"Alexandru Ioan Cuza" University Iaşi

Faculty of Physics

SUMMARY OF PhD THESIS

# CONTRIBUTIONS TO THE STUDY OF HYDROPHILIC AND PHOTOCATALYTIC PROPERTIES OF $TiO_2$ THIN FILMS DOPED WITH TRANSITION METALS

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# Introduction

The main objective in this work was to improve the photocatalytic and hydrophilic properties of titanium dioxide ($TiO_2$) thin films. To achieve this objective we have considered obtaining and characterization of undoped and doped $TiO_2$ thin films with atoms of Nb, Ni, Mo and Cr in increasing concentrations through different methods (spray pyrolysis, spin coating, sputtering). We have studied the influence of substrate nature (glass, ITO glass, Si) on the structure, morphology and, as a consequence, on the optical, photocatalytic and hydrophilic properties. For thin films with low hydrophilic properties, we tried to improve the hydrophilic behavior by depositing Pt islands on their surfaces. To study the photocatalytic properties we have considered the decomposition of some organic compounds such as oleic acid and methylene blue.

The thesis is structured in three chapters. The first chapter presents some theoretical aspects related to the mechanisms that rule the hydrophilic and photocatalytic behavior of a semiconducting material and, referring to titanium dioxide, we have reviewed the current state of research. Chapter II contains a description of the methods used to deposit and characterize the studied films, and the last chapter contains experimental results and their interpretations.

## CHAPTER I
## HYDROPHILIC AND PHOTOCATALYTIC PROPERTIES OF THE TITANIUM DIOXIDE. CURRENT RESEARCH IN THE FIELD.

Titanium dioxide is a promising photocatalytic material which, under the action of UV radiation, possesses two important properties for the environment: a high oxidation power of the organic pollutants, and a high affinity for water, being used in the purification of air, water, sterilization, self-cleaning, etc. Compared to other photocatalytic semiconductors (ZnO , CdS , $SiO_2$) , $TiO_2$ is chemical and mechanical stable, non-toxic, has a fairly low cost and a high active surface area, etc. In addition to these benefits, titanium dioxide presents a great disadvantage. The width of the optical band gap of $TiO_2$ (3.2 eV for the anatase phase), allows for photoexcitation only the radiation having a wavelength less than 390 nm (in the near UV). As a consequence, $TiO_2$ cannot effectively use solar radiation, because from sunlight spectrum only 10 % of energy is on the UV range, and about 5% is in the near UV range.

## CHAPTER II

## EXPERIMENTAL TECHNIQUES

$TiO_2$ thin films doped with different impurities was deposited on various substrates (glass , ITO/glass , Si) using three different deposition techniques:

- spray pyrolysis deposition
- sol-gel deposition ( spin coating)
- sputtering deposition

We have analyzed their structure, morphology, surface elemental composition, and correlations were made with the optical hydrophilic and photocatalytic properties.

## CHAPTER III

## EXPERIMENTAL RESULTS AND DISCUSSION

### III.1 Nb - doped $TiO_2$ thin films deposited by sol - gel method

We have obtained by spin coating method, amorphous $TiO_2$ thin films doped with ascending Nb content, very smooth, with roughness values of less than 5 nm, deposited on the glass substrates.

The Ti 2p XPS spectra of all the $TiO_2$:Nb samples demonstrate the presence of both $Ti^{4+}$ and $Ti^{3+}$ states.

From Table 3.1 it can be seen that the optical band gap increase by increasing the Nb content in the films, the explanation being made for the first time using small polaron hopping (SPH) model.

*Table 3.1 The thickness of the samples (d); the root mean square roughness ($R_{rms}$); the optical band gap ($E_g$); Ti/Nb atomic concentration ratio in the starting solutions; Ti/Nb atomic concentration ratio as resulted from XPS; the elemental composition from the XPS data*

| | d (nm) | $R_{rms}$ (nm) | $E_g$ (eV) | Ti/Nb (at.%) sol. | Ti/Nb (at.%) XPS | Elemental composition from XPS | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | O (at.%) | Ti (at.%) | Nb (at.%) | x | δ |
| $TiO_2:Nb_{0st}$ | 99 | 2,1 | 3,25 | 0,0 | 0,0 | - | - | - | - | - |
| $TiO_2:Nb_{1st}$ | 78 | 2,6 | 3,41 | 8,18 | 11,39 | 67,8 | 29,6 | 2,6 | 0,08 | 2,10 |
| $TiO_2:Nb_{2st}$ | 86 | 2,9 | 3,53 | 1,02 | 1,45 | 68,1 | 18,9 | 13,0 | 0,40 | 2,13 |
| $TiO_2:Nb_{3st}$ | 97 | 4,8 | 3,58 | 0,50 | 0,46 | 69,4 | 9,6 | 21,0 | 0,69 | 2,27 |

