Phys. Status Solidi RRL 6, No. 4, 178–180 (2012) / DOI 10.1002/pssr.201206028

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Ge(100) surfaces prepared in vapor phase epitaxy process ambient

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Received 23 January 2012, revised 16 February 2012, accepted 23 February 2012
Published online 29 February 2012

Keywords Ge(100) surfaces, MOVPE, in situ reflection anisotropy spectroscopy, hydrogen ambient

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Ge(100) substrates essential for epitaxial III–V growth were studied in the hydrogen ambient of a metalorganic vapor phase epitaxy reactor. We confirmed thermal cleaning and oxide removal by X-ray photoelectron spectroscopy, observed the (2 × 1)/(1 × 2) surface reconstruction by low energy electron diffraction, and employed reflection anisotropy spectroscopy for optical in situ analysis. Our Ge(100) spectra differ from reference data of clean surfaces prepared in vacuum, most probably due to the presence of hydrogen during the observation was correlated with Fourier-transform infrared spectroscopy showing coupled H–Ge–Ge–H stretch modes associated with a monohydride termination of the Ge(100) surface.

Vicinal Ge(100) is the common substrate for high-efficiency triple junction solar cells, since the material is lattice-matched to the subsequent III–V subcells to be grown by metalorganic vapor phase epitaxy (MOVPE) [1]. Both structural and chemical properties of Ge(100) surfaces are essential for epitaxial growth, but the process gas ambient limits the direct access to surface analysis. Present knowledge about Ge(100) surfaces is mostly based on characterization in ultra-high vacuum (UHV). In analogy to Si(100), clean Ge(100) surfaces reduce the number of dangling bonds by dimer formation, but buckling may be visible at ambient temperature. While areas of (2 × 1), (2 × 2), and c(4 × 2) symmetry may coexist on a terrace, single layer steps separate surface reconstruction domains of mutually perpendicular dimer orientation [2].

MOVPE processing of Ge(100) usually begins with thermal substrate annealing under hydrogen flow for oxide removal. According to UHV results [3, 4], temperatures of about 450–500 °C are sufficient, but carbon impurities may remain on the Ge(100) surface and influence the formation of a regular step structure [5, 6]. In UHV, the exposure of Ge(100) to atomic hydrogen leads to the formation of a (2 × 1) reconstructed monohydride surface [7]. Recently, we have shown the strong interaction of Si(100) with molecular hydrogen under MOVPE process conditions [8, 9], but no similar studies for the Ge(100) surface are available. Reflection anisotropy spectroscopy (RAS) enables in situ characterization of substrate surfaces during MOVPE processing [10]. References [11] and [12] show RA spectra of UHV-prepared, clean Ge(100) with 4° and 6° misorientation in [011] direction, respectively.

Beyond discussing the in situ RA spectra of MOVPE-prepared Ge(100), we present a thorough analysis of its chemical and structural surface properties in this Letter. Our data was intercorrelated by contamination free transfer of the samples from MOVPE ambient to UHV [13]. The annealing in H_2 ambient removed oxides and carbon from the Ge(100) substrates as confirmed by X-ray photoemission spectroscopy (XPS). While low energy electron diffraction (LEED) showed the typical, dimer-based surface reconstruction of Ge(100), Fourier-transform infrared (FTIR) spectroscopy revealed the presence of a monohydride termination after H_2 annealing. We used Ge(100) substrates with a misorientation of 6° towards the [011] di-

rection specified as "epiready" (supplier: AXT) and specific samples (CrysTec) for FTIR [7]. Without any additional wet chemical pre-cleaning, thermal oxide removal (Fig. 1) was conducted by annealing at 1000 K for 20 min in purified H_2 at a pressure of 100 mbar in a cleaned (liner, susceptor) MOVPE reactor to avoid unintentional contaminations. See Refs. [8, 13, 14] for further details.

