Ellipsometric analysis and optical absorption characterization of gallium phosphide nanoparticulate thin film

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Gallium phosphide (GaP) nanoparticulate thin films were easily fabricated by colloidal suspension deposition via GaP nanoparticles dispersed in N,N-dimethylformamide. The microstructure of the film was performed by x-ray diffraction, high resolution transmission electron microscopy and field emission scanning electron microscopy. The film was further investigated by spectroscopic ellipsometry. After the model GaP+void|SiO_2 was built and an effective medium approximation was adopted, the values of the refractive index n and the extinction coefficient k were calculated for the energy range of 0.75 eV–4.0 eV using the dispersion formula in DeltaPsi2 software. The absorption coefficient of the film was calculated from its k and its energy gaps were further estimated according to the Tauc equation, which were further verified by its fluorescence spectrum measurement. The structure and optical absorption properties of the nanoparticulate films are promising for their potential applications in hybrid solar cells.

Keywords: ellipsometry, optical energy gaps, gallium phosphide, particulate thin film

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1. Introduction

Wide-band-gap semiconductors have attracted a great deal of attention because they are strong candidate materials for light emitting diodes (LEDs) operating in the blue-to-ultraviolet region.[1] Gallium phosphide (GaP), is a popular semiconductor material[2] and is considered to be a wide-band-gap semiconductor, making it a good candidate for room-temperature device applications. GaP has potential for ultraviolet, blue, and blue–green detection applications from 250 nm to 500 nm.[3] Semiconductor nanomaterials show some new optical properties and they attract considerable attention as a possible new type of photoelectric material, arising from quantum size and dielectric confinement effects.[4−6] As an important III–V compound semiconductor, GaP nanomaterial has been widely studied.[1,7−10] It has been inferred that GaP nanoparticles exhibit a direct transition and an indirect transition from their ultraviolet and visible (UV-vis) spectra.[1,10] The ratio of the absorption and scattering coefficients of the GaP nanoparticles layer has also been calculated from its reflection spectrum via a radiative transfer theory, whose curves exhibit the energy band gaps of GaP nanoparticles.[1]

The design, manufacture and study of nanoparticle-based films have become particularly attractive because of the potential technological applications, such as catalysis, microelectronics, molecular recognition and chemical sensing.[11−15] The properties of the particulate films are dependent on the size and the surface, as well as the microstructure of the particles in the films. The optical absorption of the films depends on their optical constants and thickness. Spectroscopic ellipsometry (SE) has proven to be a successful tool for modeling the dispersion of materials in thin film form.[16−18]

In the present study, we fabricate GaP nanoparticulate thin films by colloidal suspension deposition on quartz substrates, and focus our attention on the SE and optical absorption investigation of the film. The optical constants n and k of the film are estimated by means of establishing a proper model to fit the ellipsometric data. Furthermore, the energy gaps in the film are estimated by calculating its absorption coefficient based on its k. Many relevant references are consulted, in which there is almost no report on

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the ellipsometric analysis of the GaP nanoparticulate thin films. Moreover, it is proposed that the particulate films can be applied to the design for the solar cells of the composite films with a hybrid structure.

2. Experiment

2.1. Preparation of the GaP nanoparticulate thin films

At first, GaP nanoparticles were synthesized using the benzene thermal method according to the direct reaction between anhydrous gallium trichloride and sodium phosphide: $GaCl_3 + Na_3P = GaP + 3NaCl$ in dimethylbenzene under nitrogen atmosphere at 353 K. The synthesis steps have been described in detail in Refs. [1] and [10].

