

Preliminary Studies on the Rate of Native Oxide Growth on III-V Semiconductor Surfaces by Scanning Tunnelling Microscopy

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The growth of native oxides on the GaAs(100) and InP(100) chemically etched surfaces, following exposure to air, has been investigated by scanning tunnelling microscopy (STM). These studies provide information on both the rate and progression of the native oxide growth over $100 \times 100 \text{ nm}^2$ areas of the semiconductor surfaces. The rate of oxide growth on the GaAs etched surface was found to be significantly faster than on the InP surface. On both semiconductor surfaces the oxide growth was observed to proceed via nucleation centres dispersed across the surface which eventually coalesced to form a uniform oxide layer approximately 2 nm thick. Attempts were made to reduce the rate of native oxide growth by treating the chemically etched surface with ammonium sulfide prior to air exposure. This resulted in a significant reduction in oxide growth rate on both surfaces with a thinner oxide forming on the InP surface.

Introduction

The formation of native oxides on III-V semiconductor surfaces such as GaAs and InP is a process that can strongly affect further device fabrication stages. Most initial device processing consists of etching and rinsing of the surface with different etch procedures producing different surface compositions. For GaAs, chemical cleaning procedures based on $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O}$ solutions produce, after rinsing in flowing deionized (DI) water, an oxide free surface [1, 2]. Air exposure or rinsing in static water has been found to produce a native oxide film consisting of Ga_2O_3 and As_2O_3 [3]. An acidic etch such as that mentioned above should remove surface oxides and etch the GaAs substrate, leaving a residue of elemental arsenic on the surface. Subsequent rinsing of the etched surface with dilute HCl results in removal of all or part of the elemental arsenic [4].

Etch solutions that result in clean InP surfaces, and thus realise the ability to fabricate metal-semiconductor, as opposed to metal-oxide-semiconductor, diodes have been previously examined [5]. Extensive XPS studies have been carried out on the growth of native oxides on both GaAs and InP [6] within the time scale involved in these experiments. Following the initial chemisorption of a layer of oxygen on the surface, bulk-like oxides form, primarily Ga_2O_3 and As_2O_3 , which disrupt the surface structure. It is the formation of these stable surface oxides which is investigated in this study. Further oxidation leads to the surface becoming increasingly insulating and impossible to image with STM. The three dimensional, high resolution, imaging capabilities of the STM can monitor, in real time, the evolution of the surface oxide layer formation following the exposure of the freshly etched surface to air.

Relatively little has been published to date on oxidation studies of semiconductor surfaces by STM regarding oxide growth rate or growth mechanism. Stroschio *et al.* [7, 8] have examined the structure of initial oxygen adsorption on the GaAs(110) surface in vacuum with various oxygen exposures, however this was at an atomic scale. Early steps in Si(111) 7×7 oxidation with atomic resolution have recently been studied by Avouris *et al.* [9]. Mid-desorption stages on Si(111) have been investigated by Kobayashi and Sugii [10] over a seven micron square area, noting that the desorption is not layer by layer but by the formation and lateral growth of voids approximately 2 nm in depth.

Aqueous sulfide treatments have been shown to modify the electronic properties of compound semiconductors such as GaAs [11-15] and InP [16-18] by a variety of surface probing techniques such as XPS, RHEED and SRV (surface recombination velocity). On InP [17], previous studies with $(\text{NH}_4)_2\text{S}$ solutions have reported the formation of a thin passivating indium sulfide layer (sulfur being bonded strongly to the surface) with no evidence to suggest either elemental sulfur or phosphorous-sulfur bonding. GaAs, on exposure to H_2S gas and $(\text{NH}_4)_2\text{S}$ solutions [13], produces a slightly Ga rich surface covered by one monolayer of sulfide which restricts oxidation of the GaAs surface and reduces the surface state density [14]. This contrasts with the disruptive nature of semiconductor surface oxidation which results in an increase in surface state density. The ability of these sulfur based treatments to passivate the surface has been found to degrade with time indicating that the sulfur stabilised surface is thermodynamically unstable with respect to the oxidised surface [19].

