Long Term Protection and Functionalization of GaAs Surfaces

J.D. Smith[a], T.R. Finlayson[a], U. Klemradt[b], C. Kirchner[c], M. Seitz[c] and J. Sutter[d]

[a]*School of Physics and Materials Engineering, Monash University, Victoria 3800, Australia.*
[b]*II Physik. Inst., RWTH-Aachen, D-52066, Germany.*
[c]*Centre for NanoScience, Ludwig-Maximilians University, 80539 Munich, Germany.*
[d]*HASYLAB at DESY, D-22603 Hamburg, Germany.*

X-ray reflectivity has allowed the measurement at nanometric resolution of the structures formed when a GaAs surface is passivated with (3-mercaptopropyl)trimethoxysilane (MPT). GaAs surfaces are reactive due to dangling bond formation on the surface. These vacant states provide unique physiochemical and electro-optical properties that give GaAs high sensitivity and large spatial resolution as a chemical analyte sensor. However, GaAs forms a stable oxide layer within seconds upon exposure to air, which pins the Fermi level near mid gap. Here we focus exclusively on MPT for passivation. MPT overlayers can reduce oxygen and As diffusion to and from the GaAs surface.

1. Introduction

One clear application for passivated GaAs is the potential to culture living cells directly on to the surface of the sensor. This is clearly a distinct advantage compared to bare GaAs but nevertheless a fundamental requirement for high spatial resolution [1]. However, the cultivation of cells on the surface of this material presents special difficulties, because both As and AsO_3^{3-} are toxic to living cells. When small concentrations of the toxic substances are present, the cells detach from the surface and, under the influence of larger concentrations, the cells do not survive. Therefore it is desirable to protect the cells or culture from the GaAs surface by depositing a protective layer between GaAs and the cell culture. Ideally, this protective layer would need to be dense, adherent, non-perturbative and chemically robust. MPT was chosen for these reasons [1].

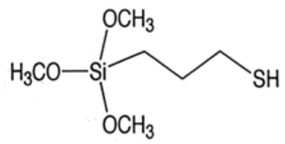

Fig. 1. MPT molecule

In general, polymers offer many advantages over epitaxially grown $Al_xGa_{1-x}As$ layers such as their mouldability, conformability, ease of deposition and low cost. Generally, deposition is straight forward and can be accomplished by techniques such as dip coating. There is also a wide choice of molecular structure and grains available [2].

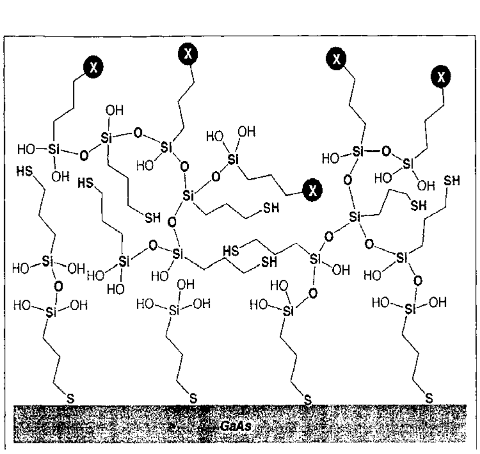

Fig.2. MPT overlayer on GaAs

The MPT monomer, is a functionalized silane comprised of a mercaptan and a trimethoxy silane group at either end of a propyl chain (Fig. 1). The molecule is 12Å in length. MPT can cross-link hence the layer is able to polymerize, increasing its chemical stability and density (Fig 2) [1,3]. Furthermore, the sulphur in the mercaptan group is known to bond covalently to both Ga and As and hence form a chemically stable layer (Fig 2) [4,1]. Sulphur is ideally suited to this substrate because of its high bond strength to GaAs and its non-perturbation of the mid-gap interface states.

Fermi level pinning originates from excess arsenic presenting antisites at the GaAs surface [5]. The antisites represent an As atom occupying the lattice site of a Ga atom. This would form a substitutional point defect.

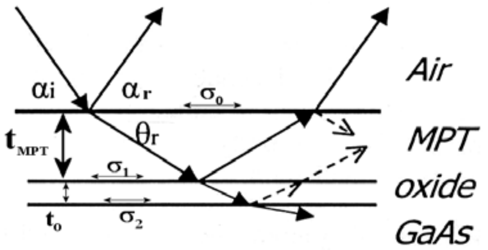

Fig. 3. Incident x-ray beam inter-acting with the sample. $\alpha_i > \theta_r$.

X-ray reflectivity was used to probe the surface giving an electron density profile from the incident electromagnetic wave interacting with the structure of the sample. Features of the curve relate to the electron density profile of the sample. The electron density profile is, however, unknown and so the process of fitting the data with physical models is mandatory for their proper evaluation. The physical models must take into account the overall structure of the material, comprised of various layers each having a thickness, t, density, ρ, and roughness, σ, on the substrate (Fig 3). Surface and/or interfacial roughness decreases the reflected intensity as it causes localized scattering of the incident x-ray beam.

