第 35 卷第 1 期
2016 年 2 月

红 外 与 毫 米 波 学 报
J. Infrared Millim. Waves

Vol. 35, No. 1
February, 2016

文章编号: 1001 - 9014(2016)01 - 0006 - 05　　DOI:10.11972/j.issn.1001 - 9014.2016.01.002

Optical properties of hydrogenated ZnO-Ga thin films studied by spectroscopic ellipsometry

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Abstract: The effects of Ga doping on structural, electrical, and optical properties of hydrogenated ZnO-Ga (GZO) thin films deposited by sol-gel technique have been investigated. From the X-ray diffraction observations, the films doped with different gallium concentrations were found to be pure wurtzite-structured ZnO. The electrical properties of the hydrogen-annealed films were improved and a lowest resistivity of $3.410\times10^{-3}\,\Omega\cdot$cm was obtained. The refractive index and extinction coefficient of ZnO-Ga thin films were determined in the range of 270 ~ 1600 nm by varying angle spectroscopic ellipsometry (VASE). The simulation was carried out using a double oscillator model, which includes the Psemi-MO equation and the rho-tau Drude equation.

Key words: GZO thin film, hydrogen treatment, spectroscopic ellipsometry, double oscillator model
PACS: 78.67.Bf

利用椭偏仪研究氢气退火处理对 ZnO-Ga 薄膜光学性能的影响

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摘要:通过溶胶凝胶技术制备了不同 Ga 掺杂含量的 ZnO 透明导电薄膜,研究了 Ga 掺杂对 GZO 薄膜结构、电学及光学性能的影响.从 X 射线衍射光谱分析,所有薄膜均表现为六方纤锌矿结构,经过氢气退火处理之后,薄膜的电学性能均得到提高,当 Ga 掺杂含量为 5 at% 时,得到薄膜的电阻率为 $3.410\times10^{-3}\,\Omega\cdot$cm.利用可变入射角椭圆偏振光谱仪(VASE)在 270 ~ 1 600 nm 波长范围内研究了 GZO 薄膜折射率和消光系数的变化,采用双振子模型对实验数据进行拟合.

关　键　词:GZO 薄膜;氢处理;椭圆偏振光谱仪;双振子模型

中图分类号:O4　　**文献标识码**:A

Introduction

Transparent conductive oxide (TCO) thin films have been widely used in optoelectronic industry, such as displays, organic light-emitting diodes, solar cells, piezoelectric transducers, gas sensors, and other optoelectronic devices[1-5]. Among the various TCO materials, Ga-doped ZnO (GZO) is regarded as a promising alternative material to indium tin oxide, owing to its low material cost, non-toxicity, high transparency, and high chemical stability[6-8]. Since cost effectiveness is an important issue in the practical application of these films, it is attractive to develop a simple and effective process to further lower fabrication cost. There are a variety of physical and chemical deposition methods for GZO thin films such as DC and RF sputtering[9], sol-gel techniques[10], spray pyrolysis[11], plasma-enhanced chemical vapor deposition[12], or pulsed laser deposition[13]. Among them the sol-gel spin coating method is the least expensive. It has been reported that hydrogen plays a beneficial role in improving electrical properties of GZO

Received date: 2015 - 03 - 12, **revised date**: 2015 - 05 - 14　　**收稿日期**:2015 - 03 - 12, **修回日期**:2015 - 05 - 14

Foundation items: Supported by the National Natural Science Foundation of China(51371093) and Program for Changjiang Scholars and Innovative Research Team in University(IRT1251)

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films[14-16].

Most previous studies have focused on the development of GZO transparent conducting oxide thin films for various applications. For example, Nayak *et al.* reported a new type of organic light-emitting diodes, which had a GZO transparent film prepared on glass substrate using sol-gel technique[6]. Tsay *et al.* fabricated UV photodetectors based on sol-gel synthesized GZO films[17]. Though there are many reports that characterized the doped ZnO films, the mechanism of the correlation between the carrier concentration and electrical and optical properties of GZO film is still not clear. Spectroscopic ellipsometry (SE) is an excellent technique for investigating the optical response of semiconductors, for measuring the spectral dependence of the dielectric function[18-20]. Recently, SE has been applied to evaluate the optical parameters (refractive index and extinction coefficient) of ZnO films[21-23].

In this paper, we have experimentally investigated the effects of Ga doping on the electronic and optical properties of hydrogenated GZO thin films prepared by simple sol-gel spin coating method. The optical constants n and k of GZO films in wide UV-V-IR spectral regions have been determined. The correlations between n, k and the carrier concentration have been founded. The results may be helpful for the development of integrated optic devices.

