## In situ study of Fermi-level pinning on *n*- and *p*-type GaAs (001) grown by molecular-beam epitaxy using photoreflectance

D. Yan and Fred H. Pollak\*

Department of Physics and New York State Center for Advanced Technology in Ultrafast Photonic Materials and Applications, Brooklyn College of the City University of New York, Brooklyn, New York 11210

T. P. Chin and J. M. Woodall

School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907-1285

(Received 17 April 1995)

We have conducted an *in situ* study of the Fermi-level pinning behavior of *n*- and *p*-type GaAs (001) surfaces in the ultrahigh-vacuum environment of a molecular-beam-epitaxy chamber using photoreflectance. As-grown surfaces as well as the effects of a few monolayers of arsenic deposition/desorption were investigated. The measured barrier heights of the as-grown  $n(V_{B,n})$ - and  $p(V_{B,p})$ -type samples (relative to their respective band edges) were 0.61 V (midgap pinning taking into account the photovoltaic effect) and 0.33 V, respectively The *in situ* deposition of a few monolayers of arsenic had no effect on  $V_{B,n}$  but caused  $V_{B,p}$  to increase to 0.60 V, i.e., midgap pinning. The desorption of the arsenic layers brought  $V_{B,p}$  close to its as-grown value but had no effect on  $V_{B,n}$ . These observations, together with earlier studies on similar but air-stabilized samples, provides evidence that As plays a crucial role in the formation of the surface Fermi levels.

Fermi-level pinning semiconductor at surfaces/interfaces is a challenging subject of investigation from both fundamental and applied points of view. After many decades of study, the origin of the surface states of GaAs (and related semiconductors) is still not completely understood.<sup>1</sup> In the case of GaAs, it is not clear that there is still an interest in metal-oxide-semiconductor effect transistor devices, since modeling results show no performance improvement over Si for submicrometer gate length structures.<sup>2</sup> However, there is still activity in the passivation of GaAs surfaces and the control of the electronic properties of metal/GaAs interfaces, e.g., Ohmic and Schottky contacts. The surface properties of  $Ga_x Al_{1-x} As$  are of interest for a number of device application. For example, the exposed surface of a  $Ga_xAl_{1-x}As/In_xGa_{1-x}As/GaAs$  pseudomorphic high electron mobility transistor determines many of the electronic properties of the device. Breakdown voltages are generally controlled by surface effects, and defect states at the  $Ga_x Al_{1-x} As$  surface also can affect the rf performance of these devices. By retarding the response of the ungated access regions of the device, surface effects can prevent the effective modulation of the channel by the gate. This effect was first discussed within a materials context,<sup>3</sup> but also has been observed for devices,<sup>4</sup> where it is highly dependent on surface treatments such as passivation and the nature of the gate etch. Therefore, there is an interest in understanding the electronic properties of various kinds of GaAs surfaces and interfaces from both fundamental and applied perspectives.

A number of recent studies have established evidence that *n*- and *p*-type GaAs (001) surfaces exhibit very different Fermi-level pinning behavior.<sup>5-11</sup> The photoreflectance (PR) study of X. Yin *et al.*<sup>5</sup> (in air) first suggested that the density of surface states on *p*-type GaAs (001) surfaces was lower than on *n*-type material. This was confirmed by the scanning tunneling microscopy (STM) investigation [in ultrahigh vacuum (UHV)] of Pashley *et al.*<sup>6</sup> Subsequently a number of PR or contactless electroreflectance studies, both in  $air^{7-10}$  and in UHV (Ref. 11) have revealed *p*-type GaAs samples with much reduced surface-state densities and a Fermi-level position closer to the band edge in relation to *n*-type material.

In this paper, we report an *in situ* study of the surface Fermi-level pinning of *n*- and *p*-type GaAs (001) structures, which contain large, uniform built-in electric fields using PR in the UHV environment of a molecular-beamepitaxy (MBE) chamber. As-grown surfaces, as well as the effects of a few monolayers of arsenic deposition/desorption were investigated. From the observed Franz-Keldysh oscillations (FKO's), it was possible to obtain the built-in electric fields and hence the barrier heights of the  $n (V_{B,n})$ - and  $p (V_{B,p})$ -type samples in a contactless manner. Our results will be compared with other recent related works.

