Passivation of GaAs (100) with an Adhesion Promoting Self-Assembled Monolayer

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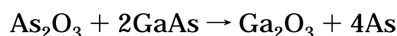
In this paper we demonstrate that photoluminescence (PL) from GaAs exposed to (3-mercaptopropyl)trimethoxysilane (MPT) exhibits a 10-fold enhancement over that of an oxidized sample. The PL enhancement is attributed to the formation of sulfur−surface bonds. We demonstrate that the MPT surface film that results from the treatment described herein is a monolayer thick by ellipsometry, and we examine the composition of the GaAs/MPT interfacial region using X-ray photoelectron spectroscopy (XPS). The XPS results indicate that the native oxide is removed by the etching procedure, and reoxidation of the surface is minimal during the subsequent deposition of MPT. The nature of the sulfur−surface bond is discussed in view of the XPS results reported here and those of previous measurements by other researchers. The self-assembled monolayers of MPT that forms on the GaAs surface leave a trimethoxy-silyl terminated surface that can be polymerized by exposure to weak acid. We demonstrate that the polymerized overlayer inhibits reoxidation of the GaAs surface better than the nonpolymerized, MPT treated surface.

Surface midgap states in GaAs are known to pin the Fermi level and therefore impede the performance of metal oxide semiconductor devices.[1] Bare arsenic atoms are thought to be one of the species present within the native oxide responsible for pinning the Fermi level.[2−6] The arsenic atoms result from chemistry that occurs at the oxide/GaAs interface. Both As_2O_3 and Ga_2O_3 will form when a clean GaAs surface is exposed to oxygen and light. However, the formation of Ga_2O_3 is thermodynamically favored,[7] and results in the reaction



$$As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As$$

leaving bare arsenic atoms embedded within the oxide near the oxide/GaAs interface. Additional evidence suggests that the As_2O_3 is also mobile at grain boundaries,[8,9] resulting in a nonuniform oxide in which an As_2O_3-rich layer is found near the oxide/air interface, and the bare arsenic atoms are found embedded within the Ga_2O_3-rich layer near the oxide/GaAs interface. To complicate matters, both Ga_2O_3 and As_2O_3 are somewhat soluble in water, and their solubilities are dependent on pH. The complicated chemistry of the GaAs native oxide has prevented the development of a simple and robust surface passivation scheme for this surface. Spicer has recently argued that the simple process used to passivate silicon is the exception rather than the rule in semiconductor surface passivation chemistry, and he suggests that a more elaborate scheme may be required for the passivation of compound semiconductors.[1] The proposed scheme suggests separate processing steps for electrical passivation (i.e., minimization of the surface midgap state density and Fermi level unpinning) and environmental protection.

Sulfur and other chalcogenides have been explored as electrical passivating agents for GaAs, and activity has been particularly brisk since Sandroff and coworkers reported substantial improvement in the electrical characteristics of GaAs following treatment with Na_2S.[10] Both Ga−S and As−S bonds have been observed by X-ray photoelectron spectroscopy (XPS) following sulfide passivation.[11−14] Because the presence of midgap states is known to quench photoluminescence (PL), PL intensity enhancement is widely used to characterize the extent of passivation following treatment.[12,15] PL enhancement is expected to occur as the result of both band unbending and reduction of surface minority trap density, and thereby reduction in the rate of surface nonradiative recombination.[16−20]

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Following the discovery of GaAs passivation with inorganic sulfides, several groups have demonstrated passivation of III–V semiconductors with thiol-type self-assembled monolayers (SAMs).[21–27] Lunt et al. examined PL enhancement from GaAs treated with a variety of SAM-forming mercaptans.[21,22] They used chemical arguments to suggest that the surface-active sites with respect to surface–S bond formation were Lewis acidic in nature, consistent with As–S and Ga–S bond formation. XPS measurements did not provide evidence for the formation of an As_2S_3 phase in the surface layer, in contrast to results on surfaces passivated with inorganic sulfides. Shin et al.[11] have argued that the nature of the sulfur–surface bond depends strongly on the composition of aqueous solutions when inorganic sulfides are used because these solutions both etch the surface and provide the passivating agent. Their results suggest that the etching methods used by Lunt et al. leave a Ga-terminated surface. Allara and co-workers have studied the surface morphology of GaAs passivated with alkanethiol SAMs.[24–26] They have shown that the SAM structure is similar to that found for alkane thiols on Au surfaces and that the SAMs can be used as resists and as insulating spacers in Schottky barrier devices.

