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Influence of Substrate Temperature on the Optical Constants of ZnO Thin Film Grown by PLD

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Abstract: Spectroscopic ellipsometry(SE) was employed to characterize ZnO thin films prepared by pulsed laser deposition (PLD) on Si (100) substrates at various temperature of 400, 500, 600 and 700 ℃. The refractive indices (n) and extinction coefficients (k) of the ZnO films were calculated in the spectral range of 400 ~ 800 nm for each deposition temperature by fitting the ellipsometic parameters based on a three-layers dispersion with Cauchy model. It was found that the optical constants were significantly affected by the substrate temperature. Through analyzing the crystalline structures and surface morphologies of ZnO thin films grown at different substrate temperature by XRD and atomic force microscopy (AFM), respectively, the variation of the refractive index can be attributed to the changes of the packing density of the thin film. After comparing the results obtained at different grown temperature, it was suggested 600 ℃ might be the optimum deposition temperature for growing dense ZnO films with high optical and crystalline quality.

Key words: spectroscopic ellipsometry; PLD; zinc oxide; optical constants
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1 Introduction

Zinc oxide is a wide and direct band-gap (3.3 eV) Ⅱ-Ⅳ semiconductor material with excitonic binding energy as large as 60 meV. It can be used in a variety of applications such as solar cells, thin films, gas sensors and transparent contacts because of its distinctive optical and electrical properties[1,2]. Much work has been focused on the fabrication of ZnO thin film via different methods such as molecular beam epitaxy[3,4], sol-gel process[5], magnetron sputtering[6,7], pulsed laser deposition[8,9] and metal organic chemical vapor deposition[10~12]. Among these technologies, PLD possesses of some unique advantages such as stoichiometric deposition, high film quality due to the high energy of the laser, and flexibility to the substrate types. It has been well known that precise control to the parameters such as oxygen pressure, substrate type and substrate temperature in PLD growth is important to obtain high quality ZnO film, and substrate temperature usually plays a core role. Undoubtedly, ZnO has become much promising in optoelectronic and optical applications such as UV detectors, short wavelength laser diodes (LDs) and light-emitting diodes (LEDs). Therefore, the research on the optical properties of ZnO films is much demanded to promoting its practical applications. Among all kinds of detection technologies, spectroscopic ellipsometry is already proven to be a non-destructive and sensitive technique and has been used to analyze the optical properties of ZnO film grown by various methods at different

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conditions such as RF-sputtering at different oxygen pressure[13], PLD at different growth temperature on glass substrate[14] and reactive sputtering at different oxygen partial pressure[15]. However, up to now there are few studies on the influences of Si substrate temperature on the optical constants of ZnO films grown by PLD.

Herein, we systemically investigated the influences of growth temperature on the optical constants of ZnO thin films grown by PLD on Si substrates. The optical constants of the films are extracted by fitting the ellipsometic spectra with Cauchy model. The variation of the refractive index can be attributed to the changes of the packing density of the ZnO thin film. The results indicated that 600 ℃ might be the optimum growth temperature to obtain dense ZnO films with homogeneous optical and crystalline quality. Our results would be useful for exploiting the applications of ZnO films grown by PLD in optoelectronic devices.

2 Experiments

ZnO films were fabricated on Si (100) substrates by using a KrF excimer plused-laser (Lambda Physik COMPexPro 102, 248 nm, 150 mJ) ablation of a sintered ceramic ZnO target prepared from the standard ceramic process. The deposition conditions are as follows: the repetition frequency of the laser is 10 Hz, the background O_2 pressure is 16 Pa, the target to substrate distance is 50 mm, the deposition time is 45 min, and the substrate temperature are 400, 500, 600, and 700 ℃, respectively.

The crystalline structures of ZnO thin films were detected by X-ray diffraction (XRD, Rigaku D/Max-rB). The surface morphologies were studied by atomic force microscopy (AFM, CSPM4000 Being Nan-Insrtuments Ltd.). The thickness and surface of the films were investigated by scanning electron microscopy (SEM, Sirion 200 FEI). The optical constants of the film were estimated by a rotating analyzer ellipsometer (EPILLA-A Shanghai Fudan Anzheng Energy Optical Network Co., LTD) in the spectral range of 400 ~ 800 nm. The incident angle was fixed at 70°.

