Photoreflectance evaluation of internal electric fields in GaAs/Si/GaAs and AlAs/Si/AlAs heterostructures

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Abstract. The possibility of controlling the band offset between layers of III–V compounds by inserting a few monolayers of silicon have given to these systems an increasing theoretical and experimental interest. Photoreflectance is a technique very sensitive to interface effects in heterostructures and particularly sensitive to effects directly related to band offsets, such as interfacial electric fields. A signature of the presence of internal electric fields is the observation of Franz-Keldysh oscillations in the photoreflectance spectra. We carried out a detailed study of Franz-Keldysh oscillations observed in the room temperature photoreflectance spectra of GaAs/Si/GaAs and AlAs/Si/AlAs, heterostructures grown by molecular beam epitaxy where the Si nominal thickness was two monolayers. The data were analyzed employing the asymptotic Franz-Keldysh theory which allowed us to calculate the magnitudes of the internal electric fields. The origin of the internal electric fields is discussed taken into account the silicon distribution as determined by secondary ion mass spectroscopy and the contribution from the inner interfaces. It is found that different contributions from degenerate heavy and light hole bands, to transitions around the Γ point of the Brillouin zone, must be expected for different heterostructures depending upon the particular characteristics of the electric fields present in each sample.

Resumen. La posibilidad de controlar el desacople de bandas entre capas de compuestos III–V al insertar monocapas de silicio ha provocado un creciente interés, tanto teórico como experimental, en esta clase de sistemas. La espectroscopía de fotorreflectancia es una técnica muy sensible a efectos interfaciales presentes en heteroestructuras y particularmente a efectos directamente relacionados con el desacople de bandas, tales como campos eléctricos interfaciales. Una característica de la presencia de campos eléctricos es la aparición de oscilaciones de Franz-Keldysh en los espectros de fotorreflectancia. En este trabajo, se han analizado las oscilaciones de Franz-Keldysh observadas en los espectros de fotorreflectancia obtenidos a temperatura ambiente en heteroestructuras de GaAs/Si/GaAs y AlAs/Si/AlAs crecidas por epitaxia de haces moleculares, donde el espesor nominal del silicio fue de dos monocapas. Los resultados fueron analizados empleando la teoría asintótica de Franz-Keldysh, lo que permitió calcular las magnitudes de los campos eléctricos internos. El origen de estos campos es analizado tomando en cuenta la distribución de silicio determinada por espectroscopía de masas de iones secundarios y la contribución de interfaces internas. Se encontró que existen diferentes contribuciones de las bandas de huecos ligeros y pesados a las transiciones electrónicas alrededor del punto Γ de la zona de Brillouin dependiendo de las características particualres de los campos eléctricos presentes en cada muestra.

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1. Introduction

For a long time GaAs and Si were considered as materials with little compatibility. Recent advances in UHV thin film growth techniques have made feasible the possibility of integrating GaAs and Si as base materials for electronic and optoelectronic devices. There are several aspects that drive the research for achieving good quality growth of the GaAs/Si system. Some of them include: i) the possibility of incorporating the important advances in GaAs-based optoelectronic devices with the more mature Si-based electronic devices technology [1], and ii) the capability of engineering the band offset of GaAs and AlAs homojunctions or GaAs-AlAs heterojunctions by inserting a few monolayers of Si in the interface [2]. Another interesting application of the GaAs-Si system is the possibility of using a few monolayers of Si on GaAs in order to block the dislocation density during the growth of GaAs on Si [3].

Perhaps the most important difficulty to solve during the growth of GaAs on Si is the large lattice mismatch between them (almost 4%). This problem has been addressed through different approaches, for example: substrate misorientation, annealing, growth of a modulation doped AlAs-GaAs superlattice or a $(\mathrm{GaAs})_{1-x}$ $(\mathrm{Si}_2)_x$/GaAs strained layer superlattice [4].