1 Experiments

The precursor solution for spin coating was prepared by dissolving an appropriate amount of zinc acetate dehydrate and gallium nitrate in 2-methoxyethanol at room temperature. Monoethanolamine (MEA) was then added to the mixture as the solution stabilizer. The concentration of gallium was varied from 0 to 10 at%. The total concentration of the sol was maintained at 0.5 M and the molar ratio of MEA to acetate was maintained at 1 : 1. The resultant solution was stirred at 60℃ for 3 h and then aged for 2 days. The ready solution was then deposited on silicon substrate using the spin-coating technique at 3000 rpm for 30 s. The as-deposited films were immediately placed into a furnace of 300℃ and for 10 min. The deposition and preheating processes were repeated for 8 times in order to get a desired thickness. Thereafter, the GZO thin films were subsequently annealed in hydrogen ambient at 450℃ for 60 min.

The crystal structure of the GZO thin films were characterized by X-ray diffractometer (Philips X′ Per Pro with Cu Kα1, 0.154056 nm) from 20° to 80°. The chemical composition was characterized by a multi-functional X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra$^{\mathrm{DLD}}$) with Al Kα radiation. The resistivity was measured by standard four-point probe method. The optical constants and film thickness were measured by spectroscopic ellipsometry. The SE standard measurements were performed using a Variable Angles Spectroscopic Ellipsometer (VASE32, J. A. Woollam) operating in the spectral range of 270 ~ 1 600 nm with a step of 10 nm. Measurements were performed at three angles of incidence (55°, 65°, 75°). The SE data for the GZO thin films were fitted by the double oscillator model.

2 Results and discussion

The XRD patterns of hydrogen-annealed GZO films with various Ga doping concentration on silicon substrates are shown in Fig. 1 (a). According to the X-ray diffraction spectrum, the films doped with different Ga concentrations are all pure wurtzite-structured ZnO (JCPDS card No. 36-1451). The corresponding X-ray diffraction peaks for (100), (002), and (101) planes at 31.7°, 34.4° and 36.2° confirm the formation of wurtzite structure of ZnO. The intensity of diffraction peaks decrease with the increase in the Ga concentration, which indicates that the doping of Ga suppress the crystalline behavior of ZnO. The FWHM of major peaks of doped GZO films increases compared with pure ZnO and confirms the grain size reduction, which is also verified by SEM images[23]. To clarify whether Ga dope into the ZnO films, X-ray photoelectron spectroscopy (XPS) measurement is performed on the GZO thin film doped with 5 at% Ga. As shown in Fig. 1 (b), the survey scan indicates no impurity above the detection limit. The Ga 2p peak located at 1117.8 eV corresponds to Ga-O bonding and the characteristic peak of metallic Ga is not observed, which confirms the doping of Ga in the ZnO crystal lattice. The SEM images of the hydrogen-annealed GZO thin films doped with different Ga concentration and cross-section views of the corresponding films are presented in Fig. 2. All the films exhibit excellent compactness and uniformity.

Spectroscopic ellipsometry is a nondestructive technique to measure the optical response of semiconductors. Measuring at several angles of incidence over a wide spectral range produces a wealth of information about the sample[24]. The ellipsometric measurement is normally expressed in terms of the parameters Ψ and Δ, which are determined from the ratio of the amplitude reflection coefficient r_p and r_s for p- and s-polarizations with the following relations[24]:

$$\rho = \tan \Psi \exp(i\Delta) = r_p/r_s \quad . \quad (1)$$

From the experimental data of Ψ and Δ, the refractive index, n and extinction coefficient, k can be extracted through a suitable dielectric function model fitting of Ψ and Δ. Film thickness is also obtained as a by-product.

In this study, double oscillator model was tentatively used to fit the experimental data. The GZO thin film is supposed to be composed of three layers: the surface roughness layer, the ZnO-Ga layer and native Si oxide layer. The Bruggeman effective medium approximation of a 50/50 vol.% mixture of the GZO underneath and voids was used to model surface roughness. The dielectric function of the ZnO-Ga layer is split up into two different absorption mechanisms,

$$\varepsilon(E) = \varepsilon_{\text{vacuum}} + \varepsilon_{\text{band gap}}(E) + \varepsilon_{\text{free carrier}}(E) \quad . \quad (2)$$

Here $\varepsilon_{\text{vacuum}} = 1$ is the dieletric constant at high energies ($E \rightarrow \infty$) when the electric polarization cannot follow the oscillation of the light field. $\varepsilon_{\text{band gap}}$ is the fundamental absorption of the semiconductor and $\varepsilon_{\text{free carrier}}$ stands for the free-carrier absorption process.

