

Effective and rapid optical characterization of sequential multilayer metal oxide nanostructures by genetic algorithm approach

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In this paper, a modified genetic algorithm (M-GA) is proposed to simultaneously determine the optical constants of each successive layer of multilayer ZnO nanostructures. The thin films were produced by different sol-gel techniques in order to use in optoelectronic applications. The multilayer pure thin films were in the form of FilmA/Substrate/FilmA and FilmA/FilmB/Substrate. Unlike conventional methods, M-GA determines optical film parameters without the need of interference fringes of the experimental optical transmittance spectrum. M-GA gives good results for multilayer and double side coated thin film systems in our calculations. R-square values higher than 0.99 are obtained for typical film thickness of a few tens of nanometers.

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1. Introduction

Multilayer films, as well as single-layer films are of technological importance for current optical communication systems with many applications such as anti-reflection coatings, wavelength division multiplexing (WDM) filters, surface acoustic wave (SAW) filters, splitting filters, or dielectric mirrors [1,2]. For accurate design of such filters, the precise determination of the thickness of each layer and wavelength-dependent optical constants of layers are necessary. Hence, the performance of these devices depends on the desired values of individual layer thickness and other optical parameters. Reliable determination of the optical properties of thin films is still a matter of concern. Ellipsometric [3, 4] and spectrophotometric measurements [5, 6] are the most common, cost-effective, and non-destructive methods to determine the optical parameters for a single layer and multilayer thin films. These methods are generally based on fitting procedures and require optimization algorithms. The solution space usually includes many local minima, and traditional minimum search algorithms generally converge to a local minimum of the cost function. In addition, methods such as the Levenberg-Marquardt algorithm and the Gauss-Newton methods are very sensitive to initial values. On the other hand, genetic algorithm (GA) is very efficient in finding the region of the absolute minimum of multi-dimensional cost functions even if the search space is vast and local minima are nearby. Further, genetic algorithms are suitable for parallel computing [7].

As with the wavelength-dependent transmittance $T(\lambda)$, the optical response is usually a complicated function of refractive index $n(\lambda)$, extinction coefficient $k(\lambda)$ and film

thickness t . It is a standard step to insert dispersion relation for $n(\lambda)$ and $k(\lambda)$ in the equations of theoretical transmittance $T_{\text{theory}}(\lambda)$ to get best fit of $T_{\text{exp}}(\lambda)$ [8, 9,10]. This procedure involves elaborate computational effort. In our previous work, GA was used for the monolayer thin film systems [10] considering the multi-constant dispersion relation for both $n(\lambda)$ and $k(\lambda)$. In addition, regardless of the dispersion relation, reliable results have been achieved on the envelope of the optical transmittance spectrum [11], the envelope of the reflection spectrum [12], and the combination of the maximum envelope of the reflection spectrum and the minimum envelope of the optical transmittance spectrum [13].

Various deposition techniques present different formations and combinations for the multilayer thin films. It is possible to deposit the bilayer films on one side or both sides of a substrate using sol-gel techniques such as dip coating (DC), ultrasonic spray pyrolysis (USP) and spin coating (SC) using the functional source materials [14-17]. Apart from the silicon and germanium elements, searches for new materials have begun to increase device performance in semiconductor technology. One of the most popular materials in the last two decades is zinc oxide (ZnO). ZnO has interesting electrical, optical, and piezoelectric properties. Si is nonpiezoelectric, and GaAs is weakly piezoelectric. The piezoelectric properties of ZnO are extremely important for the SAW filter. That is why ZnO related oxides are indicated as an alternative material to the Si and GaAs based semiconductor devices [18]. In addition, ZnO is also a low refractive index material as zinc sulfide (ZnS). It can be used to build a high dielectric reflective mirror in the desired wavelength range. These

types of filters consist of stacking alternating layers of dielectric materials of low and high reflective indices.

