

Aging and detergent washing effects of the surface of (001) and (110) GaAs passivated with hexadecanethiol

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We report on aging and detergent washing effects in GaAs wafers passivated with hexadecanethiol (HDT) $[\text{HS}(\text{CH}_2)_{15}\text{CH}_3]$. The evolution of the photoluminescence (PL) signal from GaAs was measured at room temperature as a function of time, up to 1000 h, for thiolated (001) GaAs that was solvent cleaned and etched using standard procedures, and for thiolated (110) GaAs that was obtained by cleaving in air. For 2 h of thiolation time, the decay of the PL signal from (001) GaAs and (110) GaAs could be fitted, respectively, with double and single exponential functions. This indicates that at least two different types of non-radiative recombination centers (NRRC) form on the (001) surface. The overall density of surface states formed on (110) GaAs is significantly lower than those on (001) GaAs. A single exponential decay of the PL signal has been observed for 18 h thiolated samples. The strong increase of the PL signal after detergent washing of (001) GaAs suggests that this treatment is effective in removal of some of the NRRC. The 19-fold enhancement of the PL signal, in comparison to that of the oxidized sample, has been obtained using the sample that, following the etching and detergent washing procedures, was thiolated with HDT. © 2006 American Institute of Physics. [DOI: [10.1063/1.2234538](https://doi.org/10.1063/1.2234538)]

I. INTRODUCTION

The development of II-VI and III-V semiconductor-based biosensors is strongly dependent on the ability to prepare stable semiconductor surfaces. This step poses a great challenge as the exposure of unprotected surfaces to oxygen and moisture could degrade the electrical and optical properties of compound semiconductors significantly over time. It is well known that bare (001) GaAs has intrinsic surface states with a typical density of $10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$,¹ while the cleaved (110) surfaces have been shown to be largely free of surface states that are located within the semiconductor band gap.² Exposure to oxygen and/or the air environment leads to the formation of many gap states that pin the surface Fermi level. Because the change of the surface potential strongly affects the semiconductor photoluminescence (PL), the PL signal has frequently been used to monitor the formation of nonradiative recombination centers at semiconductor surfaces. PL intensity measurements have been used to characterize the formation of sulfur-surface bonds in GaAs.³ It has been shown that photowashing, i.e., modification of the surface properties by illuminating the sample that is simultaneously washed with de-ionized water,^{4,5} reduces the density of surface states. A similar effect has been demonstrated for both silicon nitride⁶ and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (Refs. 7 and 8) treated (001) GaAs. The reduction of the density of surface states allows for the unpinning of the surface Fermi level, which

results in the modification of band bending and an increase of the PL signal due to radiative recombination.

After the discovery of GaAs passivation with inorganic sulfides,^{9,10} several groups have demonstrated passivation of III-V semiconductors with self-assembled monolayers (SAMs) of various thiols.^{3,11–13} A ten-fold PL enhancement has been reported for (100) GaAs passivated with short chain SAMs of 3-mercaptopropyl-trimethoxysilane³ (MPT) and a long chain thiol passivation of InP has demonstrated a 14-fold increase of the PL signal.¹¹ SAMs of thiols on gold have been shown to be highly oriented, uniformly dense and having a thickness in the range of 1–3 nm.^{14–16} The orientation and distribution of thiols on GaAs, however, have remained the subject of an intense investigation. Generally, the understanding of the formation of the GaAs-thiol interface is inadequate to provide an efficient and long lasting passivation of the surface of this material. Recently, we have investigated the influence of different thiols on the passivation performance of the (001) GaAs surface.^{17,18} Long-chain thiols with the same length CH_2 were found to provide better passivation efficiency (higher PL signal enhancement) if their terminal groups were hydrophobic. For the same terminal groups (CH_3 or CO_2H), it has been determined that the 15- CH_2 chain thiols passivate the surface of (001) GaAs more efficiently than the 10- CH_2 chain thiols. We have established that SAMs of hexadecanethiol (HDT) $[\text{HS}(\text{CH}_2)_{15}\text{CH}_3]$ on (001) GaAs provided the most efficient passivation among all the investigated thiols. Following these findings we succeeded in the immobilization of avidin on the surface of

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(001) GaAs.¹⁹ In this paper, we investigate the effects of aging and detergent washings in HDT-coated (001) and (110) GaAs wafers.

