TiO₂ waveguides thin films prepared by sol-gel method on glass substrates with and without ZnO underlayer

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TiO₂ thin films have been deposited on glass substrates with and without ZnO underlayer by sol-gel dip coating process. XRD patterns show the formation of anatase phase with the diffraction lines (1 0 1) and (2 0 0) in TiO₂/glass sample. In TiO₂/(ZnO/glass) sample, TiO₂ is composed of anatase phase with the diffraction line (2 0 0) but the diffraction peaks of ZnO wurtzite are also well-defined. The determination of the refractive index and the thickness of the waveguiding layers has been performed by m-lines spectroscopy. The thickness of TiO₂ thin films deduced by Rutheford Backscattering Geometry (RBS) agrees well with that obtained by m-lines spectroscopy. TiO₂/glass sample exhibits one guided TE₀ and TM₀ polarized modes. In TiO₂/(ZnO/glass) sample, only, TE₀ single mode has been excited due to cutoff condition.

Keywords: TiO₂; anatase; sol-gel; waveguides; ZnO/glass

1. Introduction

Waveguides made as thin films of metal oxides such as TiO₂ [1], Y₂O₃ [2], ZrO₂ [3], Al₂O₃ [4], GdO₃ [5], ZnO [6], are promising for integrated optical circuits and optoelectronic devices. Among the metal oxides, TiO₂ in its anatase structure has gained significant academic and industrial attention due to its interesting electrical and optical properties: high refractive index and large band gap.

Sol-gel growth process is well known for its capacity to provide TiO₂ thin films with high optical quality, suitable for waveguiding applications [7–9]. It offers also many advantages such as high purity, good uniformity of the film microstructure, low temperature synthesis, low cost, easily controlled reaction conditions and possibility to use different substrates.

Recently, the use of the double-layer structure has been proven an effective way to improve the properties of metal oxides. Several attempts have been made to modify the physical, chemical and optical properties of TiO₂ thin films by combining with other oxides such as ZnO [10], WO₃ [11] and SiO₂ [12].

In this paper, we present the preliminary results about the preparation of sol-gel TiO₂ thin films prepared on glass substrates with and without ZnO underlayer and particularly the study of their waveguiding properties.

2. Experimental

The procedure of the preparation of TiO₂ solution includes the dissolution of titanium isopropoxide in isopropanol alcohol. The solution is left under closed stirring for 10 min. Then, acetic acid is poured and stirred for 15 min. Finally, methanol is

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added and stirred for 2 h. ZnO layers are deposited on a carefully cleaned glass substrates using spray ultrasonic method. The films are prepared by spraying a solution of zinc acetate with a concentration of 0.2 M dissolved in ethanol with a spray rate of 5 ml/min. The substrate temperature is kept over the heater at 380 °C. Glass and ZnO/glass substrates are dipped into TiO₂ solution and pulled up at a constant rate of 10 cm/min. After each dipping, the obtained films are dried for 15 min. Finally, the samples are annealed at 500 °C for 1 h. TiO₂ thin films prepared on glass are denoted as TiO₂/glass and those deposited on ZnO/glass are denoted as TiO₂/(ZnO/glass).

XRD patterns are recorded on Siemens D8 diffractometer using CuK α radiation. The thickness and compositional depth profile is studied by Rutherford Backscattering Spectrometry (RBS) using a 2 MeV ⁴He⁺ ion beam. The backscattered ions are recorded by a Si detector. The waveguiding properties are investigated by a Metricon 2010/M prism coupler. A rutile prism P₂ ($n_{TE} = 2.8639$, $n_{TM} = 2.5822$) is used for coupling light of a He–Ne laser with a wavelength $\lambda = 632.8$ nm into the waveguide.

3. Results and discussion

3.1. DRX analysis

Fig. 1 shows the X-ray diffraction patterns of TiO₂ thin films prepared on glass and (ZnO/glass). Comparing the samples, one can see that the structures are different. As depicted in this figure, TiO₂/glass sample indicates the presence of the peaks belonging to anatase phase with the diffraction lines (1 0 1) and (2 0 0). The broad hump in the region extending from 20° to 35° is assigned to the glass substrate [13]. Considering TiO₂/(ZnO/glass) sample, wurtzite peaks clearly dominate the diffraction pattern [14], but the diffraction line (2 0 0) of anatase peak is also present.

