

Band bending, Fermi level pinning, and surface fixed charge on chemically prepared GaAs surfaces

E. Yablonoivitch, B. J. Skromme, R. Bhat, J. P. Harbison, and T. J. Gmitter
Bellcore, Navesink Research Center, Red Bank, New Jersey 07701-7020

(Received 31 August 1988; accepted for publication 5 December 1988)

We compare the nature of the band bending under GaAs surfaces prepared by alkaline sulfides [$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{S}$] with that under oxidized GaAs surfaces. We make the point that Fermi level pinning implies band bending, but band bending does not necessarily imply "pinning." In either case, even weak light illumination substantially flattens the bands. On ammonium sulfide treated surfaces the fixed and trapped charge density in the dark is only $\sim 5 \times 10^{11}$ electrons/cm², but these few states are mostly neutralized at low-level forward injection. This behavior should not be confused with Fermi level pinning.

Since the favorable electronic effects of the alkaline sulfides on GaAs surfaces were first¹ discovered, they have found particular application in reducing the surface recombination currents on the edges of bipolar GaAs devices. The edge recombination leakage on heterojunction bipolar transistors,² *p-n* homojunctions,³ and GaAs solar cells⁴ has been greatly improved. On the other hand, Besser and Helms⁵ and Hasegawa *et al.*⁶ have monitored the presence of band bending on these surfaces and interpreted that band bending in terms of Fermi level pinning. They claim that the reduction in surface recombination velocity (SRV) is simply due to the Fermi level being "repinned" closer to the valence-band maximum. Aside from the inconsistency of such a model with the bipolar device improvements listed above, we believe that it is incorrect to necessarily associate band bending with Fermi level pinning.

Fermi level pinning implies band bending, but band bending does not necessarily imply "pinning." Band bending is caused by the total surface charge, $Q = Q_{it} + Q_f$, which is the sum⁷ of surface trap charge Q_{it} due to defect states in the gap and surface fixed charge Q_f (e.g., ionic charge on the surface). Under surface fixed charge Q_f , the Fermi level can still move freely, while under "pinning" the density of states, D_{it} , in the gap must be so high that neither external electric fields nor bulk doping can budge the Fermi level. Furthermore, even when gap-state charge Q_{it} contributes to the band bending, it still need not imply Fermi level pinning. A surface trap charge Q_{it} as low as 10^{11} charges/cm² can bend the bands in lightly doped material, but a "pinned" surface is usually interpreted to require a significantly higher surface state density.

Therefore, the concept of Fermi level pinning must be used with great care. This is particularly true under optical or forward injection.¹ Then we are dealing with a quasi-Fermi level for electrons which can be different from the quasi-Fermi level for holes. If there is "pinning," which of the two Fermi levels is "pinned"? The paradox is resolved when we realize that "pinning" is a yes/no description of semiconductor surfaces, but real semiconductor surfaces are very complicated⁷ and require a multidimensional description. A qualitative yes/no serves only the simplest of cases such as when D_{it} is extremely high.

Our goal here is to investigate the band bending under

GaAs surfaces both in the dark and under forward optical injection. As was already pointed out in Ref. 1, under strong optical injection the carrier density itself will tend to flatten the bands. Nevertheless, there can still be a small residual band bending which can repel minority carriers and reduce the SRV. The SRV change as a function of forward injection level can then be used as a measure of Q_f as was done in Fig. 3 of Ref. 1 (Q_{it} was $< Q_f$ in that case). In this letter we seek to measure the band bending even in total darkness and therefore we use a method equivalent to the ungated field-effect transistor (FET) approach of Besser and Helms⁵ and Hasegawa *et al.*⁶ Since band bending and surface depletion reduce the channel thickness, the change in sheet conductance is a direct measure of the change in depletion layer thickness.

In our case, instead of measuring the sheet conductance between a source and drain, we measure it by rf inductive coupling to the surface channel. The apparatus in Fig. 1 is essentially identical to the contactless minority-carrier lifetime probe of Ref. 1, with the difference that we are measuring steady-state conductivity instead of pulsed conductivity.

