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Optimization of process parameters of titanium dioxide films by response surfaces methodology

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Abstract

An efficient approach for determination of the optimum process parameters for titanium dioxide coatings by using second-order response surface model is presented and investigated experimentally. Thin films were prepared by electron-beam evaporation associated with ion-beam assisted deposition by using different control factors, including starting materials, working pressure, substrate temperature, deposition rate and annealing temperature. The factorial design of the experiment was established to meet the equipment conditions and to avoid affecting the results. The main effect between various factors and interactions are independent. The significant level of both the main effects and the interaction are observed by analysis of variance (ANOVA) approach. Based on the statistical analysis, the results have provided much valuable information on the relationship between various control factors and thin film properties. Besides the optimum optical constants and surface roughness of TiO_2 thin films were obtained in the range of each parameter level. The factorial prediction model for preparation parameters of thin film was also established.

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Keywords: Thin films; Ion-beam assisted deposition; Optical properties; Response surface methodology

1. Introduction

The preparation of titanium dioxide (TiO_2) thin films have been characterized for a long time and a huge amount of information can be found in the literature. TiO_2 thin films are transparent in the visible region of the optical spectrum, possess a high refractive index, and show excellent mechanical and environmental stability. They can be prepared by various coating techniques, such as reactive evaporation [1–4], electron-beam evaporation [5–12], ion-assisted deposition [13–18], dc sputtering [19], pulsed magnetron sputtering [20], r.f. magnetron sputtering [21,22] and ion-beam sputtering [23,24]. There were large variations in the properties of TiO_2 films produced by each technique. Film refractive index, absorption, surface roughness, and microstructure seemed to depend not only on the deposition technique but also on the particular coating chamber and parameters used [25].

Ion-assisted deposition (IAD) is the bombardment of a growing film by an energetic beam of ions. The major effect of IAD is to increase the packing density of the films and reduce their adsorption of moisture and then increase their stability. As for choosing the starting material to obtain an ideal layer, it is required to decide which one is better from the standpoints both of process stability and reliability. Pulker et al. [2] suggested the use of Ti_3O_5 for the deposition of TiO_2 films, and Aoki and Ogura [26] also proved the process stability from the starting material of Ti_3O_5 by conventional electron-beam deposition. The Ti_3O_5 as a starting material is shown that the stabilized deposition

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process is obtained. But it is still left unsolved to prove whether Ti_3O_5 starting material is still best for the IAD process.

The refractive index and extinction coefficient of TiO_2 films is strongly influenced by the deposition parameters and stoichiometry of the evaporation material. Ritter [27] reported that different process parameters have significant effects on the microstructure and properties of thin films. In fact, each deposition system has its own operating range, and then it is difficult to compare the effects of the process parameters between different systems. Because of the structure of thin film is closely related to the input energy or momentum of the source atom from the specified method; therefore, it is important to study the effects of some key parameters on the properties of thin films.

Single-variable experiment is the most familiar method to characterize each parameter effect on the thin film properties. However, this approach is unable to predict the best conditions of the optical coating process. In this respect, experimental designs are appropriate tools for this purpose. Among experimental designs, second-order designs such as central composite design [28–30] allow process modeling and determination of optimal conditions. Therefore, we propose a central composite design with quadratic response surface model to optimize experimental conditions of TiO_2 thin films.

The design of experiment (DOE) method is a power technique to optimize a complex process. Using the DOE technique, one may obtain the optimum conditions associated with a specified property by performing much fewer experiments than the traditional single-variable method. The purpose of this research is to present the feasibility and reliability of the DOE method on the optimization of the process parameters. Since central composite design (CCD) is used extensively in building second-order response surface model. The CCD model was first described by Box and Wilson in 1951 [28]. Each design consists of a standard first-order design with n_F orthogonal factorial points and n_C center points, augmented by "axial points". Under our convention, axial points are points located at a specified distance from the design center in each direction on each axis defined by the coded factor levels. Thus, if there are k factors, there are $2k$ distinct axial points. Axial points are also commonly referred to as star points. A central composite design is easily built up from a standard first-order design by the addition of axial points, and possibly some extra factorial and center points. We used the central composite design for fitting a second-order model. Generally speaking, the CCD consists of a 2^k factorial with n_F points, $2k$ axial or star points, and n_C center points. There are two parameters in the design that must be specified: the distance of the axial points from the design center and the number of center points n_C. In this paper, the determination of the optimum deposition condition of ion-assisted TiO_2 thin films is based on response surface methodology, which integrates a design of experiment, regression modeling technique for fitting a model to experiment data and basic optimization. The refractive index, extinction coefficient, and surface roughness were measured to evaluate the optical characteristic of TiO_2 films. The optical properties of the resulting TiO_2 films with regard to starting material, substrate temperature, working pressure, deposition rate, and annealing temperature were investigated and discussed.

