Corrosion Resistance of Organic Layers on GaAs via X-Ray Reflectometry Characterization

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Two different solutions of (3-mercaptopropyl)trimethoxysilane (MPT) were deposited on GaAs surfaces to provide passivation against corrosion by oxygen and to prevent AsO_3^{3-} escape into the surrounding environment. Their relative effectiveness for corrosion resistance were assessed by examining their microstructures using grazing incidence x-ray reflectometry. Some success with minimizing the formation of a buried oxide layer has been achieved with processing in an argon atmosphere and using methanol rather than ethanol which is hydrophilic. Further study is required regarding the effectiveness of thiol overlayers against arsenic and oxygen diffusion on the GaAs surface.

1.   Introduction

Semiconductor passivation has been an essential requirement for bio compatibility of GaAs and other semiconductor surfaces such as silicon (Si) [1,2]. Semiconductors feature a lack of binding sites for cells so that there is always a lack of adhesion [3]. For GaAs, the situation is complicated further by the fact there are very toxic AsO_3^{3-} groups present and an unstable oxide layer [4].

Corrosion then presents itself as a major technical challenge for GaAs sensor applications and bio compatible surfaces since it facilitates device damage via oxidation and the subsequent As and AsO_3^{3-} escape into the surrounding environment [1,2,3]. In aqueous, cell-like environments the problem is magnified on account of continuous etching of the unstable oxide layer resulting in continued corrosion [3].

Passivation then presents itself as a technique to provide the necessary functional groups for cell adhesion and to provide protection against oxygen binding and subsequent As and AsO_3^{3-} escape into the local environment. Passivation by sulphur of the GaAs surface was first demonstrated by Sandroff [5] and has since grown to include passivation by selenium, tellurium, chlorine and others. The exact chemistry and mechanisms behind passivation are not yet completely understood and much further work is required.
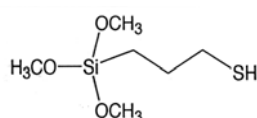

Fig. 1. MPT molecule

The passivation of GaAs via sulphur bonding is investigated by deposition of a silanol thiol-based overlayer, (3-mercaptopropyl) trimethoxysilane (MPT) (Fig. 1). The thiol group is known to bond to both arsenic and gallium and so it can form a strong coupling layer on top of the GaAs surface [1,2,3]. Previous work had suggested that the passivation of GaAs was incomplete due to a buried oxide layer found on all samples [1,2,3]. This paper reflects attempts to rectify this problem by the introduction of a cleaner environment during deposition and the substitution of methanol instead of ethanol into the depositon solution. Methanol is less hydrophilic than ethanol so it would contain less moisture but it was not known if methanol could be substituted for ethanol and what the resulting improvement would be, if any.

X-ray reflectivity was used to probe each sample due to its non-destructive nature of the samples and its ability to reveal buried interfacial layers, namely oxide or As-rich interfacial layers formed from corrosion. Features of the resultant intensity curve relate to the electron density depth profile of the sample. The process of fitting the resultant curve with a computer-

simulated model of the sample profile can give the thickness, t, density, ρ, and roughness, σ, on the substrate [6].

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. The data from other samples prepared by relatively similar processing remain to be assessed. The numeric and letters used for the sample nomenclature represent a quick way of categorizing the preparation methods. An "E" signifies etching with HCl, "M" represents a deposited monolayer and a "P" represents a thicker polymer layer.

Table 1. Samples used and preparation

Sample	Etch	Monolayer	MPT	Scan, Fit, Passivation Result
1				Great Scan, OK Fit, No Passivation
2E	X			Good Scan, Good Fit, No Passivation
4M		X		Great Scan, Poor Fit, No Passivation.
5P			X	Great Scan, Excellent Fit, Great Passivation

Sample preparation varied according to experiment type. All were $11 \times 11 mm^2$ n-GaAs (100) wafers, Te-doped to $\sim 4 \times 10^{17} cm^{-3}$, supplied by Freiberger Compound Materials GmbH, Germany. Sample cleaning involved 5 min ultrasonic treatment in acetone and ethanol and drying under a stream of nitrogen gas. Etching required 1 min in HCl (37%, Merck) followed by rinsing with de-ionized water (Millipore) and methanol (absolute grade, Merck). Monolayer deposition required 3 hours in an 11 mM solution of (MPT, Gelest) in methanol at 60°C. Polymer deposition required 34 hours in 11 mM-MPT/250 mM-HCl solution of methanol.

3. Results

Typical reflectivity curves obtained are reproduced in Figs. 2 & 3. An analysis procedure for such data has been discussed elsewhere [1,2] and uses the fitting program PCTRF [6]. The microstructural parameters arrived at from the best fits are given in Table 2. The "Best Fit (RMS)" parameter represents how well the simulated fit represents the experimental reflectivity curve and gives a good indication of the reliability of the model information obtained.

