

Surface passivation of (001) GaAs with self-assembled monolayers of long-chain thiols

Ximing Ding and Jan J. Dubowski*

Department of Electrical and Computer Engineering, Université de Sherbrooke
Regroupement québécois sur les matériaux de pointe (RQMP)
Sherbrooke, Québec, J1K 2R1, Canada

ABSTRACT

Passivation of (001) GaAs surface was investigated with self-assembled monolayers (SAMs) of a variety of thiols having various methylene chain length and terminal groups. The effect of passivation was monitored by measuring the intensity of the GaAs-related photoluminescence (PL) signal excited with lasers operating either at 683 or 248 nm wavelengths. Generally, for each case of the thiol treated surface the PL signal was more intense than that from non-treated samples. Additionally, it was found that the thiol terminal groups play an important role in determining the methylene chain orientation in the SAMs and consequently the efficiency of the passivation. The methyl terminated methylene chain formed a layer of a closely packed and relatively thick film, which resulted in a significantly increased PL signal. In contrast, carboxylic acid group (-CO₂H) terminated methylene chains formed thin and less compacted films, leading to only a slightly increased PL signal and less efficient passivation of the GaAs surface.

Key words: GaAs, surface passivation, self-assembled monolayers, thiol-semiconductor interface, photoluminescence

1. INTRODUCTION

Due to its high electron mobility and a direct bandgap structure, GaAs is an important material for electronic and photonic devices, especially those comprising low-dimensional nanostructures [1-3]. The ability to protect the freshly fabricated or chemically cleaned surface of GaAs from oxidization and/or adsorption of foreign atoms is of paramount importance for the optimized functioning of such devices. Sulfur passivation of GaAs surfaces is a well known strategy that has been applied with some success to address this issue [4]. Covalent bonds between the surface atoms and sulfur have energy states outside the III-V semiconductor fundamental bandgap. This leads to the reduced concentration of non-radiative recombination centers and, consequently, to the enhanced photoluminescence (PL) signal observed from sulfur passivated wafers. The passivating layer, when required, should be easily removable to make the atomically clean surface of III-V semiconductor

* Corresponding author: jan.j.dubowski@usherbrooke.ca

available for deposition of new material. Self-assembled monolayers (SAMs) of thiols are of potentially high interest for this application due to their relatively weak bonding provided by sulfur to Ga and/or As atoms and minimal thickness, which typically does not exceed a few nanometres. Also, SAMs of thiols are of potential interest for fabricating a variety of masks required for nano-scale patterning of GaAs, as well as for the fabrication of biological interfaces used for selective attachment and identification of different bio-molecules. Therefore, since the first report by Nakagawa and his co-workers on the passivation of (100) GaAs with octadecyl thiol (ODT) SAMs [5] many efforts have been dedicated to seeking a facile, durable and reliable approach to functionalize III-V semiconductors [6-16]. Hou et al. reported a 10-fold PL enhancement from (100) GaAs passivated with short chain SAMs of 3-mercaptopropyl-trimethoxysilane (MPT) [17]. However, the stability of the MPT coated GaAs was weak, as demonstrated by the rapid decay of the PL signal within the first 48 hours following the passivation. Long-chain thiol passivation of InP has enabled Schwartzman et al. [18, 19] to demonstrate a 14-fold increase of the PL signal intensity. They have argued that longer chain SAMs provided not only more protection due to increased thickness, but also improved packing of the monolayer due to the interchain van der Waals interactions. The closely packed organic monolayer bound to the surface reduced the number of dangling orbitals and created a physical barrier for the penetration of oxygenating species from the environment.

It has been demonstrated that passivation of the (100) GaAs surface with long alkyl thiol SAMs reduces the surface band bending and the width of the depletion region [10]. However, neither efficiency nor stability of such interface and related PL measurements have been reported. In this paper, we address this issue and investigate surface passivation of (001) GaAs with SAMs of thiols having up to 15 methylene (CH_2) chains. We also examine the influence of thiol's terminal group on the process of passivation.