In this paper we examine the formation and growth conditions of a SAM of 3-(mercaptopropyl)trimethoxysilane (MPT) on GaAs (100). We demonstrate that the SAM formation chemistry mimics the formation of polymerizable MPT SAMs on Au and Ag surfaces as demonstrated by Thompson and Pemberton.[28–30] We use PL enhancement to monitor the formation of surface–S bonds and ellipsometry to determine the thickness of the overlayer formed after exposure of GaAs to MPT. Surface composition is examined with XPS, and time-dependent PL studies are used to examine the durability of the resulting SAM/GaAs interface to reoxidation.

Experimental Section

Chemicals. (3-Mercaptopropyl)trimethoxysilane ($HS(CH_2)_3Si(OCH_3)_3$, 95%) and 99.99% semiconductor grade KOH were purchased from Aldrich Chemical Co. Reagent-grade concentrated HCl, 30% H_2O_2, NH_4OH, hexane (optima), and acetone (optima) were purchased from Fisher. 100% ethanol was from McCormick Distilling Co. Inc. All chemicals were used as received. Ultrapure water was used throughout the experiment. The n-GaAs (100) wafers with carrier concentration of 2×10^{17} cm^{-3} (Si) were purchased from Crystal Specialties Inc. Samples of 0.5×0.5 cm^2 were cut from the wafer and mounted to 1.0×2.5 cm^2 glass microscope slides. Samples were then rinsed with DI water and degreased with hexane and acetone. The samples were immersed in a solution of H_2O:H_2O_2:NH_4OH (8:1:1) for 5 s, rinsed with DI water, and blown dry with argon. They were then immersed in concentrated HCl for 1 min, rinsed with DI water and dried with argon. This step was repeated three times. The degreasing and etching steps were followed rigorously with fresh solutions for each sample.

The etched samples were immediately immersed in liquid MPT heated to 70 °C using an oil bath under argon. The samples remained in the liquid for a controlled period of time. After cooling, the samples were rinsed thoroughly with 100% ethanol to remove residual MPT on the sample surfaces and then blown dry with argon. After the MPT treatment, there was no visible change in the appearance of the GaAs surface. Some samples were immersed into 0.1 M HCl solution following MPT treatment to effect polymerization of the putative trimethoxysilyl-terminated surface. Oxygen was purged from the polymerization solution with argon, and the vessel used for the polymerization was sealed to be airtight during polymerization. After polymerization, samples were rinsed thoroughly with DI water and blown dry with argon.

Instrumentation. Photoluminescence (PL) intensities are measured with the following apparatus. A He–Cd laser (100 mW at 442 nm) is directed onto GaAs samples through a 1000 Hz chopper, which was used to accommodate phase-sensitive detection. The photoluminescence from GaAs at 837 nm was directed through a lens and a long-pass filter into a monochromator. Light intensity is measured with a photomultiplier and a lock-in amplifier (SR850 DSP, 100 ms time constant). The laser beam has a diameter of about 0.3 mm at the sample surface. An untreated, oxidized GaAs sample was used as the reference against which all PL intensities were measured. On each sample, three different spots were measured and the average value was taken as the result. The photoluminescence intensities of samples were divided by the photoluminescence intensity of the reference sample to get the relative intensities. For each sample, relative intensities after etching, MPT treatment and polymerization were compared with their relative intensities before treatment was applied. The photoluminescence enhancement factor is defined as the ratio of the relative intensity after a given process to the relative intensity of the same sample before any treatment (including etching) has been applied.

A Rudolf Research AutoEL-II automatic ellipsometer was used to measure the film thickness of various samples. A He–Ne laser (632.8 nm) light source was used at a 70° angle of incidence. The refractive index of GaAs substrate was taken as $n = 3.856$ and $k = 0.196$.[31] The refractive index of the native oxide was taken as $n = 1.800$, $k = 0.000$,[32] and the refractive index of MPT is assumed to be $n = 1.500$, $k = 0.000$. Measurements were made immediately after each treatment. On each sample, at least three different spots were measured. The thickness was calculated after each measurement using commercial software (DafIBM version 2.0), and the results were averaged.

