Infrared absorption in *n*-type ZnSe/GaAs heteroepitaxial films

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We report on the variation of the absorption coefficient α_f with wave number W, for Cl-doped n-type (9.4×10^{16}–8×10^{18} cm^{-3}) ZnSe epitaxial films grown on GaAs. Below the classical mid-infrared range of W, α_f has large values (1.6×10^{3}–2.11×10^{4} cm^{-1}) appropriate for thin-film measurements, with α_f proportional to W^{-p}. Large variations of α_f and p occur as a function of the free-electron concentration. The results are compared to a recent theoretical model by Ruda [J. Appl. Phys. **61**, 3035 (1987)], which is specific to ZnSe.

ZnSe is a good candidate for blue light-emitting devices because of its suitable direct band gap (2.7 eV at RT). However, the formation of ZnSe p-n junctions has been difficult due to problems in controlling the conductivity of bulk crystals. Tremendous progress has been made, however, with ZnSe thin films grown epitaxially on GaAs. n-type doping has been reported by many authors; however, p-type doping still remains a major problem.[1] The electrical characterization of p-type ZnSe is currently complicated by the lack of a suitable ohmic contact technology.[2] To overcome this problem, a model for the determination of free-carrier concentration from the free-carrier absorption coefficient, α_f, in the mid-infrared (600 –5000 cm^{-1}) has recently been proposed by Ruda,[3] and tested using published results for n-type bulk ZnSe crystals.[4] For a compensation ratio of 0.9 and $n = 10^{19}$ cm^{-3}, α_f up to 5×10^{4} cm^{-1} at 600 cm^{-1} can be extrapolated from this model.

This is the first report of absorption measurement in the W ranges 35–150 and 350–3000 cm^{-1} on 1.06- to 1.33-μm-thick n-type ZnSe epitaxial films grown on GaAs substrates. (The 150–350 cm^{-1} range cannot be covered due to phonon absorption in the film and substrate.) The absorption coefficient is suitable ($1.6\times10^{3} < \alpha_f < 2.11\times10^{4}$ cm^{-1}) for thin films and depends strongly on the electron concentration. For each sample $\alpha_f \propto W^{-p}$, but with values of p which are quite different according to the W range. $p_1 < 1$ in the far-infrared (range 1) and $p_2 > 1$ in the mid- infrared (range 2). The frequency of the crossover between these two ranges decreases monotonically with the carrier concentration n. The Ruda model seems to be applicable in region 2, indicating that it may have a wider applicability range than originally proposed.

The ZnSe films were grown by molecular beam epitaxy (MBE) on undoped, semi-insulating ($\rho > 10^{7}$ Ω cm), (100) GaAs substrates under a fixed set of growth conditions, namely, a substrate temperature of 275 °C and a Zn-to-Se ratio of 1:2. n-type doping of the ZnSe layers in the range 9.4×10^{16}–8×10^{18} cm^{-3} was achieved by the substitutional incorporation of a Cl atom during the MBE growth process using a $ZnCl_2$ effusion source. The doped layers were grown on an ≈0.5-μm-thick undoped ZnSe buffer layer to avoid doping interaction with the GaAs substrate. The layers were grown in a custom-designed MBE system previously used to grow ultrahigh-purity homoepitaxial ZnSe layers.[5] Room-temperature carrier concentrations and electron mobilities in the ZnSe films were derived by Hall effect measurements, while the film thicknesses were determined by cross-sectional transmission electron microscopy (see Table I).

The absorption coefficients are calculated from transmission measurements which were done using a BRUKER IFS 113v Fourier transform infrared (IR) apparatus. The measurements were made at room temperature between 35 and 5000 cm^{-1} in four overlapping regions 30–100, 80–300, 200– 600, and 450–3000 cm^{-1}. The transmission data had strong interference fringes caused by the 370-μm-thick substrate. These fringes were removed by subtracting the corresponding peak in the Fourier transform of the transmission spectra. The same procedure was performed for undoped ZnSe epitaxial thin films (1–2.38 μm thick). Their very high resistivity, $\rho > 10^{7}$ Ω cm, implies that these undoped films have negligible carrier concentrations and therefore, negligible free-carrier absorption; we use them as references.

The transmission of these samples is largely governed by the absorption coefficient of n-type ZnSe films, but also includes the reflectivities R_{ij} at each interface, and the absorption coefficient and the thickness of the various media: (1) air, (2) doped film α_f and d, (3) undoped film α_u and e, and (4) GaAs substrate α_s and D. The expressions of the transmissions (currently not available), T and T_r respectively, of the doped and reference samples for identical substrate and the undoped ZnSe layer thicknesses would have the forms

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TABLE I. Characteristics of the doped films.

