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RESEARCH ARTICLE

Optical properties of InN films grown by MOCVD

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Abstract By means of optical absorption, photoluminescence (PL), Raman scattering and ellipsometry, optical properties of indium nitride (InN) films grown by metal organic chemical vapor deposition (MOCVD) are investigated. Through absorption and PL measurements, it is proven that the band gap of high quality InN is 0.68 eV, which agrees with the recently reported value, 0.7 eV. By analysis of the Raman scattering spectrum, the comparatively low background concentration of electron results in a smaller band gap value. The transition energy of wurtzite InN at critical point is determined by ellipsometric spectra. In addition, the complex refractive index of InN at energy ranging from 0.65 to 4.0 eV is obtained for the first time.

Keywords indium nitride (InN), optical absorption, photoluminescence (PL), ellipsometry, metal organic chemical vapor deposition (MOCVD)

1 Introduction

Among III-nitride semiconductors, indium nitride (InN) has attracted much attention recently due to its novel material properties and potential applications [1,2]. Compared to GaN and AlN, InN has the smallest effective electron mass, highest mobility and peak draft velocity. It is suggested that there may be distinct advantages offered by InN in high frequency electron devices. With the development of growth technology, high quality InN thin films have been prepared by molecular beam epitaxy (MBE) or metal organic chemical vapor deposition (MOCVD). Particularly, it is discovered that the band gap of InN is 0.7 eV, which is much narrower than previous reports of 1.9 eV [3], which makes luminescence wavelength of III-nitride semiconductors covering range from ultraviolet (AlN, 6.2 eV) to infrared (InN, 0.7 eV). Owing to the narrow band gap of InN, InGaN is also considered as a potential alloy system for solar cells with high efficiency [4]. In addition, InN can be used as a terahertz emission material and good plasma filter material in thermophotovoltaic systems [5]. However, due to lack of lattice matched substrate, low InN dissociation temperature and high equilibrium N_2 vapor pressure over the film, it is difficult to grow high quality InN films. As a result, InN has been the least studied of the group of III-nitride semiconductors. Nowadays, InN thin films are usually prepared on Al_2O_3 or Si substrates through MOCVD or MBE [6–8]. The research of optical properties is significant for developing InN-based optoelectronic devices. In this paper, the optical properties of InN films grown by MOCVD are investigated by means of optical absorption, photoluminescence (PL), Raman scattering and ellipsometry.

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2 Experiments

The InN thin films for optical measurements were grown on (0001)-orientation Al_2O_3 substrates by MOCVD with a vertical reactor. Before the deposition, the substrates were nitrided at 1150°C for 3 minutes with NH_3. Then the reactor temperature was reduced down to 570°C to grow the low temperature GaN buffer. The buffer was annealed at 1100°C successively to improve the crystalline and surface morphology. Lastly, the reactor temperature was kept at 600°C to deposit InN for 4 hours. Trimethylindium (TMIn) and NH_3 were applied as In and N precursors while N_2 was used as the carrier gas. The thickness of the InN film is about 600 nm. Through Hall effect measurement, the mobility of the InN is determined to be 938 $cm^2/(V\cdot s)$ with an n type concentration of 3.8×10^{18} cm^{-3}.

All optical measurements including absorption, PL, Raman scattering and ellipsometry were implemented at room temperature (RT). The excitation source for absorp-

tion experiment is Xe lamp, and the detector is PbS. For PL measurement, a 514.5 nm Ar^+ laser is used as excitation, and an InSb detector worked at 80 K mounted on an infrared Fourier analysis system is used to detect the luminescence signal from the InN film. The Raman scattering of the InN film adopts back scattering configuration using an APEX spectrometer with a resolution of 0.5 cm^{-1}. For ellipsometry, a GES-5 ellipsometry from Sopra Company is utilized. The incidence light uses Xe lamp spectrum with an incidence angle of 75°, and the detection spectrum ranging from 0.5 to 4.0 eV.

3 Results and discussion

Figure 1 shows PL and absorption spectra of the InN film measured at RT. It can be observed that a PL peak is located around 0.69 eV. To fit the experimental data, a relation between the squared absorption coefficient and photon energy is expressed by

$$\alpha^2(h\upsilon) = A\left(h\upsilon - E_g\right),$$

where α is the absorption coefficient, h is the Planck constant, υ is the frequency of incident light, A is the fitting coefficient and E_g is the optical band gap. The optical band gap of InN is obtained as 0.68 eV from fit results as shown by the dashed line. In recent literature, the optical band gap values are reported from 0.65 to 0.8 eV by different research groups [8]. Our result agrees with the conclusion given by Cornell University, US [9,10]. The prepared un-intentional doped InN films usually are n type conduction with a background electron concentration higher than 10^{19} cm^{-3}. It is found that blueshift of absorption edge and PL peak can be induced by high background electron concentration, and the higher electron concentration brings the larger blueshift, which is called as Burstein-Moss effect. The band gap of our InN film has a small value. It is due to low electron concentration, which is proven by Raman scattering.

