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Optical properties of Nb-doped TiO_2 thin films prepared by sol–gel method

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Abstract

In this work, we studied optical properties of pure and Nb-doped TiO_2 synthesized using a sol–gel method and deposited as thin films by spin-coating followed by annealing in air at 500 °C for 1 h. The surface elemental composition was derived from X-ray photoelectron spectra, while structure and surface morphology were investigated using X-ray diffraction and atomic force/scanning electron microscopy. Finally, the optical properties were investigated by means of UV–vis spectrophotometry and spectroscopic ellipsometry.

The Nb content was determined from XPS measurements to vary between 1.8 and 4.3 at%. The XRD patterns of the deposited thin films, with a maximum thickness of about 56 nm, showed no diffraction peaks. As proven both by microscopy and spectroscopic ellipsometry studies doping TiO_2 with Nb modified the surface morphology of the samples; the grain size is increasing while the surface roughness decreases with the increase in Nb content. This is accompanied by a decrease in the refractive index and an increase of the extinction coefficient.

Keywords: Nb-doped TiO_2; Sol–gel; Thin films; Spectroscopic ellipsometry

1. Introduction

Titanium dioxide (TiO_2) is a large band gap (i.e., 3.20 eV for the anatase crystalline phase) semiconductor extensively studied due to its unique combination of chemical and physical properties used to develop various environment- and energy-related applications [1]. TiO_2 materials have thermal and chemical stability, good mechanical hardness and high UV photoactivity. TiO_2 is transparent to visible light and has high refractive index making it suitable for the development of various optical thin film applications. When exposed to UV radiation with photon energy greater than the band gap energy of the material, the TiO_2 surface becomes super-hydrophilic, self-cleaning, self-sterilizing and antifogging [1–3]. The application range of TiO_2 can be extended by improving the properties of these materials through doping with transition metal ions (Fe, Mo, Nb, Sb, V, W, etc.) [4–13].

The electrical properties of TiO_2 can be improved by doping with niobium, Nb-doped TiO_2 currently being one of the most studied transparent conductive oxides (TCO), with reported resistivity values in the order of $10^{-4}\,\Omega$ cm, that could replace high-cost indium tin oxide (ITO) as TCO electrodes [7–13]. On the other hand, Nb doping of TiO_2 can alter the structure, surface, optical properties, etc. of the material.

In this paper, work is focused on the optical properties of pure and Nb-doped titanium dioxide (<5 at%) thin films deposited on glass slides by spin-coating technique using sols prepared from titanium tetraisopropoxide (TTIP) precursor. The sol–gel method, in combination with simple techniques like spin-coating or dip coating, is highly used to obtain thin films because it offers advantages like wide composition range, large surface homogenous coverage with easy control of thickness, easy recovery of the material comparing with powders and, last but not least, it is cost-effective.

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As proven by spectroscopic ellipsometry measurements, doping TiO_2 amorphous thin films with Nb, with concentrations varying between 1.8 and 4.3 at%, affects the optical constants values. The n values of the deposited amorphous thin films are smaller than the ones characteristic to the anatase phase of ~ 2.5 and present a decrease from 2.04 to 1.94 at $\lambda = 632.8$ nm, upon increasing Nb incorporation. An opposite behavior is observed for the k values which are increasing after doping within the same wavelength range. Also, the k values reach zero in vis and IR domains this behavior being characteristic to semiconductor or dielectric thin films.

2. Materials and methods

TiO_2 was prepared using a sol–gel method by dissolving the starting precursor—titanium tetraisopropoxide (TTIP, $Ti(OiPr)_4$)—in absolute ethanol with 37% hydrochloric acid as catalyst. The volume ratio between ethanol, $Ti(OiPr)_4$ and hydrochloric acid was 12:1:1. The resulting mixture was stirred for 24 h under N_2 atmosphere. Nb-doped TiO_2 was prepared by the addition of niobium pentaethoxide ($Nb(OEt)_5$) with Nb weight ratio to Ti within 0.1–0.5%. The final solutions were again stirred for 5 h under N_2 atmosphere. Thin films were deposited onto pre-cleaned microscope glass slides by spin-coating (Laurell Technologies Lite Spin Coater) at speeds comprised between 2000 and 3000 rpm. After the spin-coating process, samples were dried at 100 °C for 1 h to remove excess organics, and then annealed in air at 500 °C for 1 h.

