

Characterisation of Semiconductors by Differential Reflectance Spectroscopy

C. Shwe^A and M. Gal

School of Physics, University of New South Wales,
P.O. Box 1, Kensington, N.S.W. 2033, Australia.

^APermanent address: Department of Physics,
University of Mandalay, Union of Myanmar.

Abstract

We have used differential reflectance (DR) spectroscopy, an optical modulation technique which does not require external modulation, to characterise bulk semiconductors and semiconductor microstructures. DR signals are the result of inhomogeneities on or below the semiconductor surface. They may be intrinsic, such as alloy fluctuations or layer thickness variations, or externally induced, such as ion implantation, hydrogenation, etc. The DR spectra are similar to spectra measured by other modulation techniques, exhibiting sharp derivative-like lineshapes at photon energies corresponding to the critical point transitions. The magnitude of the DR signal, its position and linewidth can all be used to identify and characterise fluctuations in semiconductor parameters, for example surface electric field, alloy composition, layer thicknesses, etc. It can also be used to monitor surface damage caused by different techniques, such as hydrogenation, reactive ion etching and ion implantation.

1. Introduction

Optical modulation techniques have been widely used to study semiconductors (see Cardona 1969). Due to the derivative character of the modulated spectra, these techniques are well suited to the study of optical transitions in semiconductor layer structures and bulk samples alike. Of the many different types of modulation spectroscopies, electroreflectance, photorefectance and piezoreflectance have emerged as the most popular techniques (see Pollak 1981). These methods provide useful information about semiconductor band gaps, mole fractions, quantum well barrier heights, etc. (Glembocki 1990). In all these modulation techniques, an external perturbation such as an electric field, strain or temperature is applied to the sample to introduce the desired modulation. In this paper we shall discuss, in detail, a different type of modulation technique which does not require an external perturbation, but relies on the *spatial variation* of the semiconductor parameters to introduce the modulation. This technique, called differential reflectance (DR), is a modification of a spatial modulation experiment first used by McNatt and Handler (1969). The basic principle of spatial modulation is the fact that mechanical motion can be used as a source of optical modulation for samples that are spatially inhomogeneous. Hummel and co-workers have used DR spectroscopy to study the reflectance difference of two samples having slightly different surface properties (Hummel 1990). We have modified the DR method

to measure the optical reflectance difference of two regions of the *same* sample (Gal and Shwe 1990; Gal *et al.* 1990; Shwe and Gal 1990). If the sample is not perfectly homogeneous, the two reflectivities will differ, and a differential reflectance signal will appear. The DR spectra are similar to spectra measured by other modulation spectroscopies, exhibiting sharp derivative-like lineshapes at photon energies corresponding to critical point transitions.

In addition to revealing all critical points, DR spectroscopy turns out to be a very sensitive and efficient technique to characterise semiconductor surfaces and interfaces (Shwe *et al.* 1991). This is a consequence of the differential nature of the technique: any variation between the two regions on the *surface* of the sample will translate into a DR signal, while the unaltered sub-surface region will not contribute to the DR signal. Thus, although the penetration of light may be several microns, DR can be used to study the first few hundred angstroms of a sample. We have used this method to study different surface treatments, such as ion implantation, electron beam irradiation and hydrogenation; some of which will be discussed in this paper. Similarly, layer structures, such as quantum wells and superlattices, are obvious structures to be studied by DR. We have shown (Gal *et al.* 1990; Shwe and Gal 1990) that the DR spectra of most AlGaAs/GaAs and InGaAs/GaAs quantum wells are at least as informative as the commonly measured photorelectance (PR) spectra, and in many cases DR shows superior signal-to-noise ratio to PR.

2. Differential Reflectance Spectroscopy

As in any modulation technique, differential changes in the reflectivity can be related to the perturbation of the complex dielectric function, as given by Seraphin and Bottka (1965):

$$\frac{\Delta R}{R} = \alpha \Delta \epsilon_1 + \beta \Delta \epsilon_2,$$

where R is the reflectivity, $\Delta \epsilon_1$ and $\Delta \epsilon_2$ are changes in the complex dielectric function, and α and β are the Seraphin coefficients. While in the 'conventional' modulation techniques, ΔR represents the change in reflectivity due to the perturbation (e.g. the electric field) being turned on and off, in our case ΔR represents the difference in reflectivity between two *lateral* positions on the sample, separated by Δx . Expanding $\Delta \epsilon_1$ ($\Delta \epsilon_2$) in terms of the energy gap E_G , the broadening parameter Γ , and the oscillator strength I , we can write

$$\Delta \epsilon = \left(\frac{d\epsilon}{dE_G} \frac{dE_G}{dx} + \frac{d\epsilon}{d\Gamma} \frac{d\Gamma}{dx} + \frac{d\epsilon}{dI} \frac{dI}{dx} \right) \Delta x.$$

The origin of the spatial variation of the semiconductor parameters (e.g. dE_G/dx etc.) can be diverse: alloy fluctuations, inhomogeneous doping, strain, layer thickness differences, etc. In addition to these 'built-in' inhomogeneities, one can introduce inhomogeneities by partially altering the sample surface using methods such as ion implantation, electron or optical beam irradiation and partial oxide removal. Even a fingerprint on part of the sample perturbs the surface (field) enough to be able to detect it by the DR technique.