In the present work, we aim to determine the optical constants of layered thin films formed by different sol-gel techniques using transmission spectra in the visible and near infrared wavelength range. The GA algorithm is applied to two-dimensional ZnO nanostructured thin films in different formations such as AS, BS, ASA, and ABS. The labels A, B, and S indicate DC coated film, USP coated film, and the substrate, respectively. Also, the performance of the algorithm is discussed. The film thicknesses and the constants of the selected dispersion relations for each layer are considered as tunable parameters. The proposed model based GA gives much faster and more accurate results. The parameter responsible for the absorption is compressed into a narrower region in the solution space. Hence, the global optimum solution of the fitting is realized very quickly. The algorithm has been implemented on MATLAB R2018b.

2. Materials and Methods

2.1. Experimental details

The multilayer ZnO thin films such as AS, BS, ASA, and ABS (Fig. 1) were deposited onto ultrasonically cleaned microscope glass substrates.

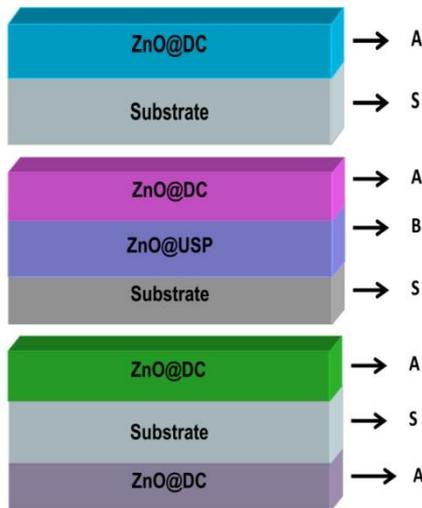


Fig. 1. Schematic representation of successive layers prepared by sol-gel techniques for pure ZnO thin films (Label "A" shows DC coated layer, label "B" shows USP coated layer and label "S" shows substrate) (color online)

For the preparation of pure layered thin films, zinc-acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was dissolved into methanol. Then monoethanolamine (MEA) was added into zinc metal salt solution, this mixture called the precursor solution, was stirred for 1 hour. This precursor solution was used in both the DC deposition system and the USP deposition system. For the DC deposition system, the withdrawal speed was fixed at 1 cm/min and the deposition time was 30 s. The two glass substrates were dipped into the precursor solution 8 times. The ZnO thin film is

deposited on both sides of the substrate in the form of ASA. Then, one side of the substrate was cleaned to obtain a ZnO thin film in the form of AS. The ZnO thin film (BS) was deposited onto glass substrates using the USP deposition system. The substrate temperature was kept constant at 400° C during the deposition process. DC and USP techniques are used consecutively to obtain bilayer ZnO thin film in the form of ABS. X-ray diffraction (XRD) diffractograms were collected with a D-Max x-ray diffractometer (Rigaku International Corp. Japan) with $\text{CuK}\alpha_1$ ($\lambda=1.5405\text{\AA}$) to obtain the structural information of the films. The optical transmittance measurement of ZnO thin films were carried out at room temperature using a PG Instruments T70 (UV/Vis/NIR Spectrophotometer).

2.2. The optical transmittance theory of layered systems

The optical properties of the thin film, in particular the film thickness (t) can be determined using the complex refractive index $\hat{n}(\lambda)=n(\lambda)+j\kappa(\lambda)$ for each wavelength. Here, the refractive index $n(\lambda)$ and extinction coefficient $\kappa(\lambda)$ are the real and imaginary parts of $\hat{n}(\lambda)$, respectively. The absorption $\alpha(\lambda)$ can be associated with the extinction coefficient through $\kappa(\lambda)=\lambda\alpha(\lambda)/4\pi$. Considering the thickness of the layer(s) and absorbance $x(\lambda)=\exp(-\alpha t)$ of the film(s) and the substrate refractive index s , the empirical expression of the optical transmittance (T) for the normal incidence of layered thin film system is given as follows,

$$T = \frac{U}{V+Y} \quad (1)$$

$$U = 64s(n_1^2 + \kappa_1^2)(n_2^2 + \kappa_2^2)x_1x_2$$

$$V = x_1x_2(Ax_1x_2 + Bx_1x + Cx_2 + D + E)$$

$$Y = x_1(Fx_1 + G) + x_2(Hx_2 + I) + J$$

If the content of the variables changes, the above equations may also be used for double layer structures such as ASA and ABS structures. In addition, as the thickness of one of the films goes to zero, the formula leads to that of a thin film on the transparent substrate. The exact formulations can be found in reference [9].

