Photoreflectance of intrinsic GaAs epitaxial layers grown by LPE with supercooling

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ABSTRACT. In this work we have characterized a set of GaAs epitaxial layers, grown by Liquid Phase Epitaxy (LPE) by using Photoreflectance Spectroscopy (PR). The variable parameter during growth was the supercooling, ΔT, which is the difference between the melt saturation temperature and the initial growth temperature. The sample crystalline quality favored the presence of Frank-Keldysh oscillations in the PR spectra. The analysis of these F-K oscillations has shown that when the supercooling increases in the range 0–14.7 °C, there is a monotonic increase in the density of ionized impurities. Further, for ΔT greater than 6.4 °C the nature of the impurities changes.

RESUMEN. En este trabajo hemos caracterizado un conjunto de películas epitaxiales de GaAs crecidas por la técnica de epitaxia en fase líquida (LPE), usando la espectroscopía de fotorreflectancia (FR). El parámetro variable durante el crecimiento fue el superenfriamiento, ΔT, que es la diferencia entre la temperatura de saturación de la solución y la temperatura inicial de crecimiento. La calidad cristalina de las muestras favoreció la presencia de las oscilaciones de Franz-Keldysh en los espectros de FR. El análisis de estas oscilaciones de F-K ha mostrado que al aumentar el superenfriamiento en el intervalo 0–14 °C, aumenta en forma monótona la densidad de impurezas ionizadas, aunque a partir de un ΔT mayor a 6.4 °C, la naturaleza de dichas impurezas cambia.

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1. INTRODUCTION

Photoreflectance spectroscopy has become to be considered as one of the more important characterization techniques for the study of semiconductor materials, mainly because it

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is a non-destructive technique and because even at room temperature it produces information equivalent to that furnished by other characterization techniques requiring low temperatures. In particular, the bandgap energy and as a consequence the stoichiometry of ternary semiconductors such as AlGaAs and HgCdTe can be obtained directly from the spectral position and the lineshape of the PR spectra [1]. Recently, it has been shown that the PR spectroscopy can be used in the determination of the Mott-Schottky parameters in the space charge region in semiconductors [2], in the study of deep levels [3], in the determination of residual impurities [4], and in the investigation of superlattices and quantum wells [5,6].

In this work we present experimental results of PR spectra measured at room temperature on GaAs intrinsic epitaxial layers deposited by liquid phase epitaxy (LPE), in which only one parameter was changed: the amount of supercooling in the melt when the layer growth starts. We show that the surface electric field at the layer is sensitive to the amount of supercooling, and discuss the type of defects introduced during the growth process.

2. THEORETICAL

In the photoreflectance spectroscopy the electric field in the space charge region of the semiconductor is modulated by the photoinjection of electron-hole pairs created by a secondary light beam [7]. The spectra obtained present some structural characteristics in the vicinity of the Van Hove singularities [8]. The spectral lineshape is determined by excitonic effects [9], dispersion processes [10], and the Mott-Schottky parameters [2]. Different regimes result from the comparison between the electrooptic energy $\hbar\Omega$ and the broadening phenomenological parameter Γ. Bottka *et al.* [1] have reviewed the applications of such regimes in terms of the spectral characteristics. The intermediate-field regime, in which we are interested in this work, takes place when $\hbar\Omega \geq \Gamma$. For these conditions the PR spectra show the presence of Franz-Keldysh oscillations, whose asymptotic expression corresponding to an M_0–type point is given by [9]

$$\frac{\Delta R}{R} = \frac{C}{\hbar\omega - E_g} \exp\left[-\frac{\Gamma(\hbar\omega - E_g)^{1/2}}{(\hbar\Omega)^{3/2}}\right] \cos\left[\phi + \frac{2}{3}\left(\frac{\hbar\omega - E_g}{\hbar\Omega}\right)^{3/2}\right], \tag{1}$$

where C is an amplitude factor, E_g is the bandgap energy, $\hbar\omega$ is the energy of the incident photon (probing light) and ϕ is a phase factor.

