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Extraction of optical constants and thickness of nanometre scale TiO_2 film *

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TiO_2 thin films were deposited on glass substrates by sputtering in a conventional rf magnetron sputtering system. X-ray diffraction pattern and transmission spectrum were measured. The curves of refraction index and extinction coefficient distributions as well as the thickness of films calculated from transmission spectrum were obtained. The optimization problem was also solved using a method based on a constrained nonlinear programming algorithm.

Keywords: TiO_2 thin films, pointwise constrained optimization approach, constrained nonlinear programming, optical constants, parameters extraction

PACC: 7820D, 7865P, 7360F

Much attention has been paid to titanium dioxide films in the past for their chemical stability, high refractive index, and high dielectric constant, which allow for their use as components in optoelectronic devices, sensors, and photocatalysts. Many deposition techniques have been used to prepare them, such as chemical vapour deposition,[1] evaporation,[2] reactive magnetron sputtering,[3] ion beam techniques,[4] and sol–gel processes.[5,6] In this paper, the optical properties of sputtered TiO_2 films on glass substrates are investigated. The dispersions of the real part, n, and the imaginary part, k, of the complex refractive index have been deduced by fitting the theoretically generated spectra to the simulated optical dispersion from the experimental transmittance spectra. A modified pointwise constrained optimization approach, double-step optimization, was used to extract the film thickness and optical constants. The new calculation method can save calculation time and enhance precision.

For most modern applications of thin dielectric or semiconductor films, the optical properties of interest cover the photon energy around fundamental absorption edge of the material. Optical transmission provides accurate and rapid information on the spectral range where the material goes from compete opacity to some degree of transparency.[7,8] As a consequence, the problem of extracting the optical constants, $\tilde{n}(\lambda) = n(\lambda) + \mathrm{i}k(\lambda)$, and the thickness ($d$) of thin films from transmission data only, is very important. Several methods were reported to solve this problem, such as a pointwise constrained optimization approach[9] and an unconstrained minimization algorithm.[10] The two methods were deduced to a nonlinear programming problem, and both were successful in extracting d and $\tilde{n}$ from transmission spectra of the computer-made film and the real one. When the above methods are used to extract parameters from the transmission of real thin film, the solution cannot be always available because of the rather complex large-scale nonlinear programming. Here a more effective procedure was introduced to enhance the efficiency of the parameters extraction method.

Firstly, we regard the problem as nonlinear programming:

minimize

$$\sum_{\lambda} [T_{\exp}(\lambda) - T(d, n(\lambda), k(\lambda))]^2 \qquad (1),$$

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then we subject it to physical constraints.

In Eq.(1) $T_{\rm exp}$ is the transmission spectra of the thin film, and T (d, n, k) is the theoretical transmission calculated by the formula.[8] The physical constraints are from Ref.[9],

$$d_{\min} \le d \le d_{\max}, \quad n_{\min} \le n \le n_{\max},$$
$$0 \le k \le k_{\max} \text{ for all } \lambda. \tag{2a}$$
$$n_{i+1} \le n_i, \quad k_{i+1} \le k_i. \tag{2b}$$
$$2n_i - n_{i-1} - n_{i+1} \le 0,$$
$$2k_i - k_{i-1} - k_{i+1} \le 0. \tag{2c}$$

Given $n(\lambda)$, $k(\lambda)$ and d for all values of wavelength λ, the theoretical transmission T is obtained. The optimization procedure is used to find the best data of three unknown d, $n(\lambda)$, $k(\lambda)$, which should satisfy Eq.(1). But for every optimization procedure, the fitting result is very sensitive to the initial values of d, $n(\lambda)$, $k(\lambda)$,[9] and the experimental data shows that bad initial values will bring about much more difficulties in parameters extraction. So, we present a double-step optimization method with which calculating time can be saved and the fitting precision is enhanced. Firstly, only the constrained condition (2a) is inserted to Eq.(1), and the retrieval parameters calculated from the nonlinear programming optimization procedure are taken as the initial values. Secondly, the full physical condition (2a–2c) and the initial values are substituted into Eq.(1), and the optimization procedure is repeated, while a constrained nonlinear programming algorithm runs with the last optimized parameters as the initial input values until the best parameters are obtained or the preset precision is reached.