X-ray photoelectron spectroscopy (XPS) survey and high-resolution measurements were used to derive the surface chemical composition of the samples using an ULVAC-PHI, 5000 VersaProbe spectrometer with monochromated Al K_α radiation (1486.7 eV). The photoelectrons were collected for a take-off angle of 45°. The calibration of binding energy (BE) scale was performed with the C 1s peak at 284.6 eV from the carbon contamination layer. Prior to XPS measurements, the samples were irradiated for 2 h with UV light from a mercury lamp to remove carbon contaminants from the surface. The surface quantification has been carried-out following the standard procedure [14] by using the core level XPS narrow spectra of found elements. Peak deconvolution has been done using the PHI—MultiPak software and the elemental concentration values were derived from peak surface areas, taking into account the sensitivity factors of the analyzed elements [15].

X-ray diffraction (XRD) patterns were obtained using a Shimadzu LabX XRD-6000 diffractometer with a CuK_α X-ray source ($\lambda = 1.54182$ Å). The morphology of the films was investigated by atomic force microscopy (AFM) using a Thermomicroscope Autoprobe LP Research system and by scanning electronic microscopy (SEM), using a JEOL 6301F microscope.

Optical transmittance spectra were recorded using a MultiSpec TEC 5 UV/VIS/NIR spectrometer. Film thickness and the dependence of the optical constants (the refraction index and the extinction coefficient) on the radiation wavelength were determined from spectroscopic ellipsometry (SE) measurements using a Horiba Jobin Yvon UVISEL NIR ellipsometter. The reflection ellipsometry measurements were collected at an angle of incidence of 70° in the range 300–1100 nm. The data analysis was performed using the Delta Psi 2 software.

3. Results and discussion

The XPS measurements show that the surfaces of the UV-cleaned deposited films are stoichiometric and mainly composed of Ti, O and Nb, with C as contaminant. The dopant has concentrations between 1.8–4.3 at% (Table 1). We denoted the TiO_2 reference sample as Nb0, and the Nb-doped TiO_2 thin films with increasing niobium contents as Nb1.8, Nb2.9 and Nb4.3, the number corresponding to the atomic concentration of each sample as determined from XPS measurements. The C contaminant adsorbed from the environment is present in the surface after the 2 h UV irradiation with a concentration up to 5.8 at%.

The deconvolution of the Ti 2p XPS high resolution spectra (Fig. 1a) showed a BE of the Ti $2p_{3/2}$ peak of 458.6 ± 0.2 eV, specific to Ti^{4+} [10,15]. The Ti $2p_{1/2}$ peak has a higher BE of 464.3 ± 0.2 eV with a separation of about 5.7 eV. No Ti^{3+}/Ti^{2+} peaks can be observed, which indicates that only stoichiometric TiO_2 is formed at the surface.

The O 1s XPS high resolution spectrum of the undoped sample (Fig. 1b) can be deconvoluted into a main component at 530.1 ± 0.2 eV, corresponding to Ti^{4+}–O bonds [15], and a secondary one at 531.2 ± 0.2 eV. The origin of this latter peak is still debated, some authors ascribing it to adsorbed OH groups [1–3] while others to different oxidized

Table 1
Atomic concentrations of the elements in the surface after UV irradiation; thickness and roughness of the samples as determined from AFM and SE measurements.

Sample	O (at%)	Ti (at%)	Nb (at%)	C (at%)	d (nm)	R_{AFM} (nm)	R_{SE} (nm)
Nb0	67.4	30.3	0	2.3	48	7.2	10.1
Nb1.8	68.8	24.6	1.8	4.8	51	5.7	4.2
Nb2.9	68.0	24.9	2.9	4.2	53	5.3	3.8
Nb4.3	68.4	21.5	4.3	5.8	56	4.2	2.9

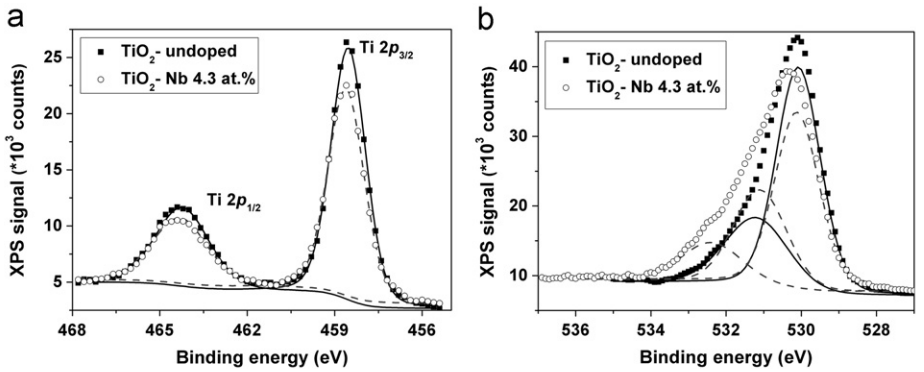

Fig. 1. Examples of (a) Ti 2p and (b) O 1s XPS high resolution spectra of pure and 4.3 at% Nb-doped TiO_2 thin films.

