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Properties of TiO_2 thin films prepared by different techniques

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TiO_2 thin films prepared by sol-gel method and by RF magnetron sputtering deposited on p-Si(111), n-GaAs(100), and glass have been investigated by XRD, XPS and AFM techniques. The characteristics of the film: colour, adherence and composition are presented in the case of thermal treatments (500 ^{0}C and 800 ^{0}C) for sol-gel deposited films as well as for RF sputtering. The TiO_2 plasma deposited film is uniform, homogeneous and stoichiometric.

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1. Introduction

The development of TiO_2 thin films is of particular interest due to the numerous technological applications of this inorganic oxide. Metal oxide semi conducting materials appear to be one of the best candidates for gas sensing, as they operate reversibly and usually have stable chemical and thermal properties over extended periods of use [1]. TiO_2 thin films are popular for such applications, where changes in the film electrical conductivity can be related to the physisorption and chemisorption of oxygen atoms [2, 3].Titanium dioxide has many excellent physical properties such as a high dielectric constant, a strong mechanical and chemical stability, as well as good insulating properties. Due to its high refractive index and optical transmittance in the visible range, TiO_2 is especially suitable as material for optical coating and protective layers for very large-scale integrated circuits [4].

TiO_2 thin films can be prepared using a variety of techniques, and the sol-gel method is attractive due to the ability to form large film surface area at a very low cost of production in a range of flexible chemical components. This method has the advantage to produce particles in a relatively shorter processing time at lower temperatures. The rheological properties of sols and gels can give rise to the formation of fibers and films and thus considerably increase the anisotropy of the material and its chemical reactivity [5]. In the sol-gel technique the stoichiometry and the high homogeneity of the final film can be controlled. In the range of nanophase materials the synthesis followed by different modes of nanoparticles film formation has led to interesting applications in non-linear optical devices [6], for information storage, frequency doubling, and in individual components in the film operating in the size regime of at most few hundreds of nanometers [7]. Structural and micro structural characterizations of thin films have been done by X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS). Apart from brookite, titania (TiO_2) has two polymorphs, both are tetragonal structures viz: anatase (TiO_2-A) lattice parameter c/a >1, gap E_g=3.18 eV, refractive index: 2.5, photo catalytically active, and rutile (TiO_2-R) lattice parameter c/a<1, gap: E_g=3.03 eV, optically active, refractive index:2.7.

Reactive sputtering is widely used in the preparation of Ti compounds thin films as TiO_2 or TiN. Generally, high fluencies of reactive gases such as oxygen are required for formation of Ti compound films during reactive sputtering of Ti metal. The deposition rate of the film drops abruptly when compounds are formed on the target surface at high fluency of the reactive gases. The pressure of reactive gases, evaporation rates and substrate temperatures are the main parameters used to influence the packing density of the films, the film crystallinity and the optical properties [4].

The purpose of this paper is to investigate the properties of TiO_2 films deposited on p-Si(111) and n-GaAs(100) by sol-gel method and RF magnetron sputtering and to compare the results in order to obtain adherent, stoichiometric and adherent films dedicated to an electromagnetic radiation sensitive structure.

2. Experimental

Titanium dioxide thin films were prepared by sol-gel method used $Ti(O\text{-}nBu)_4$ as a raw material and n-BuOH as a solvent. In order to decrease the kinetics of the hydrolysis and polycondensation of Ti $(O\text{-}nBu)_4$ it was used acetic acid as presented by C.Legrand-Buscena et al [5]. Titanium alkoxide is among the most reactive where the hydrolysis and condensation rate is very high and, therefore, is difficult to form a stable sol. Acetyl acetone is added as a chelating agent to decrease the reactivity and stabilize the sol. Acetic acid slowly added allows to initiate hydrolysis via an estherification reaction as follows:

$$C_4H_9\text{-}OH+CH_3\text{-}COOH \leftrightarrow H_2O+C_4H_9COOCH_3$$

Titanium dioxide precursor solutions were prepared firstly by stabilizing $Ti(O\text{-}nBu)_4$ dissolved in n-BuOH with acetyl acetone , stirring for 30 min. After adding acetic acid the final mixture was stirred for 30 min. at room temperature; the pH of the sols was ≤ 2. The chemical prescription used the molar ratios n_{acac}/n_{Ti}=0.3, $n_{acetic\ acid}/n_{Ti}$=0.2 to get a stable sol of concentration 2.609 M. Thin films were fabricated in a process where the substrate to be coated is immersed in a liquid (sol) and then is dried in a spinner with a well-defined speed at room temperature in air. There were deposited a sequence of 10 thin layers on cleaved substrates of p-Si(111), n-GaAs (100) and glass .Between each deposition the thin film was dried at T=100 ^oC for t=20 min. The properties of TiO_2 sol-gel films were investigated by XRD, XPS and AFM analyses after annealing at T=500 and 800^{0}C in air.