In order to explore the effect of intercalation of a few Si monolayers in III–V compounds, we have grown GaAs/Si/GaAs structures on top of GaAs/Si/GaAs and AlAs/Si/AlAs molecular beam epitaxy grown heterojunctions where Si has a nominal thickness of two monolayers. Secondary ion mass spectroscopy (SIMS) profiles showed silicon diffusion toward the GaAs adjacent regions producing a silicon distribution such that strong internal electric fields are created. Due to the high sensitivity of photoreflectance (PR) spectroscopy to surface and interface effects, it has become a powerful technique to study the internal electric fields present in several type of heterostructures [5,6] as well as its spatial origin [7]. This work reports the results of a photoreflectance characterization of the as-grown samples and of the same samples after chemically removing the top GaAs layer [8]. These results were discussed employing the asymptotic Franz-Keldysh (FK) theory and a detailed study was performed about the effective mass contributions to the calculated values of the internal electric fields. Our results indicate a strong dependence of the hole effective mass value, taken to analyze the FK oscillations above E_0, with the characteristics of the electric fields present in the sample.

2. Experiment

Intrinsic and n–type GaAs(100):Si substrates were subject to chemical cleaning prior to film deposition. Both substrates were heated at 620°C in order to remove the top

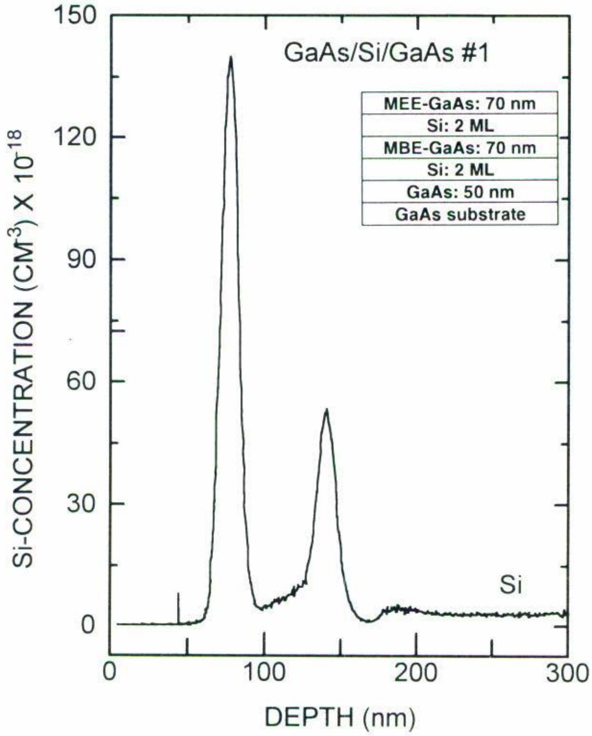

FIGURE 1. SIMS depth profile for silicon in sample GaAs/Si/GaAs #1. It is noticeable the high silicon content in the intermediate GaAs layer which forms a gradual p-n junction with the GaAs top layer.

oxide layer. Sample GaAs/Si/GaAs #1, inset Fig. 1, was deposited emplying a GaAs:Si ($n \sim 3 \times 10^{18}$ cm^{-3}) substrate. After substrate preparation, a 500 Å GaAs buffer layer was grown at 580°C. Then two Si monolayers were deposited emplying an electron-gun. Following to the growth of 700 Å of GaAs, the temperature was lowered to 480°C and kept constant to the end of the growth. After this procedure, two monolayers of Si were deposited and, finally, 700 Å of GaAs were grown by using the migration enhanced epitaxy technique.

