

Characterization of photochemically unpinned GaAs

C. W. Wilmsen,^{a)} P. D. Kirchner, J. M. Baker, D. T. McInturff, G. D. Pettit, and J. M. Woodall

IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

(Received 3 February 1988; accepted 21 April 1988)

The unpinning of the etched GaAs(100) surface has recently been reported by both photowashing and by Na₂S·9H₂O treatments. Both techniques hold promise of elucidating the mechanism by which GaAs passivation is achieved. We have identified as part of the photowashing process a separate photoactivation step. The activation step did not become apparent until we modified the photowash process in order to minimize light exposure when flowing water was not applied to the substrate. The degree of unpinning produced by this process has been found to be related to the thickness of this oxide, the presence of oxygen and water vapor and the integrated light flux incident on the sample. Photoluminescence experiments clearly show that a photoactivation step involving water vapor is required to achieve the flat-band condition. This process is relatively insensitive to the surface treatment prior to the photowash. We have observed similar photoactivation and insensitivity to surface treatment on GaAs coated with Na₂S·9H₂O. This suggests the possibility of a common passivation process.

I. INTRODUCTION

The GaAs surface has been studied for many years in order to determine the origin of surface states and ways of reducing their density. The UHV-cleaved (110) surface has been shown to be free of surface states within the energy gap, however, exposure to oxygen/air causes the creation of many gap states that pin the surface Fermi level at about 0.6 eV above the valence band edge.^{1,2} This phenomenon reduces the efficiency of some devices such as a laser diodes and prevents the realization of usable insulator gate transistors.

Recently, two different treatments (photochemical washing³⁻⁶ and coating with Na₂S·9H₂O⁷⁻⁹) have been used to hold the chemically etched GaAs surface in the unpinned state for hours and even days while exposed to air. These demonstrations open new avenues for research on the GaAs surface and should accelerate GaAs device advancement. This paper examines the characteristics of the photowashed GaAs surface, compares these with similar experiments on Na₂S·9H₂O-coated GaAs, and presents a preliminary model that satisfies most of the experimental observations.

II. EXPERIMENTAL PROCEDURES

Most of the experiments were performed on bulk *n*-type (100)GaAs doped to $n = 3 \times 10^{17} \text{ cm}^{-3}$ with Si. The *p*-type samples were 2 μ thick molecular-beam epitaxially (MBE)-grown layers doped to $p = 2 \times 10^{17} \text{ cm}^{-3}$ with Be. The as-received wafers were first degreased in sequential rinses of trichloroethene (TCE), acetone, and ethanol. Some of the wafers were then soaked in hot 1:1 H₂SO₄:H₂O and then deep etched with 6:1:1 solution of H₂SO₄:H₂O₂:H₂O in order to remove residual contamination and polish damage. The Na₂S·9H₂O-coated samples seemed to be more sensitive to this damage removal step than the photowashed samples. All samples were etched for 30 s in a 1:8:500 solution of H₂SO₄:H₂O₂:H₂O and rinsed in deionized (DI) water. Some samples then received a final chemical treatment as

listed in Table I. The wet samples were then placed on a spinner and either covered with 1-M Na₂S·9H₂O and spun dry for 1 min or were subjected to a stream of DI water under an ELH typeprojector bulb for 1 to 20 min.

The room-temperature photoluminescence (pl) of the samples excited by an ~0.25 W cm⁻² He-Cd laser was recorded soon after treatment. The level of GaAs doping was chosen so that the width of the space charge layer at the pinned GaAs surface would coincide with the adsorption coefficient of the 440-nm blue laser. Thus, the pl signal is a sensitive measure of the radiative recombination near the surface and yields combined information on the density of surface states and the surface band bending. The pl was col-

TABLE I. Effect of the last chemical treatment prior to photowashing on the luminescence of (100) GaAs.

Penultimate treatment preceding photowash	Expected results of treatment	Max. GaAs PL 440-nm excitation	Comments ^a
		28 μV	
		25	<i>p</i> -type coated
H ₂ SO ₄ :H ₂ O ₂ :H ₂ O 1:8:500	Stoichiometric	15	
		16	
		22.5	
		14	
		14.5	
H ₂ SO ₄ :H ₂ O ₂ :H ₂ O 8:1:500	Elemental As?	32	
		27	
Conc. HCl		23	10 s
Conc. H ₃ AsO ₄	Elemental As	1	10 s
Dil. H ₃ AsO ₄		10	10 s
Stagnant H ₂ O	Ga ₂ O ₃	1	20 h
30 % H ₂ O ₂		22	30 s
Dilute HNO ₃ 1:1	As ₂ O ₃	13	10 s
Dilute HNO ₃ 1:3		12	10 s

^a Times given are treatment times.

lected by a filtered photomultiplier yielding an output signal from ~ 0.5 to $32 \mu\text{V}$ for the various samples. A $2.5\text{-}\mu$ thick GaAs epilayer doped to $1\text{E}18$ p -type and capped with 300 nm of $\text{Al}_{0.9}\text{Ga}_{0.1}\text{As}$ was used as a standard for the pl measurements. Under normal operating conditions this standard yielded a pl response of $\sim 20 \mu\text{V}$.