TiO_2 thin films were deposited on glass substrates by sputtering in a conventional rf magnetron sputtering system with a base pressure 8×10^{-3}Pa. The target is titanium with a purity of 99.9% and a diameter of 60mm. The separation between the target and substrates is about 5cm. Glass substrates were firstly cleaned by standard cleaning procedures. A mixture of Ar and O_2 gases was used as sputtering gas. Throughout this work, the flow rates of Ar and O_2 was kept at 1:2. The sputtering pressure was kept at 2Pa. The films were prepared at rf power of 300W. The temperature of the substrate was maintained at 250°C and the deposition time was in a range from 10 to 60min. For convenience of description , the films are called film A, B, C and D according to the different deposition time, respectively. The x-ray diffraction (XRD) pattern of the film D is shown in Fig.1. The film shows good crystalline phase.

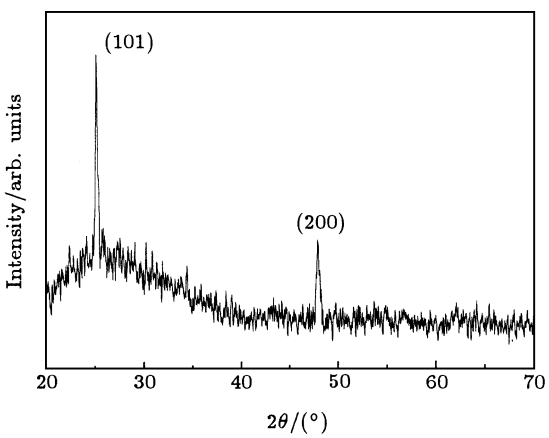


Fig.1. XRD pattern of the film D.

In the parameters extraction calculation, the two algorithms, the single-step and double-step optimization methods were compared with each other, and the results are listed in Table 1 and Fig.2. It can be seen from Table 1 that the values of the extracted thickness d of the films A to C obtained from the two methods are very close, but the calculated times are much different. Except for film B, the time elapsed by using the double-step method is nearly one tenth of that by using the single-step one. Unfortunately, the single-step optimization procedure cannot find good fitting result for some complex case, such as film D. Compared with the result obtained by the single-step method, better result can be obtained by the double-step method, as shown in Fig.2.

Table 1. Thickness extraction.

Film	Depositing time/min	$d_{\rm extracted}$/nm		Error		Time/s	
		Single	Double	Single	Double	Single	Double
A	10	40	40	0.0220	0.0279	3770	317
B	20	54.5	54.5	0.0120	0.0120	4586	4586
C	30	92.7	92.4	0.0605	0.0609	2048	300
D	60	161	297	0.682	0.1137	4578	607

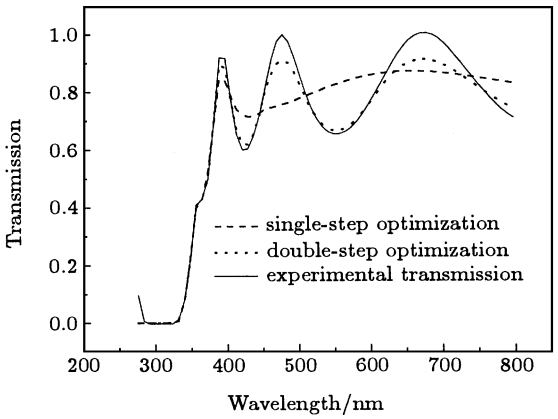


Fig.2. Comparison of the first optimization result with the second one for the experimental transmission spectrum of sample D.

The double-step and the experimental transmission spectra for the four samples are plotted in Fig.3. Good agreements were obtained expect for the film D. From the above analysis, we can see that the double-step optimization is better than the single-step one, and the former excels in calculation time and precision.

