Influence of dopants on TiO_2 thin films properties grown by pulsed laser deposition

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The work investigated doped TiO_2 thin films deposited by pulsed laser deposition method (PLD) on indium tin oxides (ITO) substrates. Titanium as target and nickel, zinc, palladium, aluminum, as dopants was used. The targets were irradiated by an Nd:YAG laser (355 nm, 5 ns, 35 mJ, 3 J/cm^2) at 40 mTorr oxygen pressure and room temperature (RT). The films were subjected to a thermal treatment at 350 ^{0}C for two hours in oxygen atmosphere. The film structure, surface morphology, composition, thickness and optical transmission were investigated. Only titanium sub-oxides were formed at RT; after annealing, the films became crystalline, corresponding to anatase phase at low dopant concentrations excepting aluminum when anatase was obtained regardless of dopant concentration. The deposition rate of the films was around 0.0052 nm/pulse. On the surface, the films present droplets with size in the range of 0.2 μm to 3 μm. The best optical transmission in the visible range was found for the films doped with the highest nickel concentration.

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1. Introduction

Titanium dioxide is a semiconductor with high importance in many fields and particularly in dye-sensitized solar cells (DSSCs) [1-8]. There is a high interest in engineering of composite TiO_2 photoelectrodes for DSSCs conversion energy improving. Different studies concerning the influence of aluminum in TiO_2 film structure with application in DSSCs are reported [9-11].

The goal of this study was to deposit doped TiO_2 films, by laser ablation on ITO substrate and to investigate the influence of dopants on the structure, morphology and optical transmission of the films.

The investigations on the structure, surface morphology, composition and transmission of the films were performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X ray spectroscopy (EDX) and optical transmission spectrometry.

2. Experimental

A Nd:YAG laser operating at 355 nm, 10 pps repetition rate, with 5 ns pulse duration, 35 mJ energy/pulse and 3 J/cm^2 fluence, was used. Titanium (99.99%) as target, and nickel (99.95%), zinc (99.95%), palladium (99.9%) and aluminum (99.9%) as dopants, were used. The dopant concentration was adjusted by changing the ratio between the number of pulses impinging the titanium and dopant target. The study was performed for the following ratio values titanium/dopant: 198/2, 196/4, 188/10, 178/20. The total number of laser pulses impinging the target was 216000.

TiO_2 doped thin films were deposited on ITO coated glass substrate (KINTEC, thickness 100 nm, sheet resistance 17.5-18 Ω/sq, transmittance 85-86% for λ=400-1000 nm). Target-substrate distance was 4.5 cm. Before deposition, the ablation chamber was evacuated to a base pressure of $3x10^{-4}$ Torr. Previous investigations on deposition of crystalline TiO_2 thin films [12] showed that an incipient crystallinity starts at 20 mTorr oxygen pressure and the best crystallinity (anatase phase) is attained at 40 mTorr; therefore during the experiments, the oxygen pressure was maintained at 40 mTorr. After deposition, the films were subjected to a thermal treatment at 350 ^{0}C for 2 hours in oxygen atmosphere. The films were characterized by a Bruker-AXS D8 Advance diffractometer (Cu $K\alpha_1$), a scanning electron microscope (Quanta Inspect F) with EDX, and a Cintra 10e spectrophotometer.

3. Results and discussion

XRD spectra of the TiO_2 films doped are presented in figures 1-4. In Fig. 1 are shown XRD spectra of the films doped with nickel deposited at RT (a) and annealed at 350 ^{0}C (b). One can see that at RT only TiO, Ti_3O, peaks are formed and Ni peak appear only at the lowest dopant concentration. After annealing, at low nickel concentrations 198/2, 196/4 ratio titanium/dopant, the film becomes crystalline corresponding to TiO_2 anatase phase, and increasing dopant concentration to 188/10 and 178/20 ratio, incipient peaks corresponding to TiO_2 crystalline phases formed.