3 Results and Discussion

Spectroscopic ellipsometry (SE) was performed to derive the optical constants and thickness of the PLD ZnO film. Two parameters related to the optical and structure properties of the samples, Ψ and Δ, were measured, which have the following relationship:

$$\rho = \frac{r_p}{r_s} = \tan\Psi \exp(i\Delta) \tag{1}$$

where r_p and r_s are the complex reflection coefficients of the polarized parallel (p) and perpendicular (s) to the plane of incidence respectively. Based on the previous reports on the spectroscopic analysis of ZnO films[15,16], Cauchy model provided better spectral fitting than that of the Sellmeier dispersion model which is an empirical model and assumes the extinction coefficient (k) is zero[17]. Therefore, Cauchy model is adopted to fit the experimental spectroscopic data in this work. As shown in Fig. 1, a three-layer model, air/ZnO film/interfacial layer/Si substrate, was used to extract the optical constants of the films. In this model, substrate layer was Si (100), whose optical constants were taken from the literature and not arrowed to vary during the fitting. The interfacial layer was effective medium approximation layer, which was assumed to be a SiO_2 layer. ZnO film layer is a homogeneous layer and its roughness is not taken into account. Three phase Cauchy dispersion model is given by:

$$\begin{aligned} n(\lambda) &= A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \\ k(\lambda) &= A_k + \frac{B_k}{\lambda^2} + \frac{C_k}{\lambda^4} \end{aligned} \tag{2}$$

where A_n, B_n, C_n, A_k, B_k and C_k are the Cauchy parameters and are determined from fitting to the experimental spectra, λ is the wavelength of the light,

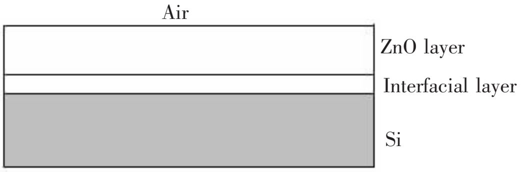

Fig. 1 Illustration of a three-layer model used in the Cauchy model fitting

n is the refractive index, k is the extinction coefficient. The film thickness was then introduced as another fitting parameter during the fitting procedure and was solved independently. The quality of the fitting was determined by minimizing the weighted test function, namely the mean-squared error (MSE) defined by the Levenberg-Marquardt algorithm[18]. Fig. 2 shows the results of the fitting with Cauchy model to the experimental data for 600 ℃ substrate temperature. It can be seen that the fitting results are very close to the experimental spectra. The thickness deduced from the fitting is about 403.9 nm, which is in agreement with the value obtained from the cross-section SEM image (~400 nm, Fig. 3), suggesting that the fitting procedure used in this work is reliable. The n and k parameters in the Cauchy model are deduced to be: $A_n = 1.900\ 25$, $B_n = 0.000\ 132\ \text{nm}^2$, $C_n = 0.006\ 05\ \text{nm}^2$, $A_k = 3.0 \times 10^{-6}$, $B_k = 3.0 \times 10^{-6}\ \text{nm}^2$, $C_k = 1.0 \times 10^{-6}\ \text{nm}^2$. The MSE was estimated to be ~0.15. The calculated optical constants n and k as a function of the wavelength at different deposition temperature of 400 ~ 700 ℃ are shown in Fig. 4(a) and (b), respectively. It can be seen that n and k decrease in the spectral range of 400 ~ 800 nm with the increasing wavelength. k is very small and near to zero for all the samples, suggesting ZnO films are transparent in this wavelength region[19]. Significantly, a clear dependence of n on the substrate temperature can be observed from the spectra. With the temperature increasing from 400 to 500 ℃, n increased first, and then decreased at the temperature range of 500 ~ 700 ℃. It is also found that k at 500 ℃ is larger than the values at other deposition temperature. It is suggested that the variation of n is related to the changes of the packing density. The packing density is determined by the grain size and grain boundary of the ZnO films. These two factors influence on the packing density in an opposite way, that is, the large grain size can result in the large packing density whereas the large grain boundary can decrease the packing density. Thinkably, the lower n corresponds to the lower packing density[15,20,21].

