Passivation of GaAs surface recombination with organic thiols

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Exposure of GaAs crystals to solutions of organic thiols resulted in substantial reductions in nonradiative GaAs surface recombination rates. This process yielded improvements in steady state photoluminescence signals that were comparable to those obtained after a $Na_2S \cdot 9H_2O$ (aqueous) treatment. Use of a series of thiols indicated that the chemically important surface electrical trap levels behaved as a polarizable, electron deficient center. X-ray photoelectron spectroscopy indicated that the thiols did not remove excess As^0 nor form detectable levels of As_2S_3-like phases, implying that neither of these factors is required for effective surface passivation chemistry.

Sandroff, Yablonovitch, and co-workers have recently reported that exposure to aqueous solutions of $Na_2S \cdot 9H_2O$ resulted in the passivation of GaAs surfaces towards nonradiative recombination.[1] These results have prompted numerous spectroscopic and electrical studies designed to understand the surface chemistry and physics of this system. Although inorganic sulfides have been found to be effective surface passivation reagents, no additional chemical reactivity trends are available for this system. We report herein that a series of organic thiols (i.e., compounds of chemical formula RSH where R is an organic functional group that can be varied) can yield a substantial reduction in nonradiative surface recombination at GaAs interfaces. We also report the results of an x-ray photoelectron spectroscopic (XPS) study that has tested some of the models for passivation chemistry in the GaAs/Na_2S and GaAs/thiol systems.

The steady-state band gap GaAs luminescence intensity was used to monitor changes in the nonradiative surface recombination rate for the various chemical treatments. Samples were thin sections of weakly doped (100)-oriented n-type GaAs (1.0-μm thick, dopant density $= 10^{15}$ cm^{-3}) with $Al_{0.4}Ga_{0.6}As$ layers (1000-Å thick, undoped) on both sides of the GaAs. The structure was grown by organometallic vapor phase epitaxy on n^+-GaAs substrates. The top $Al_{0.4}Ga_{0.6}As$ layer was etched with 0.05% Br_2–CH_3OH in order to expose the GaAs epilayer for surface treatment. Steady state photoluminescence (PL) data was obtained with irradiation at 632.8 nm (5 mW; 65 W/cm^2 on the GaAs sample) from a He/Ne laser. The PL intensity from 800 to 900 nm was collected by means of a monochromator with appropriate filters. The maximum PL at 874 nm was recorded as the figure of merit.

The GaAs surfaces were etched to leave either a near-stoichiometric surface or a surface rich in excess As^0. The near stoichiometric surface (designated as etch A) was obtained using the 0.05% Br_2–CH_3OH and 1.0 M KOH(aq) etching procedure recommended by Aspnes.[2] The As^0-rich surface was obtained by immersing a sample that had been exposed to etch A into a 1:1:100 [concentrated H_2SO_4: 30% H_2O_2(aq): H_2O] solution for 30 s, and then rinsing with H_2O and drying under N_2(g) (etch B). To avoid oxidative degradation of the surface, all PL measurements were performed under a N_2(g) atmosphere in a glass cell. Concentrations of the organic reagent were 1.0 M in diethyl ether unless otherwise specified; the GaAs sample was immersed into the desired organic solution for 20–30 min and then dried under N_2(g) before the PL signal was recorded. In some cases, the PL signal initially displayed an increase with time to a steady state value; in all cases, the quoted PL intensities were steady state PL values that were stable for periods of up to 1 h. In accord with previous observations for exposure to $Na_2S \cdot 9H_2O$(aq),[1] thorough rinsing of the GaAs after adsorption of the thiols yielded a substantial reduction in the PL intensity; thus, samples used in the PL studies were simply immersed into the reagent solution and then dried under flowing N_2. Only samples used for XPS experiments were rinsed with solvent, in order to prevent volatile thiols from being introduced into the ultrahigh vacuum (UHV) chamber.