Sample	Thickness of doped films (μm)	Free-electron concentration (cm^{-3})	Mobility ($cm^2 V^{-1} s^{-1}$)	Absorption coefficient @ 100 μm (cm^{-1})	P_1	P_2
56	1.06	9.4×10^{16}	302	$1.60\pm0.15\times10^3$	0.36 ± 0.001	3 ± 0.5
57	1.33	9.3×10^{17}	250	$4.98\pm0.15\times10^3$	0.09 ± 0.01	2.6 ± 0.2
58	1.33	8×10^{18}	207	$2.11\pm0.014\times10^4$	0	4 ± 0.2

$$T=\frac{(1-R_{12})(1-R_{23})(1-R_{34})(1-R_{41})\exp(-\alpha_f d-\alpha_u e-\alpha_s D)}{1-F[R_{12},R_{23},R_{34},R_{41},\exp(-\alpha_f d),\exp(-\alpha_u e),\exp(-\alpha_s D)]}, \quad (1)$$

$$T_r=\frac{(1-R_{13})(1-R_{34})(1-R_{41})\exp(-\alpha_u e-\alpha_s D)}{1-F'[R_{13},R_{34},R_{41},\exp(-\alpha_u e),\exp(-\alpha_s D)]}, \quad (2)$$

where F and F' are polynomial functions (taking into account the reflections at the various interfaces) whose values remain <1. So,

$$\frac{T}{T_r}=\frac{(1-R_{12})(1-R_{23})(1-F')}{(1-R_{13})(1-F)}\exp(-\alpha_f d). \quad (3)$$

Because F and F' and the refractive indices of both the doped and undoped ZnSe (which enters in R_{12}, R_{13}, and R_{23}) are not known, we make the approximation $T/T_r = \exp-\alpha_f d$. This gives what we call the "rough absorption coefficient". However, Eq. (3) is expected to be a good first approximation, because of the dominance of the exponential in comparison to the polynomial functions of R_{ij}. This simple approximation will be shown later to give the expected p values in the W range 2.

The transmission measurements were done with the ZnSe films remaining on the GaAs substrates. Both ZnSe and GaAs present absorption from phonons in the measurement range. The absorption coefficients due to phonons in both the GaAs (Ref. 6) and ZnSe (Ref. 7) have been reported previously and are shown in Fig. 1. For GaAs (Ref. 6) (Fig. 1, full line), the absorption coefficient remains very low ($\alpha < 50$ cm^{-1}) outside the 28 meV (226 cm^{-1})–42.5 meV (340 cm^{-1}) range. Its effect would be practically removed from the α_f calculation if the thicknesses of the substrates are identical.

Because the undoped ZnSe films have different thicknesses in the doped and reference samples, the ZnSe phonons should contribute directly to the rough absorption coefficient of the ZnSe doped films. Fortunately[7] (Fig. 1, dotted line), the phonon absorption exceeds 10^2 cm^{-1} only in the range 20 meV (162 cm^{-1})–39 meV (315 cm^{-1}) and so their contribution outside is negligible.

From the high α_{ph} values in both GaAs and ZnSe, the 200–300 cm^{-1} range where T and $T_r \simeq 0$ must be excluded. In fact, our α_f calculation has to be restricted below 150 and above 350 cm^{-1} to be free of any ZnSe phonon contribution.

The variations of the rough absorption coefficient of the doped ZnSe films on GaAs substrates in the wave number ranges 35–150 and 350–3000 cm^{-1} are shown in Fig. 2. Sample properties are given in Table I. At a given wavelength, α_f increases as the carrier concentration increases. In a W range increasing from 35–160 cm^{-1} to 35–1500 cm^{-1}, respectively from the lowest (9.4×10^{16} cm^{-3}) to the highest carrier concentration (8×10^{18} cm^{-3}) α_f is larger than 10^3 cm^{-1}. For samples 57 and 58, there is fine structure around 443 and 523 cm^{-1} with $\Delta\alpha < 5\times10^2$ cm^{-1}. This is because the back of the substrates has to be lapped to remove the indium used to glue them on the sample holder, then polished for the optical measurements. This introduces a slight variation in thickness (<15 μm) among the various substrates, thus stray peaks from the GaAs phonon absorption. They are easily identified as the GaAs phonons absorption peaks of Fig. 1, because of their energy, size, and shape. Figure 2 (note logarithmic scales) shows two ranges (1 and 2) for which $\alpha_f \propto W^{-p}$. The exponent p is smaller and larger than 1 for lower and higher wave numbers, respectively. From a straight line fit