The inductively coupled radio frequency (500 MHz) bridge response is directly proportional to sheet conductance. To convert it to reciprocal ohms or "mhos," it is merely necessary to calibrate it against known sheet resistance standards. The GaAs channel itself can be used as a standard if its sheet resistance is independently known, or any other standard of the identical size and shape can be used.

Typical sheet conductivity results are shown in Fig. 2.

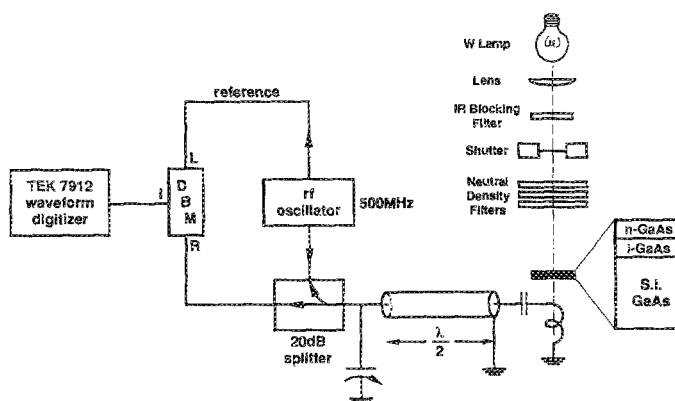


FIG. 1. Sheet conductance of an ungated FET channel is monitored by rf induction at 500 MHz, obviating the need for source and drain.

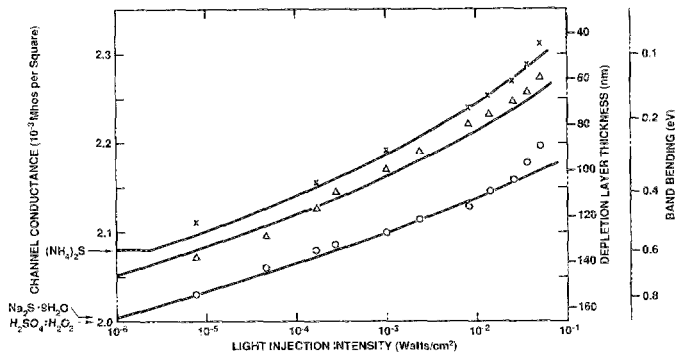


FIG. 2. O, $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ -etched surface; Δ , $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ -coated surface; \times , $(\text{NH}_4)_2\text{S}$, dried under N_2 gas. The three arrows on the left side give the dark sheet conductivities for the three respective chemical reagents. The solid lines are given by Eq. (3) using only J_0 as an adjustable parameter.

This particular sample has an epitaxially grown channel about 7500 \AA thick and doped to a net density $N = 5 \times 10^{16} \text{ cm}^{-3}$. Separating the channel from the semi-insulating substrate is a $\sim 1\text{-}\mu\text{m}$ -thick undoped buffer layer. The vertical axis of Fig. 2 reads directly in absolute sheet conductance (mhos). Since the bulk conductivity for this doping level of $n\text{-GaAs}$ is known, the sheet conductance scale can be converted directly into a depletion layer thickness scale. Thus the vertical scale in thickness units is known directly, but the zero of the thickness scale is undetermined since the absolute total channel thickness is not accurately enough known. Therefore, the absolute zero of the depletion layer thickness scale on the right-hand side of Fig. 2 was determined from the data by a model which will be described later in the letter. Once the depletion layer thickness W is known, the band bending Ψ can be derived from it by

$$q\Psi = (2\pi Nq^2/\epsilon)W^2, \quad (1)$$

where q is the electronic charge and $\epsilon \approx 13.1$ is the static dielectric constant of GaAs. This band bending is shown on the vertical scale at the far right of Fig. 2. The horizontal scale is light injection intensity from an incandescent lamp in W/cm^2 , attenuated by calibrated neutral density filters.