Then, the investigated GaP nanoparticulate thin films were fabricated by colloidal suspension deposition on quartz substrates. As we know, N,N-dimethylformamide (DMF) is a polar solvent and GaP nanoparticles are negatively charged on their surfaces due to the decomposition of the bond P–O–H. GaP nanoparticles were dispersed into the solvent DMF, considering the mutually dissolving analogue theory. The detailed steps were as follows: first, 82 mg of the as-synthesized GaP powders was added into 30-ml DMF. After ultrasonic dispersion for 30 min and centrifugal sedimentation for 20 min, the suspension was obtained. Second, the suspension for GaP nanoparticulate films was directly deposited onto the quartz substrates (40 mm×20 mm×1 mm) cleaned in an ultrasonic bath. After each deposition, the coated layer was dried at 333 K in a drying cabinet. Finally, the tender films were hardened at 433 K for 2 h to further remove residual water and DMF in the films considering that the boiling point of DMF is 426 K, and thus the GaP nanoparticulate films were obtained. The preparation method has also been applied in our previous work.[19]

2.2. Characterization

The phase compositions and microstructure of GaP nanoparticles were characterized by x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM), respectively. The XRD patterns were obtained by a D/max-rC model x-ray diffractometer using Cu Kα radiation with λ = 015418 nm from a rotating anode source and a graphite monochromator operated at 40 kV, 100 mA. The HRTEM images were collected using a JEM-2010F microscope operating at an acceleration voltage of 200 kV.

The surface microstructure of the GaP nanoparticulate thin film was observed by field emission scanning electron microscopy (FESEM) on a JSM-6700F microscope at 10 kV. The spectroscopic ellipsometric investigation of the film was performed at room temperature by using a spectroscopic ellipsometer (UVISEL-1/460-VIS-AGAS), and the photon energy was from 0.75 eV to 4.0 eV, which is located in visible to near ultraviolet range. Florescence spectrum was obtained at room temperature using a Shimadzu spectrofluorophotometer RF-540 with an excitation wavelength 300 nm.

3. Results and discussion

3.1. XRD, HRTEM and FESEM

In the XRD pattern of GaP nanoparticles shown in Fig. 1, the peaks are identified as (111), (200), (220), (311), (222), (400) and (331) reflections of zinc blende structure of GaP, in good agreement with the reported data of the crystalline bulk GaP (JCPDS card no. 12-0191). The crystallite size has been calculated by Debye–Scherrer's formula:

$$D = 0.89\lambda/\beta\cos\theta, \tag{1}$$

where D is the grain size, λ is the wavelength of the x-ray radiation used, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg diffraction angle of the XRD peak. The average size of GaP nanoparticles is estimated to be around 50 nm.

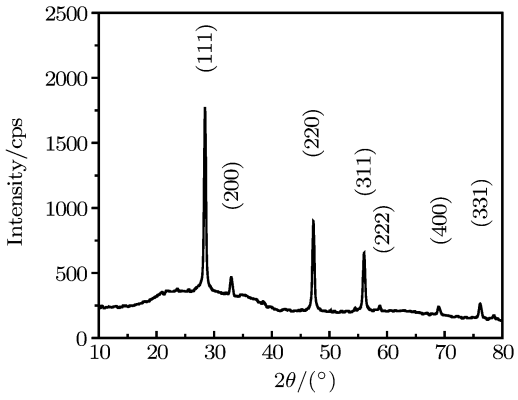


Fig. 1. The x-ray diffractogram of the GaP nanoparticles.

The morphology and microstructure of the GaP nanoparticles were studied by HRTEM, and the sample was dissolved in alcohol and a drop of solution was deposited on the copper grid. Figure 2 shows the HRTEM images of GaP nanoparticles. In Fig. 2(a), it can be seen that GaP nanoparticles are ellipsoidal and that mutual aggregation takes place among them due to their high surface energy. The lattice planes of GaP nanoparticles can be seen from Fig. 2(b), which indicate that GaP nanoparticles crystallize well. In Fig. 2(b), the spacing of the crystallographic planes in the area A is 0.31 nm, corresponding to the (111) lattice planes of crystalline GaP, and that of the area B is 0.27 nm, corresponding to the GaP (200) lattice planes (theoretically 0.314 nm and 0.272 nm, respectively, GaP JCPDS card no. 12-0191), which agrees well with the above XRD results.

