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Microstructural and photo-induced properties of silver-doped in situ crystallized TiO_2 coatings prepared by reactive magnetron sputtering

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***Abstract*- The aim of this study is to investigate the influence of in-situ crystallization on the microstructural and the photocatalytic properties of silver doped TiO_2 coatings deposited on glass slides at different temperatures. Then, a first step of this work consisted in depositing a SiN_x barrier layer on the glass slide to prohibit further diffusion of alkali elements and poisoning of the active layer.**

The second step was to synthesize pure TiO_2 and silver-doped TiO_2 films at high pressure by magnetron sputtering at the 400°C. Silver was introduced in the coatings at different contents by co-sputtering simultaneously of titanium and silver target.

The samples were characterized by X-ray diffraction, scanning electron microscopy and finally the photocatalytic activity was assessed by using the Orange G decomposition upon UV or visible irradiations.

***Index Terms*—Photocatalysis-titanium dioxide-magnetron sputtering-silver doped Titania.**

I. INTRODUCTION

In order to solve environmental problems relating to wastewaters, TiO_2 photocatalyst has been intensively studied due to its ability to degrade a wide range of organic pollutants, its physical and chemical stability, low-cost and non-toxicity [1].

Photocatalysis is a catalytic oxidation process involving a solid photocatalyst and ultraviolet radiation. It appears as one of cheaper processes, which has been established for conducting the degradation of organic molecules in aqueous or gas phase. It's a process that involves the occurrence of a chemical reaction in the presence of semiconductor TiO_2 irradiated with energy higher than its band gap [2]. The electrons e^- are excited from the valence band into the conduction band leaving holes h^+ in the valence band. Such activated electrons or holes can diffuse to the surface and generate different types of radicals or ions which are highly reactive with contacting organic compounds adsorbed on the titania surface and can decompose them [3].

Many methods can be used to prepare TiO_2 films include sol-gel method [4], chemical vapour deposition [5], sputtering process [6], vacuum evaporation [7], ion beam techniques [8], filtered arc deposition [9]. Among them the magnetron sputtering presents numerous advantages especially the high quality and homogeneity of obtained films, large-area of uniform coatings and strong adhesion. Furthermore, magnetron sputtering provides more advantages in controlling the microstructure, the morphology and hence the properties of the titania films by modifying the deposition parameters such as the working pressure, the oxygen-partial pressure, the draw distance and the substrate temperature.

However, TiO_2 has a relatively high bandgap ($Eg > 3.2$ eV) and can only excited by UV irradiation. In order to make it work under visible light irradiation, many studies proposed doping of TiO_2 with some transition metals [10]. Among these metals especially silver, have received much attention for this purpose [11]. In this work, we have investigated the structural and photocatalytic properties of undoped and silver doped TiO_2 coatings deposited on glass slides at high pressure and temperature.

II. EXPERIMENTAL DETAILS

Undoped and Ag doped TiO_2 films were deposited at 5 Pa by reactive DC magnetron sputtering using two metallic targets of Ti and single target of Ag of 50 mm diameter and 99.99% purity on glass slides substrates (75×25 mm^2). The substrates are covered in the first step by 350 nm SiN_x barrier layer to avoid alkali elements diffusion of glass and degradation of TiO_2 photocatalytic activity [12]. The experimental device is a 90-litre sputtering chamber pumped down via a turbomolecular pump system allowing a base vacuum of less than 10^{-4} Pa. The substrate-holder was heated at 400 °C by radiative effect using an electrical resistance placed behind of the substrate-holder at about 5 mm. The details of the reactive magnetron sputtering reactor are available elsewhere [13]. The distance between the targets and substrate holder was fixed at about 60 mm and the substrate holder was rotated regularly during the deposition run (60 RPM).

In all experiments, the discharge current applied to Ti targets was fixed at 0.8 A. To obtain Ag-doped TiO_2 samples with different silver ratios, Ag element was introduced in the coatings at different contents by adjusting the discharge current applied on Ag target from 5 to 8 mA. The main deposition parameters are summarized in Table 1.

