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Growth monitoring of GaAsSb:C/InP heterostructures with reflectance anisotropy spectroscopy

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Abstract

Using time-resolved reflectance anisotropy spectroscopy (RAS) we studied in situ the dynamics of surface processes of Sb-covered GaAs(1 0 0) and InP(1 0 0) under metalorganic vapour-phase epitaxy conditions. Both Sb removal during a hydride purge and Sb incorporation during GaAs and InP overgrowth were monitored enabling the investigation of group V exchange reactions.

Sb surface layers are found to be much more stable during purge with PH_3 as compared to AsH_3. Estimated activation energies are 2.5 eV for the Sb–P exchange processes and 1.1 eV for the Sb–As exchange reactions. These values reflect the low volatility of Sb compared to other group V adsorbates. During InP overgrowth Sb is rapidly buried at temperatures of 510 °C and below while it is rather persistent on the surface at temperatures of 550 °C and above. This transition indicates the existence of a highly mobile quasi-liquid InSb surface layer at temperatures above its melting point (~525 °C).

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Keywords: A1. Reflection anisotropy spectroscopy; A1. Segregation; A3. Metalorganic vapour-phase epitaxy; B1. Antimonides

1. Introduction

Recently, the $GaAs_{0.5}Sb_{0.5}$/InP material system has received increasing attention since it is a promising alternative to $Ga_{0.47}In_{0.53}As$/InP for double heterojunction bipolar transistors (DHBTs) [1]. The preferable band alignment and the better feasibility of carbon doping in GaAsSb in comparison to $Ga_{0.47}In_{0.53}As$ as the DHBT base layer are important advantages [2]. In particular, the reported absence of significant hydrogen-related passivation effects of the carbon acceptors in $GaAs_{0.5}Sb_{0.5}$:C is very promising and another potential advantage over $Ga_{0.47}In_{0.53}As$ [3].

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Epitaxial growth of $GaAs_{0.5}Sb_{0.5}$ is challenging due to the fact that there is a miscibility gap at usual MOVPE growth temperatures [4]. However, it has been demonstrated that it is possible to grow metastable $GaAs_ySb_{1-y}$ alloys within a large range of solid compositions by using V/III ratios around unity. In that case, the depletion of group V elements on the growing surface prevents the redistribution of the As and Sb atoms into GaAs- and GaSb-rich areas [5].

Another Sb-related problem is that Sb tends to segregate on the growing surface due to its large atomic radius. While literature deals mainly with Sb segregation in GaAs-based heterostructures [6,9] Sb segregation into InP layers is of prominent interest for high-speed transistor applications. Additional to segregation effects, all lattice constituents have to be switched at a $GaAs_{0.5}Sb_{0.5}$/InP heterojunction which makes the formation of an abrupt interface difficult. In DHBTs a highly mismatched interfacial layer at the emitter-base junction can lead to significant recombination losses and degrading device performance. The Sb-related growth challenges addressed up to now underline the necessity for an in situ measurement method enabling direct investigation of interface formation.

Reflectance anisotropy spectroscopy (RAS) is one of the most surface-sensitive methods for in situ monitoring of epitaxial growth. The characterization of the uppermost atomic layers involving bond symmetries and properties of adsorbates allows for a direct study of surface and interface characteristics. Only few reports about RAS studies of Sb-related MOVPE growth can be found in the literature [6–10]. Pitts et al. presented results of an Sb-rich floating layer during the growth of GaAs on GaSb [6]. Wang et al. reported on very persistent Sb surface layers on InP compared to As-terminated InP surfaces [8].

We used time-resolved RAS to study the exchange reaction of Sb with As as well as P in dependence on growth temperature and hydride purge time. Furthermore the Sb incorporation during GaAs or InP overgrowth at growth temperatures between 475 and 600 °C is compared. Since carbon doping of $GaAs_{0.5}Sb_{0.5}$ is not as restricted to low growth temperatures as of $Ga_{0.47}In_{0.53}As$ [2], temperature is an additional parameter in growth optimization with regard to segregation and memory effects.