III. EXPERIMENTAL RESULTS

A. Photowashed GaAs

Photowashing n -type GaAs, as described above, results in the growth of an oxide film whose thickness is a linear function of photowashing time as shown in Fig. 1. The oxide thickness saturates at ~ 95 nm. This rapid oxide growth occurs despite the low temperature of the process, the presumed low concentration of dissolved oxygen and the absence of an applied voltage. It should also be noted that no oxide grew if the projector lamp was turned off. X-ray photoelectron spectroscopy (XPS)-sputter profiling analysis indicates that the photowashed oxides are composed primarily of Ga_2O_3 with a small amount of As_2O_3 and elemental As. Further experiments showed that the elemental As was derived from the sputter decomposition of the As_2O_3 . The sputter profile of Fig. 2 shows that the concentration of As_2O_3 is approximately constant throughout the 95-nm layer. Thus, it appears that an oxide of Ga_2O_3 and As_2O_3 is grown but that most of the As_2O_3 is continuously washed away by the stream of DI water. This implies that the oxide layer is porous, although we possess no direct evidence to verify this conjecture.

Immediately after spin drying the photowashed sample, the integrated, room-temperature photoluminescence response to a blue laser was recorded as a function of time. A typical response curve is shown in Fig. 3. Note that the pl response is initially zero, even though the sample had been under intense illumination with flowing water for the previous 18 min. In laboratory air, however, the pl rises monotonically to a maximum in ~ 5 min and then begins to slowly

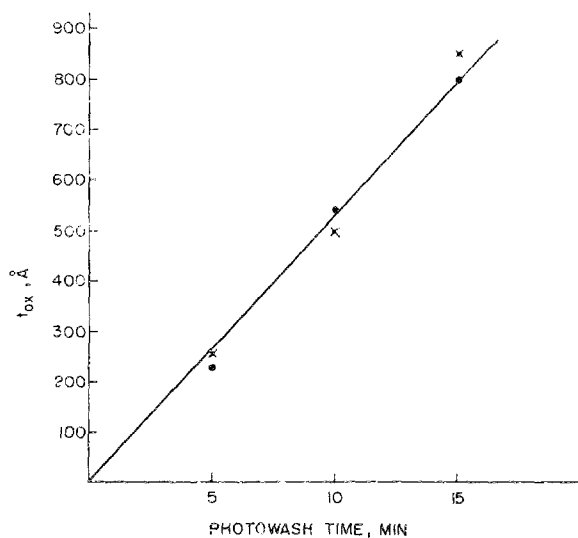


FIG. 1. Thickness of the oxide as a function of photowashing time. Sample series 44 (10/1/87); (●) Alpha step; (■) ellipsometer.

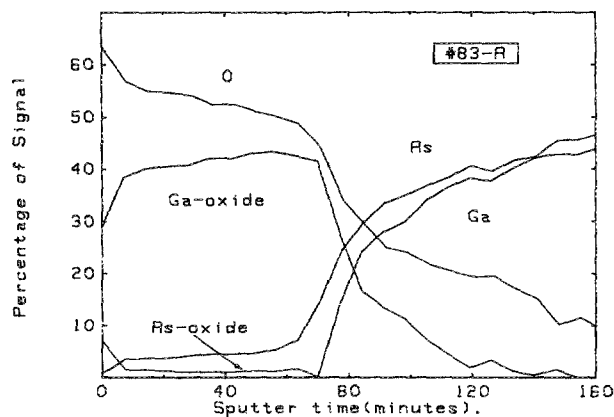


FIG. 2. XPS sputter profile of a $900\text{-}\text{\AA}$ -thick oxide grown by photowashing for 18 min.

decrease, reaching $1/e$ of the maximum in ~ 30 min. Thus, there appears to be at least three active processes: (1) growth of the oxide layer involving water and light; (2) "activation" of the GaAs surface with above band gap light in laboratory air; and (3) degradation in a similar environment. The pl versus time of n - and p -type GaAs have been found to behave in the same manner.

