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In situ characterisation of III–V substrate oxide desorption by surface photoabsorption in MOVPE

D.A. Allwood *, N.J. Mason, P.J. Walker

Clarendon Laboratory, Parks Road, University of Oxford, Oxford OX1 3PU, UK

Abstract

The thermal desorption of the oxides of several III–V substrate materials has been investigated by surface photoabsorption (SPA). GaAs, GaSb and InSb substrates were slowly heated to desorb surface oxides. SPA was performed by probing these surfaces with *p*-polarised 633 nm radiation and constantly monitoring the reflected beam intensity. Such an arrangement allows the oxide desorption to be observed clearly, non-invasively and continuously. The effect of oxidation conditions is explored and temperatures for the deoxidation of GaAs, GaSb and InSb substrates are estimated. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Oxide desorption; III–V substrate; Surface photoabsorption

1. Introduction

Epitaxial processes rely on reproducible semiconductor nucleation of very high structural integrity. Following the various possible chemical and mechanical preparative procedures, either performed by the substrate manufacturer or the grower, surface oxides on the substrates must be removed in situ before growth may commence. Such deoxidation is usually performed at a raised temperature and a further period of thermal annealing is commonly used. Since the presence of residual oxides will limit the quality of subsequent growth, removal of surface oxides is a critical process. With the possible exception of GaAs, III–V oxide removal has received very little attention and even for GaAs there is limited agreement across the different studies. This is partly because the way the substrates are prepared (anodic, acidic, alkali, plasma or ozone based etching) will affect the oxides produced on the substrate e.g. when an acid-based etch is used to prepare a GaAs substrate [1], not only are the usual As_2O_3 and Ga_2O produced (requiring deoxidation between 285–400°C) but also Ga_2O_3 which does not desorb until much higher temperatures (550–630°C). Another complication is that the majority of investigations have been performed under vacuum conditions and not under hydrogen and so the conclusions drawn may not always be appropriate to techniques such as metalorganic vapour phase epitaxy (MOVPE). Consequently, the oxide desorption mechanisms relevant to MOVPE remain somewhat unclear and a better understanding of the processes involved can only improve the quality of growth. From time to time substrate manufacturers have to change their processing and the resulting differences in oxide surface may require a change in the in situ cleaning performed prior to growth.

Unlike MBE, where in situ monitoring via RHEED patterns has allowed reproducible control of substrates before growth, MOVPE has been limited to a number of recently introduced optical techniques. These include surface photoabsorption (SPA) [2] and reflectance-difference spectroscopy (RDS [3], also called reflectance anisotropy spectroscopy, RAS [4,5]). However, RDS requires expensive optical equipment whereas SPA is a simple technique [6] requiring only p-polarised light and a detector (Fig. 1). The angle of incidence is usually held close to Brewster's angle (about 75° for GaAs) and the reflected signal recorded, hence the alternative names for SPA of '*p*-polarised reflectometry' [7] and 'Brewster reflectometry' [8]. These different names reflect different views on the optical, physical and chemical processes that are being probed on the surface

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* Corresponding author. Tel.: +44-1865-272218; fax: +44-1865-272321.

E-mail address: d.allwood1@physics.ox.ac.uk (D.A. Allwood)

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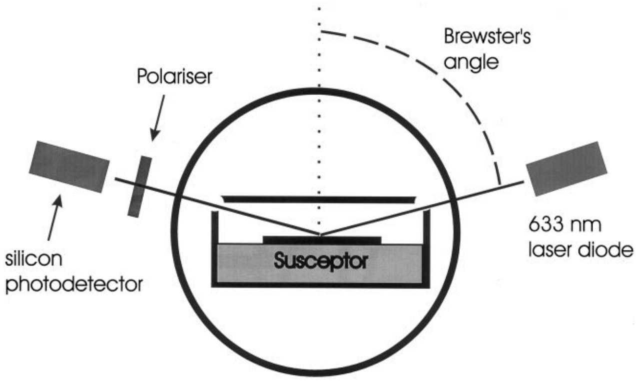

Fig. 1. Schematic cross section of MOVPE reactor and optical path for SPA.

but the apparatus is essentially the same. We report here the preliminary study of deoxidation of various III–V substrates monitored by SPA.