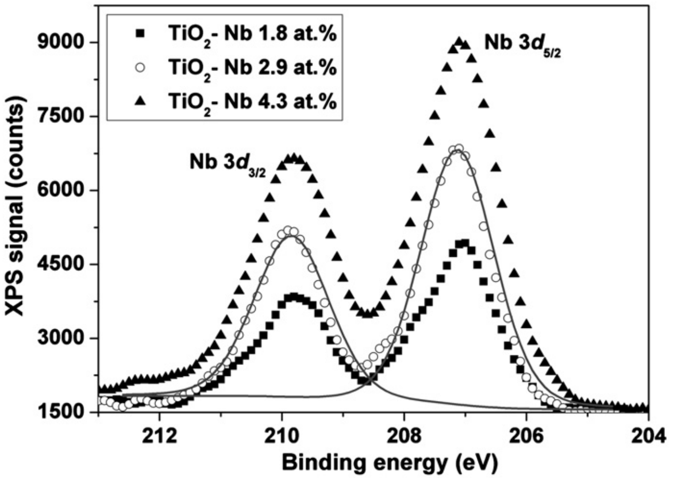

Fig. 2. Nb 3d XPS high resolution spectra of Nb-doped TiO_2 thin films.

hydrocarbon [3,16–18]. Doping TiO_2 with Nb, in a concentration of 4.3 at%, determines the apparition of a third peak with a binding energy of 532.4 ± 0.2 eV, as revealed by the XPS measurements (Fig. 1b).

The Nb 3d XPS high resolution spectra (Fig. 2) feature two peaks with BE of 207.1 ± 0.2 eV and 209.9 ± 0.2 eV, corresponding to the $3d_{5/2}$ and $3d_{3/2}$ components of Nb^{5+} oxidation state [10,15,16]. The area/intensity of the Nb 3d peaks increases with the increase of Nb concentration.

As previously reported, the XRD patterns of the pure and niobium doped TiO_2 thin films prepared with the described method do not show any diffraction peaks, suggesting that they are amorphous [19]. Considering that the anatase phase is usually formed when annealing sol–gel films with thickness > 100 nm at temperatures above 400 °C [12,13], the lack of any crystalline features can be attributed to the small thickness of the films (Table 1).

Studies of these surfaces by AFM (Fig. 3) and SEM (Fig. 4) revealed that the morphology changes with Nb doping. All samples present a granular morphology; the grains size increases with increasing dopant concentration. For the undoped film the root mean square (RMS) surface roughness has the highest value and the RMS values decrease with the increase of niobium concentration (Table 1). The scan area for surface roughness was 5 μm × 5 μm. The software used to process the AFM images and obtain the statistic data was Gwyddion v. 2.21.

Doping with Nb does not significantly affect the optical transmittance of the thin films; both pure and Nb-doped samples present transmittance higher than 75% over the entire measured spectrum (Fig. 5), with values increasing with the wavelength. As previously reported, doping with niobium of similar amorphous samples had as a result shifted towards higher energies, from 3.25 eV to 3.58 eV, of the optical band gap with increasing Nb content from 2.6 to 21 at % [19]. Similar results were also reported by other authors for Nb-doped TiO_2 films with anatase crystalline phase prepared via a sol–gel method [5,12]. Equal values or a small decrease from 3.1 eV to 3.0/2.9 eV was observed in Nb-doped anatase TiO_2 powders with high Nb contents of 10 and 20 at% prepared using a microemulsion method [4]. Sputter-deposited films show also a general tendency of optical band gap shift towards higher energies [9–11].

To model the optical constants of pure and doped TiO_2 thin films we used the “new amorphous” dispersion formula (Fig. 6), a rewriting of the Forouhi–Bloomer formula [20]. The fitting of measured parameters, delta and psi, was done by using a double layer model consisted of a dense TiO_2 layer and surface roughness, represented by a mixture of dense material and void. The optical constants of surface roughness layers were simulated using the effective medium approximation (EMA) [20].

