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Anomalous double-layer step formation on Si(100) in hydrogen process ambient

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We prepared Si(100) surfaces with anomalous atomic double-layer steps grown via chemical vapor deposition. Scanning tunneling microscopy resolved D_A-type steps, supported by low-energy electron diffraction, Fourier-transform infrared spectroscopy, and *in situ* reflection anisotropy spectroscopy, which enabled direct control of majority domain formation. We attribute the energetically unfavorable step structure to interaction of the surface with the H_2 ambient, driving a dynamic step formation process governed by surface vacancy generation, diffusion, and annihilation at step edges.

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Si(100) surfaces have been the subject of extensive investigations due to their great importance for semiconductor technology. Due to the high reactivity of the clean surface, most of the studies have been carried out in ultrahigh vacuum (UHV), where standard surface science methods can be applied. The clean Si(100) surface reconstructs by forming dimers, thus eliminating one of the two dangling bonds of the surface Si atoms.[1] In general, a $(2 \times 1)/(1 \times 2)$ reconstruction results, where regions with perpendicular dimer orientations are separated by single-layer steps,[2] while a single-domain surface requires double-layer steps.[3] Four different step types can be distinguished: single- (S) and double- (D) layer steps with dimer orientation perpendicular (A-type) or parallel (B-type) to the step edge on the upper terrace. D_B double-layer steps are considered to be energetically favorable over the combination of S_A and S_B single-layer steps, while D_A double-layer steps are considered least favorable.[3] In practice, D_B steps are obtained on vicinal Si(100) simply by annealing in UHV.[4–6] In contrast, scarce reports on D_A double-layer steps are based on application of either mechanical stress,[7] direct current (electromigration),[8] or Xe-ion bombardment.[9,10]

Hydrogen plays a major role in Si(100) semiconductor technology. Preparation conditions consisting of H_2 ambient at high temperature and near atmospheric pressure, typical for chemical vapor deposition (CVD), lead to the formation of the monohydride phase.[11,12] Hydrogen termination on Si(100) leads to a passivation of the reactive clean surface, reducing its susceptibility to oxidation and other contamination. The hydrogenated Si(100) surface prepared in UHV by application of atomic hydrogen exhibits three different surface reconstructions with increasing hydrogen chemical potential: a monohydride (2×1), a mixed (3×1), and a dihydride (1×1) phase.[13] In contrast to the situation at the clean Si(100) surface, theoretical studies of the step formation energies do not predict any preference for double-layer steps in the range of the (2×1) monohydride reconstruction.[14,15] Scanning tunneling microscopy (STM) showed a preference for single-layer steps at misorientations up to 7° in the [011] direction.[16] Other experimental studies of monohydride Si(100) mostly report on the preparation of smooth, single-layer stepped surfaces resulting from annealing in hydrogen at temperatures on the order of 1000 °C,[17–19] while some found comblike step structures depending on the direction and degree of misorientation.[20,21]

Recently, progress in III-V on Si(100) heteroepitaxy in a metalorganic chemical vapor deposition (MOCVD) environment has led to renewed interest in the preparation of Si(100) surfaces in standard MOCVD equipment[22] for the desired integration of optoelectronics with microelectronic devices. Major drawbacks are related to the formation of the crucial III-V/Si(100) interface,[23] where single-layer steps on the substrate surface induce antiphase disorder in the epitaxial film,[24] which can in principle be avoided by generating double-layer steps.[22] We have studied CVD preparation of Si(100) substrates by annealing under pure H_2 flow, verifying the complete removal of protective oxide layers by x-ray photoelectron spectroscopy (XPS)[25] and the monohydride termination of the resulting surface by Fourier transform infrared spectroscopy (FTIR).[12] *In situ* reflection anisotropy spectroscopy (RAS) measurements confirmed a strong interaction between H_2 carrier gas and the Si(100) surface.[26] While in our initial experiments single-layer steps resulted, evidenced by low-energy electron diffraction (LEED) and STM,[19] Kitahara and Ueda[27] observed a retreat of S_A steps after annealing in hydrogen. In Refs. 12,28, and 29, an imbalance in the domain distribution on Si(100) surfaces was reported.

However, here we directly display both the presence of true D_A steps on Si(100) with 2° misorientation in the [011] direction via STM and the control of their formation *in situ*, as a result of a CVD preparation process. *In situ* RA spectroscopy identifies the relevant process parameters and supports a model[9] based on surface vacancy generation, diffusion, and annihilation at step edges, which may account for the formation of this anomalous step structure.

Si(100) substrates (P-doped, 0.007–0.02 Ω cm) misoriented by 2° in [011] were wet-chemically pretreated and subsequently processed in a commercially available MOCVD system (Aixtron AIX200)[25] under *in situ* control by reflection anisotropy spectroscopy (RAS, Laytec EpiRAS 200),[26,30] which is defined by