Three different surface preparations are shown in Fig. 2: circles, a low quality surface resulting from an oxidizing etch $1:8:500$ ($\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$), rinsed in distilled water, then dried in air; presumably, this surface is highly defective and subject to Fermi level pinning; triangles, a surface oxidized as above, then soaked⁸ for 10 min in a 1 M aqueous solution of Na_2S , spun dry at 5000 rpm, leaving behind a dry polycrystalline film of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, $\sim 1 \mu\text{m}$ thick; crosses, a surface oxidized as above, then dipped in $(\text{NH}_4)_2\text{S}$, allowed to dry under N_2 gas, and measured under N_2 gas. The three arrows on the left side of Fig. 2 give the dark sheet conductivities for the three respective chemical reagents.

Under the rather weak incandescent light injection levels employed here, the minority holes are definitely in low-level injection: $p \ll 10^{10} \text{ cm}^{-3}$. Therefore, the bulk injected carrier concentration is an insignificant contributor to the sheet conductivity (about a part per 10^6). In such weak light, the main contribution to the change in sheet conductivity is the change in depletion depth of the majority carriers (about a 10% effect as seen in Fig. 2). This is quite the opposite to the higher level Q -switched laser injection condi-

tions generally¹ employed to measure carrier lifetime on the same apparatus in the past. There, the change in depletion depth was a small baseline on which the much larger bulk injected carrier conductivity was superimposed.

The most remarkable result in Fig. 2 is the very low light intensity threshold for band-flattening effects. On the sulfuric-peroxide ($\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) treated oxidized GaAs surface, the threshold intensity is $\sim 1 \mu\text{W/cm}^2$. In typical room light the band-flattening effect can already be 0.1–0.2 eV. On the higher quality alkaline sulfide treated surfaces, for a given light intensity, the bands are more flat corresponding to reduced surface recombination, and in the $(\text{NH}_4)_2\text{S}$ case to lower dark band bending as well. This should stand as a caution to many types of band-bending experiments on GaAs, particularly photoemission.⁹ Weak background light will influence the band bending measured by photoemission, Raman scattering,¹⁰ as well as by any other technique.

We will now attempt to model the functional dependence of the band bending on light intensity. In the presence of light, the electrons near the front surface will be out of equilibrium with the holes and each will have its own quasi-Fermi level. A steady state is set up, in which the recombination of electron-hole pairs is balanced by the newly created pairs diffusing to the surface. Under Shockley–Read–Hall (SRH) kinetics¹¹ the quasi-Fermi level separation ΔV near the surface is given by

$$J = J_0 \exp(q\Delta V/nkT), \quad (2)$$

where J is the available current density of electron-hole pairs, J_0 is the forward leakage current, kT is the thermal energy, and $n = 1$ for diffusive recombination or $n = 2$ for depletion region recombination. At the low injection levels considered here, the $n = 2$ component will dominate. The shift in quasi-Fermi levels will reduce the band bending by $\Psi_d \rightarrow \Psi_d - n'\Delta V$, where Ψ_d is the band bending in the dark. If the electron Fermi level is "pinned," the light will have no effect and $n' = 0$, or if the hole quasi-Fermi level tends to be "pinned," the light will flatten the bands and $n' = 1$. Taking $n = 2$, $n' = 1$, and combining Eqs. (1) and (2):

$$q\Psi_d - 2kT \ln\left(\frac{J}{J_0}\right) = \frac{2\pi Nq^2}{\epsilon}W^2. \quad (3)$$

Differentiating Eq. (3):

$$\frac{d \log(J/J_0)}{dW} = -\frac{2\pi Nq^2}{2.303\epsilon kT}W. \quad (4)$$

The left-hand side of Eq. (4) is essentially the inverse slope of the data points on Fig. 2, which is fixed independent of the absolute zero of the depletion thickness scale or the absolute units J_0 of the logarithmic current scale. Given the slope of the data points, the only unknown in Eq. (4) is W , which sets the zero of the depletion thickness scale on the right side of Fig. 2. Using that zero, our measured Ψ_d for oxidized $n\text{-GaAs}$ in the dark is $\sim 0.9 \text{ eV}$, near the generally¹² reported pinning position.