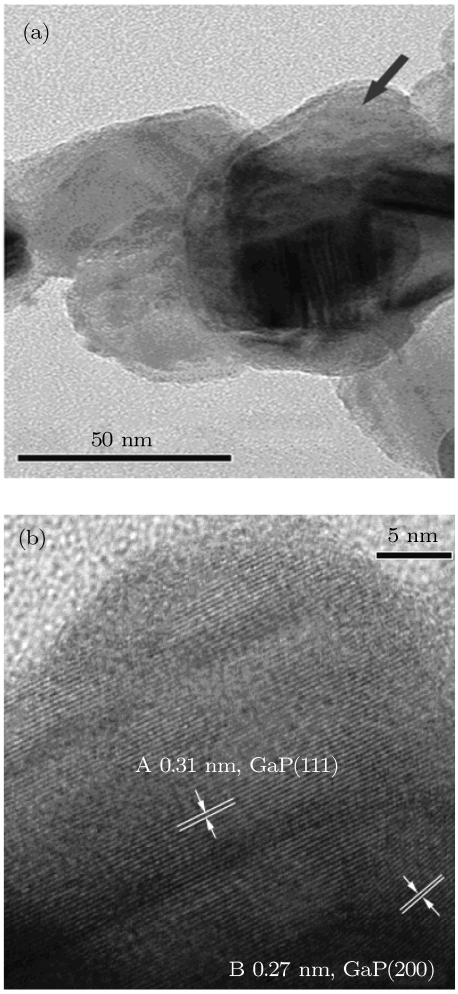


Fig. 2. HRTEM images of the GaP nanoparticles: (a) the general morphology of GaP nanoparticles; (b) the magnified HRTEM image of the region in (a) (marked with an arrow), revealing the microstructure of the GaP nanoparticles.

Figure 3 presents a typical FESEM image of the GaP nanoparticulate thin film on the quartz substrate. As shown in the image, the film seems to be composed of particles and its surface is rather rough. There are some voids in the GaP nanoparticulate film. Additionally, the morphology and the size of the GaP nanoparticles can also be seen from the FESEM image, which are consistent with the HRTEM results.

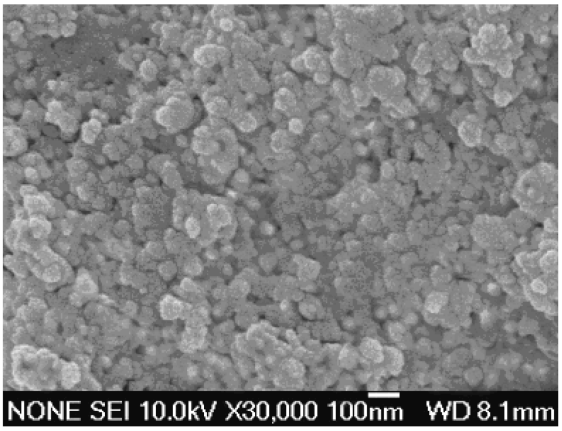


Fig. 3. FESEM image of the GaP nanoparticulate thin film.

Incidentally, such particulate films can be applied to the design for the structure of the solar cells with hybrid inorganic/organic composite films, in which bulk heterojunctions are formed.[20−25] Both the thickness and the void density of the film are the two important concerns for the application. The coated films were prepared by colloidal suspension deposition, and the depositions were operated again and again in the same way in a drying cabinet. The film thickness is connected with depositing numbers, and the thickness increases with multiple deposition. Thus, the repeated depositions can modulate the thickness of the film. Furthermore, the density of the void in the film can be adjusted by the size of the GaP nanoparticles dispersed in the suspension, depositing numbers as well as the evaporation rate of the solvent in the film. First, the void density of the film is related to the size of the deposited particles, and as we know, the smaller the dispersed GaP nanoparticles are, the smoother the surface of the film becomes. Second, the average grain size of the deposited particles is about 50 nm, which is in the order of nanometer, and therefore multiple deposition can also partly reduce the void density besides growing the film thickness. Third, the solvent evaporation rate of the nanoparticulate film has a huge influence on the void density, and

the evaporation rate can be controlled by the temperature in the drying cabinet.