3. Experimental Details

The experimental arrangement of our DR spectrometer is shown schematically in Fig. 1. Light from a 250 W tungsten filament lamp is monochromated by a 0.22 m monochromator (spectral resolution approximately 3 meV) and focussed to a fine spot on the sample. An acoustic vibrator (Bruel & Kjaer Mini Shaker type 4810) enables the sample to undergo smooth vertical vibrations in a plane perpendicular to the incident light beam. As a result, light is alternately reflected from different parts of the sample, and the reflectance difference, if present, is measured as a function of the incident photon energy. The reflected light is detected and the signal is fed into a lock-in amplifier which is synchronised to the vibration frequency of the sample. The detector output has two components: an AC component due to the reflectance difference ΔR , and a DC component R which represents the *average* reflectance of the sample. A small computer calculates the ratio $\Delta R/R$ and also controls the monochromator.

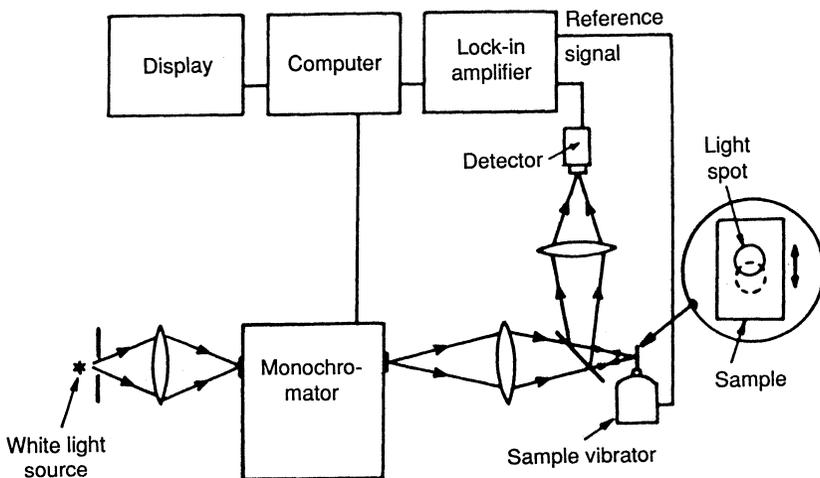


Fig. 1. Schematic diagram of the differential reflectance spectrometer.

The sample vibration amplitude can be varied by adjusting the current supplied to the driving coil of the Mini Shaker. The amplitude of vibration and the diameter of the light spot have to be chosen in such a way that the areas of the sample illuminated by the light spot are disjoint. In our experimental set-up, due to the above requirement, the spot size and amplitude of vibration are chosen to be 0.5 mm, although in some experiments we have increased (or decreased) both these values. It is observed that, for the same amplitude of vibration, the DR signals are independent of the frequency of vibration. The frequency of vibration can be varied between 10 and 140 Hz with our system. In the present experiments we have used 70 Hz as the sample vibration frequency.

For DR measurements in the 0.6 to 1.08 μm spectral range a medium area (40 mm²) silicon photodiode was used, whereas for the 0.35 to 0.6 μm spectral range a photomultiplier was used. We have found that it is advantageous to

slightly defocus the light on the detector, in order to avoid spurious signals resulting from small displacements of the light spot on the detector surface.

In DR spectroscopy, just as in any other reflection measurement, the condition of the sample surface is an important factor. Any scratch or irregularity on the surface (or part of the surface) can result in light scattering which, due to the differential nature of these measurements, can give rise to an undesired AC signal many times stronger than the real signal. By appropriate cleaning of the sample surface using methods described in the literature (Aspnes and Studna 1981), we are able to minimise the spurious signals.

