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2013 New J. Phys. 15 113049

(http://iopscience.iop.org/1367-2630/15/11/113049)

New Journal of Physics
The open access journal for physics

Domain-sensitive *in situ* observation of layer-by-layer removal at Si(100) in H_2 ambient

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New Journal of Physics **15** (2013) 113049 (10pp)
Received 11 July 2013
Published 26 November 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/11/113049

Abstract. Double-layer step formation on Si(100) substrates is a crucial prerequisite for antiphase-domain free III–V compound semiconductor heteroepitaxy. Due to its unequaled relevance in microelectronics, the (100) oriented surface of silicon is by far the most studied semiconductor surface. However, Si(100) preparation in hydrogen process gas ambient, which is commonly employed for Si and III–V device preparation, is completely different from preparation in ultra-high vacuum due to strong interaction between H_2 and the Si surface, leading to a kinetically driven different step formation. Here, we observe chemical layer-by-layer removal of surface atoms from the terraces at the Si(100) surface during annealing in hydrogen ambient. Mutually perpendicularly oriented dimers on subsequently removed monolayers induce oscillations in the *in situ* reflection anisotropy spectroscopy (RAS) signal. Scanning tunneling microscopy measurements support a model, where surface

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atom removal proceeds by formation and anisotropic expansion of vacancy islands on the terraces. We determined an activation energy E_d of 2.75 ± 0.20 eV for Si etching in H_2 ambient by transient *in situ* RAS measurements. *In situ* control of the highly reactive Si(100) surface preparation is essential for subsequent defect-free III–V heteroepitaxy.

Contents

1. Introduction

Atomic scale interface preparation and its control are essential for critical challenges in ultrahigh-performance opto-electronics. In recent years, much work has been devoted to the preparation of defect-free III–V compound semiconductors on silicon substrates by metalorganic chemical vapor deposition (MOCVD) [1–5]. Major difficulties during the heteroepitaxial growth arise from the heterointerface between the polar III–V film and the non-polar Si substrate [6]. In the initial stage of III–V nucleation, double-layer step formation of Si(100) is a crucial prerequisite for the formation of an atomically ordered III–V film free of antiphase-domains [7]. The step structure is directly related to the domain formation on the Si(100) surface [8]: while single-layer steps (S) imply a (2×1)/(1×2) two-domain surface with perpendicular dimer orientations on adjacent terraces, double-layer steps (D) are associated with single-domain surfaces where dimer orientation on the terraces is uniform. Single- and double-layer steps can be further differentiated according to the dimer orientation on the upper terrace to the step edge, so-called A-type steps (or terraces) with dimers perpendicular to the step edge, and B-type steps (or terraces) with dimers parallel to the step edge (see sketch in the insets of figures 1(a) and (b)).

In chemical vapor deposition (CVD), H_2 serves as carrier gas and leads to the formation of monohydride bonds on the Si(100) surface [9, 10]. With a view to III–V-on-silicon epitaxy we use a MOCVD reactor with H_2 as process gas in the pressure range of 50–950 mbar. However, most knowledge about Si(100) surfaces has been obtained from studies based on preparation in ultra-high vacuum (UHV), where standard surface science methods can easily