In order to further study the dependence of n on the substrate temperature, the crystalline structures of the ZnO thin films were detected by XRD, as shown in Fig. 5. Only (002) and (004) peaks were observed in the XRD patterns, indicating the preferential (002) orientation of all the ZnO films. Nevertheless, the values of the full-width at half maximum (FWHM)

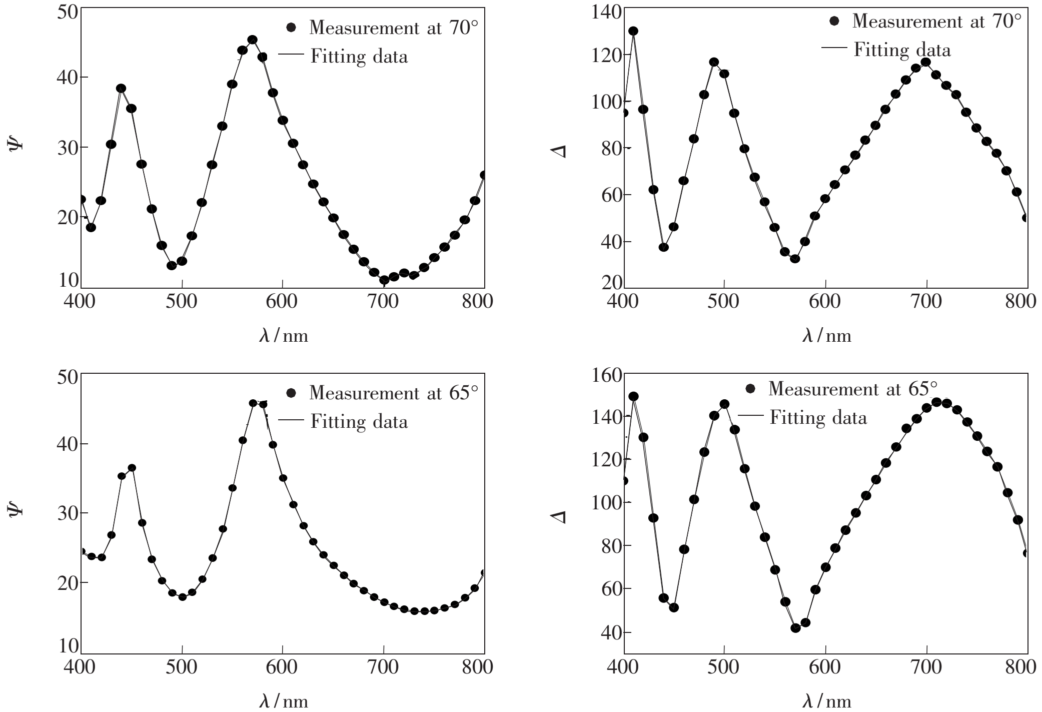

Fig. 2 The experimental and the fit (simulated by Cauchy model) Ψ and Δ on the ZnO thin film deposited at 600 ℃

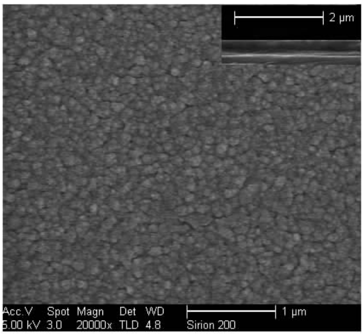

Fig. 3 SEM top-view and cross-section (inset) images of ZnO thin film deposited at 600 ℃

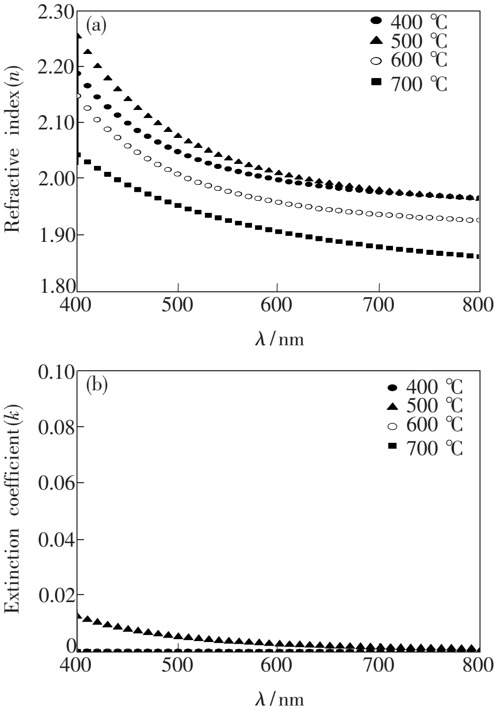

Fig. 4 The optical constants of the ZnO thin films deposited at different temperatures: (a) refractive index (n); (b) extinction coefficient (k).

