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PHOTOREFLECTANCE FOR IN-SITU
CHARACTERIZATION OF MOCVD GROWTH
OF SEMICONDUCTORS UNDER MICRO-GRAVITY CONDITIONS

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FINAL REPORT

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ABSTRACT

The goal of this project was to continue to develop the contactless electromodulation technique of photoreflectance (PR) for in-situ monitoring of MOCVD semiconductor growth for micro-gravity applications. We have demonstrated that PR can be employed in a real MOCVD reactor including rotating substrate (~ 500 rev/min), in flowing gases and through a diffuser plate. Measurements on GaAs and $Ga_{0.82}Al_{0.18}As$ were made up to 690^{o}C. The direct band gaps of $In_xGa_{1-x}As$ (x = 0.07 and 0.16) were evaluated up to 600^{o}C. In order to address the question of real time measurement, we have obtained the spectra of the direct gap of GaAs at 650^{o}C in 30 seconds and 15 seconds seems feasible.

INTRODUCTION

During the past decade metal-organic chemical vapor deposition (MOCVD) has become an important growth method for thin film semiconductors and semiconductor structures such as superlattices (SL's), quantum wells (QW's), multiple quantum wells (MQW's), heterojunctions (HJ's), etc. There is also considerable interest in studying MOCVD growth under micro-gravity conditions in space. The material and interfaces grown by MOCVD can be characterized by a variety of optical, electronic and structural methods including photoluminescence (PL), photoluminescence excitation spectroscopy (PLE), absorption spectroscopy, modulation spectroscopy, Raman and resonant Raman scattering, cyclotron resonance, Hall effect, transmission electron microscopy (TEM), etc. Each of these tools provides specific information about the material of interest. For characterization purposes in space the experimental tools should be as simple and informative as possible. Many of the methods mentioned above are specialized and sometimes difficult to employ. For example, a number of them (PL, PLE, absorption cyclotron resonance) generally require cryogenic temperatures and hence require the sample to be removed from the growth chamber.

Because of its simplicity and proven utility in the study and characterization of bulk semiconductors modulation spectroscopy [1-4] has recently gained importance for the evaluation of semiconductor thin films[1-4] and heterostructures [5,6]. This method is simple, relatively inexpensive, lightweight, and easy to use. There is a considerable data base which makes it very user friendly. The derivative nature of this technique provides maximum sensitivity to interband electronic transitions and thus to the band structure of the material being investigated. While impurity and defect levels are sometimes observed they do not dominate the spectrum as they do in PL. In addition, it is possible to perform lineshape analysis and hence to gain detailed information about the spectral feature of interest such as energy gaps and broadening parameters. The energy gap of a semiconductor can be used to deduce significant growth information such as substrate temperature and expitaxial alloy composition.

Contactless modulation methods such as photoreflectance (PR) have great potential for the in-situ monitoring of MOCVD growth as well as in-situ characterization of the material before it is removed from the growth chamber. Thus it can be used to significantly reduce the turn around time needed to modify growth conditions. This would be of great advantage for microgravity experiments. Recent studies have demonstrated that the contactless method of PR can be employed at temperatures (~600^{o}C)[7-10] corresponding to growth conditions for MOCVD and thus can be used for in-situ monitoring. While a variety of in-situ growth monitoring techniques for MOCVD have provided useful information on gas switching and complex reaction mechanisms, many fundamental issues have not been addressed. For example, the relationship between process parameters and desired materials specifications have not been studied. Thus, in-situ monitoring of MOCVD must be accomplished by directly probing the deposited material in order to achieve accurate and reliable control of this growth technique. In addition, the contactless technique of PR can yield important material information before the sample is removed from the growth chamber.

The goal of this program was to continue to develop PR as a technique to be used under microgravity conditions for in-situ monitoring of growth conditions. We have demonstrated that PR can be employed in a real MODVD system including rotating substrate (~ 500 rev/min) and flowing gases through a diffuser plate[8]. Measurements on GaAs and $Ga_{0.82}Al_{0.18}As$ were made up to 690^{o}C. The direct band gaps of the important material $In_xGa_{1-x}As$ (x = 0.07 and 0.16)[10] have been measured up to 600^{o}C. In order to address the question of real time measurements, we have obtained the spectra of the direct gap of GaAs at 650°C in 30 seconds[10] and 15 seconds seems feasible.