Figure 1(a)–(d) shows XP spectra in the range of the Ge $2p_{3/2}$, O 1s and C 1s photoemission lines of an "epiready" Ge(100) substrate and of its surface after H_2 annealing in MOVPE. 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 [14]. In the Ge $2p_{3/2}$ XP spectrum (Fig. 1(a)), the "epiready" Ge substrate exhibits peaks at 1217.5 eV and 1220.5 eV that correspond to elemental and oxidized Ge, respectively [3, 4]. Deconvolution of the oxide peak (Fig. 1(a), dotted lines) revealed main contributions from GeO_2 and smaller ones from GeO, that are shifted about +3.0 eV and +1.7 eV with regard to the elemental Ge $2p_{3/2}$ line [3]. Broad peaks at around 531 and 285 eV arise from oxygen (O 1s) and carbon (C 1s), respectively (Fig. 1(c), (d)).

The absence of both the O 1s line and the signal associated with GeO_x confirmed oxide removal during annealing in H_2. Remaining smaller peaks at about 534 eV and 525 eV are assigned to the $L_3M_{23}M_{23}$ and $L_2M_{23}M_{23}$ Auger emission lines of elemental Ge, respectively [15], also present as shoulders in the oxide spectrum. Within the sensitivity limits of our XPS setup (<1% of a monolayer), we detected no traces of impurities after annealing, neither carbon nor group III or V elements. According to Refs. [5, 6], residual carbon can only be partially removed from the Ge(100) surface by thermal annealing in UHV. In contrast, our results indicate sufficient carbon removal during thermal deoxidation (Fig. 1(d)). The absence of C 1s intensity in our spectra can be explained either by the specific surface conditioning of the supplier ("epiready"), or by a reaction with H_2 producing volatile CH_x species, or a combination of both.

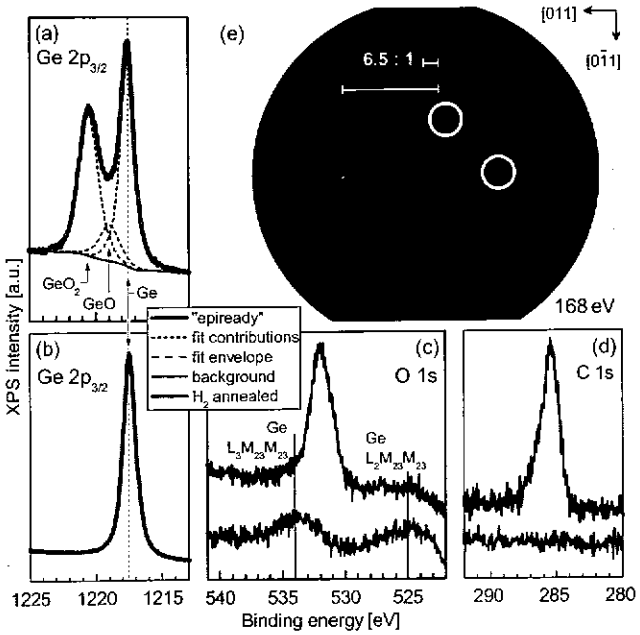

Figure 1 (online colour at: www.pss-rapid.com) XP spectra of Ge(100) "epiready" (blue) and after H_2 annealing (red) in the range of the Ge $2p_{3/2}$, O 1s and C 1s PE line with corresponding LEED pattern of the deoxidized surface.

The LEED pattern of the deoxidized Ge(100) surface (Fig. 1(e)) shows pronounced spot splitting along [011]. In consistence with UHV studies [16], half-order spots in [0$\bar{1}$1] direction indicate dimer formation on the surface and a clear prevalence (compare encircled half-order diffration spots) of the domain with dimers parallel to the step edge – corresponding to a preference for D_B-type double layer step formation typical for vicinal Ge(100) surfaces [17]. The LEED spot splitting ratio of about 1 : 6.5 compared to the distance of full-order reflexes is in good agreement with the strong vicinality of the 6° offcut Ge(100) substrate. Assuming double layer step formation, we expect an average terrace width of 2.7 nm ($\hat{=}$ 6.7 atomic distances in the surface plane). Residual disorder in the LEED pattern is most probably due to irregularities of the step structure. In analogy to Si(100) [18], dimerization occurs on both clean and monohydride Ge(100) surfaces, and our LEED pattern does not distinguish between these terminations.