This model of course depends on certain assumptions, such as the constancy of n and n' as a function of injection level. However, more rigorous numerical calculations, based on solution of the Poisson–Boltzmann equation and SRH kinetics for surface states, including both traps and fixed

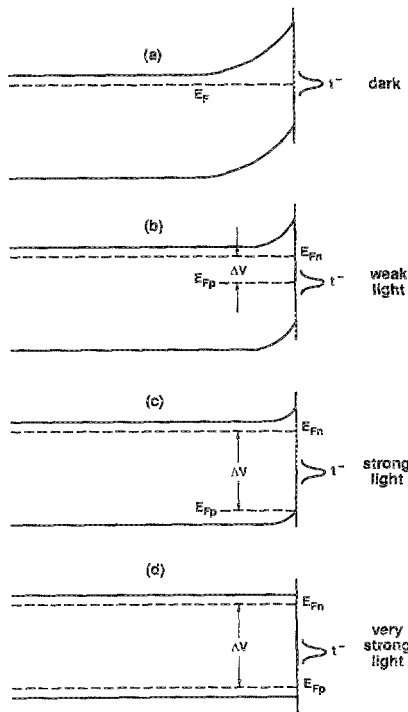


FIG. 3. (a) Band bending in the dark for the $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ case. The t^- represent the surface traps largely responsible for dark band bending. For $(\text{NH}_4)_2\text{S}$ the Fermi level stays above t^- . (b) Low injection conditions appropriate to this experiment. The electron Fermi level moves freely, but the hole Fermi level is temporarily "pinned." The bands begin to flatten. (c) Strong injection, both Fermi levels move freely, and traps t^- become empty, but some surface fixed charge Q_f remains. (d) Near degenerate injection, all band bending is screened out.

charge, have been used to justify the main assumptions. Details of this theory will be given elsewhere.¹³

We can understand the behavior of the quasi-Fermi levels by looking at Figs. 3(a)–3(d). Starting from Fig. 3(a), the usual pinning position is identified with negatively charged surface traps t^- somewhat below midgap. For the $(\text{NH}_4)_2\text{S}$ case, the density of t^- is evidently insufficient to produce complete pinning at this doping level. The smaller observed Ψ_d for this case implies $Q = 5 \times 10^{11}$ electrons/cm². Consistent with this surface charge concentration, in a more heavily doped sample ($N = 1.2 \times 10^{17}$ cm⁻³) we observe $\Psi_d = 0.2$ eV, *i.e.*, falling roughly reciprocally with the higher doping level.

The weak-light conditions of this experiment are identified with Fig. 3(b). As already emphasized, the electron Fermi level moves freely, but the hole Fermi level tends to be "pinned." The reasons for this, instead of the reverse, are that the "pinning traps" t^- are below midgap, there are more holes than electrons near the surface, and the hole capture cross section is larger. Thus the t^- occupancy is controlled by the hole Fermi level. Equation (3) is the solid line used to fit the data points in Fig. 2 with forward leakage current J_0 as the only adjustable¹⁴ parameter.

But hole Fermi level "pinning" is far from absolute. As the bands are flattened, the t^- levels are gradually emptied (with the above capture cross-section ratio), leaving only surface fixed charge Q_f to produce residual band bending. At that injection level, shown in Fig. 3(c), the hole Fermi level becomes "unpinned," just as the electron Fermi level had already been. The traps t^- are neutral and no longer bend the bands, but they can still act as recombination centers. Finally, at the highest injection levels in Fig. 3(d) all surface charge is screened out and the bands become completely flat. Figures 3(c) and 3(d) are accessible, not in this experiment, but rather in the Q -switched laser-pumping regime of Ref. 1.

For $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ -coated surfaces exposed to air, Ψ_d

tends to track the dark "pinning" level of the sulfuric-peroxide GaAs surface for doping $N \leq 10^{17}$ cm⁻³, indicating $Q_{it} \sim 10^{12}$ traps/cm², more than twice that of the $(\text{NH}_4)_2\text{S}$ surface under N_2 gas. Under strong light [as in Fig. 3(c) and using the methods of Ref. 1] these traps become emptied (neutral), leaving a fixed surface charge Q_f of $\sim 2 \times 10^{11}$ and $\sim 1 \times 10^{11}$ charges/cm² for $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{S}$, respectively.¹⁵ Nevertheless, the SRV measured at very high injection as in Ref. 1 and Fig. 3(d) and corrected for Q_f , favored $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ over $(\text{NH}_4)_2\text{S}$ by roughly a factor 3. Evidently, the t^- traps may have low recombination cross sections, even though they comprise most of the surface charge in the dark.