2. Experimental

The details of the MOVPE reactor used in these experiments have been published elsewhere [9]. Briefly, the apparatus runs at atmospheric pressure under hydrogen and its layout can be deduced from Fig. 1. The chopped 633 nm laser beam passes through the walls of the cylindrical outer fused quartz liner (and through small holes in the corners of the inner rectangular liner) and is detected by a silicon photodiode. The inside of the outer liner is kept free from deposit by a purge flow of pure hydrogen.

The only alkyls used in this study were the group V precursors tertiarybutylarsine (tBAs, 5°C, 75 sccm) and trimethylantimony (TMSb, 0°C, 8 sccm). These alkyls were used to provide an overpressure of group V to prevent incongruent evaporation (loss of group V). Total hydrogen flow through the cell was 8 slm.

All substrates were used as received from suppliers, without further cleaning or processing and were (001) orientation, on-axis and undoped. The temperatures and flow conditions used in this study are identical to those that we use during the growth of high-quality III–V semiconductor structures [10]. So we assume that under the conditions used in this study the substrates are free of oxides after the first heating and cooling cycle. A full cycle consisted of heating the substrates to a set temperature $T_{\max}$ holding at $T_{\max}$ for a fixed time and cooling. A ramp rate of 40°C min^{-1} was chosen as this is identical to the rate used on previous studies of deoxidation [1].

3. Results and discussion

Fig. 2 shows a set of six traces obtained from a GaAs substrate heated and cooled three times under tBAs ($T_{\max}$ 700°C). The temperature is shown by a solid line and should be read on the right hand side y-axis. It can be seen from the temperature trace (f) that the cooling in these cycles was uncontrolled. The first cycle, from which trace (a) was obtained, shows a change in signal intensity that includes a component due to deoxidation. In order to deconvolute this component from the background, the heating and cooling cycle was then re-

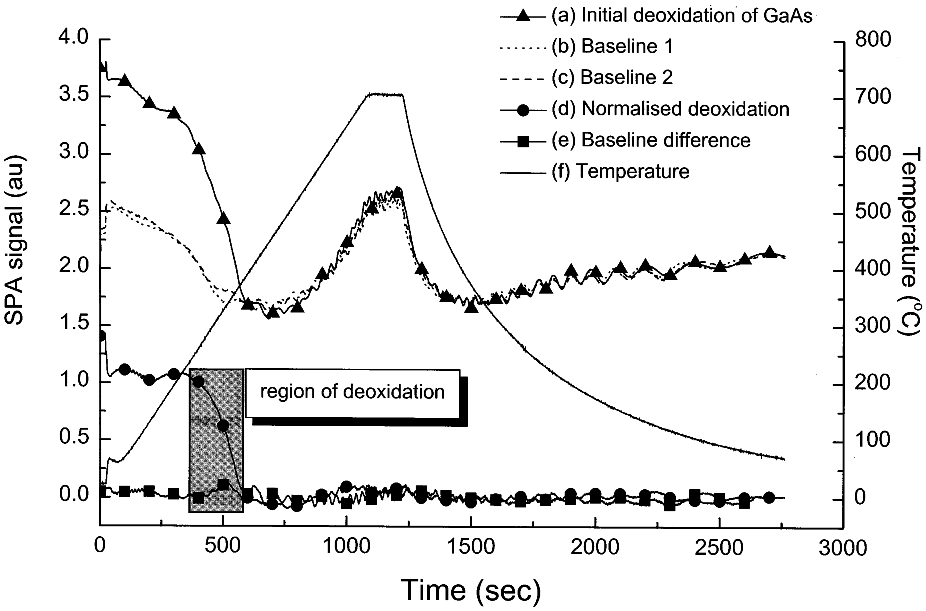

Fig. 2. Raw data and normalised traces for the optical response of a GaAs substrate surface during heating and cooling, the temperature is indicated by the solid line and should be read against the right hand side y-scale.