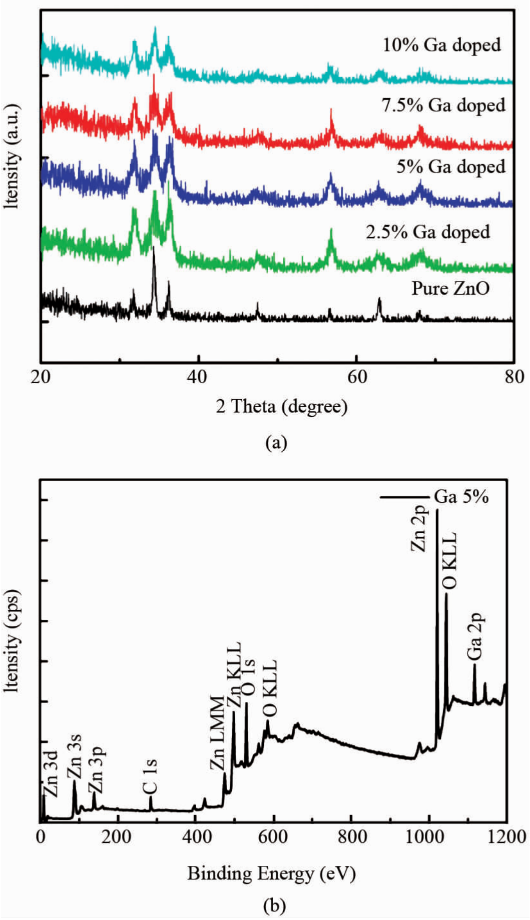

Fig. 1 (a) XRD patterns of hydrogen-annealed GZO thin films with 0 at%, 2.5 at%, 5 at%, 7.5 at%, and 10 at% of gallium; (b) X-ray photoelectron spectroscopy of the 5 at% doped GZO thin film

图1 (a) Ga 掺杂含量为 0 at%, 2.5 at%, 5 at%, 7.5 at%, 10 at% GZO 薄膜的 XRD 图谱;(b) Ga 掺杂含量为 5 at% 薄膜的 XPS 图谱

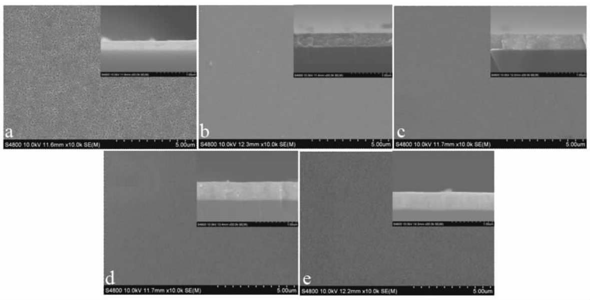

Fig. 2 (a-e) SEM images of hydrogen-annealed GZO thin films with 0 at%, 2.5 at%, 5 at%, 7.5 at%, and 10 at% of gallium; the insets are cross-section views of the corresponding films

图2 (a-e) Ga 掺杂含量为 0 at%, 2.5 at%, 5 at%, 7.5 at%, 10 at% GZO 薄膜的 SEM 图像, 插图为对应的 GZO 薄膜的横截面图像

Since ZnO is a direct band-gap semiconductor, we use the Psemi-M0 model for modeling the fundamental absorption.

$$\varepsilon_{n\_\mathrm{psemi}} = g_{M_0}(E_c, A, B, w_u, A_r, E_r) \quad , \quad (3)$$

that is a so-called Herzinger-Johs oscillator[25], designed for shaping M_0 critical points. The Herzinger-Johs function is also thoroughly disscussed by Charles C. Kim[26]. In the version used here, the shape is controlled by six parameters: the overall amplitude A, energy position E_c, the broading B of the oscillator, the parameter w_u, and the dimensionless parameters A_r, E_r, which govern the shape and asymmetry towards the highest energies.

In addition, free-carrier absorption in the near infrared (NIR) and infrared (IR) spectral range is modeled with a rho-tau Drude formula:

$$\varepsilon_{n\_\mathrm{rtDrd}} = \frac{-h^2}{\varepsilon_0\rho_n(\tau_n E^2 + ihE)} \quad , \quad (4)$$

$$\rho_n = \frac{m^*}{N_n q^2 \tau_m} = \frac{1}{q\mu_n N_n} \quad . \quad (5)$$

The fitting parameters are ρ_n and τ_m, the related parameters of interest are m^* (the carrier effective mass), N_n (the carrier concentration), μ_n (the carrier mobility), h (Plank's constant/π), ε_0 (the vacuum dieletric constant) and the single electron charge q.