2. Experimental detail

2.1. Fractional factorial experiment design

The use of fractional factorial design is among the most widely used types of designs for product and process design and for process improvement. A one-half fraction of the 2^5 design (i.e. 2^{5-1} design) with I = ABCDE is a resolution V design. The effect of a factor is defined to be the change in response produced by a change in the level of the factor. This is frequently called a main effect because it refers to the primary factors of interest in the experiment. For this design, no main effect or two-factor interaction (cross product) is aliased with any other main effect or two-factor interaction, but every main effect is aliased with a four-factor interaction, and every two-factor interaction is aliased with a three-factor interaction. We would expect the 2^{5-1} design to provide excellent information concerning the main effects and two-factor interactions.

The aim of this research was to optimize the process parameters of TiO_2 thin films prepared by electron-beam evaporation with ion-beam assisted deposition. A central composite design was carried out following the methodology described by Box et al. [28–30]. It is comprised of a 2^{5-1} design. In this design, we assume that the high and low levels of the k factors are coded to the usual ±1 levels. The experiment design includes five controllable process factors, whose levels are listed in Table 1. We follow the convention of coding the factor levels so the factorial points have coded levels ±1 for each factor. The region of interest, coded $\{-1, 1\}$, is a region determined by lower and upper limits on factor level setting combinations that are of major interest. It should be noted that some software packages will recode the levels in a central composite design before doing the analysis. In this paper, five control factors in the optical coating process for TiO_2 thin film deposition were investigated in a central composite design with the objective of optimizing experimental conditions. Using the CCD approach often lead to great economy

Table 1
Design factors and their levels

Control factors	Symbol	Factor levels	
		Low (−1)	High (+1)
Starting material	A	TiO_2	Ti_3O_5
Working pressure (Torr)	B	0.8×10^{-4}	1.0×10^{-4}
Substrate temperature (°C)	C	150	300
Deposition rate (Å/s)	D	2	3
Annealing temperature (°C)	E	200	350

and efficiency in experimentation, if the runs can be made sequentially. We were preferable to run a 2^{5-1} fractional design, including $n_F = 16$ runs, $2k = 10$ axial runs, and $n_c = 4$ center runs. Therefore, the total number (N) of the design experiments was 30 (i.e. $N = n_F + 2k + n_c$). All experiments were randomly performed. Multiple regression enables a description of the mathematical relationship between the different coded variables and the experimentally obtained responses. The resulting second-order model can be described by the polynomial expression in k design variables:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{\substack{i=1 \\ i<j}}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + \varepsilon, \qquad (1)$$

where X_i is the coded variables, the parameters β_i are the regression coefficients for linear terms, $\beta_{ij} X_i X_j$ is the interaction terms and the β_{ii} represent pure second-order or quadratic effects. The ε is the noise or error observed in the response variable Y.

In order to determine the optimum deposition conditions for the coating system or to determine a region of the factor space in which operating requirements are satisfied. Once the region of the optimum has been found, the second-order response surface model can be employed to get the optimal parameters, and an analysis can be performed to locate the optimum. In this study, coefficients for regression models, optimized conditions and response surfaces were calculated by using Design-Export® software package.

2.2. Thin film preparation and measurement

TiO_2 thin films were deposited by ion-assisted electron-beam evaporation technique. Substrates used in this experiment were N-BK7 glass with 30 mm in diameter. Prior to deposition, the substrates were undergone ultrasonic cleaning progressively in acetone and ethanol and then dried in a vacuum dryer. Two kinds of starting materials of TiO_2 and Ti_3O_5 granules were chosen to make titanium dioxide films. Titanium dioxide films have been deposited on glass substrates by ion-assisted e-beam evaporation. Fig. 1 is a schematic diagram of a vacuum thin film deposition system used for this study. The system consisted of a chamber equipped with e-beam source for evaporation, a substrate holder and an ion-beam source directed toward a substrate, both a quartz crystal monitor and an optical monitor to control evaporation. TiO_2 films were deposited by the technique of ion-assisted electron-beam evaporation. The distance between the starting material and the substrates was 935 mm. Samples were mounted onto a planetary rotation of substrate holder with a 400 mm in diameter that rotated at a speed of 36 rpm. A thermocouple was placed near the sample holder to monitor the chamber temperature. An e-beam gun was used to evaporate Ti_3O_5 and TiO_2 granules. The film thickness and the rate of deposition were controlled by both optical and quartz crystal monitors. The deposition rates of 2 Å/s and 3 Å/s were used in this research. A gridless ion source (SINTECH Ion System, ST-2000) was used to assist the deposition process. The vacuum chamber was initially pumped down by a mechanical pump and cryopump to the base pressure of less than 2×10^{-6} Torr. Oxygen, the active gas, was fed near the material source at a flow rate regulated with a needle valve. During deposition, the total chamber pressure was maintained at 2.5×10^{-4} Torr by adjusting the oxygen flow. The oxygen partial pressure was controlled at 0.8×10^{-4}–1.0×10^{-4} Torr. The ion-beam voltage was 240 V; while the ion current was 1 A. The optical thickness of TiO_2 thin film was one wavelength at 550 nm.

