

Surface potential inversion of thermal annealed GaAs (001) observed by reflectance-difference spectroscopy

R.E. BALDERAS-NAVARRO, M.A. VIDAL-BORBOLLA,
A. LASTRAS-MARTÍNEZ AND L.F. LASTRAS-MARTÍNEZ

*Instituto de Investigación en Comunicación Óptica
Universidad Autónoma de San Luis Potosí
Alvaro Obregón 64, 78000 San Luis Potosí, México*

Recibido el 20 de abril de 1993; aceptado el 17 de septiembre de 1993

ABSTRACT. Reflectance-difference spectroscopy measurements in the 2.5–3.5 eV energy range have been used to study surface potential inversion in semiinsulating GaAs (001), as induced by thermal annealing in a H₂ atmosphere at temperatures up to 600 °C. The electro-optic component of the reflectance difference spectra is dependent of both, magnitude and direction of the GaAs surface electric-field. Taking this into account, the surface potential inversion process is followed through the evolution of the linear electro-optic component of the reflectance-difference spectrum. The technique described in this paper turns out to be sensitive to atomic layers in a depth of 100–200 Å, which allows us to follow the first stages of the surface potential inversion process.

RESUMEN. Se reporta el empleo de la espectroscopía de reflectancia-diferencial para el estudio del proceso de inversión del potencial superficial en GaAs semiaislante, inducido por calentamiento en atmósfera de H₂ a temperaturas de hasta 600 °C. Tomando ventaja del hecho de que la componente electro-óptica de espectro de reflectividad superficial en GaAs (001) depende tanto de la magnitud como del sentido del campo eléctrico superficial, el proceso de inversión del potencial se sigue a través de la evolución de la forma de línea de dicha componente. La técnica descrita en este artículo tiene una resolución en profundidad de 100–200 Å, lo cual permite el estudio de las primeras etapas del proceso de inversión del potencial superficial.

PACS: 78.65.Fa; 78.20.Jq

1. INTRODUCTION

GaAs is a most important substrate material for the epitaxial growth of semiconductor films in the optoelectronics, high speed electronics and integrated circuit fields. As the device fabrication processes commonly call for the exposure of the substrate to high-temperature annealing, the study of the thermal-induced changes occurring close to the GaAs surface have received much attention in the past [1–6].

A well known surface phenomenon occurring in thermal-annealed n-type or semiinsulating GaAs is that of thermal conversion to p-type. Thermal conversion from semiinsulating GaAs to p-type was first reported almost twenty five years ago [1,2]. Since then, a series of studies carried on with, both, semiinsulating and n-type crystals have been reported,

which confirmed the early findings and made evident the complexity of the phenomena involved [3–10]. Surface thermal conversion in GaAs is commonly associated to temperature activated processes such as surface generation of As or Ga vacancies or defect complexes, and their subsequent diffusion into the semiconductor bulk [1–10].

Several experimental techniques have been employed to study p-type surface conversion in GaAs, including capacitance-voltage measurements [2,3,5,6], Hall effect [1,6,7], photoluminescence [3,4,5,7] and infrared plasma reflectance [3]. An important parameter for a technique intended for studying surface conversion is that of probing depth. For techniques such as C-V this probing depth is that of the Schottky barrier thickness, while for photoluminescence it is equal to the minority carrier diffusion length. Typically, for these two techniques we may expect probing depths of the order of 0.1–1 micrometer.

The purpose of this communication is to show that reflectance-difference spectroscopy (RDS) constitutes a sensitive probe for the study of the p-type surface conversion process. RDS probes a depth of 100–200 Å, which is at least one order of magnitude lower than that of more conventional techniques. This allows us to follow in detail the first stages of such a process.

2. REFLECTANCE-DIFFERENCE SPECTROSCOPY

RDS measures the difference in optical reflectivity between two mutually orthogonal polarizations. The working principle of RDS is based on the fact that, as the bulk optical properties of cubic semiconductors are nominally isotropic, any observed anisotropy in the reflectance spectrum should be associated to the breakdown of the cubic symmetry at the semiconductor surface [11,12]. Then, by measuring the difference in reflectance for two mutually orthogonal light polarizations, the bulk contribution to the sample reflectivity should be canceled remaining only the surface contribution.

The RD spectrum of the (001) surface of GaAs is rather complex, comprising a number of components with various physical origins. Among the physical mechanisms giving rise to RD spectra contributions we will mention linear electro-optic effects [13], surface dimmers [14] and surface roughness [15]. The results reported in this note are based on the measurement of the electro-optic contribution which, as discussed below, is directly associated to the surface potential.