The electrooptic energy is defined by

$$(\hbar\Omega)^3 = \frac{(e\hbar\epsilon)^2}{8\mu_{\|}}, \tag{2}$$

where ϵ is the surface electric field and $\mu_{\|}$ is the interband reduced mass in the direction of the electric field. The F-K oscillations can be analyzed using the energy values for the maxima and minima in such oscillations $(\hbar\omega)_j$:

$$(\hbar\omega)_j = (\hbar\Omega)F_j + E_g, \tag{3}$$

where

$$F_j = \left[\frac{3\pi\left(j - \frac{1}{2}\right)}{2}\right]^{\frac{2}{3}}, \tag{4}$$

and the j-index can take only integer successive values. This means that in an experimental plot of the $(\hbar\omega)_j$ *vs.* F_j, we will be able to determine the electrooptic energy (slope), and the bandgap energy (intersection with the vertical axis).

In the space charge region the Mott-Schottky model give us a relationship between the electric field and the density of ionized impurities, and as a consequence with the electrooptic energy:

$$\hbar\Omega \sim \epsilon^{2/3} \sim (N_d - N_a)^{1/3}, \tag{5}$$

where N_d and N_a are the density of donor and acceptor ionized impurity densities respectively.

3. EXPERIMENTAL DETAILS

The GaAs epitaxial layers were grown on n^+–GaAs substrates impurified with Si ($n \sim 2 \times 10^{18}$ cm^{-3}), by using the LPE technique with a conventional horizontal system as the one used in Ref. [11]. The growth conditions were all the same except by the initial growth temperature, T_{ig}, as indicated in Table I. In this table it is also shown the temperature at which the cooling ramp was initiated, T_i, which was in all cases approximately 3 °C above T_{ig}. The fixed parameters in each one of the growths are also indicated in Table I: the Ga and GaAs weights in the growth melt, W_{Ga} and W_{GaAs} respectively; the cooling rate, R; and the time of growth, t_g. The saturation temperature, T_s, had a value of 803.4 °C. The supercooling parameter ΔT was changed in the range from 0 to 14.7 °C, corresponding to samples labeled 108 and 100 respectively.

PR spectra were obtained at room temperature in an automatized system as described in Ref. [12]. As the modulated and exciting light source the 6328 Å–line of a He–Ne laser was used with a nominal power density of 15 mW/cm^2 chopped at a frequency of 213 Hz. The PR signal was optimized by using two crossed polarizers: a Glan-Thompson to improve the laser polarization, and an analyzer placed in front of the detector to minimize the diffusive dispersion coming from the surface sample.

4. RESULTS AND DISCUSSION

In Figs. 1 and 3 we show the photoreflectance spectra corresponding to samples presented in Table I. Spectra in Fig. 1 show the typical lineshape of a PR spectrum, presenting Franz-Keldysh oscillations at high energies. Continuous curves in Fig. 1 correspond to the best fittings of Eq. (1). In Table II we present the values for E_g, $\hbar\Omega$ and Γ, obtained from the fitting process. From the electrooptic energy, $\hbar\Omega$, and using a reduced interband

TABLE I. Growth conditions for the set of intrinsic GaAs epitaxial layers studied by photoreflectance. T_i corresponds to the temperature at which the cooling ramp in the LPE process was started, and T_{ig} is the temperature at which the melt was brought in contact with the substrate. R is the rate of cooling, and t_g the growth time. $W_{Ga} = 2.00001 \pm 0.00004$ gr; $W_{GaAs} = 92.58 \pm 0.04$ mg; $R = 0.24 \pm 0.02$ °C/min; $t_g = 10$ min.