2.3. Model based genetic algorithm for multilayer systems

The genetic algorithm is a popular and successful technique for solving optimization problems. The basis of the algorithm is based on Darwin's theory consisting of natural selection and evolution. In the previous work, the thickness of single layer (t), refractive index $n(\lambda)$ and absorption coefficient $\alpha(\lambda)$ are the genes of population and they were used to find the fitness of the solution. The implementation of GA and computational details are given in the references [10, 12]. In the present work, model based GA was adapted for layered structures. Using the normal dispersion theory, the refractive indices of isotropic thin film layers in the region $k^2 \ll n^2$ can be represented by two

constant pairs a_1 and b_1 , and a_2 and b_2 using the equations given below,

$$n_1 = a_1 + \frac{b_1}{\lambda^2} \quad (2-a)$$

$$n_2 = a_2 + \frac{b_2}{\lambda^2} \quad (2-b)$$

For the model based approach, the optical absorption α can be expressed as an exponential function of the wavelength. Optical absorptions for the layers are given by the formulae,

$$\alpha_1 = d_1 \exp(-e_1 \lambda) + f_1 \quad (3)$$

$$\alpha_2 = d_2 \exp(-e_2 \lambda) + f_2 \quad (4)$$

The main contribution of this study is the adaptation of fitness function using relevant variables for the layered structures such as ASA and ABS sample profiles. The problem then becomes finding the roots of nonlinear equations considering the multiparameter and thickness using GA with Eq. (1). The fitness function (F) is described using the related parameters for each layer and it is given as

$$F = |T(\lambda, t_1, t_2, n_1(\lambda), n_2(\lambda), a_1(\lambda), a_2(\lambda)) - T_m(\lambda)| \quad (5)$$

where $T(\lambda, t_1, t_2, n_1(\lambda), n_2(\lambda), a_1(\lambda), a_2(\lambda))$ and $T_m(\lambda)$ are the calculated and measured optical transmittance of the layered film structure, respectively. In this case, considering each layer we have defined each chromosome or individual with an array of twelve genes which represent unknown constants a_1, b_1, t_1, d_1, e_1 , and f_1 for one layer and a_2, b_2, t_2, d_2, e_2 , and f_2 for the second layer. a and b are the constants of Cauchy's equation of refractive index $n(\lambda)$ given in Eq. (2), while t is the thickness of the thin film. The parameters d, e , and f are the constants of the absorption equation $\alpha(\lambda)$ shown in Eq. (4). The parameters that generate solutions with better fitness were then selected for crossover and mutation. The algorithm starts with initialization defining minimum and maximum limits of model based parameters. A random set of solution (chromosomes) is generated at the beginning of the algorithm. The created population is then evolved by means of genetic search operations such as selection, recombination, and mutation until the desired criterion is reached. In this algorithm, the genes are encoded by N bits. In order to obtain a high enough resolution, N can be taken

as 10 bits, 12 bits, or 14 bits and the individuals are ranked from smallest to largest, according to their cost values. The crossover points are randomly selected. 6% of the individuals are mutated with randomly selected "1" bit in each gene of individuals per iteration to prevent the increase of the number of similar individuals in the population. During the mutation, the individuals to mutate are randomly selected as well.

GA has several advantages over various other numerical methods such as random walk, simplex, gradient, and damped least-square based on derivative values. If a good approximation can be guessed for the parameters, the convergence can be quite fast. The dominant term is a in the refractive index dispersion. The absorption term decreases the transmission near the band edge range. Therefore, the term e is dominant for absorption. Because, when the rate of change of the exponential function is taken into consideration, the product of the wavelength and the e parameter limits the solution space. These speed up the GA.

3. Results

3.1. Structural properties of layered ZnO systems

Typical X-ray diffraction patterns obtained from the surface of the layered ZnO thin films at room temperature are shown in Fig. 2 and Fig. 3.