Figure 2 shows the Raman spectrum of InN film measured at RT. According to selection rules, under $z(x,-)\bar{z}$ back scattering configuration, where $z(\ldots)\bar{z}$ means the incident and scattering light is along z-direction and x means the polarization of the light is along x-direction, the experimentally observable modes are E_2(high) and A_1(LO), which are located at 490 and 592 cm^{-1}, respectively. The peak located at 475 cm^{-1} is assigned as E_1(TO), which can only be observed on condition that the symmetry of the InN cell breaks. In addition, a slight peak located around 415 cm^{-1} may relate to the feature of the coupled plasmon-LO-phonon (PLP) mode [11,12]. The coupled PLP mode divides into up and low branches (PLP^+ and PLP^-). The observed peak of 415 cm^{-1} is assigned as PLP^- mode. The experiments done by Davydov et al. [12] showed that PLP^- mode could move to high frequency with increasing electron concentration, and approach the frequency of A_1(TO) (around 450 cm^{-1}). In Fig. 2, the PLP^- mode located at 415 cm^{-1}, compared with their results, is comparatively low in frequency. It means the measured InN film has low electron concentration, which is in agreement with result from Hall effect measurement. It is given that

$$\omega_\pm^2 = \frac{1}{2}\left(\omega_p^2 + \omega_{LO}^2\right) \pm \frac{1}{2}\left[\left(\omega_p^2 + \omega_{LO}^2\right)^2 - 4\omega_p^2\omega_{TO}^2\right]^{1/2},$$

where $\omega_\pm$, ω_{LO} and ω_{TO} are the frequencies of the coupled PLP^+ and PLP^- mode, LO mode and TO mode phonon. The values of them are 415, 592 and 445 cm^{-1}, respectively. The calculated plasmon frequency ω_p is 1100 cm^{-1}. The relation between ω_p and electron concentration n is as

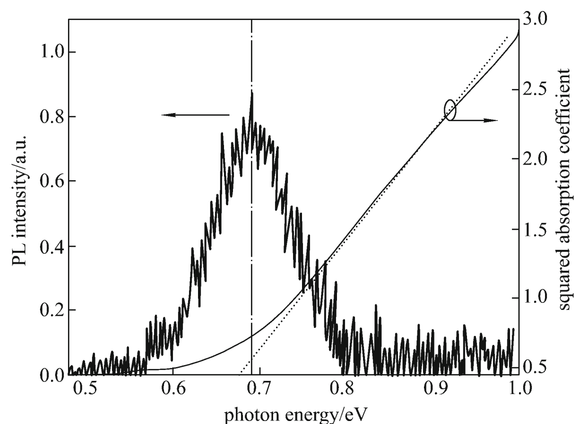


Fig. 1 Absorption and PL spectra of InN film measured at RT (the experiment data are plotted with solid line, the fitting result is plotted with dashed line)

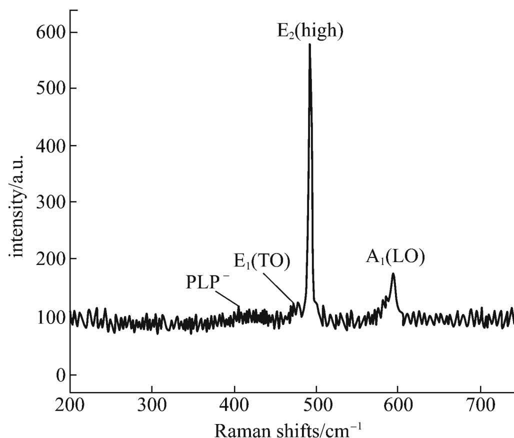


Fig. 2 Raman scattering spectrum of InN film measured at RT

follows:

$$\omega_p^2 = n_e e^2 / (\varepsilon_\infty m^*),$$

where ε_∞ is the dielectric constant of vacuum and the value is 6.7, m^* is the effective electron mass of InN, which is $0.05m_0$, the electron mass of vacuum. The electron concentration n_e of the InN film is calculated to be 4×10^{18} cm^{-3}, which is close to the Hall effect measurement result.