For shorter photowash times, i.e., thinner oxide layers, the pl follows a similar curve as Fig. 3 but the maximum response decreases linearly with the photowashed oxide thickness as illustrated in Fig. 4. This suggests that the mechanism that causes the increased blue pl is somehow related to the volume of the oxide although it could also imply that the amount of GaAs surface area covered by the porous oxide is proportional to the oxide thickness or that the surface is cleaned up proportionally by the oxidation process.

If indeed the main role of the photo-oxidation process is to "clean up" the GaAs surface, then the maximum pl signal should be very sensitive to the final cleaning step before photowashing. In order to test this, a number of different final treatments were chosen to leave the GaAs with different surface layer composition. These treatments, the expect-

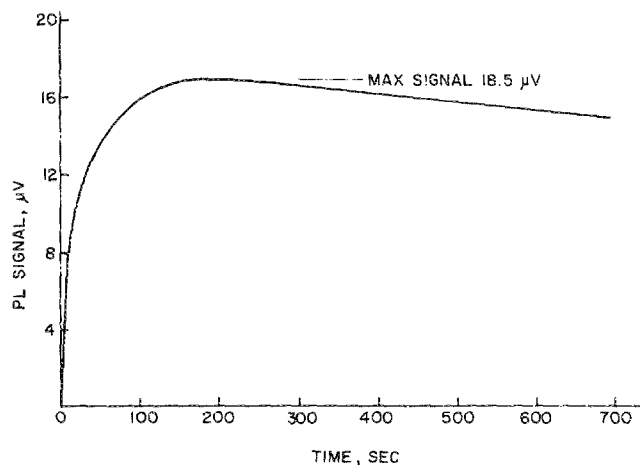


FIG. 3. Room-temperature band gap photoluminescence from a photowashed sample as a function of time. The sample was in laboratory air.

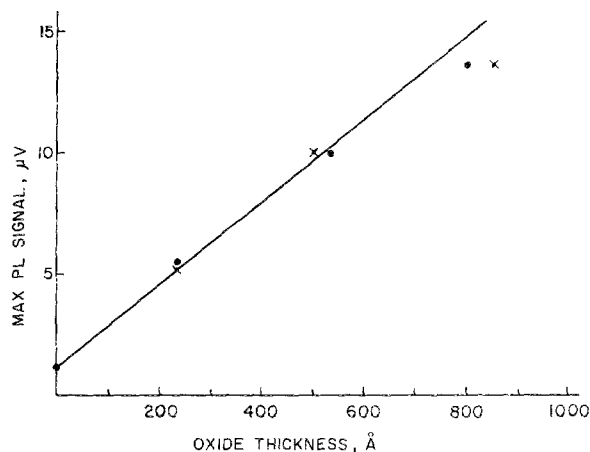


FIG. 4. Maximum pl signal for three different samples photowashed to different oxide thicknesses. (●) Alpha step, (■) ellipsometer.

ed chemical surface layer, and the maximum pl signal are summarized in Table I. Note that all but the very harshest treatment (concentrated H_3AsO_4) yield a large blue pl response. The stronger acid etches, which should leave elemental As or As_2O_3 on the surface seem, to result in a lower signal but this could also be the result of experiment variables. From Table I we conclude that photowashing does provide some surface clean up but that this is not the major function of the process.

Previously published work⁵ has found that water and/or oxygen dissolved in the water are necessary to unpin the surface. We have investigated this further. As a first test, a previously photowashed GaAs wafer was covered with water and the pl response was measured. The signal remained near zero for the duration of the 30 min test. Another photowashed wafer was placed in a small desiccator and the pl measured with the lid alternately removed and replaced. The results are given in Fig. 5(a). Note that when the lid is removed, the pl signal increases much the same as shown in Fig. 3 but now there are superimposed large and relatively rapid noise oscillations. These are caused by air currents which apparently carry water vapor to and from the sample.

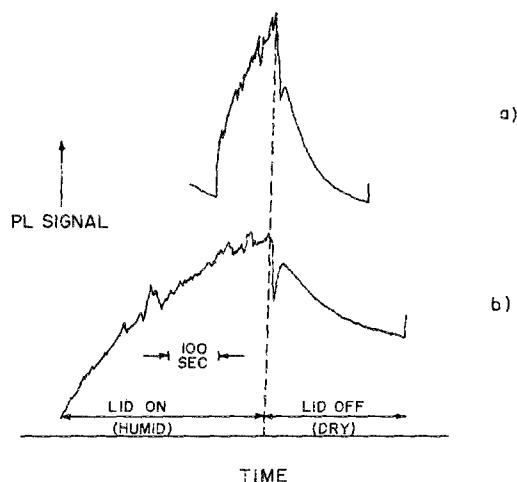


FIG. 5. The effect of a desiccant on the photoluminescence signal as a function of time. (a) Photowashed, (b) $Na_2S \cdot 9H_2O$.