Sample GaAs/Si/GaAs #2 was grown on an intrinsic GaAs(100) substrate, inset Fig. 2. After a 500 Å GaAs buffer layer grown at 580°C, the heterostructure AlAs/Si/AlAs was grown. The thicknesses were 100 Å for both AlAs layers and nominally two-monolayers for silicon. After the growth of the first AlAs layer the temperature was lowered to 520°C and maintained contant during the growth process. Then a heterostructure of GaAs/Si/GaAs was grown, where the thicknesses of the GaAs layers were 1000 Å and for silicon it was nominally two monolayers. Besides of the interest about the magnitude of the band offset, the motivation for making the latter heterostructure was to test if it was possible to improve the silicon confinement because of the stronger chemical bond between the Al and As atoms (1.98 eV) in AlAs, as compared to that between Ga and As atoms (1.59 eV) in GaAs [9]. Photoreflectance experiments were carried out at room temperature with

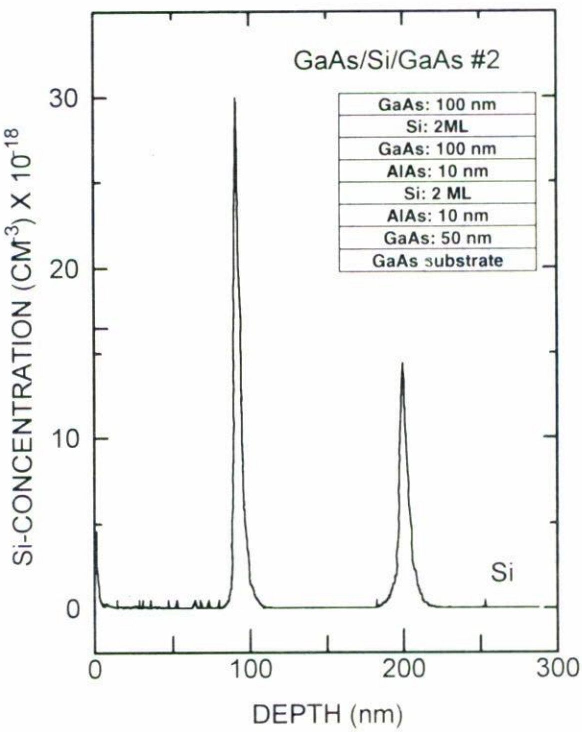

FIGURE 2. SIMS depth profile for silicon in sample GaAs/Si/GaAs #2. It is noticeable a higher silicon confinement as compared with sample GaAs/Si/GaAs #1. A gradual p-n junction between the semi-insulating GaAs layer and the silicon doped AlAs region is formed in the region adjacent to the peak around 200 nm.

a standard experimental setup employing, separately, both He–Ne (6328 Å) and Ar^+ (4880 Å) lasers as modulating sources.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the SIMS profiles of Si for the samples studied. From the analysis it was determined a larger diffusion towards the adjacent layers for the GaAs/Si/GaAs #1 sample as compared to that of sample GaAs/Si/GaAs #2. The deepest silicon layer grown at 580°C, Fig. 1, presents the largest Si diffusion. In fact, at this growth temperature Si diffused even into the GaAs buffer layer. When the topmost GaAs layer was deposited by the migration enhanced epitaxy technique at lower temperature in sample GaAs/Si/GaAs #1, the diffusion of Si within this layer was strongly reduced, as indicated by the silicon SIMS profile shown in Fig. 1.

The photoreflectance spectra of the samples taken with both He–Ne and Ar^+ lasers do not present significant differences in position and line shape of the peaks. Figures 3(a) and 4(a) show the spectra of as-grown samples. Besides the E_0 (1.42 eV) and $E_0 + \Delta_0$ (1.75 eV) GaAs signatures, additional oscillations are observed at greater energies which have been ascribed to Franz-Keldysh oscillations originating from internal electric fields. These electric fields arise from the intrinsic characteristics of the samples and their origin will be discussed latter. The oscillations were fitted to the asymptotic expressions of the Franz-Keldysh effect derived by Aspnes [10]:

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

the j–th extremum may be described by

$$j\pi = \frac{2}{3}\left(\frac{\hbar\omega_j - E_g}{\hbar\Omega}\right)^{3/2} + \frac{\pi}{2}, \tag{2}$$

where $\hbar\Omega$ stands for

$$\hbar\Omega = \left(\frac{e^2\hbar^2 F_{\rm int}^2}{8\mu^*}\right)^{1/3}, \tag{3}$$

so the extremum energies can be characterized by employing the following equations:

$$E_j = \hbar\Omega F_j + E_g, \tag{4}$$

$$F_j = \left[\tfrac{3}{2}\pi\left(j - \tfrac{1}{2}\right)\right]^{2/3}, \tag{5}$$

where $\hbar\omega$ is the energy of the probe light, $F_{\rm int}$ is the strength of the internal electric field, E_g represents the band gap energy (E_0) or the spin-orbit splitting energy ($E_0+\Delta_0$) and μ^* is the reduced effective mass of the electrons and holes involved in the transition. Due to the fact that we observed FK oscillations around E_0 and $E_0+\Delta_0$ we have the opportunity of carefully studying the problem of how the contributions from heavy and light holes must be taken into consideration. We must point out that Shen [11] *et al.* have also observed Franz-Keldysh oscillations above $E_0 + \Delta_0$ on surface-insulating-n^+ structures, but without further analysis about the relative effective mass contributions of degenerate bands. The clear presence of Franz-Keldysh oscillations above E_0 and $E_0 + \Delta_0$ is particularly interesting because it does not seem to be a general consensus in the literature as far as using a value or procedure to determine the hole effective mass of degenerate bands when studying FK oscillations or when these oscillations are used to evaluate internal electric fields. For example, some authors have addressed this problem and claim that the heavy hole contribution should be dominant [12] or take into consideration contributions from both types of holes finding that the contribution from the light holes should be 0.6 times that from the heavy holes [13]. Others make their choice without any further comment.

In this work we show that this issue requires a more detailed study and could be dependent on the characteristics of each analyzed sample. Figure 5 presents the fittings to the asymptotical model for FK oscillations associated with the E_0 and $E_0+\Delta_0$ critical

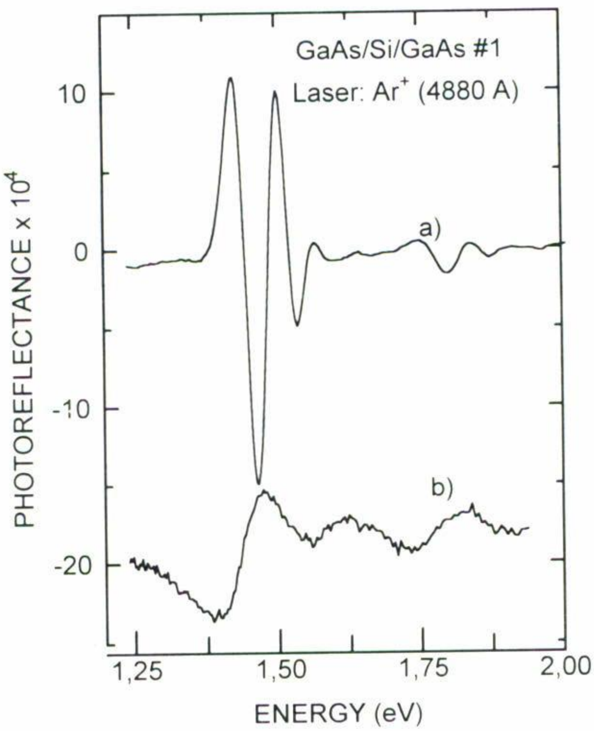

FIGURE 3. Room temperature photoreflectance spectra for a) sample GaAs/Si/GaAs #1 before chemical etching and b) after chemical etching.

points for samples GaAs/Si/GaAs #1 and #2 before chemical etching and for sample GaAs/Si/GaAs #2 after chemical etching. We may observe a similar behavior in the slope of the fittings and one could think that these small differences are due only to the different internal electric field strengths, but as we show in this work these differences could give us important information, usually not taken into account, about the effective mass contributions.