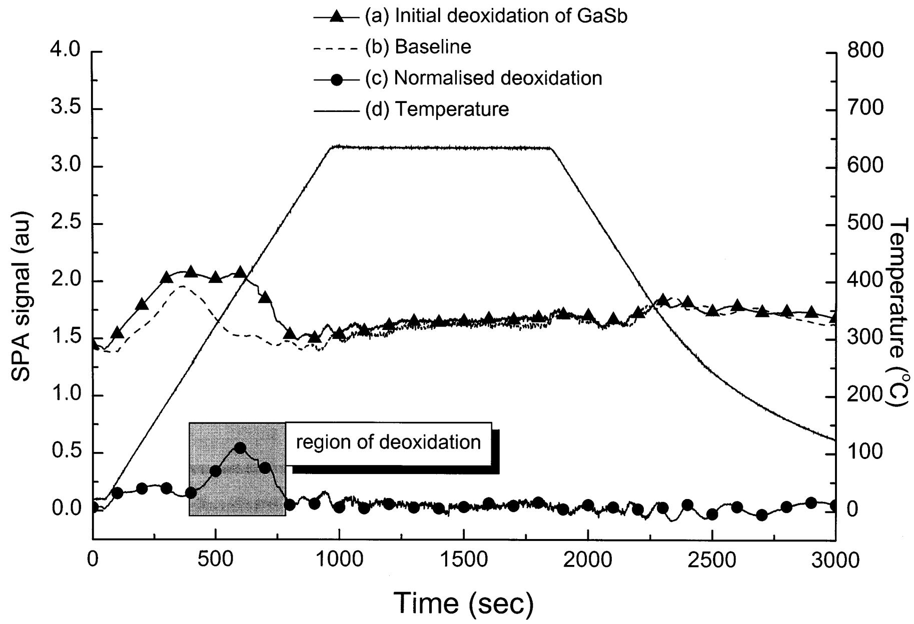

Fig. 3. Raw data and normalised traces for the optical response of a GaSb substrate surface during heating and cooling.

peated twice to get baselines from the deoxidised GaAs surface, traces (b) and (c), respectively. The fact that the traces (a), (b) and (c) coincide so closely after deoxidation suggests the technique is highly reproducible. One of these baselines is subtracted from trace (a) to give the normalised deoxidation signal (d). This trace clearly highlights the contribution from the oxide layer to the SPA signal, hence allowing the temperature range over which deoxidation occurs to be unambiguously assigned. The region of the trace where we believe deoxidation is occurring is indicated by the box. Over a large number of samples the onset of deoxidation has been found to be 260°C (+ 40°C) and the deoxidation is complete by 410°C (+ 20°C). These differences may be due to small variations in oxide thickness and composition from wafer to wafer. As a further check on the reproducibility of the SPA technique traces (b) and (c) are subtracted from one another to give (e). Trace (e) is nearly flat and at zero units on the *y*-scale confirming that the optical signal is not being perturbed by effects such as heating stress in the susceptor or fused quartz outer liner.

In order to investigate the sensitivity of the SPA signal to different group V oxides two other substrates were studied. Firstly GaSb was deoxidised under similar conditions to those used for GaAs except that the T_{max} was reduced to 650°C, the dwell time at T_{max} was increased to 30 min, TMSb was used to protect the surface and the cooling was controlled (at 40°C min^{-1}) down to 250°C. The results are shown in Fig. 3 and for reasons of clarity only one baseline is included, although both baselines were coincident. The normalised deoxidation trace (c) shows that both the temperature range (250–530°C) and the signal shape obtained from the region of deoxidation are quite different from that seen for GaAs. This is possibly due to the different group V oxide on the GaAs compared to the GaSb. In order to investigate this possibility, the deoxidation of InSb was investigated next; again a lower T_{max} (530°C) was chosen. Although this is nominally above the melting point of InSb the temperature offset from the thermocouple in our reactor is about 10° and the substrate is stable at this displayed temperature. The region of deoxidation in Fig. 4 is very close (260–530°C) to that seen for GaSb thus supporting the conclusion that this is related to the desorption of an antimony oxide. Further work on InAs and InP substrates is in progress to shed further light on this. The region of deoxidation for InSb is very close to the melting point as seen previously in high vacuum studies [11] and it is this that makes epitaxy on InSb sometimes difficult to achieve with high quality results.