II. LINESHAPE CONSIDERATIONS

Differential changes in the reflectivity can be related to the perturbation of the complex dielectric function ε ($=\varepsilon_1 + i\varepsilon_2$) by: [1,4]

$$\Delta R/R = a(\epsilon_1, \epsilon_2)\Delta\epsilon_1 + b(\epsilon_1, \epsilon_2)\Delta\epsilon_2 \tag{1}$$

where R is the reflectivity, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are the changes in the real and imaginary components of the dielectric function, respectively. The parameters a and b are the Seraphin coefficients. The functional form of $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ can be calculated provided that the form of perturbation, dielectric function and type of critical point are known.

The effects of an electric field $\vec{F}$ on $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ can be divided into two general categories. If the field F does not destroy the translational invariance, i.e., electrons and/or holes are not accelerated, the lineshape is first derivative. This is the case for EM of bound states such as excitons, impurities, quantum states of isolated quantum wells, etc[1]. In general, the energy gap (E_o), the broadening parameter (Γ) and intensity (I) are functions of F and thus we can write:

$$\Delta\epsilon = \left[\left(\frac{\partial\epsilon}{\partial E_o}\right)\left(\frac{\partial E_o}{\partial F}\right) + \left(\frac{\partial\epsilon}{\partial\Gamma}\right)\left(\frac{\partial\Gamma}{\partial F}\right) + \left(\frac{\partial\epsilon}{\partial I}\right)\left(\frac{\partial I}{\partial F}\right)\right]\Delta F \tag{2}$$

If the modulating electric field removes the translational symmetry, i.e., electrons and/or holes are accelerated, it can be shown that the low-field EM lineshape is related to the third-derivative of the unperturbed dielectric function:[1-4]

$$\Delta\epsilon \sim (\hbar\Omega)^3 \left[(\partial^3/\partial E^3)(E^2 \epsilon) \right] \tag{3a}$$

The electro-optic energy $\hbar\Omega$ is given by:

$$(\hbar\Omega)^3 = e^2 \hbar^2 F^2 / 2\mu_{||} \tag{3b}$$

where $\vec{F}$ is the modulating electric field and $\mu_{||}$ is the reduced interband effective mass in the direction of $\vec{F}$. The low-field condition is satisfied when $(\hbar\Omega) << \Gamma$.

The appropriate form for the dielectric function depends on whether the broadening is homogeneous or inhomogeneous. In the former case the lineshape function is Lorentzian while in the latter situation a Gaussian profile should be used[1,11].

If the dielectric function is given by a Lorentzian profile Eqs. (1) and (3a) can be written in the third-derivative functional form (TDFF) for low-field EM:[4]

$$\Delta R/R = \mathrm{Re}\left[A e^{i\phi} (E - E_o + i\Gamma)^{-m} \right] \tag{4}$$

where A is the amplitude, E is the photon energy, E_o is the energy gap, Γ is the lifetime broadening parameter, and φ is a phase angle which accounts for Eq (1) as well as for the influence of non-uniform fields. The parameter m is used to specify the critical point, i.e., m = 5/2 for a three-dimenstional critical point type of the direct gap of materials such as GaAs.

III. TEMPERATURE DEPENDENCE OF THE BAND GAPS OF SEMICONDUCTORS

The temperature dependence of the energy gaps of semiconductors can be described by the semi-emperical Varshni equation:[12]

$$E(T) = E(0) - \alpha T^2/(\beta + T) \tag{5}$$

where E(0) is the value of the gap at T=0 and α and β are the so-called Varshni coefficents.

More recently Lautenschlager et al[13] have proposed that E(T) can be represented by a Bose-Eistein type expression given by:

$$E(T) = E_B - a_B \left\{1 + 2\left[\exp(\theta_B/T) - 1\right]^{-1}\right\} \tag{6}$$

where E_B, a_B and Θ_B are parameters to be determined from experiment.

Thus once E(0), α and β or E_B, a_B and Θ_B are evaluated for a particular material the position of the band gap can be used to deduced the temperature of the material from Eqs. (5) or (6).

Values of E(0), α and β have been obtained for GaAs[7], $Ga_{0.82}Al_{0.18}As$[7] and InP[9]. These are listed in Table I.