Sample	T_i (°C)	T_{ig} (°C)
100	791.7	788.7
99	793.6	790.5
98	795.0	791.9
97	797.7	794.7
103	800.2	797.0
104	802.1	799.1
105	803.7	800.7
111	805.5	802.0
106	806.0	803.0
108	807.0	804.0

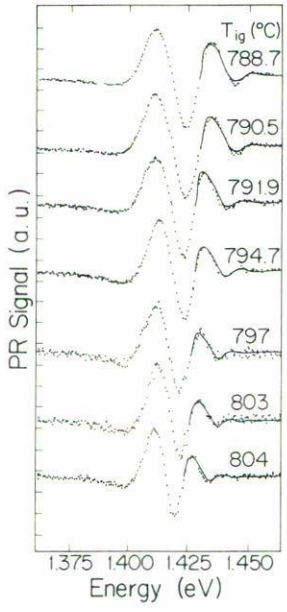

FIGURE 1. Photoreflectance spectra for GaAs films grown at different temperatures. Franz-Keldysh oscillations are observed at high energies. Note that the PR lineshape broadens as the growth temperature decreases.

mass $\mu_{\parallel} = 0.05832$ m [13], the surface electric field and the relative density of ionized impurities can be calculated. These quantities are shown in the fourth and seventh columns in Table II, respectively.

The extreme values for the F-K oscillations, $(\hbar\omega)_j$, as a function of the F_j parameter, as given in Eq. (4), are plotted in Fig. 2. As can be observed in the Fig. 2 these values

TABLE II. Parameters obtained by fitting the theoretical photoreflectance lineshape to the experimental PR spectra, for GaAs layers grown at several T_{ig}'s. E_g is the band gap energy; $\hbar\Omega$ is the electrooptic energy, ϵ is the surface electric field; Γ is the broadening parameter; ϕ is the phase; and $N(\Delta T)/N(\Delta T = 0)$ is the relative density of ionized impurities taking as a reference the impurity density for the film grown at equilibrium.

Sample T_{ig} (°C)	E_g (eV)	$\hbar\Omega$ (meV)	ϵ (KV/cm)	Γ (meV)	ϕ (rad)	$\frac{N(\Delta T)}{N(\Delta T \simeq 0)}$
788.7	1.43	4.1	6.5	4.4	4.71	2.10
790.5	1.429	4	6.3	4.1	4.71	1.95
791.9	1.428	3.7	5.6	4	4.71	1.54
794.7	1.426	3.7	5.6	3	4.71	1.54
797.0	1.426	3.4	4.9	3	4.71	1.20
803.0	1.425	3.3	4.7	2	4.71	1.10
804.0	1.425	3.2	4.5	2	4.71	1.00

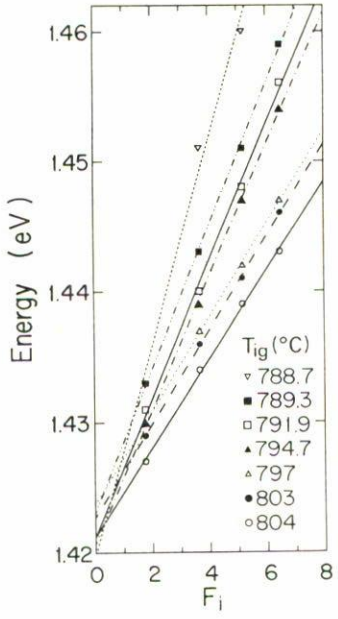

FIGURE 2. Plot of the energy position of the successive maxima and minima in the Franz-Keldysh oscillations in the PR spectra. F_j is an integer number giving the sequence of such extreme points. The linear dependence confirms the assumption of an intermediate-electric field regime.

fit quite well a linear dependence, in agreement with the assumption of an intermediate field regime. It is also observed that the electrooptic energy (slopes) increases as the supercooling does, corresponding to an increase in the surface electric field and, as a consequence, to an increase in the density of ionized impurities as ΔT increases [Eq. (5)].

In Fig. 3 are shown the PR spectra corresponding to samples grown with supercooling temperature values in the range: 1.4–4.3 °C. The important characteristic for this spectra set is that, in comparison with those of Fig. 1, we observe a shift to higher energies, related