In order to be confident about the type and thickness of oxide that we are studying we have air-exposed clean GaAs to produce a 'standard' oxide irrespective of the source of the substrate. Thus, upon completion of the experiments to obtain the traces in Fig. 2, the deoxidised GaAs samples were reoxidized by exposure to air at room temperature before being reintroduced to the reactor and deoxidised once more. Fig. 5 shows five traces, (a) and (b) that were obtained after deoxidation of a surface exposed overnight and 2 s, respectively (c) and (d) their respective baselines and (e) the temperature. Again, the post-deoxidation agreement is very precise for all four SPA traces. The two different oxide layers are distinguishable by differences in the absolute levels of the SPA signals shown in traces (a) and (b).

Although the deoxidation region for the overnight exposure is similar to that seen for the as-supplied wafers in Fig. 2, the sample exposed for two seconds appears to be deoxidised at lower temperatures. In order to examine these differences more closely the deoxidation region is magnified in Fig. 6. The baselines ((c) and (d)) in Fig. 5 were subtracted from (a) and (b) (as for Fig. 2) and the resulting traces are shown (offset vertically for clarity) with the regions of deoxidation being indicated by the boxes. The two boxes are not only different in their size and position in relation to the *x* (temperature) scale but are also different in size on the *y*-(SPA signal) scale. The differences in thickness of oxide expected from the two exposure times are quite small. Exposure of clean GaAs surfaces for the lengths of time used in this experiment have previously been estimated as 6–7 Å (2 s) and 10–13 Å (overnight) [12]. Thus it seems that a relatively small increase in oxide thickness produces a relatively large difference in optical response on heating. We intend to confirm this sensitivity to oxide thickness by performing in situ observation of oxidation. The difference in deoxidation temperature with oxide thickness seen in Fig. 6 agrees with previous observations [13]. It may be that we have

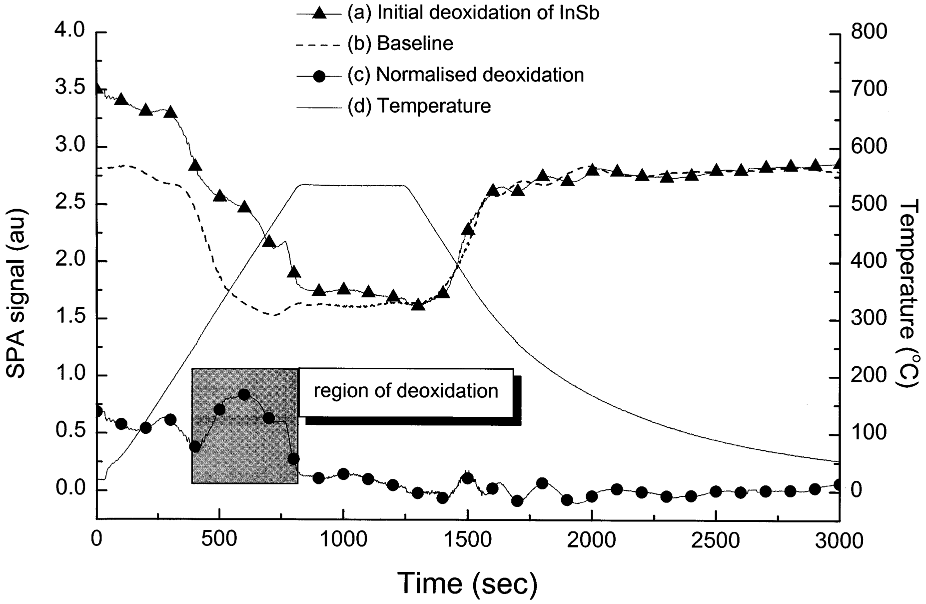

Fig. 4. Raw data and normalised traces for the optical response of an InSb substrate surface during heating and cooling.

