Optical absorption edge of semi-insulating GaAs and InP at high temperatures

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The temperature dependences of the optical absorption edges of semi-insulating GaAs and InP have been measured from room temperature to 905 °C and 748 °C, respectively, with accuracies of ±1 °C at room temperature and ±5 °C at 900 °C. The temperature dependence of the optical absorption edge is adequately reproduced by an Einstein model although the Varshni model gives an improved fit to the band gap. Finally, the widths of the absorption edges are correlated with ionicity. © *1997 American Institute of Physics.* [S0003-6951(97)00326-4]

Recent developments in optical band-gap thermometry[1–3] and rapid thermal processing have created a need for more detailed information on the temperature dependence of the optical absorption edges of common semiconductor substrates, at elevated temperatures. In direct band-gap semiconductors, the optical absorption in the vicinity of the band gap increases exponentially with photon energy.[4,5] This exponential rise in the absorption (Urbach edge) is temperature dependent, and is a manifestation of the effect of structural and thermal disorder on the electronic properties of semiconductors.[5–7] In this letter, we report optical transmission measurements of the Urbach edges of GaAs and InP wafers, from room temperature up to 905 and 748 °C, respectively, a larger temperature range than previous measurements.[2] In the most frequently cited high-temperature measurements of the band gap of GaAs, the temperature dependence of the band gap was inferred from iso-absorption measurements in the Urbach tail region.[8,9] However, the temperature dependence of the Urbach slope was not resolved;[9] this information is needed to obtain accurate measurements of wafer temperatures with band-gap thermometry. The temperature dependence of the Urbach slope for InP is reported here, to the best of our knowledge, for the first time[10] (a preliminary report is given in Ref. 10).

In the measurements reported here, semi-insulating GaAs wafers (undoped liquid-encapsulated Czochralski material) and InP wafers (Fe doped), 530 and 350 μm thick, respectively, are enclosed in a cylindrical Ta radiation cavity 5.6 cm in diameter and 20 cm long with a 2×0.9 cm optical access hole at each end. The radiation cavity containing the sample is placed in the center of a 6×110 cm stainless-steel tube in a 80 cm long tube furnace.[10] The temperature uniformity across the wafer in the radiation cavity is better than 0.5 °C, as measured by two type-*K* thermocouples, one pressed against the sample near the center of the tube and one near the edge of the tube. According to the manufacturer, the uncertainty in the absolute temperature reading of the type-*K* thermocouples is ±2.2 °C or 0.75% of the temperature reading in °C, whichever is larger. To improve the accuracy of the temperature measurements, two type-*K* thermocouples were calibrated with a commercially calibrated Pt–Pt/Rh (13%) thermocouple in a separate furnace.[10] We estimate that our temperature measurements are accurate to ±1 °C at room temperature and ±5 °C at 900 °C.

The temperature uniformity inferred from the thermocouples was confirmed by comparing the transmission spectra from various positions across the wafer at a fixed temperature. The transmission measurements were made by focusing the light from a 100 W halogen lamp at one end of the furnace tube onto the wafer. The transmitted light is collected with a lens at the opposite end of the tube and focused into a fiber bundle coupled to a 1/4 m monochromator with a cooled InGaAs photodetector. The spectral resolution of the monochromator was 0.9 nm. The transmittance spectra were recorded after the thermocouple readouts stabilized to ±1 °C.

During the measurements, the tube was evacuated and filled with 10 mbar of either Ar or dry N_2. In a first series of measurements, As fragments were placed in the tube. The As vapor pressure from the elemental As helps to protect the surface from loss of the group V and subsequent formation of droplets of In or Ga. This procedure allowed measurements on GaAs up to 790 °C and InP up to 700 °C. Prolonged measurements in this mode led to As coating on the windows on the ends of the furnace tube, which could not be totally eliminated by continuous pumping. For temperatures above 700 °C, the window coating and some visible wafer degradation made measurements unreliable (see two very large error bars in Fig. 2). Hence, for higher temperature measurements, we protected the semiconductor surfaces against group V loss by electron-beam evaporation of approximately 100 nm of aluminum oxide on both sides of the wafers. Results from the coated wafers were found to match the results from the uncoated wafers at low temperatures.

The absorption coefficient α is determined by inverting the normalized transmittance spectra. The evaporated Al_2O_3 films had an optical thickness close to λ/4 where λ is the median wavelength of interest. To ensure that the effect of this coating was properly accounted for in the transmission measurements, the absorption of protected substrates were compared with data on unprotected pieces of the same wafer and normalized. This was accomplished by measuring each substrate on an optical bench prior to insertion into the