By employing Eqs. (1)–(5) it was obtained the electric field strength and the energies of the critical points E_0 and $E_0 + \Delta_0$ whose values are shown in Table I. The internal electric field responsible for the oscillations affects simultaneously the E_0 and $E_0 + \Delta_0$ critical points, so that the field strength obtained employing the FK model to each critical point must yield the same value. When the degenerate E_0 critical point is employed to estimate the internal electric field strength, one must choose from the literature the value for the hole effective mass that one considers most appropriate. So far, to our knowledge it has not been solved theoretically the problem of how to determine a value for this important parameter when the FK model is applied to the analysis of photoreflectance spectra. On the other hand, for the non-degenerate critical point $E_0 + \Delta_0$ we have only one possible value for the hole effective mass. In our case, we employed the FK model with the oscillations around this critical point and obtained the strength of the internal electric field. With this value for F_{int} and the value of $\hbar\Omega$ obtained from the fitting to the oscillations associated with E_0, we got the effective mass value for transitions from

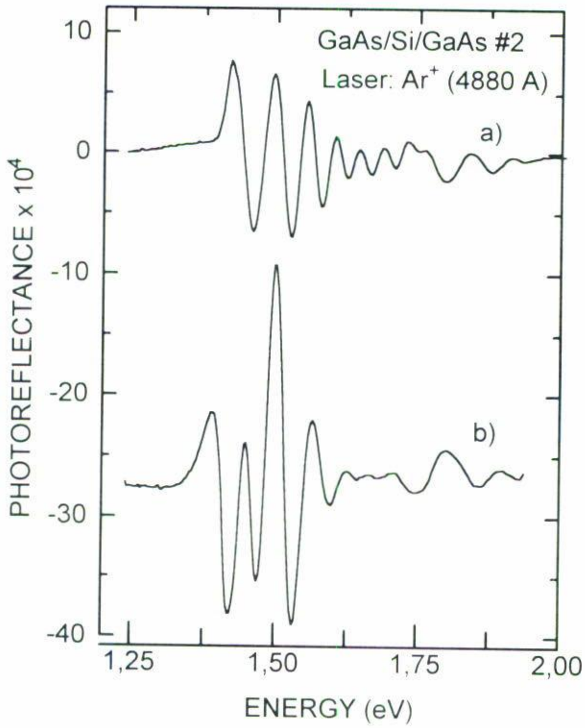

FIGURE 4. Room temperature photoreflectance spectra for a) sample GaAs/Si/GaAs #2 before chemical etching and b) after chemical etching.

E_0 at the Γ point and, therefore, it was possible to evaluate the contribution of each type of hole. The values reported in Table I were obtained employing $m_e^\Gamma = 0.067\, m_e$, for the conduction band effective mass and $m_{\text{so}} = 0.15\, m_e$, $m_{\text{lh}} = 0.087\, m_e$ and $m_{\text{hh}} = 0.62\, m_e$ for the valence band effective masses [14]. In our study we have represented the effective mass associated with transitions around the Γ point by $\mu^* = \eta m_e$, where η is a factor to be determined. For this case, if the only contribution considered arises from the heavy holes, η is equal to 0.060. On the other hand, if only light holes are assumed to contribute, η is equal to 0.038. When there is not a dominating contribution of one type of hole, it is necessary to consider a "super-effective" hole mass for the degenerate bands. The values obtained from the fittings are presented in Table I. These values differ from each other and from the value corresponding to that obtained by considering only the heavy hole contribution.