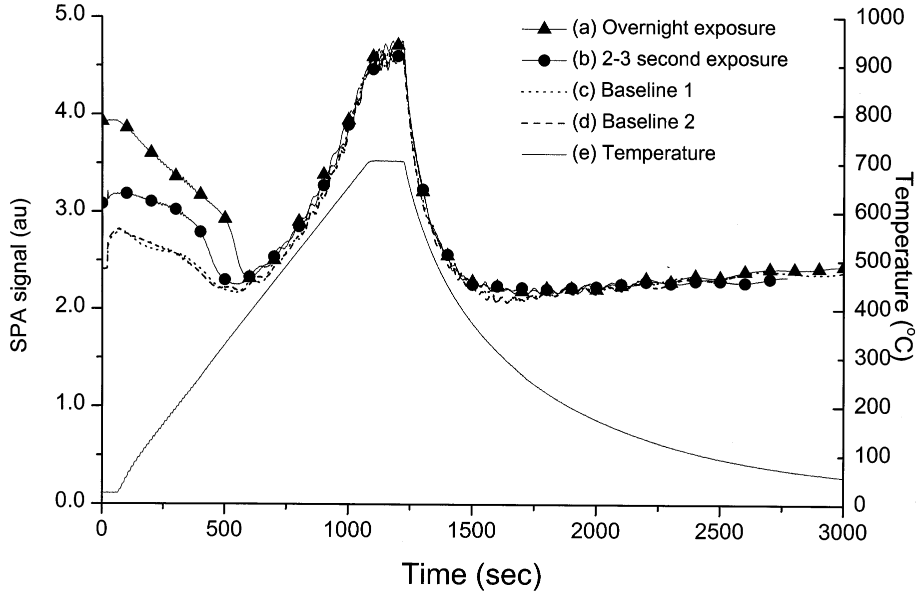

Fig. 5. Raw data for the optical response of a re-oxidised GaAs substrate surface during heating and cooling.

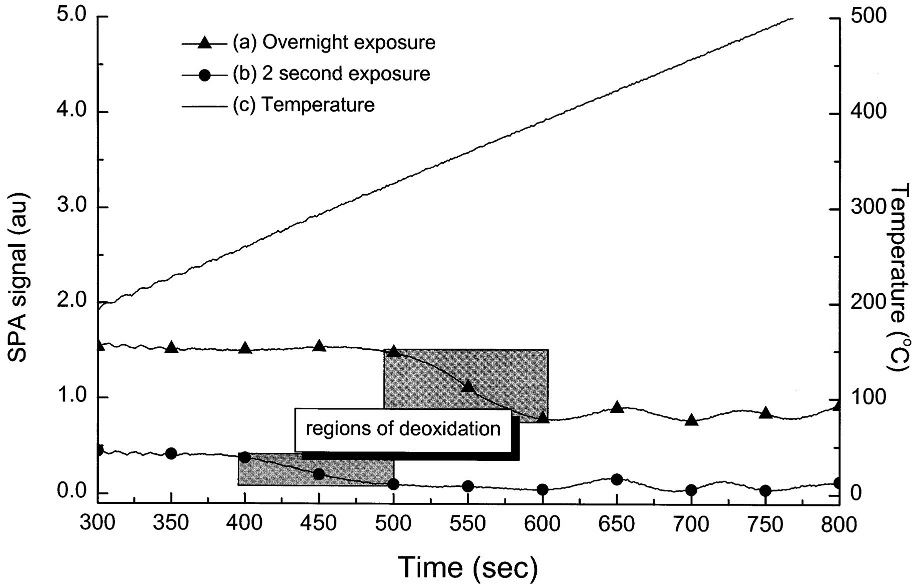

Fig. 6. Normalised traces for the optical response of a re-oxidised GaAs substrate surface during heating.

not observed this higher temperature deoxidation because our substrates are prepared by milder oxidative routes (especially when re-oxidised in air) compared to the conditions used when a high temperature (550–630°C) [1] is found to be needed for deoxidation. These observations show the necessity for close control of oxidation conditions if reproducible oxide desorption temperatures are to be obtained. This may also explain why a previous RAS [14] study reported a similar shaped optical transition but at a higher temperature range between 350 and 500°C when desorbing oxide from a GaAs substrate.

4. Conclusion

We have demonstrated, for the first time, the use of a simple optical technique (SPA) in atmospheric pressure MOVPE to identify temperatures associated with the deoxidation of both as-supplied and reoxidised III–V substrates. The technique shows a high level of reproducibility so that, even in this preliminary study, we have determined useful data for the MOVPE preparation of GaSb and InSb substrates. The importance of reproducible and controlled oxidation has been demonstrated by reoxidising a clean GaAs surface (for 2 s and overnight) resulting in different levels of optical signals and deoxidation temperatures.

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