

In-situ monitoring and analysis of GaSb(100) substrate deoxidation

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INTRODUCTION

Simple in-situ probing techniques, i.e. surface reflectance or photoabsorption have been introduced recently [1,2] for monitoring the deoxidation procedure for the GaSb(100) substrate. The latter is known to be critical for MOVPE growth. In this work we utilize surface sensitive in-situ reflectance anisotropy / difference spectroscopy (RAS/RDS) [3] that has been introduced recently also for commercial MOVPE reactors. The deoxidized substrates are characterized in addition with XPS and UPS to determine their chemical and electronic properties. The patented MOCVD–UHV transfer system is utilized here [4,5]. This additional information regarding electronic structure and chemical surface composition is essential for understanding the deoxidation process for GaSb.

Of the commercially available III–V substrates the Antimonides are most sensitive towards oxidation. Sublimation of antimony–oxides led to a porous oxide film that was approximately 100 nm thick and consisted primarily of Ga₂O₃ [6–9]. Even "Epi-ready" substrates were covered with oxide films of critical thickness. Since the Ga₂O₃–films have high desorption temperatures, i.e. between 580–640°C [10], etchants were regularly employed for removing this amorphous layer prior to epitaxy [11,12]. This additional step prevents surface decomposition by thermal deoxidation – especially when applying MBE.

MOVPE, in contrast, can utilize atomic hydrogen that is supplied by the common Sb–precursors to lower significantly the desorption temperature of Ga₂O₃ to about 400°C. The topmost Ga₂O₃ layer is reduced to Ga₂O. In a second step, this Ga₂O monolayer desorbs from the surface and exposes thereby a fresh layer of Ga₂O₃ to the reaction with atomic hydrogen [13]. Under these conditions it is interesting to clarify whether one can neglect the etching step and carry out the deoxidation step just by raising the temperature. This would eliminate a critical and expensive step in the production line.

EXPERIMENTAL DETAILS

All deoxidation experiments have been carried out with the GaSb(100) substrates mounted in a commercial AIXTRON" MOVPE–reactor (AIX–200) at a pressure of 100 mbar with H₂ as the ambient. Above 400°C the substrates were prevented from decomposition by an absolute TESb partial pressure of 7×10^{-4} mbar at a total flow of 5.5 l/min. Changes of the surface were monitored in-situ with RAS. Deoxidation was carried out between 475°–575°C. RAS signals showed the progress in deoxidation for different chemical pre-treatments, annealing temperatures, and annealing times. After deoxidation the samples were cooled down to 400°C under TESb–stabilization. Next, the TESb supply was switched off and the samples were either cooled down to ambient temperature in the reactor or were transferred into UHV utilizing the patented MOVPE–UHV transfer system [4]. After transfer the samples reached UHV–conditions ($p < 3 \times 10^{-10}$ mbar) within seconds. They were transferred into other UHV chambers for performing XPS and UPS measurements and thereby analyse the chemical and electronic properties of the deoxidised surface. "Epi-ready"–substrates and HCl–etched substrates [11,12] were used for the experiments. The HCl etching step consisted of a 5 min. bath in concentrated HCL (37%) removing the native oxide–layer. After etching the substrates were rinsed with iso–Propanol instead of H₂O to prevent rapid re–oxidation [2]. Within the next 5–10 minutes the substrates were brought into contact with an inert ambient inside of the MOCVD reactor or were transferred into a load lock chamber with UHV conditions.

RESULTS AND DISCUSSION

1) In-situ monitoring of the deoxidation step

"Epi-ready" substrates that were annealed without any chemical pre-treatment developed anisotropic, nanometer-scale 3D-structures during deoxidation. Formation of the latter was observed in-situ as a strong rise of the RAS signal during deoxidation (Fig.1). RAS enhancements can be ascribed to the formation of anisotropic 3D-structures on the surface [3]. The enhanced RAS signal vanished after deoxidation was complete. Deoxidized samples with stable RA spectra show a defect-free surface, (1x3)-reconstructed GaSb(100), with peak structures smaller than 6×10^{-3} RAS-units (Fig.2b).

HCl-etched substrates showed the following differences to "Epi-ready" substrates:

1. A slight enhancement of the RAS signal for the oxidized surface (Fig.2a). This originates from anisotropic vicinal surface mono-steps and bi-steps that are produced in the HCl etching [2,14].
2. RAS signals showed no enhancement for HCl-etched substrates during deoxidation (Fig.1).

