In situ study of Ge(100) surfaces with tertiarybutylphosphine supply in vapor phase epitaxy ambient

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A B S T R A C T

GaInP nucleation on Ge(100) often starts by annealing of the Ge(100) substrates under supply of phosphorus precursors. However, the influence on the Ge surface is not well understood. Here, we studied vicinal Ge(100) surfaces annealed under tertiarybutylphosphine (TBP) supply in MOVPE by *in situ* reflection anisotropy spectroscopy (RAS), X-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED). While XPS reveals a P termination and the presence of carbon on the Ge surface, LEED patterns indicate a disordered surface probably due to by-products of the TBP pyrolysis. However, the TBP annealed Ge(100) surface exhibits a characteristic RA spectrum, which is related to the P termination. RAS allows us to *in situ* control phosphorus desorption dependent on temperature.

1. Introduction

Ge(100) substrates are industrially relevant for several electronic applications, such as III–V based multi-junction solar cells grown by metal organic vapor phase epitaxy (MOVPE) [1]. A suitable Ge(100) surface preparation prior to heteroepitaxy is an important requirement for achieving low defect densities in the grown III–V epilayers, which directly affects device quality. Therefore, characterization of the structural and chemical properties of Ge(100) surfaces in vapor phase epitaxy (VPE) ambient is needed. However, the process gas limits the direct access to surface analysis. On that account, most knowledge about Ge(100) comes from surface science studies in ultra-high vacuum (UHV).

The Ge(100) surface atoms form dimers exhibiting a (2×1) or a buckled $c(4\times2)/p(2\times2)$ surface reconstruction [2]. Nearly exact Ge(100) substrates feature mutually perpendicularly oriented dimers on adjacent terraces separated by single layer steps. Vicinal Ge(100) surfaces with offcuts larger than 5° towards the [011] direction form double layer steps in D_B configuration which results in a single domain surface with all dimers on the terraces oriented parallel to the step edges [3,4].

Surface preparation of substrates in MOVPE ambient generally begins with a high temperature annealing in H_2 to remove oxides and other contamination. We have shown [5] that H_2 annealing of "epiready" vicinal Ge(100) substrates in VPE ambient leads to a monohydride terminated surface free of oxides and carbon. Furthermore, the Ge(100) surfaces show a predominant (2×1) surface reconstruction and D_B steps.

The growth of a high quality III–V nucleation layer usually begins with exposure of the Ge(100) surface to group V precursors after high temperature annealing [6–9]. Particularly, P termination of the Ge surface should be obtained prior to nucleation for state-of-the-art GaInP on Ge heteroepitaxy in MOVPE [10,11]. Phosphine (PH_3) and tertiarybutylphosphine (TBP) are nowadays the two main P precursors used in MOVPE systems. Ge surfaces annealed under PH_3 feature P saturation to about one atomic layer at 573–720 K in low pressure CVD systems [12]. Low energy electron diffraction (LEED) analysis of a P-terminated Ge(100) surface with 2° offcut prepared by PH_3 exposure in MOVPE ambient shows a (9×2) surface reconstruction [10]. In contrast to AsH_3, PH_3 does not etch the Ge surface [13]. However, the influence of annealing under TBP on the Ge(100) surface is still not clear.

Reflection anisotropy spectroscopy (RAS) enables *in situ* characterization of surfaces during MOVPE processing [14,15]. Defined by

$$\frac{\Delta r}{r} = 2\frac{r_{[0\bar{1}1]} - r_{[011]}}{r_{[0\bar{1}1]} + r_{[011]}},$$

RAS measures the real part of the normalized difference of the reflection of light polarized in two perpendicular directions of the surface in normal incidence geometry. In crystals with cubic

symmetry, the bulk does not contribute to the signal, so that RAS may be applied as a surface sensitive *in situ* monitoring tool [16]. Regarding Ge(100) surfaces, the clean [17] and monohydride terminated [5] vicinal Ge(100) surfaces exhibit characteristic RA spectra.

In this paper, we employ RAS for *in situ* analysis of TBP annealed vicinal Ge(100) surfaces prepared in MOVPE and correlate the spectra observed with results of X-ray photoemission spectroscopy (XPS) and LEED.