The presence of Nb in the $TiO_2$ matrix determine the superhydrophilicity (contact angles smaller than 10 degrees) of these films, with the initial values of the contact angles lower than 5 degrees, while the undoped sample shows an initial contact angle of approximately 40 degrees (Fig. 3.1). We have attributed this superiority to the presence of $Ti^{3+}$ (sustaining Wang's model),

whose area increases with increasing dopant content in the samples, and due to the increased width of the optical band gap, since it has been demonstrated that the lifetime values of the electron-hole pairs occurring upon UV irradiation in the surface region are directly proportional to $E_g$ *[Hao et al. 2002]*.

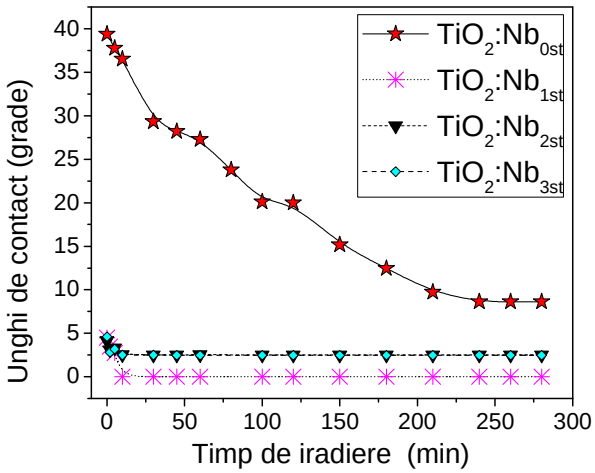


***Fig. 3.1*** *Contact angle vs. UV irradiation time plots for the pristine $TiO_2$ and $TiO_2$/Nb samples*

Studies of the decomposition of the oleic acid applied on the films surface, show that the films needed more than 30 hours to recover their initial contact angles had in the absence of the oleic acid (Fig.3.2). By continuing the UV irradiation, the contact angles keep on decreasing, tending to reach the values corresponding to the saturation of the photoactivation previously observed when investigated the hydrophilic properties of these films.

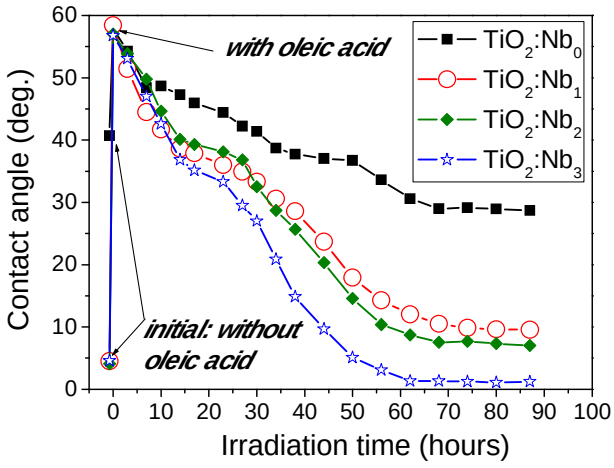


***Fig. 3.2*** *Modification of the contact angle after depositing the oleic acid layer, and its variation as a function of the irradiation time*

The optical transmittance through an aqueous solution containing methylene blue increases till 97 %, in 18 days, in the presence of the UV irradiated sample S3, and the reaction rate was found to be 0.006 $hours^{-1}$.

These Nb doped films, even highly superhydrophilic in the presence of the UV radiation, decompose the organic compounds in higher times than previously found for other dopants. This observation, together with the one that we can still detect the presence of carbon on the surface of the film, even in its superhydrophilic state with a contact angle close to 0 deg. (Fig. 3.3), show that hydrophilicity is ruled by a different mechanism than photocatalysis, even if it can provide information on the oxidation power of $TiO_2$.