2. EXPERIMENTAL DETAILS

Five long chain thiols have been investigated in this work: 1-hexadecanethiol (HDT),

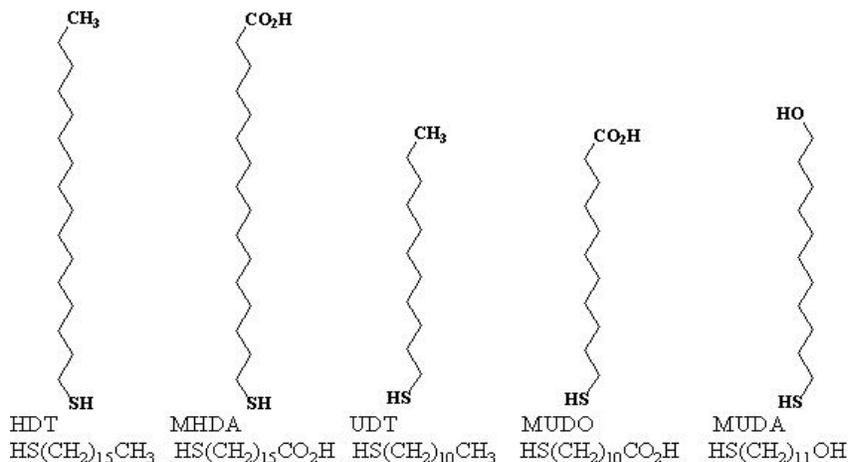


Fig. 1. Schematic diagram of five thiols structures used in this work.

HS(CH₂)₁₅CH₃), 16-mercaptohexadecanoic acid (MHDA, HS(CH₂)₁₅CO₂H), 1-undecanethiol (UDT, HS(CH₂)₁₀CH₃), 11-mercapto-1-undecanol (MUDO, HS(CH₂)₁₁OH), 11-mercaptoundecanoic acid (MUDA, HS(CH₂)₁₀CO₂H). The chemical structure of the employed thiols is schematically shown in Figure 1. The 15-methylene chain thiols (HDT and MHDA) are terminated either with hydrophobic (CH₃) or hydrophilic (CO₂H) groups. Similarly, two 10-methylene chain thiols (UDT and MUDO) are terminated either with CH₃ or CO₂H groups. The 11-methylene chain thiol is terminated with a hydrophilic OH group. The thiols were purchased from Aldrich and used as received.

The *p*-type (001) GaAs wafer (Zn-doped, 2×10^{17} atom cm⁻³, Sumitomo) was used for the deposition of the investigated thiols. Prior to SAM deposition, the wafer was cleaned in an ultrasonic bath sequentially with OpticalClear, acetone and isopropanol for 5 minutes each (all solvents were VLSI grade). The wafer was then etched in concentrated HCl for 1 minute and, subsequently, rinsed with deionized water. This etching gives a shiny and hydrophilic Ga-rich surface. We note that etching of the compound semiconductor substrate is a highly critical step in the manufacture of electronic devices. The etching procedure dictates not only the quality of surface, but also its stoichiometry, which influences the initial reactivity of the surface. For example, for the Cl₂/GaAs (001) reaction, it has been reported that the Ga-rich surface is initially more reactive than As-rich surface [20]. Since -SH in the thiol is less reactive than Cl₂, it is essential to choose the appropriate etching procedure to produce favorable surface conditions for Ga-S or As-S bonding.

After drying in nitrogen flow, the wafer was immersed in a 5 mM thiol solution in ethanol and 5% aqueous ammonia. The SAMs investigated in this work were achieved following the 18 hour immersion in the solution which was continuously purged with nitrogen and heated to 55 °C. After SAM deposition, the wafer was rinsed with hot isopropanol, methanol and water, and finally blown dried with nitrogen. In the case of carboxylic acid terminated thiols (MHDA and MUDA), the wafer was immersed in 1% HCl for 5 minutes to recuperate -CO₂H groups before rinsing in water and drying.

Tapping-mode atomic force microscope (AFM) measurements were performed with a Veeco Multimode Scanning Probe Microscope (Digital Instruments, Inc.). The applied resonant frequency and force constant were 300 kHz and 40 N/m, respectively. The scanning rate was around 2 Hz. Only one “flattening” procedure was applied to raw images before roughness analysis and drawing cross-sectional profiles. Root-mean-square (rms) roughness was measured over 500 nm × 500 nm areas.