Linear electro-optic effects in the RD spectrum of GaAs (001) arise because of the breakdown of the zincblende cubic symmetry due to the surface electric field at the oxidized surface of the semiconductor [13]. As it is well known, this field arises because of the pinning of the Fermi level at the energy of the surface states [16]. Depending of the semiconductor doping level, the surface field extends hundreds of atomic layers into the bulk with a maximum value at the surface given by

$$|E_{\max}| = \left(\frac{2qV_d N}{\epsilon_s} \right)^{1/2}, \quad (1)$$

where q is the electron charge, V_d is the surface voltage, N is the impurity concentration

and, ϵ_s is the semiconductor permittivity. The sign of the electric field depends on the conductivity type of the semiconductor.

According to Eq. (1), the amplitude of the linear electro-optic RD spectrum is proportional to the square root of the impurity level. Further, as expected for a linear electro-optical phenomenon, the phase of the electro-optic RD lineshape depends on the conductivity type of the semiconductor near the surface [12,13]. As it was shown previously [12,13], linear electro-optical component in GaAs (001) is most prominent in the spectral region around E_1 (2.92 eV) and $E_1 + \Delta_1$ (3.13 eV) optical transitions. The linear electro-optic lineshape in such a spectral region roughly consists of an oscillation with extreme points near E_1 and $E_1 + \Delta_1$.

3. EXPERIMENTAL

The RD measurements were carried out with a spectrometer which employs a photoelastic modulator to modulate the polarization of the light incident on the sample. The spectrometer is schematically shown in Fig. 1. In this set up, light coming out from a 75 watts arc Xenon lamp is focused at the entrance slit of a 0.25 m monochromator. An arrangement of two 50 cm focal length mirrors (Mg coated for enhanced UV reflectivity) directs the light beam at the output of the monochromator through a polarizer prism (quartz Rochon) and a photoelastic modulator in tandem, and focuses it on the sample surface with an angle of incidence of 3 about degrees. Upon reflection, the light beam is depolarized and focused on a UV enhanced silicon photodetector which has been matched to a TL071 operational amplifier. The photodetector/amplifier combination has a flat response up to 100 KHz [17]. The electric signal at the output of the photodetector is processed by a lock-in amplifier tuned to twice the operating frequency of the photoelastic modulator (50 KHz). The spectrometer is controlled by a microcomputer. Further details on the spectrometer are given elsewhere [18].

For the measurements we employed boat-grown semiinsulating GaAs:Cr wafers oriented in the (001) direction. The crystals were supplied by Bertram Laboratories Inc. (North Branch, New Jersey) and were used as received (the supplier indicated that the crystals were given a chemo-mechanical polish with 10 H₂O:1 NaOCl:1 Nalco 2360). For the sake of comparison, we made some measurements with samples chemically polished with a solution of 1 H₂O₂:3H₂SO₄:1 H₂O at 80 °C and no significant differences were found. Prior to mounting in the spectrometer, the samples were rinsed in isopropyl alcohol and dried with a nitrogen flux. Sample annealing was carried out in hydrogen at temperatures up to 600 °C during periods of 15–30 min. After each period of time the DR spectrum was measured at room temperature in order to determine its evolution with annealing time and temperature.

4. RESULTS

In Fig. 2 we show RD spectra for various annealing temperatures and annealing times as indicated. The RD spectrum evolution with successive annealing is complex, involving

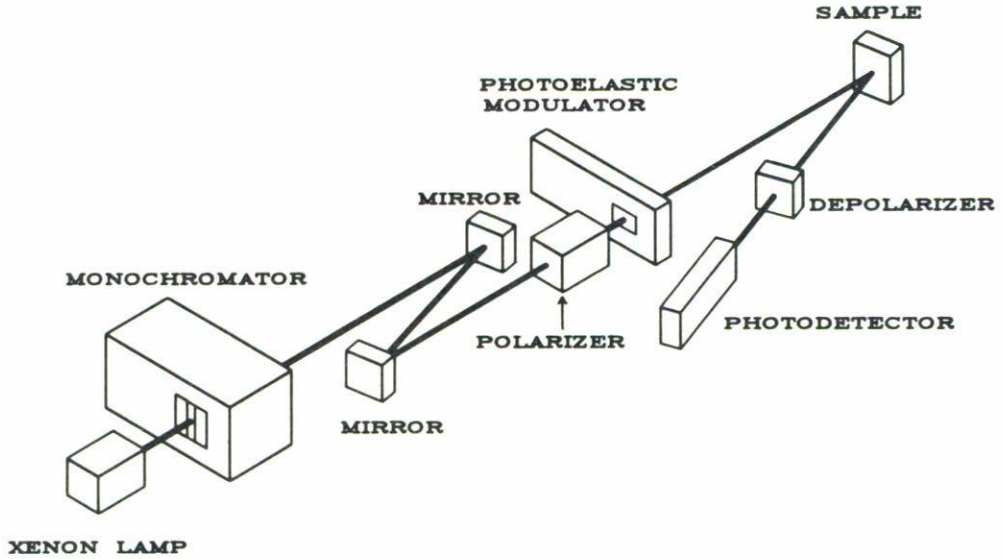


FIGURE 1. Schematics of RDS spectrometer.

