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The optical constant of $ZnSe/SiO_2$ composite thin films investigated by spectroscopic ellipsometers

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Abstract In this paper, $ZnSe/SiO_2$ composite thin films was prepared by sol–gel process. X-ray diffraction results indicate the phase structure of ZnSe particles embedded in SiO_2 composite thin films is sphalerite (cubic ZnS). The dependence of ellipsometric angle ψ with wavelength λ of $ZnSe/SiO_2$ composite thin films was investigated through spectroscopic ellipsometers. The optical constant, thickness, porosity and the concentration of $ZnSe/SiO_2$ composite thin films were fitted according to Maxwell-Garnett effective medium theory. The thickness of $ZnSe/SiO_2$ composite thin films was measured through surface profile.

Keyword $ZnSe/SiO_2$ composite thin films · Spectroscopic ellipsometers · Optical constant

1 Introduction

In recent years, composite materials have attracted much attention for applications in opto-electronic device. Especially, the application of II–VI group semiconductor composite thin films, such as CdSe, CdS, CdTe, ZnS nanoparticles embedded in strained system has attracted much attention for the fabrication of visible semiconductor laser [1–4].

As one of the wide-band gap II–VI group semiconductors, ZnSe has received much attention for its technological application in blue laser diode, IR optical window, solar cell and sensor. But there are fewer scientific reports of $ZnSe/SiO_2$ composite thin films on its fabrication and properties. S.B Yin and Lisa Chen [5] fabricated the ZnSe quantum dots in glass matrix thin films by pulsed laser evaporation. G.M Li and Nogami [6] prepared the ZnSe crystallites doped in borosilicate glass films by sol–gel method. A.A. Lipovskii et al. [7] successfully prepared the II–VI semiconductor nanocrystallite in a novel phosphate glass.

This paper presents the fabrication of $ZnSe/SiO_2$ composite thin films on $SiO_2/Si(100)$ substrate through the sol–gel process. In this paper, $ZnSe/SiO_2$ composite thin films were synthesized using relatively cheap H_2SeO_4 and $Zn(Ac)_2{\cdot}2H_2O$ as starting materials under carbon monoxide atmosphere at 500 °C. The technique of synthesis of $ZnSe/SiO_2$ composite thin films can solve the problems of the emergence of ZnO phase and escape of Se element under H_2 condition.

2 Experiment

2.1 Preparation of $ZnSe/SiO_2$ composite thin films

There are two steps of preparation of SiO_2 solution [8]. At first, the SiO_2 solution was prepared using TEOS, H_2O and $NH_4{\cdot}OH$. The TEOS was mixed with water under NH_4OH catalysis without adding ethanol, which meant no flocculation occurs when PVA was added. The volume ratio of the composition is $TEOS/H_2O/NH_4OH=5:30:2$. After a 24 stir and filtration, we can obtain a transparent and homogeneous solution. Then acetic acid was added in this solution to adjust pH to 2.5, which will slow down the speed of condensation and to delay the growth of silica gel particles. Meanwhile, the $Zn(Ac)_2{\cdot}2H_2O$ and the H_2SeO_4 (80% water solution)as starting materials were added to the solution. Finally, a 5.5 wt% PVA water solution was added to the

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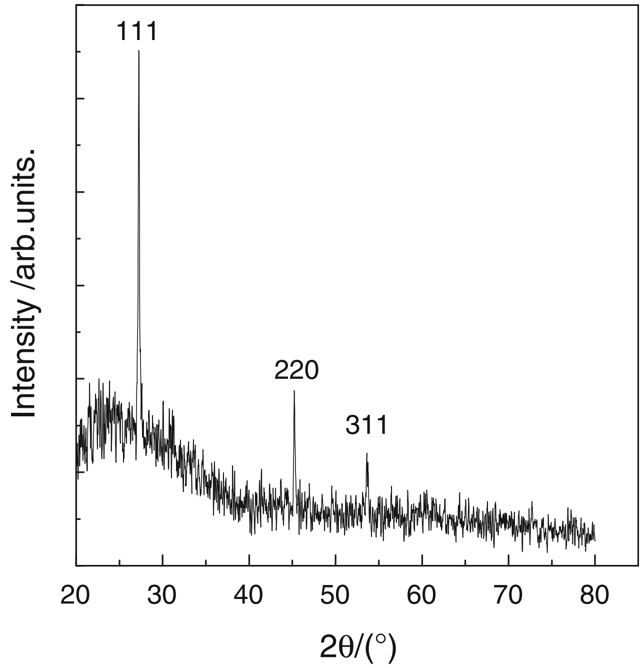