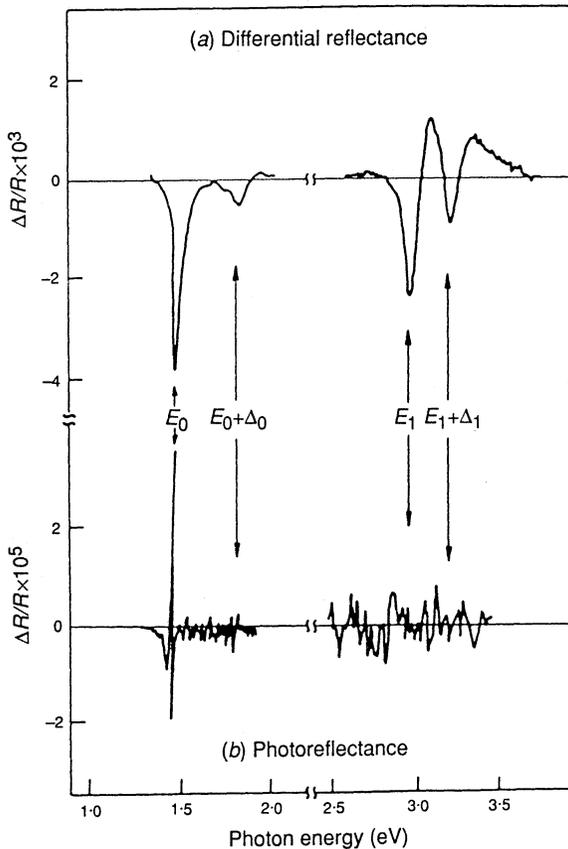


Fig. 2. Spectra of a GaAs sample implanted with 25 keV nitrogen ions, with an ion dose of 10^{12} ions cm^{-2} ($T = 300$ K): (a) differential reflectance and (b) photoreflectance.

4. Results

(a) DR of Ion Implanted Semiconductors

DR was found to be a very sensitive and efficient way to study ion implantation induced damage in semiconductors. To obtain the samples necessary for the DR measurements, we exposed one half of the surface of

the samples to the ion beam, and masked the other half with an aluminium foil during the implantation. In this way we obtained two similar samples: one implanted, the other intact. As the light spot moved across the sample, it probed the two halves of the sample that differed due to ion implantation. The resulting DR spectrum was found to exhibit sharp derivative-like features at all the critical points, similar to those found in an electroreflectance (or piezoreflectance) spectrum.

Samples used in this study were undoped (100) GaAs platelets having $5\text{ mm} \times 5\text{ mm}$ surface dimensions. The ion implantation was carried out in a Varian Extrion implanter using nitrogen ions of 25 keV energy. The ion dose, which we kept to a minimum to avoid excessive damage, was varied between 10^{10} and 10^{14} cm^{-2} . The DR spectrum of a GaAs sample implanted with 25 keV nitrogen ions, with an ion dose of $10^{12}\text{ ions cm}^{-2}$, is shown in Fig. 2a. The structure observed at 1.42 eV is the well known E_0 critical point, observed previously by electroreflectance, photoreflectance and other modulation techniques (see Cardona 1969). Apart from the E_0 critical point, the DR spectrum also shows three other critical points which are rarely seen in photoreflectance spectra. The structure at 1.76 eV corresponds to the $E_0 + \Delta_0$ transition, while the higher energy structures at 2.90 and 3.15 eV are due to the E_1 and $E_1 + \Delta_1$ transitions respectively. The energies of all the above critical points agree well with those published in the literature (Aubel *et al.* 1985). In order to compare DR with the more conventional PR technique, we measured the PR spectra of the same sample using the same experimental arrangement (except for a HeNe laser necessary for the PR experiment). The result is shown in Fig. 2b. The PR spectrum reveals only the E_0 transition, whereas all the transitions corresponding to the critical points are observed in the DR spectrum.

In addition to revealing the critical points, DR can also be used to characterise ion implantation induced damage. This is important since there are only very few experimental methods capable of detecting damage at such low ion doses and ion energies. An example of DR as a tool in characterising ion implantation is shown in Fig. 3, where we demonstrate the possibility of using DR to monitor the annealing of GaAs after ion implantation. The spectra show DR of a GaAs sample implanted with nitrogen (dose 10^{14} cm^{-2}) before (solid curve) and after (dashed curve) moderate annealing at 400°C for 30 minutes. After annealing, the amplitude as well as the width of the DR spectrum is significantly decreased. This indicates a substantial reduction in the surface damage. (The complete eradication of all damage would result in the elimination of the DR signal.)