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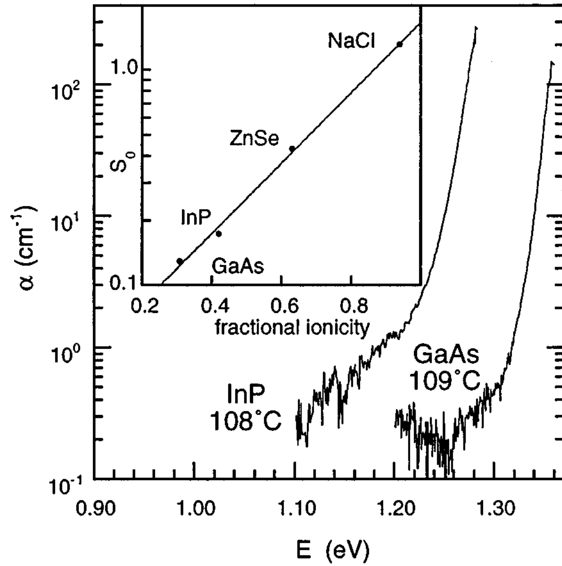

FIG. 1. Typical optical absorption spectra for semi-insulating GaAs and InP as measured in this experiment. The inset shows the exponential relationship between the coupling parameter for the Urbach slope and the fractional ionicity of representative binary compounds.

chamber. Typical absorption spectra for GaAs and InP are shown in Fig. 1.

The absorption in the Urbach region can be described by[5]

$$\alpha(h\nu)=\alpha_g \exp\left(\frac{h\nu-E_G}{E_0}\right), \qquad (1)$$

where E_0 is the characteristic energy of the Urbach edge, E_G is the extrapolated optical band-gap energy, and α_g is the optical absorption coefficient at the band-gap energy. In this letter, we will assume that the band gap is equal to the extrapolated gap E_G, although this may not give precisely the same values as other definitions of the band gap. Figure 2 shows the temperature dependence of E_G and E_0 for GaAs and InP. Both E_G and E_0 are determined by first subtracting the weakly energy dependent deep-level absorptions from the absorption data and fitting the exponential part with Eq. (1), where α_g is 8000 cm^{-1} for GaAs (Ref. 11) and 11000 cm^{-1} for InP.[12] To ensure consistency, the range $10 \leqslant \alpha \leqslant 100\ \mathrm{cm}^{-1}$ was used for the fits in the whole temperature range. At temperatures above 700 °C, the absorption below the Urbach edge increases to more than 10 cm^{-1}, although its subtraction from the absorption data still yields an exponential edge over three decades. At these temperatures, we still report the E_G and E_0 values from the 10 to 100 cm^{-1} fit range, but have also performed calculations in different ranges in order to estimate the uncertainties. Below 700 °C, the uncertainties are determined from the differences in results obtained from several runs and give error bars of ±0.7 meV for E_G and ±0.12 meV for E_0. These error bars are reported in Fig. 2. The equivalent errors in the band gap from the temperature uncertainty of ±1 °C at room temperature and ±5 at 900 °C are ±0.5 and ±2.6 meV, respectively.

In theories of the Urbach edge for crystalline semiconductors, both E_0 and E_G are proportional to the phonon

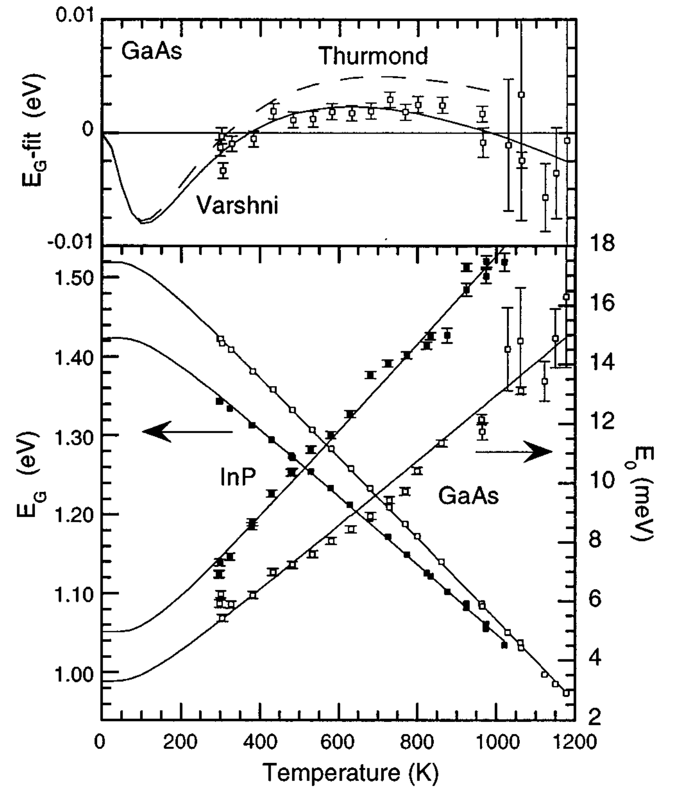

FIG. 2. Temperature dependence of the optical band gap E_G and Urbach slope parameter E_0 for semi-insulating GaAs (□) and InP (■) together with fits (solid lines) obtained with the Einstein model [Eqs. (2) and (3)]. The top part of the figure shows the difference between the GaAs band-gap data and the fit on an expanded scale.

