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Sub-bandgap refractive indexes and optical properties of Si-doped β-Ga_2O_3 semiconductor thin films

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Abstract: In this article, we present a theoretical study on the sub-bandgap refractive indexes and optical properties of Si-doped β-Ga_2O_3 thin films based on newly developed models. The measured sub-bandgap refractive indexes of β-Ga_2O_3 thin film are explained well with the new model, leading to the determination of an explicit analytical dispersion of refractive indexes for photon energy below an effective optical bandgap energy of 4.952 eV for the β-Ga_2O_3 thin film. Then, the oscillatory structures in long wavelength regions in experimental transmission spectra of Si-doped β-Ga_2O_3 thin films with different Si doping concentrations are quantitively interpreted utilizing the determined sub-bandgap refractive index dispersion. Meanwhile, effective optical bandgap values of Si-doped β-Ga_2O_3 thin films are further determined and are found to decrease with increasing the Si doping concentration as expectedly. In addition, the sub-bandgap absorption coefficients of Si-doped β-Ga_2O_3 thin film are calculated under the frame of the Franz–Keldysh mechanism due to the electric field effect of ionized Si impurities. The theoretical absorption coefficients agree with the available experimental data. These key parameters obtained in the present study may enrich the present understanding of the sub-bandgap refractive indexes and optical properties of impurity-doped β-Ga_2O_3 thin films.

Key words: gallium oxide; sub-bandgap refractive index; Si doping; effective optical bandgap; sub-bandgap absorption

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1. Introduction

In recent years, gallium oxide (Ga_2O_3) has been quickly emerging as a viable semiconductor with great application potential in several kinds of important functional devices, including power electronics, solar blind UV photodetectors, and ultra-sensitive sensors due to its super wide bandgap (WBG) and other outstanding properties[1]. Although different polymorphs of Ga_2O_3, such as the monoclinic (β), rhombohedral (α), defective spinel (γ), cubic (δ), or orthorhombic (ε) structures, have been reported, β-Ga_2O_3 has been the most widely studied one so far because of its good stability under the normal conditions. For bulk single crystals of β-Ga_2O_3, various methods have been developed to grow them[2]. For its form of thin films, they can be deposited with different techniques including pulsed laser deposition[3] and metal-organic chemical vapor deposition[4]. In the aspect of β-Ga_2O_3-based electronic devices, Schottky diode rectifiers with reverse breakdown voltages of over 2 kV have been successfully fabricated[5, 6]. Very recently, high-voltage vertical Ga_2O_3 power rectifier operating at high temperatures up to 600 K has been demonstrated[7]. Moreover, recessed-gate enhancement-mode β-Ga_2O_3 metal–oxide–semiconductor field-effect transistors (MOSFETs) and radio frequency operation of β-Ga_2O_3 MOSFET with record high transconductance have been reported[8–10]. As for β-Ga_2O_3 optoelectronic devices, β-Ga_2O_3 solar-blind photodetectors with high responsivity have been registered by different groups[11–16]. It is obvious that the technological development in β-Ga_2O_3 based devices is rather rapid, whereas the fundamental research is struggling to catch up. It is well known that impurity doping is a vital process in the fabrication of semiconductor devices including Ga_2O_3 devices. To further improve the performance of β-Ga_2O_3-based electronic and optoelectronic devices, a better understanding of the impurity doping effects on both electronic and optical properties of β-Ga_2O_3 thin films, especially, on the sub-bandgap refractive index dispersion, optical bandgap and absorption, is thus highly desirable. For the sub-bandgap refractive indexes of β-Ga_2O_3 thin film, their values were experimentally measured by Rebien *et al.*[17]. However, an explicit analytical dispersion relationship between refractive indexes and photon energy has not yet been established, although it is essentially important to understand the sub-bandgap optical properties of β-Ga_2O_3. In addition, there have been few studies on ionized impurities induced electric fields and their influence on the sub-bandgap electronic states and absorption coefficients of β-Ga_2O_3 thin films.

In this study, we attempt to present an investigation on the above-mentioned subjects. We first elucidate the distinct dispersion of the experimental sub-bandgap refractive indexes with a new model proposed by two (Bao and Xu) of the present authors for semiconducting and insulating WBG materials[18]. Then we quantitatively simulate the sub-bandgap variable-period oscillation patterns in the experimental optical spectra of β-Ga_2O_3 thin films with different Si doping concentrations, leading to the determination of effective