Fig. 1 The XRD patterns of $ZnSe/SiO_2$ composite thin films synthesized at 500 °C under carbon monoxide atmosphere for 20 min

solution to coat the silica gel (PVA/SiO_2=0.55/1 wt%) particles in order to obtain a stable gel solution and restrict the growth of the gel particles. Usually, the hydrogen bond between PVA and silica gel depends heavily on the pH value. When pH=2.5, a strong hydrogen bond is formed between PVA and silica gel. The acetic acid is also helpful to stabilize the silica gel solution. The amount of PVA is one of main factors in the preparation of the high quality, crack free, porous SiO_2 thin films.

Firstly, the wet chemical films were prepared by spin-coating method and were annealed under air condition to make complete volatilization of organic solvent and PVA at 450 °C. Afterward, the thin films were treated under carbon monoxide reduction atmosphere at 500 °C to obtain the $ZnSe/SiO_2$ composite thin films. The reactions of the synthesis of $ZnSe/SiO_2$ composite thin films are described by Eqs. 1 and 2:

$$SeO_4^{2-} + Zn^{2+} = ZnSeO_4 \quad (1)$$

$$ZnSeO_4 + 4CO \xrightarrow{\Delta} ZnSe + 4CO_2 \quad (2)$$

2.2 Characterization

The phase structure of $ZnSe/SiO_2$ films was investigated by X-ray diffraction (XRD, Rigaku D/MAX-2400, CuK_α). The relationship of ellipsometric angle $\psi - \lambda$ of $ZnSe/SiO_2$ composite thin films was investigated through spectroscopic ellipsometers (M-2000UI, J.A.WOOLAM.CO.INC). The optical constant, thickness, porosity and the concentration of $ZnSe/SiO_2$ composite thin films were fitted according to Maxwell–Garnett effective medium theory. The thickness of $ZnSe/SiO_2$ composite thin films was measured through surface profile(Dektak[3] ST).

3 Results and discussion

3.1 The XRD analysis

The XRD pattern of $ZnSe/SiO_2$ thin films synthesized at 500 °C under carbon monoxide atmosphere is shown in Fig. 1. The XRD results indicate that the phase structure of ZnSe is sphalerite (cubic ZnS).

3.2 Spectroscopic ellipsometers measurement

To interpret the spectroscopic ellipsometric experimental results of $ZnSe/SiO_2$ composite thin films with low volume