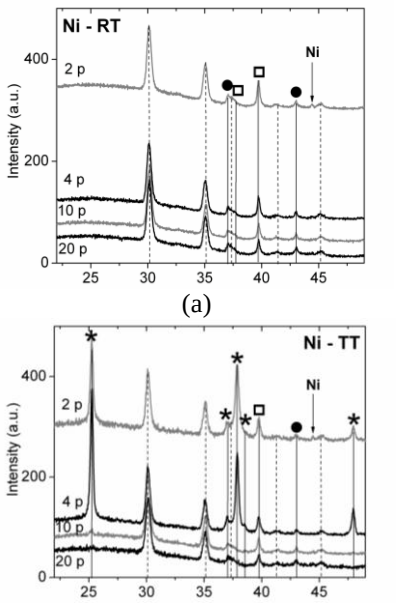


Fig. 1. XRD spectra of TiO_2 films doped with nickel (titanium/nickel laser pulses: 198/2, 196/4, 188/10, 178/20); (a) deposited at RT; (b) annealed at 350 ^{0}C.

Concerning the influence of zinc on the structural characteristics of the films, one can be seen from the Fig. 2 (a) that at RT, at low dopant concentration, no ZnO or Zn peaks formed; Increasing the dopant concentration to 188/10 and 178/20, Zn and ZnO appeared. Concerning TiO_2 formation, similar to nickel, crystalline TiO_2 anatase phase appears only after thermal treatment Fig. 2 (b) at low dopant concentration.

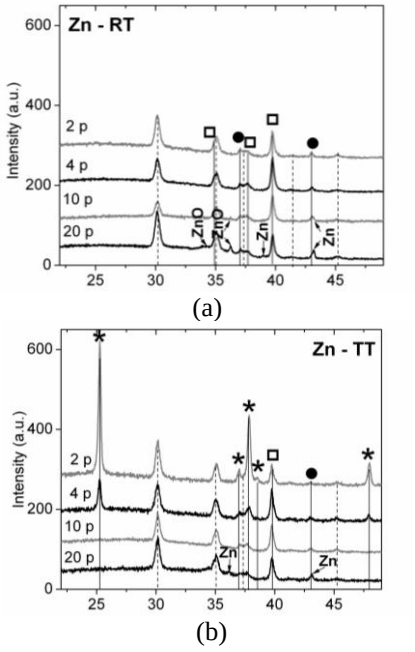


Fig. 2. XRD spectra of TiO_2 films doped with zinc (titanium/zinc laser pulses: 198/2, 196/4, 188/10, 178/20); (a) deposited at RT; (b) annealed at 350 ^{0}C.

In the case of the films doped with palladium, (Fig. 3 (a) and (b)), only peaks characteristic to Pd_3Ti are formed at RT (Fig. 3(a)) at the highest palladium concentration and Ti_3O and TiO appeared regardless of dopant concentration. After annealing, (Fig. 3(b)), PdO was formed only at the highest palladium concentration and TiO_2 anatase is formed for low dopant concentration (198/2 and 196/4).

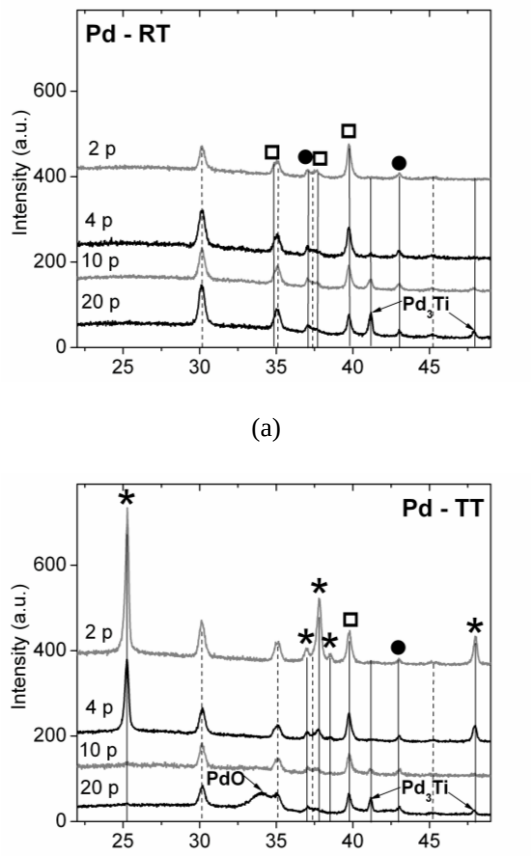
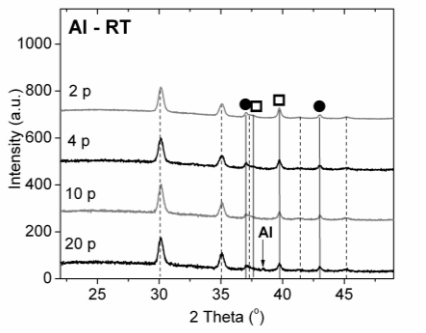
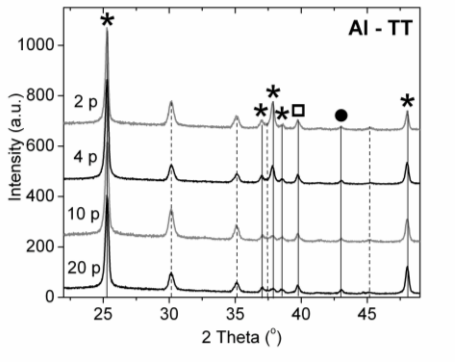