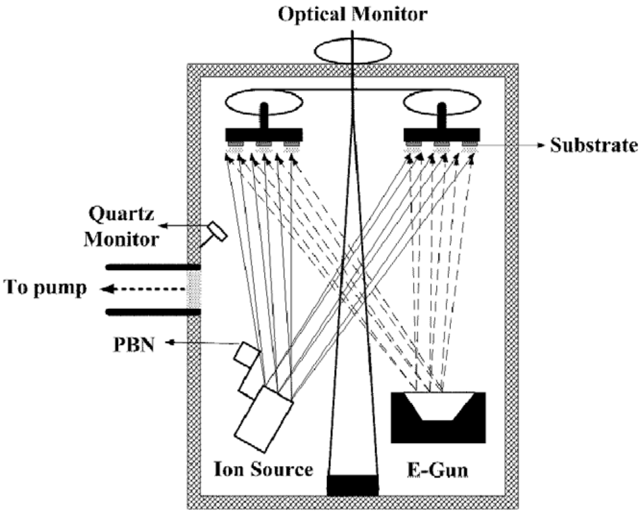

Fig. 1. Schematic diagram of an experimental setup.

Spectral transmittance and reflectance were measured using a spectrophotometer (SHIMADZU, model Solidspec-3760). The spectra of the TiO_2 films were obtained by a spectrophotometer scanning from 320 nm to 800 nm. The spectral transmittance of a film deposited from starting material of TiO_2 was compared to a film deposited from that of Ti_3O_5, as shown in Fig. 2. Refractive index, extinction coefficient and physical thickness

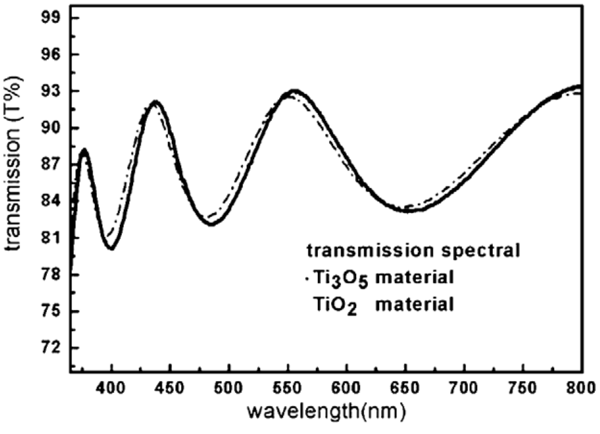

Fig. 2. Spectral transmittance of TiO_2 films prepared by different starting materials.

were calculated by the envelope method from the transmittance spectrum of the films [31]. The surface roughness was characterized by atomic force microscope (AFM). Annealing treatment of TiO_2 films in atmospheric environment at elevated temperatures of 200 °C and 350 °C was investigated. The AFM measurements were performed ex situ after deposition and annealing at both 200 °C and 350 °C, respectively. The surface roughness can be quantitatively identified by the root-mean-square roughness. For comparison, we have performed AFM measurements on the TiO_2 film surfaces that prepared by two starting materials of TiO_2 and Ti_3O_5, as shown in Fig. 3. The studied surfaces are equal to 20×20 μm in area. TiO_2 thin film deposited from starting material of Ti_3O_5 shows a surface roughness of 1.052 nm less than that of 1.176 nm for TiO_2 as starting material.

2.3. Optimization of process parameters

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response. In most RSM problem, the form of the relationship between the response and the independent variables is unknown. Thus, the first step in RSM is to find a suitable approximation for the true functional relationship between the response variable and the set of independent variables. Second, the response surface analysis is performed by means of using the fitted surface. If the fitted surface is an adequate approximation of the true response function, then analysis of the fitted surface will be approximately equivalent to analysis of the actual system. The model parameters can be estimated most effectively if proper experimental designs are used to collect the data.

The eventual objective of RSM is to determine the optimum process parameters. It is very helpful to present the results of many experiments in terms of an empirical model, that is, an equation derived from the data that express the relationship between the response and the important design factor. Residual analysis and model adequacy checking are also important analysis techniques. In this paper, a four-factor quadratic model was used as a preliminary model. An analysis of variance (ANOVA) is a necessary test procedure for applying the experimental data to verify the model being adequate. The significance level of terms in the quadratic model shall be justified by the *t*-test and one would reject the non-significance terms to reduce model. The next step is to perform the residual analysis and to find the response variables in the response surface equation. Finally, we shall find the optimal solutions in the response variables.

Response surface design is often used to build models for making predictions. Therefore, the prediction variance is of considerable important in evaluating or comparing designs. Two-dimensional contour plots or three-dimensional response surface plots of prediction variance provide a good profile of the prediction variance through out the experimental region. After software package calculation, the optimization of process parameters was obtained.

3. Results and discussion

Relevant factors and their experimental domain were selected in accordance with our preliminary result. After some preliminary experiments it was concluded that the five most important parameters which determinate the quality of TiO_2 film are investigated, as shown in Table 1. We have used a central composite design to optimize experimental conditions of IAD TiO_2 film properties.

