

Unpinned (100) GaAs surfaces in air using photochemistry

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We have unpinned the Fermi level at the surface of both *n*- and *p*-type (100) GaAs in air. Light-induced photochemistry between GaAs and water unpins the surface Fermi level by reducing the surface state density. Excitation photoluminescence spectroscopy shows a substantial decrease in both surface band bending and surface recombination velocity in treated samples, consistent with a greatly reduced surface state density ($\cong 10^{11} \text{ cm}^{-2}$). Capacitance-voltage measurements on metal-insulator-semiconductor structures corroborate this reduction in surface state density and show that the band bending may be controlled externally, indicating an unpinned Fermi level at the insulator/GaAs interface. We discuss a possible unpinning mechanism.

Although GaAs appears to be a good candidate material for high speed, high density integrated circuits, no GaAs technology has been developed that has the large, controllable barrier heights and low power consumption that can be obtained with silicon metal-oxide-semiconductor (MOS) technology. While the Si-SiO₂ system has a density of surface states of $\sim 10^{10}/\text{cm}^2$, the GaAs surface is "pinned" at 0.8 eV below the conduction band with about 10^{13} states/cm² and contains several nonstoichiometric phases, some of which are conducting.¹ Several types of GaAs metal-insulator-semiconductor field-effect transistors (MISFET's) have been fabricated,²⁻⁵ but their performance is hampered by the large surface state densities. In this letter it is shown for the first time that the surface Fermi level of both *n*- and *p*-type (100) GaAs can be unpinned in air by photochemistry. Photoluminescence (PL) is used to determine both the surface recombination velocity and equilibrium band bending,⁶ while *C-V* data are used to verify that the band bending is easily varied with gate voltage.

The experimental setup used for both the surface unpinning procedure and the photoluminescence measurement is shown in Fig. 1. The sample was held on a vacuum chuck spinner in air and was simultaneously washed with a stream of "polished", de-ionized water and illuminated with a 15-W/cm² argon laser (488 nm) to induce the unpinning photochemistry. For the photoluminescence measurements, the water was allowed to spin off and the argon laser was replaced by a shutter-chopped beam from either a 250-mW/cm² helium cadmium blue laser (440 nm) or a 250-mW/cm² helium neon red laser (633 nm). The emitted band edge photoluminescence radiation was then collected by a photomultiplier detector equipped with a bandpass filter centered at approximately 850 nm (1.4 eV), and the resulting ac signal was fed to a lock-in amplifier (along with the shutter signal). The helium cadmium laser was also successfully used to induce the photochemistry, but the lower intensity caused the surface unpinning process to take many minutes instead of seconds.

The GaAs wafers (typically $n = 2 \times 10^{17}/\text{cm}^3$) were first cleaned in hot sulfuric acid and water (1:1) to generate

a reproducible starting surface. The samples were then put on the spinner and the initial PL intensity resulting from both blue and red laser excitation was recorded. Next, the 15-W/cm² argon laser was turned on and 18 MΩ de-ionized water was squirted at the laser-illuminated spot on the spinning sample for approximately 15 s. After spinning dry, the PL intensity from blue excitation was remeasured. This illumination/washing process and remeasurement were repeated two or three times, until a maximum blue PL intensity was obtained. The PL intensity both before and after treatment was also measured using 633 nm (red) excitation. It was found that after this treatment, the PL intensity from both red and blue laser excitation increased for both *n*- and *p*-type samples, the increase being greater for blue excitation than for red and greater for *n*-type material than for *p*-type. The typical change in PL from before to after treatment is shown in Fig. 2 at time $t = 0$ for both *n*- and *p*-type samples using blue excitation. (The change in PL with time will be discussed below.) It is important to note that there is no increase in the PL intensity for the cases of either spinning the sample in air without water with the argon laser on or spinning the sample with water in the dark. Not shown in Fig. 2 is the red to blue PL ratio which when coupled with minority-carrier diffusion length measurements allows the determination of band bending and surface recombination velocity, and hence the filled surface state density. The smallest red to blue PL ratio for *n*-type samples was about 1.5.

The fact that the photoluminescence intensity increases with treatment for both *n*- and *p*-type material indicates that the surface is unpinning, and is not just being pinned at a different point. As the surface unpins, the Fermi level approaches the bulk level (flatband condition) so that the depletion layer width and the associated drift field due to band bending decrease. This by itself will reduce the number of minority carriers that recombine at the surface and cause the number that recombine radiatively in the bulk to increase. Thus the PL intensity, which had been greatly reduced by pinning, is improved. Since the blue radiation is absorbed over shorter distances than the red in GaAs, it is more sensitive to the band bending and shows a greater change with treatment. Also, since the usual pinning position is closer to

