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ZrO_2 FOR PHOTOCATALYTIC APPLICATIONS

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We report in this work on the influence of nitrogen doping on the hydrophilic and photocatalytic activity of ZrO_2 thin films, deposited by HiPIMS sputtering method, on Si substrates.

Thin films structure, elemental composition of the atomic species at the films surface and optical band gap, were derived from XRD, XPS, DRS, respectively, and are correlated to explain the wettability and photocatalytic properties of the investigated films. We have found that: N-doping induces a shift of the fundamental absorption edge from UV to visible range and determines better hydrophilic properties and better photocatalytic power for the decomposition of Rhodamine B.

Keywords: N-doped ZrO_2, HiPIMS Sputtering, wettability, photocatalysis

1. Introduction

In the conditions of the uncontrolled growth of environmental pollution, rapid solutions are needed to solve these problems. A grave environmental issue is the dye wastewater arising mainly from the textile industry, or colored glass industry [1]. Rhodamine B (RhB) is an organic compound which is toxic to the human and animal bodies. Recent studies show that, being used as a food additive in some countries, RhB can lead to oxidative stress on cells and tissue, causing cancer. When a body is exposed to high RhB quantities, even for short times, the organism can be subjected to severe poisoning [2,3]. RhB is widely used in the textile industry as a dye and accumulates in wastewaters [2]. Researchers show that, in concentrations greater than 1 mg/L, RhB causes toxicity in oyster larvae and eggs [1]. That is why, it is mandatory to investigate the ways of wastewaters treatment. Since most of the organic pollutants are resistant to chemical or biological treatments, the problem could be solved by using a “green” treatment, namely the oxidation process, through photocatalysis. As a consequence, the investigation on the materials properties used in the decomposition of organic pollutants through photocatalysis represents an important research direction.

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The purpose of this work is to make a study on zirconium oxide in the form of thin films with possible applications in photocatalysis. ZrO_2 is a non-toxic material with outstanding chemical and physical properties: high thermal and chemical and mechanical stability, low thermal conductivity, high corrosion resistance, high strength and fracture toughness, high optical transparency in the visible and near IR and high refractive index [4,5]. Since the pure material is characterized by a large optical gap [4], being absorbent in UV, in order to be able to efficiently use solar radiation, it is necessary to shift the edge of the fundamental absorption towards the visible range. In this purpose, we propose to investigate the nitrogen doping effect on ZrO_2 films hydrophilic properties and also on their photodegradation activity of RhB. The photocatalytic power of both undoped and N-doped films was investigated in the presence and in the absence of H_2O_2.

2. Experimental

Undoped and N-doped ZrO_2 films were obtained on unheated Si (100) substrates, by high power impulse magnetron sputtering (HiPIMS). Characteristic to this method, HiPIMS, is the generation of a high plasma density with high ionization degree of both sputtered material and gas, at much lower frequencies than in the conventional magnetron sputtering method, having as result the obtaining of higher quality films regarding crystallinity, adhesion to the substrate, or compactization. The Zr target (purity 99.95%, diameter 5 cm, thickness 0.3 cm) was placed at 7 cm distance from the substrate. A base pressure lower than 10^{-8} Pa was achieved in the deposition chamber, with the help of an Agilent turbomolecular pump backed by a dry scroll pump. The unipolar voltage pulses applied to the Zr target have a constant amplitude and a constant duration, of −700V and 10 μs, respectively, while the repetition frequency was 800 Hz for the undoped film, and 1250 Hz for N-doped films. To obtain N-doped ZrO_2 thin films, the sputtering gas consists in a mixture of Ar (purity: 99.999%, flow rate: 50 sccm), N_2 (purity: 99.999%, flow rate: 1 sccm) and O_2 (purity: 99.999%, flow rate: 0.1 sccm), the total pressure being kept at 0.8 Pa. The undoped film was obtained by using a mixture of Ar (50 sccm) and O_2 (1 sccm).

