Semiconductor electrical properties from the frequency dependence of the dielectric constant: application to n-type ZnSe heteroepitaxial thin films

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We discuss the derivation of the carrier concentration n and mobility of thin films from transmission and reflection in the far-infrared, through the expression of the dielectric constant when plasmon-phonon coupling is incorporated. We measure transmission of n-type-doped ZnSe on undoped ZnSe on GaAs, and derive approximate values of the absorption coefficient  $\alpha$ . We find  $\alpha \propto n^{1/2}$  at  $100 \text{ cm}^{-1}$  and constant versus wavenumber W at low W and high n. These variation laws are also found from approximate expressions of  $\alpha$  in the same conditions.

#### 1. Introduction

As the band gaps of semiconductors increase, the achievement of good ohmic contacts needed to derive the carrier concentration and mobility from the Hall effect becomes more and more difficult. For instance, in the case of ZnSe, In is widely used (without understanding the origin of he ohmicity) on n-type material [1], while Au is reported to be ohmic [2a] or not [2b] according to the authors. Both carrier concentration and mobility have been deduced from fits of the reflectivity versus wavelength measurements on bulk monocrystalline GaAs [3]. The reflectivity was computed from the real (n) and imaginary (k) parts of the refractive index, which were calculated from an expression of the dielectric constant including the phonon-plasmon coupling [4].

The situation for thin films is quite different. From their thickness, measurement can be done in transmission or in reflection, but the presence of an absorbing substrate under the film, and sometimes, as here, that of an additional absorbing buffer layer to increase the crystallinity of the doped film, requires unknown expressions for the transmission and the reflection of such systems. We derive absorption coefficients from an approximate expression of the transmission. Then we show that its variation versus doping level and wave number agrees with that derived from simple approximations of their calculation from the dielectric constant.

#### 2. Experimental techniques

The ZnSe films were grown by molecular beam epitaxy (MBE) on undoped, semi-insulating ( $\rho > 10^7~\Omega$  cm) (100) GaAs substrates under a fixed set of growth conditions, namely a substrate temperature of 275 °C and a Zn-to-Se beam equivalent pressure ratio of 1:2. The ZnSe layers were doped n-type by substitutional incorporation of Cl atoms during the MBE growth process using a ZnCl<sub>2</sub> effusion source. 1.04 to 1.52  $\mu$ m thick doped layers were grown on a ~ 0.5 to 0.76  $\mu$ m thick undoped

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ZnSe buffer layer to avoid doping interaction with the semi-insulating GaAs substrate. Undoped ZnSe 1  $\mu$ m thick was deposited on the identical substrate (reference samples). Room-temperature carrier concentrations (n) and electron mobilities ( $\mu$ ) in the ZnSe films were determined by Hall-effect measurements. They indicate carrier concentration  $n = 9.4 \times 10^{16}$ ,  $9.3 \times 10^{17}$ ,  $8 \times 10^{18}$  cm<sup>-2</sup> and mobility  $\mu = 302$ , 250 and 207 cm<sup>2</sup> V<sup>-1</sup>. s<sup>-1</sup> for samples 56, 57 and 58, respectively.

Transmission and reflection measurements were taken at room temperature using a Fourier transform infrared spectrometer (Brucker IFS 113v) with four overlapping ranges, 35–100 cm<sup>-1</sup>, 80–300 cm<sup>-1</sup>, 200–600 cm<sup>-1</sup>, and 450–5000 cm<sup>-1</sup>. The resolution was 1 or 2 cm<sup>-1</sup> in the *W* ranges 35–600 cm<sup>-1</sup> and 450–5000 cm<sup>-1</sup>, respectively. The detector was a liquid-helium cooled bolometer or a DTGS between 35 and 600 cm<sup>-1</sup> and 450–5000 cm<sup>-1</sup>, respectively. The substrate and film thicknesses were determined from their interference fringes in the far- and mid-infrared, respectively.

# 3. Results and interpretation

The transmission of the three samples is given in fig. 1. As the doping increases, the transmission of the samples decreases very rapidly. The structures are related to phonon absorption in GaAs and ZnSe. There is a dead range between 150 and  $300~{\rm cm}^{-1}$  corresponding to the important one-phonon absorption by the substrate and the ZnSe film. Analytical expressions for the transmission of stacked absorbing films on absorbing substrate are unknown until now. From approximate expressions of the transmission, and the normalization of the sample transmission T by that  $T_r$  of a substrate covered with an undoped ZnSe film, approximate values of the absorption coefficient  $\alpha$  can be deduced from the expression [5]

$$T/T_{r} \simeq \exp(-\alpha d), \tag{1}$$

where d is the thickness of the doped film.