IV. EXPERIMENTAL RESULTS

A. Measurements in an MOCVD Reactor:

The samples used in this study were undoped, semi-insulating (SI) (001) GaAs grown by the liquid-encapsulated Czochralski method and an OMVPE-grown GaAlAs/GaAs/GaAlAs heterostructure. The GaAs material is frequently used as a stubstrate for the growth of GaAs or $Ga_{1-x}Al_xAs$

structures. In-situ PR measurements were taken in a modified EMCORE OMVPE reactor. In an EMCORE growth system, precursors are introduced into a vertical, stainless steel, cold wall reactor by a multiple precursor injection manifold. Uniform carrier gas flow is provided by a perforated plate located in the top flange of the reactor. A multiple substrate rotating susceptor is directly heated by a coated carbon-filament heater. Substrate temperature is monitored by a thermocouple located 0.030" below the susceptor. Optical access into the reactor was through a pyrex viewport and a quartz gas diffuser plate. The pump beam was the 5145 A line of an air-cooled Ar-ion laser chopped at a frequency of 900 Hz.

It is important to note that even though the diffuser plate scatters some of the reflected beam it was still possible to obtain a good spectrum. Photoreflectance is a normalized optical technique and hence it is not necessary to collect every photon. The amount of light entering the detector determines the signal-to-noise ratio but does not affect the lineshape since every photon carries the same $\Delta R/R$.

Shown by the dotted lines in Fig. 1 are the PR spectra for the direct gap E_o of GaAs at six different temperatures starting with room temperature (25^oC). The temperatures denoted T_t on the various spectra are those obtained from the thermocouple reading. However, they do not correspond to the actual temperature of the material, except for the 25^oC measurement. All spectra were found independent of the pump power, indicating modulation in the low-field regime. The pump powers used were 100 mW for the 25^oC and 200^oC measurements, 300 mW for the 300^oC and 400^oC data and 500 mW for the last two temperatures. The solid lines in Fig. 1 are least-squares fits to the first-derivative of a Gaussian lineshape function (FDGF) as given by Eq. (2). Above 350^oC the data could be fit equally well by either the FDGF or the third-derivative function form (TDEF) for a three-dimensional critical point as given in Eq. (4). For the data below about 350°C the FDGF gave a somewhat better fit in relation to the TDFF. The TDFF fit is indicated by the dashed lines on the higher temperature data. The FDGF is appropriate for electromodulation of bound states such as excitons while the TDFF describes unbound states such as band-to-band transitions. The obtained energies for E_o are denoted by arrows.

The PR data for the GaAs sample indicates that there is a systematic difference between the thermocouple reading T_t and the actual substrate surface temperature T_s. At the highest temperature measurement in Fig. 1, T_t = 600°C and E_o (GaAs) = 1.049 eV. However, from Ref. 7 and Table I, this value of E_o would correspond to a surface temperature T_s = 690°C. Listed in Table II are the values of E_o, Γ, T_t and T_s, the latter deduced from the value of E_o and the data of Ref. 7 and Table I.

B. $In_xGa_{1-x}As$ (x = 0.07 and 0.16)

Another material of considerable technological interest is $In_xGa_{1-x}As$. We have studied two MBE samples of about 1 μm of $In_xGa_{1-x}As$ (x = 0.07 and 0.16) grown on 0.5 μm of GaAs on a (100) SI GaAs substrate[13]. For this thickness of epitaxial layer the lattice-mismatched strain has been relaxed. The measurements were made in the range between 15 K and 600°C. For the measurements below 300°C 5 mW of the 633 nm line of a He-Ne laser was used as the pump beam. Above this temperature several hundred mW of the 488 nm line of an Ar-ion laser were employed.

Displayed by the dotted lines in Fig. 2 are the PR spectra of the $In_{0.16}Ga_{0.84}As$ sample at 25°C, 319°C and 600°C. The solid lines are least-squares fits to Eq (4). The obtained values of E_o are designated by arrows. The 25°C spectrum displays some small Franz-Keldysh oscillations

(FKO) above the band gap. Since in the limit where the FKO are damped out[4] the lineshape is the TDFF of Eq. (4) we have used it to fit the lineshape even in the presence of small FKO.

Plotted in Fig. 3 are the temperature dependence of E_o for the x = 0.07 and 0.16 samples. The solid line is a least-squares fit to Eq. (5). The obtained values of $E_o(0)$, α and β are listed in Table I. This is the first measurement of the temperature dependence of E_o for InGaAs.