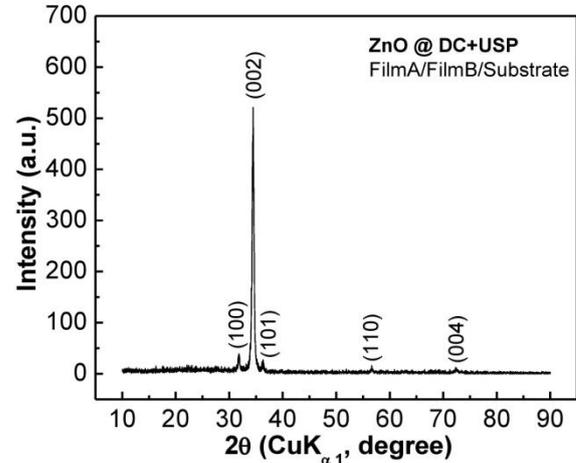


Fig. 2. XRD pattern of layered ZnO thin film in the form of ABS

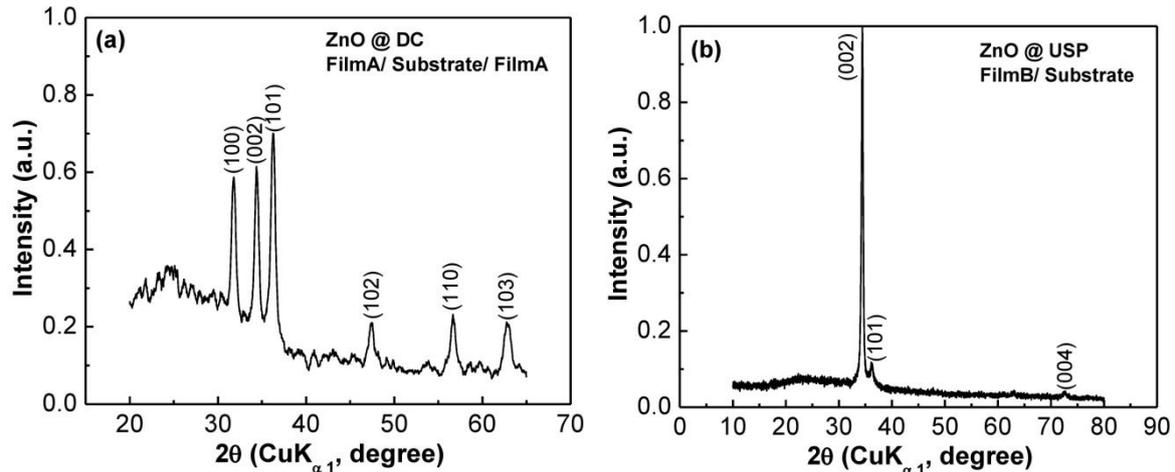


Fig. 3. XRD patterns; (a) ZnO double side coated thin film system defined as ASA formation and (b) ZnO thin film on substrate defined as BS formation

All the XRD peaks could be indexed as the ZnO wurtzite structure found in the standard reference data (JCPDS: 36–1451). Fig. 2 and Fig. 3 show the bilayer ZnO thin films in ABS formation and the ZnO thin films in ASA and BS formations, respectively. As given in the previous section, the bilayer system in ABS formation was prepared in a film structure as determined the eight-layered dip coated ZnO thin film on the USP coated ZnO film on the glass substrate. It was clearly seen that the bilayer and monolayer ZnO systems prepared by different sol-gel techniques were polycrystalline with preferred orientation along (0 0 2) plane. The XRD results pointed out that there was no impurity and/or unreacted phase of ZnO. The heating process is very critical for film growth techniques. Especially, DC technique needs pre-heat and post-heat treatments for the formation of growing planes. In the absence of heat treatment, the peaks of polycrystalline structure could not be observed clearly. However, after the pre-heat and post-heat treatment, the peaks are observed in the polycrystalline structure significantly [15].