The response surface study of central composite design refers to evaluation of the anticipated quadratic model. The model evaluation algorithm is found no aliases for the quadratic model. The evaluation of the design itself is based on advanced regression matrix analysis for the selected response surface model. The analysis of variance for response surface reduced quadratic model is shown in

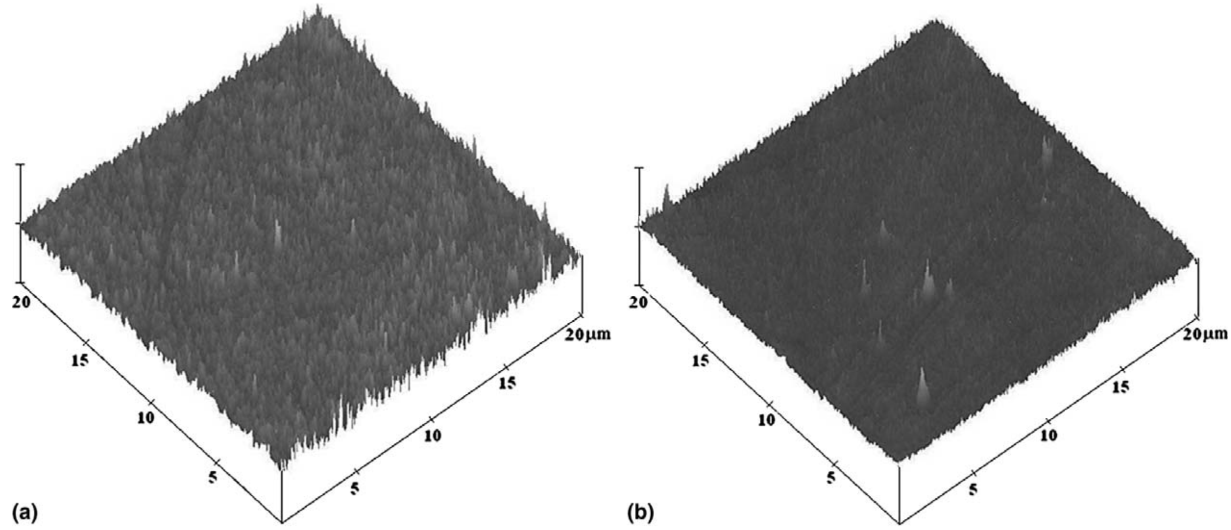

Fig. 3. AFM images showing a surface roughness of TiO_2 film prepared by two starting materials of (a) TiO_2; (b) Ti_3O_5.

Table 2. Notice that there are many significant factors in the ANOVA. The computer output contains the usual sums of squares, degrees of freedom (DF), mean squares, and test statistic F. The column F-value of 14.32 implies the model is significant. Moreover, the model's "Prob > F" value is extremely low: <0.0001. This shown that model terms are highly significant. Hence the quadratic model for response variables is adequate. In addition to the basic analysis of variance, the program displays some other useful information. The R-squared of 0.9463 is in reasonable agreement with the "Adj R-squared" of 0.8803. This indicated that it after model diagnostic is adequate. Finally, we can obtain the equations in terms of coded factors for the surface response as follows:

$$\begin{aligned} Y_1 = {} & 2.310 + 7.551 \times 10^{-3}A - 0.011B + 0.076C \\ & + 8.000 \times 10^{-3}D + 1.258 \times 10^{-3}E - 3.273 \\ & \times 10^{-3}B^2 - 0.017C^2 - 2.614 \times 10^{-3}E^2 - 9.744 \\ & \times 10^{-3}AB - 4.452 \times 10^{-3}AC - 3.625 \times 10^{-3}CD \\ & - 5.900 \times 10^{-3}CE, \end{aligned} \tag{2}$$

$$\begin{aligned} Y_2 = {} & 1.748 \times 10^{-3} + 4.583 \times 10^{-6}A - 6.597 \times 10^{-4}C + 3.340 \\ & \times 10^{-5}E + 1.817 \times 10^{-4}C^2 - 1.260 \times 10^{-4}AE, \end{aligned} \tag{3}$$

$$\begin{aligned} Y_3 = {} & 2.310 - 4.834 \times 10^{-3}A - 0.060B - 0.33C \\ & - 0.38D + 0.23E - 0.096B^2 + 0.27C^2 + 0.14E^2 \\ & - 0.16AB - 0.25CD + 0.24DE, \end{aligned} \tag{4}$$

where the measured response Y_1 is defined as the refractive index, Y_2 is the extinction coefficient, Y_3 is the surface roughness. These equations allow the prediction of any value within the experimental domain using five control factors.

Table 3 shows individual term by performing t-test for the response surface reduced model of the average refractive index response. An analysis of variance was used by Design-Expert software for the average refractive index of TiO_2 thin films. For optimization purposes it is necessary to characterize how the significant factors affect the investigated response and to define an objective of improving the response of interest. In order to obtain the optimal parameter values, the surface responses were then calculated. The quadratic response equation is represented as a solid surface in the two-dimensional diagram of Fig. 4. Fig. 4a illustrates 2-D projection contour diagram of the response surface for the refractive index of TiO_2 thin films as a function of starting material and working pressure. As the above definition, each process variable is studied at two levels, for example, low level (TiO_2 represented by -1) and high level (Ti_3O_5 represented by $+1$) on the horizontal scale of the plot. The prediction value of film's average refractive index for start material of Ti_3O_5 is higher than that of TiO_2 at low working pressure. It shows that the refractive index increases with decrease in working pressure. Ritter [1] and Pulker [2] have observed similar variations in refractive index with oxygen pressure as well as deposition rate. Fig. 4b shows a stationary ridge in the center of the plot