Experimental

All STM images for this study were obtained in air using a Nanoscope II from Digital Instruments, CA, United States, at room temperature and ambient pressure. Sample bias voltage with respect to the mechanically sharpened Pt-Ir tip was -2 V and the tunnelling current was 1 nA . No stable images were acquired with positive sample bias. Scan area for all samples was fixed at $100 \times 100 \text{ nm}^2$. The (100) GaAs samples were n-type, Si doped at a concentration of $2 \times 10^{18} \text{ cm}^{-3}$; similarly InP(100) samples were also n-type, Si doped at a $2 \times 10^{18} \text{ cm}^{-3}$ concentration. Although samples with such a high doping density are almost degenerate, ohmic contacts to the back of the substrates were formed with an indium : gallium alloy. The samples were first degreased in acetone and rinsed with methanol and DI

water. They were then etched in a 5 : 1 : 1 solution of H_2SO_4 : H_2O_2 : H_2O at 60 °C for a minute, followed by a 20 second 5 : 1 : 40 H_2SO_4 : H_2O_2 : H_2O etch. Finally, the samples were rinsed in flowing DI water, blown dry under N_2 and ohmic contacts formed. A second etch solution was also used : after again degreasing/rinsing with acetone/methanol and DI water respectively, the samples were etched in a 3 : 1 : 100 NH_4 : H_2O_2 : H_2O solution for 40 seconds, rinsed in DI water, followed by a 1 : 1 : 1 HCl : H_2O etch for 1 minute. Rinsing in flowing DI water, drying under N_2 and application of ohmic contact again completed sample preparation.

Only the first etch procedure was used for surfaces to be sulfur treated. Following etching, the samples were transferred into a beaker containing a 1 : 20 $(NH_4)_2S_x$: H_2O solution and heated with intermittent stirring for about 30 minutes on a hot plate at 60 °C. The samples were then rinsed in DI water, dried in N_2 and following the application of ohmic contacts they were thus heated in vacuum to 250 °C for 15 minutes to remove excess amorphous sulfur. This preparation is reported as providing a semiconductor surface terminated in a one atom layer of chemically bound sulfur [12].

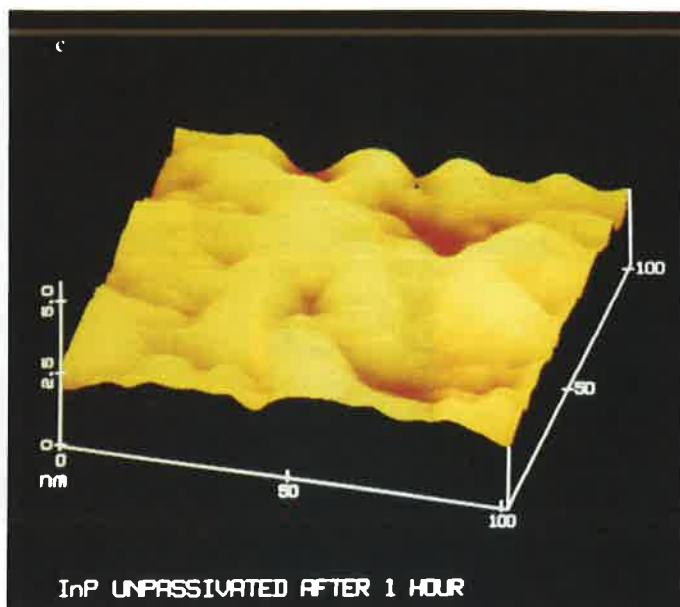
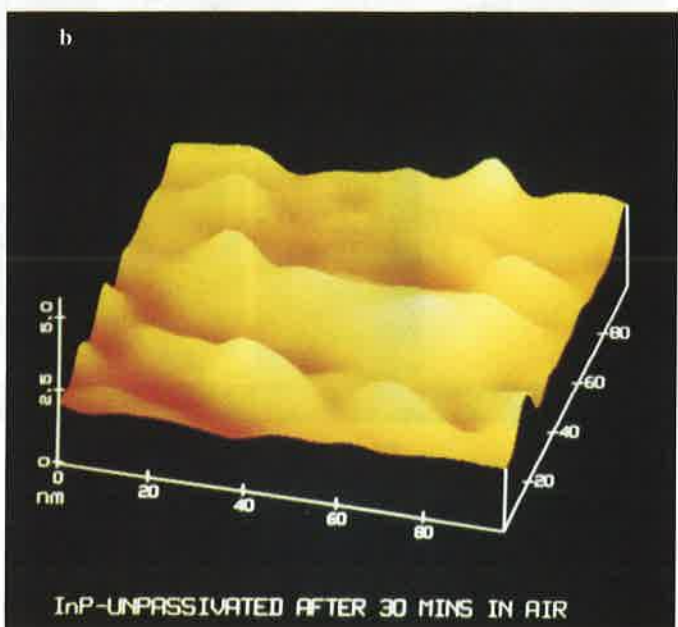
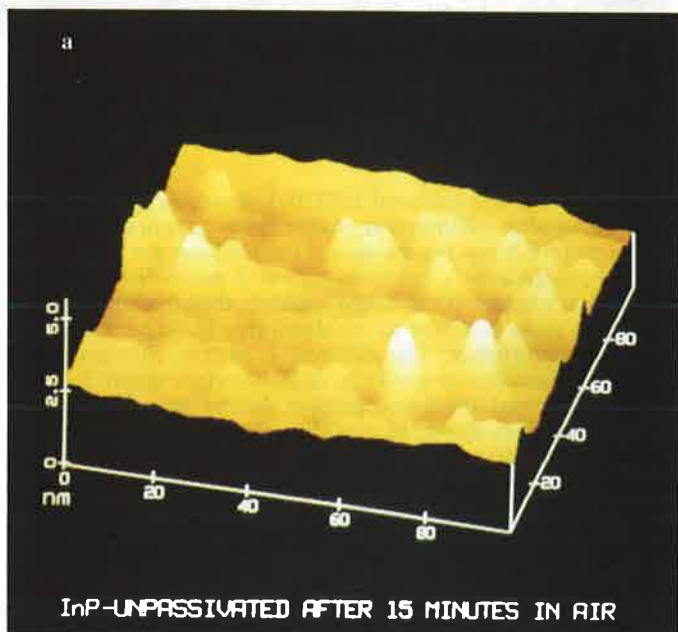