As determined from SE measurements, the thickness of the films increases with Nb concentration due to addition of niobium pentaethoxide, as the dopant source, to the TTIP solution. The surface roughness changes with Nb doping, as seen previously from AFM and SEM images. The surface roughness values determined from SE measurements are consistent with those determined from the AFM images.

The refractive index, *n*, of undoped TiO_2 thin films prepared using sol–gel [20,21], ion-assisted electron-beam evaporation [22] or plasma vapor deposition [23,24], has been previously reported to present a fast decrease in the UV region, followed by slower decrease in the vis and IR regions of the optical spectrum. Depending on the elemental

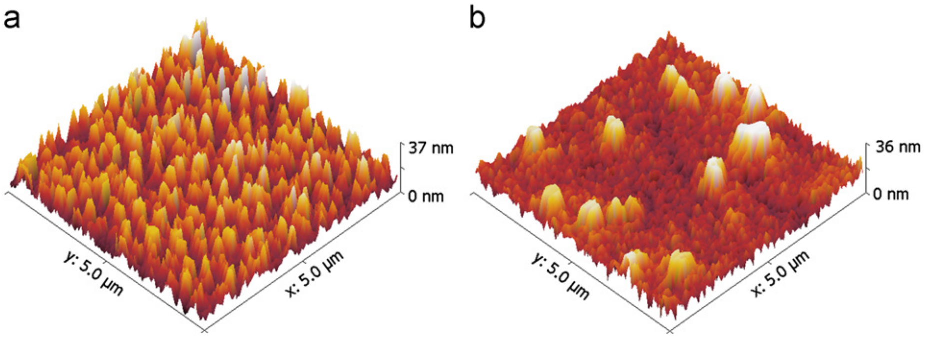

Fig. 3. Examples of AFM images of (a) pure and (b) 4.3 at% Nb-doped TiO_2 thin films.

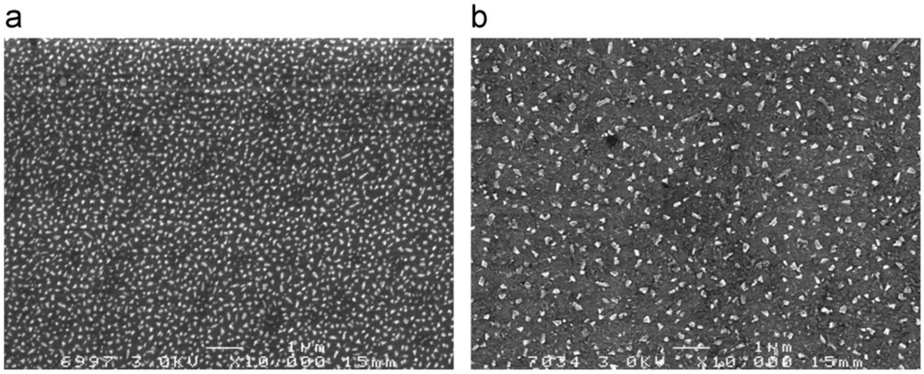

Fig. 4. Examples of SEM images of (a) pure and (b) 1.8 at% Nb-doped TiO_2 thin films.

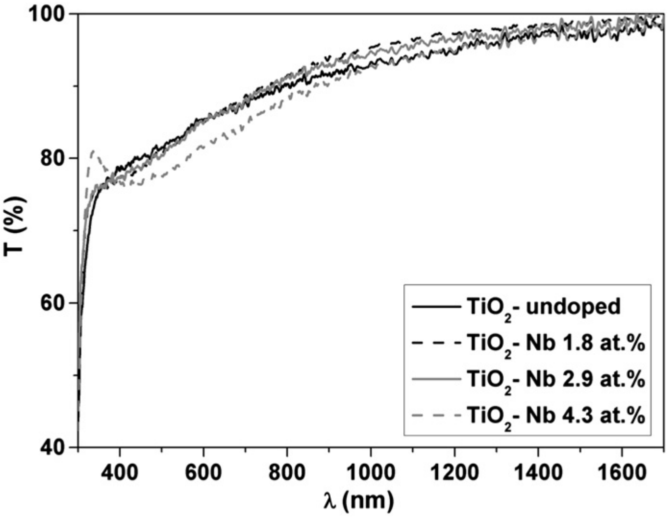

Fig. 5. Optical transmittance of the investigated samples.

composition, film crystalline structure and density, surface roughness, etc., values between 2.6 and 3.0 for $\lambda = 300$ nm and 1.9 and 2.1 for $\lambda = 800$ nm are usually common for this kind of materials. A similar behavior was found for the wavelength dependence of the extinction coefficient, k, with values usually reported to vary between 0.3 and 0.

