Photoreflectance study of Fermi level changes in photowashed GaAs

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(Received 25 September 1989; accepted 12 January 1990)

As a result of the photowashing of (100) n-GaAs ($n \approx 3\times 10^{16}\,cm^{-3}$) 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.[1-3] 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 (PR),[4,5] a contactless form of electromodulation, on a (100) GaAs surface before and after such a photochemical treatment. The observed Franz–Keldysh oscillations (FKO) are a direct measure of the magnitude of the dc surface electric field (F^s_{dc}). This quantity is related to the built-in potential and hence the surface Fermi level through the Schottky relation. We find a reduction in the built-in potential of about 25% as a result of the photowashing. 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 ($n = 3 \pm 0.5\times 10^{16}\,cm^{-3}$) of thickness 0.75 μm grown on a 0.25 μm buffer layer of GaAs:Si ($n = 2\times 10^{18}\,cm^{-3}$) 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.[5] 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 Å line of an Ar-ion laser ($\sim$600 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 electroreflectance 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^s_{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^s_{dc}.[6] It has recently been rigorously demonstrated by Shen and Pollak that for low field ac modulation in the presence of F^s_{dc} the period of the FKO are a direct

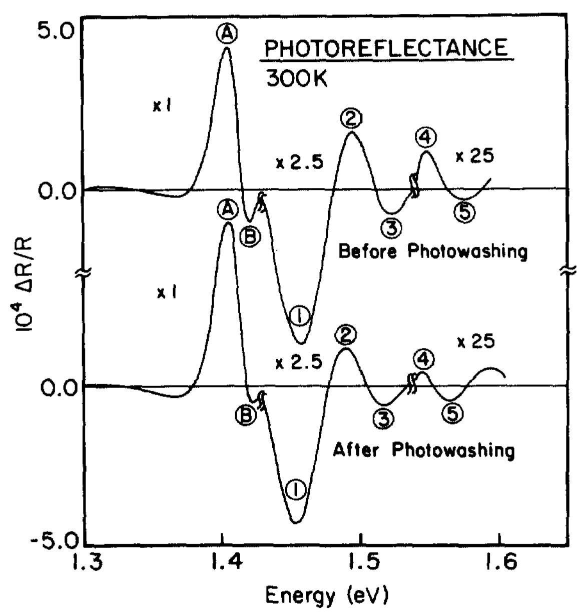

FIG. 1. (a) Photoreflectance spectrum at 300 K of a bare (100) n-GaAs ($n \approx 3\times 10^{16}\,cm^{-2}$) sample before photowashing, (b) the spectrum after the photowashing treatment. Features 1–5 are the Franz–Keldysh oscillations.

measure of F^s_{dc}, independent of doping level, i.e., the width of the SCR.[8]

The extrema in the FKO are given by[6,9]

$$m\pi = \phi + (4/3)[(E_m - E_0)/\hbar\theta^s_{dc}]^{3/2}, \quad (1)$$

where m is the index of the mth extrema, ϕ is an arbitrary phase factor, E_0 is the energy gap, E_m is the photon energy of the mth oscillation, and $\hbar\theta^s_{dc}$ is the electro-optic energy:

$$(\hbar\theta^s_{dc})^3 = e^2\hbar^2(F^s_{dc})^2/2\mu_{\parallel}, \quad (2)$$

where $\mu_{\parallel}$ is the reduced interband effective mass in the direction of $\mathbf{F}^s_{dc}$.

Plotted in Fig. 2 is the quantity $(4/3\pi)\,[E_m - E_0]^{3/2}$ as a function of m, the extrema in the FKO, before and after the PW treatment. The solid line is a least-squares fit to a linear relationship which yields the quantity $\hbar\theta^s_{dc}$. It has been shown that the FKO near the fundamental gap are dominated by the heavy-hole valence to conduction band transition.[10] Thus, using $\mu_{\parallel} = 0.055m_0$, where m_0 is the free electron mass,[11] the surface electric fields are obtained to be $F^s_{dc} = (6.85 \pm 0.2)\times 10^4$ V/cm before photowashing and $(F^s_{dc})' = (6.07 \pm 0.2)\times 10^4$ V/cm after unpinning of the Fermi level. We use the designation unprimed (primed) to indicate various quantities before (after) the PW treatment.