population.[5–7] In the Einstein model, the width of the Urbach edge is

$$E_0(T)=S_0 k\theta_E\left[\frac{1+X}{2}+\frac{1}{\exp(\theta_E/T)-1}\right], \qquad (2)$$

where the dimensionless parameter X is a measure of the structural disorder,[13] θ_E is the Einstein temperature taken as 3/4 of the published Debye temperature,[5,12,14] S_0 is a dimensionless constant related to the electron–phonon coupling, and k is the Boltzmann constant. X is expected to be zero for a perfect crystal.[13] The temperature dependence of the band gap is given by[5]

$$E_G(T)=E_G(0)-S_g k\theta_E\left[\frac{1}{\exp(\theta_E/T)-1}\right], \qquad (3)$$

where S_g is a dimensionless coupling constant and $E_G(0)$ is taken as the published band gap at liquid-He temperature.[14] A slightly better fit to the temperature dependence of the band gaps can be obtained with the expression

$$E_G(T)=E_G(0)-S_V k\theta_V\left[\frac{T^2}{\theta_V^2+\theta_V T}\right], \qquad (4)$$

proposed by Varshni[8,15] where S_V and θ_V are fitting parameters. The fits of the Einstein expressions to the temperature dependence of the gap and the Urbach parameter with S_0, S_g, and X as adjustable parameters are shown as continuous lines through the data in Fig. 2. The best-fit param-

TABLE I. Parameters describing the temperature dependence of the absorption edge obtained from the fits to the experimental data. $E_G(0)$ and θ_E are taken from the literature. We assume θ_E is 3/4 of the Debye temperature.

Parameter	GaAs	InP
$E_G(0)$ (eV)	1.51914[a]	1.4236[a]
E_G (300 K) (eV)	1.422	1.343
E_0 (300 K)(meV)	5.9	7.1
θ_E (K)	270[a]	316.5[a,b]
θ_V (K)	199.4	228.0
S_0	0.129	0.173
S_g	6.03	5.12
S_V	6.30	5.35
X	1.2	1.1

[a]Reference 14.
[b]Reference 12.

eters are listed in Table I. The measured band gap of GaAs at 300 K is 1.422 eV. For InP, the measured band gap is 1.343 eV at 297 K. These values are in good agreement with the published 300 K values of 1.424 and 1.344 eV (Ref. 14) for GaAs and InP, respectively. The values obtained for E_0 at the same temperatures are 5.9 and 7.1 meV for GaAs and InP, respectively. In Ref. 6, the Urbach edge of semi-insulating GaAs was measured with a lower monochromator resolution (4.5 nm instead of 0.9 nm) and yielded a room-temperature E_0 value of 7.5 meV. The 5.9 mev value reported here for GaAs at room temperature should be compared with 3 meV obtained in a recent theoretical calculation of the thermally induced Urbach tail.[16] Our higher value suggests a temperature-independent contribution as well, which leads to a nonzero X value when we fit Eq. (2) to the data. This X value is reported in Table I.

The top part of Fig. 2 shows the difference between the measured band gap of GaAs and the fit to the data with the Einstein model [Eq. (3)], on an expanded scale. The fit by the Varshni expression in Eq. (4) (solid curve), as well as Thurmond's widely cited fit[8] (dashed curve) are shown for comparison. Equation (4) gives a slightly better fit to the data than the Einstein model. Thurmond's curve is a fit to high-temperature absorption measurements by Panish and Casey[8,9] who quote uncertainties in E_G of between 3 and 5 meV, but give no estimate for the temperature accuracy.[9]

We believe that the Varshni model is in better agreement with the data than the Einstein model because its polynomial temperature dependence more closely matches the Debye form one would expect for a distribution of phonon modes. One can relate the Varshni temperature θ_V to the Debye temperature by matching the halfway point in the ''knee'' in the specific heat, as is done in the case of the Einstein/Debye comparison. (The specific heat is proportional to the temperature derivative of the band gap.) In this case, we find that θ_V is equal to 0.61 times the Debye temperature or 218 and 256 K for GaAs and InP, respectively, which are in reasonable agreement with the values for θ_V in Table I obtained from the fits to the data.

The constant S_0 is a measure of the strength of the coupling between the phonons and the electronic states at the conduction- and valence-band edges. In particular, the interaction with longitudinal optical phonons will increase with ionicity. The inset to Fig. 1 shows that S_0 increases approximately exponentially as a function of the fractional ionic character of the bonds in binary compounds.[17] The GaAs and InP data are from the present work while the values for the other materials are from Kurik.[7]

The simplest interpretation of the temperature-independent part of the width of the absorption edge (nonzero X) is that it is due to structural disorder. This is surprising, since the GaAs and the InP used in these experiments are high quality single-crystal materials, and one might reasonably expect the structural disorder component to be negligible. If the nonzero X is due to disorder, then structurally more perfect material, perhaps thin films grown by molecular beam epitaxy, might show sharper Urbach edges. Alternatively, we could force X to be zero in the fitting procedure and allow θ_E to be an adjustable parameter. In this case, we can still obtain a good fit to the data, but θ_E is unreasonably large. Based on these results, we are unable to say whether the nonzero value for X is due to structural disorder or is an indication that the model for the temperature dependence of the Urbach slope is incomplete.

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