For the purpose of assigning a meaning to η in terms of the heavy and light holes masses, we employed an effective hole mass ($m_{\text{eff}}^{\text{h}}$) of the form

$$\frac{1}{m_{\text{eff}}^{\text{h}}} = \frac{1}{m_{\text{hh}}} + \zeta \frac{1}{m_{\text{lh}}}, \tag{6}$$

with $0 \leq \zeta \leq 1$ and considering that ζ is a factor that weighs the light hole contribution. Then η was calculated with m_e^Γ and $m_{\text{eff}}^{\text{h}}$. The η values reported in Table I were matched

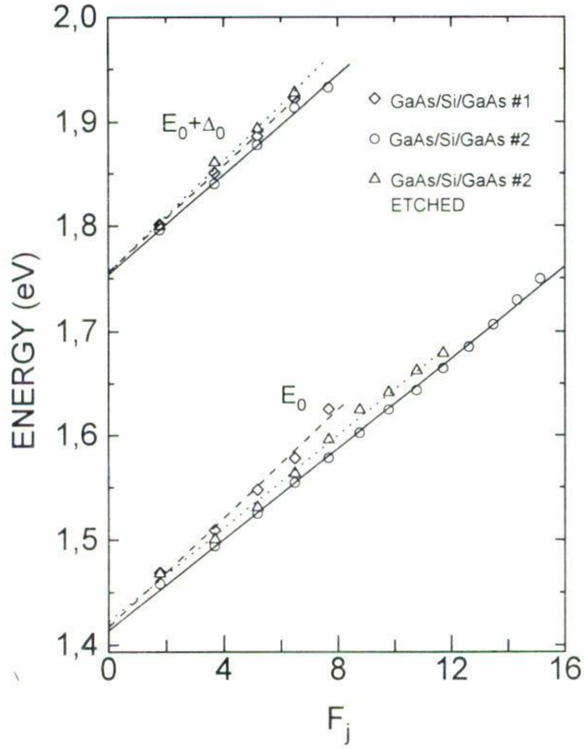

FIGURE 5. Fittings to the Franz-Keldysh model of the energies associated with the extreme in the photoreflectance spectra above E_0 and $E_0 + \Delta_0$.

TABLE I. Values for the critical points energies, internal electric fields and effective mass contributions as obtained from Franz-Keldysh analyses for the samples studied. η represents a factor associated with the effective mass contributions for transitions around E_0 *i.e.* $\mu^* = \eta m_e$.

Sample	E_0 (eV)	$E_0 + \Delta_0$ (eV)	F_{int} (V/cm)	η
GaAs/Si/GaAs #1	1.41(7)	1.75(6)	8.98×10^4	0.044
GaAs/Si/GaAs #2	1.41(4)	1.75(3)	8.15×10^4	0.061
GaAs/Si/GaAs #1 Etched	1.42(2)	1.78(4)	—	—
GaAs/Si/GaAs #2 Etched	1.42(2)	1.75(5)	9.67×10^4	0.081

when $\zeta \cong 0$ for sample GaAs/SiGaAs #1 and $\zeta \cong 0.6$ for sample GaAs/Si/GaAs #2. Therefore, under the framework of the asymptotic Franz-Keldysh theory, our results agree for one sample with the approach in which the heavy hole effective mass is dominating, while for the other sample our results are consistent with an approach in which the light hole effective mass contribution is 0.6 times that from heavy holes.

These discrepancies must be taken into consideration if one wants to determine magnitudes of electric fields by employing the oscillations above E_0 in photoreflectance experiments because there is the possibility of introducing significant errors which may be as large as 20% depending upon the particular choice of heavy and light hole mass contributions for the case of degenerate bands. The difference in the values obtained for degenerate valence band effective masses is a consequence of the particular characteristics of the internal electric fields, which gives rise to different contributions from heavy and light holes for each sample.

The origin of the dominant electric field is dissimilar for the investigated samples. Initially we try to assign this to the band offset produced by the silicon monolayers. However, as we observe from the SIMS profile of GaAs/Si/GaAs #1, we may consider that the two uppermost layers of GaAs form a p-n junction. The top GaAs layer is lightly p-type due to the growth method, while in the next GaAs layer Si is activated as an n-type dopant with an average concentration of around 5×10^{19} cm^{-3}.