Low temperature photoluminescence spectra were measured at 20 K by exciting the SAM-covered and non-covered wafers with 50 mW diode laser operating at 683 nm. A Ge-detector was employed to collect the PL signal. This PL setup was not efficient to yield a measurable PL signal at room temperature from the investigated GaAs samples. Room temperature PL was measured by exciting samples with a 248 nm excimer laser delivering 20 ns pulses. The excitation laser fluence was 0.8 mJ/cm². To minimize the possible sample inhomogeneity, the spectra for each sample were measured at three positions and the results were averaged.

3. RESULTS AND DISCUSSION

AFM images of chemically etched (001) GaAs and a sample coated with SAM of $\text{S}(\text{CH}_2)_{15}\text{CH}_3$ are shown in Figure 2. The surface of the etched sample (Fig. 2a) is almost featureless, with its RMS roughness being about 0.66 nm. This compares with RMS of 0.71 nm for (001) GaAs coated with $\text{S}(\text{CH}_2)_{15}\text{CH}_3$ (Fig. 2b). It can be seen that the thiol covered surface consists of an array of small

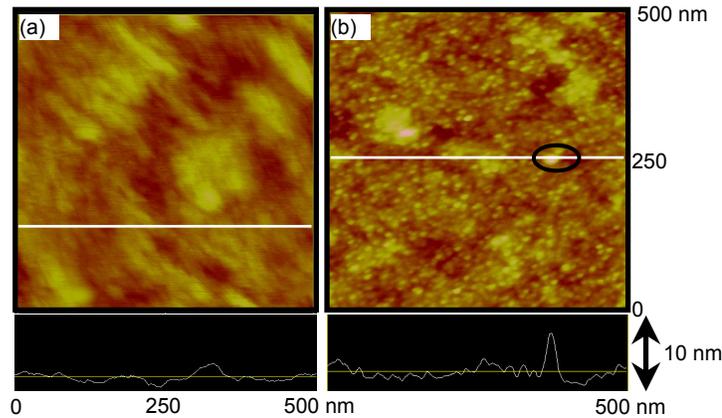


Fig. 2. Atomic force microscope images of etched (001) GaAs (a), and the sample that was immersed for 18 hours in the $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ solution (b).

domains, approximately 20 nm in diameter. Typically, domains are less than 2 nm in height, which compares with the length of a fully extended $-\text{S}(\text{CH}_2)_{15}\text{CH}_3$ thiol chain aligned at a small angle to the surface normal. The height of the observed domains is consistent with the formation of a monolayer of the $\text{S}(\text{CH}_2)_{15}\text{CH}_3$ material. Several agglomerates, as indicated by the circle in Figure 2b, could also be detected within the investigated area. Typically, they were about 5 nm in height. It is plausible that the formation of the agglomerates has been the result of an excessive exposure of the sample surface to the thiol solution. Obviously, optimization of the process of deposition of SAMs of thiols on the surface of GaAs requires a more systematic investigation.

The PL spectra from etched (001) GaAs and samples coated with SAMs of different thiols are shown in Figure 3. It can be seen that the PL signal from coated samples clearly exceeds that from the etched only wafers. The most efficient PL enhancement of 40% and 2.5 times has been observed for samples coated with $\text{S}(\text{CH}_2)_{15}\text{CH}_3$ and excited with 683 and 248 nm lasers, respectively. The absorption coefficient of GaAs at 683 and 248 nm is $1.8 \times 10^4 \text{ cm}^{-1}$ and $1.8 \times 10^6 \text{ cm}^{-1}$, respectively [21]. This corresponds to the penetration depths, respectively, 550 and 5.5 nm. Thus, it is reasonable to expect that the greater amplitude of the enhancement observed with the shorter-wavelength laser is related to more efficient probing of the near surface region of the sample. For the same terminal group (CH_3 or CO_2H), the samples coated with SAMs of thiols having longer CH_2 methylene chains have shown systematically greater amplitude of the enhanced PL signal. Also, thiols with hydrophobic terminals (CH_3) seem to provide better passivation as judged by the more intense PL signal generated in samples coated with $\text{S}(\text{CH}_2)_{15}\text{CH}_3$ and $\text{S}(\text{CH}_2)_{10}\text{CH}_3$ in comparison to that in samples with SAMs of $\text{S}(\text{CH}_2)_{10}\text{CO}_2\text{H}$, $\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ and $\text{S}(\text{CH}_2)_{11}\text{OH}$. It is worth mentioning that

the results presented in Figures 3a and b have been collected respectively for two separately prepared set of samples. This implies that a reasonable reproducibility has been achieved concerning

