Air stabilized (001) *p*-type GaAs fabricated by molecular beam epitaxy with reduced surface state density

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We present a contactless electromodulation study of undoped/p^+ GaAs (001) structures, fabricated by molecular beam epitaxy (MBE), which exhibit reduced surface state densities and surface Fermi level values closer to the band edge in relation to other p- or n-type GaAs (001) surfaces. The temperature dependence of the measured barrier height has been explained by a modified current-transport equation which contains two "pinning" levels (0.25 and 0.5 V relative to the valence band). Measurements were carried out in air and also *in situ* in the ultrahigh vacuum environment of a MBE chamber soon after growth and before the sample was removed to air.

After many decades of intense study, the origin of the surface states of GaAs is still not understood.[1] Further, except for isoelectronic heterojunctions, e.g., GaAlAs/GaAs, there is no viable technology for making either metal-oxide-semiconductor (MOS) or metal-insulator-semiconductor-like field-effect transistors with low interface state densities. In the case of GaAs it is not clear that there is still an interest in MOS field-effect transistor devices, since modeling results show no performance improvement over Si for submicron gate length structures.[2] 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. 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 presented evidence that p-type GaAs (001) surfaces have lower surface state densities in relation to n-type material.[3–7] Several authors have studied Fermi level "pinning" on n- and p-type GaAs(001) using photoreflectance (PR)[3,7–9] or contactless electroreflectance (CER)[4,6] from special structures which contain large, uniform electric fields. Pashley *et al.*[5] performed *in situ* scanning tunneling microscopy (STM) in UHV on n- and p-type bulklike material.

In this paper we present a CER and PR study of undoped (dimension $L=1000$ Å)/p^+ GaAs (001) structures (designated UP^+), fabricated by molecular beam epitaxy (MBE), which exhibit (a) a reduced surface state density and (b) Fermi level "pinning" values closer to the band edge in relation to other p or n-type GaAs (001) surfaces.[3,8,9] The CER investigation was carried out in air while the PR work was performed *in situ* in the UHV environment of an MBE chamber soon after growth and before the sample was removed to air. The effects of the *in situ* deposition of several monolayers of As on the (001) GaAs surface also has been assessed using PR. From the observed Franz-Keldysh oscillations (FKOs) using CER we have measured the barrier height $[V_B(T)=V_F(T)-V_P(T)]$ over a wide temperature range ($15<T<400$ K), where $V_F(T)$ is the surface Fermi level and $V_P(T)$ is the photovoltage. In contrast to the work of Ref. 3, where $V_P(T)$ was accounted for on the basis of current-transport theory using only one mid-gap "pinning" site, in the present study $V_P(T)$ is due to two "pinning" levels lying closer to the valence band edge. Our results also will be compared with (a) a recent study (in air) of similar MBE fabricated UP^+/UN^+ structures, including the effects of etch-induced damage,[7] and (b) the STM work (UHV) of Pashley *et al.*[5] These investigations also have found reduced surface state densities on p-type GaAs (001) in relation to n-type material.

In PR (*in situ*) the modulation was created by a chopped (200 Hz) HeNe laser (633 nm) pump beam of intensity 2 mW/cm^2. For both *ex situ* CER (no pump beam) and *in situ* PR the intensity of the probe beam was 13 μW/cm^2.

We have used a modified current-transport equation for $V_P(T)$ in order to take into account two pinning levels[10]

$$V_P(T)=(kT/q)\ln\left(\frac{\gamma P_m(1-R_0)/\hbar\omega}{[A^{**}T^2/(1+BT^{3/2})]\Sigma_{i=1}^{2}r_i(1-F_i)\exp(-qV_i/\eta_i kT)}+1\right), \tag{1}$$

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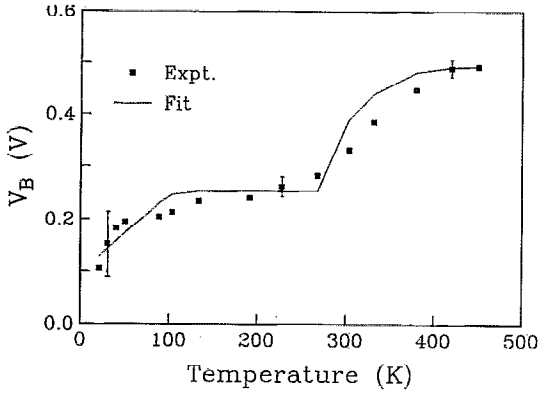

FIG. 1. The measured barrier height $V_B(T)$, in air, of a UP^+ sample as a function of temperature. Representative error bars are shown. The solid line is least-square fit to Eqs. (2) and (4).