We carried out ATR mode FTIR measurements to check for hydrogen termination after annealing and cooling in H_2 ambient. The FTIR spectrum in Fig. 2 shows two characteristic absorption lines at about 1986 and 1975 cm^{-1} assigned to coupled Ge–H stretch modes [7]. Hydrogen saturation of the residual dangling bonds of the reconstructed Ge(100) creates H–Ge–Ge–H dimers. Their antisymmetric and symmetric vibrational modes induce dipoles within and perpendicular to the surface plane, respectively. Since polarized FTIR measurements can address dipole orientations on the surface [19], we currently work on

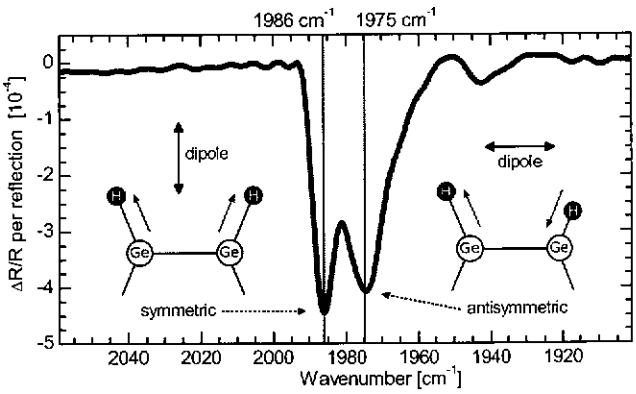

Figure 2 (online colour at: www.pss-rapid.com) FTIR spectra measured in an ATR configuration at H_2 annealed Ge(100). Clear features at 1986 and 1975 cm^{-1} agree with the symmetric and antisymmetric stretch modes of coupled Ge–H monohydrides, respectively [7].

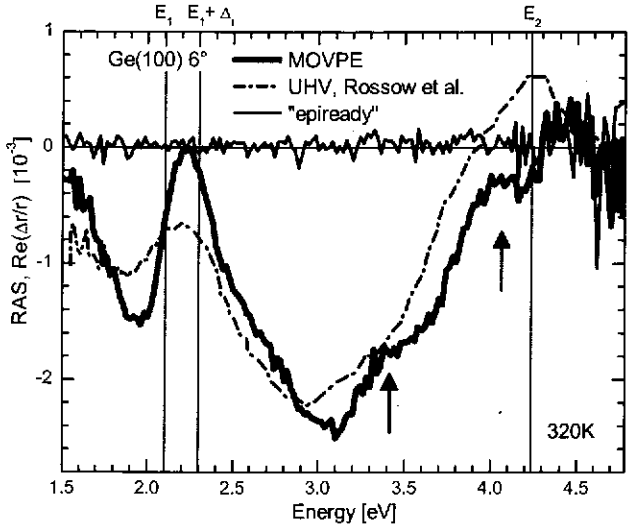

Figure 3 (online colour at: www.pss-rapid.com) In situ RA spectra of "epiready" (blue) and H_2 annealed (red) Ge(100) with 6° miscut in [011] measured at 320 K in H_2 ambient, and RAS of UHV prepared Ge(100) (dash-dotted) [12].

a quantitative analysis of surface reconstruction domains on Ge(100).

Figure 3 shows RA spectra of "epiready" and H_2 annealed vicinal Ge(100) measured in the MOVPE reactor at 320 K (after cooling in H_2 ambient) as well as the RA spectrum of clean vicinal Ge(100) prepared in UHV [12] for comparison. Due to coverage with an amorphous oxide layer, the "epiready" surface exhibits a featureless spectrum. After H_2 annealing in the MOVPE reactor, we observe a characteristic RAS signal of the Ge(100) surface (Fig. 3, red line) consisting of a broad minimum 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, respectively). Although the general features of the observed RA spectrum roughly agree with the RAS signal of clean Ge(100) prepared by annealing in UHV [12], the local maximum around 2.2 eV is more pronounced and the minimum around 3 eV is shifted slightly towards higher energies. In contrast to Ref. [12], we observed additional fine structure of the RAS signal, particularly around 3.4 eV and 4.0 eV (arrows in Fig. 3).