The structure of the films was investigated by X-ray diffractometry (XRD), in standard θ-2θ configuration, using a SHIMADZU 6000 diffractometer (CuK_α radiation, 40kV, 30mA). The average crystallite size values, were calculated with the Scherrer formula [6]:

$$D = \frac{0.9\lambda}{B_{1/2}\cos\theta} \qquad (1)$$

where θ is the Bragg angle, $B_{1/2}$ is the width measured at half height of the diffraction peak (in radians), and λ is the X-ray radiation wavelength.

A Physical Electronics-Ulvac (PHI 5000 VersaProbe) instrument (equipped with a mono-chromated Al Kα X-ray source, 1486.6 eV, power of 25W) was used to measure the X-ray photoelectron spectra (XPS) in order to obtain information on the elemental composition and the chemical state of the atomic species at the films surface. A Shirley background and Gaussian peak shapes were used to fit the spectra, for all the components.

The optical band gap (E_g) in the studied films can be found from the diffuse reflectance spectra (DRS). These spectra were obtained in the 190-1100 nm domain, using a Camspec501M spectrophotometer, provided with an integrated sphere, coated with BaSO4, against quartz as blank. From DRS, the optical absorption spectra were obtained. The Tauc expression refers to the dependence of the absorption coefficient, α, on the photon energy, hν:

$$(\alpha h\nu)^{1/n} = A(h\nu - Eg) \qquad (2)$$

where h is the Planck constant, ν is the frequency of the photon, E_g is the optical band gap energy, A is a constant which does not depend on energy, n is a factor which is 1/2 for the direct transitions and 2 for the indirect transitions of an electron. By using Kubelka–Munk function $F(R_d)$:

$$F(R_d) = \frac{\alpha}{m} = \frac{(1-R_d)^2}{2R_d} \qquad (3)$$

where R_d is the diffuse reflectance and m is the scattering factor [5], the measured reflectance spectra can be transformed into the absorption spectra [7]:

$$(Fh\nu)^{\frac{1}{n}} = A'(h\nu - Eg) \qquad (4)$$

To determine if the studied films are hydrophilic or hydrophobic, contact angle measurements were made, with a Data Physics OCA 15EC goniometer. To diminish evaporation effects and to avoid gravitational drop shape alteration, drop volumes of 500 nL (volume accuracy: 0.5 nL) were chosen. The films were photoactivated (at room temperature, 25 ºC, and 65 % environment humidity) with a high-pressure mercury lamp (150W) for 200 min, till the saturation of the photoactivation was observed. From 5 to 5 min, the contact angles were measured at 3 different locations on the films surface and each final value at each moment of time was calculated as the average of the 3 values.

RhB was the organic compound used to investigate the photocatalytic activity of the studied films, in the absence and in the presence of hydrogen peroxide (H_2O_2). The RhB solution was prepared with 3 mg/L initial dye concentration. 2 mL of 3 % H_2O_2 solution were added in 50 mL RhB solutions, to investigate the effect of H_2O_2 as co-catalyst. The films, placed with the face up on the bottom of the quartz cuvettes, were covered with 10mL of RhB solution and irradiated with a 100 W visible radiation lamp. The lamp was fixed at 10 cm from the film' s surface. To guarantee the adsorption - desorption equilibrium of the systems: photocatalyst-RhB,solution and the RhB solution itself, the systems were kept (before irradiation) 1 h in dark conditions. The absorption spectra of the RhB solutions were registered every 20 min and the dye concentration was determined with the Camspec 501M spectrophotometer at 553 nm (the RhB specific maximum absorption wavelength from the visible domain).

3. Results and discussion

The XRD patterns presented in Fig. 1 show that the undoped ZrO_2 film present a monoclinic structure (P121/c1 space group): m-ZrO_2, according to the standard JCPDS file no 98-008-2212.