We present results indicating that Sb segregation into InP is strongly enhanced at temperatures of 550 °C and above. The existence of a highly mobile quasi-liquid InSb surface layer at temperatures exceeding its melting point of 525 °C is proposed.

Structural information about an interfacial layer at the GaAsSb/InP interface in a multiple quantum well structure is given by analysing high-resolution X-ray diffraction (HRXRD) measurements.

2. Experimental

Growth was carried out in an AIX 200/4 low-pressure MOVPE system on semi-insulating InP(0 0 1) substrates with a mis-orientation of 2° toward ⟨110⟩. The growth was performed at low pressure (100 hPa) using hydrogen carrier gas. The sources used were the trimethyl-compounds of gallium, indium and antimony (TMGa, TMIn, TMSb), arsine (AsH_3), and phosphine (PH_3). CBr_4 was used for p-type doping.

The MOVPE system is equipped with a purged low-strain UV transparent viewport for normal incidence optical access. In situ measurements were performed using a LayTec EpiRas-200 spectrometer that allows RAS and reflectance measurements under standard growth conditions [11]. For simplicity reasons, RAS was measured on non-rotating samples. HRXRD was measured with a Philips MRD diffractometer. Rocking curve simulations based on the dynamic Takagi–Taupin formalism were done with the Philips X'Pert software version 3.0.

3. Results and discussion

RAS spectra of InP(0 0 1) surfaces during growth and within a growth interruption under PH_3 stabilization are shown in Fig. 1. The principal characteristic is a positive peak at around

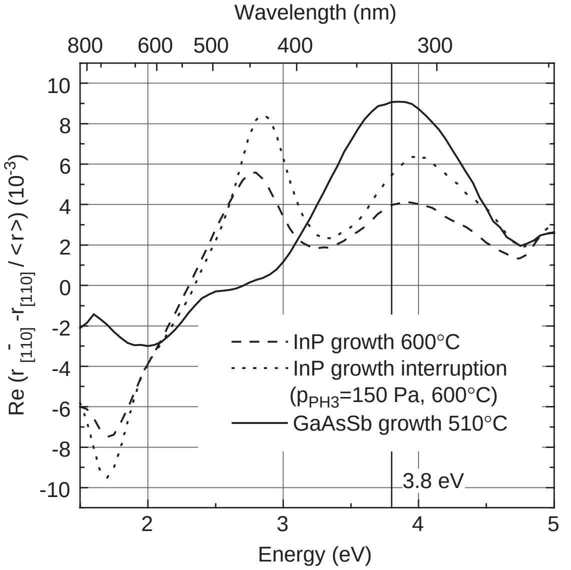

Fig. 1. RAS spectra of the InP(1 0 0) surface during growth and within a growth interruption with PH_3 stabilization compared to a GaAsSb spectrum during growth.

2.8 eV which has been assigned to P dimers oriented along the $[\bar{1}\,1\,0]$ direction [13]. A phosphorus-rich surface reconstruction with a (2×1) symmetry for the P-stabilized InP(1 0 0) surface exhibits a higher amplitude at 2.8 eV compared to a less-phosphorus-rich surface reconstruction during InP growth (Fig. 1).

All GaAsSb spectra we have observed were dominated by a broad positive feature at around 3.8 eV similar to published spectra [6,7]. A typical spectrum during growth of GaAsSb:C is shown in Fig. 1. Since the general shape of these RAS spectra is similar for InP or GaAs contaminated with residual Sb [8,9] and also GaSb [6,7,10,12], the 3.8 eV peak is related to the presence of Sb on the surface. Published RAS spectra during TMSb exposure of InP [8] as well as our own results clearly show a stronger change of the RAS signal at 3.8 eV compared to the P-dimer-related 2.8 eV peak. Therefore, a dynamic study of Sb surface coverages including exchange and interface formation processes is possible by time-resolved RAS measurements at 3.8 eV. This high energy value also results in a reduced light penetration depth further improving the surface sensitivity of the RAS measurement.