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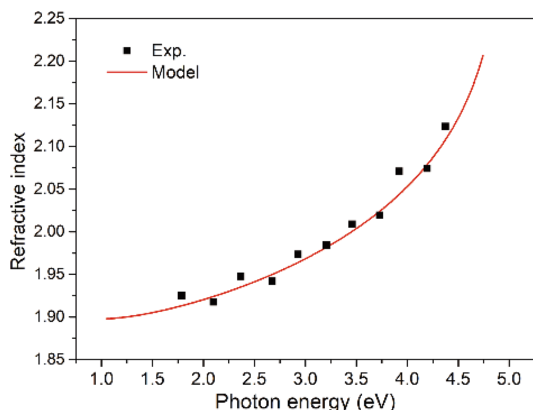

Fig. 1. (Color online) The experimental (solid squares) and calculated (solid line) refractive indexes of β-Ga_2O_3 thin film as a function of photon energy. The experimental data were from Ref. [17], while the solid line was fitted with Eq. (1).

optical bandgap values of the thin films. Finally, the sub-bandgap absorption coefficients of Si-doped β-Ga_2O_3 thin film with a given Si doping concentration are calculated under the frame of Franz–Keldysh mechanism in which the electric fields induced by ionized impurities is considered. The calculated absorption coefficients are in good agreement with the available experimental data.

2. The results and discussion

Fig. 1 shows the calculated (solid line) and the experimental (solid squares) refractive indexes of β-Ga_2O_3 thin films as a function of photon energy. The experimental data were reported by Rebien *et al.*[17] for the β-Ga_2O_3 thin films deposited onto an epitaxial GaAs buffer layer (Si doping density 1.6×10^{16} cm^{-3}) on (001)-oriented GaAs substrate wafers. X-ray diffraction revealed a nanocrystalline morphology of the thin films[17]. The theoretical line was calculated with Eq. (1). In the calculation, the parameters of E_1 = 5.098 eV, E_2 = 5.248 eV, and E_c = 4.893 eV were adopted. Here E_1 and E_2 shall be two material-dependent energy parameters, while E_c should be an effective optical bandgap of material. As shown later, E_c is dependent on doping concentration and lattice distortion degree. In addition, a background value of 1.319 was utilized for the dispersion calculation of sub-bandgap refractive index. This background refractive index may be understood as the static refractive index of material. Good agreement between experiment and model is achieved. Therefore, an explicit analytical expression is obtained as $n(E) = 1.319 + \frac{5.098-\sqrt{5.248(4.893-E)}}{E}$ for the sub-bandgap refractive indexes of β-Ga_2O_3 thin film. It is obvious that the sub-bandgap refractive index of β-Ga_2O_3 thin film exhibits a peculiar dispersion on energy. From our understanding, defects and impurities play an important role in the determination of such dispersion of refractive index in the sub-bandgap energy region. It should be noted that monoclinic phase β-Ga_2O_3 single crystal can have anisotropic refractive indexes. For instance, Bhaumik *et al.* measured temperature-dependent refractive index along crystallographic [010] and a direction perpendicular to (100)-plane (c-axis) for monoclinic phase β-Ga_2O_3 single crystal grown by the optical floating zone technique[19]. They found that the refractive index was 1.9881 and 1.9568 along [010] and the direction perpendicular to the (100)-plane, respectively, at 407 nm and 30 °C. Since photons at 407 nm have energy of 3.047 eV, the calculated refractive index was ~1.975 in Fig. 1, which is between the two anisotropic values measured by Bhaumik *et al.*[19].

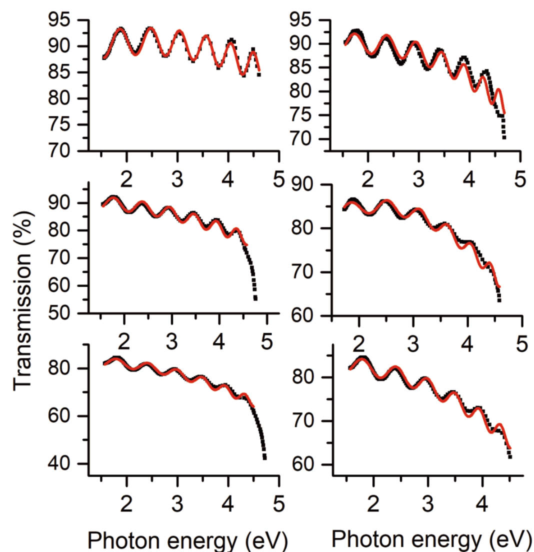

Fig. 2. (Color online) The measured transmission spectra (solid squares) and corresponding fitting curves (red solid lines) of the β-Ga_2O_3 thin films. The experimental spectra were measured by Hu *et al.*[4], while the fitting curves were obtained with Eq. (2) described in the text.