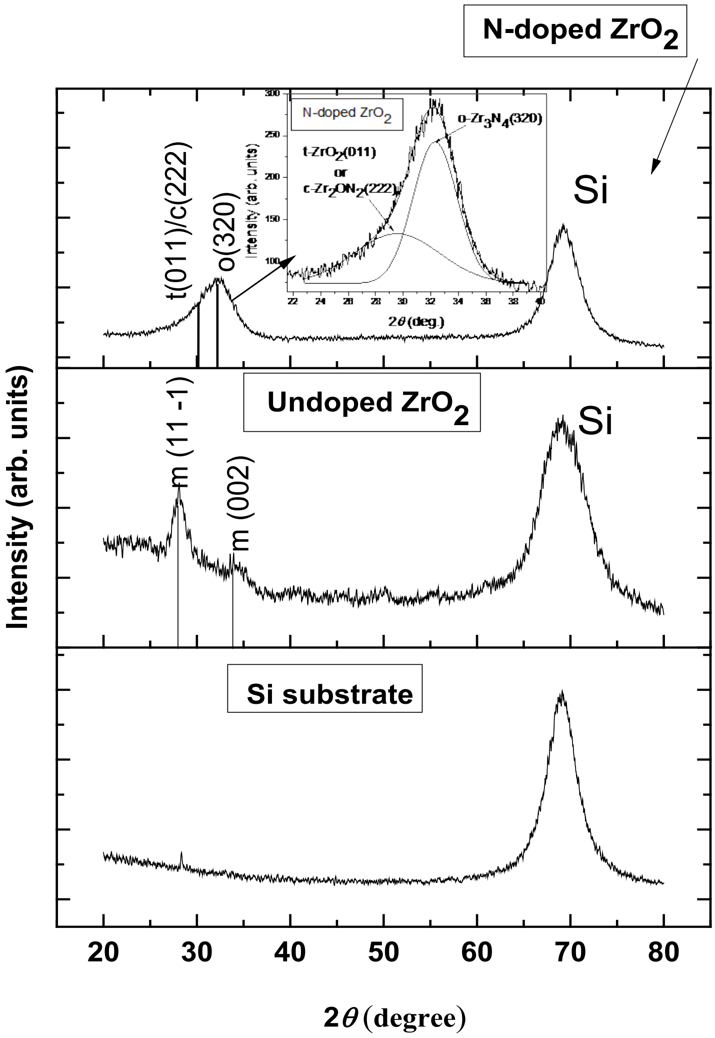


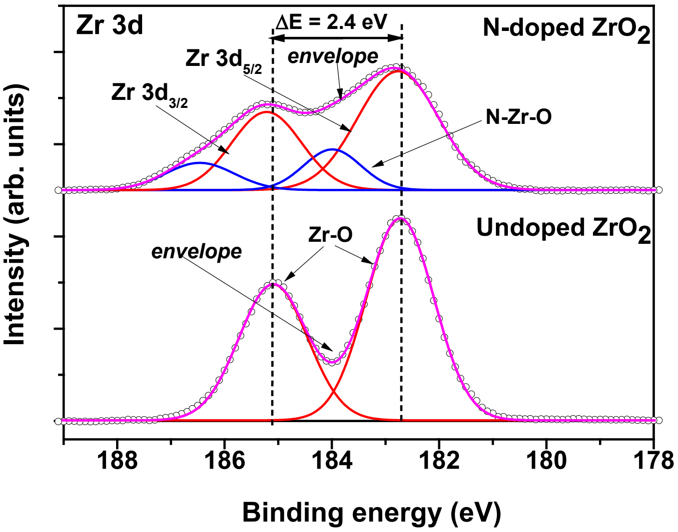
Fig. 1. The XRD patterns of the Si substrate and of the investigated films

By nitrogen doping, a phase transition takes place. According to JCPDS file no 98-008-2212 and JCPDS file no 98-003-5747, the broad peak located around