C. Real Time Measurements

In order to be useful as a control/monitoring method, it must be possible to make measurements in real time. Shown in Fig. 4 by the dotted lines is the PR spectrum of E_o of GaAs at 25°C and 650°C. The data at 650°C was taken in 30 seconds. It was found that only about 15 points are necessary to fit the lineshape (actually there are 17 points in the figure). Each point took about 2 seconds. Note that the lineshape fit (solid line) is quite good. The energy of E_o is denoted by the arrow. We believe that the data acquisition time can be reduced to one second per point for a total of 15 seconds to determine E_o and hence the temperature. Variations in temperature can be deduced in a shorter time since only a portion of the curve around the zero crossing needs to be scanned in order to evaluate shifts in E_o.

V. SUMMARY

We have made considerable progress in developing PR as an in-situ monitoring/control method for semiconductor growth. Measurements have been performed under real growth conditions including rotating substrate (about 500 rev/min.) and through a quartz diffuser plate which deflects some of the light.

We have found a systematic difference between the temperature of the GaAs substrate and a thermocouple not in contact with the sample (0.030" behind the substrate holder). A major step forward has been the substantial reduction in data acquisition time to 30 seconds so that real-time measurements are now feasible. Other important materials such as InP and $In_xGa_{x-1}As$ (x = 0.07 and 0.16) have been measured. The surface temperature of GaAs or InP substrates can be measured in real time. Also it is now possible to evaluate Al composition in GaAlAs or In content in InGaAs during actual growth.

VI. PUBLICATIONS

1. H. Shen, Z. Hang, F. H. Pollak, K. Capuder and P. E. Norris, "In-Situ Monitoring of OMVPE of GaAs and $Ga_{1-x}Al_xAs$($x \approx 0.17$) by Contacless Photoreflectance", Proceedings of the Society of Photo-Optical Instrumentation Engineers, 1186, 27 (1989).

2. Z. Hang, F. H. Pollak and H. Shen, "Photoreflectance for In-Situ Monitoring of Thin Film Growth", to be published in Vol. 1285 of the Proceedings of the Society of Photo-Optical Instrumentation Engineers.

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1. See, for example, M. Cardona in Modulation Spectroscopy (Academic, New York, 1969) and references therein.
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12. Y. P. Varshni, Physica (Utrecht) 34, 149 (1967).

13. P. Lautenschlager, M. Garriga, S. Logothetides and M. Cardona, Phys. Rev. B35, 9174 (1987).

TABLE I. Values of the Parameters $E_o(0)$, α and β for GaAs, $Ga_{0.82}Al_{0.18}As$, InP and $In_xGa_{1-x}As$ (x = 0.07 and 0.16).

MATERIAL	$E_o(0)$ (eV)	α (10^{-4} eV/K)	β (K)
GaAs[(a)]	1.512 ± 0.005	5.1 ± 0.5	190 ± 82
$Ga_{0.82}Al_{0.18}As$[(a)]	1.771 ± 0.007	6.3 ± 0.5	236 ± 73
InP	1.432 ± 0.007	4.1 ± 0.3	136 ± 60
$In_{0.07}Ga_{0.93}As$[(c)]	1.425 ± 0.006	5.0 ± 0.3	207 ± 50
$In_{0.16}Ga_{0.84}As$[(c)]	1.285 ± 0.006	5.1 ± 0.3	242 ± 50

a) Ref. 7
b) Ref. 9
c) Ref. 10

TABLE II. Variation of E_o, the Direct Band Gap of GaAs, with Temperature in an MOCVD Reactor. T_t is the thermocouple temperature while T_s is temperature deduced from E_o and the data of Ref. 7 and Table I.

E_o (eV)	T_t (^oC)	T_s (^oC)
1.428 ± 0.003	25	25
1.321 ± 0.003	200	245 ± 5
1.260 ± 0.004	300	365 ± 5
1.197 ± 0.004	400	496 ± 7
1.147 ± 0.004	500	595 ± 8
1.050 ± 0.005	600	690 ± 10

FIGURE CAPTIONS

Fig. 1 Experimental photoreflectance spectra (dotted lines) from SI (001) GaAs at various temperatures. The quantity T_t denotes the thermocouple temperature. The solid and dashed lines are least-squares filts to the first-derivative of a Gaussian form (FDGF) and a third-derivative functional form (TDFF) for a three-dimensional critical point, respectively., The obtained values of the direct gap (E_o) of GaAs are indicated by arrows.