Results in agreement with the ones reported in the literature have been found in our experiments (see Fig. 7). The values of n ranged between 2.75 and 1.95, while the values of k varied between 0.14 and 0 for the undoped sample. The optical constants, n and k, change as a result of the doping process. Due to the amorphous structure, at $\lambda = 632.8$ nm, the value of the refractive index of our samples are smaller than the ones characteristic for the anatase phase, which is reported to be approximately 2.5. Moreover, in our case n decreased from 2.04 to 1.94 at $\lambda = 632.8$ nm, upon increasing Nb incorporation. The extinction coefficient increases for the Nb-doped samples, reaching a maximum value of 0.28 at $\lambda = 300$ nm. All samples have k with zero values in vis and IR domains and this behavior is characteristic of semiconductor or dielectric thin films [9]. The SE results are in agreement with electrical measurements conducted for similar samples [25]. The room temperature electrical conductivity of the films increases from 6.6×10^{-8} to $4.5 \times 10^{-3}\ \Omega\,\mathrm{cm}^{-1}$ with the increase in the Nb concentration.

4. Conclusions

Amorphous pure and Nb-doped TiO_2 thin films with thickness in the range of 48 and 56 nm deposited on glass substrates were prepared by sol–gel method combined with spin-coating technique. Doping with Nb affects the optical properties of the samples. While the samples maintain high transmittance over the measured spectrum, both refractive index and extinction coefficient values change due to doping: smaller values are observed for n, and k presents

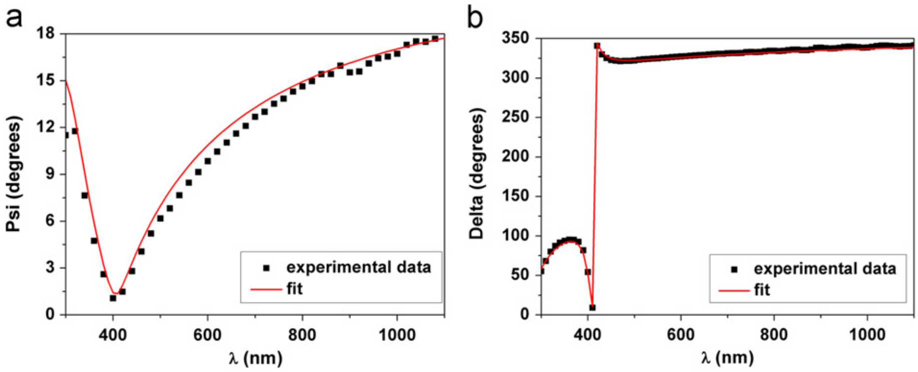

Fig. 6. Ellipsometric parameters Δ and ψ as functions of λ. Fitting with the "new amorphous" dispersion formula.

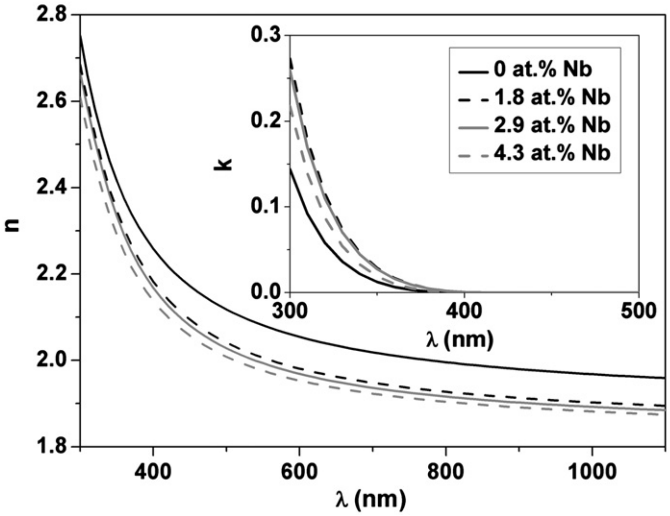

Fig. 7. Variations of refractive index and extinction coefficient with the incident light wavelength.

higher values with increasing Nb content. Also, as shown both by spectroscopic ellipsometry and microscopy techniques, doping affects the surface morphology: with increasing dopant content an increase in the grain size and a decrease in surface roughness were observed.

Acknowledgments

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