Fig. 3. XRD spectra of TiO_2 films doped with palladium (titanium/palladium laser pulses: 198/2, 196/4, 188/10, 178/20); (a) deposited at RT; (b) annealed at 350 ^{0}C.

In the case of aluminum, the dopant influence on the film structure is different concerning anatase formation. In Fig. 4(a), at RT only an incipient peak corresponding to aluminum is formed at the highest dopant concentration. After annealing, Fig. 4(b), in contrast with nickel, zinc and palladium, when TiO_2 anatase peaks were formed only at the lowest dopant concentration, in the case of aluminum, anatase phase formed for each doping ratio.



(a)



(b)

*TiO_2 anatase/•TiO/□Ti_3O

Fig. 4. XRD spectra of TiO_2 films doped with aluminum (titanium/aluminium laser pulses: 198/2, 196/4, 188/10, 178/20); deposited at RT; (b) annealed at 350 ^{0}C.

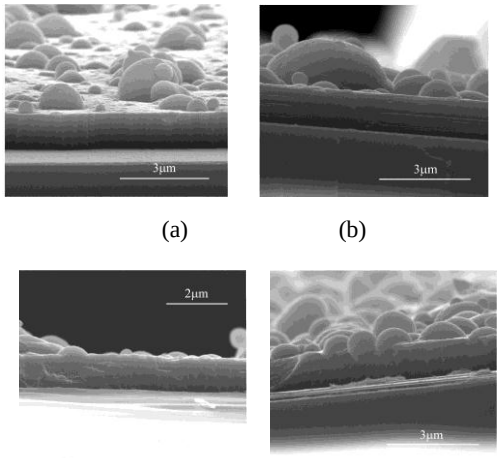
Using Debye Scherrer formula, the mean crystallite sizes of TiO_2 were determined and the results are summarized in Table 1. One can see that the average size of the doped TiO_2 particles is around 15 nm, regardless of dopant.

Table 1. TiO_2 particles average size for different dopants.

TiO_2 films doped and annealed at 350 ^{0}C	TiO_2 doped with Ni	TiO_2 doped with Zn	TiO_2 doped with Pd	TiO_2 doped with Al
Average size (nm)	15.1	14.4	15	15

In the following, SEM images (Fig. 5 (a)-(d)) of the TiO_2 doped films with the highest dopant concentration (178/20) are presented.

It can be observed that on the surface, the films present droplets ejected from the target in the ablation process. The size of the droplets attached on the film surface is in the range of 0.2 μm to 3 μm. In the cross section, the films are very compact, presenting columnar growths.



(a) (b)

(c) (d)

Fig. 5. SEM images of doped TiO_2 films after annealing process178/20 ratio titanium/dopant
(a) 20 pulses impinging nickel target;
(b) 20 pulses impinging zinc target;
(c) 20 pulses impinging palladium target;
(d) 20 pulses impinging aluminum target.

The transmission spectra of TiO_2 films doped with nickel, zinc, palladium, aluminum, are presented in figures 6-9. For the films doped with nickel (Fig. 6), as the dopant concentration increases, the film transmission increases from 22% to 40% at 500 nm.