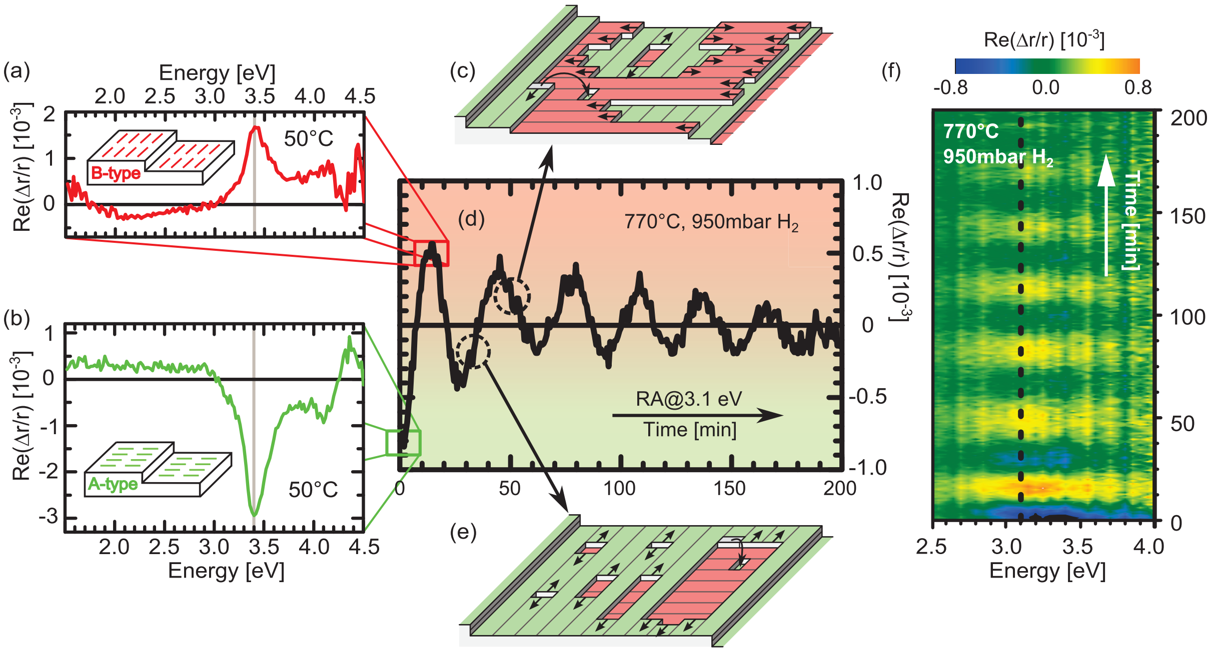

Figure 1. *In situ* RAS of Si(100) 0.1° offcut samples with preference for the A-type (b) and the B-type domain (a) obtained during preparation in H_2 ambient (see text) and measured at 50 °C. The sketches show the dimer orientation related to the step edges for the different domain types. Figure 1(f) shows continuous *in situ* RAS measurements of Si(100) with 0.1° offcut during annealing at 770 °C in 950 mbar H_2 represented in colorplot mode (41 s per RA spectrum). The dashed black line at 3.1 eV corresponds to the transient RAS measurement shown in (d) at the characteristic RAS peak of monohydride-terminated Si(100), which shifts with temperature [26] (see gray line in (a) and (b)). Positions on the transient marked with green and red squares correspond to a sample surface with A- or B-type majority domain, respectively, as shown in (a) and (b) for reference samples. In sketches (c) and (e) the vacancy formation mechanism is depicted, which explains the layer-by-layer removal process (see text).

be applied. Si(100) preparation in H_2 ambient differs considerably from well established UHV preparation. Recent studies of Si(100) surfaces prepared in nearly atmospheric H_2 pressures of a (MO)CVD reactor showed the formation of single-domain surfaces with double-layer steps in the unusual D_A step configuration [10–12]. Formation of D_A steps is in disagreement with previous experimental and theoretical reports in the literature [8, 13–16], since D_A double-layer steps are considered energetically least favorable on both clean and monohydride terminated Si(100) surfaces. At high temperature, the strong interaction of H_2 with the Si(100) surface [17] enables an interplay of several processes such as hydrogen adsorption and desorption [9, 10], Si removal (etching) or growth, diffusion of Si adatoms or vacancies, annihilation of vacancies or attachment of adatoms at step edges [11].

The presence of the H_2 ambient impedes detailed investigation of these processes on the Si(100) surface by standard surface science tools. However, *in situ* surface characterization by reflection anisotropy spectroscopy (RAS) and benchmarking of the *in situ* signals in

UHV (via an appropriate contamination-free sample transfer [18]) allows to study the Si(100) surface preparation in CVD environment and the relevant processes directly [11, 17]. Si(100) surfaces exhibit characteristic RAS signals for the clean and hydrogen-terminated surfaces [19] which enabled monitoring of hydrogen adsorption and desorption [17, 19]. The sensitivity of RAS to the surface reconstruction of monohydride-terminated Si(100) surfaces allows *in situ* observation of the domain formation on the Si(100) surface [11, 20].