3.2. Ellipsometry investigation of the GaP nanoparticulate thin film

The spectroscopic ellipsometry, with high precision and sensitivity, processing convenience and no harm to samples, is one of the most adopted measuring methods in analysing the optical properties of thin films. In ellipsometric analysis, a conventional method to simulate the optical variation of thin film is to model the film with a stack of layers having different compositions. Effective medium approximation (EMA) is the most frequently used approach to model the optical properties of polycrystalline thin films, which includes purity, void and surface roughness.

In this work, the Bruggeman EMA is also applied to model the film. The SE data, ellipsometric angles ψ and Δ, of the film in the energy range 0.75 eV–4.0 eV are obtained. The experimental data are analysed using a model, GaP+void|SiO_2, to describe the structure of the GaP nanoparticulate film (shown in Fig. 4). In addition, the model thus uses the layer GaP+void because many voids, seen from the FESEM image of the GaP nanoparticulate film, are in the film. The fitting results are obtained by the DeltaPsi2 software. A good fit is found between the model fit and the experimental data. The standard deviation is only 0.1036. The thickness of the film is about 964.1 nm, and GaP nanoparticles account for 92.74% and voids for 7.26% in the GaP+void layer.



Fig. 4. Fit model GaP+void|SiO_2 of the GaP nanoparticulate film on the quartz substrate for SE (generated by the DeltaPsi2 software).

We employ the dispersion formula for nanocrystalline materials proposed by Forouhi and Bloomer (F–B),[26] which is derived on the basis of the extinction coefficient k for a single electron transition in the proximity of the interband energy gap (E_g),

$$k(E) = \frac{A(E - E_g)^2}{E^2 - BE + C}. \tag{2}$$

Unlike Tauc's model, which is more commonly employed to evaluate the optical gap of amorphous semiconductors, the F–B dispersion model does fulfill the causality principle,[26] making it possible to arrive at the corresponding expression rigorously for the refractive index, $n(E)$, through Kramers–Kronig relations:

$$n(E) = n(\infty) + \frac{BE + C}{E^2 - BE + C}, \tag{3}$$

where E_g corresponds to the optical band gap, $n(\infty)$ is the refractive index at optical frequencies, A is inversely proportional to the lifetime of the excited states, and B is related to the energy difference between the bonding and anti-bonding states.[26] C depends on both A and B. Results for the optical constants n and k of the GaP nanoparticulate film, obtained by calculating from the five parameters using Eqs. (2) and (3), are shown in Fig. 5.

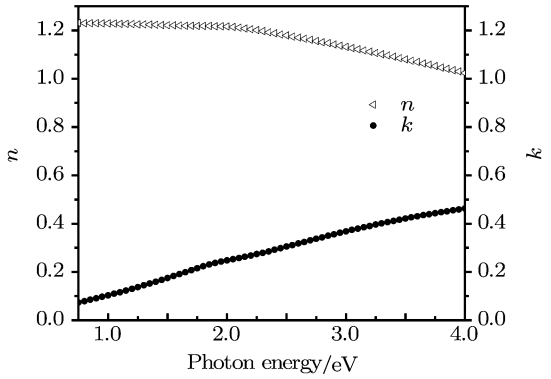


Fig. 5. Calculated values of n and k of the GaP nanoparticulate film.

The value of n varies a little (1.03–1.23) in the range of photon energy from 0.75 eV to 4.0 eV. Being of the order of 10^{-1}, the data of k indicate a good absorption of the film in the energy range. The voids in the GaP nanoparticulate film have probably made the value of n decrease. Additionally, the spectra of optical constants n and k for bulk GaP in the mid-infrared range have been reported by Kleinman and Spitzer,[27] in which the value of n varies near 3.

3.3. Optical energy gaps of the GaP nanoparticulate thin film

To further reveal the meaning of extinction coefficient k, we plot k as a function of wavelength for the GaP nanoparticulate film. Figure 6 shows $k(\lambda)$ of the film in the wavelength range of 300 nm–1600 nm. The shape of $k(\lambda)$ of the film is consistent with that of the absorption spectra of GaP nanoparticles shown in our previous papers.[1,10] Thus, extinction coefficient

k is also one of the important parameters displaying optical absorption characteristic of the materials. As shown, for wavelengths in the range of 300 nm–700 nm the absorption of the film is strong.

