Effects of N_2, O_2, and H_2O on GaAs passivated by photowashing or coating with $Na_2S{\cdot}9H_2O$

C. W. Wilmsen
NSF ERC for Optoelectronic Computing Systems and Department of Electrical Engineering, Fort Collins, Colorado 80523

P. D. Kirchner and J. M. Woodall
IBM TJ Watson Research Center, Yorktown Heights, New York 10598

(Received 5 April 1988; accepted for publication 6 June 1988)

The photoluminescence (PL) from the surface region of GaAs passivated by photowashing or coating with $Na_2S{\cdot}9H_2O$ is shown to be sensitive to the gas ambient. Both water vapor and oxygen must be present in order to obtain a large PL signal. The effects are activated by the measuring laser light.

Recently, two passivation techniques which greatly reduce the surface state density of GaAs have been reported; photowashing[1-3] and coating[4-6] with $Na_2S{\cdot}9H_2O$. These are important discoveries since the performance of most GaAs devices and circuits are improved by the lowering of the surface state density.[5] In addition, it may now be feasible to fabricate surface control devices such as metal-oxide-semiconductor field-effect transistors, particularly if the mechanism for passivation can be more fully understood and controlled.

We previously[7,8] have shown that photowashing causes an oxide to grow on the GaAs surface and while both Ga_2O_3 and As_2O_3 are formed, most of the As_2O_3 is washed away leaving a layer of Ga_2O_3 with only a trace of As_2O_3. It has also been shown that band-gap photoluminescence from the surface region of the GaAs after photowashing or coating with $Na_2S{\cdot}9H_2O$ is initially very low but increases with time under laser illumination, i.e., both passivation processes appear to be photoactivated.[9] As a result of continued study of these passivation techniques, we have found the magnitude of the photoluminescence signal is sensitive to the sample ambient. This communication reports the results of this investigation and compares them with the previously reported gas sensitivity of bare GaAs surfaces.[10,11]

The samples were fabricated from bulk *n*-type (100) GaAs doped to 3×10^{17} with Si. The wafers were degreased in sequential rinses of TCE, acetone, and ethanol and then etched for 30 s in a 1:8:500 solution of H_2SO_4:H_2O_2:H_2O and rinsed in DI water. The wet samples were then placed on a spinner and either covered with 1 m $Na_2S{\cdot}9H_2O$ and spun dry for 1 min or were subjected to a stream of DI water under an ELH projector bulb for 18 min. This later procedure grew a 950-Å-thick oxide. A 250-mW/cm^2 440 nm provided the excitation for the photoluminescence measurements.

A typical room-temperature photoluminescence (PL) versus time plot for both photowashed and $Na_2S{\cdot}9H_2O$ coated GaAs are shown in Fig. 1. The two curves have the same basic shape, i.e., they both start near zero signal and rise to a maximum value (this is designated the "activation" region) and then decrease in magnitude ("aging") at a rate much slower than the initial rise. The rate of rise and fall of the PL signal from the $Na_2S{\cdot}9H_2O$ coated sample is about 5–10 times slower than that of the photowashed. The PL signal typically increased by a factor of 30–60 over the initial, "unactivated" sample. The following analysis examines the effects of gas ambients on the "activation" portion of the PL versus time curves. The ambients are also expected to effect the "aging" region but this has not been investigated.

This study was limited to the gases that primarily make up laboratory air. CO_2 was also briefly examined and found to be similar to N_2. The effect of water vapor was initially investigated by placing the sample in a small desiccator filled with calcium sulfate and alternately removing and replacing the desiccator lid. In this way the ambient was cycled from humid to dry air and the effects were continuously monitored by recording the PL signal. The results of this cycling are shown in Fig. 2 for both photowashed and $Na_2S{\cdot}9H_2O$ coated GaAs samples. With the lid off and the sample exposed to air, the PL signal increases in the same manner as shown in Fig. 1 except now there is a large superimposed noise signal. This noise is the result of air currents that apparently are dried by the surrounding desiccant. Note that

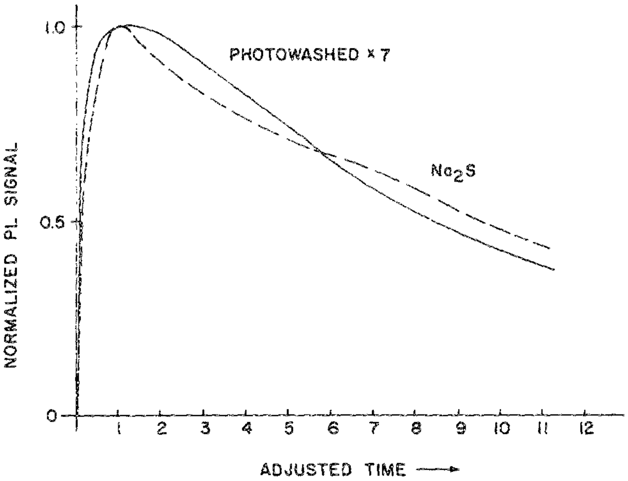

FIG. 1. Comparison of the photoluminescence vs time curves for photowashed and Na_2S coated GaAs.

