Stability of biofunctionalized GaAs surface

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ABSTRACT

For a semiconductor based biosensor, functionalization of the surface and the stability of the semiconductor-biomolecule interface are the primary issues to be addressed by researchers. We have investigated a variety of strategies to passivate (001) GaAs surface with a long chain hexadecanethiol ($C_{16}H_{33}SH$: T16). GaAs substrates were cleaned and etched either with ArF excimer laser irradiation in an atmospheric environment or with conventional wet etchants. The effect of surface passivation and stability of the interface were evaluated using photoluminescence (PL) measurements. Significant cleaning of the (001) GaAs surface has been achieved with an ArF laser, as evidenced by the up to 4-fold increase of the PL signal. This compares to the 12-fold enhancement of the PL signal from samples that were alternately etched in solutions of NH_3/H_2O and HCl/ethanol. A combination of a diluted base and an acid possibly provides the cleanest surface and therefore the highest surface functionalization efficacy and long term stability upon thiolation.

Key words: GaAs, photoluminescence, self-assembled monolayer, alkanethiol, laser cleaning

1. INTRODUCTION

In the quest for developing II-VI and III-V semiconductor material based photonic biosensing devices, it is highly desired to prepare a versatile interface which stabilizes the semiconductor surface and provides links to probing biomolecules. Long chain alkanethiols with reactive terminal groups play an active role in this field. It has been demonstrated that alkanethiols form self-assembled monolayers (SAMs) on the surface of GaAs and InP [1-4] and are capable of passivating surface states and creating a physical barrier protecting the surface from exposure to oxygen, ambient moisture and other adventitious contaminants. In addition, reactive terminal groups on alkanethiol such as amine (-NH_2) and carboxylic acid (-CO_2H) are utilized to directly or indirectly immobilize probing biomolecules (protein, DNA, etc.) on the surface [5-8].

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We have endeavoured to passivate GaAs surface with long chain alkanethiols with a variety of terminal groups and functionalize the surface with biotin and avidin, aiming to fabricate a reliable interface to immobilize probing biomolecules [4-6] and to develop quantum semiconductor based biosensing devices. Calculations have shown that alkanethiol-GaAs passivation results from covalent S-As bonding which removes surface states from the bandgap [9]. This in turns results in enhanced photoluminescence (PL) intensity of GaAs. Further investigation has shown that PL intensity of alkanethiol passivated GaAs decreased following single exponential decay dynamics [10]. Stability of the GaAs-thiol interface remains to be a critical issue and it needs to be well understood for successful application. In this paper, we report on the stability of biofunctionalized GaAs surface that was subjected to various surface cleaning and etching procedures.

2. EXPERIMENTAL DETAILS

All chemical reagents are Aldrich products. The nominally undoped (001) GaAs was purchased from Atomergic Chemetals Corp. (ACC, New York).

GaAs substrates were sequentially degreased with opticlear, acetone and isopropanol (IPA) for 5 minutes each in an ultrasonic bath followed by etching and thiolation. Two wet chemistry recipes were employed to etch an oxide layer on GaAs surface. In recipe I, substrates were etched with 37% HCl/H_2O for 1 minute then rinsed with DI water and blown dry with N_2. In recipe II, degreased substrates were etched in $NH_3.H_2O/H_2O$(v/v 1:20) for 30 seconds, followed by rinsing with DI water and blowing dry with N_2 flow. Next, these substrates were etched with 37% HCl/ethanol (degassed, v/v 1:10) for 30 seconds and rinsed with ethanol. The whole etching procedure was repeated again and the substrates were stored in degassed ethanol till thiolation without intermediate exposure to air. Room temperature thiolation was carried out by immersing freshly etched substrates in a 5-10 mM T16/ethanol solution for 20 hours. For high temperature thiolation, substrates were immersed in a 5-10 mM anaerobic solution of T16 /ethanol-$NH_3.H_2O$ (20:1 v/v) and heated at $55^{o}C$ for 18 hours under continuous N_2 flow.