II. EXPERIMENTAL DETAILS

The nominally undoped (001) GaAs wafer (Atomergic Chemical Corp.) was used for the deposition of the investigated thiol. HDT was purchased from Sigma-Aldrich, Inc. Prior to exposure to the thiol solution, the samples were cleaned and etched following the procedure described elsewhere.¹⁸ In some cases, the etched samples were additionally washed in a commercial detergent solution (Roche Diagnostics). After drying in nitrogen flow, the samples were immersed in a 5 mM thiol solution in ethanol and 5% aqueous ammonia which was degassed with nitrogen flow for 2 h. The two sets of SAMs samples investigated in this work were achieved following 2 and 18 h immersions in the solution that was continuously purged with nitrogen and heated to 55 °C. After SAM deposition, the samples were rinsed with hot isopropanol, methanol, and water, and finally blow dried with nitrogen. The (110) samples were prepared by cleaving the (100) GaAs wafer and immediately immersing them in the thiol solution.

The PL measurements have been carried out at room temperature in the band gap emission region of GaAs ($\lambda \approx 870$ nm) using a Philips PLM-150 high speed photoluminescence mapping system, which is equipped with a constant power excitation source operating at 532 nm and an IR array of InGaAs detectors. The sample was located on a computer controlled XYZ mapping stage (10 μm spatial resolution in *X* and *Y* directions and 1 μm resolution in *Z* direction). Typically, a PL map was collected at a 100 μm step, which for a 5×5 mm² sample gave the intensity result based on an average from 2500 points. Freshly cleaved (110) and a freshly etched (001) surfaces were used as the reference for PL measurements on (110) GaAs and (001) GaAs, respectively.

The thickness of films on (001) GaAs was determined with an Alpha-SE ellipsometer (J. A. Woollam Co., Inc.) using an incident angle of 70° and a wavelength of 632.8 nm as reference. In order to minimize the effect of sample inhomogeneity, the final results were obtained by averaging the measurements from three different points on the sample. The thickness was calculated using a parallel three-layer model.

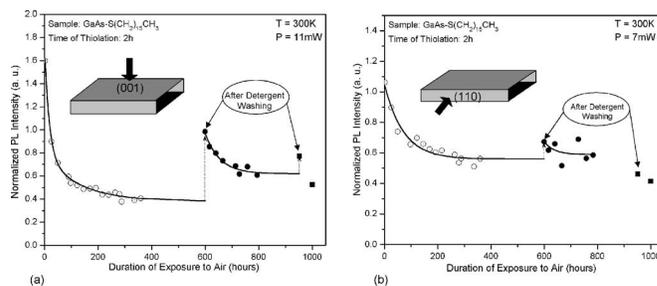


FIG. 1. Time dependence of the normalized photoluminescence intensity for (001) GaAs (a) and (110) GaAs (b) passivated with $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$. The inset shows the photoluminescence measurement configuration. The solid lines are the result of fitting.

III. RESULTS AND DISCUSSION

A. (001) and (110) GaAs: 2 h thiolation

Figure 1 shows the time dependence of the normalized PL signals from (001) and (110) GaAs samples following their 2 h exposure to the HDT solution. It can be seen that the initial ($t < 1$ h) normalized PL signal from (001) surface is significantly greater than that of the cleaved (110) surface. This enhancement can be attributed to the effective suppression of the surface states that are present on the surface of (001) GaAs, while a significantly smaller concentration of such states exists on the freshly cleaved surface of (110) GaAs. For $t < 600$ h, the PL signal shown in Fig. 1(a) could be fitted with a double exponential function,

$$I(t) = I_0 + A_f e^{-t/\tau_f} + A_s e^{-t/\tau_s}, \quad (1)$$

where t is time, A_f and A_s are the amplitudes of the fast and slow decay components, respectively, their respective decay time constants are τ_f and τ_s , and I_0 represents the background PL intensity. The value of $I(t)=1$ corresponds to the state where the PL intensity from the thiolated sample would be identical to that of a freshly etched sample. The results of fitting that have been summarized in Table I show that the overall decay could be described by a fast component with $\tau_f \approx 17$ h, followed by a slow component with $\tau_s \approx 131$ h. The slower decay rate and a higher value of $I_0 + A_s$ would generally indicate a more stable and durable surface. However, the value of $I_0 + A_s = 0.78$ indicates that in this case the efficiency of passivation is rather poor. Qualitatively, a similar two-slop decay of PL intensity has been reported for (100) GaAs samples coated with a short chain $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ thiol.³ In our case, however, the rate of

TABLE I. Fitting parameters obtained from Eqs. (1) and (2) to describe the temporal behavior of the PL signal from thiolated (001) and (110) GaAs samples for $t < 600$ h.