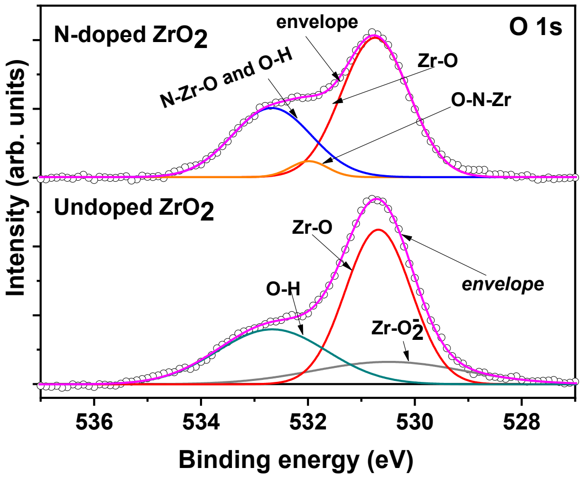
32.3 deg., could be assigned both to the tetragonal crystalline structure (P42/nmc space group): t-ZrO_2 (011) and to the orthorhombic crystalline structure (Pna21 space group): o-Zr_3N_4 (320), respectively. The deconvolution of the mentioned broad peak, using a Gaussian fit (Fig. 1-inset), confirms the above observation. The first peak, centred at 30.89 deg., can be assigned to t-ZrO_2 lattice, while the one centred at 32.442 deg. was assigned to o-Zr_3N_4 lattice. However, the accurate determination of the crystalline structure is very difficult due the reduced number of visible diffraction peaks [8,9]. For this reason, according to the literature [8,10] the peak located at 30.89 deg. can also be attributed to the cubic structure of zirconium oxynitride (Ia-3 space group, JCPDS file no 98-005-4208): c- Zr_2ON_2 (222). A decrease of the average crystallite size from 7.5 nm for the undoped film, to 4.5 nm for the N-doped one is observed, that will sustain the better hydrophilic and photocatalytic properties of the doped film.

The XPS spectra of undoped and N-doped ZrO_2 films were collected to investigate the surficial chemical composition of catalysts. The deconvoluted spectra of the Zr 3d, O 1s and N1s are shown in Fig. 2.

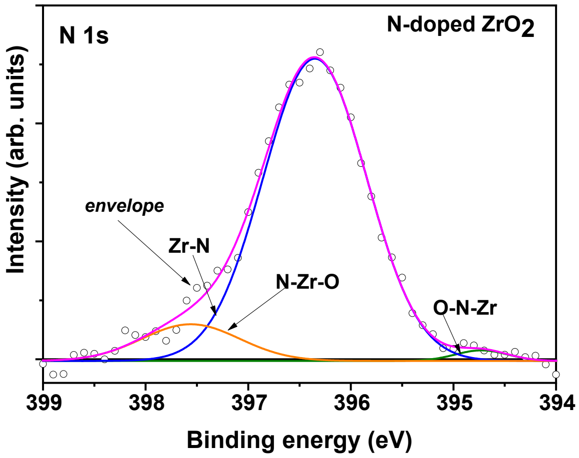
The high-resolution spectrum of Zr 3d of the undoped ZrO_2 film clearly displays the two peaks at 182.73 eV and 185.10 eV assigned to Zr $3d_{5/2}$ and Zr $3d_{3/2}$ core level and a spin orbit splitting of 2.4 eV which is consistent with the values for zirconium oxide [11]. The deconvolution of asymmetrical Zr 3d XPS signal revealed four components for N-doped ZrO_2 sample (Fig. 2a).



(a)



(b)



(c)

Fig.2. Zr 3d (a), O 1s (b) and N1s (c) XPS spectra of the studied films

The splitting of both Zr $3d_{5/2}$ and Zr $3d_{3/2}$ peaks evidently shows that the nitrogen atoms were included in the ZrO_2 lattice. The main peaks originated from Zr-O bonds were slightly shifted to the higher binding energy to 182.82 eV and 185.21 eV, and the less intense doublet located at 183.99 eV and 186.46 eV could be attributed to Zr-N bonds with about 21.70 % contribution from the total Zr-nonmetal (O and N) bonds. Correlated with XRD analysis, the existence of Zr-N and Zr-O bonds sustains that nitrogen atoms enter into the ZrO_2 matrix by substitution.

Fig.2b shows the O 1s XPS spectra of undoped and N-doped ZrO_2 films. The spectrum corresponding to the undoped ZrO_2 has a main peak at 530.68 eV, a shoulder at 532.67 eV and a third peak located at about 530. 47 eV. The peaks were assigned to Zr-O and O-H bonds (from adsorbed moisture), while the peak superposed with the main one could be assigned to the presence of vacancies occupied by the adsorbed oxygen or to the local asymmetry of the crystalline lattice. In the O1s XPS spectra of N-doped sample the peaks attributed to the adsorbed water is superposed with the peak centered at 532.48 eV related with O-Zr-N bonds. The small peak at 531.97 eV could include the contribution of N-O single bonds from O-N-Zr.