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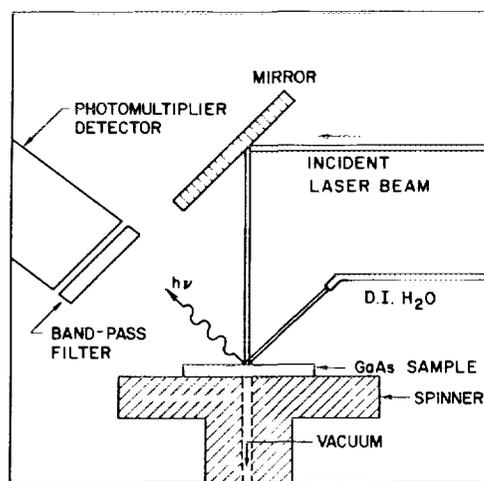


FIG. 1. Experimental setup for the unpinning procedure and the PL measurements. The sample is spun on a vacuum chuck spinner, and for the unpinning is exposed to an argon laser and washed in 18 M Ω de-ionized water. Photoluminescence is measured using shutter-chopped lasers in the red and blue, and a photomultiplier detector equipped with a 1.4-eV band-pass filter.

the valence band than the conduction band, it is expected that less of an improvement would be observed in *p*-type material than in *n*-type. This is consistent with the data in Fig. 2. The actual Fermi level position can be determined by comparing the relative PL intensities at 633 nm (red) and 440 nm (blue) to the theoretical ratio obtained from the computer simulation described in Ref. 6. The minority-carrier diffusion length was needed for this analysis and was found to be 0.5 μm using the electron beam induced current (EBIC) method.^{7,8} For low surface recombination velocities and flatband condition, it would be expected that the red and blue relative PL intensities would be nearly equal, but in pinned samples the measured ratio of the 633 nm intensity to the 440 nm intensity ranged from 8 to 15, consistent with strong band bending and a large surface recombination velocity. After the samples had been treated the ratio decreased to about 2. According to the simulations, these values correspond to a change from a surface barrier height

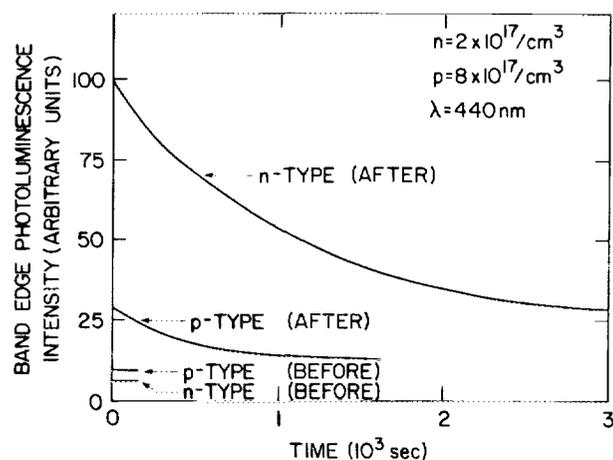


FIG. 2. 440 nm excitation band edge photoluminescence intensity vs time for *n*-type and *p*-type samples after the unpinning treatment. Pinned levels are included for reference.

(band bending) of 0.8 eV and a surface recombination velocity of 10^7 cm/s to ~ 0.1 eV and 10^4 cm/s, respectively.

The density of *filled* surface states can also be approximated, since the total charge in the filled states is about equal to the charge in the depletion region. For $N_D = 2 \times 10^{17}/\text{cm}^3$, a 0.8-V barrier height (i.e., pinned) yields a 760- \AA depletion width. Multiplying by the fixed charge density, N_D yields a density of filled surface states of $1.5 \times 10^{12}/\text{cm}^2$. Although the total surface state density for the pinned material is not known, its value should be within the range of reported values ($\sim 10^{13}/\text{cm}^2$) and their energies are believed to be relatively localized at ~ 0.8 eV below the conduction band.^{1,9-12} The large density of unfilled states in the pinned material is the cause of the extremely large surface recombination velocity. On the other hand, a surface barrier height of 0.1 V (i.e., unpinned) yields a depletion width of 280 \AA and a density of filled surface states of about $5 \times 10^{11}/\text{cm}^2$. The position of the Fermi level in this case indicates that all states at the point 0.8 eV below the conduction band are now filled, so that while the density of filled states has only changed by a factor of 3, the total density of surface states has been reduced by at least a factor of 15 to 20. Also, since these midgap surface states are now completely filled, the surface recombination velocity should be greatly reduced, which is in agreement with the simulation results given above.

The possibility that the Fermi level might be unpinned immediately suggested the formation of MIS capacitors for controlling the band bending. Despite its obviously poor dielectric properties, polymethylmethacrylate (PMMA) was used as the insulator because it was found that it could be spin coated on the treated surface without an immediate decrease in the PL intensity. This result indicated that PMMA was relatively nonreactive with GaAs, and that its application did not cause repinning. Capacitors were made by spinning ~ 1000 \AA of PMMA onto GaAs samples which had Au-Ge ohmic contacts on the backsides, and capacitance-voltage measurements were made at 20 kHz using a ring/dot Hg probe. Figure 3 shows *C-V* plots for such MIS capacitors made from both the original and the treated samples. The plot for untreated samples [Fig. 3(a)] shows no change in capacitance over a large range in gate voltage which is indicative of a firmly pinned surface. This behavior is somewhat anomalous in that the absolute value of the capacitance corresponds to that of the dielectric alone (i.e., does not include the pinned depletion layer capacitance), which suggests that either the surface states are very fast or that the PMMA is a "leaky" dielectric. As the literature gives a time constant for these states¹³ of ≈ 1 ms for MIS structures using a variety of inorganic dielectrics, the later explanation is more likely. Whatever the reason for the unusual behavior of the sample of Fig. 3(a), the important point is that the data show that the surface Fermi level is pinned. This is in contrast to the *C-V* data of treated samples [Fig. 3(b)] which show the characteristic shape of an MIS capacitor at high frequency,¹⁴ with a clear transition from accumulation to depletion. The maximum capacitance in Fig. 3(b) is consistent with the PMMA insulator capacitance, and it scaled correctly for different film thicknesses. In addition, the minimum capaci-

