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Theoretical and Experimental Studies of Polarized Infrared Reflectance of Bulk Wurtzite ZnO Semiconductor

(Kajian Teori dan Eksperimen bagi Spektrum Pantulan Inframerah Terkutub untuk Semikonduktor ZnO Wurtzit Pukal)

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ABSTRACT

Polarized infrared (IR) reflectance spectrum studies of bulk wurtzite ZnO are presented. The features of the polarized IR reflectance spectra and the optical characteristics of ZnO were investigated. Based on the anisotropic dielectric function model, the experimental IR reflectance spectra were numerically fitted by the theoretical IR reflectance spectra. The obtained transverse optical (TO) and longitudinal optical (LO) frequencies, i.e., $\omega_{TO\perp}(\omega_{TO||})$ and $\omega_{LO\perp}(\omega_{LO||})$ are 411 cm^{-1} (384 cm^{-1}) and 589.8 cm^{-1} (572 cm^{-1}), respectively. These results are compared with the reported values measured from the other techniques. Good agreement has been obtained.

Keywords: Dielectric function; polarized infrared reflectance; wurtzite; ZnO

ABSTRAK

Kajian spektrum pantulan inframerah (IR) terkutub untuk ZnO wurtzit pukal dibentangkan. Ciri-ciri spektrum pantulan IR terkutub dan sifat-sifat optik ZnO telah dikaji. Berdasarkan model fungsi dielektrik anisotropi, spektrum pantulan IR eksperimen telah dipadankan dengan spektrum pantulan IR teori. Frekuensi-frekuensi melintang optik (TO) dan membujur optik (LO) yang diperoleh, iaitu $\omega_{TO\perp}(\omega_{TO||})$ dan $\omega_{LO\perp}(\omega_{LO||})$ ialah 411 cm^{-1} (384 cm^{-1}) dan 589.8 cm^{-1} (572 cm^{-1}) masing-masing. Keputusan ini telah dibandingkan dengan nilai-nilai yang dilaporkan daripada teknik-teknik ukuran yang lain. Persetujuan yang baik telah diperoleh.

Kata kunci: Fungsi dielektrik; pantulan inframerah terkutub; wurtzit; ZnO

INTRODUCTION

Zinc oxide is one of the important II-VI compound semiconductors that crystallize preferentially in the wurtzite (α-) structure. The strong interest in ZnO is due to its direct wide band gap energy, i.e., ~3.4 eV and high excitonic binding energy, i.e., ~60 meV at 300 K (Klingshirn 2007). These unique properties make ZnO and ZnO related compounds promising candidates for the development of short wavelength optical devices, as well as for the optics and optoelectronics applications, such as transparent conducting electrodes for flat panel displays and solar cells (Ozgur et al. 2005). In addition, ZnO is also used for the fabrication of the piezoelectric, catalytic and sensory devices (Kim et al. 2010; Wang 2007).

Several optical techniques such as infrared (IR) spectroscopic ellipsometry, IR reflectance and Raman scattering measurements have been used to study its optical properties (Ashkenov et al. 2003). Attention in this paper is focused on the IR reflectance properties of α-ZnO. Previously, Venger et al. (1995) used the normal incidence reflectance formula to analyze the anisotropy of α-ZnO in IR reflectance spectra. However, for α-crystal, oblique incidence polarization measurements are necessary because at certain angles of incidence, extra anisotropic features in α-crystal can be significantly observed in the *p*-polarized IR reflectance spectrum (Engelbrecht & Helbig 1993). Thus, in the analysis of IR spectra for α-crystal, the effects of the angle and polarization must be taken into consideration.

Generally, the optical parameters can be determined via numerical fitting by using a suitable theoretical model. Classical dielectric function, which assumes the damping constants are identical in the transverse optical (TO) and longitudinal optical (LO) modes have been frequently used in the analysis of IR reflectance spectra. However, it was shown that the modified dielectric function (MDF) that assumes the TO and the LO damping constants are not identical is more appropriate to characterize the optical parameters because of anharmonic effect (Gervais & Piriou 1974; Kasic et al. 2000; Lockwood et al. 2005). In this work, the investigation of the optical parameters is based on the MDF by means of oblique incidence polarization measurements.