X-ray photoelectron spectra (XPS) of the samples were collected in order to examine the composition of the GaAs/MPT interface following treatment. A VSW twin X-ray source was used in this study. X-ray photoelectron spectra were taken with Al Kα radiation (1486.7 eV) with the anode operating at 435 W of power. A cylindrical mirror analyzer (CMA, Physical Electronics Inc., Model 15-255GAR) was operated at a fixed

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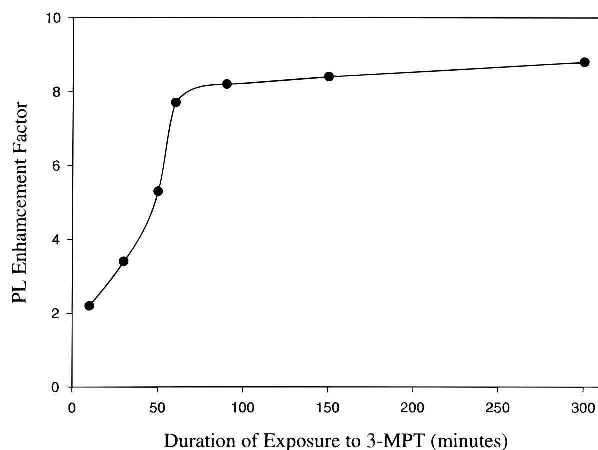

Figure 1. Photoluminescence enhancement versus duration of exposure to MPT. The line is included as a guide to the eye. All points were measured on the same sample. After 90 min the enhancement factor remains nearly constant.

pass energy of 25 eV. XPS measurements were carried out on samples without treatment (bare sample), etched samples, MPT-treated samples, and polymerized samples. For each sample, Ga (3d) and As (3d) core level spectra were collected. Peakfit (Jandel Scientific) nonlinear curve-fitting software was used for data analysis. The spectra were fit to sums of Lorentzian line shapes. By peak fitting, the components associated with GaAs, oxides, and sulfur-bonded species in the spectra were identified.

Overlayer Formation and Structure

Figure 1 shows PL intensities of etched samples exposed to liquid MPT at 70 °C as a function of exposure time. The sample was removed from the MPT, rinsed with ethanol, and dried with argon, and then the PL measurement was made. The sample was immediately returned to the liquid MPT after the PL measurement. The PL intensity of the etched GaAs sample always increases upon exposure to MPT. On the basis of previous reports of PL intensity increase following exposure to organic thiols, we take this as evidence of sulfur−surface bond formation, resulting in passivation of midgap states on the GaAs surface. The PL enhancement factor increases sharply, reaching a value of 8.2 after 90 min following exposure to the MPT and reaches a plateau. After 5 h of total exposure to MPT the PL enhancement factor has increased to 8.8, only slightly higher than the value after 90 min. In subsequent studies of surface treatment the GaAs is exposed to the warm MPT for a duration of 90 min. Numerous trials were performed, and the enhancement factor ranged from 13 to 7 with an average value of 10. There appears to be a correlation between the magnitude of the enhancement factor immediately after etching and the initial enhancement factor immediately after MPT treatment, suggesting that variations in the GaAs surface morphology are responsible for the variability of the initial enhancement factor after MPT treatment.