Table 2
ANOVA table for response surface reduced quadratic model

Source	Sum of squares	DF	Mean square	F-value	Prob > F
Model	10.92	16	0.680	14.32	<0.0001
Residual	0.62	13	0.048		
Lack of fit	0.61	9	0.068	55.27	0.0008
Pure error	4.943×10^{-3}	4	1.236×10^{-3}		
Cor total	11.54	29			
Root MSE	0.22	R-squared	0.9463		
Dep mean	2.55	Adj R-squared	0.8803		
CV	8.57	Pred R-squared	0.5608		
PRESS	5.07	Adeq precision	14.6370		

Table 3
Individual term by performing t-test for the response surface reduced model of the refractive index

Factors	Coefficient estimate	DOF	Standard error	t for H_0 Coeff = 0	Prob > $\lvert t \rvert$
Intercept	2.310	1	2.263×10^{-3}		
A	7.551×10^{-3}	1	1.218×10^{-3}	6.20	<0.0001
B	−0.011	1	1.322×10^{-3}	−8.47	<0.0001
C	0.076	1	1.444×10^{-3}	52.56	<0.0001
D	8.000×10^{-3}	1	1.322×10^{-3}	6.05	<0.0001
E	1.258×10^{-3}	1	1.322×10^{-3}	0.95	0.3546
B^2	-3.273×10^{-3}	1	1.392×10^{-3}	−2.35	0.0311
C^2	−0.017	1	2.095×10^{-3}	−8.26	<0.0001
E^2	-2.614×10^{-3}	1	1.210×10^{-3}	−2.16	0.0454
AB	-9.744×10^{-3}	1	1.558×10^{-3}	−6.25	<0.0001
AC	-4.452×10^{-3}	1	1.513×10^{-3}	−2.94	0.0091
CD	-3.625×10^{-3}	1	1.600×10^{-3}	−2.27	0.0368
CE	-5.900×10^{-3}	1	1.600×10^{-3}	−3.69	0.0018

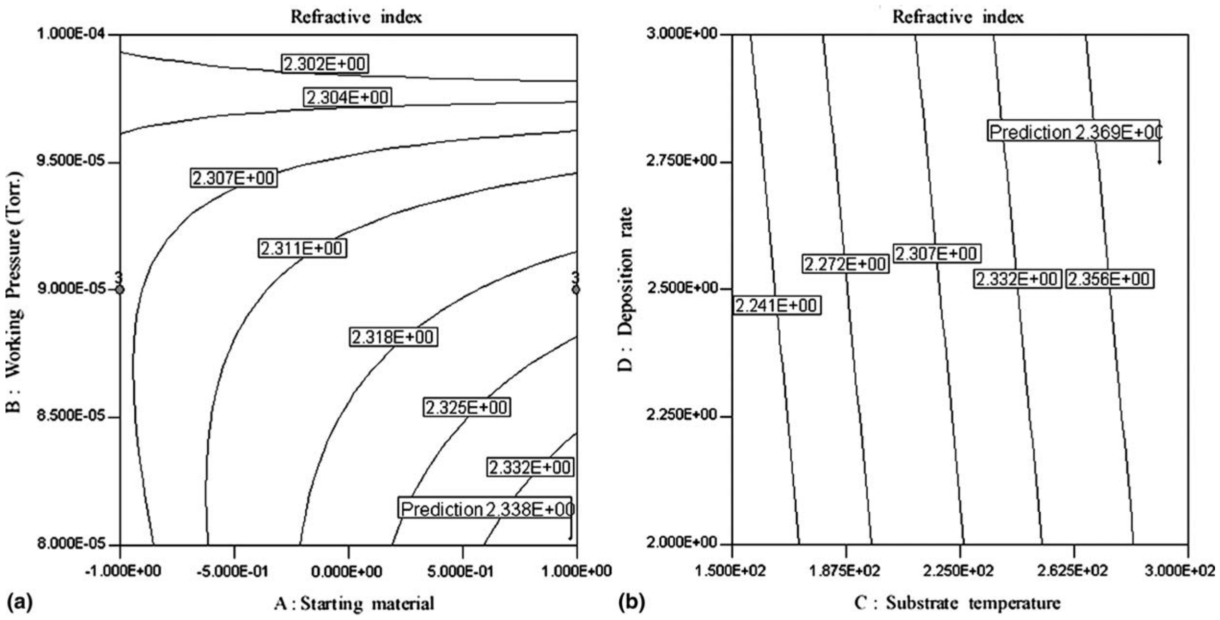

Fig. 4. A response surface and contour plot showing the refractive index as a function of (a) starting material and working pressure; (b) substrate temperature and deposition rate.

with a decreasing response to the left of the center line of maximum response. It also shows response surface for the refractive index with respect to the substrate temperature and deposition rate. We found that increasing the substrate temperature caused a higher refractive index of TiO_2 thin films. The refractive index with the increase of substrate temperature might be due to the improved packing density of the films. This result is in agreement with the work of others who have found the higher refractive index of the films deposited either at higher rates of deposition or at low working pressure [5,12]. For comparison, the value of the optimal process parameters for the refractive index of TiO_2 films prepared by two starting materials is presented in Table 4.