The dried gel was obtained after heating at 100^{0}C. Thereafter the gel was subjected to a Thermal Gravimetry Analysis (TGA) on a PYRIS DIAMOND TG/DTA-Perkin Elmer, temperature range (25-1500)^{0}C.

The XRD analysis was performed in a DRON 2.0 system in air with a beam current I=20 mA at an accelerating voltage U=30 kV using Mo anticathode ($K_{\alpha 1}$=1.5405Å).

The XPS spectra were obtained with VG ESCA 3 MKII Spectrometer using monochromatized Al k_α radiation (1486.6 eV) the analysis chamber was maintained at ultra high vacuum (p~10^{-9} torr) and the sample position was oriented at θ=45^0 in respect to the analyzer. The XPS spectra were recorded with a 20 eV window, 50 eV resolution and 256 channels recordance. Data collection was made using a computer interface digital pulse counting system. The spectra were processed using SDP v2.3 software which allows smoothing and deconvolution of the curve.

The RF plasma magnetron deposition was performed on a VARIAN R 3119- European certified. The deposition condition for a thickness of 50 nm TiO_2 film were: oxygen controlled atmosphere at a flow rate of 30 sccm monitories by a ultraflo US mass flow controller model 80-5, vapor pressure 5×10^{-3} Torr and a deposition rate between 0.3-1Å/s. The TiO_2 sputtered films deposited on p-Si(111) and n-GaAs(100) were investigated by AFM analysis regarding the surface quality and by XPS for the surface composition

The AFM analysis was performed on AFM system model NOMAD QUESANT Instrument Corporation (USA).

3. Results and discussion

The TGA analysis of dried gel evidenced (Fig. 1) four temperature regions as follows: below 100^{0}C, between 100 to 275^{0}C, from 275 to 413^{0}C and from 413 to 546^{0}C. In the first region the weight loss is the result of water evaporation from the surface of TiO_2 powder. The temperature range (100-275)^{0}C is related to the weight loss from the evaporation of butanol, acetyl acetone and acetate groups which is not a part of gel structure. The temperature range (275-413)^{0}C is attributed to the loss of butoxide, acetylacetonate and acetate groups from gel structure. For temperatures up to 546 ^{o}C occurs the combustion of organic constituents in the gel and starts the crystallization of the anatase form. After 546^{0}C it does not appear any thermal effect.

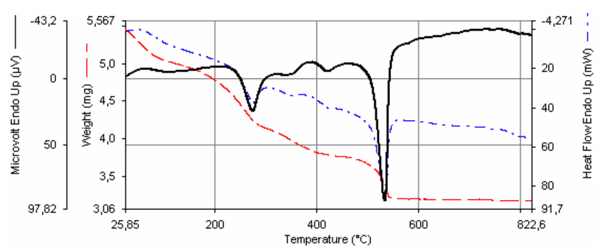


Fig. 1-TGA analysis of TiO_2 dried gel.

The XRD analysis of sol-gel TiO_2 thin films deposited on glass and annealed at 500^{0}C (Fig. 2) revealed a peak at 25^0 attributed to anatase phase on the background of the glass amorphous phase. The TiO_2 film deposited on glass is semi-transparent and whitish. The adherence is good both on glass and on silicon. Regarding the modification of the substrate type the crystallization process does not depend on the support and the anatase crystallization process begins at 480^{0}C [5]. The XRD spectrum of TiO_2/p-Si(111) annealed at 500^{0}C presents peaks corresponding to anatase form at 25^0 and 38^0 and a peak at 28 · 5 ^{0} of silicon.