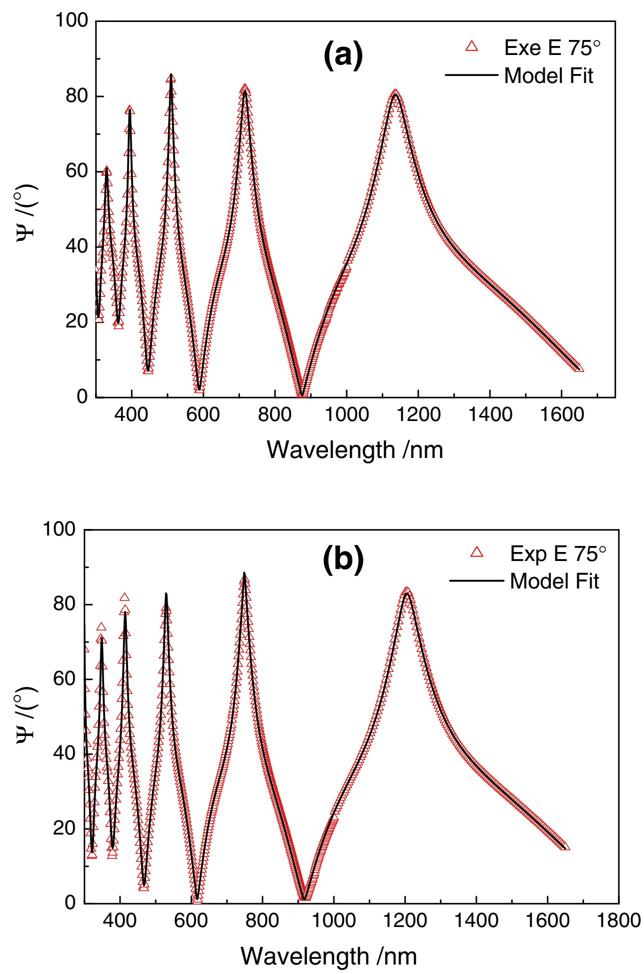

Fig. 2 The experimental and fitting ψ value of one layer $ZnSe/SiO_2$ composite thin films (**a**) pure SiO_2 thin films, (**b**) 10%$ZnSe/SiO_2$ composite thin films

Table 1 The fitting results of different one layer films according to M–G effective medium theory

Sample	Zn^{2+}/TEOS (before heat-treated) (/mol%)	$ZnSe/SiO_2$ (before heat-treated) (/mol%)	Porosity (/vol.%)	Thickness[a] (/nm)	Thickness[b] (/nm)
1	0	0	38.6	277.7	270
2	10	4.66	38.3	312.4	350
3	15	6.07	38.5	344.5	390
4	20	11.29	26.7	339.8	380
5	25	10.08	22.2	360.5	390
6	30	15.44	38.1	361.5	400

[a] The thickness was surveyed through spectroscopic ellipsometers.
[b] The thickness was surveyed through surface profiler.

fractions of ZnSe semiconductor, Maxwell-Garnett effective medium theory [9] is used to calculate the optical constant of $ZnSe/SiO_2$ composite thin films. According to Maxwell–Garnett effective medium theory, the effective dielectric permittivity of composite thin films is given by Eq. 3 as follows:

$$\frac{\varepsilon_{effe} - \varepsilon_h}{\varepsilon_{effe} + 2\varepsilon_h} = f_1 \frac{\varepsilon_1 - \varepsilon_h}{\varepsilon_1 + 2\varepsilon_h} + f_2 \frac{\varepsilon_2 - \varepsilon_h}{\varepsilon_2 + 2\varepsilon_h} \quad (3)$$

where ε_h is the dielectric permittivity of SiO_2 thin films ε_1 is the dielectric permittivity of ZnSe orbicular particle random embedded in SiO_2 thin films, f_1 represents the volume fraction of ZnSe particles in SiO_2 thin films, ε_2 is the dielectric permittivity of air void of SiO_2 thin films and f_2 represents the volume fraction of air void, $\varepsilon_{effe} = \varepsilon'_{effe} + i\varepsilon''_{effe}$ denotes the effective complex dielectric permittivity of composite thin films(with real part ε'_{effe} and imaginary part ε''_{effe}). The underlying assumptions are (1) spherical inclusion geometry, and (2) dipole interaction only.