Table 5 shows individual term by performing *t*-test for the response surface reduced model of the average extinction coefficient. Fig. 5 demonstrates a saddle contour plot of the response surfaces for the extinction coefficient of TiO_2 thin films. Response surfaces show that the average refractive index (Y_2) is a function of the starting material and the annealing temperature. Nevertheless the working pressure and deposition rate have no significant effect on the extinction coefficient of the films. For two kinds of starting materials (nominally TiO_2 and Ti_3O_5), the optimal

Table 4
Comparison of the optimal process parameters for the refractive index of TiO_2 thin film using two starting materials

Process parameter	Starting material	
	TiO_2	Ti_3O_5
Working pressure (Torr)	8.79×10^{-5}	7.00×10^{-5}
Substrate temperature (°C)	330.0	330.0
Deposition rate (Å/s)	3.5	3.5
Annealing temperature (°C)	172.9	174.8

Table 5
Individual term by performing *t*-test for the response surface reduced model of the extinction coefficient

Factors	Coefficient estimate	DF	Standard error	t for H_0 Coeff = 0	Prob > $\|t\|$
Intercept	1.748×10^{-3}	1	7.366×10^{-5}		
A	4.583×10^{-6}	1	4.856×10^{-5}	0.094	0.9256
C	-6.597×10^{-4}	1	5.893×10^{-5}	−11.19	<0.0001
E	3.340×10^{-5}	1	5.394×10^{-5}	0.62	0.5416
C^2	1.817×10^{-4}	1	8.197×10^{-5}	2.22	0.0364
AE	-1.260×10^{-4}	1	5.472×10^{-5}	−2.30	0.0303

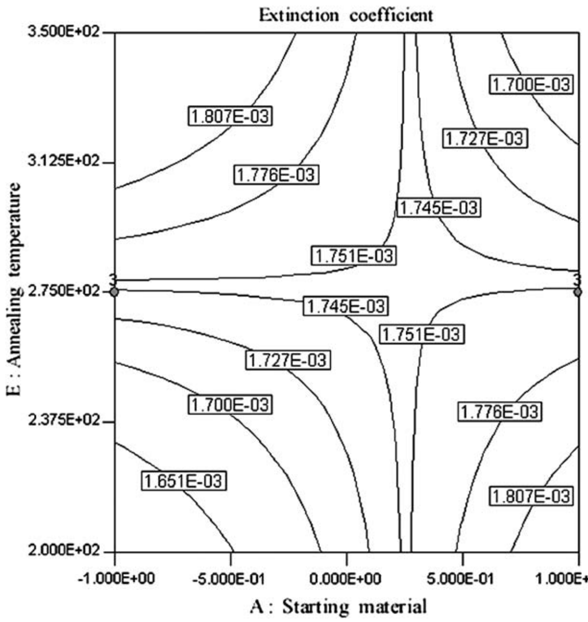

Fig. 5. A response surface and contour plot showing the average extinction coefficient as a function of starting material and annealing temperature.

Table 6
Summary of the optimal process parameters for the extinction coefficient of TiO_2 thin film

Process parameter	Starting material	
	TiO_2	Ti_3O_5
Working pressure (Torr)	–	–
Substrate temperature (°C)	330	330
Deposition rate (Å/s)	–	–
Annealing temperature (°C)	125.0	425.0

process parameters of the average extinction coefficient are substrate temperature for 330 °C and annealing temperature for 125 °C, respectively. Table 6 shows the optimal process parameters for the extinction coefficient of TiO_2 films prepared by two starting materials. However, the working pressure and deposition rate are not significant.

We center our attention in the variation of the optical properties of TiO_2 films at different annealing temperatures. Some publications [6,12,18,19,21,23,24] have showed that the annealing temperature has a strong influence on the structure of the film and results in the decrease of extinction coefficient. The as-deposited films are oxygen deficient and absorb sufficient oxygen from the ambient atmosphere on post-deposition annealing treatment. In this study, two sets of the TiO_2 films were annealed at different temperatures of 200 °C and 350 °C for 24 h. The optical measurements showed that annealing treatment could modify the density of TiO_2 thin films which change their refractive indices and extinction coefficients.

Table 7 shows individual term by performing t-test for the response surface reduced model of the surface roughness. It can be seen from Fig. 6a that a response surface and saddle contour plot of showing the surface roughness (Y_3) as a function of the starting material and working pressure. Fig. 6b illustrates a rising ridge contour plot of the response surface for the surface roughness with respect to substrate temperature and deposition rate, respectively. The optimal process parameters for the surface roughness of TiO_2 films prepared by two starting materials are summarized in Table 8.