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Table1. Sputtering parameters for synthesis of undoped and Ag doped TiO_2 coatings.

Ar flow rate (sccm)	220	Target (metallic)	**Ti**	**Ag**
Oxygen flow rate (sccm)	10	Discharge current (A)	0.8	0.005→0.008
Total pressure (Pa)	5	Pulse frequency (kHz)	50	-
Run duration (h)	2	Substrate temperature (°C)	400	
Draw distance (mm)	60			

The structure of the films was characterized by X-ray diffraction in the Bragg-Brentano (θ/2θ) geometry using Bruker D8 focus diffractometer equipped with a cobalt anode ($CoK_{\alpha1+\alpha2}$radiations). The morphology of the coatings is assessed by means of scanning electron microscopy (SEM) using a JEOL JSM 7800F equipped with energy dispersive spectroscopy (EDS) for chemical composition measurements.

The photocatalytic activity was evaluated by following in real-time the Orange G decomposition (100 ml) during 2 h with an initial concentration C_0 = 10 mg.l^{-1} upon UV irradiation from a UV–vis xenon light source (Lot-Oriel) emitting with a constant irradiance (15 mW. m^{-2}). The distance between the samples and the light source was fixed at 15 cm. The experimental setup is described elsewhere in details [12]. Since the degradation reaction is a pseudo one-order kinetic, the photocatalytic activity is expressed in terms of the apparent rate constant K' in min^{-1}.

The photo-induced hydrophilic character of the films was studied by measuring the contact angle of constant volume water droplets deposited in ambient air on the coatings surface using DIGITROP device type after different irradiation times. The angle measurement was performed in ambient air and each angle value is an average of about five measurements on the entire coating surface.

III. RESULTS AND DISCUSSION

A. *Structural and morphological characterization*

TiO_2 layers enriched in different percentages of silver were analyzed by X-ray diffraction (Fig 1). Indexing of the diffraction peaks was carried from the 01-089-4921-JCPDS and 01-087-0720-JCPDS card number. TiO_2 crystallizes in the anatase phase with a preferred orientation along the plane (101) and along (004) for undoped TiO_2 and neither traces of parasitic phase were detected in the films. The presence of metallic Ag is visible even for Ag content as low as 1 at/.% and the Ag crystallizes in the FCC structure. By increasing the silver content, the intensity of all peaks increases, which leads to the conclusion that the particles of Ag and TiO_2 grains grow gradually. For low percentages (1 and 2 at.%), silver is dispersed in the matrix of TiO_2. For larger percentages (7 and 10 at.%), the silver particles precipitate onto the surface of the coatings and TiO_2 crystallizes more coarsely in its anatase structure.

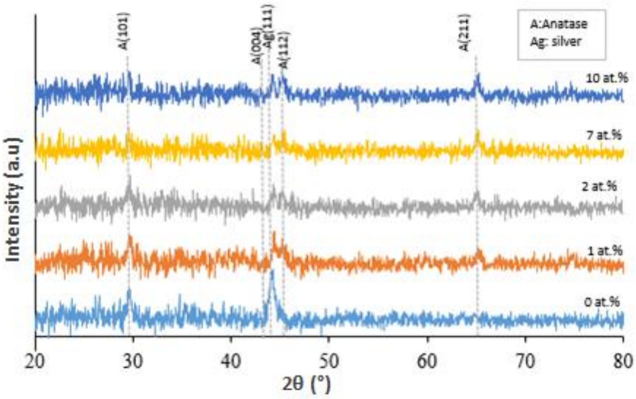

Fig 1. X-ray diffractograms of Ag-doped TiO_2 coatings in-situ annealed at 400°C.

Fig 2 shows the SEM top surface views of the coatings. It can be seen clearly that the undoped TiO_2 films exhibits a large porous morphology Fig (2(a)).