Table 2. Results of fits obtained for samples

Sample FIT	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)
1	0.0	-	-	-	15.4	1.006	10.7	0.171
2E	3.7	-	-	-	23.1	1.106	4.3	0.90
4M	9.2	49.6	3.148	0.0	-	-	-	0.156
5P	7.8	164.9	1.523	7.5	-	-	-	0.102

4. Discussion/Conclusions

Samples 1 and 2E showed clear signs of a corrosion layer which was not surprising since no protective layer was deposited on to the surface. However, it was not expected that after etching, the regrown oxide would be thicker and have a greater density. From Table 2 it can be seen that the new density is 1.106 gcm^{-3} compared to 1.006 gcm^{-3} and the thickness is 23.1Å compared to 15.4 Å. This represents a 50 percent increase in the layer thickness and about a 10 percent increase in density. This can partially be explained by the variance in oxide growth conditions since different thicknesses and densities depend on oxygen concentration, temperature, exposure time and even surface roughness. The reduction in buried roughness from 10.7Å to 4.3Å is not understood at this time. It seems obvious from the RMS values that sample 1 will most likely require an As-rich, interfacial layer added to the model in order to complete the fit process.   Samples 4M and 5P had a monolayer and the thicker polymer layer applied to their surfaces. Compared to the previous ethanol batch [1,2] the coverage and thickness of the new methanol layers depended more on the deposition time than the solution used. For example,

the methanol batch had a 34 hour deposition time which was 70.8 percent of the time of 48 hours used for previous samples [1,2]. The methanol batch therefore was expected to have polymer layers about 260×0.708=184Å in thickness since the average before was 260 Å. It was found from Table 2 that a thickness of 164.9Å agrees pretty much with a linear relationship between deposition time and layer coverage and thickness.

The methanol batch of samples showed a marked improvement regarding passivation effectiveness of the GaAs surface. This result appears to be a consequence of the cleaner argon environment during deposition rather than the change to a methanol solution. Future work will concentrate on determining the exact cause for this improvement and correctly characterizing it. Data has been collected for several other samples with various preparation procedures, but these are yet to be analysed.

Sample 4M (Table 2 and Fig. 3) has a clear oxide layer and can be used as a comparison to sample 5P which doesn't. The fit for sample 4M data is poor because the model used in the fitting program is not complete. This sample shows some corrosion and so needs an additional oxide layer added to the fitting model. This will only be included if it improves the fit considerably.
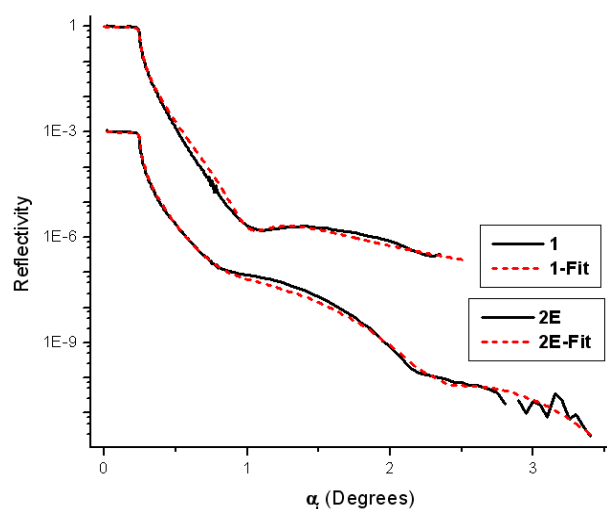

Fig. 2.   Reflectivity profiles for a native untreated sample 1 and a piece of GaAs that has been etched, sample 2E. Sample 2E has been offset 3 orders of magnitude for clarity.
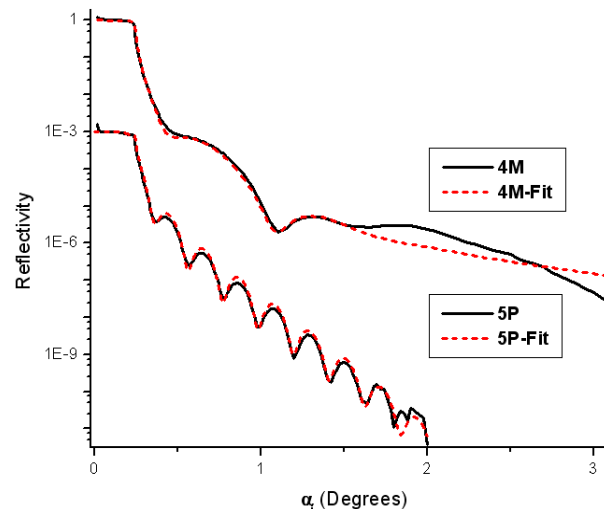
Fig. 3.   Reflectivity profiles for sample 4M which has been treated with a monolayer. Sample 5P has a polymer layer applied and has been offset for clarity.

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