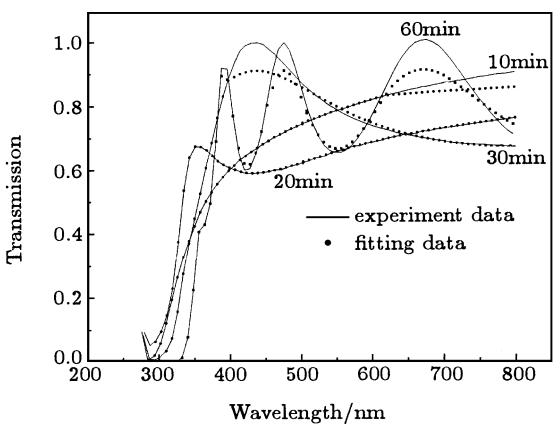


Fig.3. The measured and retrieved values of the transmission from TiO_2 thin films prepared with different depositing time.

As Ernesto *et al*[10] pointed out, the pointwise constrained optimization approach can retrieve the correct thickness and optical constants of the film, and it does not rely on the existence of the interference fringes. From Fig.3 and Table 1 it can be seen that the thickness of the film ranges from 40 to 300 nm. With increasing thickness, interference fringes appear and the highest precision can be obtained at a thickness of 54.5nm. The optical constants of the four TiO_2 films, n and k, vary with increasing wavelength from 300 to 800nm, as shown in Fig.4. Within the visible light region the refraction index of these films ranges mainly from 2 to 2.5, and their extinction coefficients are very close to zero. These calculated optical constants decrease sharply for wavelength below 300 nm. The distribution of the refraction index and extinction coefficient is similar to those in Refs.[11] and [12].

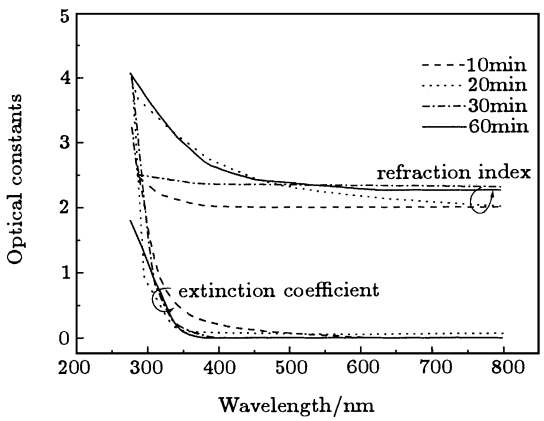


Fig.4. Retrieved optical constants for different films versus wavelength.

In conclusion, thin TiO_2 films have been prepared on glass substrates by rf magnetron sputtering technique. The thin films show good optical quality and crystalline phase. A modified pointwise constrained optimization approach, double-step optimization, was used to extract the film thickness and optical constants. The new calculation method can save calculation time and enhance precision.

References

[1] Nishida K, Morisawa K, Hiraki A, Muraishi S and Katoda T 2000 *Appl. Surf. Sci.* **159–160** 143

[2] Zarate R A and Fuenzalida V M 2004 *Vacuum* **76** 13

[3] Zhao K, Zhu F, Wang L F *et al* 2001 *Acta Phys. Sin.* **50** 1390 (in Chinese)

[4] Fernandez L A, Espinos J P, Belderrain T R *et al* 1994 *Thin Solid Films* **241** 198

[5] Hu L H, Dai S Y and Wang K J 2003 *Acta Phys. Sin.* **52** 2135 (in Chinese)

[6] Wang B L and Hu L L 2004 *Chin. Phys.* **13** 1887

[7] Bron M and Wolf E 1980 *Principles of Optics* (London: Pergamon)

[8] Heavens O S 1991 *Optical Properties of Thin Films* (New York: Dover)

[9] Chambouleyron I, Martinez J M, Moretti A C and Mulato M 1997 *Appl. Opt.* **38** 8238

[10] Ernesto G B, Chambouleyron I and Martinez J M 1999 *J. Comput. Phys.* **151** 862

[11] Amassian A, Desjardins P and Martinu L 2004 *Thin Solid Films* **447–448** 40

[12] Kunio O, Naohiro M and Akira S 1996 *Thin Solid Films* **281–282** 427