FIGURE 1. - STM images of the chemically etched InP(100) surface : (a) after 15 minutes exposure to air, (b) after 30 minutes exposure to air, (c) after 1 hour exposure to air.

Results and discussion

The STM images shown in figures 1a, b, c are of the InP(100) surface 15, 30 and 60 minutes, respectively, after etching. Little difference in rate of oxide growth or growth mechanism was distinguished between the two etches used. Oxide nucleation centres were seen to appear and coalesce over the course of an hour, after which stable tunnelling images were not obtained. Although these surface oxides do not produce a sufficiently good insulating barrier for device fabrication, they can inhibit the tunnelling current making it impossible to stably image the surface.

For InP(100) surfaces, an oxide growth pattern of an initial chemisorbed stage followed by a nucleation process has been previously proposed by Hollinger *et al.* [21], based on photoemission studies. GaAs(100), after the same etches, exhibited the same type of growth mechanism - however the rate of oxidation was much quicker ; after, on average, 20 minutes no stable images were observed. Occasionally it was impossible to obtain stable images on GaAs(100) directly after etching - this may be due to variations in the quality of the etched surface. A nucleation based model for the oxidation of the GaAs(110) surface has also been proposed by Landgren *et al.* [20] - all our observations would confirm this form of nucleation growth as opposed to a layer by layer mechanism.

Recent STM investigations in air on multiquantum well structures [22] observe a quicker degradation in images of wells fabricated on GaAs as opposed to InP over a time scale comparable to what we have seen. The authors also note that surface oxidation may be accelerated by the tunnelling current. Stroschio *et al.* [7, 8] note an increase in the density of filled states (i.e. those probed at negative sample bias) near adsorbed oxygen sites but this is prior to the formation of bulk oxides on the semiconductor surface. A section through the oxide layer (figure 2) before it becomes uniform reveals an approximate 2 nm thickness which remains constant until the final image (figure 1c) where oxide coverage of the surface is virtually a complete uniform layer.

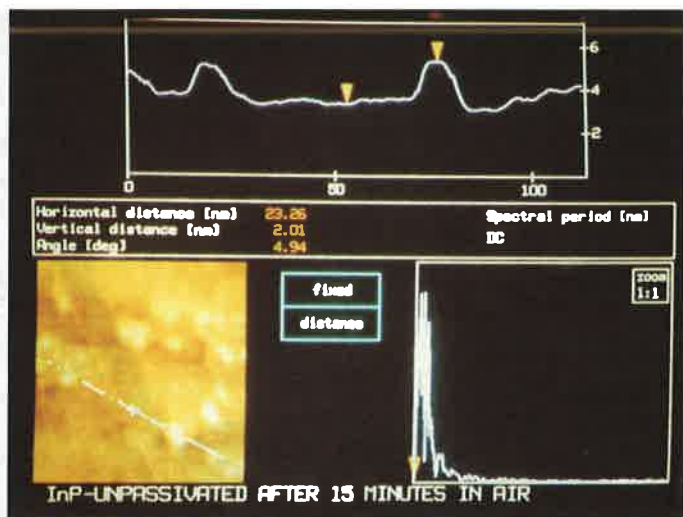


FIGURE 2. - A section through the native oxide nucleation centres revealing an approximative 2 nm thickness.