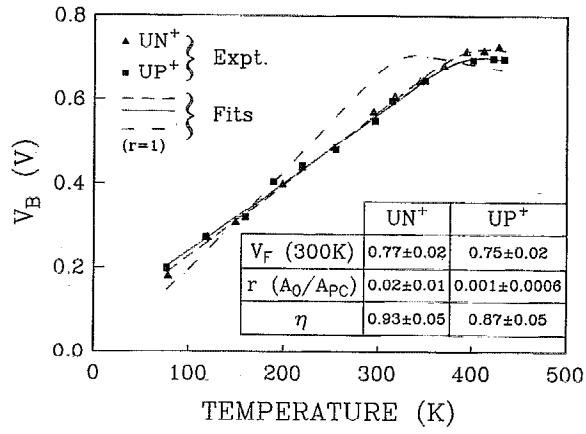

FIG. 2. The measured barrier height $V_B(T)$, in air, of UN^+ (triangles) and UP^+ (squares) samples as a function of temperature from Ref. 3. The solid (UN^+) and dashed (UP^+) lines are least-square fits to a current-transport equation with one pinning level (V_F). The obtained values of V_F, r, and η are shown in the inset. The dot-dashed line is a least-squares fit for the UN^+ sample with $r=1$.

where P_m is the light intensity, γ is the quantum efficiency (=1), R_0 is the reflectivity of the light at the semiconductor surface (=0.34), $\hbar\omega$ is the photon energy of the light, A^{**} is the modified Richardson constant (which is proportional to the effective mass of the carrier), and B is a constant defined in Ref. 3. The parameters V_i, r_i, η_i, and F_i are the position (relative to the band edge), geometry factor, ideality factor, and occupation probability, respectively, of the ith level. The geometry term r was introduced in Ref. 3 to take into account the fact that only a fraction of the surface has states to accommodate the saturation (dark) current. The factor $(1-F_i)$ has been introduced so that when a certain level (particularly $i=1$) is full it no longer contributes to V_P. The important fitting parameters are η_i, r_i, and V_i.

In addition, there must be the right amount of charge on the surface of the "parallel plate capacitor" UP^+ (or UN^+) structure to produce the measured field, i.e., V_B. This charge/area also determines the Fermi leve, V_F. Thus we also have

$$V_B(T)=Q(T)/C, \quad Q(T)=qN_0\sum_{i=1}^{2} n_i r_i F_i(T),$$

$$C\approx \epsilon\kappa_0/L, \tag{2a}$$

$$F_i(T)=\int_{-\infty}^{\infty}\{\exp[(E'-V_i)^2/2\sigma_i^2]/(2\pi)^{1/2}\sigma_i\}$$

$$\times\{\exp[(E'-V_F)/kT]+1\}^{-1}dE', \tag{2b}$$

so that

$$V_B(T)=(qN_oL/\epsilon\kappa_0)\sum_{i=1}^{2} n_i r_i F_i(T). \tag{3}$$

where $\epsilon_0(=12)$ is the static dielectric constant of GaAs, κ is the permittivity of free space, N_o is the density of atoms on the surface (6.3×10^{14} cm^{-2}), n_i is the number of charges that can be put on each site r_i, and $\sigma_i=10$ meV for both levels.

Shown by the solid line in Fig. 1 is a least-squares fit of the data to Eqs. (1) and (3). The obtained values of the relevant parameters are $\eta_1=1.75$, $V_1=0.25$ V, $r_1=4\times10^{-4}$, $n_1=1$, $\eta_2=0.88$, $V_2=0.5$ V, $r_2=4\times10^{-4}$, and $n_2=1$. Thus there are two "pinning" levels at 0.25 and 0.5 V above the valence band.

For comparison purposes we show in Fig. 2 the values of $V_B(T)$ as as function of temperature for GaAs (001) UP^+ (squares) and UN^+ (triangles) structures (in air) from Ref. 3. The dashed (UN^+) and solid (UP^+) lines are least-squares fits to Eq. (1) with $i=1$ (i.e., only one pinning level at V_F). The obtained values of the relevant parameters are listed in the inset.

Above about 250 K the curve of Fig. 1 is similar to the UP^+ (and UN^+) sample of Fig. 2, a major difference being that the saturation value of $V_B(T)$ is only about 0.5 V (V_2), instead of 0.75 for the UP^+ (and UN^+) sample of Fig. 2. Another important observation is that $V_B(T)$ in Fig. 1 saturates at about the same temperature (≈425–450 K) as the corresponding material of Fig. 2.

Another significant difference between Figs. 1 and 2 is the low-temperature behavior. For the former sample there is a plateau at about 0.20–0.25 V between 100–250 K and then $V_B(T)$ turns over and approaches zero. The presence of this plateau indicates that there is another "pinning" level (V_1) at about 0.2–0.25 V above the valence band edge.

