content goes up, however, a fast recombination rate caused by a large number of lattice defects will severely undermine photocatalytic capability. Following uniform ions doping, it is difficult to achieve high photo-generating efficiency under visible light while keeping the recombination ratio at a sufficiently small value so as to maintain a high carrier concentration within film.

Recent study pointed out that Fermi level drops at crystallite interface can result in depletion layer with internal electric field [4]. Theoretically, if the direction and intensity of these fields could be manipulated, internal charge transfer could be accelerated and carrier recombination will be inhibited. Based on sol–gel method, Cen's group covered the La-doped film with an undoped TiO<sub>2</sub> layer and observed improved photocatalytic capability [5]. Zhang also reported similar results observed in their work on Mn doped TiO<sub>2</sub> [6]. Such investigations imply internal electric fields, which usually exist between layer with different Fermi level, could be used to accelerate carrier separation in film catalyst. Since recombination ratio in a heavy doped TiO<sub>2</sub> layer is rather high, the thickness of heavy doped layer has to be much smaller than other layers. However, confined by the sol–gel method, studies above could not control layer thickness precisely and failed to prepare ultrathin, heavy doped layers. As a result, after comparing two different kinds of primary double-layer structures, Zhang and Cen both came to a disappointing and inaccurate conclusion that heavy doped layers are meaningless for multilayer films. Up to now, the influence of internal electric fields on carrier separation in TiO<sub>2</sub> films has not been studied in detail.

Unlike sol–gel method, RF magnetron co-sputtering is an ideal approach to prepare multilayer films while controlling thickness and doping content in each layer precisely. It is well known that intensity of internal electric fields depend on the value of Fermi level drop at crystallite interfaces. Considering Fermi level depends on ion content, we can modulate sputtering power of each target dynamically in sputtering process and thereby control Mo content in each layer. This novel approach enables us to deposit layers containing various Mo content in different orders, so makes it much easier to reveal the real potential of internal electric fields in multilayer films.

## 2. Experimental details

Samples are deposited on titanium substrate for AC impedance experiment, while glass substrate was used for samples studied in the investigation of UV–Vis. absorption test. A Mo cube (2 × 2 × 2 mm) was fixed on the TiO<sub>2</sub> ceramic target and the sputtering area ration ( $S_{\text{Mo}}/S_{\text{Ti}}$ ) is 1/70. A TiO<sub>2</sub> ceramic target and a Mo-embedded TiO<sub>2</sub> ceramic target were used. Besides area ratio, sputtering yield  $Y$ , a parameter indicates how many atoms could be sputtered out of the target surface by each ion ( $\text{Ar}^+$ ), was also considered in the accurate rectification of Mo content, given that  $Y_{\text{TiO}_2}/Y_{\text{Mo}}$  is 1.66 when the energy of  $\text{Ar}^+$  is 300 eV.

The vacuum chamber was evacuated to  $2 \times 10^{-3}$  Pa before sputtering and the sputtering pressure was kept at 0.5 Pa (Ar). During sputtering process, oxygen was infused into vacuum chamber to inhibit TiO<sub>2</sub> decomposition (pressure ratio of  $\text{O}_2/\text{Ar}$  was 1/143). Since we have confirmed the optimized Mo content as well as the corresponding sputtering power (60 W) in similar experiment conditions in previous work, we continue to use this power value to yield an appropriate Mo content for the uniformly-doped layer [7]. The power of TiO<sub>2</sub> target was fixed on 300 W in deposition, while sputtering power of the Mo-embedded target was modulated as zero, 60 W and 300 W, corresponding to layer T (TiO<sub>2</sub>), L (light doped layer) and H (heavy doped layer), respectively. Samples obtained were annealed at 500 °C in air for 2 h. Fig. 1 gives a brief illustration of all layer-assemble modes investigated in this study.

Crystal structure was characterized by X-ray diffraction (XRD-D8, Bruker) at a scanning speed of 00B0 4°/min (Cu target,  $K\alpha = 0.1542$  nm). Surface morphology was characterized by atomic force microscope (AFM, Bruker). Chemical composition and valence states were measured on X-ray

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