In a first experiment, the influence of purging an Sb-covered GaAs or InP surface with either AsH_3 or PH_3 at different temperatures was investigated. The Sb coverage was generated by a 2 min purge with TMSb at a partial pressure of 0.9 Pa in all experiments. Partial pressures of AsH_3 and PH_3 during purging were 91 and 227 Pa, respectively. The RAS transients at 3.8 eV for GaAs are shown in Fig. 2a. The 3.8 eV signal increased rapidly after switching on the TMSb and then reached a stationary level. Only at the lowest temperature (475 °C) a noticeable delay in Sb deposition was observed, probably due to the incomplete TMSb decomposition.

After switching off TMSb the transients exhibit an exponential-like decay monitoring Sb removal from the surface, a process which is more efficient at higher temperatures (Fig. 2a). At 600 °C, AsH_3 supply for approximately 30 s was sufficient to change the surface from Sb-rich to As-terminated. Here and in the following experiments, RAS spectra measured at the end of the particular purge or growth step confirmed the re-establishment of Sb-free GaAs or InP surfaces. The temperature dependence of the Sb–As exchange processes has been analysed by determining the initial slope of RAS signal decay. The estimated activation energy for the Sb–As exchange is 1.1 eV (see the Arrhenius plot in Fig. 3). It should be noted that this activation energy describes not surface exchange reactions alone, but also includes precursor decomposition and desorption processes.

The time dependence of the RAS transient was quite different for the PH_3 purge of the Sb-covered InP surface (Fig. 2b). Besides the significantly longer times needed for Sb removal compared to AsH_3, the decay exhibits a distinct plateau region where the Sb desorption nearly stops. One can speculate that the plateau region during the Sb–P exchange represents a transition from Sb desorption supplied from excess Sb on the surface to a relatively stable thin In–Sb surface layer. This would imply that the Sb–Sb bond energy is lower compared to In–Sb. Again the initial slope of the transient (time interval between 340 and 360 s) has

