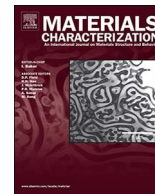




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Characterization of thin films prepared by co-sputtering iron and titanium precursors and thermal oxidation under air atmosphere

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ABSTRACT

Nanocomposites of metal oxides are useful materials for operation in many energy conversion systems. In this study, such nanocomposites were prepared by oxidation of mixtures of iron and titanium precursor metallic thin films at 520 °C under air atmosphere. The metallic films with different iron percentages were obtained by radio frequency (RF) magnetron sputtering on glass and silicon substrates. The films were characterized by means of X-ray Diffraction (XRD), Raman spectroscopy, UV–Vis spectroscopy, High Resolution Scanning Transmission Electron Microscopy (HRSTEM), Ellipsometry and X-ray Photo-electron Spectroscopy (XPS). The results show that these films present mainly two nanometric phases, namely Fe₂O₃ and TiO₂. A phase separation was observed; the film surface was found to be iron rich oxide or clusters of iron rich oxide (Fe_xO_y, x > y), whereas titanium accumulated deeply in the bulk, forming TiO₂ far below the film surface. A red shift of optical absorption as well as a relatively stable high refractive index (varying between 3.1 and 3.5) over a broad band of optical frequencies was observed for the films containing higher iron initial concentrations.

1. Introduction

Nanocomposites of metal oxides are useful materials in energy conversion systems. Extensive earlier experimental findings indicate that inert oxides such as titanium oxide can greatly improve the reactivity of iron oxide, for example, over multiple redox cycles [1]. The promotion or inhibition of solid state reaction in nanocomposite films, such as phase formation, phase separation, segregation, crystallization, etc., plays an important role in ultimate performance of the films. The extraordinary interest in nanocomposite materials is mainly due to the vast range of properties that can arise from the combination of the peculiar characteristics of each component [2]. TiO₂ has been studied as photo catalyst as well as in many other applications. However, its large band gap which approaches 3.2 eV, depending on the phase structure (rutile: ~ 3.0 eV [3], anatase: ~ 3.4 eV [4] and brookite: ~ 3.3 eV [5]), confines its uses to only the UV region of the electromagnetic spectrum. Hence, lowering the band gap of titania below 3 eV to shift the optical response to the visible light range is a highly active area of research with attention focused on the improvement of the catalytic activities of TiO₂ through doping, metal loading and

semiconductor mixing.

Depending on preparation methods, iron oxide can be found in several phases such as magnetite (Fe₃O₄), wustite (FeO) and trioxide (α-Fe₂O₃, β-Fe₂O₃, γ-Fe₂O₃, and ε-Fe₂O₃) among others. The three most common forms of iron oxides are magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and hematite (α-Fe₂O₃). Formation and reactivity of iron oxide at the nanoscale are rather complicated. For instance, Both Fe₂O₃ and FeO can be detected in 20% iron oxide– silica aerogel calcined at 500 °C [6]. Hematite, which is the main phase detected in the present investigation, is an interesting n-type semiconductor material with a band gap of about 2.2 eV [7]. It has been investigated for its application in environmental purification [8] as well as for water splitting [9] despite the unfavorable position of the conduction band. For instance, photo-electrochemical (PEC) water splitting at Au-modified nanocrystalline TiO₂ films have been studied [10] as alternative materials to TiO₂ and the inverse opal photonic crystals (PC) design has been applied to photocatalytic iron oxides [11] and binary oxides [12]. It has been found that coupling a SOFC (Solid Oxide Fuel Cell) with an external reducer, using Fe-Ti-O as an oxygen carrier is a good candidate for electricity generation [13]. Fe₂O₃ can be considered as a sensitizer for

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TiO₂, since it has a flat band potential of 0.32 V versus NHE (Normal Hydrogen Electrode). Some authors [14] have published a correlation between the enhanced photo reactivity and higher surface activity resulting from the addition of metal oxides to TiO₂. This suggests that hetero elements incorporated to TiO₂ may create novel binary metal oxide photo catalysts with better performance. It has been pointed out that an efficient way to use the majority of sunlight may be found in the composites of nano semiconductors such as TiO₂-Fe₂O₃ [15,16]. Therefore, these kinds of nanocomposites should gain more attention. So far, most of the studies focus on developing Fe₂O₃-TiO₂ powder photocatalyst by various methods [17,18,19] such as hydrothermal and sol-gel. However, there are some drawbacks of the practical use of the powder photocatalyst [20]; [1] separation of powder from water is difficult; [2] the suspended powder tends to aggregate, especially, at high concentrations. Therefore, developing supported photocatalysts is of obvious practical significance. For instance, Zhang and Lei, prepared Fe₂O₃-TiO₂ coatings supported on activated carbon fiber by metal organic chemical vapor deposition [21] and Jin Kawakita et al. [22] fabricated coatings of nano-sized composite of TiO₂ and Fe₂O₃ by the warm spray process for photo-electric conversion function by TiO₂ and electron charge/discharge function by Fe₂O₃. In order to improve the conductivity of hematite, Ti-doped (up to 19.7% by atomic ratio) micro-nanostructured hematite films have been prepared by an in situ solid-state reaction method [23]. Mechanical milling has been used to prepare nanometric iron-titanium oxides for anodic materials in lithium cells [24].