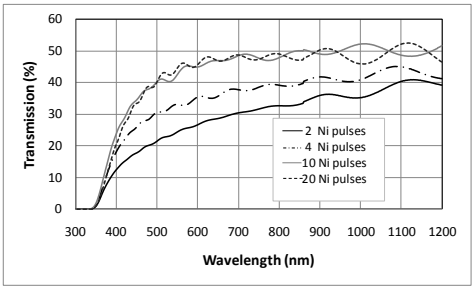


Fig. 6. Nickel doped TiO_2 films transmission spectra.

In the case of TiO_2 films doped with zinc (Fig. 7), the film transmission increases up to dopant concentrations of 188/10, when is maximum, and decreases for 178/20, the transmission being about 28% in the visible range at 500 nm.

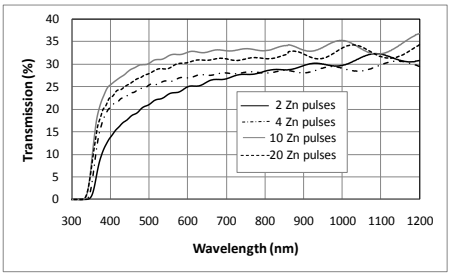


Fig. 7. Zinc doped TiO_2 films transmission spectra.

Using palladium as dopant, the optical transmission is very low as is presented in Fig. 8. One can see that as the amount of dopant increases, the film transmission decreases to about 2% at 500 nm for the highest palladium concentration (178/20).

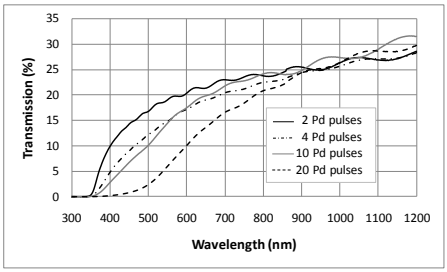


Fig. 8. Palladium doped TiO_2 films transmission spectra.

Concerning the influence of aluminum on the film transmission one can be seen from the Fig. 9 a similar behavior to zinc; the maximum transmission of 35% occurs at ratio 188/10 at 500 nm.

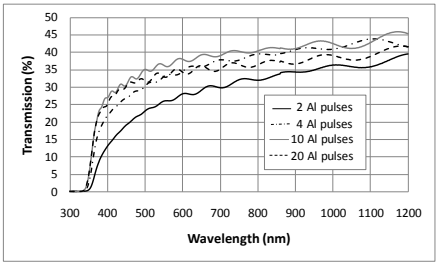


Fig. 9. Aluminum doped TiO_2 films transmission spectra.

In Table 2 are presented deposition rates of the doped TiO_2 films and atomic concentration of the dopant as function of titanium/dopant ratio. It can be seen that the deposition rate was around 0.0052 nm/pulse in all cases, excepting zinc deposition rate which was a little bit higher.

From EDX measurements, atomic concentration of the dopant was also determined. If the number of the laser pulses impinging on dopant target increases, dopant concentrations increases as are summarized in the Table 2.

Table 2. Deposition rate and atomic concentration of doped TiO_2 films.

Dopant	Ratio dopant/titanium	Deposition rate [nm/pulse]	Average deposition rate [nm/pulse]	Atomic concentration (%)
Nickel	2/198	0.0057	0.00525	1.1
	4/196	0.0056		1.6
	10/188	0.0046		5
	20/178	0.0051		7
Zinc	2/198	0.0060	0.00597	2.9
	4/196	0.0061		5.5
	10/188	0.0061		6.2
	20/178	0.0057		10.5
Palladium	2/198	0.0053	0.00527	1.3
	4/196	0.0053		1.7
	10/188	0.0054		4.8
	20/178	0.0051		10.8
Aluminum	2/198	0.0053	0.00525	2.3
	4/196	0.0048		3.6
	10/188	0.0058		10.4
	20/178	0.0051		16.5

4. Conclusions

Crystalline doped TiO_2 films anatase phase were obtained using PLD method after annealing treatment at low nickel, zinc, palladium dopant concentration while aluminum favored formation of TiO_2 anatase phase regardless of dopant concentration. The films presented some droplets on the surface with sizes in the range of 0.2 μm to 3 μm. The size of the grains in the film structure was around 15 nm. The deposition rate was around 0.0052 nm/pulse excepting Zn with 0.0059 nm/pulse. The best optical transmission was for the films doped with nickel at 178/20 ratio.

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