The N 1s XPS spectrum (Fig. 2c), obtained for N-doped ZrO_2, was deconvoluted in the two main components centered at 396.35eV and 397.56eV corresponding to the Zr-N (Zr_3N_4 zirconium nitride) and formation of N-Zr-O bonds, respectively, confirming the formation of oxynitride ($ZrO_{2-x}N_x$). In $ZrO_{2-x}N_x$ the nitrogen atoms may have more positive charge than nitrogen atoms of Zr_3N_4 and, consequently, a higher binding energy. The very small shoulder located at 394.73 eV can be a contribution of N-O bond from O-N-Zr groups.

When the photocatalytic activity of a material is investigated, information on the optical band gap energy is a required. To efficiently use the solar radiation, namely the visible part, which is about 45% of the solar spectrum, it is desired to have materials absorbent in the visible range. So, researchers try to modify the materials, while keeping other important characteristics, so that to be able to absorb in visible.

To calculate the optical band gap, the value $n = ½$ was taken in the relation (4), a characteristic value for the direct allowed transition which dominates over the optical absorption, according to ref. [5]. From the linear part of the dependences $(Fh\nu)^2 = f(h\nu)$, the extrapolated values of the optical bandgap, E_g, can be obtained for $Fh\nu = 0$, for each dependence (Fig. 3).

Undoped ZrO_2 has outstanding properties mentioned above, but it is absorbent in UV, so we expect a high value for E_g. Indeed, from Fig.3, E_g was found to be 3.8 eV for the undoped film. By nitrogen doping, an increase in the absorption of visible light can be accomplished, E_g decreasing to 2.4 eV.

From Fig.3 one can observe that there is a quasimonoton decrease of the contact angle of films' surface with the de-ionized water. The initial values of the contact angles can be correlated with the surface roughness of the samples. It is known that, in the case of hydrophilic surfaces, when the contact angles are under 90 deg., a higher roughness results in smaller contact angle values [12, 13]. The initial values of the contact angles, 90 deg. and 83 deg. for the undoped and N-doped film respectively, suggest that the N-doped film has a slightly more open surface.

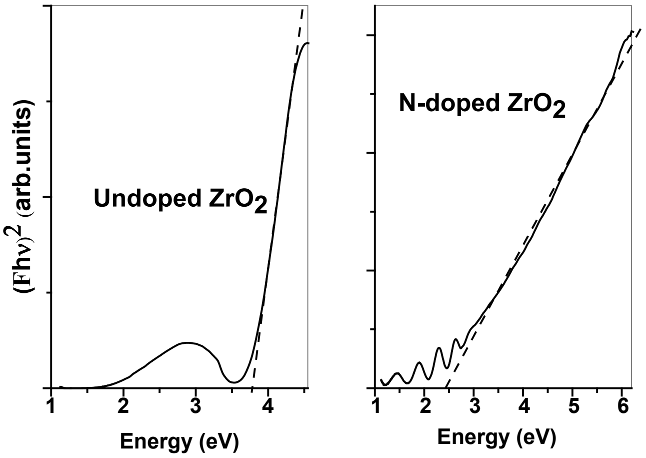


Fig. 3. The dependences $(Fh\nu)^2 = f(h\nu)$, for the investigated films

Contact angles can offer information on the surface tension (surface energy per unit of area), through the dependence [12]:

$$\sigma_S = \sigma_L^{3/2}\Phi^{-2}(1 + \cos\beta), \quad (5)$$

where β is the contact angle, σ_L is the surface tension of water (71.78×10^{-3} N/m at 25 °C) and $\Phi = 1.0$ J/m^2. According to (5) higher contact angles correspond to lower surface tension values, for hydrophilic surfaces.