THEORY

Dielectric properties greatly depend on the crystal symmetry. For α-crystal with *c* axis along the growth direction ($c||z$) and perpendicular to the propagation

direction ($c \perp x$), the dielectric function is given by Gervais & Piriou (1974):

$$\varepsilon_j(\omega) = \varepsilon_{\infty,j}\left(\frac{\omega_{LOj}^2 - \omega^2 - i\omega\gamma_{LOj}}{\omega_{TOj}^2 - \omega^2 - i\omega\gamma_{TOj}}\right). \quad (1)$$

where ε_∞ is the high-frequency dielectric constant, ω_{LO} and ω_{TO} are respectively, the LO and TO phonon frequencies. and γ_{LO} and γ_{TO} are the LO and TO phonon damping constants, respectively. The subscript *j* stands for the parallel (∥) and the perpendicular (⊥) vibration modes with respect to the optical crystal axis *c*, respectively.

The *s*- and *p*-polarized IR reflectivity for two layers media, i.e., R_s and R_p can be evaluated, respectively, by using (Dumelow et al. 1993):

$$R_s = \left|\left(q_{z1} - q_{z2}\right)/\left(q_{z1} + q_{z2}\right)\right|^2, \quad (2)$$

$$R_p = \left|\left(\varepsilon_{\perp 2}q_{z1} - \varepsilon_{\perp 1}q_{z2}\right)/\left(\varepsilon_{\perp 2}q_{z1} + \varepsilon_{\perp 1}q_{z2}\right)\right|^2, \quad (3)$$

where q_z represents the wave propagation in a uniaxial medium. The equations of q_z for the *s*- and *p*-polarization are, respectively, given by:

s-polarized: $$q_{zi}^2 = \varepsilon_{\perp i}(\omega/c)^2 - q_z^2, \quad (4)$$

p-polarized: $$q_{zi}^2 = \varepsilon_{\perp i}(\omega/c)^2 - \left(\varepsilon_{\perp i}/\varepsilon_{\parallel i}\right)q_z^2. \quad (5)$$

ω and *c* are, respectively, the angular frequency and the velocity of light in the vacuum (3×10^8 m s^{-1}). The subscript *i* denotes the layer's media, i.e., $i = 1$ for the medium of incidence and $i = 2$ for the measured sample. q_x is the in-plane wave vector component given by:

$$q_x = \sqrt{\varepsilon_1}(\omega/c)\sin\theta, \quad (6)$$

where ε_1 is the dielectric of the medium of incidence (vacuum), taken to be isotropic, i.e., $\varepsilon_1 = \varepsilon_{\parallel 1} = \varepsilon_{\perp 1} = 1$. θ is the angle of incidence.

Materials and Methods

One side polished commercial undoped bulk ZnO wafer growth by hydrothermal method was used in this study. The size of the sample was about 1.1 × 1.1 cm^2 and the thickness was about 1 mm. Overall, the ZnO sample exhibited a predominantly clean and smooth surface morphology.

Room temperature *s*- and *p*-polarized far IR reflectance measurements have been carried out on the ZnO sample by using a Fourier transform IR spectrometer (Spectrum GX FTIR, Perkin Elmer). A wire grid polarizer was used in the polarization measurements. The angle of incident was set to 30° by using a variable angle reflectance accessory. The measurements were taken at frequencies ranging from 300 to 700 cm^{-1}. The spectra were recorded using 512 scans at a resolution of 4 cm^{-1}.

Results and Discussion

Figure 1 shows the polarized IR reflectance spectra in the range of 300-700 cm^{-1} for bulk α-ZnO. Lines for the $LO_{\parallel(\perp)}$ and $TO_{\parallel(\perp)}$ phonon frequencies of α-ZnO are also shown in Figure 1. A reflection band located between the TO and LO frequencies can be clearly observed.