2. Sample preparation

Samples were prepared with the aim of assessing the effectiveness of different preparation procedures. The samples that gave acceptable reflectivity (based on quality of fit (RMS)) are listed in Table 1. We are yet to evaluate the other samples.

Table 1. Samples used and preparation

Sample	Etch	Monolayer	MPT	Scan Result, Fit Result, Passivation Result
A2	X	X		Good, Average Fit, No Passivation
A3			X	Good, No Fit, Little Passivation
A4		X	X	Good, Very Good Fit, Good Passivation
A6	X	X	X	Excellent, Very Good Fit, Good Passivation
C1P		X		Good, No Fit, No Passivation

Sample preparation varied according to experiment type. All were 11x11mm^2 n-GaAs (100) wafers, Te-doped to ~4x10^{17}cm^{-3}, supplied by Freiberger Compound Materials GmbH, Germany. Sample cleaning involved 5 min ultrasonic treatment in acetone and ethanol, drying under a stream of N_2 gas. Etching required 1 min in HCl (37%, Merck) followed by rinsing with de-ionized water (Millipore) and ethanol (absolute grade, Merck). Monolayer deposition required 2 hours in a 11 mM solution of (MPT, Gelest) in ethanol at 50° C. Polymer deposition required 48 hours in 11 mM-MPT/250 mM-HCl solution of ethanol. After polymer deposition, the polymer coated samples where baked for 3 hours at 120° C in air.

3. Results

Typical reflectivity curves obtained are reproduced in Fig. 4. An analysis procedure for such data has been discussed elsewhere [6] and uses the fitting program PCTRF [7]. The microstructural parameters arrived at from the best fits are given in Table 2. The "Best Fit (RMS)" parameter represents how well is the fit to the experimental reflectivity curve and gives a good indication of the reliability of the model information obtained from the fit.

Table 2. Results of fits obtained for samples

Sample	σ_0 (Å)	t_{MPT} (Å)	ρ_{MPT} (gcm^{-3})	σ_1 (Å)	t_{oxide} (Å)	ρ_{oxide} (gcm^{-3})	σ_2 (Å)	Best Fit (RMS)
A2	8.7	19.9	2.377	3.1	27.7	5.077	1.9	0.033
A4	10.8	272.2	1.384	19.8	10.1	4.116	5.2	0.101
A6	10.2	277.8	1.403	21.1	10.0	4.229	4.7	0.102

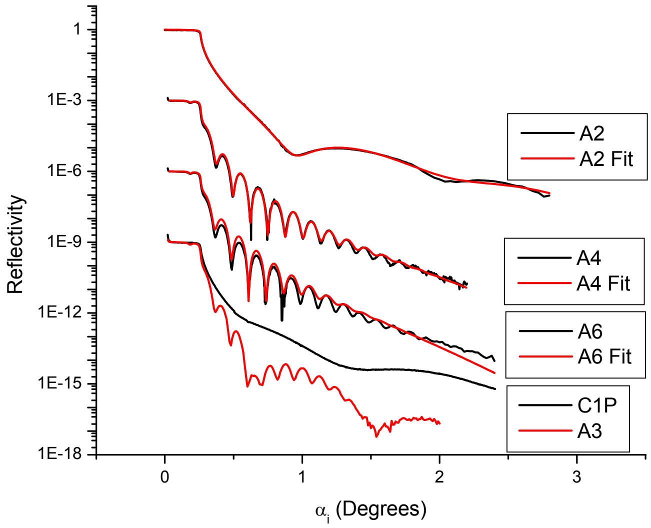

Fig. 4. Reflectivity profiles for various treatments of a GaAs surface. With the exception of A2 & A2 Fit all profiles are offset with respect to absolute reflectivity for clarity.

4 Discussion/Conclusions

All samples examined using x-ray reflectometry showed the presence of an oxide layer of thickness depending on deposition processes. It has also become clear that prior etching of the GaAs substrate before MPT deposition has little or no effect on the final oxide layer thickness or quality and therefore can be avoided. Samples A4 and A6 clearly showed the presence of an oxide layer of 10Å and that it was unchanged by prior etching (Fig. 4, Table 2).

Furthermore, the prior addition of a monolayer of MPT was found to produce considerable improvement to the passivation abilities of the MPT overlayer as samples with an applied monolayer, A4 and A6, had large reductions in the thicknesses of their respective oxide layers compared to samples where no monolayer was present, as in A3 (Fig. 4, Table 2). Although it is clear that some oxide was present when the samples were studied, its origin is unclear. There is so much that is unknown about the exact formation of oxides on type III-IV semiconductors, in general, that it is impossible to say if the oxide layer exhibited regrowth after complete removal or if the oxide present was residual from a prior native layer. Certainly it would be advantageous to discover the exact origin of the oxide layer found as this could aid in further passivation attempts in future work.

Current passivation techniques preclude the immediate use of GaAs material as a biosensor due to oxide layer formation and the release of As species from the surface. For this reason it would be impossible to use GaAs material as a biosensor without further developments to passivation technologies. However, with a continued analysis and further work, focusing on many of the yet unexplained mechanisms required for GaAs passivation, progress will be made, resulting in a system that will suit this proposed application.

Acknowledgments

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