Supplying alternate ambients of various wet and dry gases confirms the need for water vapor in attaining the large pl response. The rapid response (< 1 s) indicates that the interface and/or oxide bulk are very sensitive to water vapor and readily communicate with the ambient gases. When the desiccator lid is replaced, water vapor is removed from the sample and the pl signal rapidly decreases. Removing the lid does not restore the pl signal to its original value, but rather the signal begins to increase from the value reached while in the dry atmosphere.

B. $Na_2S \cdot 9H_2O$

Coating with a layer of $Na_2S \cdot 9H_2O$ has also been reported^{7,8} to unpin the GaAs surface. In this process, a 1-M solution is placed on the etched wafer and either spun dry or dried with a stream of N_2 . This procedure does not grow an oxide: in fact the strongly basic $Na_2S \cdot 9H_2O$ solution dissolves the surface oxides. Thus, the process of photowashing and $Na_2S \cdot 9H_2O$ coating are quite different. Even so, the measured photoluminescence characteristics appear quite similar.

For the characteristics presented here, the $Na_2S \cdot 9H_2O$ coated samples were prepared on the same or similar GaAs wafers used in the photowashed experiments and the photoluminescence test procedures were identical to those used for the photowashed devices. The blue pl response versus time for a typical sample freshly coated with $Na_2S \cdot 9H_2O$ is illustrated in Fig. 6. The general shape and features of this curve are very similar to the curve given in Fig. 3 for photowashed GaAs. The time scale for the two curves, however, differ by a factor of 7 and the pl reaches a maximum in ~ 35 min and decreases to the $1/e$ value in 5 h. Thus $Na_2S \cdot 9H_2O$ coated GaAs appears to have a photoactivated or possibly minority carrier activated step, much the same as photowashed GaAs. The shape of the activation portion of the pl versus time curve for $Na_2S \cdot 9H_2O$ coated samples is somewhat variable but consistent results are obtained if the sample is allowed to sit in air for 10 min after spin drying. Again *n*- and *p*-type GaAs yield the same pl versus time behavior.

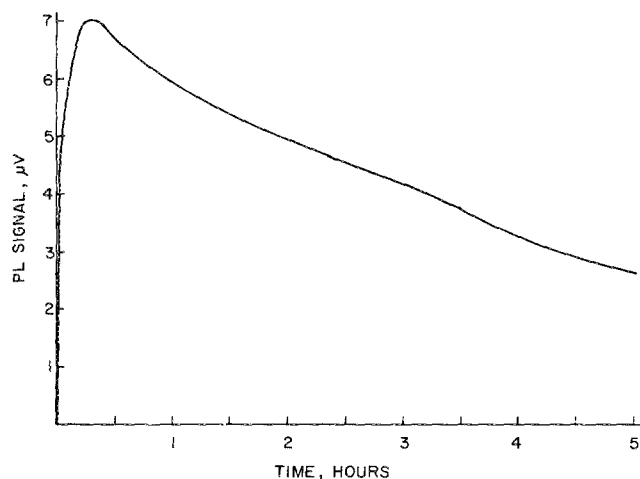


FIG. 6. Room-temperature band gap pl of GaAs coated with $Na_2S \cdot 9H_2O$ as a function of time. The sample was in laboratory air.

The pl of the $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ coated GaAs responded to a dry atmosphere in a manner similar to the photowashed samples. As shown in Fig. 5(b), all relevant features are replicated, including the speed at which the pl signal responded to air currents. The response to wet and dry gases are also quite similar for the two unpinning methods.

The sensitivity of the $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ to the final surface treatment was investigated. There appears to be two different factors that effect pl signal: nonstoichiometry and wettability. It was found that the pl signal was not strongly dependent on the final chemical etch if the etch left the surface near stoichiometry. Thus, Br-MeOH and $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (in various ratios) yield approximately the same maximum pl response. Other etches had a stronger effect on the pl than they did on the photowashed samples. This follows from the fact that photowashing consumes several tens of nm of the GaAs surface and provides a continual washing of the surface.

The final treatment also effects the wetting of the surface, i.e., the physical form of the $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ coating. We have observed continuous polycrystalline coatings, dendritic growth, and small isolated islands. These different coatings seem to effect the value of the maximum pl signal but no clear correlation has been established. There could also be some effects on the speed of the response to the dry atmosphere, but again no correlation has been established.