It is tempting to identify the t^- traps with excess elemental arsenic (As^0). Preferential oxidation of Ga is thought to generate As^0 on GaAs surfaces. We found that $(\text{NH}_4)_2\text{S}$ dissolves intentionally evaporated As^0 films at the rate of ~ 3 Å/s, while Na_2S solutions are relatively ineffective at dissolving such films. This suggests that the dissolution of As^0 is responsible for the lower concentration of t^- produced by $(\text{NH}_4)_2\text{S}$. [($\text{NH}_4)_2\text{S}$ -treated surfaces are sufficiently "unpinned" to allow four-point probe resistance measurements for n -GaAs doping levels $N \geq 10^{17}$ cm⁻³]. Under either reagent, air oxidation increases the t^- concentration within about 20 or 30 min, and shifts Ψ_d to the dark "pinning" position of sulfuric-peroxide GaAs.

In conclusion, the alkaline sulfide treated GaAs surfaces have a relatively modest density of trapped and fixed surface charge ($Q_{it} + Q_f$) in the dark. Upon low-level forward injection, the trapped charge is neutralized, leaving only a small residual band bending. This should not be confused with Fermi level pinning.

¹E. Yablonovitch, C. J. Sandroff, R. Bhat, and T. Gmitter, *Appl. Phys. Lett.* **51**, 439 (1987).

²C. J. Sandroff, R. N. Nottenburg, J.-C. Bischoff, and R. Bhat, *Appl. Phys. Lett.* **51**, 33 (1987).

³M. S. Carpenter, M. R. Melloch, M. S. Lundstrom, and S. P. Tobin, *Appl. Phys. Lett.* **52**, 2157 (1988).

⁴P. D. DeMoulin, S. P. Tobin, M. S. Lundstrom, M. S. Carpenter, and M. R. Melloch, *IEEE Electron Device Lett.* **EDE-9**, 368 (1988).

⁵R. S. Besser and C. R. Helms, *Appl. Phys. Lett.* **52**, 1707 (1988).

⁶H. Hasegawa, H. Ishii, T. Sawada, T. Saitoh, S. Konishi, Y. Liu, and H. Ohno, *J. Vac. Sci. Technol. B* **6**, 1184 (1988).

⁷E. H. Nicollian and J. R. Brews, *MOS Physics and Technology* (Wiley, New York, 1982).

⁸The 10 min soak step was inadvertently omitted from the original procedure in Ref. 1.

⁹W. E. Spicer, I. Lindau, P. Skeath, C. Y. Su, and P. Chye, *Phys. Rev. Lett.* **44**, 420 (1980).

¹⁰L. A. Farrow, C. J. Sandroff, and M. C. Tamargo, *Appl. Phys. Lett.* **51**, 1931 (1987).

¹¹A. S. Grove, *Physics and Technology of Semiconductor Devices* (Wiley, New York, 1967).

¹²H. H. Weider, *J. Vac. Sci. Technol.* **17**, 1009 (1980).

¹³B. J. Skromme (unpublished).

¹⁴For average photon energy of ~ 2 eV, the W/cm² can be converted to A/cm². The fitted J_0 's for sulfuric-peroxide, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{S}$, are, respectively, $\sim 4 \times 10^{-7}$, $\sim 10^{-8}$, and $\sim 3 \times 10^{-9}$ A/cm². If the trapping level t^- is at the same energy position in all three cases, then these J_0 can be used to derive reasonable SRVs for $n = 2$ surface recombination.

¹⁵In fact, the behavior of SRV as a function of injection reported in Ref. 1 cannot be obtained without fixed charge and further implies that the donor-like trap density in the band gap must be $<$ fixed charge. These statements will be justified in Ref. 13.