Fig. 2 shows measured sub-bandgap transmission spectra (solid squares) of the Si-doped β-Ga_2O_3 thin films grown on c-plane sapphire substrates by Hu *et al.*[4]. The flow rates of SiH_4 were 0.00, 0.04, 0.08, 0.12, 0.16, and 0.20 standard cubic centimeter per minute (sccm) for the six samples grown and measured by them. By utilizing the below dispersion relationship of refractive index in the sub-bandgap energy region proposed by Bao and Xu[18],

$$n(E) = n_0 + \frac{E_1 - \sqrt{E_2(E_c - E)}}{E}, \tag{1}$$

where n_0 is a background refractive index, i.e., static refractive index, the transmission spectrum of thin film due to the thin-film interference effect may be formulated as[18]

$$I_t = I_{t0} + I_{t1}e^{-\frac{8\pi dkE}{hc}} + 2\sqrt{I_{t0}I_{t1}}e^{-\frac{4\pi dkE}{hc}}\cos\left[\frac{4\pi d}{hc}\left(E_1 - \sqrt{E_2(E_c - E)}\right)\right], \tag{2}$$

where I_{t0} is the intensity of the primary transmitted light, I_{t1} is the intensity of the first-order transmitted light after experiencing the double-round reflections inside the thin film, d is the film thickness, k is the extinction coefficient of the thin film, E is the photon energy, h is the Planck constant, c is the light speed in vacuum, $E_{1(2)}$ is the material dependent energy parameter, and E_c is the effective optical bandgap of material. It should be noted that the whole phase variable in the cosine function of the interference term (i.e., the third term in the right-hand side of Eq. (2)) in Eq. (2) shows a particular dependence on photon energy (or wavelength), resulting in a variable-period oscillation pattern in the sub-bandgap energy (i.e., $< E_c$).

The solid lines in Fig. 2 represent the simulation curves

Table 1. Determined effective optical bandgap values vs. flow rates of SiH_4.

Sample	a	b	c	d	e	f	g
Effective bandgap (eV)	4.952	4.923	4.920	4.918	4.865	4.823	4.770
Flow rates of SiH_4 (sccm)	0.00	0.02	0.04	0.08	0.12	0.16	0.20

with Eq. (2). Good agreement between theory and experiment is achieved, which leads to the determination of several key parameters such as the film thickness and effective optical bandgap. The determined thin film thickness was ~500 nm. It is regrettable that there were no experimental thickness data of the thin films reported in Ref. [4]. The obtained effective optical bandgap values are tabulated in Table 1. The experimental flow rates of SiH_4 are listed in Table 1 too. From Table 1, the effective optical bandgap of intentionally undoped β-Ga_2O_3 thin film was 4.952 eV. Available bandgap values of β-Ga_2O_3 crystal are quite scattered, i.e., 4.7–5.04 eV, probably due to different theoretical approaches, doping concentrations, and crystal orientations[20–25]. The obtained value in the present study is well within the range of 4.7–5.04 eV. A clear tendency is the shrinking behavior of the effective optical bandgap with the flow rate of SiH_4. For instance, when the flow rate was increased from 0 to 0.20 sccm, the effective optical bandgap decreases from 4.952 to 4.770 eV. Such tendency indicates that the effective optical bandgap of Si-doped β-Ga_2O_3 thin films shrinks with increasing the Si doping concentration. From our point of view, the shrinking of the effective bandgap with the rise of doping concentration is mainly due to the penetrating of wave functions of intrinsic electronic states at band maxima into bandgap under the action of electric fields induced by ionized dopants. As the dopant density increases, the average magnitude of electric fields increases and then results in the longer (deeper) penetration length. As a result, the effective bandgap shrinks.

It is well known that ionized dopants in solid can produce electric fields around them inside solid. Such ionized-dopant-induced electric fields may result in some significant effects, such as their substantial impact on the band-edge absorption of insulating solids[26–28]. Fig. 3 presents the measured (open circles) and theoretical (thin green line: Urbach model; thick red line: electric field effect) sub-bandgap absorption coefficients of β-Ga_2O_3 with impurity density of 2.52×10^{24} m^{-3}. As the Urbach model is a widely used model in the calculation of sub-bandgap absorption spectrum, here we employed it to calculate the absorption spectrum of β-Ga_2O_3 for comparison. The experimental data were from Ref. [29]. By considering the effective optical bandgap of ~4.70 eV[30, 31], the sub-bandgap absorption coefficients of β-Ga_2O_3 were hence calculated for photon energies less than 4.7 eV. Note that the absorption coefficients were plotted in a semi-logarithmic scale in Fig. 3. For the electric field effect, the calculation formula of sub-bandgap absorption coefficient is as follows[28]

