

# Oblique-Incidence Infrared Reflection in Thin ZnO Films Deposited on Sapphire by Gas-Source MBE

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**Abstract.** Properties of polar optical phonons in *n*-ZnO thin films are investigated by infrared reflection spectroscopy. Although there exist degenerate electrons in the concentration of  $5 \times 10^{18} \text{ cm}^{-3}$  in the buffer layer, observation of the  $A_1(\text{LO})$  phonon-plasmon coupled mode permits us to evaluate the electron concentration in the films grown on the buffer layer. The electron concentration is found to attain to  $7 \times 10^{16} \text{ cm}^{-3}$  in undoped, 500-nm-thick films, while the damping energy of the  $E_1(\text{LO})$  mode remains to be as large as  $45 \text{ cm}^{-1}$  in those thin films.

**Keywords:** ZnO/sapphire, infrared reflection, LO phonons, plasmon

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## INTRODUCTION

High quality thin films of ZnO, adaptable for blue and ultraviolet devices, have been reported to be grown by molecular beam epitaxy (MBE).<sup>1,2</sup> It has emerged recently from a transport measurement that, if sapphire is employed for the substrate of MBE, degenerate electrons are induced in the buffer layer;<sup>3,4</sup> the concentration ranges from  $4 \times 10^{18}$  to  $1.5 \times 10^{19} \text{ cm}^{-3}$ , depending on the conditions of gas-flow and thermal treatment. These degenerate electrons affect the sheet electric conductivity and the Hall coefficient of the ZnO film/buffer system significantly.

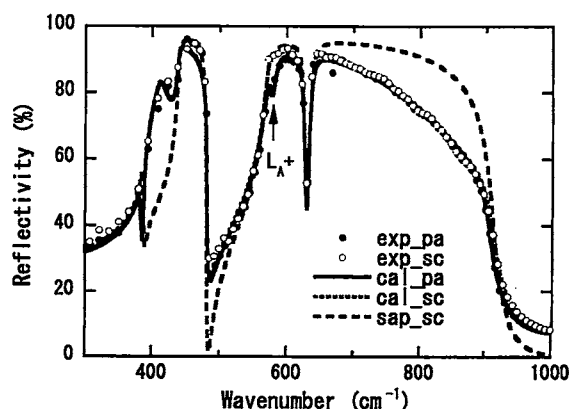
In this work we study the properties of polar optical phonons in thin MBE-grown films of *n*-ZnO by infrared spectroscopy. The result shows that, despite the existence of degenerate electrons in the buffer layer, observation of the  $A_1(\text{LO})$  phonon-plasmon coupling by the linearly-polarized oblique-incidence reflection enables us to evaluate the electron concentration in the films grown on the buffer layer.

## RESULTS AND DISCUSSION

ZnO is grown on the *a*-surface of sapphire by radical-source MBE. The buffer layer is grown to a thickness of 20 nm and then annealed for 20 min at 600 °C. *n*-ZnO films are grown with the *c*-surface of the wurtzite structure on this buffer layer. The thickness of the films and the nominal Hall

concentration of electrons in the samples examined are listed in Table 1.

Reflection spectrum is measured with an FT/IR spectrometer at an angle of incidence of  $10^\circ$  with *s*- and *p*-polarized infrared beams. All the measurements are performed at room temperature.



**FIGURE 1.** Reflection spectra of sample “3469”. Solid and open circles are the experimental data, and solid and dotted lines are calculated spectra. The broken curve is the spectrum of sapphire. Notations p and s show polarization of incident light and a and c signify the orientation of the plane of incidence seen by crystal axes of sapphire.

Figure 1 shows the spectra taken for the sample “3469” with the plane of incidence parallel to the *c*-

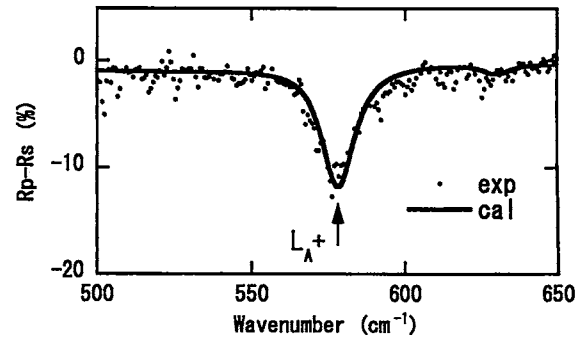
and  $a$ -axes of sapphire for  $s$ - and  $p$ -polarizations, respectively. Although the ZnO film is very thin, its contribution to the spectrum of Fig. 1 is clearly identified by the deviation from the spectrum of sapphire. With the effect of free carriers incorporated into the dielectric function in terms of the Drude model, the overall experimental data can be reproduced by the theoretical calculation based on the four-parameter semi-quantum oscillator model.<sup>5,6</sup>

Note that the  $A_1(\text{LO})$ -plasmon coupled mode,  $L_{A^+}$ , appears around  $578\text{ cm}^{-1}$  only in the  $p$ -polarization. The difference,  $R_p - R_s$ , in the reflectivity between  $p$ - and  $s$ -polarizations agrees with the theoretical curve very well, as shown in Fig. 2.