components associated to oxide layers, surface roughness [15] and linear electro-optic effects [13]. It is not the purpose of this paper to discuss in detail the overall evolution of the RD spectrum which will be considered elsewhere. Instead, we will focus on the evolution of the electro-optic component around 3.0 eV which, as stressed above, is directly associated to the surface potential. Inspection of the upper curve of Fig. 2 shows that the linear electro-optic component for the non-treated sample is small, indicating that the surface electric field is small as expected for a semiinsulating sample. After a first annealing at 550 °C we observe a large change in the RD lineshape, which is associated to the desorption of oxide layer on the GaAs surface. After this first annealing, we do not observe an appreciable increase in the electro-optic component. After annealing at 580 °C (fifth curve from top to bottom) we do observe a significant change in the RD lineshape which is due to an increase of the GaAs surface roughness [15]. No appreciable change in the electro-optic component is still found. In contrast, after annealing at 600 °C (bottom curve) a large increase in the RD electro-optic component is observed, indicating that an increment in the surface field had finally occurred.

We further note that the RD electro-optic component corresponds to that of a p-type material [12]. To make this more evident, in Fig. 3 we show the bottom curve of Fig. 2 along with the RD spectra for, both, a p-type GaAs sample doped with Zn accepters at a level of $4 \times 10^{17} \text{ cm}^{-3}$ and an undoped sample doped with residual donors at a level of $5.5 \times 10^{16} \text{ cm}^{-3}$. The coincidence of the oscillators around 3 eV (which correspond to the electro-optic component lineshape [13]) in the RD spectra for the annealed sample and the p-type sample is remarkable. In contrast, for the n-type sample such an oscillation is out of phase by π radians.

We note that RDS as employed in this paper probes a surface whose width is either the light penetration depth or the surface barrier width, whichever is smaller. For a photon energy of 3 eV the light penetration depth in GaAs is about 170 angstroms, while the

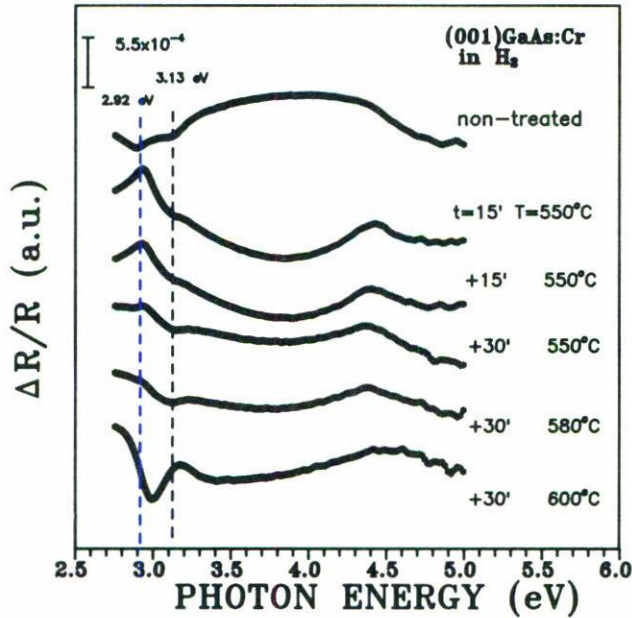


FIGURE 2. RDS spectra for Cr-doped GaAs (001) single-crystals, for various annealing temperatures and annealing times as indicated.