0021-8979/88/183287-03$02.40

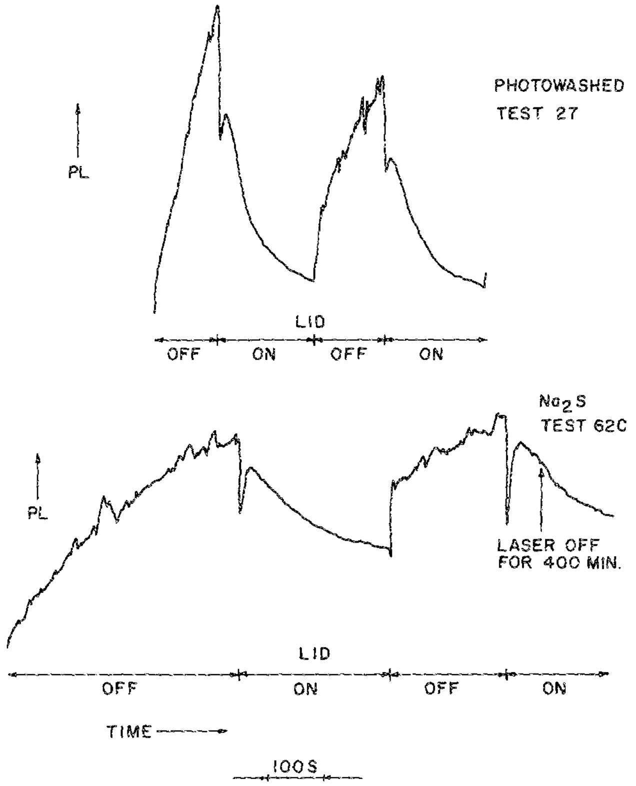

FIG. 2. Photoluminescence of GaAs in a desiccator with and without the lid, (a) photowashed GaAs, and (b) Na_2S coated GaAs.

the PL signal responds in somewhat less than a second. Placing the lid on the desiccator causes the sample ambient to dry out. The initial steep drop in the signal followed by an increase in the PL are thought to be artifacts of the test procedure and may be caused, respectively, by a slight distortion in the laser beam when the lid is in place and by air movement due to the closing of the lid. The main effect of water vapor deprivation is a dramatic drop in the PL signal as the ambient dries out. For the $Na_2S\cdot 9H_2O$ coated sample, this decrease is dependent on the laser light. Thus, if the laser beam is blocked for some period of time and then allowed to once again shine on the same region of the sample, the magnitude of the PL signal is found to be unchanged during the dark period. Removing the desiccator lid readmits water vapor and the PL signal starts to rise again.

To investigate the effects of gases, the sample was placed in a small box containing several air holes. The test gases flowed into the box, directly onto the sample surface, but, when the gases were turned off, the sample ambient changed rapidly from that of the test gas to laboratory air. The effects of dry N_2 on the PL signal are shown in Fig. 3. These curves are very similar to that for dry air given in Fig. 2, except the large noise signal is not present since the sample is always in a closed container and not subjected to air currents.

Bubbling the N_2 through water also does not change the PL response (Fig. 4). This implies that water vapor alone does not provide the catalysis necessary for increasing the PL signal, and that there must be some cooperative interaction involving water vapor and some other gas. As shown in Fig. 5, this gas is O_2. The data clearly shows that dry O_2 has the same effect as dry N_2 but that wet O_2 provides the necessary ambient to "activate" the surface.