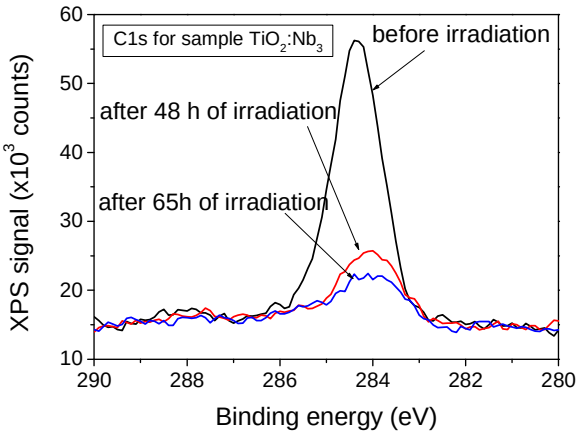


***Fig. 3.6*** *C 1s XPS spectra of the film S3 covered with oleic acid, before the UV irradiation, and after 50 hours and 65 hours after irradiation*

### III.2 Nb - doped $TiO_2$ thin films deposited by spray-pyrolysis method

Undoped $TiO_2$ and Nb-doped $TiO_2$ thin films have been deposited by spray pyrolysis method on ITO/glass substrates. All the as-deposited films are amorphous, as shown by X-Ray Diffraction (XRD). Under certain conditions of heat-treatment in air, the films deposited by pyrolysis became pure anatase and a slight decrease of average crystallite size was observed with the increase of the Nb content.

The heat-treated samples are superior as concern the hydrophilic properties, then their as-deposited counterparts (Fig. 3.4), fact explained by the anatase phase development in the heat-treated samples. Ana tase phase has a higher active area, leading on one hand to a higher adsorption capacity of water molecules and, on the other hand, increases the density of allowed energy states in the optical band gap, resulting a reduction of the electrons-holes recombination rate. Remarkable are not only the obtaining of contact angles less than 3 degrees in very short times, but also the long recovery time (more than 6 days for the heat treated samples) (Fig. 3.5).

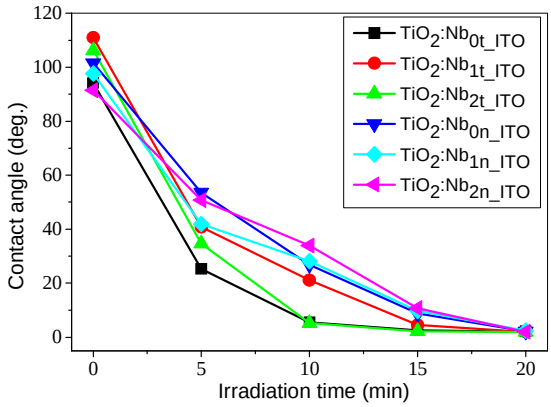


***Fig.3.4*** *Contact angle as a function of the irradiation time*

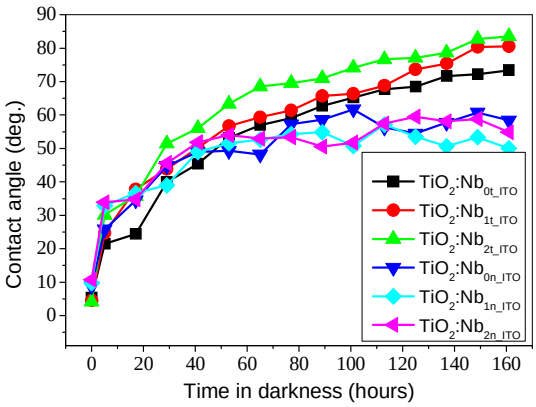


***Fig.3.5*** *Contact angle versus time dependences, as monitored during the back-reaction regime*

### III.3 Ni - doped $TiO_2$ thin films deposited by spray-pyrolysis method

Undoped and Ni-doped $TiO_2$ thin films were deposited by the spray pyrolysis method on glass and ITO (Indium tin oxide)/glass substrates heated at 100 ºC. The as deposited films were amorphous as indicated by XRD analysis. Thin films deposited on the glass substrates remains amorphous after heat treatment, except the undoped one which developed the anatase phase. The heat treatment drives to the appearance of the anatase phase for samples deposited on ITO/glass substrates, with the average crystallite size values under 14 nm.

X-Ray Photoelectron Spectroscopy (XPS) analysis confirmed the presence of Ni embedded in the $TiO_2$ matrix. We have found out that, by Ni doping, hydrophilic properties decrease for the $TiO_2$ films (Fig.3.6), with increasing dopant concentration, depending on the nature of the substrate that brings its own contribution on their structure and morphology of the studied samples.