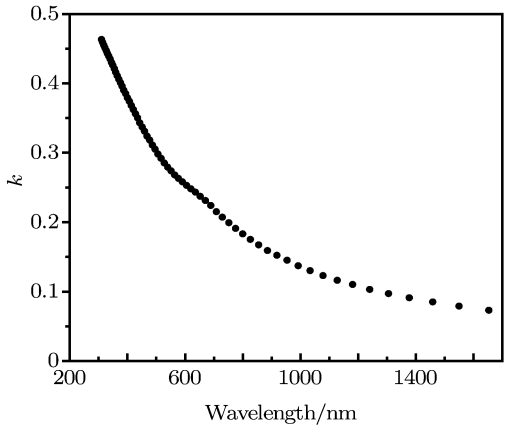


Fig. 6. Optical constant k of the GaP nanoparticulate thin film as a function of wavelength.

Once the extinction coefficient $k(\lambda)$ is known, the absorption coefficient $\alpha(\lambda)$ can be calculated from the following equation[28,29]

$$\alpha = 4\pi k/\lambda, \tag{4}$$

where λ is the wavelength of light. The absorption coefficient $\alpha(\lambda)$ of the GaP nanoparticulate film is presented in Fig. 7, and it is also compatible with the absorption spectra of GaP nanoparticles in our previous work.[1,10]

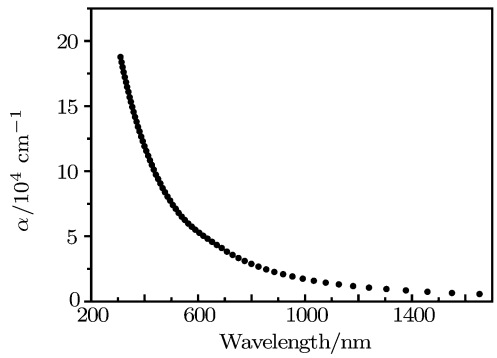


Fig. 7. Optical absorption coefficient of the GaP nanoparticulate thin film as a function of wavelength.

The optical energy gap is an important parameter for describing solid-state materials. The optical energy gaps can be estimated from the absorption coefficient using the following Tauc equation[30,31]

$$\alpha h\nu = F(h\nu - E_g)^m, \tag{5}$$

where $h\nu$ is the energy of the incident photons, F is the proportionality factor, m is the power indicating the nature of optical transition in the film, which is 2 for indirect transition and 1/2 for direct transition, and E_g is the optical energy gap between the valence band and the conduction band. The usual method for the determination of the value of E_g involves plotting $(\alpha h\nu)^{1/m}$ against $(h\nu)$. The optical gaps have been determined from the plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus $h\nu$, respectively (shown in Figs. 8(a) and 8(b)). By extrapolating the straight parts of these relations to the $h\nu$ axis, indirect and direct energy gaps have been determined for the GaP nanoparticulate film. The estimated optical gaps are about 2.43 eV ($m = 2$) and around 3.07 eV ($m = 1/2$). The method has also been used in Refs. [30] and [32].

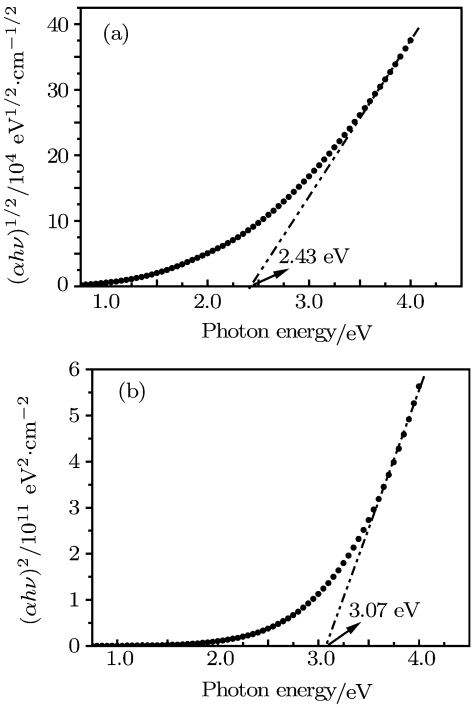


Fig. 8. Energy gaps of the GaP nanoparticulate thin film under different transition mechanics: (a) plots for $(\alpha h\nu)^{1/2}$ versus $h\nu$; (b) plots for $(\alpha h\nu)^2$ versus $h\nu$.