It is known for GaAs that inhomogeneous oxide desorption can produce surface texture [10]. Such a texture can be found on "Epi-ready" substrates if the deoxidation process is stopped in the region of RAS-enhancement (Fig.3). This effect enables one to monitor the desorption of the oxide layer via the RAS signal. When deoxidation is completed "Epi-ready" and HCl-etched substrates show identical RAS spectra (Fig.2b).

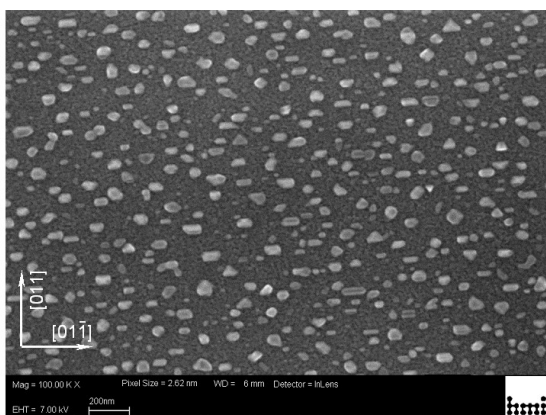


Fig.3 SEM image of the anisotropic surface at maximum RAS enhancement. 3D-structures have heights between 10-30 nm as measured by AFM (not shown here).

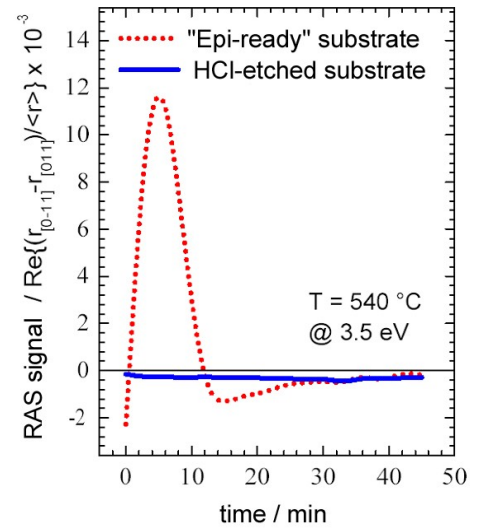


Fig.1 Thermal deoxidation of „Epi-ready“ GaSb(100) substrates shows a strong modulation of the RAS signal around 3.5 eV in the absence of a pre-etch with HCl.

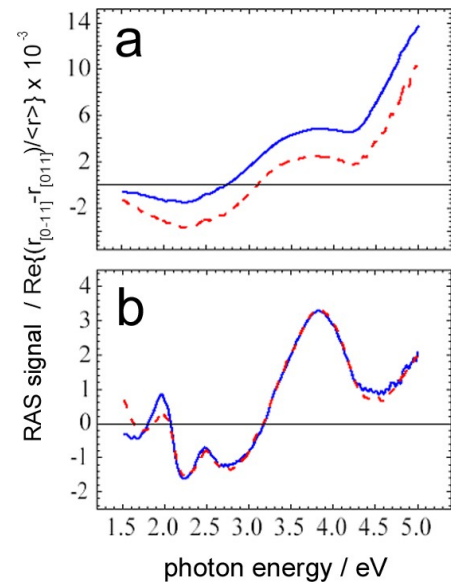


Fig.2 In-situ RA-spectra of oxidized (a) and deoxidized (b) "Epi-ready" and HCl-etched substrates. Note that HCl-etched substrates show an enhancement of the RAS signal prior to deoxidation (a). After deoxidation both substrates show identical RAS spectra (b).

II) Deoxidation at different temperatures

"Epi-ready" substrates were deoxidized at different temperatures and monitored by RAS. Each spectrum was an average and was normalized (Fig.4) and the spectra were compared for different substrates and temperatures. In this representation stable RAS spectra have constant values. The spectra of the deoxidized surface corresponds to $\Delta RAS = 0$. One can see now the enhancement arising due to anisotropic 3D-structures that were formed during deoxidation at different annealing temperatures. At a temperature of 575°C no more enhancement can be detected. The rate of reaching the maximum RAS enhancement showed an exponential increase with the annealing temperature. The deoxidation process for GaSb(100) is thermally activated (Fig.5).