Laser irradiation of degreased only samples was carried out with an ArF excimer laser delivering 15 ns long pulses of 50 mJ/cm^2 fluence, and at repetition rate of 5 Hz. The laser beam was projected through a 4.8 mm diameter metal mask using a 3X demagnification system. Samples were irradiated with up to 500 pulses. Four nominally same samples were prepared by laser irradiation for subsequent study of the PL modification by $C_{16}H_{33}SH$ (T16) in ethanol at room temperature, T16 in ethanol and $NH_3 \cdot H_2O$ at room temperature, T16 in ethanol and $NH_3 \cdot H_2O$ at $55^{o}C$, and avidin in TBS solution at room temperature.

PL response from the investigated samples was measured at room temperature in the band gap emission region of GaAs (868 nm) using a PL mapper (Philips PLM-150). The PL signal was excited with a laser operating at 532 nm and the signal was collected with an IR array of InGaAs

detectors. Typically, PL intensity maps were collected with a 100 μm step, which for a sample of 5 mm × 5 mm gave a result averaged over 2500 points.

3. RESULTS AND DISCUSSION

The pseudo color intensity PL maps of laser irradiated (001) GaAs are displayed in Fig.1. An example of a series of spots, from 1 to 12, that were obtained by irradiation with 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200 and 500 pulses, respectively, is shown for one of the initial samples in Fig. 1a. The effect of exposing such samples to $C_{16}H_{33}SH$ (T16) in ethanol at room temperature, T16 in ethanol and $NH_3·H_2O$ at room temperature, T16 in ethanol and $NH_3·H_2O$ at 55°C, and avidin in TBS solution is illustrated in Figs. 1b to 1e, respectively. PL intensity at each laser irradiated spot for
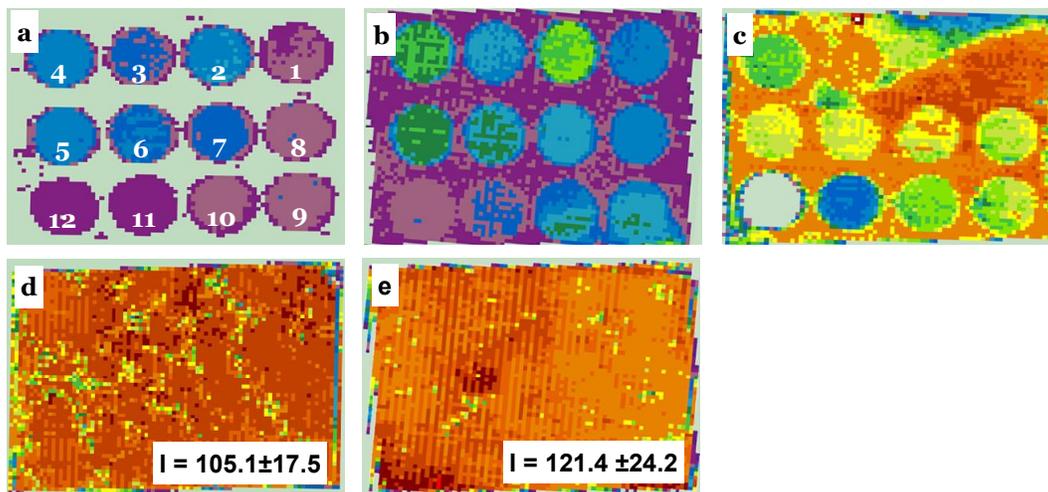

Fig. 1. Photoluminescence maps of a degreased only (001) GaAs sample that following laser irradiation with different number of pulses (a) was exposed to $C_{16}H_{33}SH$ in ethanol at room temperature (b), $C_{16}H_{33}SH$ in ethanol and $NH_3·H_2O$ at room temperature (c), $C_{16}H_{33}SH$ in ethanol and $NH_3·H_2O$ at 55°C (d), and avidin in TBS (e). The pulse number at spots 1-12 was 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, and 500, respectively.
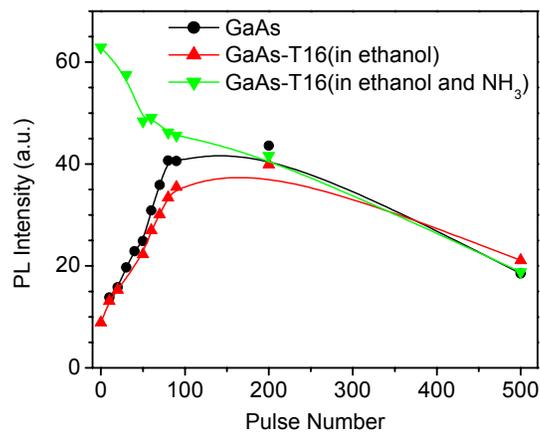