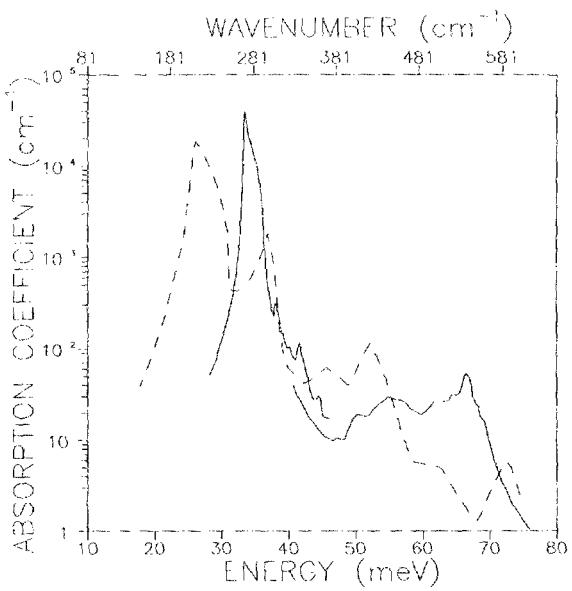

FIG. 1. Absorption coefficient vs wave number and energy for GaAs [full line, from Ref. 6; the small mismatch between the various parts of the curve is from the original paper of Ref. 6(c)] and ZnSe (dotted line, from Ref. 7).

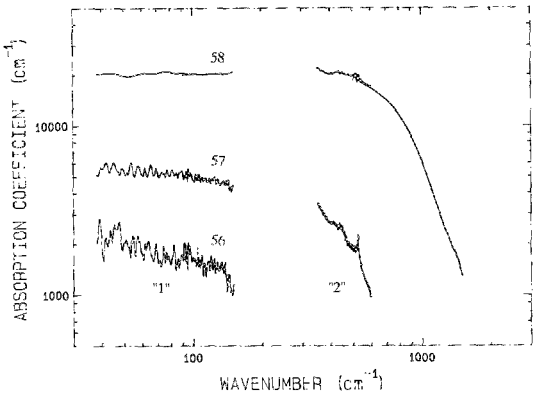

FIG. 2. Absorption coefficient α_f vs wave number W for doped thin films 56, 57, and 58 (see Table I for their characteristics).

of $\alpha(W)$ over the entire 1 range and the upper 2 range, the p_1 and some approximate p_2 values are given in Table I. The p_2 values are close to 2.5 for the lower carrier concentrations 9.4×10^{16} and 9.3×10^{17} cm^{-3}, but significantly higher (around 4), for the higher carrier concentration 8×10^{18} cm^{-3}. In contrast, p_1 values decrease monotonically from 0.36 to 0 as the carrier concentration increases to 8×10^{18} cm^{-3}. Thus, in wave number range 1, both the absorption coefficient and the derivative of the logarithmic absorption coefficient exhibit very significant variations with the electron concentration. The α_f magnitude is approximately quadratic with n, while no obvious law appears for p_1.

The detailed comparison with the previous measurements of Dutts *et al.*[4] and with the Ruda model predictions[3] will be done in a forthcoming paper. However, some new factors can already be pointed out.

From the wave number and the p_2 values, the Ruda model is expected to apply in our higher W range 2. Thus, the range of applicability of this model can be widened from 900 cm^{-1} (11 μm) to 150 cm^{-1} (60 μm) as the free-electron concentration decreases from 8×10^{18} to 9.4×10^{16} cm^{-3}. The lower limit of 15 μm quoted by Ruda would approximately correspond to $n=10^{18}$ cm^{-3}. The p_2 values for $n=9.4\times10^{16}$ and 9.6×10^{17} cm^{-3} agree with the value of 2.5 predicted by the Ruda model in this electron concentration range, which corresponds to a dominance of optical phonon scattering in the free-electron absorption. However, when $n=8\times10^{18}$ cm^{-3}, the model predicts a dominance of impurity scattering in the free-carrier absorption (FCA), leading to $p_2=3.5$, whereas we find a slightly higher value of $p_2=4$. Quite generally, the Ruda model predicts an increase of p as the compensation ratio (n/total concentration of impurities) decreases from the unity value corresponding to perfect doping efficiency. This ratio has been shown previously[8] to decrease below 1 when $n>10^{18}$ cm^{-3} for Cl doping by MBE, which might explain our higher value. More data are required to clarify this point.

The α_f values investigated here are much higher than those obtained for bulk crystal in the classical FCA range, so that no direct comparison can be made with the previous results.[4] However, in the same carrier concentration range 10^{17}–10^{18} cm^{-3} our p_2 values agree reasonably with those quoted (2.7) by Dutts *et al.*[4]

The absorption in W ranges 1 and 2 have very different p values, suggesting that they involve different physical processes. From its wave number range, α_f in range 1 might originate from phonon-plasmon coupling.[9]

In conclusion, we have shown here for the first time, free-electron absorption from doped ZnSe thin films. It can be measured directly for doped epitaxial ZnSe films on semi-insulating GaAs substrates. The free-carrier absorption coefficient is more important in the far-infrared range (35–150 cm^{-1}) reported here for the first time. α_f varies approximately as W^{-p_1}. Both α_f and p_1 have large variations with the electron concentration which suggests they may be used for contactless measurement of carrier concentrations in thin ZnSe films. In the mid-infrared range, the classical FCA is found.

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