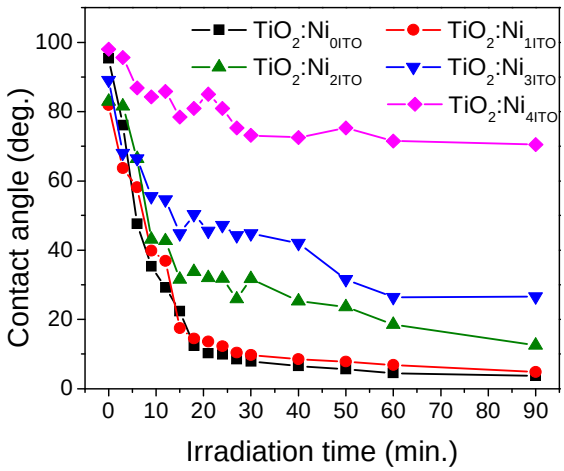


***Fig. 3.6*** *Contact angle as a function of the irradiation time for the sample deposited on ITO/glass substrate*

### III.4 Mo - doped $TiO_2$ thin films deposited by spray-pyrolysis method

Undoped and Mo-doped $TiO_2$ thin films have been obtained by the spray pyrolysis method on glass and Si substrates. The as-deposited films were amorphous, while the heat treated ones are polycrystalline, having an anatase phase, or mixed anatase/rutile phases, as a function of the substrate used; the development of the rutile phase is enhanced, as a combined effect of both doping and substrate nature.

XPS analysis revealed the fact that Mo enters the $TiO_2$ matrix as $Mo^{5+}$ state; the films retained a smaller amount of Mo (0.1 at. % and 0.2 at. %) compared to the amounts from the solution synthesis report (Table 3.2).

***Table 3.2.*** *Dopant concentrations in the initial solutions; dopant concentrations resulting from XPS; the anatase average crystallite size ($D_A$) and rutile ($D_R$), the weight percentage of the anatase phase ($W_A$) and the optical band gap ($E_g$).*

| Sample | Mo $(at.\%)_{sol.}$ | Mo $(at.\%)_{XPS.}$ | $D_A$ (nm) | $D_R$ (nm) | $W_A$ (%) | $E_g$ (eV) |
|---|---|---|---|---|---|---|
| $TiO_2$:$Mo_{st0}$ | - | - | 12,3 | - | 100 | 3,58 |
| $TiO_2$:$Mo_{st1}$ | 0,5 | 0,1 | 12,1 | - | 100 | 3,55 |
| $TiO_2$:$Mo_{st2}$ | 1 | 0,2 | 12,1 | - | 100 | 3,53 |
| $TiO_2$:$Mo_{Si0}$ | - | - | 13,2 | 4,9 | 60 | - |
| $TiO_2$:$Mo_{Si1}$ | 0,5 | 0,1 | 13,1 | 9,9 | 42 | - |
| $TiO_2$:$Mo_{Si2}$ | 1 | 0,2 | 13,4 | 12,5 | 26 | - |

Mo doping induces a shift of the optical band gap values towards lower energies, which is beneficial to the photocatalysis, but the shift is very small, as a consequence of the small amount of Mo embedded in $TiO_2$ matrix (as seen from XPS).

The films hydrophilic behavior under UV irradiation (Fig.3.7) show that superhydrophilicity is reached by all the irradiated samples with one exception: the undoped $TiO_2$ sample deposited on Si substrate. The anatase films obtained on glass substrates present excellent hydrophilic properties (contact angles very close to 0 deg. after less than 12 min of UV irradiation), independent on Mo doping, while the anatase/rutile films obtained on Si substrates have lower performances (contact angles of about 9 and 5 deg. for the doped films, after 60 min of UV irradiation, and 29 deg. for the undoped film) which are enhanced by Mo doping.