Table 7
Individual term by performing t-test for the response surface reduced model of the surface roughness

Factors	Coefficient estimate	DF	Standard error	t for H_0 Coeff = 0	Prob > $\lvert t \rvert$
Intercept	2.31	1	0.087		
A	-4.834×10^{-3}	1	0.047	−0.10	0.9193
B	−0.06	1	0.051	−1.17	0.2592
C	−0.33	1	0.056	−5.91	<0.0001
D	−0.38	1	0.051	−7.43	<0.0001
E	0.23	1	0.051	4.41	0.0003
B^2	−0.096	1	0.053	−1.79	0.0897
C^2	0.27	1	0.078	3.51	0.0025
E^2	0.14	1	0.047	3.01	0.0075
AB	−0.16	1	0.060	−2.66	0.0160
CD	−0.25	1	0.062	−4.07	0.0007
DE	0.24	1	0.062	3.96	0.0009

Many response surface problems involve the analysis of several responses. We optimized the process with respect to three responses, including the refractive index, extinction coefficient and surface roughness. After optimization of multiple responses, the process parameters were determined by the software package. A comparison of the optimal process parameters of IAD TiO_2 films between TiO_2 and Ti_3O_5 starting materials is given in Table 9. For the optimal process parameters of the starting material of TiO_2, the prediction value of film's average refractive

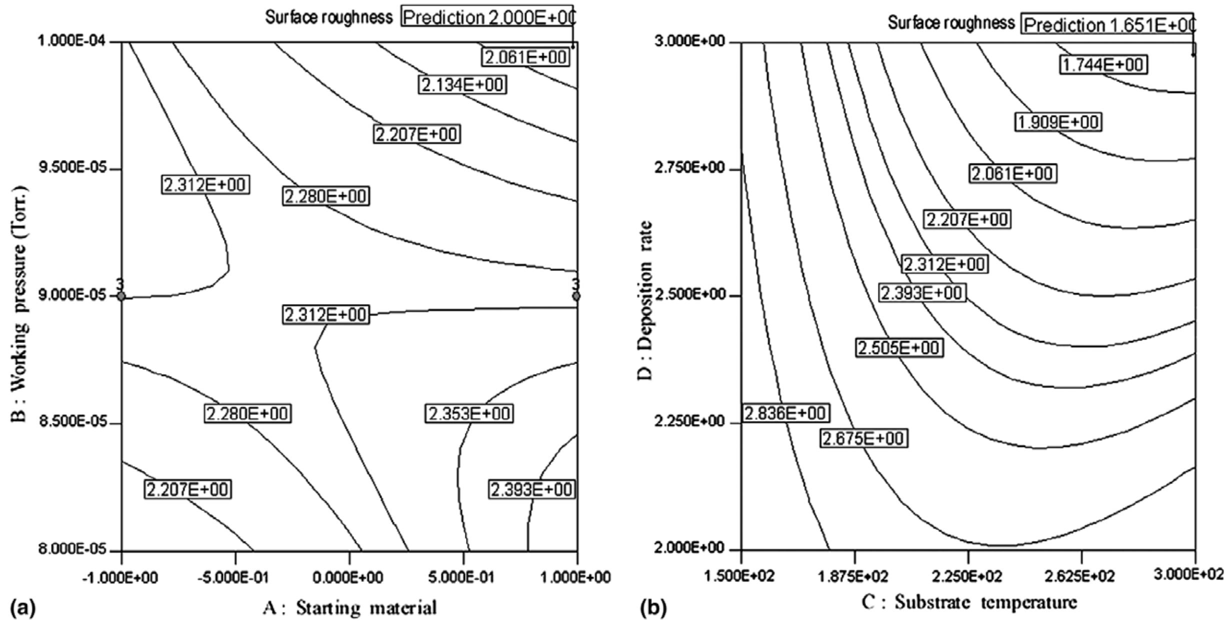

Fig. 6. A response surface and contour plot showing surface roughness as a function of (a) starting material and working pressure; (b) substrate temperature and deposition rate.

Table 8
Summary of the optimal process parameters for the surface roughness of TiO_2 thin film

Process parameter	Starting material	
	TiO_2	Ti_3O_5
Working pressure (Torr)	9.704×10^{-5}	8.726×10^{-5}
Substrate temperature (°C)	197.8	207.9
Deposition rate (Å/s)	2.356	2.472
Annealing temperature (°C)	137.7	339.3

Table 9
Comparisons between TiO_2 and Ti_3O_5 starting materials for the optimal process parameters of IAD TiO_2 thin film

parameter	Starting material	
	TiO_2	Ti_3O_5
Working pressure (Torr)	8.808×10^{-5}	7.021×10^{-5}
Substrate temperature (°C)	329.8	329.9
Deposition rate (Å/s)	3.0	3.5
Annealing temperature (°C)	112.0	302.2
Refractive index	2.391	2.419
Extinction coefficient	8.575×10^{-4}	1.152×10^{-3}
Surface roughness	1.25	1.23

index, extinction coefficient and surface roughness are determined to be 2.391, 8.574×10^{-4} , and 1.25 nm, respectively. For TiO_2 film with Ti_3O_5 as starting material, the average refractive index of 2.419, the average extinction coefficient of 1.152×10^{-3} and surface roughness of 1.23 nm were also obtained. The above results suggest that the optical constants and surface roughness of IAD TiO_2 films are extremely important factors prior to its application in any optical devices.