(b) DR of Hydrogenated GaAs

DR spectroscopy has also been used to study the condition of the surface of GaAs after hydrogenation in a conventional hydrogen plasma apparatus (see Pearton *et al.* 1987), and we found evidence for significant surface damage due to the hydrogenation process. Our measurements show that defect states

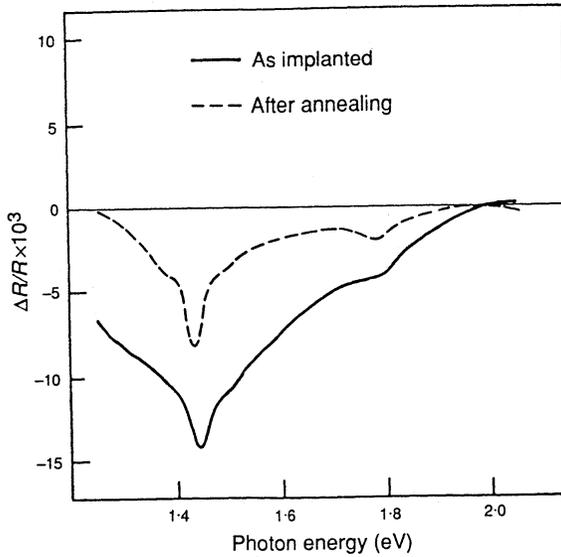


Fig. 3. Differential reflectance spectra ($T=300$ K) of a GaAs sample implanted with 25 keV nitrogen ions (dose 10^{14} ions cm^{-2}) before (solid curve) and after (dashed curve) annealing at 400°C for 30 minutes.

are created by the impinging (hydrogen) ions and that the density of these defects increases linearly with ion energy (Shwe *et al.* 1991).

The samples used in the hydrogenation experiments were liquid encapsulated Czocharalski (LEC)-grown, (100) oriented, semi-insulating GaAs platelets with dimensions $8\text{ mm} \times 4\text{ mm} \times 0.5\text{ mm}$. Hydrogen plasma exposure was performed in a conventional asymmetric diode reactive ion etching system. The plasma was excited by an 8 MHz RF source; the gas pressure during the discharge was 40 Pa. The power density could be varied between 0.004 and 0.06 W cm^{-2} , which resulted in target bias voltages between 20 and 100 V. At the high (gas) pressures used in these experiments, the bias voltage may be used as an approximate measure of the maximum ion bombardment energy (Smith *et al.* 1989). While under plasma exposure, half of the sample was masked with a 0.3 mm thick silicon wafer to obtain the reference (unhydrogenated) sample.

In Fig. 4 we show the result of a typical hydrogenation process in which special care was taken to *avoid* damage: the sample was protected from *direct* ion impact using a small 'umbrella' above the sample and was therefore affected (hydrogenated) by only very low energy, neutral H atoms that were able to diffuse into the gap between the 'umbrella' and the sample (see Fig. 4*a*). We attribute the origin of the DR signal from GaAs samples indirectly exposed to the hydrogen plasma (Fig. 4*b*) to the difference in the surface electric field due to hydrogenation. We base our assumptions on the strong similarities existing between the DR signals and electroreflectance signals, in which the electric field induced reflectance differences are measured. Although hydrogen may alter the band gap, we believe that such a low concentration of hydrogen on

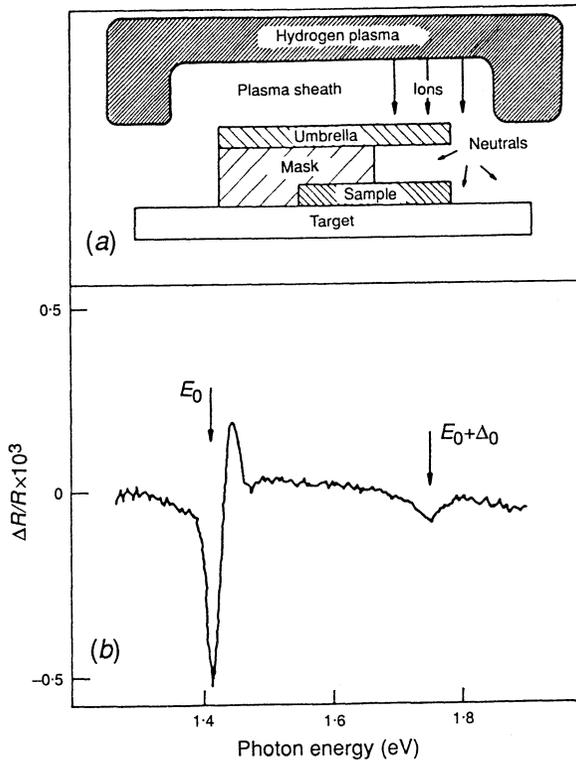


Fig. 4. (a) Experimental arrangement for the indirect exposure of a GaAs sample to the hydrogen plasma. (b) Differential reflectance spectrum ($T = 300$ K) of a GaAs sample indirectly exposed to the hydrogen plasma (40 Pa, 0.06 W cm^{-2}) for 30 minutes.

the surface of an indirectly exposed sample is unlikely to change the band gap by approximately 50 meV, which would be necessary to cause the observed signal.