Thicknesses of GaAs surface layers were measured by ellipsometry. The results are summarized in Table 1. Each entry in the table is the average over several samples. Each sample was measured at least three times on three different spots, and averaged. The standard deviations of thicknesses determined on each individual sample were typically ±1 Å except in the case of polymerized samples as discussed below. The averages shown in Table 1 are averages over several samples and the uncertainties reflect sample-to-sample variations. The average thickness of the native oxide on as received GaAs samples is 43 ± 12 Å. After etching, the average measured thickness of 6 samples is 24 ± 1 Å assuming $n = 1.800$ for the oxide. The decrease of film thickness indicates that an oxide layer has been removed, and the small uncertainty reflects a uniform etching procedure. However, the thickness of the etched samples is not zero. Osakabe and Adachi[32b] observed similar results in studies of GaAs etching procedures. They suggest that the finite measured overlayer thickness is the result of either surface roughness following etching or the formation of a new surface film during the brief exposure (about 5 min) to air during the ellipsometric measurement. XPS results discussed below indicate that neither Ga oxides nor As oxides form during an exposure of this duration, suggesting that if a surface film forms, it may be composed of physisorped species such as O_2 and H_2O. If we assume that surface roughness is responsible for the observed finite overlayer thickness or that the surface film which forms on the clean GaAs surface will also form on the MPT treated surface, we can use the difference between the etched and MPT treated samples to estimate the thickness of the MPT overlayer. We have analyzed the ellipsometric data of MPT treated samples with a single layer model using the refractive index of the oxide layer ($n = 1.8$) and the expected refractive index of the MPT overlayer ($n = 1.5$) as limiting cases. When $n = 1.800$ is used, the average thickness of etched samples is 24 ± 1 Å, and the average thickness of films on MPT-treated samples is 36 ± 6 Å. Thus the MPT layer thickness is 12 ± 7 Å. When $n = 1.500$ is used, the average thickness of etched samples is 27 ± 1 Å, and the average thickness of MPT treated samples is 42 ± 7 Å. In this case an MPT layer thickness of 15 ± 7 Å is found. Comparison of these values with the length of MPT molecule (12 Å), leads us to conclude that the films are composed of a single monolayer.

Table 1. Film Thickness (Å) by Ellipsometry[a]

refractive index	$n = 1.800$	$n = 1.500$
bare sample	43 ± 12	
etched sample	24 ± 1	27 ± 1
MPT-treated sample	36 ± 6	42 ± 6
difference from etched surface	$\delta = 12 \pm 7$	$\delta = 15 \pm 7$
polymerized sample		66 ± 20
difference from etched surface		$\delta = 39 \pm 20$

[a] Three to six trials of each sample type were measured. Each trial represented a different sample of the GaAs wafer, and three spots on the surface were measured for each trial. The standard deviation in the film thickness of individual trials was ±1 Å, with the exception of the polymerized samples, which exhibited larger variations. Uncertainties listed in this table reflect trial-to-trial variations in film thickness.

The PL results and the film thickness are consistent with the formation of a monomolecular layer of MPT on the GaAs surface, which has the same structure as that of MPT on Au surfaces demonstrated by Thompson and Pemberton.[28] We therefore expect that the putative trimethoxysilyl-terminated surface will polymerize following exposure to weak acidic aqueous solutions. We have measured PL intensities of MPT-treated samples exposed to 0.1 M HCl at room temperature measured as a function of exposure time. The results indicate that surface passivation characterized by PL intensity is

largely unaffected by exposure of the surface to the weak acid for a period of up to 4 h. PL enhancement factors of the acid-exposed surfaces were essentially identical with the MPT-treated surface before exposure to the acid. Slight variations on the order of ±5% were observed after 4 h exposure, but the average PL enhancement factor of 6 trials was unchanged. In contrast, a 12 h exposure always resulted in about a 50% decrease in the PL enhancement factor. All subsequent polymerized samples were exposed to 0.1 M HCl following MPT treatment for 4 h. Table 1 indicates that polymerized overlayers exhibit substantial variations in thickness, both on a single sample and between samples. The polymerization process is clearly affecting the morphology of the overlayer. It is possible that the polymerization process results in a nonuniform overlayer with high- and low-density regions of the polymerized MPT. In this case variability in the overlayer thickness would effectively roughen the sample surface and thereby increase the "thickness" as measured by ellipsometry. Associated variability in the optical properties of the overlayer might corrupt the "thickness" measured ellipsometrically even further. Etching of the GaAs substrate through pinholes in the MPT overlayer would have a similar roughening effect. Film thickness variations in the polymerized overlayer may also result from adsorption of water to the hydroxyl-terminated surface that forms after the polymerization process. The unchanged PL enhancement factors following polymerization indicate that the change in surface morphology is not the result of changes in surface bonding characteristics such as sulfonate formation.[33] Passivation durability studies described below also suggest that the initially formed passivating thiol/GaAs interface survives the polymerization process largely intact. Localized surface probes such as scanned probe microscopies may be required to fully understand the observed variability in the ellipsometrically measured polymerized overlayer thickness.