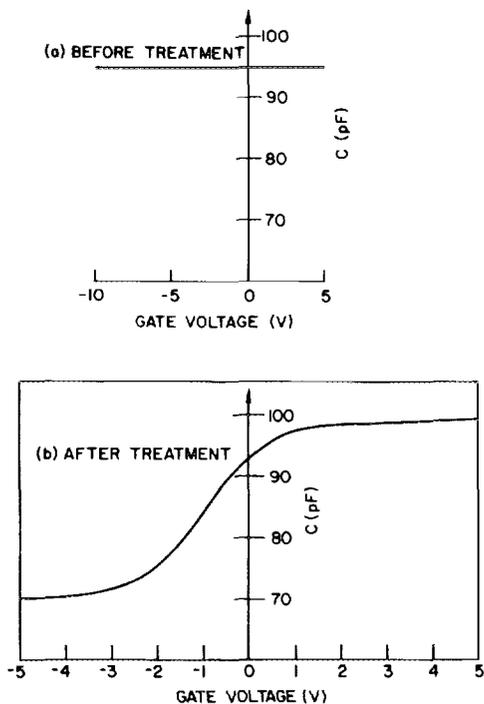


FIG. 3. High frequency (20 kHz) capacitance vs gate voltage for an *n*-type GaAs MIS structure: (a) without the unpinning treatment and (b) with the unpinning treatment.

tance agrees with the theoretical value for maximum depletion of $2 \times 10^{17}/\text{cm}^3$ doped GaAs to within 2–3%, and the voltage range over which the CV swing occurs is consistent with the theoretical value of ≈ 6 V. The observed threshold voltage and the amount of CV swing confirm that the surface has been successfully unpinning and indicate that the surface state density has been drastically reduced.

The *C-V* data presented thus far were for samples either before or very soon after treatment. Measurement of the time dependence of the PL data, however, revealed a gradual degradation and typical results for the blue response of both *n*- and *p*-type material are shown in Fig. 2. These data were taken in air at room temperature, and they show a roughly exponential decay with a characteristic time of 20–30 min. While this decay is certainly a problem if one wants to make any long-term use of the unpinning surface, it is helpful in analyzing the various mechanisms involved. For this reason, the decay has been studied as a function of temperature and ambient. Initial results indicate a very strong dependence on temperature such that, while the characteristic decay time decreased to several minutes at 50 °C, no decay was observed at 77 K after an hour. In addition, it was found that the PL intensity was stable in N_2 , even up to 100 °C. Finally, it should be noted that the PL intensity was seen to degrade in air even with a PMMA film on the surface, and with no observable change in the decay rate.

In order to explain the source of the GaAs surface states responsible for pinning, two recent models have been proposed: the defect model¹⁵ and the effective work function (EWF) model.¹⁶ The defect model proposes that the pinning is caused by point defects such as vacancies and antisite defects. It is unlikely, however, that a photostimulated “washing” with water would be sufficient to “dissolve” such

physical defects, or that the weak bonding of water or OH groups to the surface would counteract their effect. On the other hand, the EWF model suggests that the pinning states are due to excess As. It is known that the oxidation of the GaAs results in the formation of excess As, Ga_2O_3 , and As_2O_3 on the surface.¹⁷ Since As oxide and As are highly soluble in oxygenated water, the unpinning mechanism could be that both species are being photochemically washed away, leaving behind an As-free, passivating Ga oxide layer. It is also possible that the surface is entirely free of oxides.^{18,19} According to the EWF model, either condition would result in an unpinning surface. The observed gradual degradation of the PL intensity after the treatment would then be explained either by the residual Ga oxide layer inhibiting (but not preventing) re-oxidation and hence causing a slow regeneration of As and As oxide on the surface or by the gradual re-oxidation in air of an oxide-free surface.¹⁹ Either of these explanations is consistent with the observed degradation after coating with PMMA since such films are known to be extremely permeable to O_2 . It is also supported by the strong temperature dependence, which suggests an activated process, and by the fact that the degradation does not occur in an N_2 ambient.

In summary, we have described a simple procedure which can be used to greatly reduce the surface state density of GaAs and thereby unpin the Fermi level. This unpinning is of both technological and scientific importance. For device and circuit fabrication, it demonstrates the feasibility of improved GaAs MISFET'S. More fundamentally, the effect itself offers a tool for improving our understanding of compound semiconductor surfaces.

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