To determine the composition of the thiol-treated GaAs surfaces, a series of high resolution x-ray photoemission spectra on thoroughly rinsed GaAs surfaces were collected. XPS experiments were performed on 10^{17} doped bulk (100) n-GaAs; two nominally identical GaAs samples were etched simultaneously, and one was subsequently exposed to the thiol solutions before introduction into the vacuum chamber. The contributions of various surface species to the As 3d and Ga 3d regions were determined using standard curve-fitting techniques. Although the instrumental resolution for the Al source full width at half-maximum [(FWHM) of Au $4f_{7/2}$ line is 1.1 eV] precluded direct separation of the XP signals from As^0 and substrate As_{GaAs}, the presence of As^0 on GaAs surfaces could be reliably deduced from deviations in the expected 3:2 area ratio for the substrate As_{GaAs} spin orbit doublet peaks. As expected, the GaAs surface exposed to etch B displayed a large ($\sim 3 \times 10^{-9}$ mole/cm^2) coverage of excess As^0; the As^0 was introduced deliberately in the etching process so that its subsequent reactivity with the thiol solutions could be easily monitored by XPS. The Ga 3d region was fit with two doublets each constrained to 3:2 area ratios.

Figure 1 displays the steady state low level injection PL data obtained for a GaAs epilayer sample that had been exposed to a series of sulfur-containing reagents. The data were

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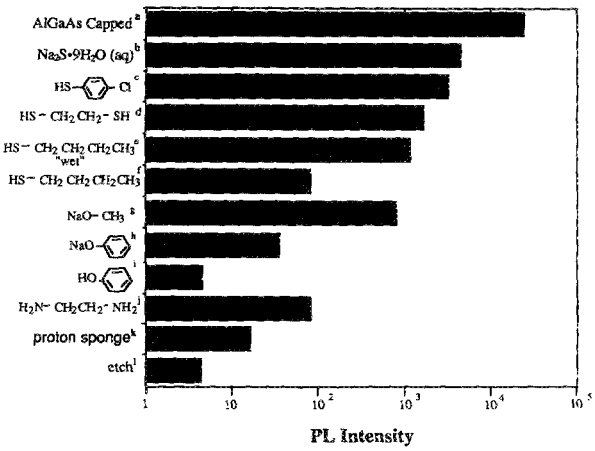

FIG. 1. Bar graph of the steady state PL intensity at 874 nm, in arbitrary units, of GaAs exposed to a variety of organic reagents. The concentration of each compound was 1.0 M in diethyl ether, and exposure times were 30 min. For all systems investigated, the magnitude of the PL signal induced by a given reagent was identical for either the stoichiometric surface (obtained by use of etch A) or the As^0-rich GaAs surface (obtained by use of etch B). (a) Sample as grown with $Al_{0.4}Ga_{0.6}As$ overlayer (see text). (b) PL intensity after treatment with 1.0 M $Na_2S{\cdot}9H_2O$ in water. (c) 4-chlorothiophenol. (d) 1,2-dithiolethane. (e) 1-butanethiol; sample immersed in the liquid. (f) 1-butanethiol; treated identically to the other organic compounds. (g) sodium methoxide. (h) sodium phenoxide. (i) phenol. (j) ethylenediamine. (k) 1,8-bis(dimethylamino)naphthalene. (l) Etch A after removal of the top AlGaAs layer.

obtained under conditions in which the PL signal was very sensitive to changes in the GaAs surface recombination velocity (S); thus, the PL signal intensity varied by over 10^3 for the various systems evaluated. The lattice matched $GaAs/Al_{0.4}Ga_{0.6}As$ interface showed the highest PL signals, which is in accord with the low surface recombination velocity (10^2 cm/s) of this system. The highly defective GaAs/air interface had a very high surface recombination velocity, and yielded very low levels of PL intensity (Fig. 1). Treatment of the air-etched GaAs surface with $Na_2S{\cdot}9H_2O$ has been reported previously[1] to reduce the low level injection S value from $> 10^5$ to 10^3 cm/s, and our PL data was in accord with this observation. We also observed that exposure to alkyl and aryl thiols effected large reductions in the low level injection S value; furthermore, these effects were comparable in magnitude to the $Na_2S{\cdot}9H_2O$ (aqueous) treatment (Fig. 1).