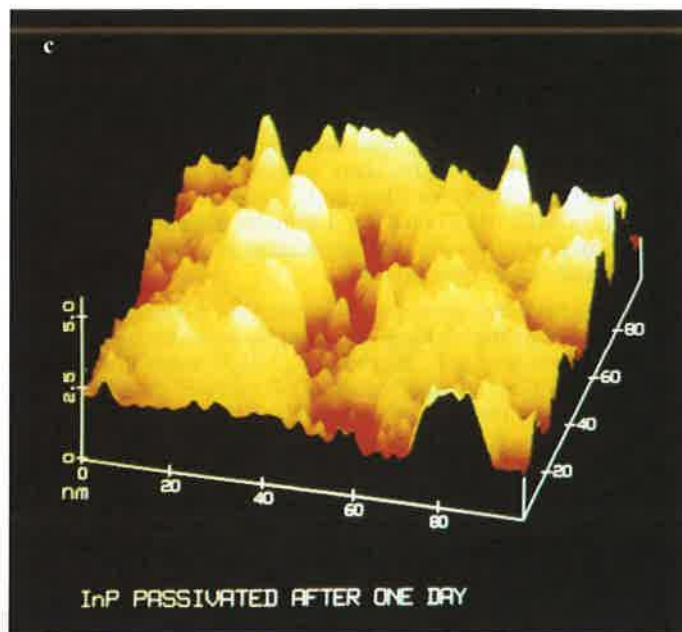
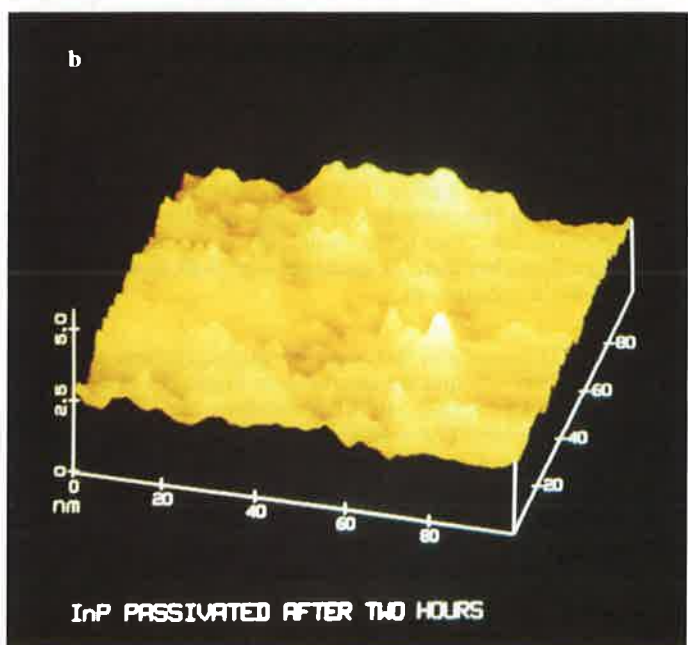
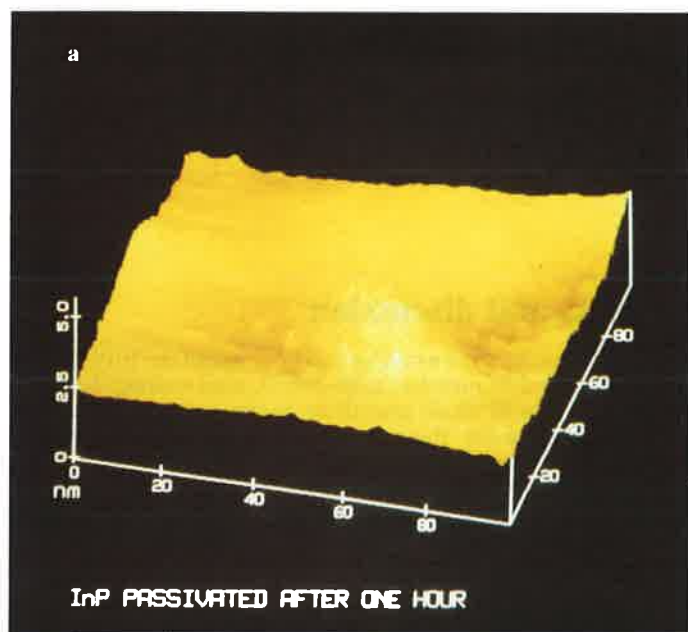


FIGURE 3. - STM images of the sulfur treated InP(100) surface : (a) after 1 hour exposure to air, (b) after 2 hours, (c) after 1 day.