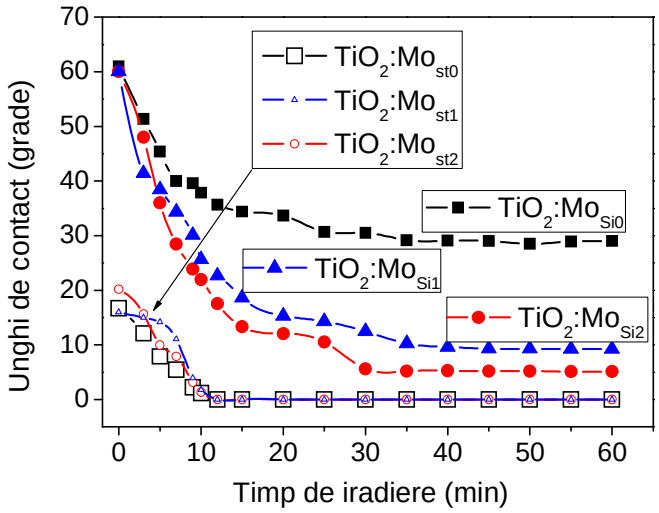


***Fig. 3.7*** *Contact angle as a function of the irradiation time for all the studied samples [Adomnitei et al. 2014]*

A study on the relationship between hydrophilicity and the amount of the adsorbed hydroxyl groups was performed based on FT-IR results realized on all the films, before and after irradiation, and explains the superiority of the anatase phase concerning the hydrophilic properties. Mo enhances wettability of the samples deposited on Si but, in the mean time, it determines a rise in the rutile weight percentage, as a combined effect with the substrate nature.

Studies of the decomposition of the oleic acid, applied on films surfaces, confirm that the films with higher hydrophilic performances are also good photocatalysts, and we mention all the films deposited on glass substrates, which decompose the oleic acid in 7 to 17 h, as a function of doping.

### III.5 Cr - doped $TiO_2$ thin films deposited by RF magnetron sputtering method

Undoped and Cr-doped $TiO_2$ thin films were deposited by RF magnetron sputtering (13.56 MHz) on heated glass substrates (300 °C).

The as deposited films are polycrystalline. Chromium induces a phase transformation from anatase to rutile and the all the crystallites size decreases with the increase in the Cr concentration.

The optical band gap values ($E_g$) of the studied films, decrease from 3.31 eV for the undoped sample to 2.57 eV for the sample with the highest Cr content, pointing out that these films deserve attention in studying their self cleaning properties. In the same time, the films did not show the promising hydrophilic properties (Fig.3.7). The explanation could be related to the different Cr concentrations. For high dopant concentrations, as in our case, the recombination

rate of the photogenerated electrons and holes could increase as a consequence of the decrease of the distance between trapping sites.

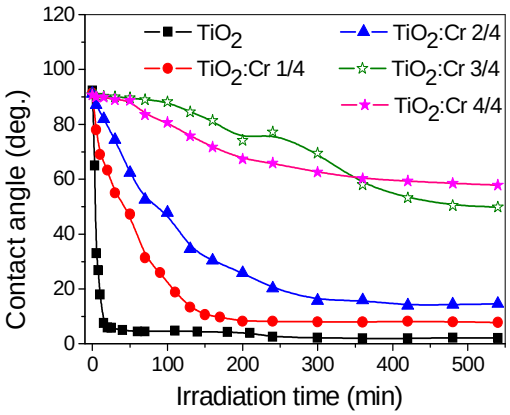


***Fig. 3.7*** *Contact angle as a function of the irradiation time for the $TiO_2$ films having different Cr percentages*

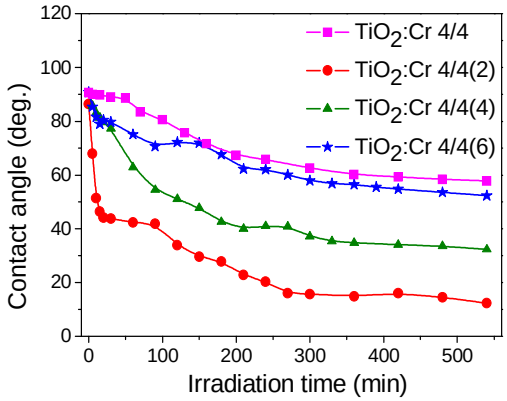


***Fig. 3. 8*** *Contact angle as a function of the irradiation time for the $TiO_2$ films with the highest Cr concentration ($TiO_2$:Cr 4/4), having different Pt islands deposited on their surfaces*

The $TiO_2$ film having the highest Cr content ($TiO_2$:Cr 4/4) presents the worse hydrophilic properties, but it is in the mean time the most absorbent in visible, so it deserves an improvement of its self cleaning properties. We want to test a surface modification method for the enhancement of its hydrophilic properties. In this purpose we have deposited an increased number of Pt islands on its surface, letting a large enough surface area of $TiO_2$ to be exposed to the radiation. From Fig. 3.8 it can be seen an improvement in hydrophilic properties by Pt islands covering. We may remark also the sharp decrease of the contact angle of the film with 2 Pt islands, till 44 deg. in about 17 min of UV irradiation. Probably there is an optimum Pt coverage area, lower than 0.07% (2 islands), for which better hydrophilic properties can be achieved, but this will be a challenge for the future.