The absorption coefficients of the doped ZnSe films versus the wavenumber, W, are shown in fig. 2 on a log-log plot. For low wavenumber, the  $\alpha$ 

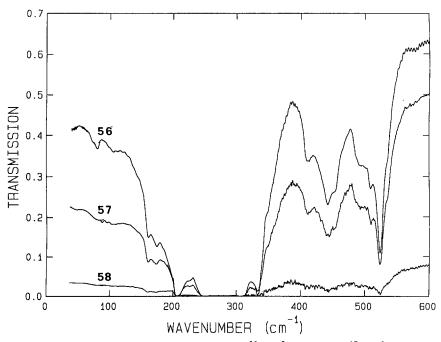


Fig. 1. Transmission versus wavenumber of the samples 56 ( $9.4 \times 10^{16} \text{ cm}^{-3}$ ), 57 ( $9.3 \times 10^{17} \text{ cm}^{-3}$ ), and 58 ( $8 \times 10^{18} \text{ cm}^{-3}$ ).

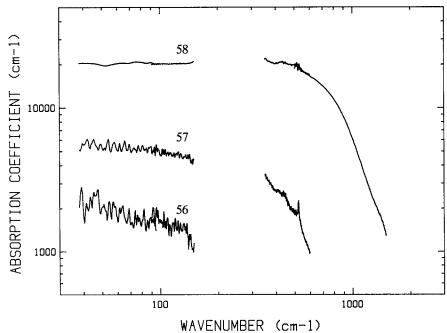


Fig. 2. Approximate absorption coefficient versus wavenumber of the samples 56 ( $9.4 \times 10^{16}$  cm<sup>-3</sup>), 57 ( $9.3 \times 10^{17}$  cm<sup>-3</sup>), and 58 ( $8 \times 10^{18}$  cm<sup>-3</sup>).

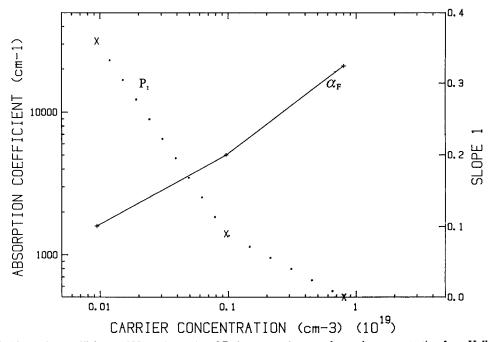


Fig. 3. Absorption coefficient at  $100 \, \mu \text{m} \, (\alpha_F, +)$  and  $P_1$  (see text,  $\times$ ) versus the carrier concentration from Hall effect.

value is constant below about 700 cm<sup>-1</sup> at the higher doping level, while at lower doping level, it increases more and more rapidly with W. The  $\alpha$  values at 100 cm<sup>-1</sup> (100  $\mu$ m) versus the doping level n in an ln-ln scale are shown in fig. 3.  $\alpha$  varies approximately as  $n^{1/2}$ .

The carrier concentration n and the mobility  $\mu$  can be extracted from the plasmon frequency  $W_p$  and its damping constant  $\gamma_e$ , through

$$W_{\rm p}^2 = nq^2/4\pi c^2 K_{\infty} m^*,$$
 
$$\gamma_{\rm e} = \frac{q}{2\pi c m^* \mu},$$

where q, c and  $m^*$  are the electron charge, the light velocity and the carrier effective mass, respectively.

The optical constants  $n_{\text{opt}}$  and k, or

$$\alpha = 4\pi k W, \tag{2}$$

of doped films can be calculated from  $W_p$  and  $\gamma_e$ , from the variation of the complex dielectric K constant with frequency. Taking into account the plasmon-phonon coupling, the expressions of the dielectric constant K and of its real  $K_1$  and imaginary part  $K_2$  can be written

$$K = K_{\infty} + \frac{W_{\text{TO}}^{2}(K_{0} - K_{\infty})}{W_{\text{TO}}^{2} - W^{2} - i\gamma_{p}W} - \frac{K_{\infty}W_{p}^{2}}{W(W + i\gamma_{e})},$$
(3)

$$K_{1} = K_{\infty} + \frac{W_{\text{TO}}^{2} (K_{0} - K_{\infty}) (W_{\text{TO}}^{2} - W^{2})}{(W_{\text{TO}}^{2} - W^{2})^{2} + \gamma_{p}^{2} W^{2}} - \frac{K_{\infty} W_{p}^{2}}{W^{2} + \gamma_{p}^{2}}, \tag{4}$$

$$K_{2} = \frac{W_{\text{TO}}^{2} (K_{0} - K_{\infty}) \gamma_{p} W}{(W_{\text{TO}}^{2} - W^{2})^{2} + \gamma_{p}^{2} W^{2}} + \frac{K_{\infty} W_{p}^{2} \gamma_{e}}{(W^{2} + \gamma_{e}^{2}) W},$$
(5)

with

$$K_1 = n_{\text{opt}}^2 - k^2, \quad K_2 = 2n_{\text{opt}}k,$$
 (6)

where  $W_{\text{TO}}$  is the wavenumber of the TO mode at the center ( $\Gamma$ ) of the Brillouin zone along with its damping constant  $\gamma_{\text{p}}$ , and  $K_0$  and  $K_{\infty}$  are the DC and optical constants of the semiconductor.