Moving to sulfur passivated InP(100), figure 3a shows this surface 1 hour after sulfurisation - native oxide growth on this region of the surface is just beginning and the oxide seems to form thinner (approximately 1 nm from figure 4) more dispersed oxide nucleation centres. This would indicate that the sulfur treated surface is more resistant to the disruptive oxide formation than the untreated surface. This different growth mechanism was not found on the sulfur treated GaAs(100) surface where the oxide growth followed the same pattern as the untreated surface, though at a much slower rate, with a comparable oxide thickness being formed after a 24 hour exposure to air. Figures 4b and c are images acquired after 2 hours and 24 hours, respectively, following sulfurisation. Stable imaging of both GaAs(100) and InP(100) was possible up to a day after sulfur treatment.

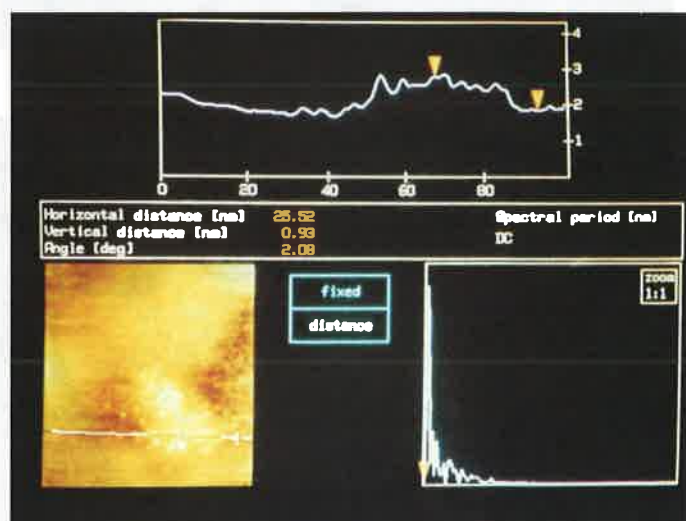


FIGURE 4. - A section through the native oxide nucleation centres on the sulfur treated surface - oxide thickness is now approximatively 1 nm.

Scan areas were, as mentioned before, set at $100 \times 100 \text{ nm}^2$. On reducing to $10 \times 10 \text{ nm}^2$ and $5 \times 5 \text{ nm}^2$ areas on the passivated samples no atomic resolution was found even though surface

roughness was of the order of 0.5 nm. This may be due to the fact that sulfide treatments reduce the surface state density [14] causing a corresponding decrease in the signal to noise ratio of the I-V tunnelling characteristic. The surface flatness observed on the passivated samples would confirm that oxidation on the etched surfaces is not merely a chemisorbed layer but introduces a considerable degree of surface and sub-surface disruption to produce a native oxide layer 2 nm thick. For oxide layers thicker than 2 nm it has proven impossible to obtain stable reproducible tunnelling images.

Conclusions

STM images of native oxide growth on GaAs(100) and InP(100) were obtained, both for chemically etched and sulfur treated surfaces, in air. The mechanism of oxide growth on all surfaces investigated was found to be via a coalescing of oxide nucleation centres rather than layer by layer, where the oxide thickness on the untreated surfaces is approximately 2 nm.

With etched GaAs(100) it was possible to obtain stable images no more than 20 minutes after etching whereas etched InP images were obtained up to an hour after etching. Both GaAs(100) and InP(100) were imaged up to 24 hours after sulfurisation, oxide thickness on the treated InP surface being thinner than on the untreated surface. This ability to obtain stable images after periods up to a day indicates the passivating ability of the chemically bound sulfide layer. Inhibited growth of surface oxides following surface passivation provides a period within which post etch processing can be carried out without the presence of a substantive surface oxide. This is particularly important for GaAs where the rate of oxide growth is substantially faster than for InP.

Acknowledgements

We would like to thank the National Metrology Laboratory in Eolas for providing the facilities to carry out the experimental work and one of us, P.M., acknowledges financial support from Eolas under the Applied Research Award Scheme. We would also like to thank Mr. Al. Devine for technical assistance in preparing the figures.

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