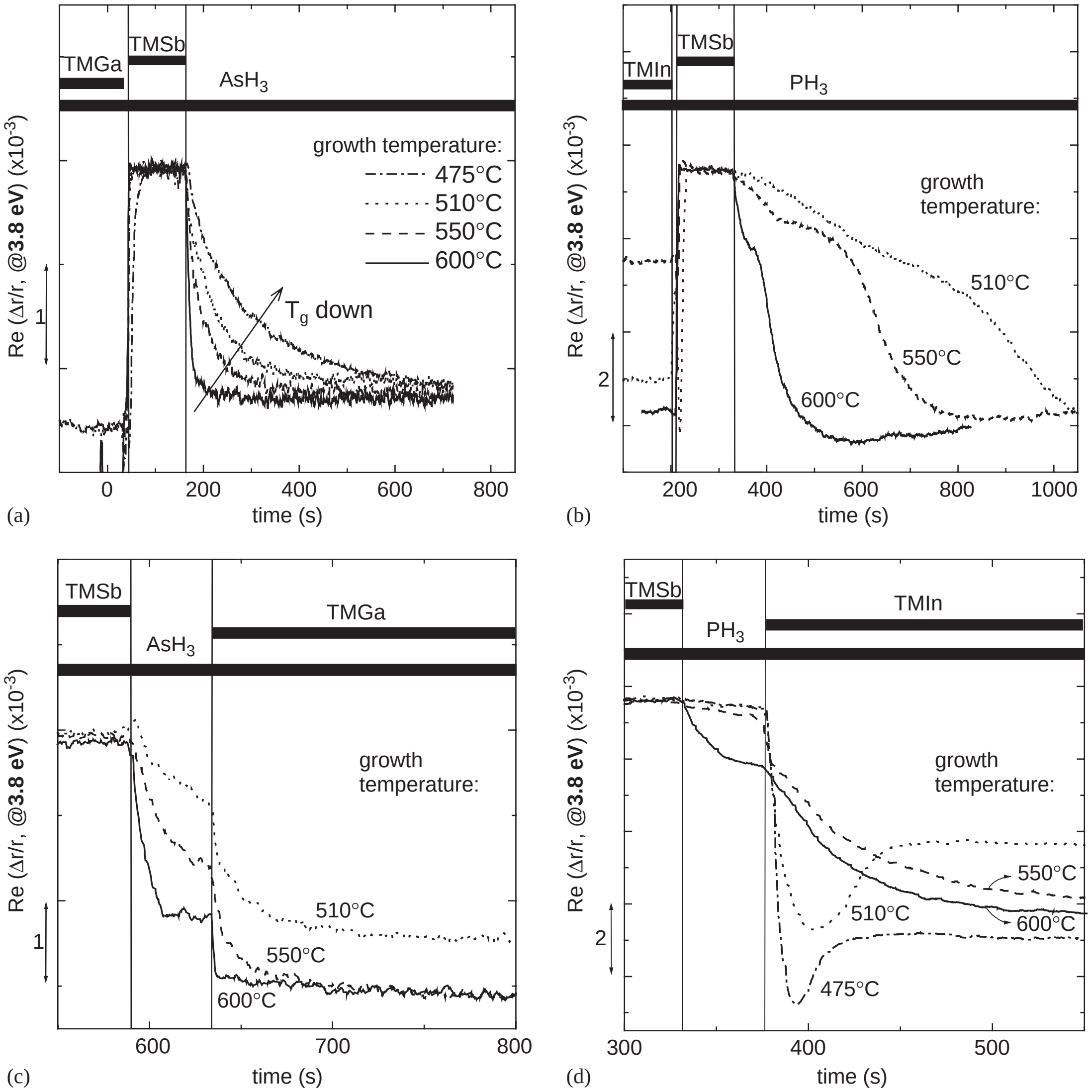

Fig. 2. Time-resolved RAS measurements (3.8 eV) for GaAs (a,c) and InP (b,d) surfaces during hydride purge and overgrowth. The upper pictures (a,b) show RAS transients during a long purge with (a) AsH_3 ($p = 91$ Pa) or (b) PH_3 ($p = 227$ Pa). The lower viewgraphs (c,d) show RAS transients during GaAs (c) and InP (d) overgrowth after a 45 s hydride purge. Transients are offset vertically for clarity.

been used to estimate the activation energy of the Sb–P exchange processes (Fig. 3). The determined 2.5 eV are a measure for the persistence of the Sb coverage during PH_3 purge. The large difference between the Sb–As and Sb–P reactions may also be related to a less efficient pyrolysis of PH_3 compared to AsH_3, which is probably not balanced by the higher PH_3 input partial pressure. Also, different bond strengths of Ga–Sb and In–Sb would influence the surface processes that have been investigated. Similar in situ studies of exchange reactions of As by P on GaAs and P by As on InP were done by Jönsson et al. [14] and Zorn [15], respectively. The calculated activation

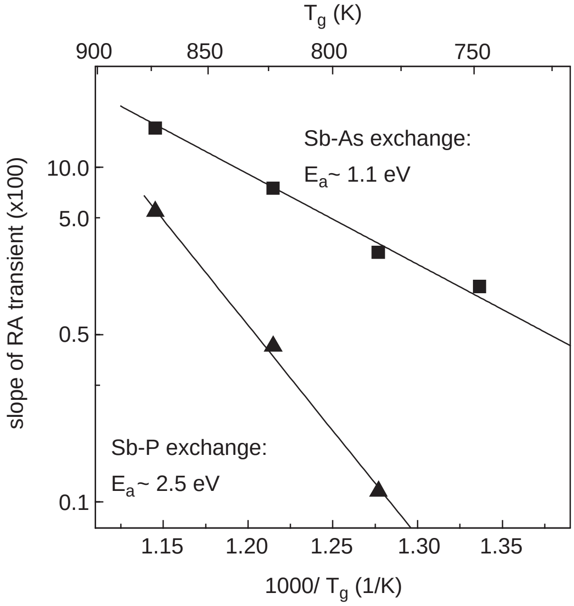

Fig. 3. Arrhenius plot of the initial slope of RAS transients during AsH_3 and PH_3 exposure of Sb-covered GaAs and InP surfaces. The respective transients are shown in Fig. 2a and b. The slopes are taken at times between 167 and 180 s in the GaAs–Sb transient (Fig. 2a) and between 340 and 360 s in the InP–Sb transient (Fig. 2b).