Fig. 2. Photoreflectance spectra (dotted lines) of E_o of $In_{0.16}Ga_{0.84}As$ at 25^{o}C, 319^{o}C and 600^{o}C. The solid lines are fits to a TDFF. The obtained energies are indicated by arrows.

Fig. 3. Temperature dependence of E_o of $In_{0.07}Ga_{0.93}As$ and $In_{0.16}Ga_{0.84}As$. The solid lines are fits to Eq. (5).

Fig. 4. Photoreflectance spectra (dotted lines) of E_o of GaAs at 250^{o}C and 650^{o}C. The solid line is a fit to a lineshape function which yields the band gap energies denoted by arrows. The 650^{o}C spectrum was taken in only 30 seconds.

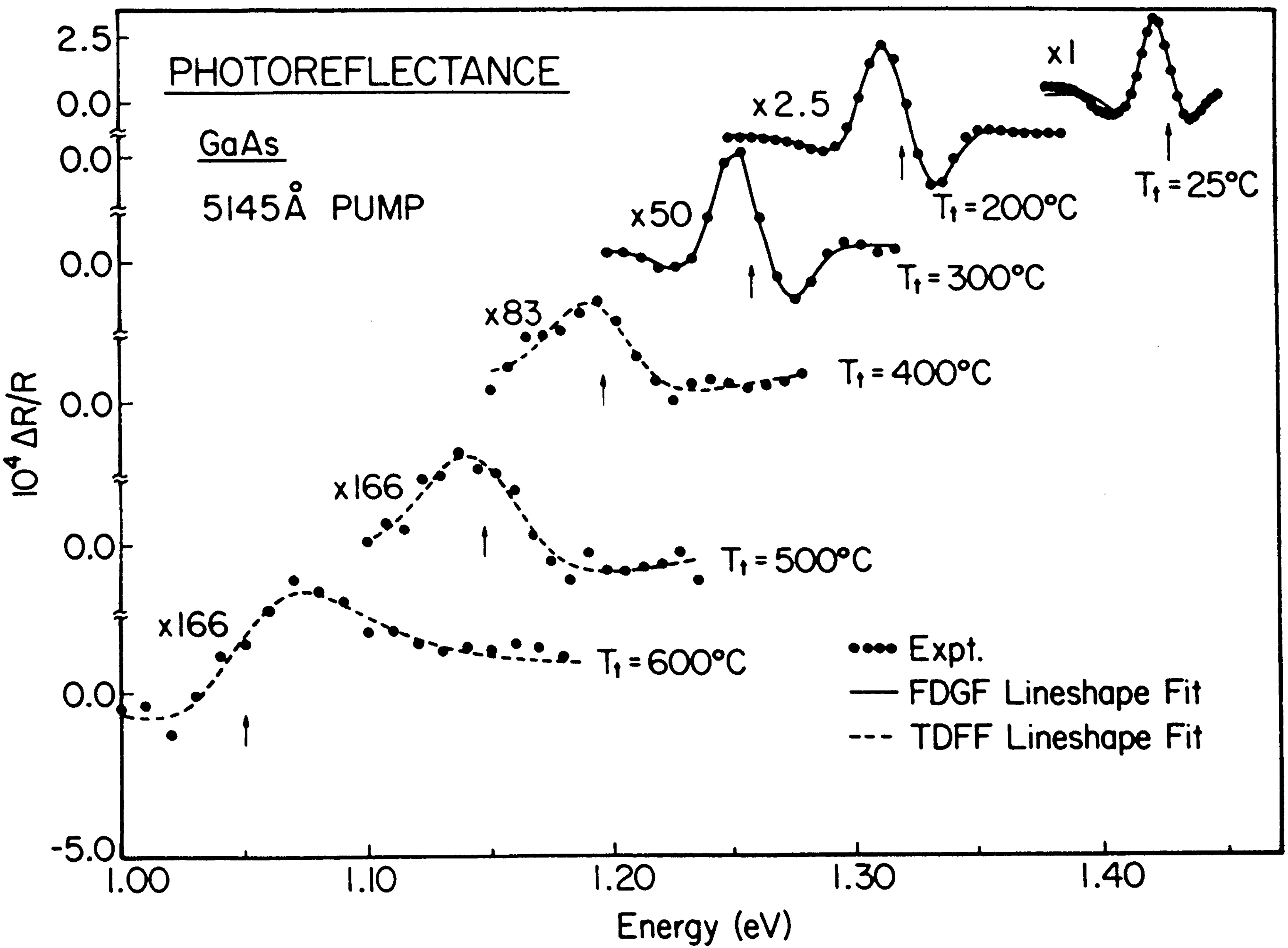
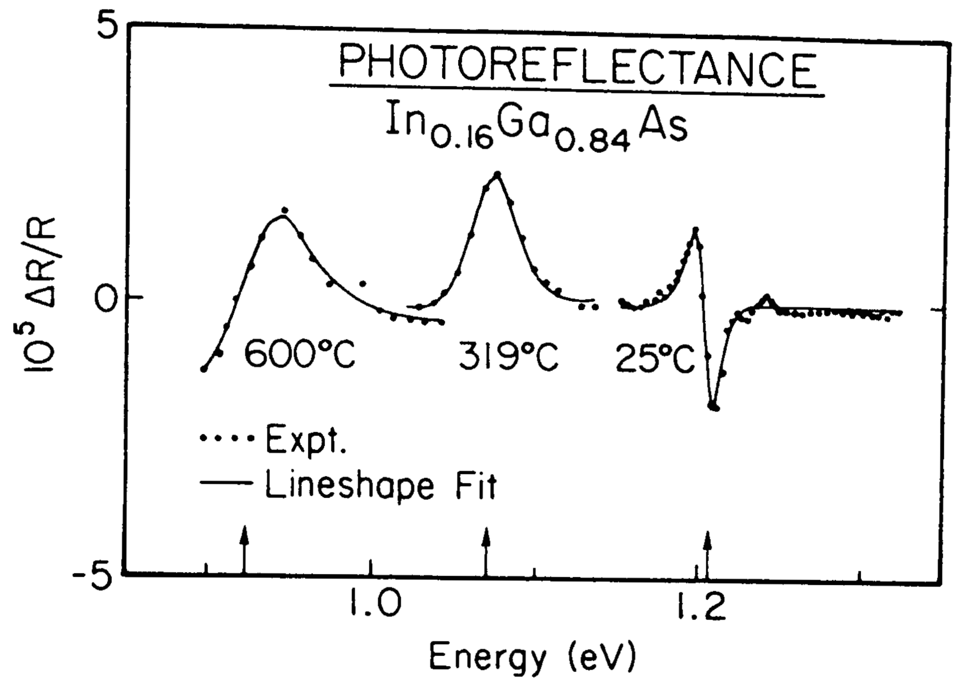
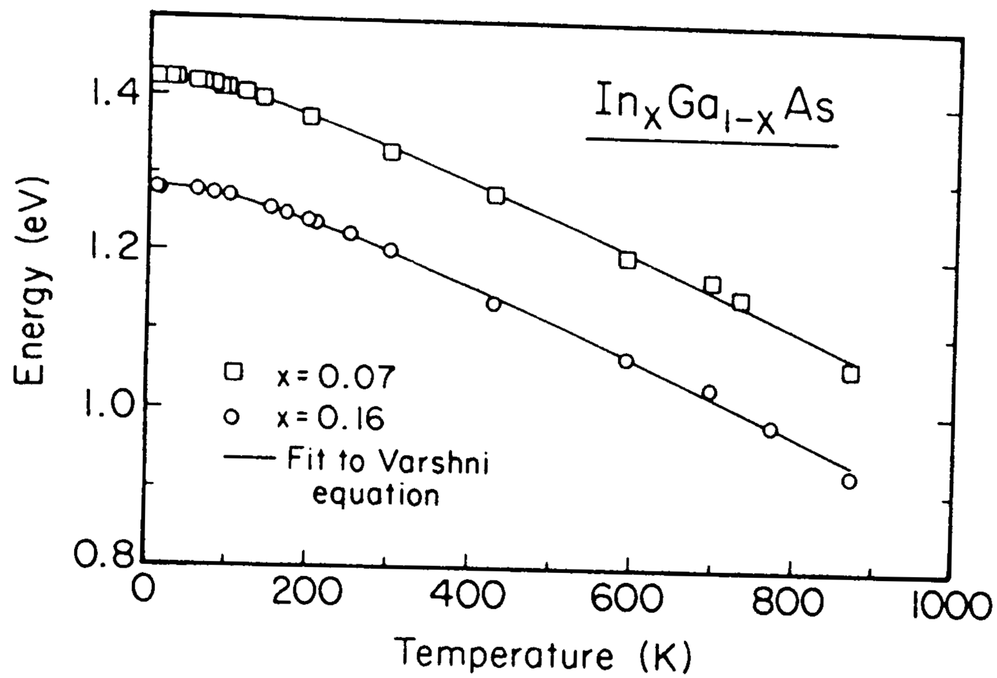