In addition to demonstrating that a class of thiols is effective in reducing the recombination velocity of GaAs surfaces, the data for the series of compounds depicted in Fig. 1 also yields valuable chemical information concerning the nature of the important nonradiative surface recombination centers. While simple unhindered aryl and alkyl thiols were effective in reducing the surface recombination velocity, additional experiments with weak donors, such as thiophene (C_4H_4S) and dimethylsulfide [$(CH_3)_2S$], indicated that such compounds did not effect a large change in the PL signal. This trend parallels that commonly observed for the binding constants of sulfur ligands with transition metal Lewis acid centers,[3] and is consistent with the hypothesis that effective coordination to the recombination site is an important component of improving the PL signal. Additionally, the trend in PL intensity observed for the various heteroatom bases of S > N,O suggests that the surface site is "soft" in character[3] and prefers type *b*, or polarizable ligands, as opposed to being protic in character and being only sensitive to the pK_a of a compound. This would be expected for a polarizable, electron deficient site, such as perhaps As^0, or possibly Ga atoms in a GaAs lattice, but is not consistent with expectations for an oxide-type acceptor site.

Figure 2 displays monochromatic Al $K\alpha$ XPS data for the As 3*d* and Cl 2*p* regions of a stoichiometric (etch A) and As^0-rich GaAs surface (etch B) before and after exposure to 4-chlorothiophenol (4-Cl-C_6H_4-SH). As shown in Fig. 2(b), although the presence of persistent Cl signals indicated that the 4-chlorothiophenol had adsorbed on the GaAs surface, exposure to the thiol did not result in elimination of excess As^0. Additionally, no detectable As_2S_3 ($< 1\times10^{-10}$ mole As_2S_3-cm^{-2} surface coverage) or other As–S type oxidized As signal was observed on the thiol-exposed GaAs surface. Fits to the As 3*d* region are displayed in Fig. 3, and clearly indicate the presence of As^0 and lack of an As_2S_3-type phase after exposure to the thiol. The small intensity at higher binding energies with respect to the As_{GaAs} peak resulted from the presence of As^0; clearly detectable signals would have been observed in this region even with small ($\approx 2\times10^{-10}$ mole/cm^2) coverages of As_2S_3-type phases. Consistent with prior work,[4] near-monolayer coverages of As_2S_3-type phases were readily observed after exposure of GaAs to 1.0 M $Na_2S{\cdot}9H_2O$(aq), but exposure to the thiols used in the present work did not yield detectable signals for an As_2S_3-type phase under the same instrumental conditions. The lack of As_2S_3 formation and residual presence of As^0 was also verified for exposure to other thiols, including 1,2-dithiolethane [HS-(C_2H_4)-SH] and 1-butanethiol [HS-(C_4H_9)]. Additionally, no changes were observed in the Ga 3*d* peak for any of the surface treatments. Occasionally, low but detectable levels of Ga oxide were observed on etched GaAs surfaces. The position of the oxidized Ga 3*d* peak was in excellent agreement with prior literature values for thin Ga oxides on etched GaAs surfaces,[5] and this peak,

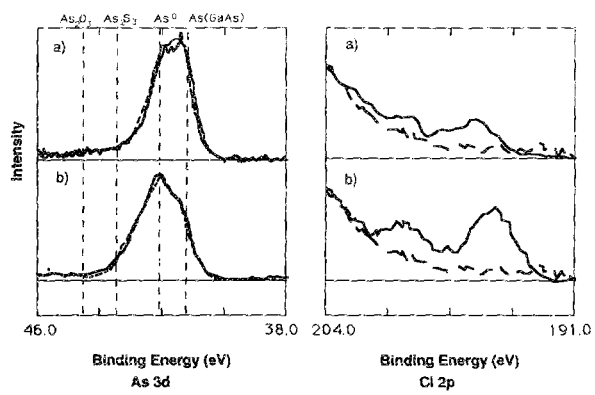

FIG. 2. As 3*d* and Cl 2*p* XPS regions for *n* GaAs (a) etched with Etch A (dashed line), and for GaAs then exposed to1.0 M 4-chlorothiophenol in CCl_4 for 30 min (solid line). (b) as (a) except GaAs initially etched with etch B.