IV. DISCUSSION

From the variety of previously published experimental data and the work presented here, it is clear that both the photowashed and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ treatments sufficiently reduce the density of surface states to allow easy movement of the surface Fermi level, i.e., unpin the surface. However, the apparent need for photo (minority carrier) activation and the sensitivity of the processes to water vapor cannot be explained by a simple surface state model. Thus, we propose a model that includes both the condition of the surface and the effects of the overcoating layer. We consider this model only as a starting point for the understanding of the unpinning process, since additional work will be required in order to finalize a satisfactory model.

Primarily, we wish to explain the apparent activation, i.e., the increase in photoluminescence signal with time, when there is incident light or possibly injected minority carriers. The sensitivity of GaAs treated with either $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ or photowashing to the simultaneous presence or absence of both oxygen and water vapor, suggests that an oxidation process is taking place. However, the fast response time and the reversibility of the photoluminescence signal to the presence or absence of water vapor, indicates that the formation or decomposition of an interfacial oxide layer is not likely. Sulfurization can also be ruled out.

It therefore appears that the two treatments create a low-surface state density and that no chemical reactions with the substrate are involved in the activation process. During the activation process the incident light must interact with the water and/or oxygen in such a manner to either create an appropriate adsorbate which neutralizes the remaining surface states or forms a dipole layer which bends the bands

towards flat band. This later explains the dependence of the pl signal on the oxide thickness as seen in Fig. 4. However, the fact that *n*- and *p*-type GaAs respond in the same way requires the dipole to be reversed on the two conductivity types.

The model does not provide direct evidence for the cause of unpinning, but to some extent, this can be inferred from what is known about the chemical nature of the etched/photowashed GaAs surface. The photowashing process removes water soluble compounds and coupled with light can remove As_2O_3 and elemental As. This leaves the surface covered with the wide band gap, thermodynamically stable compound, Ga_2O_3 . The initial chemical condition of the surface is relatively unimportant since the photowashing will remove it anyway, although more slowly for contaminated surfaces.

The 1-M $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ will etch away the Ga and As oxides as well as elemental As. However, this treatment is probably more sensitive to the final chemical etch. This may explain why the best results in this study were obtained with a final etch in either Br-MeOH or $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ since these leave a stoichiometric surface that gets covered with a thin stoichiometric oxide, which is initially free of elemental As. We have not experimentally investigated the reaction between $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and GaAs, however, the thermodynamics appear favorable. In fact, the Ga-As-O and the Ga-As-S ternary phase diagrams are similar,^{10,11} as are the properties of the reaction products. Thus, one might expect similar chemical (and perhaps electrical) behavior for oxidized and sulfurized GaAs surfaces.

ACKNOWLEDGMENTS

The authors are indebted to Dr. Alan C. Warren for his assistance. One of us (C.W.W.) wishes to acknowledge the financial support for the NSF/ERC Grant No. CDR8622236.

^{a)} Colorado State University, Fort Collins, CO 80523.

¹W. E. Spicer, I. Lindau, P. Skeath, and C. Y. Su, *J. Vac. Sci. Technol.* **17**, 1010 (1980).

²W. Gudot and D. E. Eastman, *J. Vac. Sci. Technol.* **13**, 831 (1976).

³S. D. Offsey, J. M. Woodall, A. C. Warren, P. D. Kirchner, T. I. Chappell, and G. D. Pettit, *Appl. Phys. Lett.* **48**, 475 (1986).

⁴P. D. Kirchner, A. C. Warren, J. M. Woodall, C. W. Wilmsen, S. L. Wright, and J. M. Baker, *J. Electrochem. Soc.* (in press).

⁵N. A. Ives, G. W. Stupian, and M. S. Leung, *Appl. Phys. Lett.* **50**, 256 (1987).

⁶S. M. Beck and J. W. Wessel, *Appl. Phys. Lett.* **50**, 149 (1987).

⁷E. Yablonoich, C. J. Sandroff, R. Bhat, and T. Gmitter, *Appl. Phys. Lett.* **51**, 439 (1987).

⁸C. J. Sandroff, R. N. Nottenberg, J. C. Bischoff, and R. Bhat, *Appl. Phys. Lett.* **51**, 33 (1987).

⁹B. J. Skromme, C. J. Sandroff, E. Yablonoich, and T. Gmitter, *Appl. Phys. Lett.* **51**, 2022 (1987).

¹⁰C. D. Thurmond, G. P. Schwartz, G. W. Kammlott, and B. Schwartz, *J. Electrochem. Soc.* **127**, 1366 (1980).

¹¹H. Matino, *Solid State Electron.* **17**, 35 (1974).