In this paper, we present experimental evidence that chemical Si surface atom removal occurs in highly reactive H_2 ambient and proceeds in a layer-by-layer fashion on nearly exact Si(100) surfaces. Since step edge atoms exhibit a reduced coordination compared to terrace atoms, one might expect surface atom removal due to interaction with H_2 to proceed primarily at the step edges [21]. In contrast, we show that a process analogous to that observed with Xe ion bombardment in UHV occurs [22, 23].

2. Experimental

2.1. Experimental setup

Sample preparation took place in an Aixtron AIX-200 MOCVD reactor equipped with an *in situ* reflection anisotropy (RA) spectrometer (LayTec EpiRAS 200). The process temperature was measured by thermocouples inside the graphite susceptor. We cleaned reactor parts (liner and susceptor) and sample carriers with regard to III–V residuals to avoid unintentional contamination of the samples. A dedicated MOCVD-to-UHV sample transfer system enabled contamination-free access to surface science tools [18] such as scanning tunneling microscopy (STM) (Specs Aarhus 150). The STM was equipped with tungsten tips which were prepared by electrochemical etching.

2.2. Sample preparation

We used Si(100) substrates with $0.10 \pm 0.05^\circ$ misorientation in [011] direction with optional wet-chemical pretreatment before CVD processing [24, 25]. The Si preparation started with annealing for 30 min at 1000 °C in H_2 process gas at a pressure of 950 mbar to remove oxides and other contamination [25], followed by growth of a 0.25 μm thick Si buffer layer at 950 °C and a H_2 pressure of 200 mbar using SiH_4 (10% in H_2). Afterwards samples were annealed in H_2 ambient for 10 min at 1000 °C and 950 mbar. After fast cooling from 1000 to 500 °C (heating system off) and simultaneous H_2 pressure change from 950 to 100 mbar within 5 min, the sample surface exhibits a strong prevalence for the A-type domain (see RAS and STM measurements).

2.3. In situ reflection anisotropy spectroscopy (RAS) measurements

In situ monitoring of the surface preparation by RAS enabled control of the domain formation on monohydride-terminated Si(100) surfaces [11]. The RAS signal is sensitive to the surface reconstruction of monohydride-terminated Si(100) surfaces [11, 20]. Due to the definition of RAS

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

domains with mutually perpendicular dimer orientation exhibit RA spectra with opposite sign. Since RAS integrates over the entire probed surface area, the measured amplitude of the signal reflects the domain ratio on the surface [2, 11] (as shown for the monohydride terminated Si(100) surface in figures 1(a) and (b)).

Continuous *in situ* RAS measurement in color-coded representation (colorplot) (see figure 1(f)) or single transient mode (see figure 1(d)) enable observation of processes on the Si(100) surface such as H adsorption/desorption [17] or domain formation [11] dependent on the applied process parameters.

3. Results and discussion

3.1. In situ RAS signals of 0.1° misoriented Si(100)

After standard Si preparation (see section 2) and fast cooling from 1000 to 500 °C (heating system off) and simultaneous pressure change from 950 to 100 mbar within 5 min, the sample exhibited the characteristic RA spectrum of monohydride-terminated Si(100) [11, 20], shown in figure 1(b) measured at 50 °C. It consists of peak structures around the critical point energies of Si, E_1 and E_2, at 3.4 eV and around 4.3 eV, respectively, as well as a shoulder around 4 eV (green line). According to the strong negative peak at 3.4 eV, the RA spectrum corresponds to a Si(100) surface with a preference for the A-type domain [11]. Comparison of the RAS signal amplitude at 3.4 eV to RA spectra of [11, 20] indicates a domain ratio of about 75:25 with an A-type majority domain.