2. Experimental

We used Ge(100) substrates with a misorientation of 6° towards the [011] direction without any additional wet chemical pre-cleaning. Substrate preparation was carried out in an Aixtron AIX-200 MOVPE reactor. Reactor parts (liner, susceptor) and sample carriers were cleaned of III–V residues to avoid unintentional contaminations of the samples. The reactor is equipped with an *in situ* RA spectrometer (LayTec EpiRAS 200). The RA spectra are baseline corrected to avoid anisotropies originating from the viewport window [16]. A dedicated MOVPE-to-UHV sample transfer system [18] enabled XPS (Specs Focus 500 and Phoibos 100) and LEED (Specs ErLEED 100-A) measurements. XP spectra were analyzed using the CASAXPS commercial software [19]. The surface preparation consists of a 20-minute long annealing step at 1000 K at 100 mbar under 5500 l/min of H_2 to remove oxides and other contamination. Subsequently, we anneal the sample under 1.03×10^{-4} mol/min of TBP at 920 K for 5 min. Afterwards the sample was cooled down to 570 K, at which point the TBP flow was switched off.

3. Results and discussion

In order to evaluate the effect of TBP annealing on the Ge(100) surface, the characterization of the clean and monohydride terminated Ge(100) surfaces is included as a reference for direct comparison. Fig. 1 shows the characteristic RA spectra of a monohydride terminated (thin red line), a clean (broken gray line), and a TBP annealed (thick black line) vicinal Ge(100) surface. The RA spectrum of the monohydride terminated surface consists of a broad minimum at around 3 eV and a narrow one at 1.9 eV as well as local maxima around the critical point (CP) energies of Ge(100) (E_1 and $E_1+\Delta_1$ at about 2.2 eV and E_2 at 4.3 eV) [5]. If we further anneal the monohydride terminated surface under N_2 at 570 K and then cool down again to RT, a slightly different RA spectrum (broken gray line) evolves. While the shape of the spectrum is similar, the characteristic features at 1.9 eV and 3 eV present lower intensities and are slightly shifted towards lower energies. The spectrum is similar to RA spectra of UHV prepared vicinal Ge(100) surfaces [17,20], thus indicating a H-free surface. After exposure to TBP as described above, the RA spectrum of the Ge(100) surface at RT (Fig. 1, black line) consists of a broad negative minimum at 2.3 eV (matching the Ge(100) $E_1+\Delta_1$ critical point), a broad positive maximum at 3.7 eV and a shoulder at 1.9 eV.

We carried out XPS and LEED measurements to explore the chemical configuration and reconstruction of the surface after annealing in TBP. Fig. 2(c)–(e) shows XP spectra in the range of the Ge $2p_{3/2}$, P 2p and C 1s photoemission lines of the Ge(100) substrate after annealing in H_2 (red line) and exposure to TBP (black line). The influence of band bending was corrected in the XPS data by matching the energetic positions of the elemental Ge photoemission (PE) signals between the samples [21]. For easier viewing, we add an offset to separate both XP spectra. After H_2 annealing, we detect neither C (Fig. 2e) nor any contributions related to oxygen or oxides (Fig. 2c). The reader is referred to Ref. [5] for further details. After annealing under TBP, a shoulder at 129 eV, matching the P 2p line, confirms the presence of P (Fig. 2d). The deconvolution of the P 2p XP spectra (Fig. 2d) enabled the determination of the intensities related to the P 2p, Ge $3p_{1/2}$ and Ge $3p_{3/2}$ peak. Moreover, we measured C on the surface (Fig. 2e, black line). Since C was absent after H_2 annealing [5], the C contamination probably comes from a by-product from the pyrolysis of the metalorganic source. Neither traces of As, Ga nor other elements typically found in a MOVPE ambient were detected after TBP annealing. The peak intensity of the Ge $2p_{3/2}$ peak is significantly reduced after the annealing procedure in TBP compared to the H_2 annealed surface (Fig. 2c) due to coverage of the surface by P and C. From the attenuation of the signal intensity of the TBP annealed sample, we roughly estimated the