The GaAs samples used in this study consisted of an undoped layer of thickness L (=1000 Å) fabricated by MBE on top of an  $n^+$  ( $p^+$ ) buffer on an  $n^+$  ( $p^+$ ) substrate. We designate these special structures as  $UN^+$  $(UP^+)$ . The  $n^+$  ( $p^+$ ) doping level in the buffer was  $2 \times 10^{18}$  cm<sup>-3</sup> ( $2 \times 10^{18}$  cm<sup>-3</sup>). The surface Fermi level, together with the Fermi levels of the buffer/substrate layers, form a "parallel plate capacitor" across the undoped layer with a large and uniform electric field, whose strength is a direct measure of the surface barrier height. The PR investigations were carried out *in situ* at 300 K, with the samples in the MBE growth chamber. Measure-

4674

ments were first performed on an as-grown sample which had been transferred to a UHV buffer chamber of the MBE system  $(1 \times 10^{-11} \text{ Torr})$ . The sample was then returned to the MBE chamber for the deposition of 3-4 ML of As and finally desorption was accomplished by heating the material to 450 °C. The PR apparatus has been described in the literature.<sup>12</sup> The 633-nm line of a HeNe laser chopped at 200 Hz was used as the modulation source (pump beam). The probe beam was a 100-W tungsten halogen lamp dispersed by a  $\frac{1}{4}$ -m monochromator. The pump beam intensity was about 2 mW/cm<sup>2</sup>, whereas that of the probe beam was about 13  $\mu$ W/cm<sup>2</sup>.

Shown in Fig. 1 are the PR spectra at 300 K of the asgrown, arsenic-deposited, and arsenic-desorbed  $UN^+$  and  $UP^+$  structures. All samples exhibited well-defined FKO's. The built-in electric field (F) can be evaluated from the FKO's. The extrema in the observed FKO's are given by<sup>12</sup>

$$m\pi = \frac{4}{3} \{ [2\mu_{\parallel}(E_m - E_g)^3]^{1/2} / q\hbar F \} + \phi , \qquad (1)$$

where *m* is the index of the *m*th extrema,  $E_m$  is the photon energy of the *m*th extrema,  $E_g$  is the energy gap, *F* is the electric field,  $\mu_{\parallel}$  is the reduced interband mass in the direction of  $\vec{F}$ , and  $\phi$  is an arbitrary phase factor. From Eq. (1), the electric field *F* was obtained by fitting the quantity  $(4/3\pi)(E_m - E_g)^{3/2}$  as a function of index *m* to a straight line using  $\mu_{\parallel} = 0.055$  (Ref. 13) (in units of the free-electron mass).

In the  $UN^+$  ( $UP^+$ ) structures the barrier heights,  $V_{B,n}$  ( $V_{B,p}$ ), are related to F (as measured from the FKO's) by<sup>5,12</sup>

$$V_B = FL + (kT/q) + SCC , \qquad (2)$$

where the second and third terms are the Debye length and space-charge layer corrections (SCC), respectively.

It has been observed that such structure exhibit a photovoltaic effect at 300 K. Therefore, the surface Fermi level,  $V_F$ , is related to the measured barrier height,  $V_B$ , by<sup>5,10,12</sup>



FIG. 1. In situ photoreflectance spectra at 300 K for asgrown, arsenic-deposited, and arsenic-desorbed  $UN^+$  and  $UP^+$ samples.

$$V_F = V_B + V_P , \qquad (3)$$

where  $V_P$  is the photovoltage. Typically the value of  $V_P$  at 300 K is about 100 mV.<sup>5,10-12</sup>

Shown in Fig. 2 are the measured barrier heights  $V_{B,n}$  (solid circles) and  $V_{B,p}$  (open circles), relative to the respective band edges, for the as-grown, arsenic-deposited, and arsenic-desorbed situations.

For the as-grown samples, the measured barrier heights are  $V_{B,n} = 0.61$  V and  $V_{B,p} = 0.33$  V. These results are consistent with a number of other observations, both in  $air^{5,7-10}$  and in UHV.<sup>11</sup> For the *n*-type sample, correcting for the photovoltaic effect, the value of  $V_F$  is about 0.7 V, i.e., midgap pinning. Note that  $V_{B,n}$ remains constant for all the various procedures and also is in agreement with measurements in air. Alperovich, Paulish, and Terekhov<sup>11</sup> also found in their UHV investigation that for *n*-type material the Fermi level is firmly pinned, i.e., independent of various surface treatments. In their study of etched-induced damage in dry etched GaAs Glembocki et al.<sup>9</sup> also observed that  $V_{B,n}$  was unchanged by the various treatments. On the other hand, both Refs. 9 and 11 report that  $V_{B,p}$  could be increased, i.e., moved towards midgap, by various surface modifications. Alperovich, Paulish, and Terekhov found that p-type material could be cycled from an "unpinned"  $(V_{B,p} \approx 0.3 \text{ V})$  to a midgap pinning  $(V_{B,p} \approx 0.6 \text{ V})$  position by successive depositions of Cs and O<sub>2</sub>. These results are similar to our own observations (see Fig. 2).