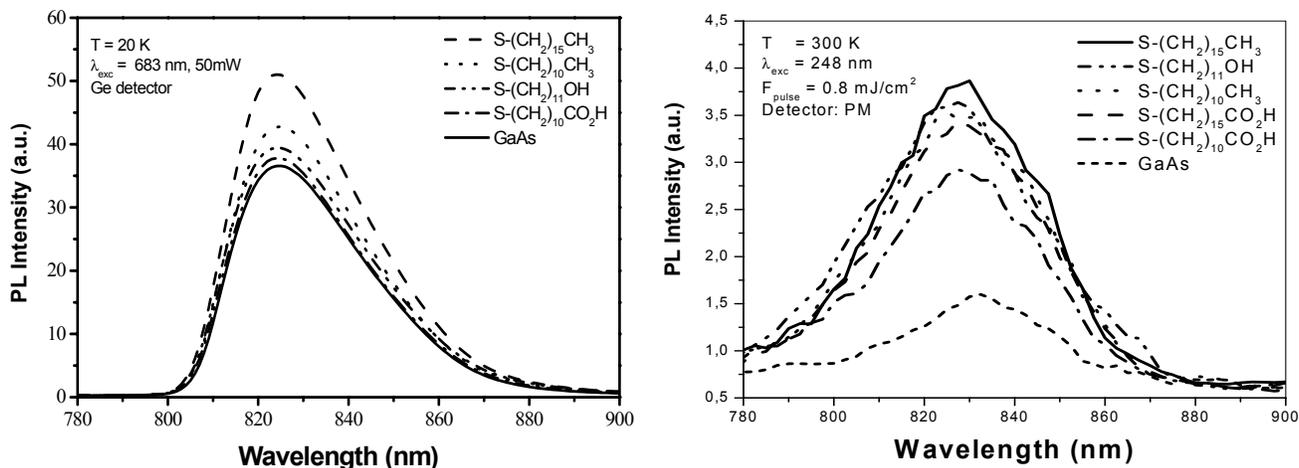


Fig. 3. Photoluminescence spectra of freshly etched (001) GaAs and samples covered with SAMs of different thiols.

sample surface preparation and deposition of SAMs of the investigated thiols. Stability of the (001) GaAs-thiol interface has been confirmed by the PL measurements, which were repeated after 4 weeks. Effectively, the same amplitude of the PL signal enhancement was observed for all the interfaces investigated in this work.

The preliminary attenuated total reflection Fourier transform infra-red spectroscopy (ATR-FTIR) experiments [22] have shown that the alkyl chain orientation in the thiol SAM is dictated by the terminal group. As shown in Figure 4, when the substrate is hydrophilic (etched with 37% HCl in our case), hydrophobic terminated alkyl incline towards the substrate normal while the hydrophilic

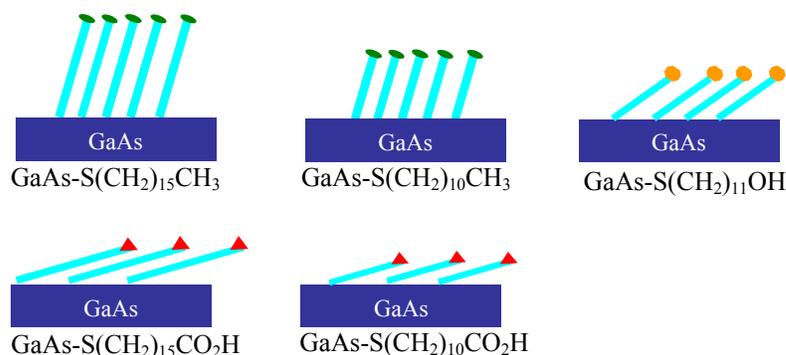


Fig. 4. Relative alkyl chain orientations for various thiols investigated in this work.