In this type of *indirect* exposure to hydrogen, there is no evidence for surface damage. However, when the sample is exposed *directly* to hydrogen, as is common practice, the DR spectra change considerably: broad below-bandgap signals are observed in addition to the sharp critical point transitions that are found in the shielded samples. Such a DR spectrum is shown in Fig. 5, where a sample was directly exposed to hydrogen plasma for 30 minutes (input power 5.0 W , maximum ion energy 100 eV). These broad bands, which were found to increase in amplitude with increasing ion energy, are due to the defect states that are created by the impinging ions. Very similar DR spectra, displayed in the insert of Fig. 5, were observed for samples directly exposed to argon plasma (under the same experimental conditions as in the case of direct hydrogen plasma exposure). This suggests that the defect states are caused by ion impact and are independent of the chemical nature of the impinging ions. The density of defect states, determined from the DR spectra, shows a linear dependence on maximum ion energy (Shwe *et al.* 1991).

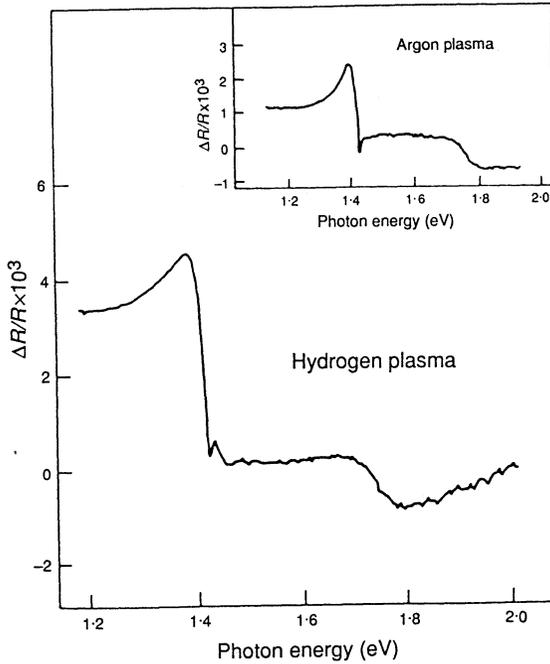


Fig. 5. Differential reflectance spectrum ($T = 300$ K) of a GaAs sample directly exposed to the hydrogen plasma (40 Pa, 0.06 W cm^{-2} , 100 eV maximum ion energy) for 30 minutes. The insert shows the DR spectrum ($T = 300$ K) of a GaAs sample directly exposed to the argon plasma for 30 minutes under the same conditions.

(c) DR of Doped Layers and Heterostructures

The DR spectra reported in this and the following subsection result from *intrinsic* inhomogeneities in the sample, such as fluctuations in one or more of the following parameters: strain, surface electric field, alloy composition (in ternary or quaternary compounds), layer thickness, dopant distribution, etc. The samples discussed in this subsection, therefore, were neither irradiated nor treated in any way. They were high quality as-grown samples, with one or more of the above-mentioned inhomogeneities present. The light spot is alternately reflected from two arbitrary parts of the sample. Due to the intrinsic inhomogeneities, this results in the differential reflectance signal.

The DR spectrum of an LEC-grown semi-insulating GaAs substrate sample is shown in the insert of Fig. 6. The structureless spectrum is an indication that the bulk GaAs is homogeneous. However, when a $2.0 \mu\text{m}$ thick n-type GaAs layer ($n = 1.0 \times 10^{18} \text{ cm}^{-3}$) was grown by molecular beam epitaxy on the above substrate, DR showed the structures displayed in Fig. 6. The prominent structure at 1.42 eV is the E_0 critical point of undoped GaAs. The emergence of this structure is due to the spatial fluctuations in the

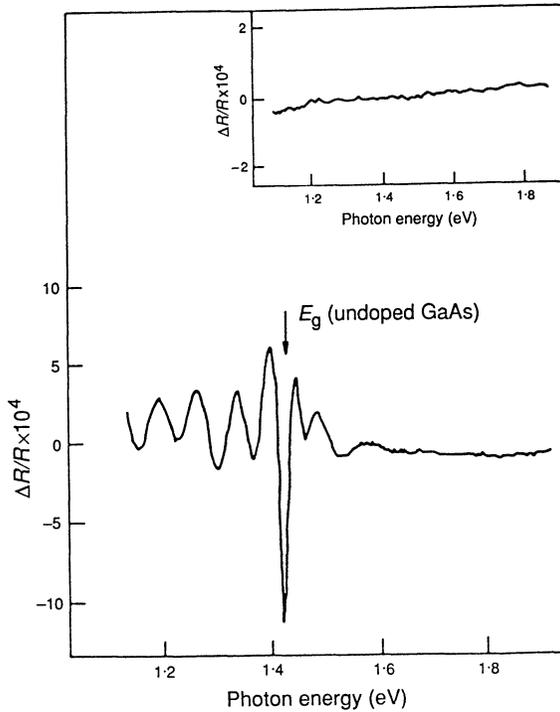


Fig. 6. Differential reflectance spectrum ($T = 300$ K) of a $2 \mu\text{m}$ thick n-type ($n = 1.0 \times 10^{18} \text{ cm}^{-3}$) GaAs epilayer grown on a semi-insulating GaAs substrate. The insert shows the DR spectrum ($T = 300$ K) of the same substrate before the epilayer growth.