The film formation occurs during the reaction. That is why, (002) orientation is kinetically preferred, the (001) and (101) peaks of ZnO disappear. When the USP and DC techniques are used successively, the heat treatment in the USP technique is more dominant at the structural properties of the film (Fig. 2).

3.2. Optical properties of layered ZnO systems with various film formations

Fig. 4 displays the measured optical transmittance of the DC type ZnO, USP type ZnO, and DC/USP type thin films in the range 300 nm to 900 nm. Even though the deposition rate depends on the number of immersions, the film thickness is limited to a certain value in the DC technique. The thickness of the ZnO thin film deposited by the USP technique is bigger than the thickness of the ZnO film deposited by DC technique, therefore the optical transmittance spectrum is mainly dominated by the USP type film. The modification of the transmission spectrum due to the change of refractive index and film can be clearly seen in Fig. 4. The refractive index of the substrate is

relatively constant and optical transmittance is flat in the range of 380–900 nm. The approximate value of the substrate refractive index is taken as 1.52 for the calculations. The most important parameter affecting the wavelength dependence of the optical transmittance spectrum is the film refractive index. Therefore, the first step in the calculations is the determination of the limits for the refractive index. For some materials, the refractive index exhibits a rapidly decreasing behaviour with increasing wavelength. In such materials, oscillations in the optical transmittance spectrum are observed when the appropriate film thickness and the wavelength region are taken into account. Firstly, we set the region of variables a_1 , b_1 , t_1 , d_1 , e_1 , and f_1 for one layer and a_2 , b_2 , t_2 , d_2 , e_2 , and f_2 for other layer of interest. How the parameters affect the optical transmission spectrum is explained in reference [10]. Secondly, GA generates the corresponding values and finds the value of the fitness function. When the fitness function becomes smaller than the previous calculation, the sum of squares due to error (SSE) and adjusted R -square (R^2) values are calculated. For example, the results obtained from single layer thin film on the substrate with the parameters determined from GA can be taken as a constant for the ABS structure. Hence, the range of some optical parameters can be narrowed or fixed. This treatment can speed up the GA. When optical transmittance spectra and fitted spectra overlap, it is decided that the optimization process is finished. To test the operation of the algorithm in layered structures an optical transmittance spectrum of the synthetic sample as in the film formation of *ASA is used. The optical transmittance spectrum is generated using with the parameters ($t_1=t_2=283\text{nm}$; $n(\lambda)=1.88+5.894\times 10^{-14}/\lambda^2$) and the substrate refractive index $n_s = 1.52$). Then, GA is run for the synthetic sample and the obtained values of fitting parameters are given in Table 1. A good graphical fit ($R^2=0.990$) is observed between the generated optical transmittance spectrum and calculated optical transmittance spectra using GA as shown in Fig. 5.

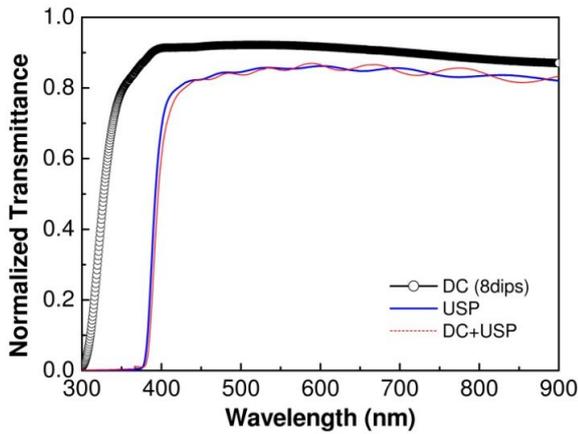


Fig. 4. Experimental optical transmittance spectrum of bilayer and monolayer ZnO thin film, DC coated with symbol "o" for DC with dip number 8 (AS), solid line for USP (BS) and dashed line DC and USP (ABS) (color online)