3.2. RBS analysis

Determination of the thickness of thin films is a topic of fundamental and technological

Fig. 1. XRD patterns of TiO₂/glass and TiO₂/(ZnO/glass) samples.

Fig. 2. Experimental and simulated RBS spectra of TiO₂/glass sample.

importance. Therefore, RBS analysis [15, 16] is also introduced to measure the thickness, simultaneously with the stoichiometry of TiO₂ films. Fig. 2 shows the RBS spectra of both experimental and simulated data of TiO₂/glass sample using the Rump simulation. The film thickness is 144 nm and the composition ratio of O/Ti is obtained to be 1.94:1.

3.3. Waveguiding measurements

For the waveguiding characterization, the m-lines spectroscopy based on prism coupler with a totally automated set-up has been used. It is

well-known that the m-lines spectroscopy is a convenient and efficient technique of launching laser into the planar waveguiding thin films for exciting the modes and obtain the optogeometric parameters, such as the thickness and the refractive index [17]. The mode excitation is provided by the measuring of the reflected intensity as a function of the incidence angle on the entrance face of the prism, where the coupling is detected by the occurrence of dark lines. Using the ray optics in the case of planar waveguides such as TiO₂ thin films, the corresponding effective index can thus be deduced [18]:

$$N_m = n_p \sin[A_p + \arcsin(\sin i_m / n_p)] \quad (1)$$

where n_p is the refractive index of the prism, A is the prism angle and i_m is the incident angle. The dispersion equations for TE and TM polarizations can be found using Maxwell equations and interfaces conditions [19]:

For TE polarization

$$k_0 d \sqrt{n_f^2 - N_m^2} = \arctan \sqrt{\frac{N_m^2 - n_a^2}{n_f^2 - N_m^2}} + \arctan \sqrt{\frac{N_m^2 - n_s^2}{n_f^2 - N_m^2}} + m\pi \quad (2)$$

For TM polarization

$$k_0 d \sqrt{n_f^2 - N_m^2} = \arctan \frac{n_f^2}{n_a^2} \sqrt{\frac{N_m^2 - n_a^2}{n_f^2 - N_m^2}} + \arctan \frac{n_f^2}{n_s^2} \sqrt{\frac{N_m^2 - n_s^2}{n_f^2 - N_m^2}} + m\pi \quad (3)$$

where n_f , n_a , n_s are the film, the air and the substrate refractive index, respectively; d is the thickness of the film and k_0 is the free-space wave vector.

Fig. 3 shows the recorded waveguiding modes of TiO₂/glass and TiO₂/(ZnO/glass) samples.

To achieve the waveguiding regime, the refractive index of the guiding layer must be greater than the refractive index of the substrate (or the underlayer) and the refractive index of the surrounding medium (air). Since TiO₂ oxide has

(a)

(b)

(c)

Fig. 3. Optical guided modes of TiO₂/glass and TiO₂/(ZnO/glass) samples: (a) TiO₂/glass TE₀; (b) TiO₂/glass TM₀; (c) TiO₂/(ZnO/glass) TE₀.

higher refractive index than air, glass and ZnO ($n_{\text{TiO}_2} > n_{\text{ZnO}} > n_{\text{glass}} > n_{\text{air}}$), the waveguiding can only be performed in TiO_2 films [20, 21]. As depicted in Fig. 3, $\text{TiO}_2/\text{glass}$ sample shows the presence of the fundamental TE_0 and TM_0 modes from which we can measure the refractive index and the film thickness under the assumption that the refractive index of the film is isotropic, i.e. $n_f(\text{TE}) = n_f(\text{TM})$. The m-lines measurements for $\text{TiO}_2/(\text{ZnO}/\text{glass})$ sample show only one guided TE_0 polarized mode from which the effective index can be measured. By using this value and that of the thickness of TiO_2 (132.8 nm) in the dispersion equations of guided modes (equations 2 and 3), the value of the refractive index is determined. The results are listed in Table 1.

The measured values of the refractive index are in good agreement with that of the samples obtained by sol-gel methods [7, 22, 23]. The deduced value of the thickness agrees well with that obtained by RBS measurements. No appreciable change in the values of the refractive index supports the assumption that the refractive index of the film is isotropic. As a consequence, calculations using only one TE_0 mode and one TM_0 mode are acceptable.