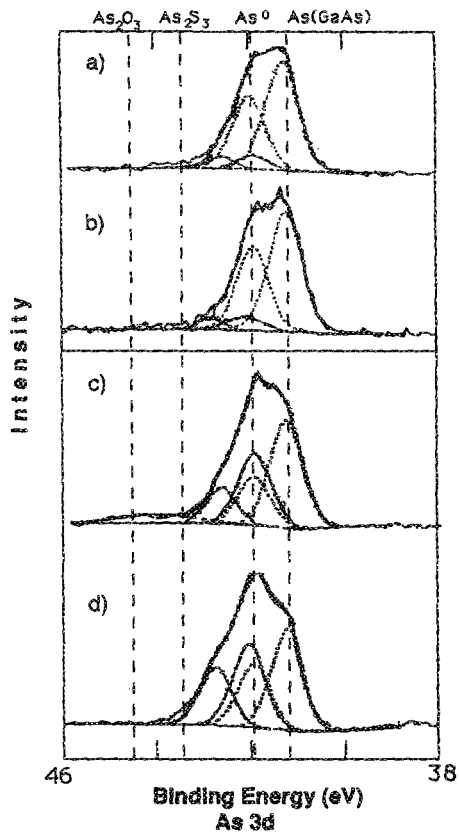

FIG. 3. Fits to the As 3*d* XPS region for the spectra of Fig. 2. (a) Etch A. (b) Etch A, followed by exposure to 1.0 M 4-chlorothiophenol in CCl_4 for 30 min. Note the small intensity for As^0, and the lack of As–S or As–O peaks. (c) Etch B. Note the large intensity for As^0 needed to fit the As 3*d* peak, as expected for this etching process. (d) Etch B, followed by exposure to 1.0 M 4-chlorothiophenol in CCl_4 for 30 min. Note the lack of As–S or As–O peaks, as well as the lack of change in the As^0 intensity after exposure to the thiol solution.

when present, was not removed by exposure to the thiol solutions. The PL intensity increases of Fig. 1 were observed whether or not the Ga oxide peaks were detectable by XPS. In fact, the only systematic change in the XPS detectable on thiol-treated GaAs surfaces was due to XP lines from the thiol itself; this result was verified even on stoichiometrically etched (etch A) surfaces that had little or no detectable As^0, As oxides or Ga oxides before immersion into the thiol solutions (Table I).

This behavior is not expected based on several hypotheses for the surface chemistry responsible for the $Na_2S \cdot 9H_2O$/GaAs passivation process.[4,6-8] The removal of excess As^0 [6,7] and/or formation of an epitaxial, defect-free, layer of As_2S_3[4,8] have been proposed to explain the improved electrical properties of GaAs that has been exposed to 1.0 M $Na_2S \cdot 9H_2O$(aq). In contrast, the comparable steady state PL intensities for the simple alkyl and aryl thiols (Fig. 1), combined with the XPS data for these systems (Fig. 2, Table I), indicates that effective passivation of GaAs surface recombination can occur without such gross changes in surface stoichiometry. The trends of Fig. 1 do indicate, however, that effective passivation of GaAs surface recombination can occur without such gross changes in surface stoichiometry. The trends of Fig. 1 also imply, however, that effective binding to the important chemical recombination site is required, and that S donors are substantially more effective than "harder," less polarizable, O and N bases. The recent results of Sandroff *et al.*[9] showing that selenium is a superior passivant to sulfur is consistent with these results, since selenium is even more polarizable than sulfur. Given the potentially low density of recombination centers that could be responsible for the variation in surface electrical characteristics,[10] it is not surprising that spectroscopies with sensitivity limits of 0.1–1.0 monolayers cannot uniquely identify the chemically important surface species of many passivated surfaces, such as the thiol-treated GaAs surfaces studied herein. Although the XPS work discussed herein only pertains to thiol-treated GaAs surfaces, similar conclusions can be made for GaAs exposed to $Na_2S \cdot 9H_2O$(aq), and these results will be discussed in a separate manuscript.

In conclusion, we have identified a series of donor-type reagents that are extremely effective in reducing nonradia-

TABLE I. XPS data of GaAs exposed to nonaqueous solutions of thiols. Binding energies of Ga and As species given with respect to C 1*s* = 285.0 eV.

		Ga 3*d*		As 3*d*			As 2*p*					
Sample	x-ray[a] source	Ga (GaAs) eV	Ga (Ga_2O_3) eV	As (GaAs) eV	As (As_2O_3) eV	As (As^0) eV	As (GaAs) eV	As (As_2O_3) eV	As (As^0) eV	Ga/As 3*d* region[b]	S 2*s* eV	C 1*s* eV
Etch A[c]	Al	19.2	20.0	41.0	···	41.7				1.7		285.3
+ 1.0 *M* 4-Cl–C_6H_4–SH in CCl_4 (30 min)	Al	19.2	20.1	41.1	···	41.8				1.1		285.2
+ 1.0 *M* 4-Cl–C_6H_4–SH in CCl_4 (30 min)	Mg	20.0	20.9	42.0	···	···				1.0	227.6	285.1
Etch B	Al	19.7	20.6	41.6	44.4	42.3	1323.3	1325.6	1324.1	1.5		284.7
+ 1.0 *M* 4-Cl–C_6H_4–SH in CCl_4 (30 min)	Al	19.4	···	41.2	···	42.0	1323.0	1325.2	1323.9	1.6		285.1