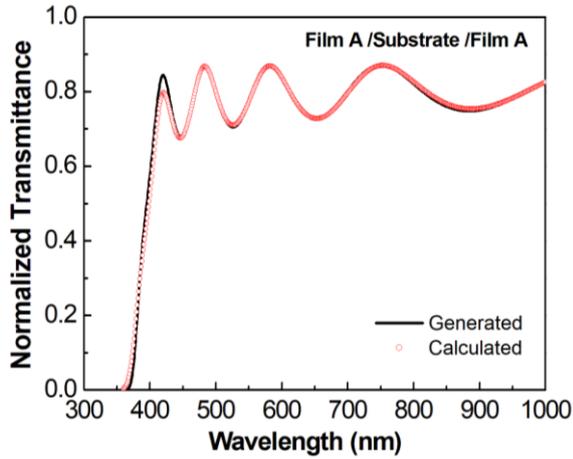


Fig. 5. Computer generated optical transmittance spectrum (solid line) and calculated optical transmittance spectrum by GA (symbol "o") for ZnO thin film in the form of *ASA (color online)

GA is also run for the ZnO thin films for the ASA and ABS structures. The parameters given in Eq. (2), Eq. (3) and Eq. (4) calculated by GA and R^2 are given in Table 2 and Table 3. Generally, a good graphical fit is observed between the generated optical transmittance spectrum and calculated optical transmittance spectra obtained by GA which are shown in Fig. 6 and Fig. 7.

Table 1. Calculated optical constants from the model based GA for the computer generated as deposited *ASA layered ZnO thin film samples. Film thickness t is in nm

Sample Order		
*ASA		
a	1.8765	1.8761
b ($\times 10^{-14}$)	5.67	5.66
d ($\times 10^{11}$)	9.69	1.20
e ($\times 10^7$)	7.23	7.24
f ($\times 10^{-2}$)	- 6.28	11.58
t ($\times 10^2$)	2.845	2.850
R^2	0.990	

Table 2. Calculated optical constants from the model based GA for the computer generated as deposited ASA layered ZnO thin film samples. Film thickness t is in nm

Sample Order		
ASA		
a	1.2237	1.0881
b ($\times 10^{-13}$)	1.75	0.66
d ($\times 10^{11}$)	2.01	2.01
e ($\times 10^7$)	8.30	8.30
f ($\times 10^{-2}$)	2.99	2.71
t ($\times 10$)	4.59	4.56
R^2	0.991	

Table 3. Calculated optical constants from the model based GA for the ABS layered ZnO thin film sample. Film thickness t is in nm

Sample Order			
	A	B	S
a	1.8765	1.8765	
b ($\times 10^{-14}$)	5.67	5.67	
d ($\times 10^{11}$)	9.69	9.69	
e ($\times 10^7$)	7.23	7.23	
f ($\times 10^{-2}$)	- 6.28	- 6.28	
t ($\times 10^2$)	2.845	2.845	
R^2	0.988		

The optical absorption spectrum obtained from the calculated optical transmittance spectra by GA was used to determine the optical band gap of each layer (A, B) in the ASA and ABS film structures. Considering the Tauc's relation, the optical band gap of the layers in the films can be calculated using the following equation [19]

Table 4. Calculated refractive index $n(\lambda)$ at 532nm from the model based GA parameters, and optical band gap value E_g of each layers from Eq. (6), optical band gap values E_g^{inf} of whole film system from Eq. (7) for the layered ZnO thin film samples

Sample Order		n (for 532nm)	E_g (eV)	E_g^{inf} (eV)
*ASA	A	2.077	3.36	3.26
	A	2.076	3.35	
ASA	A	1.842	4.01	3.88
	A	1.323	4.01	
ABS	A	1.454	3.92	4.00
	B	1.451	4.01	