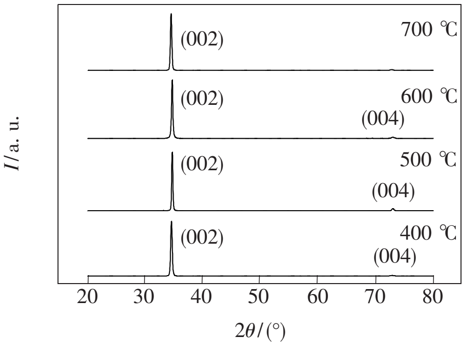

Fig. 5 XRD patterns of ZnO thin films deposited at different temperatures

Table 1 FWHM of XRD (002) peaks of ZnO film deposited at different substrate temperature

Substrate temperature (℃)	400	500	600	700
FWHM	0.305°	0.258°	0.306°	0.277°

of the (002) peaks are different at different growth temperature, as shown in Table 1. It can be seen that the FWHM at 500 ℃ is smaller than others. Except at 500 ℃, the FWHM at 700 ℃ is smaller than that at 400 ℃ or 600 ℃. We note that the FWHM values are related to the average grain size of the films. The smaller FWHM value usually corresponds to the larger grain size[22].

To evaluate the grain size and grain boundary of the ZnO films, AFM measurements are carried out, as shown in Fig. 6. Obviously, the surface morphologies of the films change remarkably with the temperature increasing. It is found that the film deposited at 400 ℃ is composed of fine grains and the grains pack together tightly [Fig. 6(a)], which makes the grain boundaries cannot be distinguished easily. However, the film at 500 ℃ is the mixture of fine grains and large grains so that the average grain size is much large than that at 400 ℃ [Fig. 6(b)], which may response to the small FWHM value at 500 ℃. Due to the large grain size, the packing density of the film at 500 ℃ is higher than that at 400 ℃, resulting in the larger refractive index of the ZnO film at 500 ℃ [Fig. 4(a)]. Although the FWHM value and the grain size of the film at 400 ℃ are almost equal to that at 600 ℃, their refractive indices are very different. From the Fig. 6(c), the grain boundaries at 600 ℃ can be distinguished clearly. Therefore, it is suggested the packing density of the film at 600 ℃ might be much smaller than that at 400 ℃, which is responsible for its smaller refractive index. From the Fig. 6(d), the grain size of the film at 700 ℃ is much larger than that at 400 ℃ and 600 ℃, which is consistent with the FWHM values. Nevertheless, the film at 700 ℃ also shows large grain spacing and large surface roughness, which may result from the column growth of the ZnO grains at this temperature. As a result, the packing density at 700 ℃ is smaller than that at other temperature. This