[a] Al = Data taken with monochromatic Al *Kα* x rays (1486.6 eV) on a Surface Science Instruments Model 100. Mg = Data taken with Mg *Kα* x rays (1254 eV) on a VG Mark II. "···" indicate that the peaks were undetectable due to either sensitivity or resolution.
[b] Ga/As ratio for substrate peaks and does not include contributions from oxides, or As^0.
[c] Etch A = 1.0 M KOH (15 s), 0.5% Br_2/Methanol (15 s), repeated 3 times and ending in KOH. Etch B = Etch A + 30 s 1:1:100 (H_2SO_4:30% H_2O_2:H_2O).

tive recombination at GaAs surfaces. The surface recombination velocities produced by these thiols (as measured by the low-level injection changes in PL intensity) are not as low as values obtainable with the GaAs/$Al_{0.4}Ga_{0.6}As$ interface, but are comparable to the best known chemical systems to date. The trends in chemical reactivity are consistent with the hypothesis that the important recombination sites on the GaAs surface act as a soft, polarizable, electron deficient center. Such trends in reaction chemistry should be useful in extending the passivation process to other classes of donors, and might allow development of superior GaAs electrical surfaces for use in numerous optoelectronic applications. The structural information obtained from use of a variety of chemical reagents is complementary to, and in many ways more desirable than, spectroscopic analyses, because the low density of important recombination levels may not be detectable with gross stoichiometry changes of the surface. Further chemical studies of the GaAs system using other ligands have the potential to yield even superior electrical surfaces, and full details on such studies will be discussed in future reports.

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[1] B. J. Skromme, C. J. Sandroff, E. Yablonovitch, and T. Gmitter, Appl. Phys. Lett. **51**, 2022 (1988); C. J. Sandroff, R. N. Nottenburg, J. C. Bischoff, and R. Bhat, Appl. Phys. Lett. **51**, 33 (1987); E. Yablonovitch, C. J. Sandroff, R. Bhat, and T. Gmitter, Appl. Phys. Lett. **51**, 439 (1987).
[2] H. J. Stocker and D. E. Aspnes, Appl. Phys. Lett. **42**, 85 (1983).
[3] J. E. Huheey, *Inorganic Chemistry*, 3rd ed. (Harper, New York, 1983), pp. 312–325.
[4] C. J. Sandroff, M. S. Hegde, L. A. Farrow, C. C. Chang, and J. P. Harbison, Appl. Phys. Lett. **54**, 362 (1989).
[5] P. J. Grunthaner, R. P. Vasquez, and F. J. Grunthaner, J. Vac. Sci. Technol. **17**, 1045 (1980); J. Massies and J. P. Contour, J. Appl. Phys. **58**, 806 (1985); C. F. Yu, D. V. Podlesnik, M. T. Schmidt, H. H. Gilgen, and R. M. Osgood, Jr., Chem. Phys. Lett. **130**, 301 (1986).
[6] C. J. Spindt and W. E. Spicer, Appl. Phys. Lett. **55**, 1653 (1989).
[7] G. D. Pettit and J. M. Woodall, J. Vac. Sci. Technol. B **6**, 1180 (1988); C. W. Wilmsen, P. D. Kirchner, and J. M. Woodall, J. Appl. Phys. **64**, 3287 (1988).
[8] Y. Nannichi, J.-F. Fan, H. Oigawa, and A. Koma, Jpn. J. Appl. Phys. **27**, L2367 (1988).
[9] C. J. Sandroff, M. S. Hegde, L. A. Farrow, R. Bhat, J. P. Harbison, and C. C. Chang, J. Appl. Phys. **67**, 586 (1990).
[10] W. E. Spicer, Z. Liliental-Weber, E. Weber, N. Newman, T. Kendelewicz, R. Cao, C. McCants, P. Mahowald, K. Miyano, and I. Lindau, J. Vac. Sci. Technol. B **6**, 1245 (1988).