Sample	I_0	A_f	A_s	τ_f (h)	τ_s (h)
(001) GaAs: 2 h thiolation	0.38	0.94	0.40	17.3	130.7
(001) GaAs: 2 h thiolation with detergent wash	1.04	0	0.26	∞	101.0
(001) GaAs: 18 h thiolation	1.07	0	0.55	∞	84.1
(001) GaAs: 18 h thiolation with detergent wash	1.81	0	0.55	∞	60.7
(110) GaAs: 2 h thiolation	0.56	0	0.49	∞	71.2

TABLE II. PL intensity from cleaved (110) GaAs and etched (001) GaAs before and after detergent washing (DW). Measurements taken nominally with the same laser excitation power $P \approx 11$ mW.

Substrate	Initial PL intensity (a.u.)	PL intensity before DW (a.u.)	PL intensity after DW (a.u.)
(110) GaAs	114.8 ^a	102.8 ^b	109.6
(001) GaAs	(33.1–35.7) ^c	30.2 ^d	52.2

^a2 h after cleaving.

^b12 h after cleaving.

^c(0.5–17) h after etching.

^d20 h after etching.

the fast decay is at least three times slower than the slowest rate reported in Ref. 3.

The temporal behavior of the PL signal from the thiol coated (110) GaAs [Fig. 1(b)] can be fitted with a single exponential function of the form

$$I(t) = I_0 + A_s e^{-t/\tau_s}. \quad (2)$$

The fitting parameters listed in Table I indicate that the PL intensity in that case decays with a τ_s constant equal to about 71 h. The slower decay and the relatively large value of $I_0 + A_s = 1.05$ for this sample indicate a more efficient surface passivation process and/or increased resistance of the (110) surface to the formation of nonradiative recombination centers (NRRC).

Following 600 h of exposure in an air environment, both samples were washed with a detergent solution. It can be seen in Fig. 1 that said treatment significantly increased the normalized PL signal from (001) GaAs (from 0.4 to 1.0), but only a small increase of such a signal was observed from (110) GaAs (from 0.6 to 0.7). Similarly, it can be seen that detergent washing of (001) GaAs after 900 h partially restores the intensity of the PL signal, but essentially does not change the signal from (110) GaAs. Pronounced increases of the PL signal observed for (001) GaAs following its washing with detergent suggests that such a treatment removes some NRRC. A similar increase of the PL signal from (100) GaAs was observed by Wilmsen *et al.*,^{4,5} and it was suggested that the reduced density of surface states had been achieved due to the oxide reducing photowash process.

The PL signal decays for both detergent washed samples (after 600 h) could be fitted with a single exponential function and $\tau_s = 55$ and 37 h for (001) GaAs and (110) GaAs, respectively. It appears that the surface of the investigated (001) GaAs was either not sufficiently cleaned before thiolation, or the 2 h treatment with HDT was not sufficient to efficiently passivate it.

The results of a comparative study on the influence of detergent washing on the PL intensity of an etched (100) GaAs and that of a cleaved (110) GaAs have been summarized in Table II. It can be seen that the detergent treatment practically does not affect the PL signal from cleaved (110) GaAs. The absence of such an effect suggests that the concentration of NRRC in this case was minimal or that the efficiency of removing defects from (110) GaAs was low. In contrast, a significant influence of detergent treatment on PL signal has been observed for (001) GaAs. For the case re-

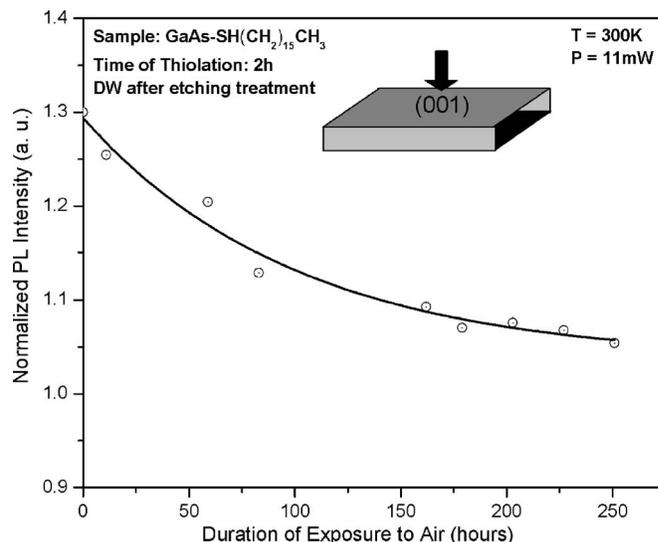


FIG. 2. Time dependence of the normalized photoluminescence intensity for (001) GaAs passivated with $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ after the detergent washing treatment. The time of thiolation was 2 h.