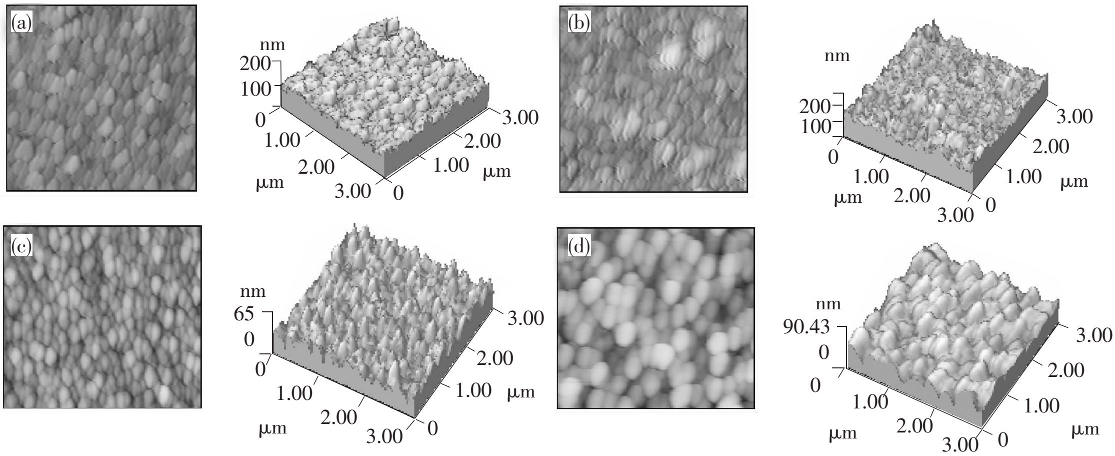

Fig. 6　AFM phase and three-dimensional images of ZnO thin films deposited at different substrate temperatures (a)400 ℃; (b) 500 ℃; (c)600 ℃; (d)700 ℃.

may explains the smallest n at 700 ℃. On the other hand, the smaller RMS corresponds to the better surface quality. The grain size's root-mean-square (RMS) values of the ZnO films obtained from AFM are 15.2, 23.8, 6.5, 8.5 nm for 400, 500, 600, 700 ℃ substrate temperature, respectively. The RMS value at 500 ℃ are much larger than the others, indicating the worse film quality. The RMS value at 600 ℃ is smallest as compared with the results at other growth temperature.

For optoelectronic applications, film with high structural and optical qualities is much desired. The film quality is determined by the surface roughness, packing density, uniformity of the grain size, and the optical properties such as refractive index. Based on our results, it is suggested that 600 ℃ might be a optimum temperature for PLD ZnO film growth.

4　Conclusion

ZnO thin films were deposited on Si (100) substrate by PLD at various temperature from 400 ~ 700 ℃. By using Spectroscopic ellipsometry, the optical constants of the ZnO films were extracted by fitting the ellipsometric spectra with Cauchy model. The influences of the substrate temperature on the optical constants were systemically investigated. According to the crystalline structures measured by XRD and surface morphologies detected by AFM, the changes in the optical constants at different growth temperature have been further discussed. We found that the refractive index is dependent on the packing density of the ZnO thin film. The lower n corresponds to the lower packing density. Significantly, the packing density is a combined result of the grain size and the grain boundary. Our results demonstrate the possibility to control the optical properties by varying the substrate temperature. On the other hand, homogeneous ZnO film with high structural and optical qualities is obtain at the growth temperature of 600 ℃. These results could be important to exploit the optoelectronic applications of ZnO films.

References:

[1] Kang H S, Kand J S, Kim J W, *et al.* Annealing effect on the property of ultraviolet and green emissions of ZnO thin films [J]. *J. Appl. Phys.*, 2004, **95**(3):1264-1250.

[2] Ohta H, Kawamura K, Orita M, *et al.* Current injection emission from a transparent p-n junction composed of p-$SrCu_2O_2$/n-ZnO [J]. *Appl. Phys. Lett.*, 2002, **77**(4):475-477.

[3] Wang X J, Buyanova I A, Chen W M, *et al.* Optical characterization studies of grown-in defects in ZnO epilayers grown by molecular beam epitaxy [J]. *Phys.* B: *Condensed Matter*, 2007, **401-402**:413-416.

[4] Sun Jianwu, Lu Youming, Liu Yichun, *et al.* Hole scattering mechanisms in nitrogen-doped p-type ZnO films grown by plasma assisted molecular beam epitaxy [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(3):437-440 (in Chinese).

[5] Shou Y K, Wei C C, Chin P C. Investigation of annealing-treatment on the optical and electrical properties of sol-gel-derived zinc oxide thin films [J]. *Superlattices and Microstrutures*, 2006, **39**(1-4):162-170.

[6] Sato Y, Sato S. Preparation and some properties of nitrogen-mixed ZnO thin films [J]. *Thin Solid Films*, 1996, **281-282**: 445-458.

[7] Wen Jun, Chen Changle. Structural and photoluminescence properties of N-doped ZnO thin films grown by RF magnetron sputtering [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(5):856-860 (in Chinese).

[8] Sun X W, Kwok H S. Optical properties of epitaxially grown zinc oxide films on sapphire by pulsed laser deposition [J]. *J. Appl. Phys.*, 1999, **86**(1):408-411.

