

Photoreflectance of GaAs and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ at elevated temperatures up to 600 °C

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We report a modulation spectroscopy experiment on GaAs and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ at elevated temperatures. Using the contactless electromodulation method of photoreflectance, the direct gaps (E_0) of these materials have been observed from 77 K to 600 °C. The latter temperature is comparable to molecular beam epitaxy, metalorganic chemical vapor deposition, growth temperatures, etc. Our results are at the highest temperature yet reported for E_0 (GaAs) in a reflectance experiment and the first observation of E_0 ($\text{Ga}_{1-x}\text{Al}_x\text{As}$) at elevated temperatures. From the latter, the Varshni coefficients [Physica 34, 149 (1967)] for $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ were determined.

Modulation spectroscopy is a powerful technique to study and characterize semiconductors.¹⁻⁶ The most widely used of these methods is electromodulation¹⁻⁷ (electric field modulation reflectivity or transmission) since it yields the sharpest structure (related to the third derivative of the optical constants¹⁻⁴) and is sensitive to surface (interface) states and electric fields.^{3,5,6} Photoreflectance (PR)^{2,3,5-8} is a particularly used form of electromodulation (EM) since it is contactless and hence can be performed *in situ* under a variety of sample conditions including different temperatures. While many EM experiments from cryogenic temperatures to 300 K have been performed,¹⁻⁸ there has been no report of work at elevated temperatures.

The ability to perform modulated optical measurements in semiconductors over a wide temperature range, including elevated temperatures, has many fundamental as well as applied ramifications. The temperature dependence of the interband electronic transitions can yield information about electron-phonon interactions, excitonic effects, etc.⁹ The variation of energy gaps with temperature in semiconductors is described by the Varshni expression¹⁰ which involves two parameters. Experimental values of these parameters can be used to test recent theories.^{9,11} From an applied point of view the ability to measure band gaps at elevated temperatures (~ 600 °C) corresponding to growth conditions of molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), etc., opens up many new possibilities. By using PR the temperature of the substrate material could be measured in a contactless manner. *In situ* monitoring of the growth of epitaxial layers could be performed.

In this letter, we report PR measurements of the direct gaps (E_0) of undoped, semi-insulating (SI) $\langle 100 \rangle$ GaAs and

$\langle 100 \rangle \text{Ga}_{0.82}\text{Al}_{0.18}\text{As}/\text{GaAs}$ from 77 K to 600 °C. The 600 °C measurement is the highest temperature at which E_0 of GaAs has been observed in a reflection experiment. A recent investigation using scanning ellipsometry has measured E_0 (GaAs) up to 500 K.⁹ Absorption measurements have been performed up to 1000 K.⁹ For $\text{Ga}_{1-x}\text{Al}_x\text{As}$ this is the first optical result at elevated temperatures. For both materials E_0 can be evaluated to about ± 5 meV at 600 °C. From the temperature variation of E_0 we have determined the Varshni coefficients for the two materials. For GaAs our values are in good agreement with Ref. 9. This is the first determination of these parameters for $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

The $\langle 100 \rangle$ GaAs sample used in this experiment was undoped, SI material grown by the liquid-encapsulated Czochralski method. The $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}/\text{GaAs}$ sample was fabricated in a Varian GEN II MBE system at the United Technologies Research Center. It was grown on a GaAs buffer layer (not intentionally doped) of 0.8 μm thickness on a SI $\langle 100 \rangle$ GaAs substrate. The substrate temperature was 590 °C. From the growth conditions the $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ epilayer was 1 μm thick. The Al composition was determined from the position of E_0 using the relation $E_0(\text{Ga}_{1-x}\text{Al}_x\text{As}) = E_0(\text{GaAs}) + 1.45x$ for $x < 0.4$.¹²

The PR apparatus used in this experiment has been described in Ref. 13. The pump beam was the 5145 Å line of an Ar-ion laser with a power density of about 100 mW/cm² on the sample and chopped at 500 Hz. The sample was mounted in a heating system with optical access similar to that described in Ref. 9. The vacuum in our chamber was 10^{-6} Torr. The temperature was measured by a chromel-constantan thermocouple mounted directly onto the sample. In order to eliminate blackbody radiation from the sample at temperatures above about 450 °C, we used a filter consisting of water (about 1 in. in thickness) in a container with flat quartz windows.