fundamental bandgap energy of GaAs. These fluctuations in the bandgap energy, in this case, are the result of spatial variations in the strain or the surface field at the substrate–epilayer interface. In addition to the dominant E_0 peak, interference fringes, arising from thickness non-uniformities in the epilayer, are also observed in the DR spectrum. The onset of the interference peaks indicates the photon energy at which the doped layer is transparent to the incident light. Since the DR technique is sensitive enough to pick up slight variations in the thickness of the layer, it results in the well-defined interferences peaks (which can be used for layer thickness determination). When the layer thickness is less than approximately 2000 \AA , the interference fringes disappear, and only the critical point transitions are observed.

The DR spectrum of an AlGaAs/GaAs single heterostructure (1000 \AA thick undoped AlGaAs layer on $1 \mu\text{m}$ thick undoped GaAs grown on semi-insulating GaAs substrate), shown in Fig. 7a, reveals two structures. One at 1.42 eV is the transition associated with the fundamental gap of GaAs, while the other at 1.66 eV is that associated with the fundamental gap of AlGaAs (mole fraction $x = 0.19$). The DR signal from the AlGaAs originates from the spatial variation in the aluminium mole fraction x of the ternary compound $\text{Al}_x\text{Ga}_{1-x}\text{As}$, whereas the GaAs related structure is the result of variations in surface field and/or

strain in the GaAs layer caused by the AlGaAs capping layer. The PR spectrum of the same sample is shown in Fig. 7*b*. It is to be noted that both spectra have similar lineshapes and comparable linewidths. This demonstrates the possibility of using DR as a sensitive technique for the determination of mole fraction in ternary (or quaternary) compounds. We have also studied other heterostructures, such as InGaAs/GaAs and CdTe/CdZnTe, and have observed similar types of DR spectra arising from microscopic non-uniformities in the layers.

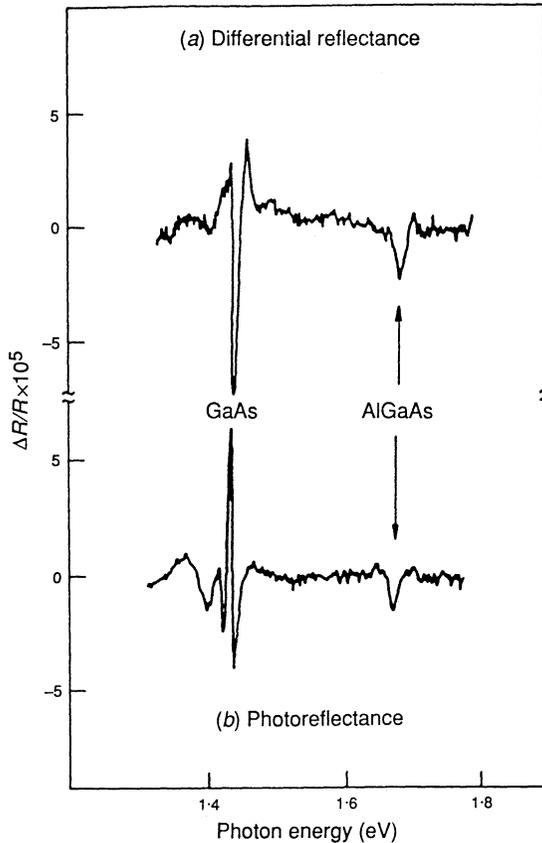


Fig. 7. (a) DR spectrum and (b) PR spectrum ($T = 300$ K) of an AlGaAs/GaAs heterostructure [1000 Å thick undoped AlGaAs (Al mole fraction of 0.19) layer on 1 μm thick undoped GaAs, grown on semi-insulating GaAs substrate].

(d) DR of AlGaAs/GaAs and InGaAs/GaAs Quantum Wells

The DR spectrum of an AlGaAs single quantum well (thickness 55 Å and Al mole fraction $x = 0.31$) is shown in Fig. 8*a*. The arrows indicate the calculated transition energies for the well using Bastard's (1981) envelope function approximation. Here $nC-mH$ ($nC-mL$) represents the transition between the n th conduction level and the m th heavy (light) hole valance level. The

DR spectrum reveals all the allowed transitions of the quantum well; whereas the PR spectrum of the same sample, displayed in Fig. 8b, is less informative than DR (for this particular sample).