In general, differences in the atomic order of probed (100) surfaces such as cleanliness, surface reconstruction, domain ratio, and chemical configuration affect shape and amplitude of RA spectra [20]. If the signal originates from the surface reconstruction, the presence of mutually perpendicular reconstruction domains results in a linear reduction of the amplitude [21]. The impurity concentration on the surface mainly affects the signal intensity, too [11]. In contrast, hydrogen saturation of dangling bonds [7] usually changes the shape of the RAS signal as observed for monohydride termination on vicinal Si(100) [22]. Since our findings exclude significant contamination of our MOVPE prepared Ge(100) surfaces (Fig. 1) and confirm the presence of monohydride dimers (Fig. 2), we assume that both the more pronounced signal shape between 1.8 eV and 2.3 eV and the additional fine structure beyond 3 eV are characteristic of the monohydride Ge(100) surface. The limited stability of the hydrogen bonds [23] should enable us to prepare clean Ge(100) by thermal hydrogen desorption under flow of alternative process gases such as N_2 or Ar [24]. The confirmation of characteristic RA spectra which distinguish between both surface configurations of Ge(100) will enable dedicated in situ investigations of hydrogen adsorption and desorption characteristics [9] on Ge(100) in dependence on temperature, pressure, and process gas in the MOVPE reactor.

We confirmed oxide and carbon removal from Ge(100) substrates by hydrogen annealing in MOVPE ambient with XPS and characterized the $(2 \times 1)/(1 \times 2)$ surface reconstruction with LEED. ATR mode FTIR spectroscopy revealed coupled H–Ge–Ge–H stretch modes indicating a monohydride termination of our Ge(100) surfaces. In situ RA spectra showed characteristic deviations from UHV reference data of clean Ge(100). In particular, we assigned the more pronounced features between 1.8 eV and 2.3 eV as well as the additional fine structure beyond 3.0 eV to the monohydride termination of the surface.

Acknowledgement This work was supported by the BMBF (Project 03SF0329C). E. Barrigón was supported by the Spanish Ministerio de Ciencia e Innovación (TEC2008-01226, TEC2009-11143) and by the Comunidad de Madrid (S2099/ENE1477) and the Consejo Social of the UPM.

References

[1] R. R. King et al., Appl. Phys. Lett. **90**, 183516 (2007).
[2] H. J. W. Zandvliet, Phys. Rep. **388**, 1 (2003).
[3] K. Prabhakaran and T. Ogino, Surf. Sci. **325**, 263 (1995).
[4] J. Oh and J. C. Campbell, J. Electron. Mater. **33**, 364 (2004).
[5] S. Gan et al., Surf. Sci. **395**, 69 (1998).
[6] J. S. Hovis et al., Surf. Sci. **440**, L815 (1999).
[7] Y. J. Chabal, Surf. Sci. **168**, 594 (1986).
[8] H. Döscher et al., Appl. Phys. Lett. **97**, 151905 (2010).
[9] S. Brückner et al., Appl. Phys. Lett. **98**, 211909 (2011).
[10] P. Weightman et al., Rep. Prog. Phys. **68**, 1251 (2005).
[11] T. Yasuda et al., Phys. Rev. Lett. **74**, 3431 (1995).
[12] U. Rossow et al., J. Vac. Sci. Technol. B **18**, 2229 (2000).
[13] T. Hannappel et al., Rev. Sci. Instrum. **75**, 1297 (2004).
[14] H. Döscher et al., J. Cryst. Growth **315**, 10 (2011).
[15] E. Antonides et al., Phys. Rev. B **15**, 1669 (1977).
[16] C. Tegenkamp et al., Phys. Rev. B **65**, 235316 (2002).
[17] J. E. Griffith et al., J. Vac. Sci. Technol. A **6**, 493 (1988).
[18] H. Döscher et al., Appl. Surf. Sci. **257**, 574 (2010).
[19] A. Dobrich et al., J. Vac. Sci. Technol. B **29**, 04D114 (2011).
[20] H. Döscher and T. Hannappel, J. Appl. Phys. **107**, 123523 (2010).
[21] N. Witkowski et al., Surf. Sci. **600**, 5142 (2006).
[22] R. Shioda and J. v. d. Weide, Appl. Surf. Sci. **130–132**, 266 (1998).
[23] J. Y. Lee et al., J. Chem. Phys. **118**, 1929 (2003).
[24] H. Döscher et al., J. Cryst. Growth **318**, 563 (2011).