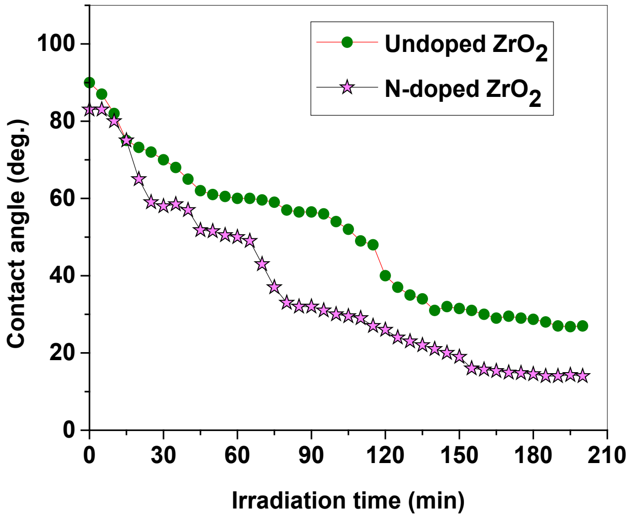


Fig. 4. Contact angle as a function of the irradiation time for the studied films.

As seen from Fig. 4, the N-doped ZrO_2 films show better hydrophilic properties reaching contact angles of 14 deg. in 200 min time of irradiation, approaching super-hydrophilicity (contact angles around 10 deg.), while the undoped film reaches contact angle saturation values of only 27 deg. An explanation could be related to the presence of the HO groups observed on the both films surface (Fig. 2b), but the finer grained surface of N-doped sample favors a better adsorption of the water molecules.

The photodegradation dependences of RhB under visible light irradiation on undoped and nitrogen doped ZrO_2 are shown in Fig. 5.

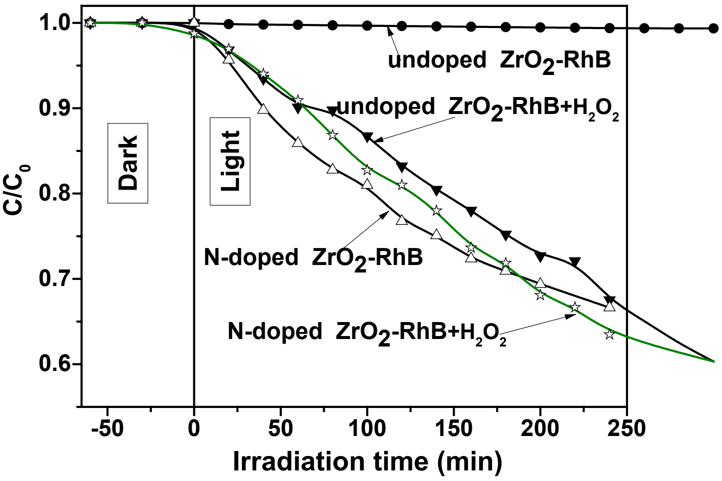


Fig. 5. Photodegradation trends of RhB as a function of irradiation time, in the presence and in the absence of H_2O_2

Under dark condition, the RhB concentration remained constant for all measurements. The photocatalytic process, coupled with H_2O_2 action, greatly promoted the decolorization of RhB in 250 min time of irradiation. Specifically, the degradation efficiency of RhB by the undoped ZrO_2 under illumination was only 0.2%, while in the presence of H_2O_2 was 33%, Noticeably, in the same time interval, the dye decolorization efficiency on ZrO_2 photocatalyst was enlarged (35%) when nitrogen and zirconia are coupled. The addition of hydrogen peroxide in N-doped ZrO_2 – RhB photoreaction system does not improve significantly the degradation yield (40%). This indicates that the photodegradation process and the presence of nitrogen atoms in the crystalline matrix of zirconia are not independent but synergistically promoted. The presented results suggest that the decolorization of RhB in aqueous solution was caused, firstly, by the photocatalytic activity of doped thin film sample under visible light irradiation, in contrast to the undoped system in which the photocatalytic efficiency is dependent of the H_2O_2 presence. An explanation of the improved photocatalytic activity in the presence of H_2O_2 is given by the fact that, by irradiation, H_2O_2 decompose, generating reactive oxygen species, like $HO^\bullet$, which bring a supplementary contribution to the decomposition of RhB.