Obviously, the gaps of the GaP nanoparticulate film are closer to the values of the GaP nanoparticles (2.58 eV and 3.05 eV) presented in our previous papers.[1,10] In addition, we propose that due to the above moderate band gaps, the GaP nanoparticulate film can also be used in the design of solar cells and the dye sensitization treatment is unnecessary.[10]

3.4. Verification of the energy gaps from the fluorescence spectrum

The room temperature fluorescence spectrum of the GaP nanoparticulate film is presented in Fig. 9,

which shows four distinct emitting bands at 2.64, 2.74, 3.00 and 3.10 eV, respectively. It is obvious that two emissions corresponding to blue light (a strong emission centred at around 2.64 eV and a weak one centred at about 2.74 eV) and two broad violet emissions centered at around 3.00 eV and 3.10 eV, respectively, can be observed in the figure.

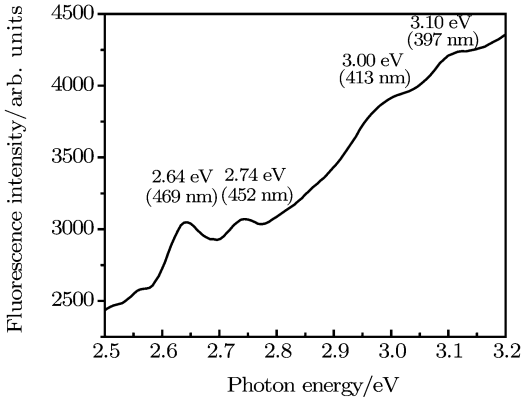


Fig. 9. Fluorescence spectrum of the GaP nanoparticulate film at room temperature.

The doublet bands at 3.00 eV and 3.10 eV, respectively, can be attributed to the direct transitions, and the doublet at 2.64 eV and 2.74 eV, respectively, can be assigned to the indirect transitions. As reported in Refs. [19] and [33], the split-off valence bands of the film are generated due to the spin–orbit-splitting of the GaP nanoparticles. The 3.00- and 3.10-eV emissions are due to the transitions from Γ_6 conduction band ($\Gamma_6^{\rm c}$) to Γ_7 valance band ($\Gamma_7^{\rm v}$) and from Γ_6 conduction band ($\Gamma_6^{\rm c}$) to Γ_8 valance band ($\Gamma_8^{\rm v}$), respectively, while the 2.64- and 2.74-eV emissions come from the transitions of $X_1^{\rm c} \rightarrow \Gamma_7^{\rm v}$ and $X_1^{\rm c} \rightarrow \Gamma_8^{\rm v}$, respectively.

The fluorescence spectrum measurement further confirms that optical energy gaps of the GaP nanoparticulate film exhibit a direct transition and an indirect transition, which is compatible with the result from the SE investigation.

4. Conclusion

The investigated GaP nanoparticulate thin films were prepared by spin-coating method on the quartz substrates. The nanoparticulate film had some voids. The film was investigated by SE and its constants n and k were obtained by fitting the ellipsometric data in the energy range of 0.75 eV–4.0 eV after the proper model was built and EMA was adopted. The value of n of the film varies a little from 1.03 to 1.23 and k of the film is of the order of 10^{-1}. According to the absorption coefficient calculated from k, the optical band gaps of the film were estimated to be around 2.43 eV as an indirect transition and about 3.07 eV as a direct transition, by using Tauc equation, which have also been verified from its fluorescence spectrum. We expect that the structure and optical absorption properties of the GaP nanoparticulate films could allow it to find some applications in solar cells in the future.