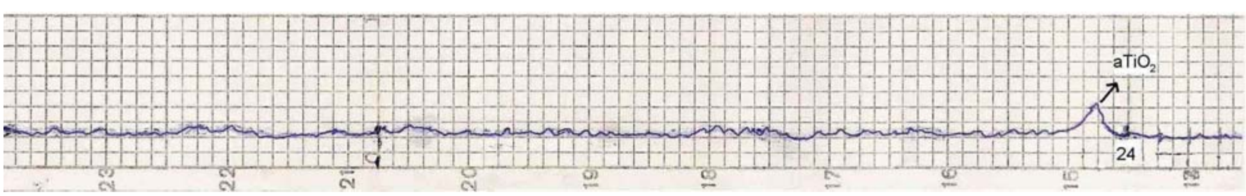
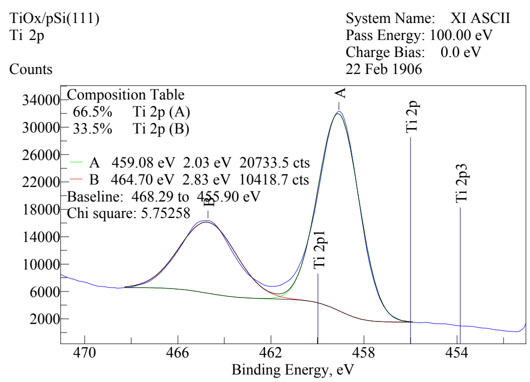


Fig. 2. XRD spectrum of TiO_2/glass annealed at 500^{0}C

The XPS investigation at the surface of TiO_2 films deposited on p-Si(111), n-GaAs(100), and glass by sol-gel method and RF magnetron sputtering put into evidence a stoichiometric compound. For XPS analysis the binding energies were calibrated with reference to C 1s at 285 eV. The measurement conditions were p=10^{-9}torr, U_{me}=3.2 kV, RX: U=14 kV, I=20 mA, P=280 W, Flod gun U=3 V, I=0.02 mA. As a general remarks, the C line is enhanced due to air adsorption (after annealing at 800 ^{o}C). The organic part of the gel is decomposed, the signal of oxygen arises from the line 532 eV corresponding to absorbed oxygen and the line 529.33 corresponds to TiO_2. In

Fig. 3a and 3b we present the XPS analysis on TiO_2/p-Si(111) deposited by sol-gel and annealed at 500^{0}C (3a) and 800^{0}C (3b). The typical spectrum for titanium with the line shapes of $2P_{1/2}$ and $2P_{3/2}$ corresponds to a concentration ratio of 33.5% to 66.5%. This suggests that the oxidation state of TiO_2 may be obtained from spin-orbit splitting of $2P_{1/2}$ and $2P_{3/2}$ electron bands of titanium [1]. Regarding the signal arised from silicon, in the main part it proceed from SiO_2.



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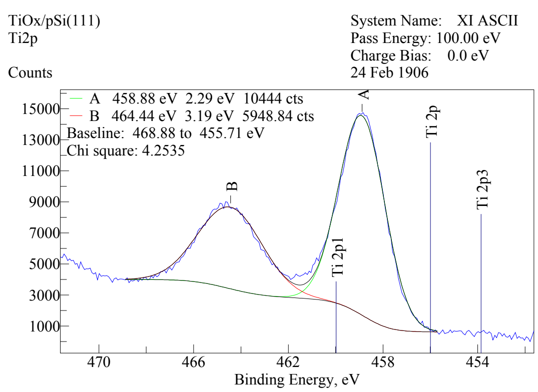
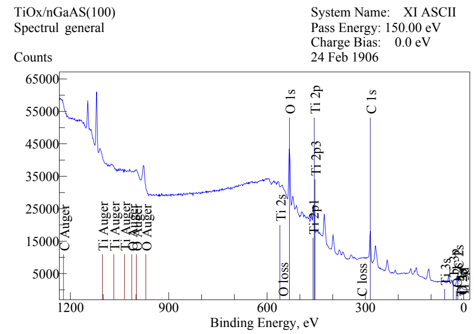


b

Fig. 3. XPS spectrum of Ti for TiO_2 film (sol-gel) annealed at 500 ^{0}C (a) and 800 ^{0}C (b).

For TiO_2 sol-gel thin film deposited on n-GaAs (100) and annealed at 800 ^{o}C the general XPS spectrum is shown in Fig. 4 (a). The spectrum is focused on the peak lines Ti-Auger, Ti-2s, Ti-$2P_{1/2,}$ Ti-$2P_{1/2}$, O-Auger, C-1s, O-1s; in the range (0-450)eV the binding energies are related to the Auger lines for Ga and As and the lines for Ga-3d and As-3d. For titanium lines the concentration ratio $2P_{1/2}$to $2P_{3/2}$ is 35% to 65%. The sample TiO_2 /n-GaAs has at its surface an uniform white film, the sample TiO_2/p-Si is a non - uniform film part, and for TiO_2/glass sample, the film is uniform, transparent but with poor adherence. In the oxygen signal of TiO_2/glass annealed at 500 ^{o}C, the peak from 529.64 eV is attributed to TiO_2 in a preparation of 87.6%. Titanium peak positions corresponds to the oxidation state Ti^{4+} [1].



