Photoreflectance study of Fermi level changes in photowashed GaAs

H. Shen
Geo-Centers, Inc., U.S. Army Electronics Technology and Device Laboratory, Fort Monmouth, New Jersey 07703

Fred H. Pollak
Physics Department, Brooklyn College of CUNY, Brooklyn, New York 11210

J. M. Woodall
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 25 September 1989; accepted 12 January 1990)

As a result of the photowashing of (100) n-GaAs \( (n \approx 3 \times 10^{16} \text{~cm}^{-3}) \) a decrease of about 25% in the surface potential was found using the contactless electromodulation method of photoreflectance. This corresponds to a reduction in the surface state density by about a factor of 2.

Recently a photochemistry passivation technique has been reported which greatly reduced the surface state density of GaAs.\(^1\) Photowashing (PW) in air by Offsey et al.\(^1\) resulted in an enhanced photoluminescence excitation intensity and MIS structures made on such treated samples behaved as if the surface had been unpinned. An important aspect of this approach is its impact on previous notions concerning Fermi level pinning. In order to gain more information about this procedure we have measured photoreflectance and photoreflectance. This corresponds to a decrease of about a factor of 2 in the surface state density.

The sample used in this study was an epitaxial layer (100) n-GaAs:Si \( (n = 3 \pm 0.5 \times 10^{16} \text{~cm}^{-3}) \) of thickness 0.75 \( \mu \text{m} \) grown on a 0.25 \( \mu \text{m} \) buffer layer of GaAs:Si \( (n = 2 \times 10^{18} \text{~cm}^{-3}) \) on an \( n^+ \) GaAs substrate. The carrier concentration in the epitaxial layer was evaluated from \( C-V \) measurements. The PR apparatus has been described in the literature.\(^2\) A 1 mW HeNe laser chopped at 200 Hz was used as the pump beam. The GaAs surface was first cleaned in hot sulfuric acid and deionized (DI) water \((1:1)\) for about 2 min to generate a reproducible starting surface.\(^2\) Under projector bulk illumination with the wafer spinning at several thousand revolutions per min the surface of the wafer was sprayed with DI water for about 20 min. This procedure forms a stable oxide.\(^2\)

To unpin the Fermi level at the GaAs-oxide surface the material was simultaneously washed and illuminated for about 1 min using the 5145 \( \text{Å} \) line of an Ar ion laser \((-600 \text{~mW/cm}^2)\).\(^3\)

Displayed in Fig. 1(a) is the PR spectrum at 300 K of the GaAs sample after cleaning in the hot sulfuric acid/water bath. The large features labeled A and B around 1.40 eV arise from excitonic effects in a portion of the space-charge region (SCR) where the electric fields are low enough not to quench the exciton.\(^6\) Similar phenomenon have been reported for electrolyte electoreflectance in GaAs\(^7\) and PR of InP.\(^6\) Features 1–3 have been magnified by a factor of 2.5 while peaks 4 and 5 are amplified by a factor of 25. The peaks denoted 1–5 are FKO originating in the SCR and are related to \( F_{dc} \). In Fig. 1(b) is plotted the PR spectrum at 300 K immediately after the photowashing treatment to unpin the Fermi level. It took about 5 min to measure the entire data. The spectrum of Fig. 1(b) is similar to that of Fig. 1(a) except that the period of the FKO has decreased. The line shapes of the spectral features of both Figs. 1(a) and 1(b) were found to be independent of pump beam intensity.

In the case of low field ac modulation in the presence of a large dc electric field the period of the FKO provides a direct measure of \( F_{dc} \).\(^6\) It has recently been rigorously demonstrated by Shen and Pollak that for low field ac modulation in the presence of \( F_{dc} \) the period of the FKO are a direct

![Fig. 1. (a) Photoreflectance spectrum at 300 K of a bare (100) n-GaAs \( (n \approx 3 \times 10^{16} \text{~cm}^{-3}) \) sample before photowashing. (b) the spectrum after the photowashing treatment. Features 1–5 are the Franz–Keldysh oscillations.](image-url)
measure of $F_{de}^2$, independent of doping level, i.e., the width of the SCR.\(^8\)

The extrema in the FK0 are given by\(^6,9\)

$$m \pi = \phi + (4/3) \left\{ \left( E_m - E_0 \right) / \hbar \omega_{de} \right\}^{3/2},$$

(1)

where $m$ is the index of the $m$th extrema, $\phi$ is an arbitrary phase factor, $E_0$ is the energy gap, $E_m$ is the photon energy of the $m$th oscillation, and $\hbar \omega_{de}$ is the electro-optic energy:

$$\hbar \omega_{de}^3 = e^2 R (F_{de}^2) / 2 \mu_i,$$

(2)

where $\mu_i$ is the reduced interband effective mass in the direction of $F_{de}$.