XPS was used to examine the composition of the GaAs surface following four stages of treatment. The bare samples are as received, and the etched, MPT-treated and polymerized samples are prepared as described above. Samples were loaded into the XPS chamber within 5 min following treatment, and ultrahigh vacuum was attained within about 45 min after loading the samples. All spectra were analyzed by fitting to sums of Lorentzian line shapes. In the As (3d) and Ga (3d) regions etched samples were used to determine the peak parameters for the GaAs peaks composed of two Lorentzian components representing the $3d_{3/2}$ and $3d_{5/2}$ contributions, and bare samples were then used to determine peak parameters for oxide peaks widths. Peak widths thus determined were fixed in subsequent analysis. Binding energy shifts from the $3d_{5/2}$ peak of the GaAs component were held constant at the literature values of the respective constituents including native oxides[13] and Ga−S[14] and As−S[12,14] species. Figure 2 shows the As (3d) spectra of a set of four samples along with composite spectral fits, and the curve-fitting results are given in Table 2. Comparison of the bare and etched samples indicates that As oxides

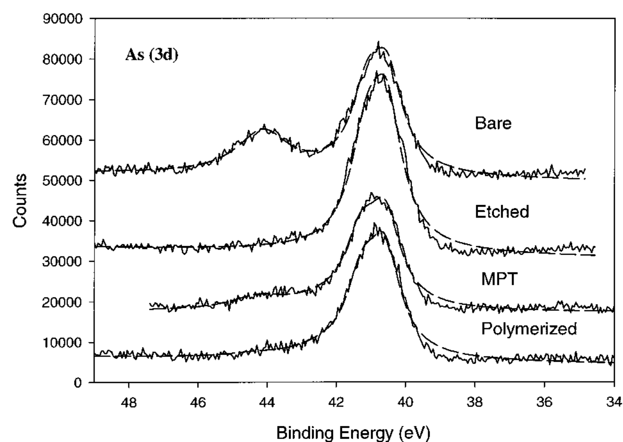

Figure 2. XPS spectra of four samples in the As (3d) region. The dashed lines are results of fits to sums of Lorentzian line shapes. Fitting parameters are given in Table 2.

Table 2. Nonlinear Regression Analysis of the XPS As(3d) Region Spectra[a]

		binding energy shift (eV)	peak width	% area
bare sample	As−oxide peak	3.6	0.9150	29.7
	GaAs $3d_{3/2}$ peak	0.6	0.5526	31.3
	GaAs $3d_{5/2}$ peak	0.0	0.5526	39.0
etched sample	GaAs $3d_{3/2}$ peak	0.6	0.5526	42.4
	GaAs $3d_{5/2}$ peak	0.0	0.5526	57.6
MPT-treated sample	As−oxide peak	3.7	0.9150	10.0
	As−S peak	1.8	1.2200	7.8
	GaAs $3d_{3/2}$ peak	0.7	0.5526	34.6
	GaAs $3d_{5/2}$ peak	0.0	0.5526	47.6
polymerized sample	As−oxide peak	3.8	0.9150	2.5
	As−S peak	1.9	0.9715	5.8
	GaAs $3d_{3/2}$ peak	0.7	0.5526	35.8
	GaAs $3d_{5/2}$ peak	0.0	0.5526	55.9

[a] Binding energy shifts are measured relative to the As−Ga ($3d_{5/2}$) peak at 40.7 eV.