terminated alkyl chains have a tendency to run almost parallel to the substrate surface. In addition, they have a high affinity to ambient water and oxygen, which may account for their relatively lower surface passivation efficiency. In contrast, the hydrophobic terminated SAMs, such as GaAs-S(CH₂)₁₅CH₃ and GaAs-S(CH₂)₁₀CH₃ tend to be highly organized and closely packed. Therefore they are more effective in protecting the surface of GaAs from contacting ambient oxygen and moisture. Furthermore, longer chain SAMs offer a thicker diffusion barrier, hence GaAs-S(CH₂)₁₅CH₃ gave stronger enhancement of the PL signal when compared with GaAs-S(CH₂)₁₀CH₃.

4. CONCLUSIONS

We have investigated the passivation efficiency of the surface of (001) GaAs with self-assembled monolayers of thiols comprising relatively long methylene chains. Generally, based on the observations of the enhanced photoluminescence signal, it has been determined that the 15-CH₂ chain thiols more efficiently passivate the surface than the 10-CH₂ chain thiols. Although qualitatively similar, the amplitude of PL enhancement was found to depend strongly on the wavelength of the PL signal exciting laser. When compared with the etched only sample, a 40% PL signal enhancement has been observed for the S(CH₂)₁₅CH₃-GaAs interface excited with the 683 nm laser. The same interface yielded a 2.5 times increased PL signal if excited with the 248 nm laser. We attribute this increased ratio of the enhancement to the increased surface sensitivity of the PL measurements carried out with the UV excitation source. SAMs with same-length CH₂ chains provided better results (more enhanced PL signals) if their terminal groups were hydrophobic. Hydrophobic terminated SAMs tend to be highly organized and closely packed, which leads to the more efficient surface passivation through the sulfur interaction with Ga and/or As atoms. Stability of the (001) GaAs-thiol interface has been confirmed by the PL measurements, which repeated after 4 weeks, showed effectively the same enhancement.

Acknowledgements

The funding for this research has been provided by the Canadian Institutes for Health Research and Canada Research Chair Program. We are greatly indebted to Dr. Mike Post (NRC, Canada) for making available to us his excimer laser setup.

REFERENCES

- [1] P. Baumgartner, C. Engel, G. Abstreiter, G. Böhm, G. Weimann, "Fabrication of lateral *n*pn-phototransistors with high gain and sub- μ m spatial resolution", Appl. Phys. Lett. **66**(6), 751(1995)
- [2] P. Baumgartner, C. Engel, G. Abstreiter, G. Böhm, G. Weimann, "Fabrication of in-plane-gate transistor structures by focused laser beam-induced Zn doping of modulation-doped GaAs/AlGaAs quantum wells", Appl. Phys. Lett. **64**(5), 592(1994)
- [3] K. Adlkofer, M. Tanaka, H. Hillebrandt, G. Wiegand, E. Sackmann, T. Bolom, R. Deutschmann, G. Abstreiter, "Electrochemical passivation of gallium arsenide surface with organic self-assembled monolayers in aqueous electrolytes", Appl. Phys. Lett., **76**, 3313 (2000).
- [4] J. Shin, K.M. Geib, C.W. Wilmsen and Z. Lilliental-Weber, "The chemistry of sulfur passivation of GaAs surfaces", J. Vac. Sci. Technol. **A8**(3), 1894-1898 (1990), and references therein.