In the range of optical frequency, we can obtain the refractive index n and the extinction coefficient k of the composite thin films from the effective complex dielectric function value according to Eqs. 4 and 5.

$$n = \left\{ \frac{1}{2} \left[\sqrt{\varepsilon'^{2}_{effe} + i\varepsilon''^{2}_{effe}} + \varepsilon'_{effe} \right] \right\}^{\frac{1}{2}} \quad (4)$$

$$k = \left\{ \frac{1}{2} \left[\sqrt{\varepsilon'^{2}_{effe} + i\varepsilon''^{2}_{effe}} - \varepsilon'_{effe} \right] \right\}^{\frac{1}{2}} \quad (5)$$

According to Maxwell–Garnett effective medium theory , we adjusted the factor f_1 and f_2 to calculate the optical constant of composite films system. Then the $\psi-\lambda$ relationship is obtained according to the calculated n and k. The $\psi-\lambda$ fitting is described as follows:

The complex reflectance ratio ρ of thin films can be described by Eq. 6:

$$\rho = R_p / R_s = \frac{\left(r_{01p} + r_{12p}e^{-i2\beta}\right)\left(1 + r_{01p}r_{12p}e^{-i2\beta}\right)^{-1}}{\left(r_{01s} + r_{12s}e^{-i2\beta}\right)\left(1 + r_{01s}r_{12s}e^{-i2\beta}\right)^{-1}} \quad (6)$$

where R_p and R_s represent the reflection coefficient of p- and s-polarized light respectively. r_{01p}, r_{12p}, r_{01s} and r_{12s} represent the Fresnel reflection coefficient of p- and s-polarized light in 01 (between air and film) interface and 12 (between film and substrate) interface, β is the phase difference of two light beams.

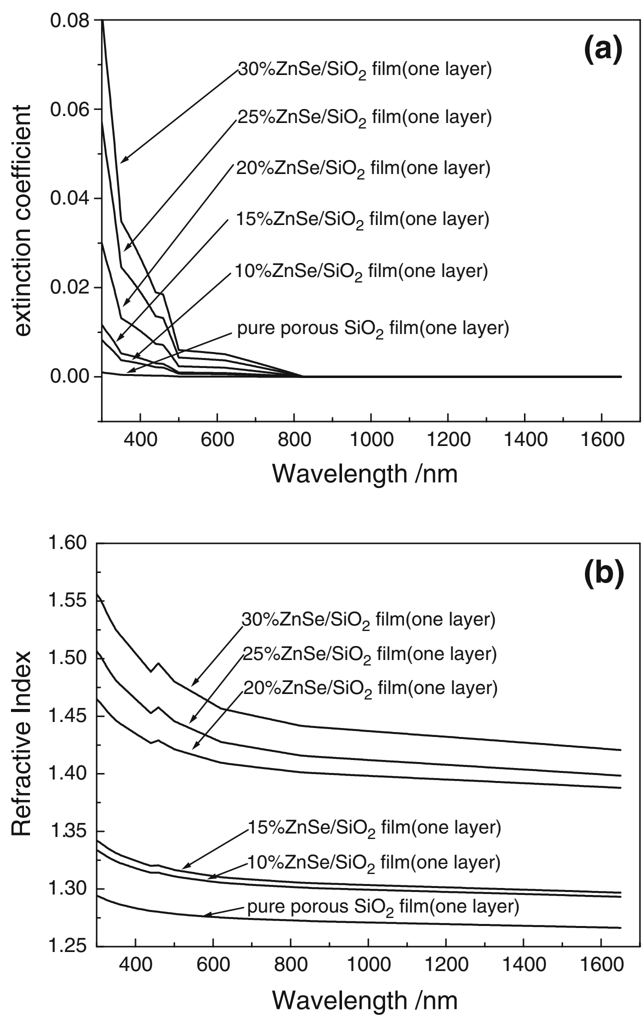

Fig. 3 The relation between optical constant and wavelength (**a**) extinction coefficient, (**b**) refractive index

The complex reflectance ratio ρ of thin films is a function of ellipsometric factors of ψ and Δ:

$$\rho = \tan\psi \cdot e^{i\Delta} = f(n_1, n_2, n, \phi, d, \lambda, k) \tag{7}$$

where n_1, n_2 and n represent the refractive index of air, substrate and films respectively. ϕ and λ represent the incident angle and wavelength of incident light, respectively. d and k represent the thickness of films and extinction coefficient of thin films, respectively. In our experiment, the relationship of $\psi-\lambda$ was fitted under 75° incident angle after n, d and k were adjusted. Figure 2 is the experimental and fitting results of $\psi-\lambda$ of one layer ZnSe/SiO_2 composite thin films:

Table 1 is the fitting results of the molar ratio of ZnSe/SiO_2, porosity and thickness of one layer ZnSe/SiO_2 composite thin films according to Maxwell–Garnett effective medium theory. Column 2 and column 3 represent the original molar ratio of Zn^{2+} (or SeO_4^{2-})/SiO_2 in TEOS solution and the actual moral ratio of ZnSe/SiO_2 in composite thin films, respectively. The results reveal that the molar ratio of ZnSe/SiO_2 increases with the increasing of original molar concentration of Zn^{2+}, SeO_4^{2-} in solution. The actual molar ratio of ZnSe/SiO_2 of thin films is approximately 1/2 of the original molar ratio of $Zn^{2+}(SeO_4^{2-})$/SiO_2 in solution. We can control the concentration of ZnSe in ZnSe/SiO_2 composite thin films by adjusting the original concentration of Zn^{2+} and SeO_4^{2+} in solution. The porosity of ZnSe/SiO_2 composite thin films was about 38–22%, which is consistent with every sample concerning the experimental error. The thickness of single layer ZnSe/SiO_2 composite thin films will increase with the increase of the molar ratio of ZnSe/SiO_2 . The thickness of one layer pure SiO_2 thin films is 277.7 nm and the thickness of one layer ZnSe/SiO_2 thin films is more than 300 nm.

The relationship between extinction coefficient, refractive index and wavelength is shown in Fig. 3.

Figure 3 indicates that the extinction coefficient and refractive index increase with the increasing of ZnSe/SiO_2 molar ratio. The extinction coefficient of pure SiO_2 thin films is invariable at the wavelength 300–1650 nm without any particular absorption region. The value of extinction coefficient is approximately 1.22×10^{-4}. The extinction coefficient of ZnSe/SiO_2 composite thin films increases in wavelength less than 800 nm and sharply increases in wavelength less than 500 nm. This results indicate that the absorption of ZnSe/SiO_2 composite thin films increases when wavelength is less than 800 nm. In Fig. 3(a), there are five different absorption regions which correspond to 800–500 nm, 500–458 nm, 458–441 nm, 441–350 nm, 350–300 nm, respectively. In the 800–500 nm region, the extinction coefficient of ZnSe/SiO_2 composite thin films is slightly larger than that of pure SiO_2 films for the quantity of lattice defects of sphalerite ZnSe crystal, such as $V_{Zn^{2+}}$, $V_{Se^{2-}}$, $O_{Se^{2-}}$, which induce the complicated absorption mechanism including free excited absorption and lattice defect absorption. A sharp absorption in 500–458 nm correspond to the band-to-band absorption of sphalerite ZnSe crystal. There is a relatively smooth curve in the 458–441 nm region without special absorption. In the 441–350 nm and 350–300 nm, wurtzite ZnSe phase structure and ZnO phase emerge, which sharply increase the absorption of ZnSe/SiO_2 thin films. The refractive index curve also reveals the existent of ZnSe crystal.

4 Conclusion

In conclusion, the ZnSe/SiO_2 composite thin films was prepared by a sol–gel process. XRD indicate the ZnSe embedded in the SiO_2 thin films is sphalerite. The spectroscopic ellipsometers and Maxwell–Garnett effective medium theory are used to measure and to evaluate the optical experimental results. The results reveal that the actual molar ratio of ZnSe/SiO_2 of thin films is approximately one half of the original molar ratio of $Zn^{2+}(SeO_4^{2-})$/SiO_2 in solution. The porosity of ZnSe/SiO_2 composite thin films is approximately 30%. The thickness of one layer SiO_2 thin films is 277.7 nm and the thickness of one layer ZnSe/SiO_2 thin films is more than 300 nm.

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