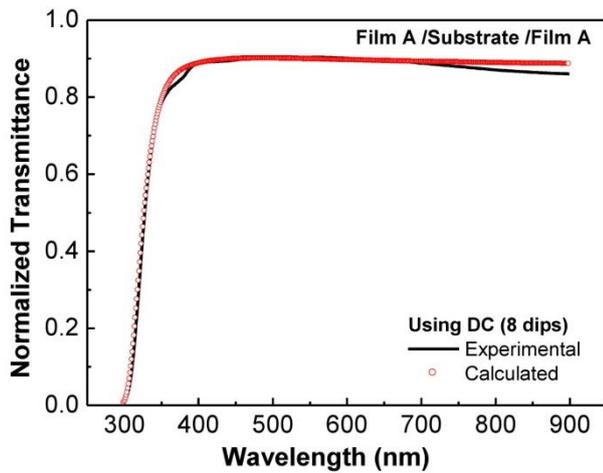


Fig. 6. Experimental optical transmittance spectrum with solid line and calculated optical transmittance spectrum by GA with symbol "o" for ZnO thin film in the form of ASA (color online)

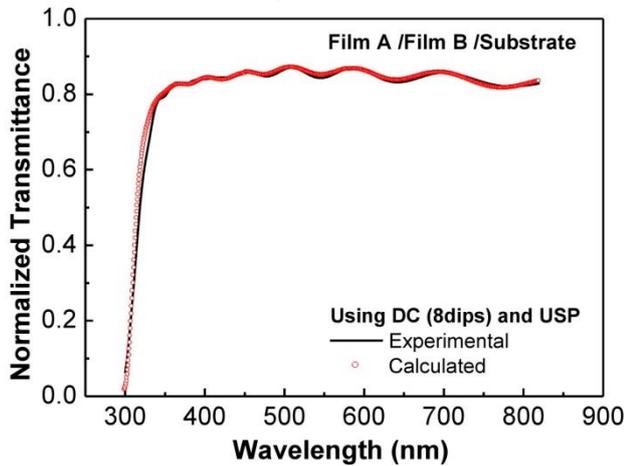


Fig. 7. Experimental optical transmittance spectrum with solid line and calculated optical transmittance spectrum by GA with symbol "o" for layered ZnO thin film in the form of ABS (color online)

$$ahv = A(hv - E_g)^n \quad (6)$$

where A is the probability parameter for the transition, E_g is the band gap energy of the material, $h\nu$ is the incident photon energy, and n is the transition coefficient. The value of n is known to be 2 for the measurement of an indirect band gap and 1/2 for a direct band gap. Calculated optical transmittance from model based GA serves the variation of $(ahv)^2$ vs the photon energy ($h\nu$) of each layer of the film systems indirectly according to Eq. (6). The direct band gap of each layer was carried out by taking the intersection of the extrapolated lines from the linear vertical and horizontal regions near the band edge of the $(ahv)^2 = 0$ curve. In addition, the optical band gap of the optical system consisting of layers was determined with an alternative method considering the inflection point [20]. The optical band gap (E_g^{inf}) of the overall film system can be found approximately according to the empirical formula:

$$E_g^{inf} (nm) = \frac{1240.8}{\lambda_c} \quad (7)$$

where λ_c (nm) is the critical wavelength value at which the second derivative of the optical transmittance spectrum equals zero. The optical band ranges obtained by both methods and refractive index values calculated with GA are shown in Table 4. When the optical band gaps obtained by the two methods are compared, it is observed that the band gap values are close to each other. It can be said that the small differences between these values are due to the substrate between the layers.

4. Conclusions

In this work, we presented the modified model based GA method to determine the optical constants of each layer of ZnO thin films prepared by different sol-gel techniques in the form of FilmA/Substrate/FilmA (ASA) and FilmA/FilmB/Substrate (ABS). To improve the convergence of fitness function, the terms responsible for the absorption, which are confined into narrower regions in the solution space, have been proposed. Hence, the global optimum solution of the fitting is realized very quickly. The experimental optical transmittance spectrum of the layered samples was used for testing the proposed model based GA. R-square values obtained for the model modified to the multilayer samples show that the proposed formulations can estimate the optical transmittance spectrum with the optical constants to a high degree of accuracy. We can conclude that the modified model based GA method successfully fits the calculated transmittance spectra with the experimentally measured spectra over the wavelength range of 300-800 nm for layered metal oxide thin films. Our results show that the assumption of absorption limitation was justified. Altogether, the M-GA method gave very good results for layered thin films whose typical thicknesses are about a few tens of nanometers, which can not be calculated by conventional methods.

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