ported in Table II, such a treatment increased the PL intensity by about 1.7 times. Taking into account that the oxidized (001) GaAs sample excited under the same conditions exhibited a PL signal about ten times weaker ($I_{\text{PL}} = 3.5$), this indicates that the cleaning, etching, and detergent washing procedures are responsible for the 15-fold enhancement of the initial signal from (001) GaAs. The thiolation procedure has further increased this signal to $I_{\text{PL}} = 67.9$, which gives a total of 19-times enhancement with respect to the initial signal from the highly oxidized (001) GaAs sample. We have further investigated the role of detergent washing by following the evolution of the PL signal from a thiolated (001) GaAs sample that was treated with detergent directly after the etching procedure. The results shown in Fig. 2 and the related fitting parameters listed in Table I demonstrate that such a treatment suppresses fast decay from the time dependent PL signal. This proves that the detergent treatment is capable of efficiently removing some of the NRRC defects left at the surface of HCl treated (001) GaAs.

The x-ray photoelectron spectroscopy (XPS) measurements have indicated a significant reduction of the oxygen content related to the presence of As_2O_3 or As_2O_5 on the detergent washed surface of (001) GaAs.²⁰ Thus, it is reasonable to expect that the defects in question are related to the presence of various arsenic oxides. It has been reported that detergent treatment could be efficient in reducing the surface roughness of chemically modified mica.²¹ We expect that such treatment could also reduce the concentration of oxide-rich surface precipitates, or it could lead to some other chemical changes of the surface of GaAs. Nevertheless, the reactivity of detergent with different substrates and its exact role in the cleaning and/or passivation of the surface of GaAs have yet to be fully investigated.

B. (001) GaAs: 18 h passivation

The results of an aging effect study in samples exposed to the HDT solution for 18 h are shown in Fig. 3. It can be

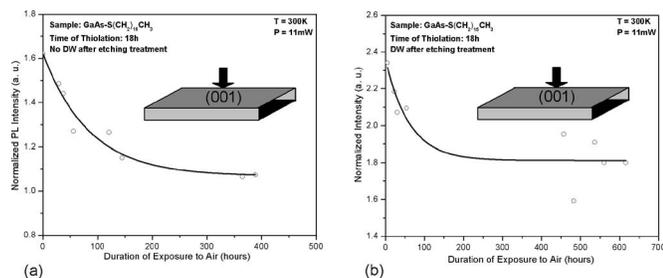


FIG. 3. Time dependence of the normalized photoluminescence intensity for (001) GaAs passivated with $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ without detergent washing (a) and with detergent washing that followed the HCl deoxidation treatment (b). The time of thiolation was 18 h.

seen that, initially, the PL signal from a nondetergent treated sample is $I(0) \approx 1.6$, which is comparable to the signal from the etched only (001) GaAs exposed for 2 h to a HDT solution [see Fig. 1(a)]. However, the decay is now much slower and $I(t) > 1$ remains even at 400 h, which for the same aging time compares with $I(t) \approx 0.4$ observed for the sample in Fig. 1(a). A significantly enhanced PL signal with $I(0) \approx 2.3$ has been observed for the 18 h thiolated sample that, following the HCl treatment, was exposed to detergent washing. Considering that the etching procedure alone typically resulted in an over eight-fold enhancement of the PL signal, the 15-fold and 19-fold increases of the PL signal with respect to the oxidized bulk GaAs discussed in this and the previous paragraph, respectively, compare favorably to the results reported in literature.³ The PL signal from the sample in Fig. 3, even after 600 h is about 1.8 times stronger than that from freshly etched and detergent treated samples. The time dependence of the normalized PL intensity from a nondetergent treated (001) GaAs [Fig. 3(a)] and a detergent washed sample [Fig. 3(b)] could be fitted with a single exponential function. The fitting parameters, which are listed in Table I, confirm quantitatively the superior passivation efficiency of the thiolation process that involves the detergent washing procedure.