on the GaAs surface are removed by the concentrated HCl etching method. Small oxide peaks are observed in the spectrum of the MPT-treated sample and polymerized samples. The fact that the etched sample does not have an oxide peak indicates that the oxide peaks in the MPT-treated and polymerized samples results either from incomplete initial etching or from oxide formation resulting from the treatment process itself. The latter possibility seems unlikely, however, since it would be expected to result in diminished PL intensity with increasing treatment time, which is inconsistent with the PL results described above. Furthermore in this set of samples the polymerized sample has a smaller oxide component than the MPT-treated sample. The Ga (3d) spectra shown in Figure 3 exhibit the same oxide peak intensity trend, which also suggests that incomplete initial oxide removal or adventitious surface oxidation during treatment processes are responsible for the observed oxide peaks and that oxide formation is not inherent to the treatment procedures used in these studies. For MPT-treated and polymerized samples, a third peak in the As (3d) spectra with 1.8 eV shift from GaAs $3d_{5/2}$ component was also present. Spindt et al.[14] assign a peak with a 1.7 eV shift in the As (3d) spectrum of $(NH_4)_2S$-treated GaAs (100) to As_2S_3. On the basis of these results, the third spectral component in the As (3d) spectrum of MPT-treated GaAs provides evidence for the formation of As−S bonds on the MPT-modified GaAs surfaces.

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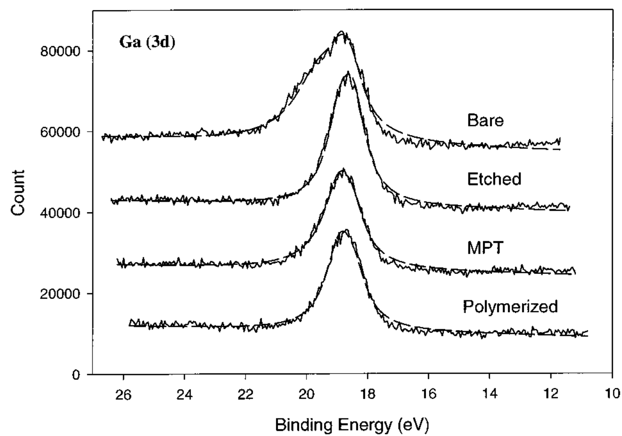

Figure 3. XPS spectra of four samples in the Ga (3d) region. The dashed lines are results of fits to sums of Lorentzian line shapes. Fitting parameters are given in Table 3.

The magnitude of the As–S peaks in XPS spectra are low compared to the results of Spindt et al.[14] We also observe that the magnitude of the As–S component is lower in the polymerized samples than in the MPT-treated samples. Yet the PL intensity enhancement indicates clearly that surface–sulfur bonds are forming. Spindt et al.[14] and Shin et al.[11] have demonstrated that Ga–S formation can also occur in sulfide-passivated GaAs by careful examination of the Ga (3d) spectral region using high-resolution UV photoemission and angle-resolved XPS. Their instruments were able to resolve the Ga–S peak from the Ga peak. Lower resolution XPS instrumentation such as that used in our studies are incapable of resolving the Ga–S peak, and as a result this surface species is easily overlooked. Lunt et al.[21] have examined the As (3d) region of GaAs passivated with organic thiol self-assembled monolayers and found no evidence for As–S bond formation. Our results indicate a small As–S component. On the basis of the studies of Shin et al.,[34] it appears that this difference may simply result from the nature of the GaAs surface following the etching procedure. Examination of the Ga (3d) region of the MPT-treated and polymerized samples suggest the presence of an additional peak beneath the main Ga (3d) envelope. The results of peak fitting in the Ga (3d) region are given in Table 3. This additional component manifests itself visually as a slight broadening of the Ga (3d) peak. By fixing the Ga (3d) width to the value obtained for the etched sample, the new component is identified at a binding energy shift consistent with the assignment of Spindt et al.[14] This may provide evidence for the formation of Ga–S bonds, though we cannot unambiguously rule out contributions from Ga_2O_3 with our present resolution.

Passivation Durability

PL intensity changes with time were measured on both polymerized and nonpolymerized samples in order to study the durability of MPT-modified samples to environmental degradation. Figure 4 is the PL intensity change of a pair of samples stored in a lightproof container filled with argon between measurements.