The apparent rate constants, which give the efficiency of RhB photodegradation, were calculated with the values of maximum absorption and concentration values, C, at t time. They were determined from the plot of $\ln(C/C_0)$ as a function of the irradiation time, t (Fig. 6). All the reactions followed the first-order kinetics, as seen from the fairly good linear relationships presented in Fig. 6:

$$\ln(C/C_0) = -k_{app} \cdot t \tag{6}$$

where C is the dye concentration at the moment t, C_0 is the initial dye concentration, and k_{app} is the apparent equilibrium constant for the adsorption of the dye.

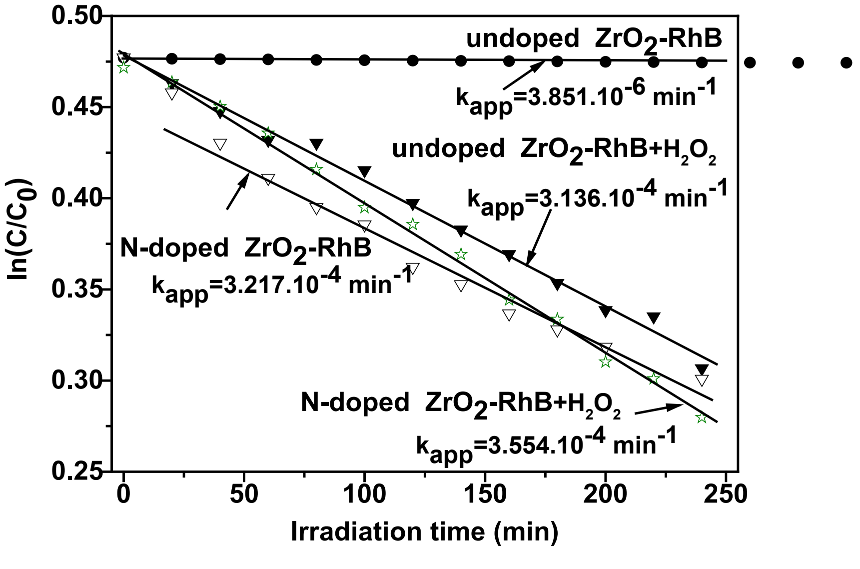


Fig. 6. Plots of $\ln(C/C_0)$ vs. irradiation time on the studied films, in the presence and in the absence of H_2O_2

The apparent rate constants were found to be $3.851 \cdot 10^{-6}$ min^{-1} for undoped zirconia, in the absence of H_2O_2, and about 100 times higher for the others photoreaction systems studied. These results suggest that all the doped systems show a higher photocatalytic activity for the RhB degradation in the visible light region. The higher photocatalytic activity could be associated with the smaller crystallite size of the N-doped films and its better hydrophilic properties, which determine the decrease of the electrons (e^-) and holes (h^+) recombination rate, the charge carriers being able to reach the surface of the photocatalysts, where the organic molecules decomposition can take place, by redox reactions [14]:

$$h^+ + RhB \rightarrow CO_2 + H_2O + other\ products \quad (7)$$

$$e^- + O_2 + RhB \rightarrow CO_2 + H_2O + other\ products \quad (8)$$

$$HO^{\cdot} + RhB \rightarrow CO_2 + H_2O + other\ products \quad (9)$$

The $HO^{\bullet}$ is the main active radical in the photodegradation process. The incorporation of N 2p in the zirconia matrix determines the narrowing of the band gap, facilitating the interbands electron transition.

4. Conclusions

We have obtained undoped and nitrogen-doped zirconia thin films by high power impulse magnetron sputtering. By N-doping of zirconia films, we have succeeded to obtain:

-Finer grained films,

-A shift of the fundamental absorption edge, from the UV domain, for the undoped film, to visible domain for N-doped film, an important finding, desired in photocatalysis,

-Better wettability properties by irradiation, the N doped ZrO_2 approaching super-hydrophilicity,

-Better activity in decomposing RhB, even in the absence of the co-catalysts.

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