In Fig. 3 (a ~ j), the experiental data (green dots) and fitting results (red lines) of hydrogen-annealed GZO films with various doping concentrations by two oscillation formulas are shown. The fitting lines are consistent with the experimental data. The fitted film thicknesses (247.9, 358.6, 428.8, 453.6, 458.5 nm) match the values measured by a field emission scanning electron microscope (246.3, 356.8, 423.9, 461.7 and 461.1 nm, respectively), which confirm the accuracy of our model further. Besides, the film thickness increases with Ga doping. Weber and Botnaras *et al.* also discovered the similar phenomenon in ZnO: Ga and ZnO: Ga, In films[27]. A possible explanation could be an inhibited growing of zinc oxide nuclei by the Ga doping, if the crystals grow not only 2-dimensionally but also 3-domensionally. It will result in a thicker film.

Figure 4 shows the changes of refractive index (n) and extinction coefficient (k) of hydrogen-annealed GZO films as a function of wavelength in the range of 270 ~ 1600 nm. For GZO films, we find that the refractive index decreases gradually with the increase of the Ga doping concentration. This can be mainly attributed to an increase of the carrier concentration in the GZO thin films as confirmed by Hall Effect measurement in Fig. 5[24]. Kim and Qiao *et al.* also found that the refractive index was inversely related to the carrier concentration[28-29]. It is well known that Ga doped ZnO films can act as an effective donor as a result of substitutional introduction of Ga^{3+} into the Zn^{2+} site, generating free electrons. With the increasing dopant concentration, the carrier concentration in the GZO films is increased. On the other hand, from Fig. 4b, we can see that the extinction coefficient increases steeply at short wavelengths and increases monotonously at long wavelengths. It can be attributed to the absorption edge and the increase of the free carrier absorption, respectively. The increase of the doping concentration results in the increase of the extinction coefficient in the near infrared and infrared spectral range. It is due to the increase of carrier concentration.

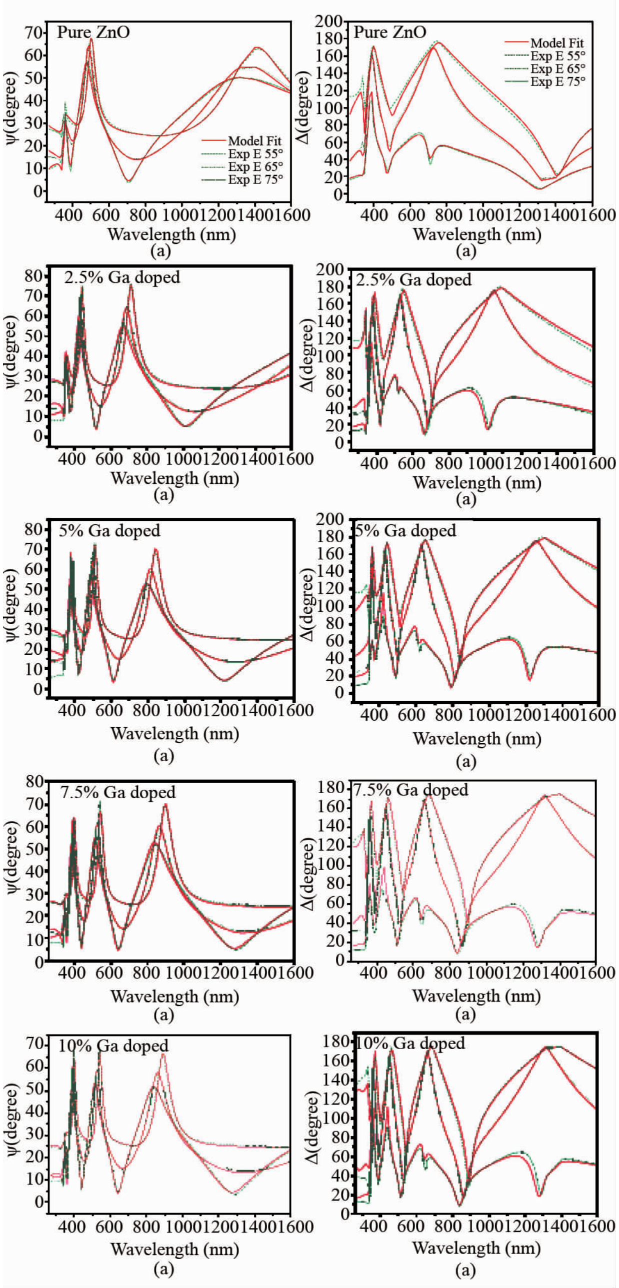

Fig. 3　(a ~ j) Measured ellipsometry data (green dots) and fitting results by the double oscillator model (red line) of hydrogen-annealed GZO thin films