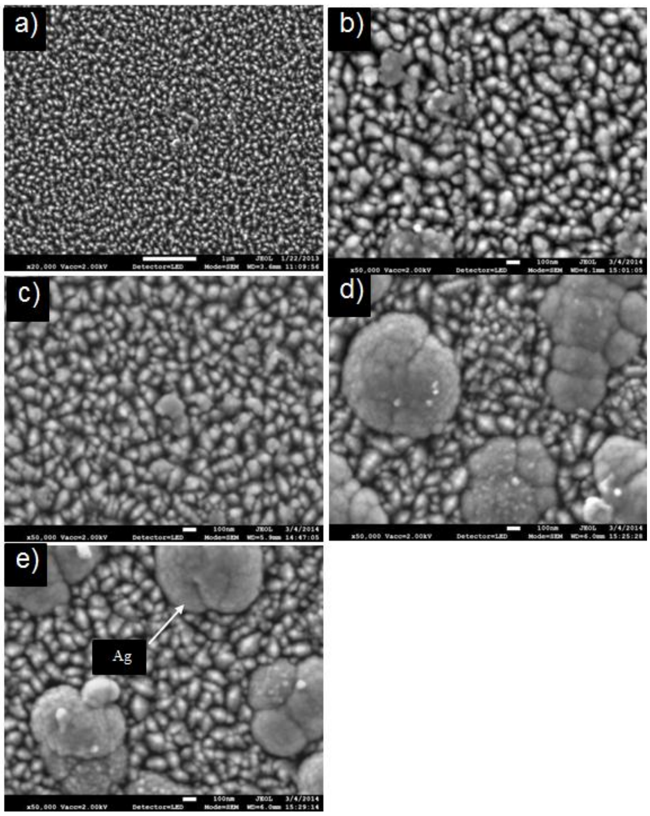

Fig 2.Top surface SEM micrographs of the surface of the synthesized TiO_2 with various percentages of Ag: a): 0 at.%; b): 1 at.%; c): 2 at.% ; d): 7 at.% and e): 10 at.%.

The layers formed with low percentages of Ag (Fig 2 (b) and (c)) show a homogeneous and granular surface with no Ag traceless. By increasing the percentage of Ag, the Ag particles begin to agglomerate on the surface (Fig 2 (d) and (e)). These observations confirm the results obtained by the X-ray diffractograms.

B. Photocatalytic properties

The evolution of the apparent rate constant K' as a function of silver content is compared for the films deposited at 400 °C under UV irradiation and visible light (Fig 3). Under UV irradiation, the apparent constant K' of TiO_2 is about 2.10^{-3} $.min^{-1}$. It increases to 2.5 10^{-3} $min.^{-1}$ for about 1 at.% Ag and falls to $0.7.10^{-3}$ min^{-1} for Ag contents higher than 7 at.%. Under visible light, it was found that as pure TiO_2 is not active under visible light, increasing Ag content increases quite linearly K' up to $1.2.10^{-3}$ min^{-1} for about 7 at.% Ag and then decreases K' for higher Ag contents.

Above the optimum content, the Ag particles begin to act as recombination centers thereby reducing the photocatalytic activity of the layers. Similar behavior was also observed for TiO_2 layers doped Fe^{III}, Zn^{II} and La^{III} [13-16].

Previous research of the effect of addition of Zn and Fe [15] has shown that even if the profile was similar to the variation, the optimal concentration varies with the nature of the metal ions used. In general, comparing the optimum content of the silver ions with Fe^{III} of Zn^{II} and it was found that the optimum content for the silver ions is considerably lower than that of Fe^{III} and Zn^{II}. This difference could be related to the degree of oxidation and the ionic radius of different metal ions. For a similar Ti^{IV} ionic radius (61 pm), Fe^{III} (55 pm) and Zn^{II} (74 pm) ions could enter the TiO_2 lattice by substituting Ti^{IV} in the lattice sites [15-17]. In addition, they may also exist as ions in the pore network of TiO_2. However, it is impossible for Ag ions whose ionic radius equal to 115 pm to act as interstitial ions in the matrix of TiO_2. The silver ion can only replace Ti^{IV} in lattice sites like solid solution [18].