The explanation was based on FT-IR and XPS analysis, performed on the UV irradiated and non-irradiated films, which gives information on the relationship between hydrophilicity and the amount of the adsorbed hydroxyl groups.

## Conclusions

- I have improved the spray pyrolysis deposition system existing in the laboratory, establishing optimum conditions for achieving the desired thin films.
- By doping the $TiO_2$ thin films with Nb, they do not become absorbant in the visible region as it was desired, however the hydrophilicity and the photocatalytic properties are improved. Among other models in the literature, which were proposed to explain the hydrophilicity mechanism, I have sustained the Wang's model, related to the presence of $Ti^{3+}$ states with increased area, as Nb concentration increases in $TiO_2$ films.
- I have shown that hydrophilicity is governed by a different mechanism than photocatalysis, even if it can provide indirect information about the $TiO_2$ oxidation power. At the films surface, even for contact angles close to 0 deg., the presence of carbon sill can be detected, confirming the idea that superhydrophilic surfaces are not simple "clean surfaces".
- Mo doping induces a very small shift of the optical band gap values towards lower energies, and better hydrophilic and photocatalytic performances; the thin films deposited on glass substrates (only anatase phase) are more efficient than those deposited on Si substrates (mixed anatase/rutile phases), contributing to the debate in the literature regarding the photocatalytic and hydrophilic performances of the anatase $TiO_2$ versus rutile $TiO_2$.
- Cr-doping induces an increase in the rutile weight percentages, a more compact structure, a significant red shift of the $TiO_2$ absorption edge, but poor hydrophilic properties.
- We have chosen the worst hydrophilic sample and we have covered it with Pt islands. Its hydrophilic properties evidently improve, more obvious for a metal coverage of 0.07% (2 islands).
- We have explained the appearance of the $Ti^{3+}$ state only in the titanium XPS spectra of the irradiated film without Pt, by the electron transfer from the oxygen atom of a coordinated water molecule, or of a hydroxyl group, to $Ti^{4+}$ or $Cr^{3+}$, activated by the UV radiation, taking into account their reduction potentials. For the irradiated Pt covered films, the $Ti^{3+}$ state is not present, probably because Pt accepts the excited electrons that appear by irradiation easier than $Ti^{4+}$. Instead, for these films, a supplementary Ti state, rarely reported in the literature, located at higher binding energies than the one corresponding to $Ti^{4+}$, was evidenced and explained by more powerful Ti-O bonds, close to double bonds, based on FT-IR analysis.