In a fully depleted SCR the surface electric field and built-in potential V_{bi} are related by[12]

$$(F^s_{dc})^2 = (2eN/\epsilon_0)(V_{bi} - kT/e), \quad (3)$$

where N is the net impurity concentration ($N = n$ in our case) and ϵ_0 is the static dielectric constant.[12]

The relative change in the built-in potential

$$\Delta V_{bi}/V_{bi} = (V'_{bi} - V_{bi})/V_{bi}, \quad (4)$$

can be evaluated from Eq. (3) and the above measured variations in F^s_{dc} due to PW. Using $N = 3\times 10^{16}$ cm^{-3} we find $\Delta V_{bi}/V_{bi} \approx 25\%$. The absolute values of V_{bi} can also be determined from Eq. (3). However, while $\Delta V_{bi}/V_{bi}$ is relatively insensitive to N, the absolute values are almost linear dependent on this quantity. We find using $N = (3 \pm 0.5)\times 10^{16}$

$$V_{bi} = 0.62 \pm 0.1 \text{ V}.$$

Within experimental error (due mainly to the error bars on N) this value is in good agreement with other determinations of the Fermi energy on a free GaAs surface.[13]

The samples used in this study were photowashed according to the procedure of Ref. 1. However, since the PR facility was not equipped with photoluminscence excitation (PLE) spectroscopy, it was not possible to evaluate the "base line" PLE reference to determine if the PW treatment produced the lowest possible surface state density. In fact, the PR result of $V'_{bi}/V_{bi} \approx 0.75$ instead of $(F^s_{dc})' = 0$ indicates that less than optimal conditions were produced.

Nonetheless, we will show that this result indicates that the PW procedure used still leads to a significant reduction in surfaces states. The actual reduction depends on the model used to describe the energy distribution of midgap state density. We shall consider two cases: one where D, the density of surface states for a given surface, is uniform in energy as discussed in Ref. 12 and one in which there is a delta function in energy.[14,15] For the first case we choose E_{cn}, the charge neutrality level, to be 0.7 eV above the valence band edge, E_v, for 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_v. We estimate D by determining Q_{sc},[12] the space charge density for $n = 3.0\times 10^{16}$ cm^{-3} and $V_{bi} = 0.62$ V. This value is 5.1×10^{11} cm^{-2}. Using the relations $Q_{ss} = Q_{sc}$ and $Q_{ss} = D(E_f - E_{cn})$,[12] where Q_{ss} is the surface charge density in excess of Q_{sc}, we find $D = 5\text{–}10\times 10^{12}$ eV^{-1} cm^{-2}. This number agrees with previous observations for etched GaAs surfaces.[17] For the delta function all that we can say is that the charge density Q_{ss} at the pinning energy is $> 5.1\times 10^{11}$ cm^{-2}. Therefore, the density of states is actually much larger. Using this model and the fact that pinning is observed for samples doped $n > 1\times 10^{18}$ cm^{-3} suggests that Q_{ss} for this case[15,18] is on the order of 1×10^{13} 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 (USS) 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, $Q'_{sc} = (0.86\times Q_{sc}) = 4.4\times 10^{11}$ cm^{-2}. Since E_f has moved by $(0.62 - 0.47)$ eV $= 0.15$ eV, D' is now 1.8×10^{12} eV^{-1} cm^{-2} by the USS calculation. For the delta function model Q_{ss} has dropped to 4.4×10^{11} cm^{-2}. Thus, in either case we have achieved a significant reduction in pinning sites for samples that have been photowashed.

Gaskill *et al.* have recently reported PR measurements of (100) n-GaAs ($n = 1.3\times 10^{16}$ cm^{-3}) subjected to various chemical treatments, including photowashing.[19] They find

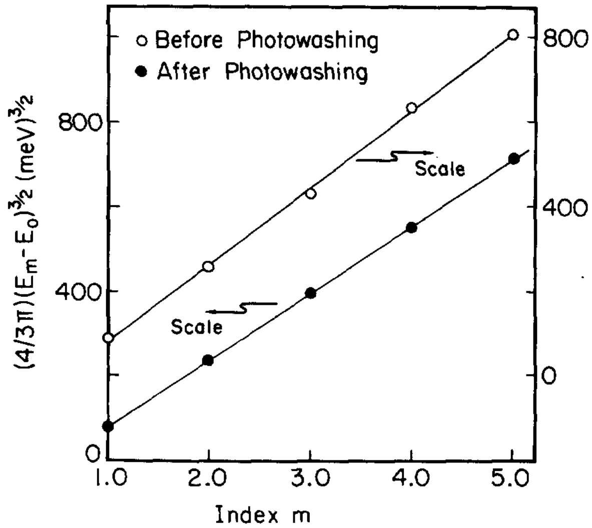

FIG. 2. The quantity $(4/3\pi)\,[E_m - E_0]^{3/2}$ as a function of FKO index m before and after photowashing. The solid lines are least-squares fits to a linear function.

that the PW procedure (or Na_2S 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 Pollak[8] has demonstrated rigorously that if the modulating field is small compared to F^s_{dc}, the period of the FKO always yields F^s_{dc}, 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.

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