Values of several important quantities obtained from the present study are listed in Table 1.

We have  $575.5\text{ cm}^{-1}$  for the  $A_1(\text{LO})$  mode in insulating films. In addition, referring to the literature we have  $0.29m_0$  for the effective mass of a conduction electron and the infrared dielectric constant,  $\epsilon_\infty = 3.76$ , for  $E//c$ . With the aid of these quantities the observed energy of  $L_{A^+}$  gives the electron concentration to be  $7.4 \times 10^{16}\text{ cm}^{-3}$  for the undoped sample "3469" and  $\sim 5 \times 10^{15}\text{ cm}^{-3}$  for the nitrogen-doped sample "2782". It

is likely that nitrogen doping produces acceptors to almost compensate donors. It also follows from the present results that the 20-nm-thick buffer layer of our samples contains degenerate electrons in the concentration of the order of  $5 \times 10^{18}\text{ cm}^{-3}$ .



**FIGURE 2.** Experimental (•) and calculated (—) spectrum of  $R_p - R_s$  of sample "3469" in the region of the upper branch  $L_{A^+}$  of the  $A_1(\text{LO})$ -plasmon coupled mode. The data of  $p_a$  and  $s_c$  shown in Fig. 1 are used for  $R_p$  and  $R_s$ , respectively, to obtain the spectra.

**TABLE 1.** Thickness  $d$  of ZnO film, dopant, nominal Hall concentration  $n_H$ , optically determined electron concentration  $n$ , energy of  $A_1(\text{LO})$ -plasmon coupled mode  $L_{A^+}$ , and damping energies  $\gamma_A$  and  $\gamma_E$  of  $A_1(\text{LO})$  and  $E_1(\text{LO})$  modes, respectively.

Sample	$d$ (nm)	dopant	$n_H$ ( $\text{cm}^{-3}$ )	$n$ ( $\text{cm}^{-3}$ )	$L_{A^+}$ ( $\text{cm}^{-1}$ )	$\gamma_A$ ( $\text{cm}^{-1}$ )	$\gamma_E$ ( $\text{cm}^{-1}$ )
2782	490	nitrogen	$1.8 \times 10^{17}$	$5 \times 10^{15}$	575.7	10	26
3469	500	none	$2.6 \times 10^{17}$	$7.4 \times 10^{16}$	578.6	13	45

Another point to be observed is a prominent reduction of the reflectivity in the region from 650 to  $900\text{ cm}^{-1}$  in comparison with the reststrahlen band of sapphire. This is caused by the extinction of the infrared light due to a strong damping of the  $E_1(\text{LO})$  mode, being located around  $591\text{ cm}^{-1}$ , of the ZnO film. This property is common to the films thinner than  $1\text{ }\mu\text{m}$ . Correspondingly, the full width at half maximum

(FWHM) of the X-ray rocking curve is  $600\text{--}650$  arcsec for the (0002) reflection and  $1100\text{--}1200$  arcsec for the (10-11) reflection in  $\sim 500\text{-nm}$ -thick films, which are about twice as large as the values of FWHM in  $\sim 1\text{-}\mu\text{m}$ -thick films. The damping energy of the  $E_1(\text{TO})$  mode, on the other hand, is  $10$  to  $12\text{ cm}^{-1}$  regardless of the thickness of the films.

## ACKNOWLEDGMENTS

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## REFERENCES

1. A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma and M. Kawasaki, *Nature Mater.* **4**, 42-46 (2004).
2. A. Tsukazaki, M. Kubota, A. Ohtomo, T. Onuma, K. Ohtani, H. Ohno, S. F. Chichibu and M. Kawasaki, *Jpn. J. Appl. Phys.* **44**, L643-L645 (2005).
3. H. Tampo, A. Yamada, P. Fons, H. Shibata, K. Matsubara, K. Iwasa, S. Niki, K. Nakahara and H. Takasu, *Appl. Phys. Lett.* **84**, 4412-4414 (2004).
4. K. Koike, K. Hama, I. Nakashima, G. Takada, M. Ozaki, K. Ogata, S. Sasa, M. Inoue and M. Yano, *Jap. J. Appl. Phys.* **43**, L1372-L1375 (2004).
5. F. Gervais and B. Piriou, *J. Phys. C: Solid State Phys.* **7**, 2374-2386 (1974).
6. N. Kuroda, T. Kitayama, Y. Nishi, K. Saiki, H. Yokoi, J. Watanabe, M. W. Cho, T. Egawa and H. Ishikawa, *Jap. J. Appl. Phys.* **45**, 646-650 (2006).