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**References (selection)**


- Adomnitei C., Luca D., Girtan M., Sandu I., Nica V., Sandu A.V., Mardare D., *Journal of Optoelectronics and Advanced Materials* 15 (2013) 519-522
- Adomnitei C., Tascu S., Luca D., Dobromir M., Girtan M., Mardare D., *Bulletin of Materials Science* xx (2015) xxx - (acceptată pentru publicare)
- Adomnitei[1] C., Cornei N., Luca D., Girtan M, Sandu I., Vasilache V., Dobromir M., Mardare D., *Journal Of Optoelectronics and Advanced Materials* 17 (5-6) (2015) 889 - 893
- Adomnitei[1] C., Ghiorghita L., Mardare D., *14th International Balkan Workshop on Applied Physics*, Constanţa, Romania, July 2-4, 2014, (poster)
- Adomnitei[3] C., Tascu S., Mita C., Mardare D., *10th International Conference on Physics of Advanced Materials* (ICPAM 10) 22 - 28 September 2014, Universitatea "Alexandru Ioan Cuza" din Iasi, Romania, (poster)
- Apetrei R., Catrinescu C., Mardare D., Teodorescu C. M., Luca D., Thin Solid films 518 (2009) 1040–1043
- Crisan D., Dragan N., Raileanu M., Crisan M., Ianculescu A., Luca D., Nastuta A., Mardare D., *Appl. Surf. Sci.* 257 (2011) 4227-4231
- Fujishima A., Rao T.N., Tryk D.A., *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 1 (2000) 1–21
- Fujishima A., Zhang X., Tryk D.A., *Int. J. Hydrogen Energ.* 32 (2007) 2664–2672
- Hao W. C., Zheng S. K., Wang C., and Wang T. M., *J. Mater. Sci. Lett*. 21(20), 1627 (2002).
- Hashimoto K., Irie H., Fujishima A., *Japanese Journal of Applied Physics*, 44 (2005) 8269-8285
- Mardare D., Cornei N., Luca D., Dobromir M., Irimiciuc S.A., Pungă L., Pui A., Adomniței C., Journal Of Applied Physics, 115 (2014) 213501
- Mardare D., Stancu A., Tiron V., Manole A., Adomnitei C., Florea D., *J Vac Sci Technol A*, xxx (2015) - trimisă spre publicare
- Mardare D., Yildiz A., Girtan M., Manole A., Dobromir M., Irimia M., Adomnitei C., Cornei N. and Luca D., *Journal of Applied Physics* 112 (2012) 073502
- Mardare[1] D., Yildiz A., Girtan M., Manole A., Dobromir M., Adomnitei C., Florea D., Cornei N., Luca D., *NanoSEA 2012 – International Conference on NANO-strutures Self-Assembly*, 25-29 june 2012, Sardinia, Italy
- Oja A.I., Junolainena A., Miklib V., Danilsona M., Krunks M., *Applied Surface Science* 256 (2009) 1391–1394
- Rusu G.I., Rusu I., Stamate M., Introducere în fizica semiconductorilor, Ed. Plumb, Bacau (1997)
- Thompson T.L., Yates J.T. Jr., *Chem. Rev.*, 106 (2006) 4428-4453
- Wang R., Hashimoto K., Fujishima A., Chikuni M., Kojima E., Kitamura A., Shimohigoshi M. & Watanabe T., *Nature*, 388 (1997) 431-432
- Yu J.C., Yu J., Ho W., Jiang Z., Zhang L., *Chem Mater* 14 (2002) 3808-3816


**ISI Thomson articles:**

1. Mardare D., Cornei N., Luca D., Dobromir M., Irimiciuc S.A., Punga L., Pui A., Adomnitei C., Synthesis and hydrophilic properties of Mo doped $TiO_2$ thin films, ***J Appl Phys*** 115 (2014) 213501

(**Factor de impact: 2,185; AIS: 0,721**)

2. Mardare D., Yildiz A., Girtan M., Manole A., Dobromir M., Irimia M., Adomnitei C., Cornei N., Luca D., Surface wettability of titania thin films with increasing Nb content, ***J Appl Phys*** 112 (2012) 073502

(**Factor de impact: 2,210; AIS: 0,796**)

3. Adomnitei C., Luca D., Girtan M., Sandu I., Nica V., Sandu A.V., Mardare D., Nb-dopped $TiO_2$ thin films deposited by spray pyrolisis method, ***J Optoelectron Adv M*** 15 (2013) 519

(**Factor de impact: 0,563; AIS: 0,111**)

4. Adomnitei C., Tascu S., Luca D., Dobromir M., Girtan M., Mardare D., Nb doped $TiO_2$ thin films as photocatalytic materials, ***B Mater Sci*** xx (2015) xxx (acceptată pentru publicare)

(**Factor de impact: 0,87; AIS: 0,293**)

5. Adomnitei C., Cornei N., Luca D., Girtan M., Sandu I., Vasilache V., Dobromir M., Mardare M., The influence of Ni doping on the surface wettability of $TiO_2$ thin films, ***J Optoelectron Adv M*** 17 (5-6) (2015) 889 - 893

(**Factor de impact: 0,563; AIS: 0,111**)

6. Mardare D., Stancu A., Tiron V., Manole A., Adomnitei C., Florea D., Sensing gas properties of Cr-doped $TiO_2$ thin films in $CO_2$ atmosphere, ***J Vac Sci Technol A***, xx (2015) - trimisă spre publicare

(**Factor de impact: 2,14; AIS: 0,473**)

7. Mardare D., Tascu S., Adomnitei C., Luca D., Dobromir M., Mita C., Increasing surface hydrophilicity of Cr-doped $TiO_2$ thin films by depositing Pt on their surfaces, *Journal of Catalisys*, xx (2015) - trimisă spre publicare

(**Factor de impact: 6,073; AIS: 1,484**)