energies were 0.8 eV for the P–As exchange reaction and 1.64 eV for the As–P exchange by exposing GaAs to PH_3. The higher values found for the Sb–As and Sb–P exchange processes could be explained by the lower volatility of Sb in comparison to As and P.

In a second set of experiments, the Sb-covered surface was purged with AsH_3 or PH_3 for 45 s. Then GaAs and InP growth was continued. The corresponding RAS transients for different growth temperatures are shown in Fig. 2c and d for GaAs and InP, respectively.

By switching on the TMGa to grow GaAs, the decay of the RAS signal at 3.8 eV became steeper, indicating a faster Sb incorporation compared to the Sb removal during AsH_3 purge. SIMS measurements confirm the incorporation of Sb over several tens of nanometers at $T_g = 510\,^\circ C$ and $T_g = 550\,^\circ C$. In our study, no clear dependence of segregation length on growth temperature was observed. The findings of Pitts et al. [6] that Sb acts as an increasingly perfect surfactant at higher temperatures could not be confirmed. SIMS measurements showed that no significant Sb incorporation occurred at 600 °C, which agrees with the RAS decay showing that Sb is already removed during the preceding purge step of 45 s.

Fig. 2d compares the RAS transients of InP overgrowth at different temperatures. In the lower temperature range ($T_g \leqslant 510\,^\circ C$) the RAS signal decreased rather quickly indicating a fast incorporation of the residual Sb. The Sb segregation length is smaller for the lower temperature (475 °C).

A remarkable change of the transients could be observed at growth temperatures above 510 °C. Here, the RAS signal exhibits a slow monotonous decay monitoring a very persistant Sb surface coverage. The remarkable change of the transients between 510 and 550 °C is an indication for an existing InSb surface layer. We suppose that this surface layer changes its properties due to melting at around 525 °C [16]. The formation of a highly mobile quasi-liquid InSb surface layer at temperatures above 525 °C explains a strongly enhanced Sb segregation, which is confirmed by SIMS measurements. Significant amounts of Sb were detected by SIMS even after 100 nm InP overgrowth.

From the presented results it can be concluded that a reduced Sb carry-over into InP requires growth temperatures lower than approximately 525 °C. However, at those low temperatures rather long AsH_3 purge times are necessary in order to remove excessive Sb from the GaAsSb surface.

To investigate this, GaAsSb:C/InP multiple quantum well structures were grown at a temperature of 510 °C comparing AsH_3 purge times of 10 and 120 s. Fig. 4a presents the RAS transients at 3.8 eV for both cases (straight line: 10 s AsH_3 purge; dashed line: 120 s AsH_3 purge). The very similar shape of the transients of different MQW periods confirms the reproducibility of the growth sequence. However, the transient detail shown reveals a faster decrease of the RAS signal during InP well growth after the long hydride purge. This indicates a reduced Sb incorporation in the InP layer which is confirmed by HRXRD measurement.