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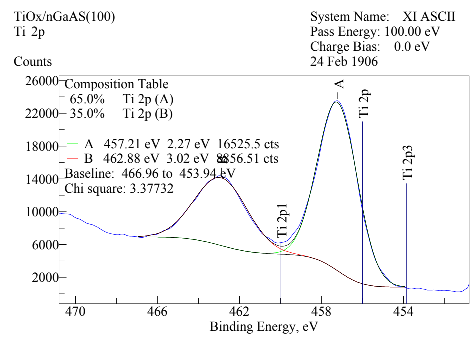
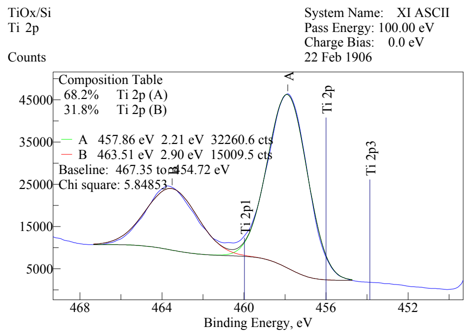


b

Fig. 4. XPS spectrum of TiO_2/n-GaAs film annealed at 800^{0}C, (a)-general spectrum, (b)-Ti line.

In this study we deposited TiO_2 thin films on p-Si(111) and n-GaAs(100) using radio-frequency (RF) magnetron sputtering in order to understand the role of different techniques on the quality of TiO_2 films. The XPS analysis (Fig. 5) put into evidence a signal of O-1s from TiO_2/Si that arises from oxygen in oxide (530.79 eV) in a proportion of 71.7% and from adsorbed oxygen (532.00 eV) in a proportion of 28.3%. The titanium signal from TiO_2 is very clear ($2P_{1/2}$ 31.8 % and $2P_3$ 68.2%) and does not exist other compounds as e.g titanium oxide species (Fig. 5). The same observations are consistent also with TiO_2 film on GaAs-for titanium signal the composition indicates a clearly and accurate TiO_2 stoichiometric compound ($2P_{1/2}$ 28.4%, $2P_{3/2}$ 71.6%)

For RF magnetron sputtering of TiO_2 films deposited on Si and GaAs the AFM characteristics are presented in Fig. 6. For Silicon the wafer surface was not prepared at a optical quality. The surface area investigated was 5μm ×5μm and RMS diagram was 3.587 nm. For TiO_2/Si film the RMS deviation is 10.69 nm and mean deviation is 0.007 nm TiO_2 film of a thickness 50 nm is uniform with a average height of 26.65 nm. For TiO_2 films at an equivalent thickness of λ/4 at 1μm, the initial surface morphology is changed. It is observed a cluster structure of the semi arranged layer. Optical quality of the deposited layers is influenced by the wafer surface quality.



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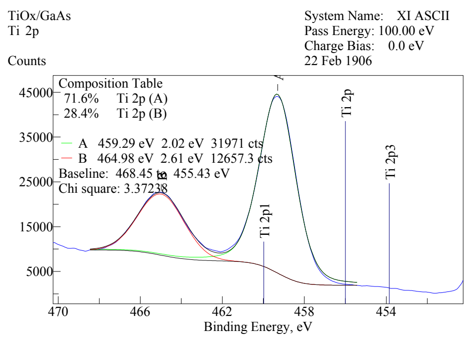

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Fig. 5. XPS spectrum of Ti in TiO_2 film (RF magnetron sputtering) a-TiO_2/Si, b-TiO_2/GaAs.