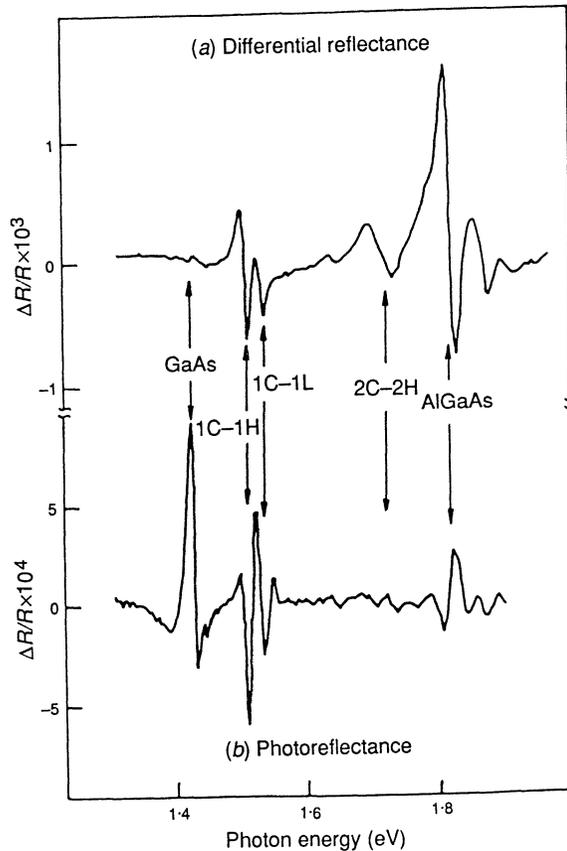


Fig. 8. (a) DR spectrum and (b) PR spectrum ($T = 300$ K) of an AlGaAs/GaAs single quantum well (with a well width of 55 Å and Al mole fraction of 0.31).

The distinct and well-defined signals representing the quantum well transitions signify the spatial fluctuations of its energy levels as a result of variations in the well parameters in the region probed by the incident light. There is now increasing evidence from a number of different experiments (Warwick *et al.* 1990) that quantum well interfaces of the highest quality are not atomically smooth, as originally thought. These spatial fluctuations in the well parameters are the most likely causes of the DR signals. It is interesting to note that the oscillations observed in the DR spectrum at energies above the AlGaAs band gap (1.82 eV) may be Franz-Keldysh oscillations. Since these oscillations are characteristic of electric field modulation (Cardona 1969), inhomogeneities in the surface field distribution may also contribute to the DR signals.

We have also studied InGaAs/GaAs quantum wells. In this lattice mismatched system, the origin of the DR signals in addition to alloy fluctuations and interface

roughness is most likely strain. The DR spectrum of an $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ single quantum well (thickness 110 Å and $x=0.24$) is compared with the calculated transitions (Ji *et al.* 1987) in Fig. 9a. The agreement is excellent, demonstrating the value of DR as a spectroscopic tool. It is interesting to note that the DR signal corresponding to the GaAs band gap in Fig. 9a is much stronger than the corresponding transition in the AlGaAs/GaAs quantum well (see Fig. 8a). This behaviour can be attributed to the spatial variation of strain in the GaAs capping layer on the InGaAs layer. It has also been shown previously that in the InGaAs/GaAs system the compressively strained InGaAs layer introduces an amount of tensile strain in the GaAs capping layer (Gal *et al.* 1988).

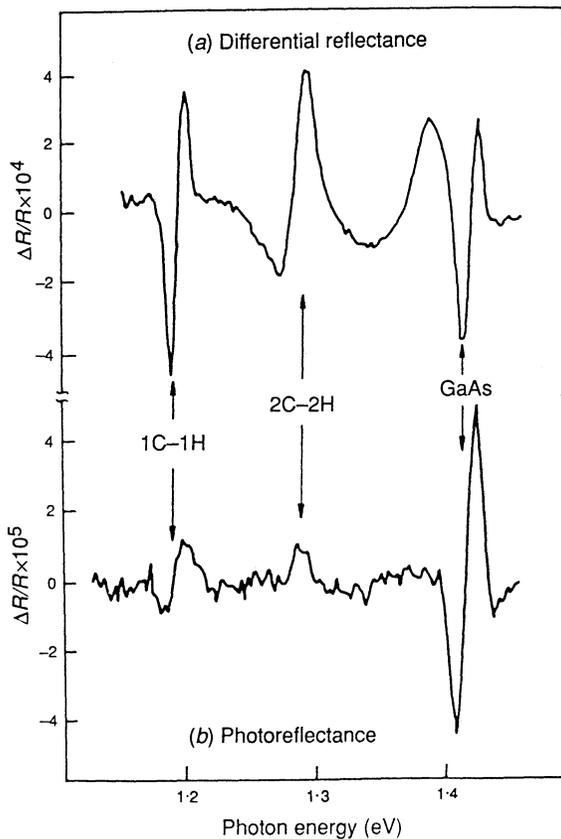


Fig. 9. (a) DR spectrum and (b) PR spectrum ($T=300$ K) of an InGaAs/GaAs single quantum well (with a well width of 110 Å and In mole fraction of 0.24).