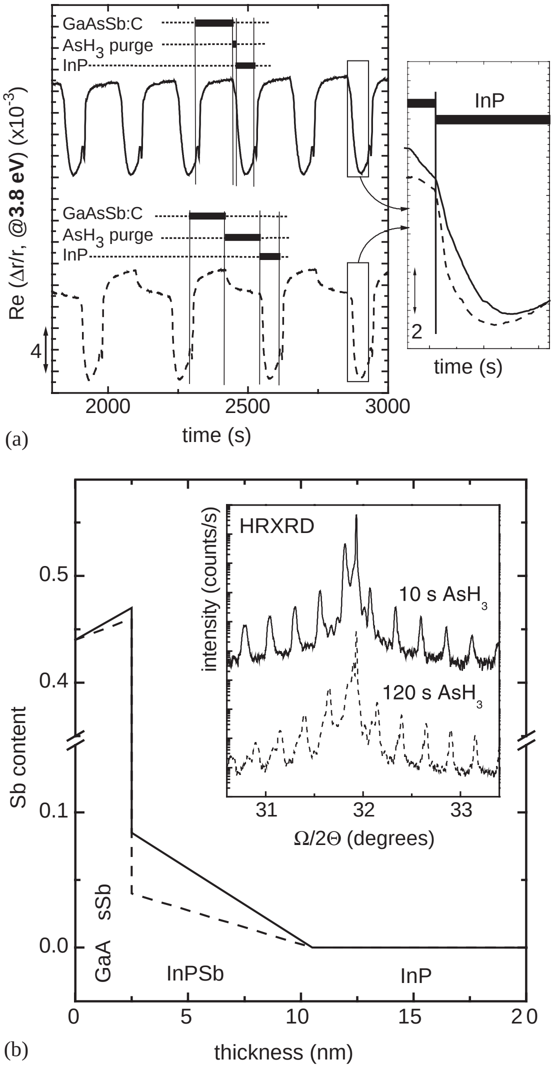

Fig. 4. (a) RAS transients at 3.8 eV of 15 × GaAsSb:C/InP MQW structures employing AsH_3 purge times of 10 s (straight line) and 120 s (dashed line) after GaAsSb growth. On the right side a magnified part of the transients shows distinct differences in the slope during InP barrier growth. (b) Sb content in the GaAsSb/InP MQW structure as obtained by fitting HRXRD measurements with simulated rocking curves. The simulation assumes a graded 8 nm thick InPSb interfacial layer with either 8% or 4% Sb on the side of GaAsSb for the 10 s (straight line) and 120 s AsH_3 purge (dashed line), respectively. Measured rocking curves of both MQW structures are shown in the inset.

The Sb content in the GaAsSb:C/InP MQW structure as obtained by simulation of HRXRD rocking curves is shown in Fig. 4b. Measured rocking curves of both MQW structures are shown in the inset. To simulate the rocking curves reasonably, a graded 8 nm thick InPSb interfacial layer had to be introduced. A concentration of 8% Sb on the side of $GaAs_{0.54}Sb_{0.46}$ and pure InP on the opposing side are assumed for the sample with the 10 s long AsH_3 purge. The simulation of the HRXRD measurement of the sample with the long AsH_3 purge indicates that the Sb concentration is reduced to 4% over the same grading length. The extracted thickness of the InPSb layer is nearly half of the overall InP thickness (18 nm). This agrees well with the appearance of the RAS transient minimum within the InP growth step (Fig. 4a, detail), demonstrating a good correlation of in situ and ex situ measurement.

4. Summary

In this work, time-resolved RAS measurements were used to study the dynamics of Sb surface coverages during hydride purge and overgrowth in dependence on temperature. The RAS signal at 3.8 eV was utilized to investigate Sb–P und Sb–As exchange reactions on InP and GaAs. AsH_3 purging of Sb-covered GaAs is more efficient at higher temperatures. PH_3 purging of InP–Sb is characterized by an unusual non-monotonic transient RAS signal. Activation energies of 1.1 eV (Sb–As) and 2.5 eV (Sb–P) were determined for the overall exchange processes including source pyrolysis, exchange on the surface and desorption. These values are higher than those reported for As–P exchange which points to the persistence of an Sb coverage on GaAs and InP surfaces.

An enhanced Sb segregation into InP at temperatures of 550 °C and above is found. We assume that this is related to a highly mobile quasi-liquid InSb surface layer at temperatures exceeding the InSb melting point of 525 °C.

Structural properties of GaAsSb:C/InP MQW structures grown at 510 °C are presented. A prolonged AsH_3 purge time after growth of the GaAsSb:C results in a reduced Sb concentration of approximately 4% in an 8 nm thick graded interfacial InPSb layer.

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