The temperature range between 700 and 800 °C is critical for D_A-type step formation on the 2° misoriented Si(100) surface [11]. Figure 1(f) shows continuous *in situ* RAS measurements (41 s per spectrum) in color-coded representation (colorplot) of a 0.1° Si(100) sample during annealing at 770 °C and a H_2 pressure of 950 mbar after preparation of a preferential A-type domain surface as described above. In the beginning the surface exhibits the spectra of the monohydride-terminated Si(100) surface with a preferential A-type domain indicated by the strong negative intensity around 3.1 eV (peaks shift with increasing temperature toward lower energies [26]). During further annealing we observe an alternating change in the sign of the RAS peak around 3.1 eV in the colorplot.

For better illustration of the observed changes in the RAS signal with time, figure 1(d) shows a RAS transient at 3.1 eV (see black dotted line in figure 1(f)). The chosen energy corresponds to the characteristic RAS peak of the monohydride terminated Si(100) surface at 770 °C. The transient clearly shows an oscillation of the peak amplitude with a constant period of 30.8 min and slowly decreasing amplitude. According to the definition of the RAS signal, we observed a switch of the majority amongst the two mutually perpendicular dimer orientations whenever the RAS peak changes its sign: starting from a predominantly A-type surface (green square), the increasing B-type surface area decreases the RAS amplitude due to the implicit integration over the probed surface area. Reaching equal domain distribution, the RAS signal cancels out completely and once the former minority domain prevails, the signal changes its sign.

The prevalence of the B-type domain can be preserved on the surface, if we cool down the sample directly after evolution of the positive RAS peak (red square) with maximum cooling rate (heater off) and simultaneous reduction of the H_2 pressure from 950 to 50 mbar. Thereby, we obtain a sample with preference for the B-type domain with a positive RAS peak at 3.4 eV.

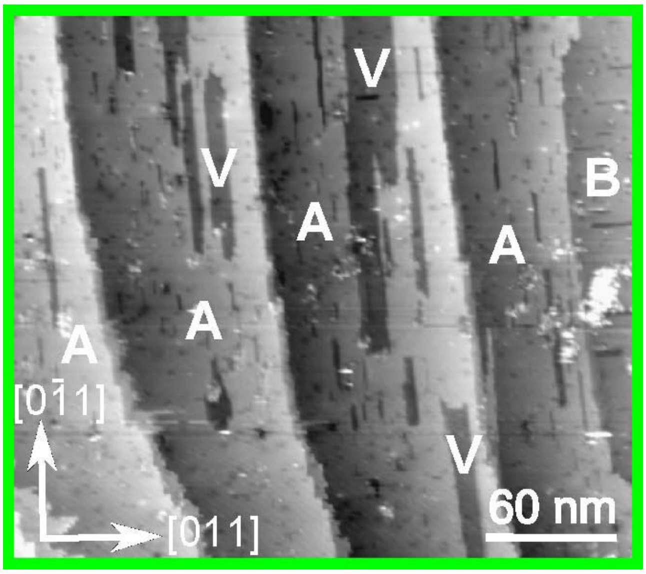

Figure 2. STM measurement of Si(100) with 0.1° offcut. Sample surface was prepared by fast cooling with simultaneous pressure ramp. A and B denote the domain type of the terraces and V marks vacancy islands ($I_t = 290\,\text{pA}$, $V_t = 1.24\,\text{V}$, empty state image).

The corresponding RAS signal of a reference sample is shown in figure 1(a). Here, the RAS amplitude at 3.4 eV indicates a domain ratio of about 63:37 with a B-type majority domain.

3.2. Atomic surface structure

STM measurements showed the surface structure of an Si(100) 0.1° sample which was cooled quickly with the same pressure ramp as the sample of figure 1(b) (see figure 2). The surface exhibits large A-type terraces (dimer rows parallel to step edges) and small B-type terraces (dimer rows perpendicular to step edges). The steps run slightly curved along [0$\bar{1}$1] direction. The surface mainly exhibits D_A steps, but in some locations narrow B-type terraces remain. On the A-type terraces we also observe missing dimer rows forming vacancy islands of the B-type domain (indicated by Vs). The vacancy islands exhibit an elongated shape extended along the direction of the dimer rows.