The presence of spatial inhomogeneities in InGaAs, even in high quality MBE-grown layers, has been observed by others. Penna *et al.* (1984) reported 1.5 meV bandgap variations over a distance of 1 mm in lattice matched MBE-grown InGaAs/InP layers from photoluminescence (PL) studies. We have also confirmed the existence of such inhomogeneities in our samples, using PL measurements. The observed variation in the PL peak energy (corresponding

to the lowest energy transition in the quantum well) was found to be as large as 3.5 meV over distances of 2–3 mm (Shwe and Gal 1990). Since our samples are strained layers, our larger value compared with that of Penna *et al.* is understandable.

The PR spectrum of the same sample is displayed in Fig. 9b. The transition energies from PR and DR spectra agree, within the experimental resolution of the spectrometer. The most striking feature is the superiority of signal-to-noise ratio in the DR spectrum compared with the room temperature PR spectrum.

5. Conclusions

We have used differential reflectance spectroscopy to characterise bulk semiconductors and microstructures. The DR spectra originate from the intrinsic inhomogeneities in the semiconductor parameters, such as strain, surface field, alloy composition, layer thickness, dopant distribution, or externally induced surface treatments, such as ion implantation, hydrogenation, electron or optical beam irradiation. The DR spectra reveal sharp critical point structures as those measured by other modulation techniques. The DR spectra are as informative as photoreflectance spectra of the same samples and show a superior signal-to-noise ratio. As a consequence of the differential nature, DR spectroscopy shows a potential application for the study of surface damage in semiconductors.

Acknowledgments

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References

- Aspnes, D. E., and Studna, A. A. (1981). *Appl. Phys. Lett.* **393**, 316.
- Aubel, J. L., Reddy, U. K., Sundaram, S., Beard, W. T., and Comas, J. (1985). *J. Appl. Phys.* **58**, 495.
- Bastard, G. (1981). *Phys. Rev. B* **24**, 5693.
- Cardona, M. (1969). In 'Modulation Spectroscopy' (Eds F. Seitz *et al.*), p. 1 (Academic: New York).
- Gal, M., Orders, P. J., Usher, B. F., Joyce, M. J., and Tann, J. (1988). *Appl. Phys. Lett.* **53**, 113.
- Gal, M., and Shwe, C. (1990). *Appl. Phys. Lett.* **56**, 545.
- Gal, M., Shwe, C., Tann, J., McMillan, P., Gross, M., and Shi, R. (1990). Proceedings Society of Photo-Optical Instrumentation Engineers (SPIE) **1286**, 136.
- Glembocki, O. J. (1990). Proceedings SPIE **1286**, 2.
- Hummel, R. E. (1990). Proceedings SPIE **1286**, 146.
- Ji, G., Huang, D., Reddy, U. K., Henderson, T. S., Houdre, R., and Morkoc, H. (1987). *J. Appl. Phys.* **62**, 3366.
- McNatt, J. L., and Handler, P. (1969). *Phys. Rev.* **178**, 1328.
- Pearton, S. J., Corbett, J. W., and Shi, T. S. (1987). *Appl. Phys. A* **43**, 153.
- Penna, A. F. S., Jagdeep, S., Chang, T. Y., Burroughs, M. S., Nahory, R. E., Tamargo, M., and Cox, H. M. (1984). *Solid State Commun.* **51**, 425.
- Pollak, F. H. (1981). Proceedings SPIE **276**, 142.
- Seraphin, B. O., and Bottka, N. (1965). *Phys. Rev.* **139**, A560.
- Shwe, C., and Gal, M. (1990). *Appl. Phys. Lett.* **57**, 1910.
- Shwe, C., Gal, M., and Gross, M. (1991). *J. Vac. Sci. Tech. A* **9**, 2683.
- Smith, A. M., Beilby, B. N., and Horwitz, C. M. (1989). *J. Vac. Sci. Technol. A* **7**, 3332.
- Warwick, C. A., Jan, W. Y., Ourmazd, A., and Harris, T. D. (1990). *Appl. Phys. Lett.* **56**, 2666.