Due to the reflectivity for *s*-polarization measurement is only depend on $\varepsilon_\perp$ as described from the equations mentioned above, thus one set of phonon parameters is sufficient to fit the *s*-polarized IR reflectance spectrum. However, for *p*-polarization measurement, the reflectivity depends on both $\varepsilon_\perp$ and $\varepsilon_\parallel$, thus two set of phonon parameters are required to fit the *p*-polarized IR reflectance spectrum. The phonon parameters are adjusted until the

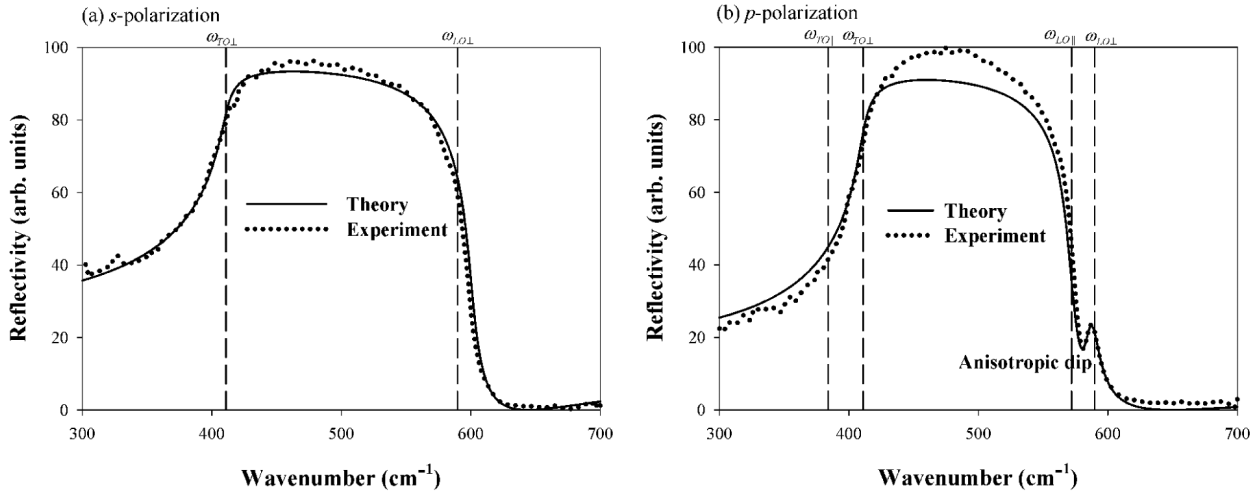

FIGURE 1. Room temperature (a) *s*- and (b) *p*-polarized IR reflectance spectra of bulk α-ZnO measured at an incident angle of 30°. The solid and dotted lines indicate the theoretical and experimental IR reflectance spectra, respectively

theoretical spectra give the best fit to the experimental spectra for both the *s*- and *p*-polarization measurements. From Figure 1, it can be seen that the theoretical spectra are in good agreement with the experimental spectra. The best-fit parameters are listed in Table 1. The obtained parameters are reasonable compared with the reported values measured from the other techniques such as Raman scattering and IR spectroscopic ellipsometry (Ashkenov et al. 2003). The average discrepancy is less than 1%.

TABLE 1. Optical parameters for polarized IR reflectance spectra of bulk α-ZnO

	ε_∞	ω_{TO}(cm^{-1})	ω_{LO}(cm^{-1})	γ_{TO}(cm^{-1})	γ_{LO}(cm^{-1})
⊥	3.70*	411	589.8	10.5	11.0
∥	3.78*	384	572.0	10.0	12.2

*Ashkenov et al. (2003)

From the *p*-polarized IR reflectance spectrum, a significant dip can be observed at 580.5 cm^{-1}, this resonance like feature is related to the phonon anisotropy in the α-ZnO. In general, for air/semi-infinite crystal system and in the absence of phonon damping, this dip occurs when $R_p = 0$. Consequently, (3) can be written as:

$$q_{z2} = \varepsilon_{\perp 2} q_{z1}. \quad (7)$$

Equation (7) contains multiple solutions. However, only one of the solutions precisely describes the frequency position of the anisotropic dip ω_d, i.e., occurs under the condition $\omega_{LO\parallel} < \omega_d < \omega_{LO\perp}$. However, this dip will be slightly changed in its position and this resonance feature will be gradually broadening when damping is present.

CONCLUSION

In conclusion, experimental and theoretical polarized IR reflectance studies on bulk α-ZnO have been reported. Through this study, a complete set of the lattice vibrational parameters for bulk α-ZnO has been obtained. The obtained optical phonon modes are in good agreement with the reported values. In the near future, these results will be used as the basis for the attenuated total reflection studies on the surface phonon polaritons characteristics of α-ZnO.

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