We also have examined an as-grown UP^+ GaAs (001) structure at 300 K using PR *in situ* in a MBE chamber before removal to air. In this case also a reduced surface state density was observed. It was found that $V_B(300)\approx0.36$ V, in good agreement with the data of Fig. 1 but considerably lower than the UP^+ sample in Fig. 2. After the deposition of several monolayers of As the barrier height, V_B (300), increased to about 0.6 V, similar to Fig. 2, i.e., a midgap pinning level.

In a recent PR investigation of UP^+/UN^+ GaAs (001) MBE structures in air Glembocki *et al.*[7] also have found evidence for reduced surface state densities on p-type surfaces. As a function of temperature it was found that $V_B(T)$ satu-

rated at about 425–450 K for both UP^+ and UN^+ samples with values of 0.3 and 0.7 V, respectively.

Of the possible reasons which could account for the lower surface-state densities observed in UP^+ structures compared with UN^+ configurations, a likely explanation may be related to a recent STM result by Pashley *et al.*[5] to characterize the electronic properties of MBE grown GaAs (001) surfaces with $(2\times4)/c(2\times8)$ reconstructions. 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 modulation spectroscopy experiments on UN^+ structures, i.e., they always exhibit midgap "pinning."[3,7–9] 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 valance band edge, i.e., not midgap Fermi level pinning. This behavior could account for the observations of the present study and Ref. 7 since these samples also had (001) surfaces grown by MBE. However, this can only be part of the explanation, since the Pashley *et al.* results were obtained in UHV on pristine surfaces while our surfaces and Ref. 7 had been air exposed. Therefore, in addition to the above argument we must account for the stability in air of our low surface-state density UP^+ structures.

We suggest that this stability is due to photoelectrochemical properties of the p-type surface of GaAs. It is well known that many n-type compound semiconductor surfaces including GaP surfaces, are unstable against greater than band-gap energy photon illumination in aqueous solutions while p-type GaAs (Ref. 11) and GaP (Ref. 12) surfaces are stable under these conditions. The obvious photoelectrochemical difference between n- and p-type surfaces is the minority carrier type which under illumination crosses the semiconductor/electrolyte interface. For illuminated n-GaAs the reaction is $GaAs+6e^+ \Leftrightarrow Ga^{3+}+As^{3+}$, which leads to photo-oxidation/etching, i.e., Ga and As oxides and elemental As. It is reasonable to conclude from the stability of p-type photochemical electrodes that the electron minority carrier current into the solution results in surface passivation. In illuminated p-GaAs the reaction is $GaAs+3e^- \Leftrightarrow Ga+As^{3-}$ and $As^{3-}+3H^+ \Leftrightarrow AsH_3$, which leads to passivation, i.e., Ga oxide. If so, this would account for the air stability of our UP^+ structures. We plan to confirm this in future studies by STM characterization of these surfaces.

One of the important findings of this study was the qualitative change in the nature of the surface defects as the concentration of the defects was reduced by improved MBE growth of UP^+ structures over those reported in the past.[3,8] Previously we had found midgap pinning for both air exposed and metallized UN^+ and UP^+ structures, i.e., $|E_{\text{band edge}}-E_{F-\text{surface}}|\sim0.75$ eV.[8] This pinning has been correlated with the presence of elemental arsenic which exists at equilibrium at the interface of GaAs and its native oxide, i.e., Ga_2O_3 and As_2O_3. There is some controversy as to the fundamental relation of the As with the pinning energy or pinning states. It could be argued either that the presence of As would correlate to surface native defects[13] in the GaAs which would pin the Fermi level at their respective defect levels; or the presence of As would pin the Fermi level via its work function. The As work function would fix the Fermi level at exactly midgap whereas the native defects would be expected to pin near midgap at slightly different energies, separated by about 0.2 V, depending on the conductivity type, nearer the conduction band edge for n type and nearer the valence band for p type. However, for pinning to occur it requires a sufficient density of states of the pinning sites, about 10^{13} cm^{-2}, for previous midgap pinned structures.

It is interesting to note that in the study of UP^+ samples the 0.7 V pinning site has been greatly reduced. What is uncovered then are two new pinning levels at 0.5 and 0.25 V above the valence band whose density is about 2.5×10^{11} cm^{-2} (rN_0). This density is sufficient to measure in our experiment but is insufficient to firmly pin the Fermi level, i.e., to dominate Schottky barrier formation at metal/GaAs interfaces. We conclude therefore that these new levels are most likely related to surface native defects and, while present at small concentration, are not a factor in the midgap pinning at metal/GaAs interfaces. Rather these results add support to the model which suggests that midgap pinning at metal/GaAs interfaces is directly correlated with As acting via its work function.

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