Fig. 2. Dependence of PL intensity on pulses number from ArF laser irradiation. The solid lines are drawn to guide eyes.

cases presented in Fig. 1a, b and c is plotted in Fig. 2. For laser only processed GaAs, PL intensity increased with accumulated irradiation and reached the maximum at 100 ~ 200 pulses. Further irradiation resulted in decreased PL intensity. Treatment in a solution of T16/ethanol at room temperature did not change PL intensity of either laser-irradiated spots or non-irradiated area (Fig. 1b). When 5% of $NH_3.H_2O$ was present in T16/ethanol solution, the PL intensity of the non-irradiated area became remarkably higher. The laser irradiated spots showed enhanced PL intensity, but the enhancement decreased with pulse number and no enhancement was observed for more than 200 pulses of irradiation (Fig. 1c). By heating the T16/ethanol solution at $55^{o}C$, or immersing the laser irradiated substrate in a protein solution (avidin in Tris buffer saline, pH = 7.4), a significantly increased PL intensity was observed from both laser-irradiated spots and the non–irradiated area. This increase was sufficient to wash away the laser fabricated patterns (spots), as seen in Figs. 1d and 1e.

It is reasonable to expect that the observed increase of the PL intensity at the early stage of laser irradiation is related to the laser-induced surface cleaning and removal of PL reducing non-radiative recombination centers. Total etch depth of GaAs irradiated with 100 pulses of an ArF laser delivering 50 mJ/cm^2 per pulse in a reactive atmosphere of Cl_2 at 1.5×10^{-5} Torr, is expected to be less than 1 nm [11]. Thus, the low pulse number irradiation in an atmospheric environment (a relatively non-reactive atmosphere), would lead to the negligible removal of Ga and As. Instead, some surface impurities and precipitates (e.g., carbon adsorbed from air atmosphere) and weakly bound micro-inclusions responsible for the reduced PL signal could be ejected by laser radiation. It has been reported that irradiation of GaAs in air with 118 mJ/cm^2 XeCl and 75 mJ/cm^2 KrF lasers leads to the formation of a Ga_xO_y layer [12,13]. In vacuum, the efficient removal of carbon has been reported with a 53mJ/cm^2 pulse of an ArF laser irradiating GaAs, while over a thousand pulses were required to eliminate the Auger oxygen peak (originating from various surface oxides) under similar conditions of irradiation [14]. The removal of C and O from vacuum irradiated GaAs with 532 nm pulses has also been reported [15]. Thus, while as-etched sample could be coated primarily by AsO_x, which is volatile and relatively easily removed by laser irradiation, we expect that the concentration of Ga_xO_y has significantly increased in the 500-pulse sample irradiated in an atmospheric environment. This could explain the 50% decrease in the PL intensity signal from its maximum observed for the 100-pulse irradiated sample (see Fig. 2).

The presence of surface oxides is expected to inhibit attachment of thiols to GaAs. The unchanged PL signal observed from the as-etched and laser irradiated sample following immersion in a T16/ethanol solution (triangle 'up' symbols in Fig. 3) illustrates such a case. In contrast, the presence of $NH_3.H_2O$ in the solution, which is expected to efficiently remove arsenic oxides [16], will facilitate the attachment of thiols. The increased intensity of the PL signal observed for the ethanol/$NH_3·H_2O$ treated sample, as illustrated by triangle 'down' symbols in Fig. 3, supports this hypothesis. The reduced PL enhancement with increasing number of laser pulses is likely related do the increasing concentration/thickness of the laser formed Ga_xO_y layer. A continuous layer of Ga_xO_y would explain the absence of the PL enhancement for spots irradiated with 200 and more pulses, as observed in Fig. 2.

During processing at elevated temperature (55°C), both Ga_xO_y and AsO_x are dissolved in $NH_3.H_2O$. For example, Ozasa et al [17] reported that pH 7.7 buffer solution could remove an oxide layer from GaAs surface. We expect that Tris buffer saline (pH 7.4) acted as an etchant in our protein deposition test and also removed the surface oxide layer. Thus, alkanethiol has equally passivated the laser irradiated spots as well as the non-irradiated area observed in Fig. 1d. It also appears that physisorbed avidin on the freshly etched surface of GaAs enhanced the PL intensity via the charge effect [5]. Three weeks after these two samples were exposed to ambient environment, overall PL intensity dropped to 80% but PL intensity pattern was not recovered, indicating that protein deposition and high temperature thiolation permanently and equally modified the overall surface, without measurable physical damage to the surface even with 500 pulses of laser irradiation.