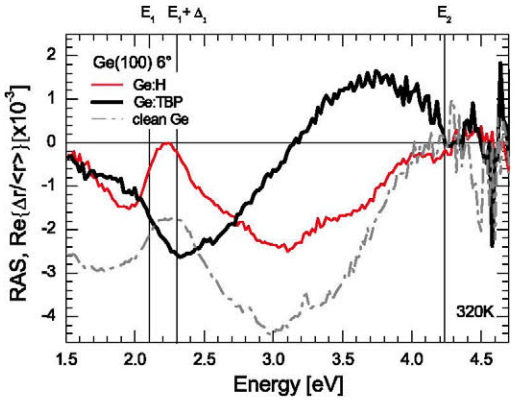

Fig. 1. *In situ* RA spectra of monohydride terminated (thin red line), clean (broken gray line) and TBP annealed (thick black line) Ge(100) with 6° miscut in [011] measured at 320 K in H_2 ambient. Vertical lines indicate the critical points energies of Ge(100). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

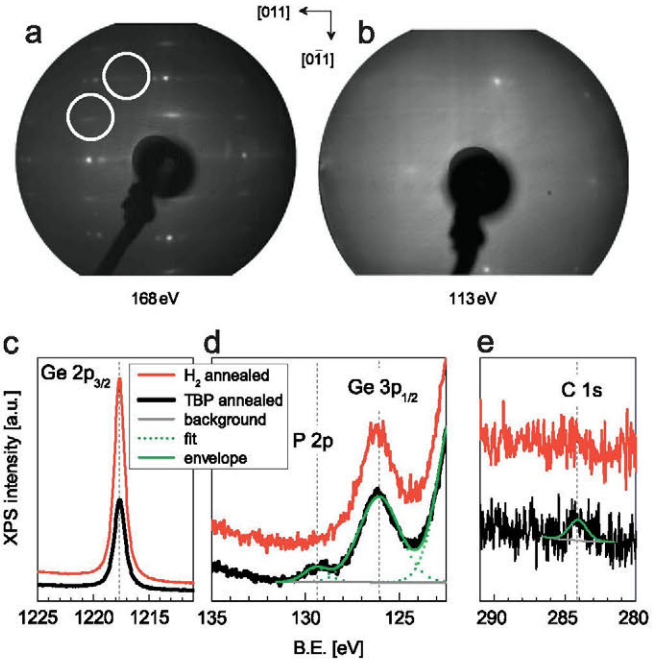

Fig. 2. LEED patterns of the Ge(100) surface after H_2 (a) and TBP annealing (b) as well as XPS measurements of the Ge(100) surface after H_2 annealing (red) and TBP annealing (black) in the range of the Ge $2p_{3/2}$ (c), P 2p (d) and C 1s (e) PE line. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

thickness of the coverage by applying a simple two-layer model. If we assume that the upper layer absorbs intensity according to the Beer–Lambert law and an electron mean free path of 9 Å is considered in that energy range [22,23], we can determine a layer thickness of about 3.3 Å containing P and C. In addition to this, from the intensity ratio P 2p/Ge 3p we estimated a coverage of the TBP annealed Ge surface of about 2.1 Å equivalent to 1.5 monolayers (ML) of P using the same model and assumptions as above and an electron mean free path of 29 Å according to the different energy range [22,23]. Regarding C, it is difficult to quantify its amount due to the low and noisy C 1s signal measured. According to Shimamune [12], P termination prepared in UHV is self-limited to 1 ML. However, dissociation of TBP as well as adsorption and desorption of P can include certain quantities of excess P atoms [24].

The LEED pattern of the monohydride Ge(100) surface (Fig. 2a) shows half-ordered spots along the [0$\bar{1}$1] direction and spot splitting along the [011] direction, which indicates a predominant (2×1) surface reconstruction with D_B steps and terraces of equal width, respectively [5]. On the contrary, for the TBP annealed Ge surface (Fig. 2b) we observe a (1×1) LEED pattern with a high background, which indicates a disordered surface. According to the literature, the P-terminated Ge(100) surface with 2° offcut shows a (9×2) surface reconstruction [10]. Since our XPS analysis confirms the presence of C and more than one ML of P on the Ge surface, we assume that the high background in the LEED pattern is related to the presence of excess of P and TBP by-products on the surface. Surface disorder caused by excess of P and TBP by-products has been reported in other material systems such as P-rich GaP(100) surfaces [25]. Despite the observation of a disordered surface indicated by the LEED pattern, we do obtain a different and characteristic RA signal when annealing under TBP, indicating at least some degree of ordered anisotropic structures on the Ge surface. In general, differences in the atomic order of probed (100) surfaces -such as cleanliness, surface reconstruction and chemical configuration- affect shape and amplitude of RA spectra [26]. Considering that (1) P induces changes on the surface reconstruction [10]; (2) the thickness estimation for the P coverage from XPS measurements is more than 1 ML of P; and (3) carbon [20] and TBP fragments [25] mainly reduce the observed signal intensity, we believe that the RA spectrum of Fig. 1 might arise from the surface reconstruction of the P terminated Ge(100) surface underneath a layer of TBP fragments.