The above results can be understood on the following basis. The STM investigation of Pashley *et al.*<sup>6</sup> has established that the mechanism for Fermi level pinning in *n*-type GaAs (001) is the formation of kink sites, which pin the Fermi level close to midgap at all doping levels. For *n*-type samples, the surface forms the exact density of acceptorlike kink sites needed to "pin" the surface Fermi-level midgap by compensating the donors forming the space charge region, i.e., the kink-site density increases with increasing *n* doping. This suggests that the MBE growth of *n*-type GaAs will inherently result in surface Fermi-level "pinning." This is consistent with various



FIG. 2. Measured barrier heights  $V_{B,n}$  (solid circles) and  $V_{B,p}$  (open circles) for as grown, arsenic-deposited, and arsenic-desorbed situations.

modulation spectroscopy experiments on *n*-type structures, i.e., they always exhibit midgap "pinning."<sup>5,9,11</sup> For *p*-type samples the kinks do not form donor sites, hence there is no driving force to form kinks, since they will not assist midgap "pinning" for high doping levels. Hence, the highly doped *p*-type, as-grown samples showed a surface Fermi level near the valence-band edge, i.e., not midgap Fermi level "pinning."

The results of this experiment, together with earlier studies on similar but air-stabilized samples, strongly suggests that Fermi-level pinning is due to As-related surface states, not defect-induced states.<sup>14</sup> This observation also is consistent with the recent *in situ* work of Alperovich, Paulish, and Terekhov.<sup>11</sup>

The work of D.Y. and F.H.P. was supported in part by NSF Grant No. DMR-9120363, ARO Contract No. DAAL-03-92-G-0189, and the NY State Science and Technology Foundation through its Centers for Advanced Technology Program.

- \*Also at the Graduate School and University Center of the City University of New York, New York, NY 10036.
- <sup>1</sup>See, for example, J. M. Woodall, P. D. Kirchner, J. L. Freeouf, D. T. McInturff, M. R. Melloch, and F. H. Pollak, Philos. Trans. R. Soc. London **344**, 521 (1993).
- <sup>2</sup>M. V. Fischetti and S. E. Laux, IEEE Trans. Electron Devices **ED-38**, 650 (1991).
- <sup>3</sup>S. R. Blight, R. H. Wallis, and H. Thomas, IEEE Trans. Electron Devices ED-33, 1447 (1986).
- <sup>4</sup>J. C. Huang et al., IEEE MTT-S Dig. 39, 713 (1991).
- <sup>5</sup>X. Yin, H.-M. Chen, F. H. Pollak, Y. Cao, P. A. Montano, P. D. Kirchner, G. D. Pettit, and J. M. Woodall, J. Vac. Sci. Technol. A 10, 131 (1992).
- <sup>6</sup>M. D. Pashley, K. W. Haberern, R. M. Feenstra, and P. D. Kirchner, Phys. Rev. B 48, 4612 (1993).
- <sup>7</sup>F. H. Pollak, J. Vac. Sci. Technol. B 11, 1710 (1993).

- <sup>8</sup>J. M. Woodall, in *Diagnostic Techniques for Semiconductor Materials Processing*, edited by O. J. Glembocki, F. H. Pollak, S. W. Pang, G. Larrabee, and G. M. Crean, MRS Symposia Proceedings No. 324 (Materials Research Society, Pittsburgh, 1994), p. 141.
- <sup>9</sup>O. J. Glembocki, A. J. Tuchman, K. K. Ko, S. W. Pang, A. Giordana, and C. E. Stutz, in *Diagnostic Techniques for Semiconductor Materials Processing* (Ref. 8), p. 153.
- <sup>10</sup>D. Yan, E. Look, X. Yin, F. H. Pollak, and J. M. Woodall, Appl. Phys. Lett. **65**, 186 (1994).
- <sup>11</sup>V. L. Alperovich, A. G. Paulish, and A. S. Terekhov, Phys. Rev. B 50, 5480 (1994); Surf. Sci. (to be published).
- <sup>12</sup>F. H. Pollak and H. Shen, Mater. Sci. Eng. **R10**, 275 (1993).
- <sup>13</sup>S. Adachi, J. Appl. Phys. 58, R1 (1985).
- <sup>14</sup>W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, J. Vac. Sci. Technol. 16, 1422 (1979).