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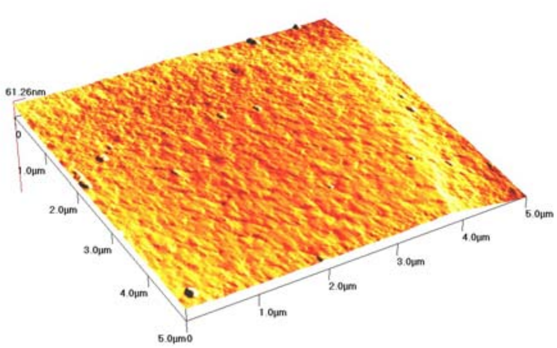
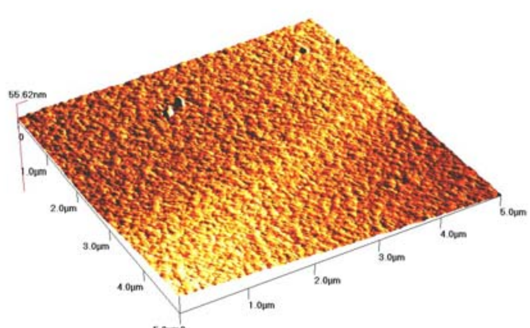
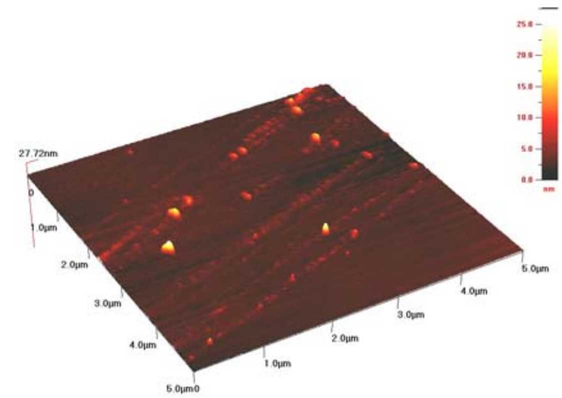


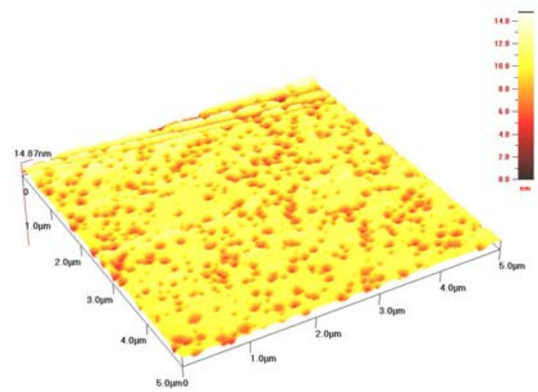
Si wafer



50 nm TiO_2/Si



GaAs wafer



50 nm TiO_2/GaAs

Fig. 6. AFM pictures of magnetion sputtered TiO_2 films

The GaAs wafer is polished optically with a RMS of 9.82Å, average height of 2.774 nm with a mean deviation of 5.013Å at an image resolution of 500. It is clearly observed that after the deposition of TiO_2/GaAs thin layers, the obtained structure is arranged periodically with a RMS of 1.121 nm, an order of magnitude better than TiO_2/Si.

The TiO_2 sol-gel thin films deposited on GaAs (TiO_2/n-GaAs (100)) annealed at T=800^{0}C has the aspect presented in Fig. 7. The film is no uniform with a cluster of microcrystallites. For this thin film we remark that TiO_2 is completely crystallized at 800^{0}C.

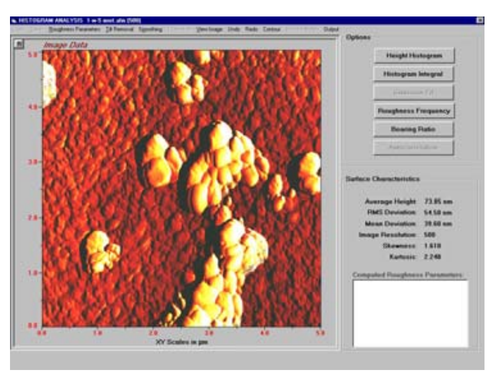


Fig. 7. AFM image of TiO_2/n-GaAs(sol-gel) annealed at 800 ^{o}C.

4. Conclusions

In the present study the principal characteristics of TiO_2 films deposited on p-Si(111), n-GaAs(100) by sol-gel techniques and by RF magnetron sputtering techniques were investigated. The estimated thickness of sol-gel films was <1μm obtained by successive deposition of 10 layers from a titanium n-butoxide sol in the presence of acetic acid. XPS analysis led to a detailed knowledge about the chemical properties of the film samples. TiO_2 films deposited by both techniques are found to be stoichiometric. Surface quality investigated by AFM shows an uniform aspect for TiO_2 deposited by RF sputtering. The XRD analysis performed on TiO_2 sol-gel films put into evidence the presence of anatase phase on glass and Si substrates. The TGA analysis recorded the different stages to the route of crystallization of titanium oxide.

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