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References

[1] Zhang Q, Zhang Z and Zhou Z 2008 *Appl. Phys.* B **93** 589
[2] Liu Z G, Bai Y J, Cui D L, Hao X P, Wang L M, Wang Q L and Xu X G 2002 *J. Cryst. Growth* **242** 486
[3] Beck A L, Collins C J, Wang S, Yang B, Campbell J C, Yulius A, Chen A and Woodall J M 2002 in *Lasers and Electro-Optics Society*, 2002 LEOS 2002 *The 15th Annual Meeting of the IEEE*, Vol. **2** p. 837
[4] Brus L E 1983 *J. Chem. Phys.* **79** 5566
[5] Wang Y and Herron N 1987 *J. Phys. Chem.* **91** 257
[6] Leung K M 1986 *Phys. Rev.* A **33** 2461
[7] Chen L Y, Luo T, Huang M X, Gu Y L, Shi L and Qian Y T 2004 *Solid State Commun.* **132** 667
[8] Gao S M, Cui D L, Huang B B and Jiang M H 1998 *J. Cryst. Growth* **192** 89
[9] Zhang Q X and Zhang Z C 2008 *Appl. Phys.* A **91** 631
[10] Zhang Q X, Zhang Z C and Wang B P 2008 *J. Phys.* D: *Appl. Phys.* **41** 185403
[11] Mukherjee B and Ravishankar N 2007 *Nanotechnology* **18** 025603
[12] Kim T W, Lee D U and Yoon Y S 2000 *J. Appl. Phys.* **88** 3759
[13] Wong E M and Searson P C 1999 *Appl. Phys. Lett.* **74** 2939
[14] Gittins D I, Susha A S, Schoeler B and Caruso F 2002 *Adv. Mater.* **14** 508
[15] Sathaye S D, Patil K R, Paranjape D V and Padalkar S R 2001 *Mater. Res. Bull.* **36** 1149
[16] Lin Y Y, Mo D, Gong K C and Zhang G P 1993 *Chin. Phys.* **2** 816

[17] Zhang X J, Ma H L, Li Y X, Wang Q P, Ma J, Zong F J and Xiao H D 2006 *Chin. Phys.* **15** 2385

[18] Gao X Y, Feng H L, Ma J M and Zhang Z Y 2010 *Chin. Phys.* B **19** 090701

[19] Wang B P, Zhang Z C and Zhang N 2010 *Solid State Sciences* **12** 1188

[20] Cheyns D, Vasseur K, Rolin C, Genoe J, Poortmans J and Heremans P 2008 *Nanotechnology* **19** 424016

[21] Krebs F C, Thomann Y, Thomann R and Andreasen J W 2008 *Nanotechnology* **19** 424013

[22] Beek W J E, Wienk M M and Janssen R A J 2004 *Adv. Mater.* **16** 1009

[23] Beek W J E, Wienk M M and Janssen R A J 2005 *Adv. Funct. Mater.* **16** 1112

[24] Arango A C, Johnson L R, Bliznyuk V N, Schlesinger Z, Carter S A and Hörhold H H 2000 *Adv. Mater.* **12** 1689

[25] Huynh W U, Dittmer J J and Alivisatos A P 2002 *Science* **295** 2425

[26] Forouhi A R and Bloomer I 1986 *Phys. Rev.* B **34** 7018

[27] Kleinman D A and Spitzer W G 1960 *Phys. Rev.* **118** 110

[28] Pankove J I 1971 *Optical Processes in Semiconductors* (New Jersey: Prentice-Hall) p. 88

[29] Swanepoel R 1983 *J. Phys.* E: *Sci. Instrum.* **16** 1214

[30] Zaki M F 2008 *J. Phys.* D: *Appl. Phys.* **41** 175404

[31] Sun Z, Tay B K and Lau S P 2000 *Diam. Relat. Mater.* **9** 1979

[32] Jayasimhadri M, Cho E J, Jang K W, Lee H S and Kim S I 2008 *J. Phys.* D: *Appl. Phys.* **41** 175101

[33] Yue L Y, Zhang Z C and Chen X 2006 *Trans. Nonferrous Met. Soc. China* **16** 863