On the other hand, preparation and nanostructuring of mixed oxide thin films where two single oxides of different optical properties are mixed together [25,26] can be considered as one of the common approaches for tailoring the photonic properties of the materials, such as refractive index and frequency-selective light trapping and absorption. Knowledge of phase and element distribution as well as evolution of the nanoscale morphology of the Fe-Ti thin films during oxidation is thus of considerable importance. The present work is devoted to the structural and optical characterization of thin films prepared by RF magnetron co-sputtering Fe and Ti precursor metallic films on glass and Si substrates and subsequent oxidation at relatively low temperature and under air atmosphere. The surface of these films was found to be composed of iron rich nanospheres with 10 nm diameter or less.

2. Material and methods

Films that are mixtures of metallic iron and titanium were deposited on glass substrates by radio frequency magnetron sputtering of pure Ti (99.8%) target with Fe (99.5%) in the form of circular sheets superimposed on the Ti target (Fig. 1). The ratio of the Fe sputtered area to the total sputtered area of Ti was changed, in order to obtain various composites. It was possible to change the concentration of Fe in Ti-Fe thin films by changing the relative area covered with Fe sheets. The base pressure of the system was 3.10–3 Pa and the sputtering Ar gas (99.99) pressure was at 5.10–1 Pa. The RF power was fixed at 10 W/cm² and the substrate temperature in this case did not exceed 100 °C. After sputtering, the metallic (mixture of Ti and Fe) films were oxidized in air under atmospheric pressure at 520 °C during 8 h.

The preparation conditions and sample designations are summarized in Table 1.

The oxidized films were characterized by XRD (Siemens D8000) using Cu K α radiation at normal incidence in the 2 θ range of 20–80° with 40 keV, 35 mA. Raman spectra were recorded with a Bruker Senterra Raman spectrometer equipped with a laser source radiating at wavelength = 532 nm and power = 10 mW. X-ray photoelectron spectroscopy (XPS) depth profiling was carried out on a Kratos Nova system using Al K α (1486.6 eV) radiation. Both elemental and topographical scanning transmission electron microscopy images were taken in a FEI STEM of type Talos F200A. Focused Ion Beam (FIB) was used to prepare thin cross section of the film for TEM analysis and

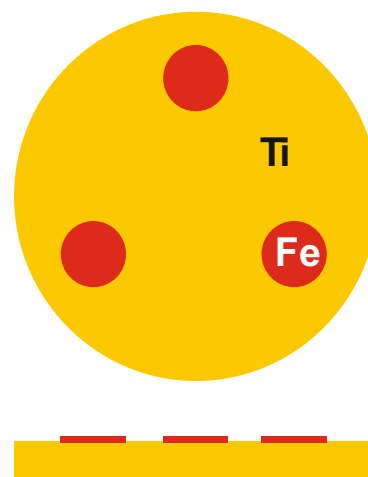


Fig. 1. Schematic of the Ti target (yellow) on which Fe discs (red) are superimposed for the deposition of Ti-Fe mixture by magnetron sputtering. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Sample preparation conditions.

| Sample designation | Iron percentage in term of sputtered area ratio (S_{Fe}/S_{Ti}) (%) | Deposition time (min) | Oxidation time (h) at 520 °C |
|--------------------|---|-----------------------|------------------------------|
| S ₁ | 10 | 3 | 8 |
| S ₂ | 17 | 3 | 8 |
| S ₃ | 22 | 3 | 8 |

UV-Vis spectrometry (Shimadzu UV 3101 PC spectrometer) was used to record the optical absorbance spectra. Ellipsometry was performed using a Jobin Yvon UVISEL NIR Spectroscopic Phase Modulated Ellipsometer with an automatic goniometer. The ellipsometric measurements were collected at an angle of incidence of 70° across the spectral range 190–830 nm. It should be noted that the analysis results of samples S₂ and S₃ are not very different. So the exposed results will be focused on S₁ and S₃ except where is useful.

3. Results and discussion

3.1. XRD and Raman spectroscopy

Fig. 2 shows the XRD patterns of the films that were deposited on glass substrates. Both anatase (a) which is characterized by the most intense diffraction peak at 25.5° corresponding to the (101) planes and rutile (r) which is characterized by the (110) reflection at 27.6° are visible in the explored region of XRD. It can be seen that no inter metallic FeTi is detected in these films. The other reflections can be assigned to α -Fe₂O₃ and the intensity of these reflections increased with the increase of the Fe content.

The formation of these phases (anatase, rutile and hematite) is confirmed by Raman spectra displayed in Fig. 3. Many peaks of the Raman spectra, as shown for samples S₁ and S₃, matches that of typical hematite (α -Fe₂O₃), rutile and anatase. Factor group analysis suggests 7 Raman-active vibrational modes (2A_{1g} + 5E_g) for hematite corundum structure, situated at 226, 245, 292, 301, 411, 497, 613 cm⁻¹ [27]. Also, the Raman lines appearing at 225, 245, 291, 410, 495, and 611 cm⁻¹ are characteristic of α -Fe₂O₃ [28]. All of them are clearly observed in the spectra of samples S₁, S₂ (not shown) and S₃, revealing the presence of α -Fe₂O₃. Raman modes bands for rutile are reported around 144–147, 238–240, 447–448, and 610–612 cm⁻¹ [29,30] or 143, 450, 612, 826 [31] while for anatase are found around 144, 394,

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