PHOTOREFLECTANCE
GaAs
5145Å PUMP
x1
x2.5
x50
x83
x166
x166
T_t = 25°C
T_t = 200°C
T_t = 300°C
T_t = 400°C
T_t = 500°C
T_t = 600°C
Expt.
FDGF Lineshape Fit
TDFF Lineshape Fit
$10^4 \Delta R/R$
2.5
0.0
-5.0
1.00
1.10
1.20
1.30
1.40
Energy (eV)

FIG. 1



PHOTOREFLECTANCE
In0.16Ga0.84As
600°C
319°C
25°C
Expt.
Lineshape Fit
5
0
-5
10^5 ΔR/R
1.0
1.2
Energy (eV)

FIG. 2



$In_xGa_{1-x}As$
x = 0.07
x = 0.16
Fit to Varshni equation
Energy (eV)
1.4
1.2
1.0
0.8
Temperature (K)
0
200
400
600
800
1000

FIG. 3

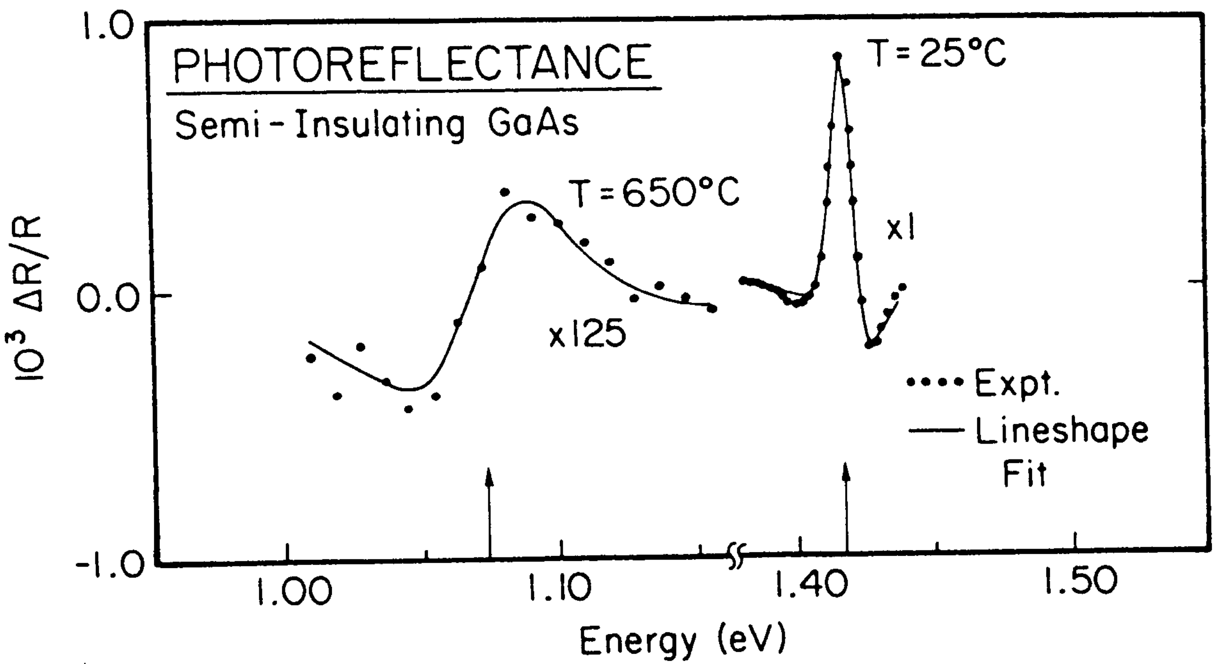

PHOTOREFLECTANCE
Semi-Insulating GaAs
T = 650°C
x125
T = 25°C
x1
Expt.
Lineshape Fit
1.0
0.0
-1.0
10^3 ΔR/R
1.00
1.10
1.40
1.50
Energy (eV)

FIG. 4