Shown by the dotted lines in Fig. 1 are the PR spectra for $E_0(\text{GaAs})$ at $T = 25, 250,$ and 610 °C. The dotted lines in Fig. 2 are the experimental data for the

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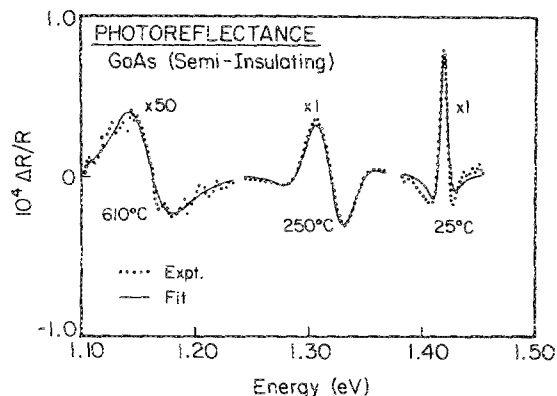


FIG. 1. Experimental photoreflectance spectra (dotted lines) of the direct gap of GaAs at 25 °C, 250 °C, and 610 °C. The solid line is a least-squares fit to Eq. (1).

$\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ sample in the vicinity of $E_0(\text{Ga}_{0.82}\text{Al}_{0.18}\text{As})$ at 25, 324, and 620 °C. The highest temperature spectra for GaAs and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ required scans of 20 and 15 min, respectively. The line shapes of all spectra were found to be independent of pump beam intensity, i.e., low-field modulation regime.^{2,3} The phase of the signals is taken relative to that of the pump beam.

The solid lines in Figs. 1 and 2 are a least-squares fit to the Aspnes low-field derivative functional form³:

$$\Delta R/R = \text{Re}[Ae^{i\theta}(E - E_0 + i\Gamma)^{-m}], \quad (1)$$

where A is the amplitude, θ is a phase factor, E is the photon energy, E_0 is the energy gap, and Γ is a phenomenological broadening parameter. The parameter m is related to critical point type and order of the derivative. Since E_0 of GaAs and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ are three-dimensional interband transitions, $m = 5/2$ was used for the fit in Figs. 1 and 2.³ For GaAs the fit to the experimental data is quite good for all three temperatures. For $E_0(\text{Ga}_{0.82}\text{Al}_{0.18}\text{As})$ at 25 °C there is an oscillation on the high-energy side of the feature which cannot be fit by Eq. (1). We shall return to the question of the fit of $E_0(\text{Ga}_{0.82}\text{Al}_{0.18}\text{As})$ in a section below. Even in the temperature range where the fit to Eq. (1) is not so good it is still possible to obtain the energy of $E_0(\text{Ga}_{0.82}\text{Al}_{0.18}\text{As})$ from the three-point fit method.³ From Figs. 1 and 2 at the highest

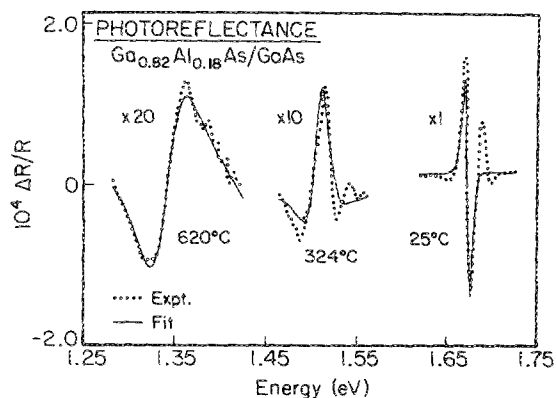


FIG. 2. Experimental photoreflectance spectra (dotted lines) of the direct gap of $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ at 25 °C, 324 °C, and 620 °C. The solid line is a least-squares fit to Eq. (1).

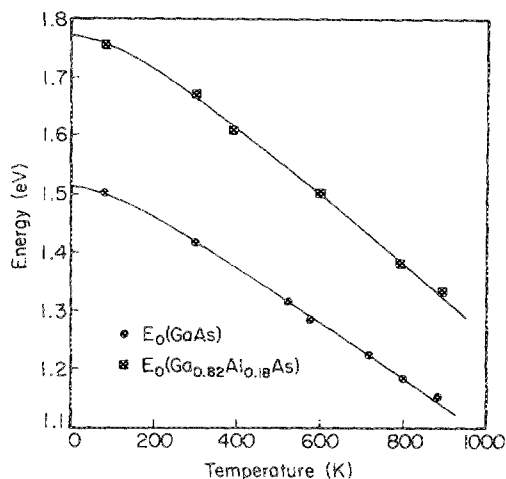


FIG. 3. Temperature dependence of the direct gaps of GaAs (circles) and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ (squares). The solid lines are least-squares fits to Eq. (2).

temperatures, it is possible to obtain the energy of E_0 of either material to ± 5 meV.