[9] Ye Zhigao, Zhu Liping, Peng Yingzi, *et al.* Fabrication and magnetic properties of Co-doped ZnO thin films by pulsed laser deposition [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(3):486-490 (in Chinese).

[10] Grola R C, Wmanetogly N W, Liang S, *et al.* Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on ($01\bar{1}2$) sapphire by metalorganic chemical vapor deposition [J]. *J. Appl. Phys.*, 1999, **85**(5): 2595-2602.

[11] Li Xiangping, Zhang Baolin, Dong Xin, *et al.* Study on the properties of ZnO films prepared by photo-assisted MOCVD [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(1):139-143 (in Chinese).

[12] Liu Xuedong, Gu Shulin, Li Feng, *et al.* The effect of carrier gas H_2 used during MOCVD-growth on the properties of N-doped ZnO [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(3):441-446 (in Chinese).

[13] Gioffre M, Angeloni M, Gagliardi M, *et al.* The influence of oxygen on the optical properties of RF-sputtered zinc oxide thin films [J]. *Supperlattics and Mirostructures*, 2007, **42**(1-6):85-88.

[14] Shan F K, Liu G X, Lee W J, *et al.* Transparent conductive ZnO thin films on glass substrates deposited by pulsed laser deposition [J]. *J. Cryst. Growth*, 2005, **277**(1-4):284-292.

[15] Zhang J P, He G, Zhu L Q, *et al.* Effect of oxygen partial pressure on the structural and optical properties of ZnO film deposited by reactive sputtering [J]. *Appl. Surf. Sci.*, 2007, **253**(24):9414-9421.

[16] Miao L, Tanemura S, Tanemura M, *et al.* Thickness-dependent optical properties of ZnO thin films [J]. *J. Mater. Sci.: Mater. Electron.*, 2007, **18**:S343-S346.

[17] Liu Y C, Hsieh J H, Tung S K. Extraction of optical constants of zinc oxide thin films by ellipsomerty with various models [J]. *Thin Solid Films*, 2006, **510**(1-2):32-38.

[18] Herzinger C, Snyder P, Johs B, *et al.* InP optical constants between 0.75 and 5.0 eV determined by variable-angle spectroscopic ellipsometry [J]. *J. Appl. Phys.*, 1995, **77**(4):1715-1724.

[19] Tan S T, Chen B J, Sun X W, *et al.* Blueshift of optical band gap in ZnO thin films grown by metal-organic chemical-vapor deposition [J]. *J. Appl. Phys.*, 2005, **98**(1):013505-1-5.

[20] Mohamed S H, Abd El-Rahman A M, Salem A M, *et al.* Effect of rf plasma nitriding time on electrical and optical properties of ZnO thin films [J]. *J. Phys. Chem. Solids*, 2006, **67**(11):2351-2357.

[21] Senadim E, Tü Zemen, Kavak H, *et al.* Influence of oxygen pressure of ZnO/glass substrate produced by plused filtered cathodic vacuum arc deposition [J]. *Phys. B: Condensed Matter*, 2007, **390**(1-2):366-372.

[22] Liu Z W, Ong C K. Synthesis and size control of ZnO nanorods by conventional pulsed-laser deposition without catalyst [J]. *Mater. Lett.*, 2007, **61**(16):3329-3333.

基片温度对 PLD 制备 ZnO 薄膜光学常数的影响

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摘要： 光谱椭偏仪被用来研究用脉冲激光沉积方法在 Si(100)基片上，温度分别为 400，500，600，700 ℃制备的 ZnO 薄膜的特性。利用三层 Cauchy 散射模型拟合椭偏参数，计算了每个温度下制备的 ZnO 薄膜在 400 ~ 800 nm 波长范围内的折射率(n)和消光系数(k)。发现基片温度对光学常数有很大的影响。通过分析 XRD 表征的晶体结构和 AFM 表征的薄膜表面形貌，发现折射率的变化归因于薄膜堆积密度的变化。为了获得具有较好的光学和薄膜质量的 ZnO 薄膜，相比与其他沉积温度 600 ℃或许是最佳的沉积温度。

关　键　词： 光谱椭偏仪；PLD；氧化锌；光学常数

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