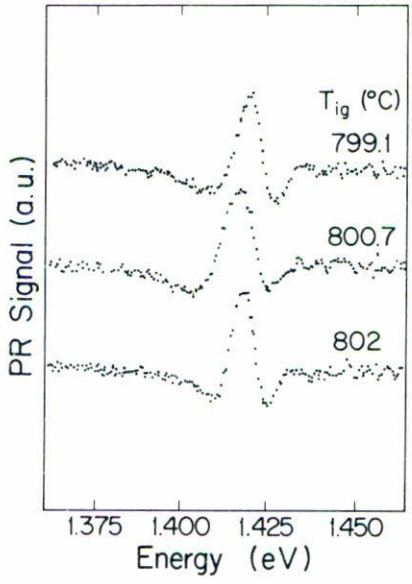

FIGURE 3. Photoreflectance spectra for GaAs layers grown at temperatures in the range 799–802 °C slightly below the equilibrium temperature. There is a change of phase when compared to the PR spectra of Fig. 1, and attenuation of the Franz-Keldysh oscillations.

to a change in the spectral phase by approximately $\pi/2$. In this way, the PR spectra give us an indication that, when the growth temperature changes from 803 to 802 °C there appears an abrupt change of phase which is kept for the samples grown at 800.7 and 799.1 °C. The PR spectra recover their original phase when the T_{ig} values are lower or equal than 797 °C.

It has been shown [14] from the photoluminescence spectra in the same set of samples that, when the layer is grown out of equilibrium conditions ($\sim$ 802 °C), there appears in the PL spectrum a low-energy band associated to antisite defects of the type Ga_{As} produced by a deficiency of As in the melt-crystal interface during the growth process of the epitaxial layer. This deficiency is established when the melt is brought in contact with the substrate, giving rise to an As gradient concentration that keeps the flux of arsenic from the solution toward the interface along the layer growth process. The growth limited by the diffusion of the solute (As) into the solvent (Ga) is one of the basic principles of the LPE method [15]. We know [16] that the GaAs intrinsic epitaxial layers grown in equilibrium by LPE have a residual impurity density in the range: 10^{14} to 10^{15} cm^{-3} and that they are n–type. On the other side, the antisite defect Ga in As sites behaves as a p-type impurity [17].

Based on the above statements we can now give an explanation for the abrupt changes observed in the PR spectra of Fig. 3. When the growth process starts at a few degrees from the equilibrium temperature, the Ga_{As} antisites concentration in the epitaxial layer increases with the supercooling and becomes comparable or higher than the residual impurity density. This results in the growth of a highly compensated layer with an inverted conductivity (from n– to p–type). It is known, on the other hand, that strong

changes in the resistivity [18] (through high compensation), or changes in the type of conductivity [19], produce a phase change in the PR spectrum. Another characteristic in the set of PR spectra shown in Fig. 3 is that the F-K oscillations are attenuated as compared to the spectra shown in Fig. 1, because of electric field inhomogeneities [20], possibly due to a high compensation mechanism.

When the supercooling increases the point is reached where spontaneous nucleation process in the growth solution starts and we have the so called "two-phase growth". In our case this point occurs at about 797 °C. In this growth regime it is expected that GaAs microprecipitates will incorporate in the epitaxial layer producing crystalline defects besides those related to antisites. In Fig. 1 it is observed that for samples grown at temperatures from 797 down to 788.7 °C, the PR spectra recover and maintain the phase corresponding to those layers grown near equilibrium temperature, as can be confirmed in the sixth column of Table II. Such a phase recovering can be explained in terms of defects produced in the two-phase growth having an n–type nature, which increase in density as ΔT increases, neutralizing the antisite defects thus recovering the PR phase and the F-K oscillations. This type of defect would be responsible for the exciton broadening observed in the PL spectra when the supercooling parameter is higher than 7 °C.

5. CONCLUSIONS

In summary, in this work we have shown that the photoreflectance spectroscopy at room temperature is a highly sensitive technique to detect the presence of defects in intrinsic GaAs epitaxial layers grown by LPE. In particular, the PR detects in a clear way the antisite defects that appear when the growth takes place at temperatures lower than those of the equilibrium, in the supercooling region.

An increase in the antisite defect density as we increase the supercooling produce a high compensation and a change in the type of conductivity from n to p, originating an abrupt phase change in the PR spectra, as well as an attenuation in the F-K oscillations. The PR phase and F-K oscillations are recovered when an n–type structural defect due to a two-phase growth mechanism neutralizes the antisite Ga_{As}, a process which dominates for T_{ig}'s lower than 797 °C.

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