Figure 3(a) shows the measured and fitted ellipsometric spectra from 300 to 1900 nm. As the wavelength range covers the band edge emission wavelength of InN film, some critical parameters can be obtained from these spectra, for example E_0. The relation between standard ellipsometric parameters ψ, Δ and complex refractive index ratio ρ is given by

$$\rho = r_p / r_s = \tan\psi \exp(i\Delta),$$

where r_p and r_s are the reflectances of light parallel to the incident plane (p) and perpendicularity to the incident plane (s), respectively. The fitting process adopts Adachi model [13] with an air/InN/GaN buffer/Al_2O_3 multilayer. For direct band gap III-V semiconductors, the shape of the conduction band bottom is parabolic. Considering the transitions to deep energy levels, the dielectric constant is approximately given by

$$\varepsilon(E) = \frac{A_0}{E_0^{1.5}} f(\chi_0) + \sum_{r=1}^{\infty} \frac{A_{0x}}{r^3} \frac{1}{E_0 - (G_0/r^2) - E - i\Gamma_0} + \frac{-B_1}{\chi_1^2} \ln(1 - \chi_1^2) + \sum_{r=1}^{\infty} \frac{B_{1x}}{(2r-1)^3} \frac{1}{E_1 - [G_1/(2r-1)^2] - E - i\Gamma_1},$$

where

$$f(\chi_0) = \frac{2 - \sqrt{1+\chi_0} + \sqrt{1-\chi_0}}{\chi_0^2},$$

$$\chi_0 = \frac{E + i\Gamma_0}{E_0},$$

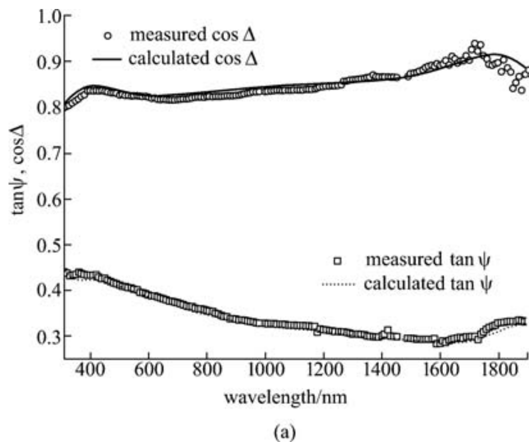
$$\chi_1 = \frac{E + i\Gamma_1}{E_1},$$

and A_0, E_0, A_{0x}, G_0, Γ_0, B_1, E_1, B_{1x}, G_1, Γ_1 are the fitting parameters.

The complex dielectric constants of Al_2O_3 substrate and GaN are used from Refs. [14,15]. In Fig. 3(a), the dashed/solid line and square/circle dots are the simulated and experimental data of $\tan\psi$ and $\cos\Delta$. In Fig. 3(b), the calculated complex refractive index of InN dependence on photon energy is shown, where the real part of complex refractive index is n and the imaginary part is k. The fitted parameters are $A_0 = 2.3338$, $E_0 = 0.6605$, $A_{0x} = 0.2336$, $G_0 = 0.2050$, $\Gamma_0 = 0.0255$, $B_1 = 2.5441$, $E_1 = 3.7670$, $B_{1x} = 2.3851$, $G_1 = 1.9377$, $\Gamma_1 = 1.3254$. According to these parameters, E_0 and E_1 are obtained. It is shown that E_0 is consistent with the results measured by optical absorption and PL. In addition, a mutation of n and k is observed around 0.7 eV, which is the band edge energy of InN. As the k is in proportion to the absorption coefficient α, the dispersion curve of k is directly related to the optical properties of InN. Thus, the drastic increase of k near 0.7 eV originates from band edge absorption and slight increase near 3.7 eV is related to the transitions between deep energy levels in conduction band and valence band.

4 Conclusion

The optical properties of InN film grown by MOCVD are investigated. The band gap of InN is determined to be



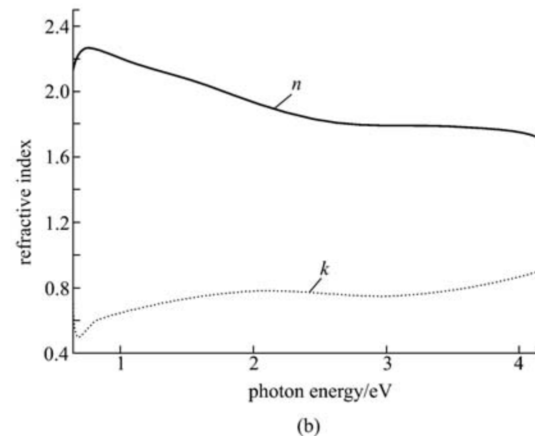


Fig. 3 Measurement results of InN. (a) Measured and fitted ellipsometric spectra; (b) obtained complex refractive index of InN

0.68 eV by means of optical absorption, PL, Raman scattering and ellipsometry, which agrees well with recent research. From the relation between the frequency of PLP^- mode and electron concentration, electron concentration of the measured InN film is calculated as 4×10^{18} cm^{-3}, which is close to Hall effect measurement result. Furthermore, the critical point $E_0 = 0.66$ eV at Brillouin zone and the dispersion curve of n and k of InN are obtained by ellipsometric spectra.

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