- [5] O. S. Nakagawa, S. Ashok, S.W. Sheen, J. Martensson, D.L. Allara, "GaAs interfaces with octadecyl thiol self-assembled monolayer - structural and electrical-properties", *Jap. J. Appl. Phys.*, Part 1, **30(12B)**, 3759-3762 (1991).
- [6] S. R. Lunt, P. G. Santangelo, N. S. Lewis, "Passivation of GaAs surface recombination with organic thiols", *J. Vac. Sci. Technol.* **B9(4)**, 2333-2336 (1991).
- [7] S. R. Lunt, G. N. Ryba, P. G. Santangelo and N. S. Lewis, "Chemical studies of the passivation of GaAs surface recombination using sulfides and thiols", *J. Appl. Phys.*, **70(12)**, 7449-7467(1991).
- [8] C. W. Sheen, J. X. Shi, J. Maarensen, A. N. Parikh and D. L. Allara, "A new class of organized self-assembled monolayers: alkane thiols on gallium arsenide(100)", *J. Am. Chem. Soc.*, **114(4)**, 1514-1515 (1992).
- [9] R. C. Tiberio, H. G. Craighead, M. Lercel, T. Lau, C. W. Sheen and D. L. Allara, "Self-assembled monolayer electron beam resist on GaAs", *Appl. Phys. Lett.*, **62(5)**, 476-478 (1993).
- [10] H. Ohno, M. Motomatsu, W. Mizutani and H. Tokumoto, "AFM Observation of Self-Assembled Monolayer Films on GaAs (110)", *Jpn. J. Appl. Phys. Part I*, **34(2B)**, 1381-1386 (1995).
- [11] J. F. Dorsten, J. E. Maslar and P. W. Bohn, "Near-surface electronic structure in GaAs (100) modified with self-assembled monolayers of octadecylthiol", *Appl. Phys. Lett.*, **66(14)**, 1755-1757 (1995).
- [12] V. N. Bessolov, M. V. Lebedev, A. F. Ivankov, W. Bauhofer and D. R. T. Zahn, "Electronic properties of GaAs(100) surface passivated in alcoholic sulfide solutions", *Appl. Surf. Sci.*, **133(1)**, 17-22 (1998).
- [13] T. Baum, S. Ye and K. Uosaki, "Formation of self-assembled monolayers of alkanethiols on GaAs surface with in-situ surface activation by ammonium hydroxide", *Langmuir*, **15(25)**, 8577-8579 (1999).
- [14] H. Ohno, L. A. Naghara, W. Mizutani, J. Takagi and H. Tokumoto, "Preparation of self-assembled mercaptoalkanoic acid multilayers on GaAs (110) surfaces", *Jpn. J. Appl. Phys.*, Part I, **38(1A)**, 180-185 (1999).
- [15] M. V. Lebedev, D. Ensling, R. Hunger, T. Mayer and W. Jaegermann, "Synchrotron photoemission spectroscopy study of ammonium hydroxide etching to prepare well-ordered GaAs(100) surfaces", *Appl. Surf. Sci.*, **229(1-4)**, 226-232 (2004).
- [16] V. L. Alperovich, O. E. Tereshchenko, N. S. Rudaya, D. V. Sheglov, A. V. Latyshev and A. S. Terekhov, "Surface passivation and morphology of GaAs(100) treated in HCl-isopropanol solution", *Appl. Surf. Sci.*, **235(3)**, 249-259 (2004).
- [17] T. Hou, C. M. Greenlief, S. W. Keller, L. Nelen and J. F. Kauffman, "Passivation of GaAs (100) with an Adhesion Promoting Self-Assembled Monolayer", *Chem. Mater.*, **9(12)**, 3181-3186 (1997).
- [18] M. Schwartzman, V. Sidorov, D. Ritter and Y. Paz, "Surface passivation of (100) InP by organic thiols and polyimide as characterized by steady-state photoluminescence", *Semicond. Sci. Technol.*, **16(10)**, L68-L71 (2001).
- [19] M. Schwartzman, V. Sidorov, D. Ritter and Y. Paz, "Passivation of InP surfaces of electronic devices by organothiolated self-assembled monolayers", *J. Vac. Sci. Technol.* **B21(1)**, 148-155 (2003).
- [20] W. S. Simpson, D. K. Shuh, W. H. Hung, M. C. Hakansson, J. Kanski, U. O. Karlsson and J. A. Yarmoff, "Role of surface stoichiometry in the Cl₂/GaAs(001) reaction", *J. Vac. Sci. Tech.* **A14(3)**, 1815-1821 (1996).
- [21] A. Dargys and J. Kundrotas, *Handbook on Physical Properties of Ge, Si, GaAs and InP*, Vilnius, Science and Encyclopedia Publishers, 1994.
- [22] X. Ding et al., to be published.