图 3　(a ~ j) 氢化后 GZO 薄膜椭偏光谱实验数据和采用双振子模型拟合的结果

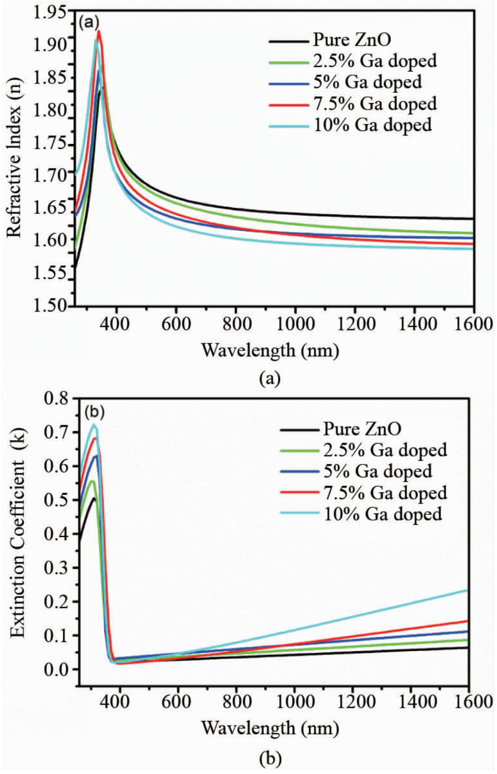

Fig. 4　Refractive index, *n* and extinction coefficient, *k* of hydrogen-annealed GZO films as a function of the wavelength

图 4　通过拟合得到的氢化后 GZO 薄膜折射率和消光系数随波长的变化关系

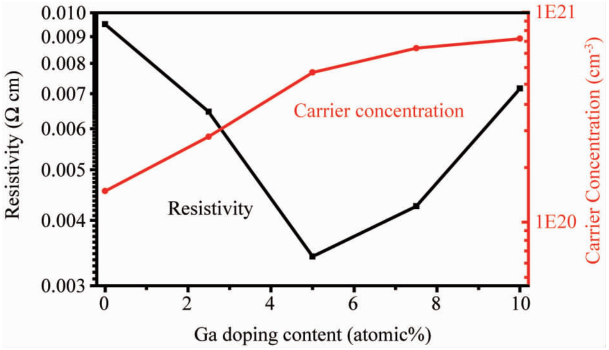

Fig. 5　Resistivity and carrier concentration of GZO thin films as a function of dopant concentration

图 5　氢化后 GZO 薄膜电阻率和载流子浓度随掺杂浓度的变化关系

Therefore, the refractive index and the extinction coefficient of the GZO films can be tuned effectively by varying the carrier concentration, which is important for the applications in designing integrated optic devices.

The dependence of the electrical resistivity, carrier concentration of the hydrogen-annealed GZO films on the doping concentrations is shown in Fig. 5. A lowest resistivity of 3.410×10^{-3} Ω · cm is obtained with 5 at% Ga doping concentration. When the Ga doping concentration is larger than 5 at%, vast amounts of crystal defects and lattice distortion exist, which result in a decrease in mobility, and consequently an increase in resistivity [30].

3　Conclusions

In this paper, the ellipsometric data for several angles of incidence of the hydrogenated GZO thin films on silicon substrate were analyzed. The Psemi-M0 model for modeling direct fundamental absorption and a rho-tau Drude model for free carrier absorption were used in the fitting process. The model yields good fitting results for ellipsometric spectra range from 270 nm to 1600 nm. According to the X-ray diffraction spectrum, the films doped with different gallium concentrations were found to be pure wurtzite-structured ZnO. A lowest resistivity of $3.410\times10^{-3}\ \Omega\cdot\mathrm{cm}$ is obtained for the ZnO film doped with 5 at% of Ga by hydrogen-annealing at 450℃ for 60 min. The optical properties of GZO films can be tuned effectively by varying the carrier concentration, which is important for applications in designing integrated optic devices.

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