PL spectra of GaAs prepared with both I and II recipes, and consequently passivated with T16 are displayed in Fig. 3. The recipe II etched GaAs shows higher PL intensity than that of recipe I etched materials. This increased PL signal could be due to the more efficient removal of surface
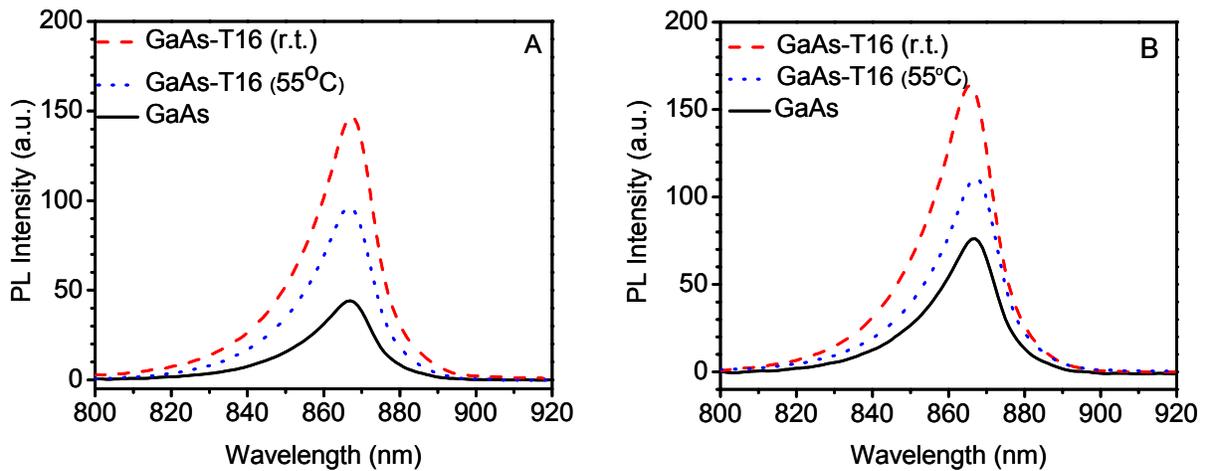

Fig. 3. PL spectra of (001) GaAs and GaAs passivated with T16. GaAs was etched with recipe I (A) and with recipe II (B).

contaminants in agreement with the results of Jun et al [18], which have indicated that a combination of a dilute base and an acid solution produced lower level of C and O residues on the surface of GaAs. Consequently, PL intensity of all samples was significantly enhanced after thiolation, indicating effective formation of covalent bonds between alkanethiol molecules and GaAs surface.

The stability of long chain alkanethiol passivated GaAs was investigated by monitoring the PL intensity decay behavior. PL decay curves of bare GaAs and passivated GaAs are plotted in Fig. 4. To quantitatively analyze PL decay dynamics, the curves were fitted with a single exponential function:

$$I_{(t)} = I_0 + Ae^{-t/\tau},$$

where t is the duration time from the moment that the sample was etched or thiolated, τ is the decay constant, A is the fitting parameter, I_0 refers to the PL intensity after the sample is exposed to

ambient environment for infinite long time, and $I_0 + A$ corresponds the PL intensity immediately after the sample was made. The fitting parameters are listed in Table 1.