3.3. Analysis of RAS signal oscillations

We conclude that the oscillations result from monolayer (ML) removal from the surface: removal of one ML Si atoms from an A-type terrace results in a B-type terrace and vice versa. The decreasing amplitude during the oscillation indicates a reduction of the maximum prevalence for both majority domains. While the detection of an oscillating signal as a result of a layer-by-layer process is reminiscent of reflection high energy electron diffraction (RHEED) oscillations (applicable only in UHV), the RAS signal has distinctly different properties: RHEED oscillations originate from periodic filling/removal of each new layer; in [22, 27] the maximum intensity refers to a completely removed ML, accordingly. In contrast, RAS is sensitive to the majority dimer orientation on the terraces, and the RAS oscillations are due

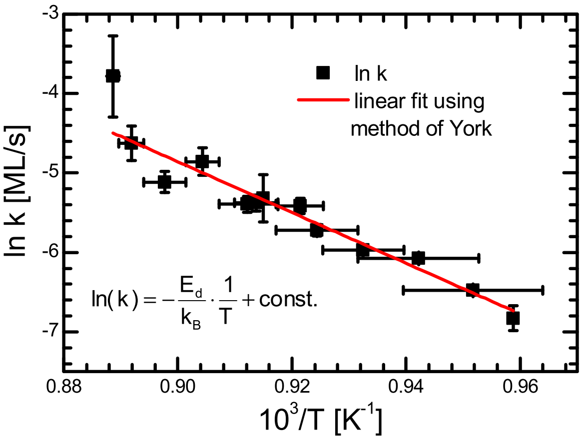

Figure 3. Arrhenius plot of the etching rate k of Si. Data was taken from RAS transients at 3.1 eV measured in 950 mbar H_2 in the temperature range 770–852 °C. From the slope of linear fit using the computation method of York [28] (red line), we determined an activation energy E_d of 2.75±0.20 eV.

to the oscillating prevalence of the two domain types. Hence, unlike RHEED, RAS oscillations directly reflect the domain content, with maximum amplitude in the case of double-layer stepped surfaces (whereas a smooth single-layer stepped surface would result in zero signal). RAS detects monolayer removal from specifiable terraces at the Si(100) surface, which enables *in situ* control of the majority dimer orientation. The oscillating RAS signal in figures 1(d) and (f) corresponds to an alternating formation of preferential A- and B-type domain surfaces, which implies a Si layer-by-layer removal process. The constant oscillation period indicates uniform removal of a bilayer for every period of the oscillation during H_2 annealing.

The process must imply differences in the surface structure during the decreasing and increasing slopes of the transient, where the magnitude of the RAS signal indicates equal domain prevalence, but the different gradients of its time dependence lead again to the development of either A- or B-type majority domains, respectively. Accordingly, we can rule out processes based only on removal from the terrace step edges. Si removal starting from the step edges of a preferential A-type domain surface would result in a regular sequence of S_A and S_B steps and continuous Si removal in step flow mode and, thus, a decreasing RAS amplitude which approaches zero without oscillations.

3.4. Si etch process

The *in situ* RAS measurements enabled us to study the Si etch process in H_2 ambient on nearly exact Si(100) surfaces. We applied continuous *in situ* RAS measurements during annealing in the temperature range between 650 and 900 °C at high H_2 pressures of 950 mbar. Data was obtained at constant temperatures of 770 °C (see figure 1) and 820 °C and during slow heating ramps (3.3 and 2.5 K min^{-1}) from 650 to 900 °C. From the transient *in situ* RAS measurements at 3.1 eV, we derived etching rates k (ML s^{-1}) for Si removal in 950 mbar H_2 ambient dependent on temperature.

Figure 3 shows the resulting Arrhenius plot from the etching rates k measured in a temperature range between 770 and 852 °C. Assuming a first order reaction, we applied a linear fit in consideration of x and y errors using the computation method of York [28] (red line). From the slope of the fit, we calculated an activation energy E_d of 2.75±0.20 eV. Our value agrees within the error margins with data published by Gallois *et al* [29], who obtained an activation energy E_d of 3.25±0.43 eV for Si etching in H_2 ambient from rates at 1052–1277 °C. Gallois *et al* assumed that SiH_2 is the main reaction species in this temperature range. Since our value of E_d is also well below the sublimation energy of Si (4.5 eV [30]), our result indicates Si etching processes by formation of SiH_x species.