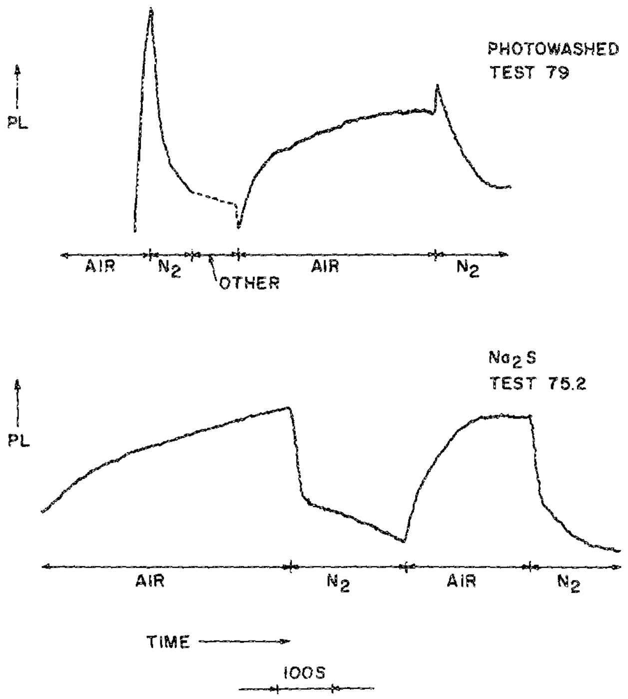

FIG. 3. Effects of dry N_2 on the photoluminescence of GaAs, (a) photowashed, and (b) Na_2S coated.

Both the photowashed and $Na_2S\cdot 9H_2O$ coated samples have approximately the same response to the various gas/water vapor combinations, although the $Na_2S\cdot 9H_2O$ responded more slowly. In addition the $Na_2S\cdot 9H\ O_2$ coated samples were much more sensitive to the amount of water vapor in the test gas than were the photowashed samples, however a more refined method of introducing the water vapor is required to characterize this phenomenon.

It appears that the observed changes in the PL signal from photowashed and $Na_2S\cdot 9H_2O$ treated GaAs are due to a cooperative interaction involving H_2O, O_2, and light. At

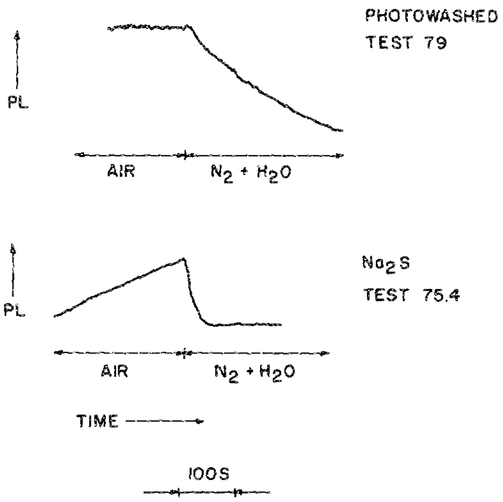

FIG. 4. Effects of wet N_2 on the photoluminescence of GaAs, (a) photowashed, and (b) Na_2S coated.

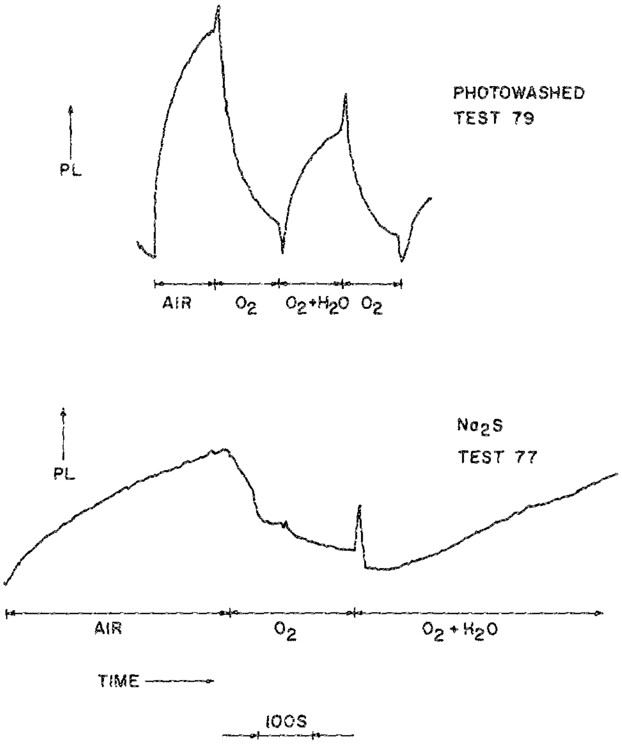

FIG. 5. Effects of wet and dry O_2 on the photoluminescence of GaAs, (a) photowashed, and (b) Na_2S coated.