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Table 3. Nonlinear Regression Analysis of the XPS Ga(3d) Region Spectra[a]

		binding energy shift (eV)	peak width	% area
bare sample	Ga–oxide peak	0.9	0.9851	60.4
	GaAs $3d_{3/2}$ peak	0.4	0.4993	19.4
	GaAs $3d_{5/2}$ peak	0.0	0.4993	22.2
etched sample	GaAs $3d_{3/2}$ peak	0.4	0.4993	45.0
	GaAs $3d_{5/2}$ peak	0.0	0.4993	55.0
MPT-treated sample	Ga–oxide peak	0.9	0.9851	15.6
	Ga–S peak	0.55	0.5798	26.1
	GaAs $3d_{3/2}$ peak	0.4	0.4993	29.3
	GaAs $3d_{5/2}$ peak	0.0	0.4993	29.0
polymerized sample	Ga–oxide peak	0.9	0.9851	1.629×10^{-5}
	Ga–S peak	0.55	0.5608	42.6
	GaAs $3d_{3/2}$ peak	0.4	0.4993	26.0
	GaAs $3d_{5/2}$ peak	0.0	0.4993	31.4

[a] Binding energy shifts are measured relative to the Ga–As ($3d_{5/2}$) peak at 18.5 eV.

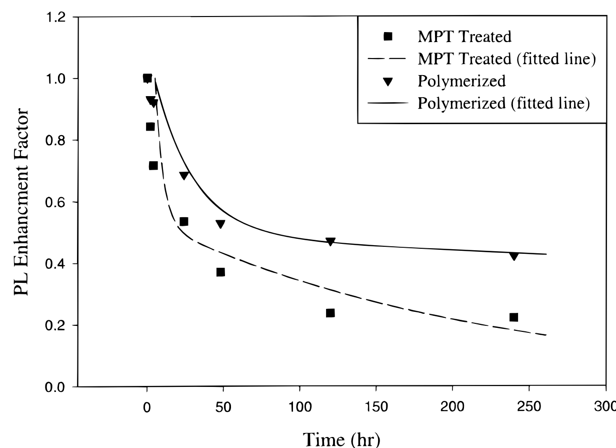

Figure 4. Photoluminescence intensity versus time for MPT-treated and polymerized-MPT-treated GaAs samples. The lines are fits to a double exponential decay function (Equation 1). Fitting results are given in Table 4.

Table 4. Nonlinear Regression Analysis of Photoluminescence Decay from MPT-Modified GaAs[a]

		A	B	τ (h)	τ' (h)
ambient conditions	MPT-treated sample	0.6246	0.3713	1.7	298.6
	polymerized sample	0.5158	0.4784	5.7	301.8
controlled conditions	MPT-treated sample	0.4712	0.5283	4.9	203.7
	polymerized sample	0.5006	0.4900	24.6	1676.7

[a] Photoluminescence time traces were fit to a double exponential decay function, eq 1.

Both samples exhibit PL intensity decay with time, which appears to include a fast and a slow component. We have fit the data to a phenomenological equation defined by eq 1 using commercial software (Sigma Plot 4.0):

$$PL = Ae^{-t/\tau} + Be^{-t/\tau'} \qquad (1)$$

In this equation t is time, A and B are positive constants with a value of $A + B = 1$, and τ and τ' are fast and slow decay rates, respectively. Larger decay times represent slower PL intensity decay rates, and a coating is expected to exhibit slower decay rates and a larger value of B as it becomes more durable. The results of the fit are given in Table 4, and they demonstrate that the polymerized samples exhibit improved resistance to

surface deterioration following MPT treatment. Similar results have been obtained for samples stored in ambient lab conditions (exposed to normal room lights and air). Though the decay rates were faster under ambient conditions, the polymerized sample exhibited substantially longer decay rates than the nonpolymerized samples. These studies provide evidence that the polymerization process results in a cross-linked self-assembled monolayer of MPT on the GaAs surface and are consistent with the expected chemistry under the assumption that the surface following MPT treatment is trimethoxysilyl terminated. The fact that the PL decays more rapidly in air than in argon suggests that photooxidation may play a role in the deterioration of GaAs surface passivation following MPT treatment. This observation suggests that the improved durability of the polymerized sample against PL deterioration may result from reduced oxygen permeability through the cross-linked overlayer.

Conclusions

The results of the study presented here are consistent with the formation of a single monolayer of MPT on the surface of GaAs having a structure similar to that proposed by Thompson and Pemberton.[28–30] PL durability studies are consistent with the formation of a polymerized SAM on the surface of GaAs under conditions used here. Following the results of Thompson and Pemberton,[29,30] we expect that the MPT SAM on GaAs will promote adhesion between silicate glasses and the GaAs surface.

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