4. Conclusions

In this research, the response surface methodology has been demonstrated to be an adequate tool to improve the analytical results of the thin film deposition process. Using the quadratic response surface model, one may obtain the optimum conditions associated with a specific property by performing much fewer experiments than the traditional single-variable method.

TiO_2 thin films prepared by ion-assisted e-beam evaporation technique have been optimized by second-order response surface methodology. The analysis of variance (ANOVA) for response surface quadratic model was conducted to find the sensitive parameters and predict the optimum conditions. We have observed both optical properties and surface roughness for titanium dioxides from different control factors. On one hand the refractive index of the films increased with decrease of working pressure, increase of deposition rate, and substrate temperature. On the other hand the extinction coefficient decreased with the increase of annealing temperature. Further, AFM analysis shows that the surface roughness of TiO_2 films increases with the annealing temperature. Compared with two starting materials, the starting material of Ti_3O_5 shows the IAD titanium oxide films with high refractive index and low surface roughness. Its extinction coefficient can be improved by annealing at higher temperature. We find that starting material of Ti_3O_5 for the TiO_2 thin film deposition presents more stable characteristics in the process.

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References

[1] E. Ritter, J. Vac. Sci. Technol. 3 (1966) 25.
[2] H.K. Pulker, G. Paesolk, E. Ritter, Appl. Opt. 15 (1976) 2986.
[3] H. Küster, J. Ebert, Thin Solid Films 70 (1980) 43.
[4] S.C. Chiao, B.G. Bovard, H.A. Macleod, Appl. Opt. 37 (1998) 5284.
[5] H.W. Lehmann, K. Frik, Appl. Opt. 27 (1988) 4920.
[6] K.N. Rao, M.A. Murthy, S. Mohan, Thin Solid Films 176 (1989) 181.
[7] K.N. Rao, S. Mohan, J. Vac. Sci. Technol. A8 (1990) 3260.
[8] Y. Leprince-Wang, K. Yu-Zhang, Surf. Coat. Technol. 140 (2001) 155.
[9] F. Waibel, E. Ritter, R. Linsbod, Appl. Opt. 42 (2003) 4590.
[10] L. Sun, P. Hou, Thin Solid Films 455–456 (2004) 525.
[11] H. Selhofer, E. Ritter, R. Linsbod, Appl. Opt. 41 (2002) 756.
[12] K.N. Rao, Opt. Eng. 41 (2002) 2357.
[13] F. Varnier, J. Vac. Sci. Technol. A 8 (1990) 2155.
[14] M. Gilo, N. Croitoru, Thin Solid Films 283 (1996) 84.
[15] Q. Tang, K. Kikuchi, S. Ogura, H.A. Macleod, J. Vac. Sci. Technol. A 17 (1999) 3379.
[16] Y. Leprince-Wang, D. Souche, K. Yu-Zhang, S. Fisson, G. Vuye, J. Rivory, Thin Solid Films 359 (2000) 171.
[17] D. Bhattacharyya, N.K. Sahoo, S. Thakur, N.C. Das, Thin Solid Films 360 (2000) 96.
[18] C.C. Lee, H.C. Chen, C.C. Jaing, Appl. Opt. 44 (2005) 2996.
[19] D. Mardare, G.I. Rusu, Mater. Lett. 56 (2002) 210.
[20] P.S. Henderson, P.J. Kely, R.D. Arnell, H. Bäcker, J.W. Baradley, Surf. Coat. Technol. 174–175 (2003) 779.
[21] N. Martin, C. Rousselot, D. Rondot, F. Palmino, R. Mercier, Thin Solid Films 300 (1997) 113.
[22] N. Martin, D. Baretti, C. Rousselot, J.Y. Rauch, Surf. Coat. Technol. 107 (1998) 172.
[23] J.C. Hsu, C.C. Lee, Appl. Opt. 37 (1998) 1171.
[24] W.H. Wang, S. Chao, Opt. Lett. 23 (1998) 1417.
[25] J.M. Bennett, E. Pelletier, G. Albrand, J.P. Borgogno, B. Lazarides, C.K. Carniglia, R.A. Schmell, T.H. Allen, T. Tuttle-Hart, K.H. Guenther, A. Saxer, Appl. Opt. 28 (1989) 3303.
[26] T. Aoki, S. Ogura, OSA Tech. Digest Ser. 9 (1998) 207.
[27] E. Ritter, Appl. Opt. 20 (1981) 21.
[28] G.E.P. Box, K.B. Wilson, J. Roy. Statist. Soc. Ser. B 13 (1951) 1.
[29] G.E.P. Box, N.R. Draper, Empirical Model-Building and Response Surfaces, Wiley, New York, 1987.
[30] D.C. Montgomery, Design and Analysis of Experiments, sixth ed., John Wiely & Sons, New York, 2005.
[31] J.C. Manifacier, J. Gasiot, J.P. Fillard, J. Phys. E 9 (1976) 1002.