It is well known that etching of GaAs in an HCl acid solution may produce microscopic roughness on the surface²² that could affect the electrical properties of interfaces as it was observed, e.g., for the GaAs–SiN interface.⁶ Thus, chlorine and other contaminants such as elemental As or As_2O_3 left on the surface after the etching procedure,⁴ in addition to insufficient passivation (due to the short time of the thiolation) may be responsible for the weak and rapidly decaying PL signal from (001) GaAs as seen in Fig. 1. In general, recombination via a single trapping level in the band gap is represented by the Shockley-Read mechanism.²³ The likely process behind the PL decay observed in etched but nondetergent treated samples concerns two different types of surface states.²⁴

C. Ellipsometric measurements

Our ellipsometric measurements suggest that the thickness of the native oxide developed within $t < 15$ min on the surface of a freshly etched (001) GaAs sample is in the range of 1.4– 2.30 ± 0.03 nm. Following the detergent treatment, a reduced oxide thickness by up to 0.4 nm has been observed. Table III summarizes the thickness measurements for freshly

TABLE III. Thicknesses of oxide and hexadecanethiol SAMs on (001) GaAs before (l_{BDW}) and after (l_{ADW}) detergent washing. θ is the tilt angle of the thiol from the normal of the surface.

Sample	l_{BDW} (nm)	l_{ADW} (nm)	θ
GaAs	2.30 ± 0.02	1.94 ± 0.01	...
after HCl treatment			
GaAs– $\text{S}(\text{CH}_2)_{15}\text{CH}_3$ 2 h thiolation	1.18 ± 0.36	1.11 ± 0.05	55°
GaAs– $\text{S}(\text{CH}_2)_{15}\text{CH}_3$ 18 h thiolation	1.74 ± 0.30	1.74 ± 0.21	32°

etched (001) GaAs and HDT SAMs on (001) GaAs samples thiolated for 2 and 18 h. The SAM thickness on the 2 h thiolated sample is 1.18 nm and that on the 18 h thiolated increased to 1.74 nm.

The thickness of SAMs of the alkyl chains that adopt a fully extended, all-*trans* configuration, and which would be oriented normal to the surface should be 2.04 nm. Thus, our measurements suggest that the 2 and 18 h HDT SAMs have their alkanethiol chains tilted at 55° and 32° from the surface normal. It is possible that incomplete coverage of the surface with the 2 h SAM would result in an underestimated thickness and an overestimated value of the tilt angle. We note that the 55° tilt angle observed for the 2 h thiolated sample is close to the 57° tilt angle for HDT SAMs on GaAs that has been previously reported.^{25,26} The detergent washing procedure, in both cases of thiolated samples, did not measurably change the value of measured thiol thicknesses. We consider this result to be strong evidence of the robust link between the fabricated HDT SAMs with GaAs and their stability in an air environment.

IV. CONCLUSIONS

We have investigated the process of (001) and (110) GaAs surface passivations with hexadecanethiol [$\text{HS}(\text{CH}_2)_{15}\text{CH}_3$]. The two-exponential decay of the photoluminescence (PL) signal from short time (2 h) thiolated (001) GaAs samples indicates the presence of at least two different types of surface traps that neither were removed by the GaAs conventional surface preparation procedure nor could they be neutralized by the thiolation process. In contrast, the PL decay from cleaved (110) GaAs samples that were thiolated for 2 h exhibited only one-exponential behavior. For both orientations, however, the PL signal diminished to below the “fresh” sample level within less than 20 h. Significantly improved passivation results have been demonstrated with samples that were thiolated for 18 h. The 19-fold increase of the PL signal from (001) GaAs has been observed for the sample that, prior to thiolation, had been washed with a commercial detergent. This is the greatest room-temperature PL enhancement ever reported for the passivated surface of bulk GaAs. The detergent treated surface also shows a significantly improved resistance to the aging effect, with the PL signal intensity remaining almost two times stronger than that of the freshly treated (001) GaAs even after 600 h. The cleaved surface of (110) GaAs is practically inert to the detergent treatment, which indicates that either

the concentration of defects that could be removed by detergent washing was negligible or the efficiency of removing such defects was less effective. The likely role of the detergent in the enhanced PL signal lies in the efficient removal of hydrophobic surface residues, such as As and As_2O_x left by the chemical etching procedure. However, the exact mechanism of the detergent-based reaction with GaAs has yet to be elaborated. The deposited SAMs survive the detergent washing procedure, which we take as evidence of their strong and stable link with (001) GaAs.

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