To check for the origin of the RA signal, we carried out the following experiment. A P-terminated surface was prepared by TBP exposure at 920 K and cooled down to 570 K in the presence of TBP. Afterwards, the TBP was switched off and the temperature was raised to 850 K at a rate of 3.4 K/min under H_2, while RA spectra were measured continuously. The color-coded results of the described experiment (see Fig. 3a) show a clear change in the RA spectra with temperature. Representative initial and final spectra (Fig. 3b) of the observed evolution in the color plot represent the P terminated and the clean Ge(100) surfaces, respectively. Their principal features agree very well with the RT spectra from Fig. 1. In the range of 570–695 K and beyond 730 K, the spectra indicate no significant change of the surface. The XPS analysis of the resulting surface after the temperature ramp confirms no traces of P, but C is still present. If TBP is introduced again in the reactor, the RA spectrum associated with P termination re-emerges. Summarizing, in Fig. 3 we observe the transition from a P-terminated to a clean Ge surface by RAS, since Ge–P bonds cannot be re-established once they are broken at high temperatures in H_2 ambient. This transition also indicates that the RA spectrum of the TBP annealed sample is mainly surface related. Furthermore, we show that P desorption from the Ge(100) surface begins at 695 K and at 730 K desorption is

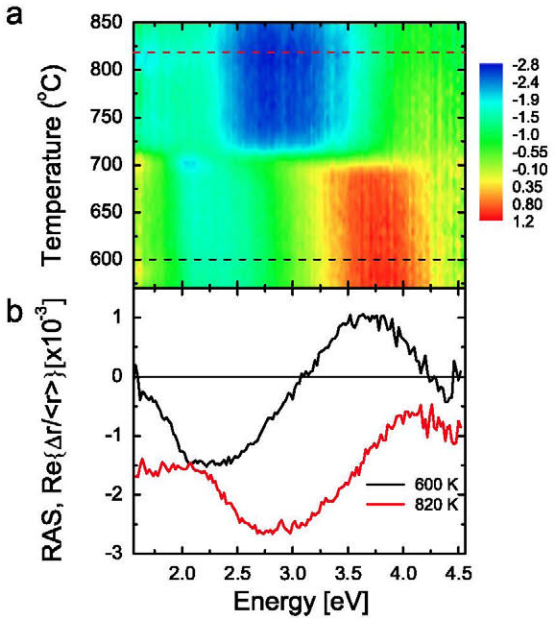

Fig. 3. (a) Color-coded representation of a continuous *in situ* RAS measurement (colorplot) at a Ge(100) surface while the sample temperature was ramped up from 570 to 850 K at a rate of 3.4 K/min without TBP supply. Color coded scale represents the intensity of the RA signal. (b) RA spectra of the dotted lines in (a). The RA spectrum at 600 K (black) corresponds to the P-terminated surface while the RAS curve at 820 K (red) is related to the clean Ge surface. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

complete. This temperature range is in good agreement with the data published by Shimamune [12] for low pressure CVD systems.

4. Conclusions

The vicinal Ge(100) surface after annealing in TBP at high temperature shows a characteristic RA spectrum, different from those reported for clean or monohydride terminated Ge surfaces. XPS measurements showed coverage of the surface with more than 1 ML of phosphorous and some carbon, leading to a disordered surface as indicated by the LEED pattern. Since carbon was not present on H_2 annealed samples, we conclude that C probably stems from a TBP pyrolysis by-product. The confirmation of a characteristic RA spectrum of a P terminated Ge(100) surface will enable dedicated *in situ* investigations of phosphorus adsorption and desorption kinetics on Ge(100) and of their dependence on temperature, pressure, and different P partial pressures in the MOVPE reactor.

Acknowledgments

This work was supported by the BMBF (Project 03SF0329C) and by the Spanish Ministerio de Economía y Competitividad (Projects TEC2009-11143, TEC2011-28639-C02-01 and SIGMA-MODULOS IPT-2011-1441-920000) and the Consejo Social of the UPM. The authors acknowledge Matthias May and Thomas Hänsel for the XPS discussion.

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