In fact, the graphical interpretation of equation 2 and equation 3 (effective index as a function of thickness) shows that the excitation of the optical modes takes place when the film thickness is greater than some minimum value $d_{\min}$ (cutoff thickness). In other words, as the film thickness gets thinner, the mode approaches its cutoff and then, no mode is supported by the waveguides. The number of these modes is also related to the film thickness. The value of $d_{\min}$ differs for each mode, and is defined by the condition of total internal reflection at the interface of the guiding layer and the substrate [19]:

$$d_{\min}(\text{TE}) = \frac{1}{k_0 \sqrt{n_f^2 - n_s^2}} \left(\arctan \sqrt{\frac{n_s^2 - n_a^2}{n_f^2 - n_s^2}} + m\pi \right) \quad (4)$$

$$d_{\min}(\text{TM}) = \frac{1}{k_0 \sqrt{n_f^2 - n_s^2}} \left(\arctan \frac{n_f^2}{n_a^2} \sqrt{\frac{n_s^2 - n_a^2}{n_f^2 - n_s^2}} + m\pi \right) \quad (5)$$

where $n_f = n_{\text{TiO}_2}$, $n_s = n_{\text{glass}}$ or n_{ZnO} and $n_a = n_{\text{air}}$. n_{ZnO} has previously been calculated using m-lines spectroscopy and it is about 1.94. Calculated values of cutoff thickness are presented in Table 2.

It is obvious that the $d_{\min}$ depends on the differences of the index squares rather than the indices themselves. This explains the excitations of two fundamental modes (TE_0 and TM_0) for $\text{TiO}_2/\text{glass}$ sample, because the high value of the difference $n_f^2 - n_s^2$ between TiO_2 and glass gives a smaller values of $d_{\min}(\text{TE})$ and $d_{\min}(\text{TM})$ compared to the thickness of TiO_2 thin films. For $\text{TiO}_2/(\text{ZnO}/\text{glass})$, the value of the thickness of TiO_2 is higher than $d_{\min}(\text{TE})$ and smaller than $d_{\min}(\text{TM})$ due to the low value of $n_f^2 - n_s^2$ between the two films of TiO_2 and ZnO. Since n_a (air) is smaller than n_f , the cutoff thickness of TE_0 mode is slightly smaller than the cutoff thickness of TM_0 mode. As a result, only the fundamental TE_0 mode has been excited. So, to excite the TM_0 modes in the case of $\text{TiO}_2/(\text{ZnO}/\text{glass})$ sample, we have to prepare thicker TiO_2 thin films.

4. Conclusions

TiO_2 thin films have been grown on glass substrates with and without ZnO underlayer by sol-gel dip coating process. The obtained TiO_2 films are in anatase phase. The investigation of waveguiding measurements reveals the excitation of one guided TE_0 and one TM_0 polarized mode for $\text{TiO}_2/\text{glass}$. $\text{TiO}_2/(\text{ZnO}/\text{glass})$ sample supports only the TE_0 modes. The excitation of TM modes has been unsuccessful. This can be explained by the fact that the excitation of the optical modes is performed when the film thickness is greater than some minimum value of the thickness which is considered as cutoff condition. Moreover, the cutoff thickness is dependent on the differences of the index squares of the substrate and the surrounding.

Table 1. Measured values of the optogeometric parameters of TiO₂/glass and TiO₂/(ZnO/glass) samples.

Sample	Film thickness (± 0.1) [nm]	Effective index N(TE ₀) ($\pm 10^{-4}$) [nm]	Effective index N(TM ₀) ($\pm 10^{-4}$) [nm]	Refractive index ($\pm 10^{-4}$) [nm]
TiO ₂ /glass	132.8	1.7773	1.5744	2.1378
TiO ₂ /(ZnO/glass)	132.8 (assumed)	1.7783	-	2.1391

Table 2. Calculated values of cutoff thickness of TiO₂/glass and TiO₂/(ZnO/glass) samples.

Samples	d _{min} (TE) [nm]	d _{min} (TM) [nm]
TiO ₂ /glass	62.45	93.54
TiO ₂ /(ZnO/glass)	124.66	167.02

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