Shown in Fig. 3 are the experimental values of E_0 for GaAs (circles) and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ (squares) as a function of temperature including the 77 K measurement. The solid lines are a least-squares fit to the Varshni empirical relation^{9,10}

$$E_0(T) = E_0(0) - \alpha T^2 / (\beta + T). \quad (2)$$

The obtained values of $E_0(0)$, α , and β for the two materials are listed in Table I. For $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ these are the first values of the Varshni coefficients.

At the present time we do not fully understand the line shape of $E_0(\text{Ga}_{0.82}\text{Al}_{0.18}\text{As})$ at 25 °C. Possible explanations are Franz-Keldysh oscillations (FKO) due to built-in dc fields⁵ or interference effects from the $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}/\text{GaAs}$ interface.¹³ Further work is needed to understand the line shape of $E_0(\text{Ga}_{0.82}\text{Al}_{0.18}\text{As})$ in our structure.

Photoreflectance could also be used as a high temperature, contactless *in situ* monitoring technique for (a) growth techniques such as MBE, MOCVD, etc., or (b) processing methods. For example, the temperature of GaAs substrates could be evaluated to ± 10 °C (based on ± 5 meV accuracy for E_0 and Fig. 3) to within a depth of only several thousand angstroms from the growth surface. Topographical scans¹⁴ could be performed to evaluate temperature uniformity. At present the two main techniques to evaluate substrate temperatures over a wide range are infrared pyrometry¹⁵ and

TABLE I. Values of the parameters $E_0(0)$, α , and β for GaAs and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$.

Material	$E_0(0)$ (eV)	α (10^{-4} eV K ⁻¹)	β (K)
GaAs	1.512 ± 0.005^a	5.1 ± 0.5^a	190 ± 82^a
	1.517 ± 0.008^b	5.5 ± 1.3^b	225 ± 174^b
$\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$	1.771 ± 0.007^a	6.3 ± 0.5^a	236 ± 73^a

^a This work.

^b Reference 9.

thermocouples in intimate contact with the back of the substrate holder. Both of these techniques have serious drawbacks. Thermocouples measure the temperature at the back of a relatively thick block of Mo to which the substrate is mounted with molten In which may vary considerably in thickness and distribution from run to run. The actual surface temperature of the substrate is thus known to within only about $\pm 50^\circ\text{C}$. This problem becomes even worse as the use of In-free substrate holders becomes more widespread since the thermocouple is no longer in contact with the wafer in any way. Infrared pyrometry is useful only above about 450°C . The pyrometer must be constantly recalibrated since the viewport may become coated. This recalibration procedure can itself become a source of error. It is also important to pick a pyrometer with a narrow, short wavelength spectral window so that the temperature measured is that of the wafer and not the heater filaments behind it.

Substrate temperatures at only a single point can be evaluated by using reflection electron diffraction to observe the transition temperature at which the $\langle 100 \rangle$ GaAs surface reconstruction switches from As stabilized to Ga stabilized.¹⁵ This is taken as a measure of the bulk congruent sublimation temperature of GaAs, reported to be between 625 and 638°C .¹⁶

Photoreflectance overcomes all of these problems since it directly measures the optical spectrum of the wafer to within several thousand angstroms from the surface. Also, it can readily be performed over a wide temperature range including $T < 450^\circ\text{C}$. It is relatively immune to viewport coating since it is a normalized technique. In addition, the quality and composition of epilayers such as $\text{Ga}_{1-x}\text{Al}_x\text{As}$ could be determined during actual growth procedures. Experiments are presently under way to determine the minimum thickness of a $\text{Ga}_{1-x}\text{Al}_x\text{As}$ epilayer needed to observe a PR signal.

In summary, we report the first modulation spectroscopy experiment at elevated temperature. Using the contactless electromodulation method of PR we have observed the direct gap of GaAs and $\text{Ga}_{0.82}\text{Al}_{0.18}\text{As}$ up to 600°C , temperatures comparable to MBE or MOCVD growth conditions. We have for the first time evaluated the Varshni coeffi-

cients for $\text{Ga}_{1-x}\text{Al}_x\text{As}$. The ability to perform EM at elevated temperatures, particularly PR, has many fundamental and applied applications.

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