Without adding another element to titanium oxide in its production, the oxygen is the only electron acceptor. However when the addition of Ag, two additional acceptor species are introduced: Ag^+ and Ag.

The most important advantage of adding Ag is to improve the efficiency of charge separation which increases the lifetime of the charge carriers. Thus, a greater number of holes reach the interfacial region of the layer, leading to the production of super-active groups such as: $HO_2^{\bullet}$, $OH^{\bullet}$ and H_2O_2 [19].

The high photoactivity of TiO_2 enriched Ag compared to that of pure TiO_2 under UV irradiation is attributed to the fact that silver acts as an electron trap in the surface layers. This speeds up the rate of electrons transfer to molecular oxygen, inhibiting thereby the recombination of photogenerated electrons and holes [20].

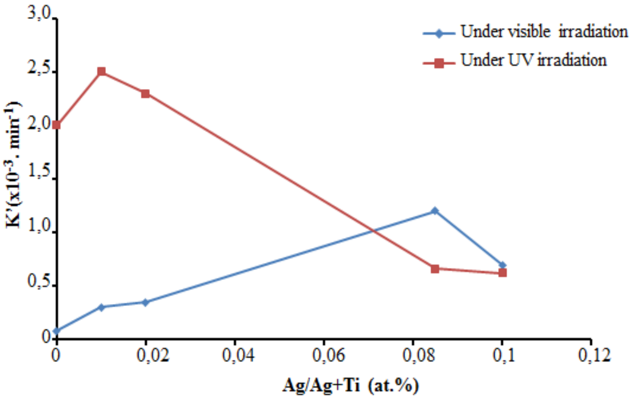

Fig 3. Evolution of the apparent rate constant K' as a function of Ag at.% for the coatings synthesized at 400°C.

The hydrophilicity of films which have the highest photocatalytic activity was investigated by measurements of the water contact angle. Fig 4 shows the changes in this angles induced by UV light irradiation for different times (0, 15, 30, 60 and 120 min).

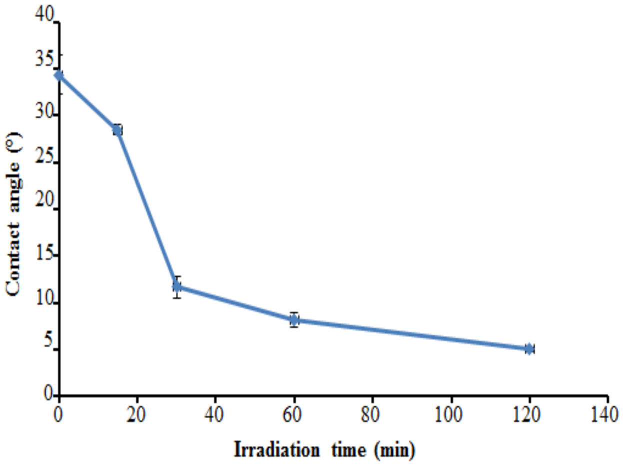

Fig 4. Contact angle evolution of of 7 at.% Ag doped TiO_2 according to the irradiation time.

The contact angle decreases with increasing the irradiation time to a value equal to 5 ° for 2 h after irradiation. This was explained by the fact that the UV-light-induced hydrophilicity of the TiO_2 is related to the dissociative adsorption of water molecules from the ambient air at Ti^{4+} photo-reduced to Ti^{3+}, which is typically situated at the oxygen bridges on the surface [21- 22].

IV. CONCLUSION

The efficiency of undoped and Ag doped porous TiO_2 thin films deposited by reactive magnetron sputtering at high pressure on heated glass slides substrates at 400 °C) was investigated. XRD analysis reveals that all the films crystallized only in the anatase structure. The morphology of the layers is porous. Under visible light, the photocatalysis processes show that 7 at.% Ag-doped TiO_2 thin film is attractive for photocatalytic applications. Under UV irradiation, however, the 1 at.% Ag doped TiO_2 films revealed 25% more Orange photodegradation as compared to the undoped TiO_2.

Finally, the hydrophilicity of films which have the highest photocatalytic activity was verified.

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