Plotted in Fig. 2 is the quantity $(4/3 \pi) \left\{ \left( E_m - E_0 \right) \right\}^{3/2}$ as a function of $m$, the extrema in the FK0, before and after the PW treatment. The solid line is a least-squares fit to a linear function in energy. 14.15 For the first case we choose $Q_{sa}$, the space charge density for intrinsic GaAs.16 This of course is the location of the surface Fermi level for intrinsic GaAs as $D$ approaches zero. The measured value of $V_{bi} = 0.62$ V places $E_f$ (Fermi level before PW) between 0.75 and 0.80 eV above $E_c$. We estimate $D$ by determining $Q_{sa}$, the space charge density for $n = 3 \times 10^{16} \text{ cm}^{-3}$ and $V_{bi} = 0.62$ V. This value is $5.1 \times 10^{11} \text{ cm}^{-2}$. Using the relations $Q_{sc} = Q_{sa}$ and $Q_{sa} = D(E_f - E_c)$,12 where $Q_{sa}$ is the surface charge density in excess of $Q_{sc}$, we find $D = 5 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$. This number agrees with previous determinations for etched GaAs surfaces.17 For the delta function all that we can say is that the charge density $Q_{sc}$ at the pinning energy is $> 5.1 \times 10^{11} \text{ cm}^{-2}$. Therefore, the density of states is actually much larger. Using this model and the fact that pinning is observed for samples doped $n > 1 \times 10^{18} \text{ cm}^{-3}$ suggests that $Q_{sa}$ for this case\(^15,18\) is on the order of $1 \times 10^{13} \text{ cm}^{-2}$.

After the PW treatment we find $V_{bi} = 0.465$ V which means that $E_f$ is now closer to the conduction band edge. The sample is thus approaching the flat-band condition with a lower surface state density than before PW. This is consistent with both the uniform surface state (US) density and metal cluster models but not necessarily the defect models\(^12,14\) if a new level has been created by the PW. Since it has been shown that PW drives $p$-type as well as $n$-type material flat band\(^1\) the case for a new defect level nearer the conduction band is not convincing. For $V' = 0.465$ V, $Q_{sc} = (0.86 \times Q_{sc}) = 4.4 \times 10^{11} \text{ cm}^{-2}$. Since $E_f$ has moved by $0.62 - 0.47 = 0.15$ eV, $D'$ is now $1.8 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$ by the US calculation. For the delta function model $Q_{sa}$ has dropped to $4.4 \times 10^{11} \text{ cm}^{-2}$. Thus, in either case we have achieved a significant reduction in pinning sites for samples that have been photowashed.

Gaskell \textit{et al.} have recently reported PR measurements of (100) $n$-GaAs ($n = 1.3 \times 10^{16} \text{ cm}^{-2}$) subjected to various chemical treatments, including photowashing.19 They find

![Fig. 2](image-url)
that the PW procedure (or Na2S treatment) of a bare GaAs surface reduces the built-in potential by about 0.1 eV, i.e., about 15%. However, they did not perform a detailed analysis of the FKO or changes in the surface state density.

Reference 19 (as well as other publications by this group) erroneously states that modulated reflectance experiments average the effect of the nonuniform field in the FKO, i.e., when the penetration depth of the light becomes comparable to the depletion width. However, the detailed analysis of Shen and Pollak8 has demonstrated rigorously that if the modulating field is small compared to \( F_0 \), the period of the FKO always yields \( F_0 \), independent of the relation between the penetration depth of the light and the width of the space charge region.

In conclusion, we have used the contactless electromodulation method of PR to evaluate the changes in the surface potential of n-GaAs due to a PW procedure. The reduction of only 25% in \( V_{bi} \) corresponds to a decrease of about a factor of 2 in the surface density responsible for Fermi level pinning.

Acknowledgment: The authors H.S. and F.H.P. acknowledge the partial support of the New York State Science and Technology Foundation as part of its Centers for Advanced Technology program.

---

\(^8\) Also at Graduate School and University Center, City University of New York, New York, New York 10036.


\(^3\) C. W. Wilmsen, P. D. Kirchner, and J. M. Woodall, J. Appl. Phys. 64, 3287 (1988).


\(^8\) H. Shen and F. H. Pollak, Phys. Rev. (submitted)

\(^9\) Equation (9) in Ref. 6 incorrectly stated the expression for the extrema in the FKO as \( m \pi = \phi + (16/3)[(E_m - E_o)/\hbar]^{1/2} \) although the correct equation was used to interpret the experimental results.

\(^10\) The dominance of the conduction to heavy-hole valence transitions in FKO was demonstrated by M. Chandreskhar and F. H. Pollak, Phys. Rev. B 15, 2127 (1977).