$$\alpha(\omega, F) = R(\omega)\frac{\omega_F^{3/2}}{8\pi(\omega_g-\omega)}\exp\left[-\frac{4}{3}\left(\frac{\omega_g-\omega}{\omega_F}\right)^{3/2}\right], \quad (3)$$

where $R(\omega) = \frac{2e^2M_0^2}{cn(\omega)m_0^2\hbar\omega}\left(\frac{2\mu}{\hbar}\right)^{3/2}$, e is the electron charge, M_0 comprises the matrix element having the dimensions of momentum, c is the light speed in vacuum, $n(\omega)$ is the frequency-dependent refractive index, m_0 is the mass of free electron, $\hbar \equiv h/2\pi$, $\mu = m_e^* m_h^*/(m_e^* + m_h^*)$ is the reduced mass with $m_{e(h)}^*$ as the effective mass of the electrons (holes) in the conduction (valence) band. Here ω_F is defined as[28]

$$\omega_F = \left(\frac{e^2F^2}{12\hbar\mu}\right)^{1/3}, \quad (4)$$

where F is electric field induced by ionized dopants. Calculation formulas and descriptions of its magnitude (i.e., dependence on dopant concentration) and distribution (i.e., distance dependence) within a crystal can be referred to as in Ref. [28]. $E_g = \hbar\omega_g$ is the fundamental bandgap of the crystal. Note that the units of Eqs. (3) and (4) are the S.I. units. In the calculation of sub-bandgap absorption coefficient of β-Ga_2O_3 thin film, $n = 2.14$[18], $m_e^* = 0.3m_0$[32], $m_h^* = 10m_0$, $N = 2.52 \times 10^{24}$ m^{-3}, and $E_g = 4.70$ eV[30, 31] were adopted. For the effective mass of holes, its value has not been determined so far because of rather flat valence bands and anisotropy around Γ point. Herein, we tentatively assume that it is ten times of m_0, much larger than the effective mass of electrons, i.e., as argued in Ref. [33–35]. When the impurity atoms with density of 2.52×10^{24} m^{-3} are singly charged, the resulting average electric field was 4.256×10^6 V/m. Clearly, the calculated absorption coefficients are in good agreement with the experimental data for photon energies <4.70 eV. However, a larger deviation between the theoretical Urbach line[36] and the experimental data exists. These results advocate that the electric fields induced by ionized Si impurities could be the major factor of sub-bandgap absorption in doped β-Ga_2O_3 thin films. As a final remarking note, we would like to point out that the sub-bandgap electronic states and optical properties in WBG semiconductors may be more complicated than the present understanding, for instance, the recent observation of the long persistent phosphorescence in the sub-bandgap region in ZnO under the sub-bandgap excitation[37, 38]. Further investigation about this issue needs to be done.

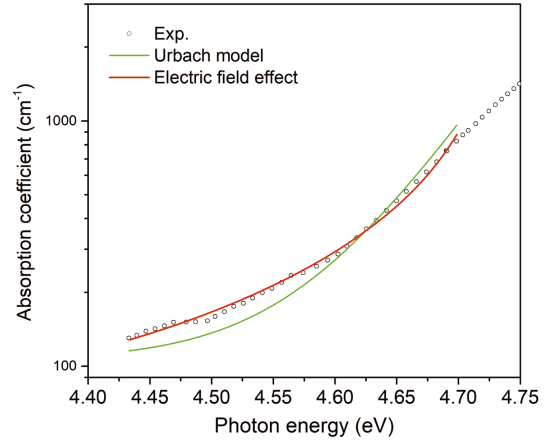

Fig. 3. (Color online) Measured (open circles) and calculated (solid lines) sub-bandgap absorption coefficients of β-Ga_2O_3 thin film with an impurity density of 2.52×10^{24} m^{-3}. Note that the plot is drawn in a semi-logarithmic scale. The original experimental data was from Ref. [29].

3. Conclusions

In conclusion, the dispersion of the refractive index of β-Ga_2O_3 thin film in the sub-bandgap energy region was elucid-

ated. Based on the peculiar dispersion of sub-bandgap refractive index, the variable-period oscillation patterns in the measured sub-bandgap transmission spectra of Si-doped β-Ga_2O_3 thin films with different doping concentrations were quantitatively interpreted. It is found that the effective optical bandgap of the films decreases with increasing the Si doping concentration. Under the frame of Franz–Keldysh mechanism due to the electric fields, the sub-bandgap absorption coefficients of β-Ga_2O_3 were calculated. It is shown that the electric fields induced by ionized Si impurities should be responsible for the sub-bandgap absorption in β-Ga_2O_3 thin films. These new findings not only deepen the existing understanding of the sub-bandgap refractive indexes and optical properties of β-Ga_2O_3, but also may promote the further device applications of this unique WBG oxide semiconductor.

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