Therefore, n and  $\mu$  can be extracted for doped semiconductors from the determination of their plasmon frequency  $W_p$  along with its damping constant  $\gamma_e$ , as soon as the effective mass of the carrier is known ( $m^* = 0.17$  [6] in ZnSe). However, only numerical values of  $W_p$  and  $\gamma_e$  can be extracted from fits of the optical constants  $n_{\text{opt}}$  or  $\alpha$  through expression (3) to (6), and we have also shown previously that only approximate values of  $\alpha$  can be extracted at that time from optical measurements on thin films. So, we look for approximate analytical expressions of  $\alpha$  to determine its variation law with the doping level and the wavenumber.

From the carrier concentration and mobility values determined from the Hall effect, 92.7  $< W_p$   $< 830 \text{ cm}^{-1}$ , and  $182 < \gamma_e < 265 \text{ cm}^{-1}$ , so at low wavenumber  $W \le 100 \text{ cm}^{-1}$ , the approximations

$$K_1 \simeq -K_{\infty} W_{\rm p}^2 / \left( W^2 + \gamma_{\rm e}^2 \right), \tag{7a}$$

$$K_2 \simeq K_\infty W_p^2 \gamma_e / (W^2 + \gamma_e^2) W \tag{7b}$$

can be done, with  $nk \approx k^2 - n^2$ , which gives on all the doping range  $k \approx 1.6n$ . From the expression of  $K_1$ ,  $K_1 \approx 1.56k^2$ , so from eq. (7a),  $k \propto W_p$  and  $\alpha \propto n^{1/2}$  as found experimentally. For the higher doping level, approximation (7a) still almost holds up to around  $700 \text{ cm}^{-1}$ , and from (2) and (7a)  $\alpha$  is independent of W around  $700 \text{ cm}^{-1}$ . Our experimental  $\alpha$  values for the higher doping level are independent of W in a much larger range ( $W < 700 \text{ cm}^{-1}$ ). This might occur from a larger range than expected for the validity of the previous approximation, or because errors have been introduced from our approximate way to derive the experimental  $\alpha$  values at low wavenumber.

## 4. Conclusion

The carrier concentration and mobility can only be derived from a numerical fit of the refractive index n or of the absorption coefficient  $\alpha$  of doped semiconductors through the addition of a term taking into account the plasmon-phonon coupling in the dielectric constant of the material. However, in the case of thin films, additional problems occur from the unknown analytical ex-

pressions of their transmission or reflection on an absorbing substrate and eventually an additional absorbing buffer sublayer as in our case.

We have derived approximate values for the absorption coefficient  $\alpha$  of n-type-doped ZnSe thin film. It was found to be proportional to  $n^{1/2}$  around 100 cm<sup>-1</sup>, and for our higher doping level to be approximately constant below 1000 cm<sup>-1</sup>. In certain ranges, approximate analytical expressions of  $\alpha$  versus the doping level and the wavenumber can be derived, which agree with the variations found experimentally.

A first step has been done here in the determination of the carrier concentration and mobility in thin doped film from optical measurement through the determination of approximate values of the absorption coefficient, the derivation of approximate analytical functions of  $\alpha$ , and the verification that they give the right law of  $\alpha$  variation with doping and wavenumber in some par-

ticular case. The general derivation of n and  $\mu$  requires the determination of the general expressions for the transmission and the reflection of stacked thin absorbing films on thick absorbing substrate. Work along these lines is in progress.

### References

- For example, R.G. Kaufman and P. Dowbor, J. Appl. Phys. 45 (1974) 4487.
- [2] (a) For example, M. Taike, M. Migita and H. Yamamoto, Appl. Phys. Lett. 56 (1990) 1989;(b) J.M. de Puydt, M.A. Haase, H. Cheng and J.E. Potts, Appl. Phys. Lett. 55 (1989) 1103.
- [3] For example, H.R. Chandrasekhar and A.K. Ramdas, Phys. Rev. B 21 (1980) 1511.
- [4] For example, J.S. Blakemore, J. Appl. Phys. 53 (1982) R123.
- [5] A. Deneuville, G. Lindauer, D.B. Tanner, R.M. Park and P.H. Holloway, Appl. Phys. Lett. 57 (1990) 2458.
- [6] D.T. Marple, J. Appl. Phys. 35 (1964) 539.