Recipe II etched GaAs is slightly less stable (smaller τ) than that of recipe I did. Since recipe II etching leaves less oxide and C residues, the surface is more vulnerable to attacks from ambient moisture and oxidation which makes the surface deteriorate faster. After thiolation, the samples prepared with the recipe II showed greater I_0 and τ, which indicates those samples have higher alkanethiol coverage and better long term stability. Even after seven weeks (~1200 hours) exposure to ambient environment, passivated GaAs shows comparable PL intensity to freshly etched sample. For recipe II etched GaAs, although room temperature thiolated sample shows higher initial PL intensity ($I_0 + A$), it decays slightly faster (smaller τ) and I_0 is comparable to that of samples thiolated at 55 °C. Some alkanethiol molecules most likely physisorbed or loosely bound to GaAs surface during the room temperature thiolation process. Physisorption and loose binding were reduced however at elevated temperature. However, loosely bound or physisorbed alkanethiol molecules migrate on the surface or are cleaved upon attacks from ambient environment and lose direct
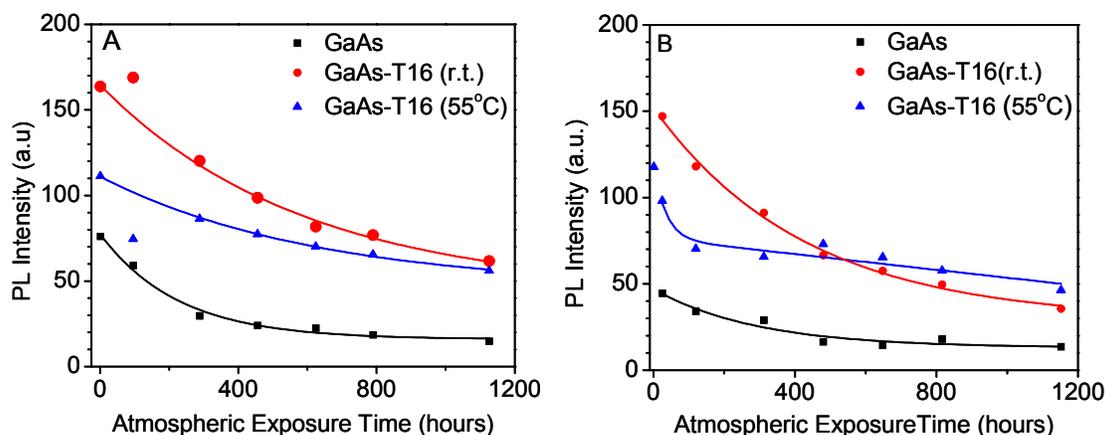

Fig. 4. PL decay curves of GaAs and GaAs passivated with alkanethiol (T) at room temperature and 55°C. GaAs substrates were etched with NH_3/H_2O and HCl/ethanol (A) and with 37% HCl (B). The solid lines are obtained by fitting experimental points with the first order exponential decay function.

Table 1. Parameters used to fit curves in Fig. 4.

Samples	GaAs was etched with recipe I			GaAs was etched with recipe II		
	GaAs	GaAs-T (r.t.)	GaAs-T, 55°C	GaAs	GaAs-T, r.t.	GaAs-T, 55°C
I_0	13.02	28.80	34.49	15.96	43.56	45.75
A	33.98	123.03	85.06	61.48	120.95	65.30
τ	293.55	431.50	69.26	226.47	587.37	630.06
I_0+A	47	151	119.55	15.96	43.56	45.75

connection to GaAs surface, which induces PL intensity decaying faster. Eventually, only those sites cleaned by wet etching covalently bind to alkanethiol molecules and contribute to PL enhancement. Therefore, samples thiolated at room temperature and $55^{o}C$ showed comparable I_0 and long term stability, both of them showing superior performance to samples etched with recipe I and thiolated at $55^{o}C$, as reported previously [10].

4. CONCLUSIONS

The soft ArF excimer laser irradiation at 50 mJ/cm^2 and wet chemistry etching procedures were employed to clean GaAs surface prior to surface thiolation. Laser irradiation in an atmospheric environment removes non-radiative recombination centers, such as some surface oxides and carbon residues, for low number of pulses ($N \leq 100$). However, it leads to surface deterioration (oxidation) for greater number of pulses as indicated by the reduced GaAs photoluminescence intensity. A combination of a 2-step etching in dilute $NH_3.H_2O/H_2O$ and HCl/ethanol, without exposing the etched surface to the air environment, allows the efficient removal of non-radiative recombination centers, as suggested by the significant enhancement of the photoluminescence signal. Freshly etched substrates were passivated with long chain alkanethiol either at room temperature or at $55^{o}C$. In both cases, the PL intensity was significantly enhanced indicating effective surface passivation. Even though room temperature thiolation shows greater immediate passivation efficiency (higher initial PL intensity), samples thiolated at $55^{o}C$ exhibit slower decay of the PL signal, which likely suggests a more efficient (dense) alkanethiol coverage.

ACKNOWLEDGEMENTS

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