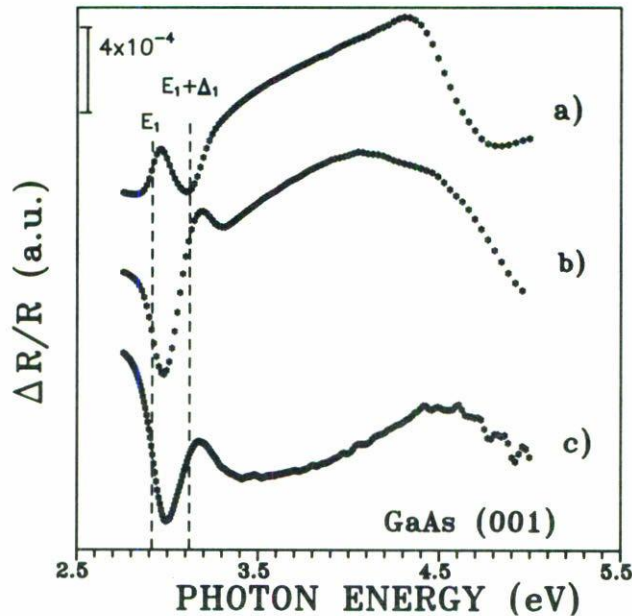


FIGURE 3. GaAs (001) RDS spectra. a) Undoped n-type crystal; $n = 5.6 \times 10^{16} \text{ cm}^{-3}$. b) Zn-doped p-type sample; $p = 2.9 \times 10^{18} \text{ cm}^{-3}$. c) Bottom curve of Fig. 2.

surface barrier width depends on the doping level near the surface and is smaller than 200 angstroms for n and $p > 5 \times 10^{18} \text{ cm}^{-3}$. In any case, the technique probes only the region where there exists a band bending, in contrast to techniques such as photoluminescence

or plasma reflection which probe a neutral region beyond the surface barrier as well. A depth resolution of 200 Å allows RDS to study the first stages of the surface potential inversion process with greater detail than more conventional techniques.

In conclusion, we have shown in this paper that RDS constitutes a sensitive probe for the study of surface potential evolution in GaAs (001) surfaces under thermal annealing. Further, although the measurements reported in this paper were done *ex situ*, RDS is well suited to carry out in situ measurements. The depth resolution attainable with RDS indicates that a quantification of the parameters characteristic of the early stages of the diffusion process, such as the diffusion coefficient for the p-type thermal impurities is possible. Presently, work is under progress in our laboratory in this direction.

ACKNOWLEDGMENTS

The authors would like to thank H. Navarro-Contreras for critical reading of the manuscript. This work was supported by Secretaría de Educación Pública (Fondo para la Modernización de la Educación Superior), Consejo Nacional de Ciencia y Tecnología, Organization of American States and Fondo de Ayuda para la Investigación.

REFERENCES

1. M. Toyama, *J.J. Appl. Phys.* **8** (1969) 1000.
2. E. Muñoz, W.L. Snyder and J.L. Moll, *Appl. Phys. Letts.* **16** (1970) 262.
3. S.Y. Chiang and G.L. Pearson, *J. Appl. Phys.* **46** (1975) 2986.
4. Nguyen Hong Ky, L. Pavesi, D. Araujo, J.D. Ganiere and F.K. Reinhart, *J. Appl. Phys.* **70** (1991) 3887.
5. W.Y. Lum and H.H. Wieder, *Appl. Phys. Lett.* **31** (1977) 213.
6. S. Chichibu, N. Ohkubo and S. Matsumoto, *J.J. Appl. Phys.* **28** (1989) 1750.
7. N. Ohkubo, M. Shishikura and S. Matsumoto, *J. Appl. Phys.* **73** (1993) 615.
8. Richard A. Morrow, *J. Appl. Phys.* **69** (1991) 3396.
9. D.C. Look, P.W. Yu, W.M. Theis, W. Ford, G. Mathur, J.R. Sizelove, D.H. Lee and S.S. Li, *Appl. Phys. Letts.* **49** (1986) 1083.
10. J. Lagowski, H.C. Gatos, C.H. Kang, M. Skowronsky, K.Y. Ko and D.G. Lin, *Appl. Phys. Lett.* **49** (1986) 892.
11. D.E. Aspnes and A.A. Studna, *Phys. Rev. Lett.* **54** (1985) 1956.
12. S.E. Acosta-Ortíz and A. Lastras-Martínez, *Solid. State. Commun.* **64** (1987) 809.
13. S.E. Acosta-Ortíz and A. Lastras-Martínez, *Phys. Rev.* **B40** (1989) 1426.
14. I. Kamiya, D.E. Aspnes, H. Tanaka, L.T. Florez, J.P. Harbison and R. Bhat, *J. Vac. Sci. Technol.* **B10** (1992) 1716.
15. L.F. Lastras-Martínez and A. Lastras-Martínez (to be published elsewhere).
16. W. Monch, *Surf. Sci.* **132** (1983) 92.
17. L.F. Lastras-Martínez, M.D. Thesis, Universidad Autónoma de San Luis Potosí (1990).
18. L.F. Lastras-Martínez, A. Lastras-Martínez and R.E. Balderas-Navarro, *Rev. Sci. Instrum.* **8** (1993) 2147.