present, the detail mechanisms of this interaction are not clear, but since three components are required it would seem that a catalytic action takes place which breaks up the H_2O molecules, possibly into OH^-. The new molecules either attach themselves to active gap states in such a manner so as to passivate them or they form a dipole layer which bends the surface bands of the GaAs. Chemical reactions can be ruled out because the PL enhancement process was shown to be reversible which is not possible for strong bonds such as oxidation. It is thought that the adsorption takes place either on the GaAs surface or in the bulk overcoating matrix. For photowashed GaAs the adsorption bond appears to be weak since the PL enhancement can be removed simply by placing the sample in a vacuum in the dark. On the other hand the $Na_2S\cdot 9H_2O$ treated samples are stable in the dark and appear to require energy from the laser (or possibly some other source) to reverse the PL signal. In addition the surface state density must be low or it would not be possible to increase the PL signal by such a large magnitude.[8] The low surface state density is attributable to the photowash/$Na_2S\cdot 9H_2O$ treatments which first "clean up" the surface and then hold it in this low surface state density condition.

Nagai and Noguchi[10] used PL measurements to investigate the effects of gases on GaAs cleaved in air. They report that O_2 containing gases irreversibly reduced the PL signal. Following this work, Streetman and coworkers[11] applied PL measurements to chemically etched GaAs. They found that exposure to N_2 decreased the PL signal similar to our findings. However, contrary to our coated samples, dry O_2 increased the signal (this may have been caused by some water vapor in their gas or by air back streamed into the test chamber). The effects of exposure to both N_2 and O_2 were reversible. The magnitude of their PL signal change with gas ambient appears to be small compared to our observations which showed the PL signal to increase 30–60 times above that of the bare GaAs substrate. In addition our tests on chemically etched samples in air showed an initial rise of the PL and then a rapid decay to near zero. There have been a number of other investigations of the degradation of the PL signal from bare GaAs surfaces[12-15]. Guidotti *et al.*[15] investigated the effects of ambients and reports that wet ambients slowed or even enhanced the PL response over that of dry ambients. Thus, in contrast to the photowashed/$Na_2S\cdot 9H_2O$ samples, the bare GaAs was unstable and much less responsive.

In summary, GaAs surfaces, which have been treated by either photowashing or $Na_2S\cdot 9H_2O$ are very sensitive to ambient gases. Without the presence of H_2O, O_2, and light, the surface remains in an unactivated condition. The surface appears to be "activated" by the adsorption of H_2O or OH^-. There appears to be some similarity between the gas sensitivity of the photowashed/$Na_2S\cdot 9H_2O$ coated and bare GaAs. However, further work is required to determine if the same mechanisms are causing the observed effects.

The authors are indebted to David Petit and David McInturff for their assistance. The technical discussions with E. Yablonovitch and C. Sandroff on the $Na_2S\cdot 9H_2O$ coating process are also gratefully acknowledged. One of us wishes to acknowledge the financial support of the NSF/ERC, Grant No. CDR8622236.

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

[2] S. M. Beck and J. E. Wessel, Appl. Phys. Lett. **50**, 149 (1987).

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

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

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

[6] B. J. Skromme, C. J. Sandroff, E. Yablonovitch, and T. Gmitter, Appl. Phys. Lett. **51**, 33 (1987).

[7] P. D. Kirchner, A. C. Warren, J. M. Woodall, C. W. Wilmsen, S. L. Wright, and J. M. Baker, J. Electrochem. Soc. (to be published).

[8] C. W. Wilmsen, P. D. Kirchner, J. M. Baker, D. McIntorff, G. D. Pettit, and J. M. Woodall, J. Vac. Sci. Technol. B **6**, 1180 (1988).

[9] J. M. Woodall, G. D. Petit, T. Chappell, and H. J. Hovel, J. Vac. Sci. Technol. **16**, 1389 (1979).

[10] H. Nagai and Y. Noguchi, Appl. Phys. Lett. **33**, 312 (1978).

[11] S. D. Lester, T. S. Kim, and B. G. Streetman, J. Appl. Phys. **60**, 4209 (1986).

[12] T. Suzuki and M. Ogawa, Appl. Phys. Lett. **31**, 473 (1977).

[13] H. Booyens, J. H. Basson, A. W. R. Leitch, M. E. Lee, and C. M. Stander, Surf. Sci. **130**, 259 (1983).

[14] H. J. Hovel and Guidotti, IEEE Trans. Electron Devices **ED-32** 2331 (1985).

[15] D. Guidotti, Eram Hasan, H. J. Hovel, and M. Albert, Appl. Phys. Lett. **50**, 912 (1987).