Similarly the origin of the electric field for the GaAs/Si/GaAs #2 sample is mostly associated with th GaAs/AlAs interface with some additional contribution of a gradual p-n junction, similar to that described above, due to the Si interdiffusion into the neighboring AlAs layer rather than due to a band offset. In order to corroborate this assignment we etched away the topmost GaAs layer in both samples. Fig. 3(b) shows the photoreflectance spectrum for the sample GaAs/Si/GaAs #1 after the removal of the p-type top GaAs layer. In this figure it is noticeable the similarity between this spectrum and that of an n-type GaAs crystal [15] ($n \sim 10^{18}$ cm^{-3}). For sample GaAs/Si/GaAs #2, Fig. 4(b), after etching away the topmost GaAs layer, one can observe a reduction in the number of oscillations and a slight increment of the spacing between them. The persistence of the oscillations and the similarity with those appearing before the chemical etching suggest that the innermost interfaces are mostly responsible for the measured internal electric field. In Fig. 5 it is shown the fitting to the asymptotic Franz- Keldysh model of the E_0 and $E_0 + \Delta_0$ oscillations. The calculated magnitude of the electric field for this sample is 1×10^5 V/cm, Table I.

We can observe from the inset in Fig. 2 that the thickness of the top GaAs layer, before chemical etching, is larger than the penetration depth for the 4880 Å laser wavelength in GaAs (around 800 Å). However, there is evidence that even when the penetration depth at a given wavelength is smaller than the film thickness, it is still possible to modulate inner interfaces because of the acceleration produced on photo-carriers by internal electric fields [15]. In the case of the GaAs/Si/GaAs #2 sample, the large band offset between GaAs and AlAs, in addition to the silicon distribution in the AlAs layer, gives rise to an intense internal electric field which accelerates the photoexcited majority carriers toward the GaAs-AlAs interface producing the observed Franz-Keldysh oscillations. This explains the fact that the oscillations and the electric field strength are so similar before and after etching. Studies carried out by employing differential photoreflectance spectroscopy on the same samples support the assumption that the dominant internal electric field originates at the GaAs/AlAs interface [16]. However, it should be stressed that the obtained electric field strength is a sort of weighed average value of the electric fields present in the surface and in the interface between the successive layers. These electric fields act simultaneously upon the free carriers.

The possibility of an optical interference origin for the oscillations is ruled out because we do not have sharp GaAs/Si interfaces.

4. CONCLUSIONS

We have carried out room temperature photoreflectance studies of molecular beam epitaxy grown GaAs/Si/GaAs and AlAs/Si/AlAs thin film heterostructures. Depending upon the growth procedure, we observed silicon diffusion, to a different extent, toward the adjacent GaAs or AlAs. Two factors were noticed to improve Si confinement: the use of AlAs as surrounding layers and the growth of GaAs layers by migration enhanced epitaxy at a lower temperature. The silicon diffusion precluded the observation of band offset effects and was heavily responsible for the appearance of internal electric fields easily detected and evaluated due to presence of Franz-Keldysh oscillations in the photoreflectance spectra of both type of samples used for this study, Figs. 3 and 4.

Due to the presence of FK oscillations above $E_0 + \Delta_0$ it was possible to estimate the magnitude of the internal electric field employing the spin-orbit splitting hole effective mass, avoiding the indefinition of what value of the effective mass should be employed when applying the FK asymptotic theory to oscillations above E_0. Our results indicate a sample dependent hole effective mass contributions and disagree with the usual criteria taken to analyze Franz-Keldysh oscillations above E_0 in the sense that it is not correct to generalize a single value for the hole effective mass when dealing with degenerate valence bands. It was also determined that, depending on the particular choice of the hole effective mass, the calculated strength of the electric field from the PR spectra may lead to errors of up to 20%. Moreover, in our sample the total internal electric field measured by PR experiments had various contributions mainly arising from the surface and from the electric fields originated at interfaces between layers with high and low silicon content, being dominant the interfacial electric fields.

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