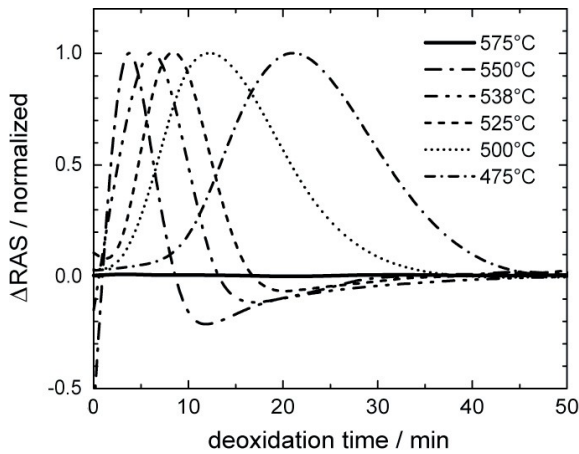


Fig.4 Modulation in RA-spectra due to the formation of anisotropic 3D-structures on the substrate surface at different temperatures. RAS spectra of deoxidized GaSb-surface correspond to $\Delta RAS = 0$.

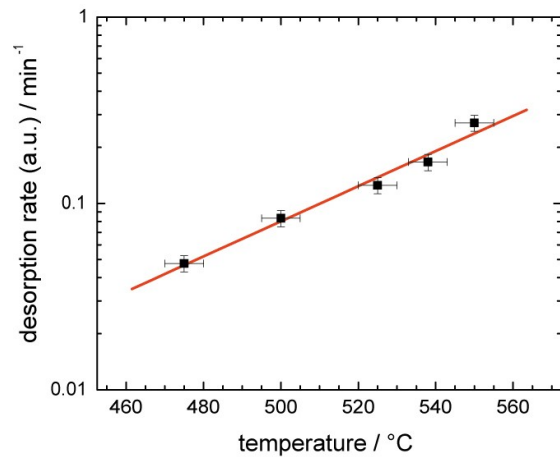


Fig.5 The oxide desorption rate follows the rise of RAS enhancements with an exponential dependence.

III) Chemical and electronic properties of the surfaces

Different surfaces of the substrates were investigated with UPS and XPS spectroscopy. The chemical surface compositions were analysed with XPS (Table in Fig.6) and agreed with the chemical depth profiles of thermal GaSb oxides [8,9].

Surface	Sb-oxide	Ga-oxide	GaSb (substrate)	Sb (elementary)
"Epi-ready" oxidized (A)	Sb ₂ O ₅	Ga ₂ O ₃	few	/
HCl-etched oxidized (a)	Sb ₂ O ₄ *	residuals of Ga ₂ O ₃	yes	/
"Epi-ready" partial deoxidized (B)	not clarified**	Ga ₂ O ₃	yes	/
"Epi-ready" / HCl-etched complete deoxidized (C,b)	/	/	yes	yes

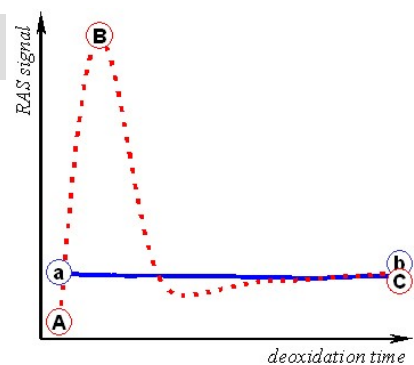


Fig.6 XPS characterization of different surfaces for deoxidation of GaSb(100).

Two results require further explanation:

* Etched GaSb(100) shows a top layer of Sb₂O₄ – XPS measurements on Sb powder [15] suggest this to be the contact layer between oxygen and GaSb and the starting point for GaSb-oxidation.

** No identification of Sb-oxides on partially deoxidized "Epi-ready" substrates due to rough surface morphology.

With the deoxidation step completed no difference between "Epi-ready" and HCl-etched substrates was detectable within the accuracy limits.

UPS spectra for completely deoxidized "Epi-ready" and HCl-etched substrates showed also identical Fermi energies and work functions. The surfaces were free of oxygen and carbon for both the substrates. The UPS spectra were clearly structured and showed sharp peaks at same energies especially for the higher valence bands.

SUMMARY

The deoxidation process of "Epi-ready" and HCl-etched substrates was investigated under MOVPE conditions. "Epi-ready" substrates showed a thermally-activated oxide desorption process that was monitored with RAS. After complete deoxidation no major difference in RAS, XPS and UPS spectra was detected between "Epi-ready" and HCl-etched substrates.

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