3.5. Layer-by-layer removal

The occurrence of vacancy islands, as observed in the STM images in figure 2, substantiate Si removal from the terraces during cooling in H_2 ambient. Even though the interaction with the surface in the Si removal process during H_2 annealing differs from that in removal by Xe ion bombardment under UHV conditions [22, 23], the resulting layer-by-layer removal mechanism is similar, relying on vacancy formation on the terraces. For the alternating formation of preferential A- and B-type layers during Si removal on nearly exact Si(100) substrates, we consider a mechanism that consists of (i) generation of vacancies on the terraces, (ii) anisotropic diffusion of vacancies (faster parallel than perpendicular to the dimer rows) [31] and (iii) nucleation of vacancy islands with anisotropic expansion parallel to the dimer rows [23], as well as (iv) partial suppression of vacancy nucleation on the subjacent Si layer due to refilling by diffusing Si adatoms [23, 32] (see figures 1(c) and (e)).

We conjecture that vacancies nucleate during annealing in H_2 and coalesce to elongated vacancy islands oriented parallel to the dimer rows of the Si terrace with long S_A step edges in agreement with our STM results (figure 2) and [23, 31]. Formation of elongated vacancy islands minimizes the surface energy compared to many small vacancies spread over the terraces. Starting from a surface with preference for A-type terraces (figure 1(d), green areas), the vacancies expand (black arrows) parallel to the step edges uncovering the subjacent B terrace layer (red areas). Broadening of the vacancy islands perpendicular to the dimer rows is enhanced by merging of several islands on a terrace layer. The preferential growth of the vacancy islands parallel to the dimer rows of the corresponding Si layer induces mutually perpendicular expansion of the islands on A- and B-type terraces. Removal of the subjacent Si layer ((figure 1(d), green areas in the vacancy islands) is limited by the width of the vacancy islands in the first layer and suppressed by refilling with diffusing Si adatoms detached from the step edges of the upper (A-type) layer [23, 32]. Refilling of subjacent vacancies in the second layer depends on the temperature dependent mobility of adatoms and the width of the first vacancy island. Only after formation of wide vacancy islands in the first terrace layer, nucleation of vacancy islands in the subjacent Si layer may begin (figure 1(e). As a result A- and B-type majority domains continuously alternate, which is directly observed by an oscillating RAS signal. The attenuation of the oscillation amplitude with annealing time is likely the result from increasing imperfection of the above process resulting in left over dimer rows of former terraces.

4. Conclusion

In conclusion, our RAS observations revealed that annealing in near ambient H_2 pressure in the critical temperature range between 700 and 850 °C strongly influences the domain formation on nearly exact Si(100) surfaces due to ML removal. Layer-by-layer removal leads to alternating majority domains with mutually perpendicular dimer orientations detected as oscillations in the RAS signal. *In situ* RAS enabled analysis of the etch kinetics and revealed an activation energy of 2.75±0.20 eV which indicates SiH_x formation. The transient RAS measurement showed that Si removal processes in H_2 ambient are crucial for understanding the domain formation of Si(100) surfaces in CVD ambient. The strong dependence of the domain formation on temperature and H_2 pressure implies a highly sensitive surface preparation of nearly exact Si(100) substrates which requires precise *in situ* control as the basis for subsequent III–V heteroepitaxy.

In a previous publication we explained the formation of the energetically unfavorable D_A steps on vicinal 2° offcut Si(100) substrates by vacancy generation on the terraces and subsequent vacancy diffusion to and annihilation at the step edges. Here we showed Si removal from the terraces of 0.1 misoriented Si(100) substrates during processing in H_2 ambient. It is very likely that this removal process also takes place on smaller terraces such as those on 2° misoriented substrates. Therefore, our model for step formation based on vacancy generation [11] is supported by the results presented here.

Acknowledgments

This work was supported by the BMBF (project no. 03SF0404A) and the German Research Foundation (DFG project no. HA 3096). HD acknowledges support by a Marie Curie International Outgoing Fellowship from the European Research Council (Project 'Solar Fuel by III–Vs', no. 300971).

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