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

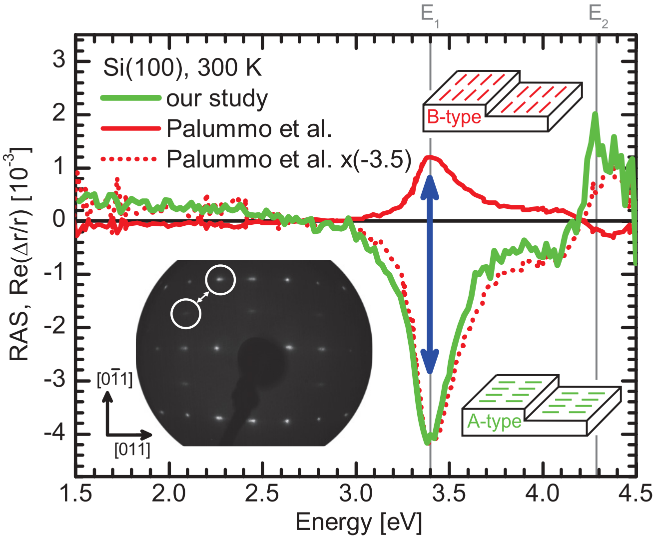

FIG. 1. (Color online) LEED pattern (144 eV) and corresponding *in situ* RA spectra of a monohydride terminated Si(100) surface with 2° misorientation in [011] (green line) indicating a strong prevalence of the *A*-type domain (lower sketch) as well as RAS data from Ref. 32 (red line) of a monohydride terminated nominal Si(100) sample with a preferential *B*-type domain (upper sketch). For comparison, the scaled data (factor −3.5) of Ref. 32 (red dotted line) is also depicted.

Subsequent contamination-free sample transfer to UHV[31] enabled dedicated surface investigations by XPS, LEED, and STM as well as correlation to our *in situ* results. XPS verified the absence of surface contamination apart from traces of residual background arsenic (<0.05, typically 0.01 ML). STM characterization was carried out with a commercial setup (SPECS 150 Aarhus STM) operating at a residual pressure $<4 \times 10^{-10}$ mbar in constant-current mode with etched tungsten tips.

After deoxidation[25] and Si growth,[12] we prepared the samples by cooling at a rate of $\sim$8 K/min from 1000 to 500 °C at a pressure of 950 mbar H_2 at the end of the CVD process. On similarly prepared Si(100) samples, we already showed a strong domain imbalance by LEED and FTIR measurements.[12,28] The LEED pattern, shown in the inset of Fig. 1, exhibits high-intensity half-order spots in the [011] direction, while in the [0$\bar{1}$1] direction the half-order spots are suppressed (as indicated by the circles in the figure). Hence, dimers oriented in the [011] direction, perpendicular to the step edges (see the sketch in the lower inset), and therefore of type *A*, dominate the surface. Figure 1 also shows the corresponding *in situ* RA spectra measured at 50 °C (green line). The spectrum exhibits features around the critical point energies E_1 and E_2 of Si, a strong peak at 3.4 eV and a smaller one around 4.3 eV, respectively, as well as a shoulder around 4.0 eV. The RA spectrum with regard to its peak positions agrees perfectly with data of nearly exact Si(100) surfaces terminated with monohydrides.[32,33] However, direct comparison to the RA spectrum of Ref. 32 (Fig. 1, red line) shows differences in amplitude and sign of the signal. Reference 32 showed the sensitivity of RAS to the surface reconstruction of monohydride terminated Si(100) by experimental and theoretical results. Domains with mutually perpendicular dimer orientation exhibit RAS signals with opposite sign. Since RAS integrates over the entire probed surface area, the measured signal reflects the preferential dimer orientation which enables domain quantification by linear scaling (blue arrow).[22] When comparing experimentally and theoretically derived RA spectra, in Ref. 32, the authors estimated a domain imbalance of 60:40, with a *B*-type domain majority for their sample obtained by electromigration on a nearly exact Si(100) surface. From our FTIR results,[12,28] we infer a domain distribution of about 82:18 with an *A*-type majority domain. Comparison of the peak intensity at 3.4 eV of our RA spectrum to the spectrum of Ref. 32 scaled by a factor −3.5 (dotted gray line) indicates a domain ratio of about 85:15, in good agreement with the FTIR results.[28]

LEED, *in situ* RAS, and FTIR[28] enable independent quantification of the domain ratio of our MOCVD prepared Si(100) samples on a large scale. We observed a strong majority of the *A*-type domain on the Si(100) samples after CVD processing. Remarkably, this result would imply the presence of unfavorable D_A-type steps on the surface. We applied STM to resolve the surface structure on an atomic to microscopic length scale.

Figure 2(a) shows a typical STM image of this Si(100) surface where a step structure of terraces with rather straight edges was observed. The difference in height of these terraces corresponds to two atomic layers. In some step edge locations, short stripes of variable length extend perpendicularly from the straight step edges onto the lower terrace (black arrow), but in many places the straight step edges are sharp without an intermediate fringe or terrace (one example is indicated by a white arrow). To study the structure at the step edges in more detail, we carried out STM measurements with atomic resolution. Figure 2(b) shows an area around a step edge clearly resolving individual Si surface atoms. Rows of pairs of atoms are separated by a deeper trough than the one separating atoms within one pair. We identify these pairs as Si dimers, where each Si atom is terminated by a single hydrogen atom, according to previous results.[12,28] The dimer rows run parallel to the step edge both on the terrace above the step edge and on the terrace below the step edge. The step height was confirmed to correspond to a double atomic layer step. Hence, the step type was identified as a D_A-type step referring to a double-layer step with dimer rows parallel to the step edge. Accordingly, the straight step edges in the large area image of Fig. 2(a) can be identified as *A*-type step edges, and the short stripes extending perpendicular from the *A*-type step edges correspond to residual dimer rows of the *B*-type terrace. In the surface region shown in Fig. 2(a), the dominance of the *A*-type terraces is evident and the absence of an intermediate ledge in many locations implies a high proportion of true D_A-type steps. We obtained similar images at several locations on the sample within the scanning range of our STM (2×2 μm^2).

Our observation of D_A-type steps after standard CVD preparation is in disagreement with previous experimental[6,16] and theoretical[3,5,14,15] reports in the literature, where D_A steps were found to be the energetically most unfavorable step type on both the clean and monohydride Si(100) surface.

The sensitivity of RAS to the dimer orientation on Si(100):H enables us to (i) observe and quantify the formation

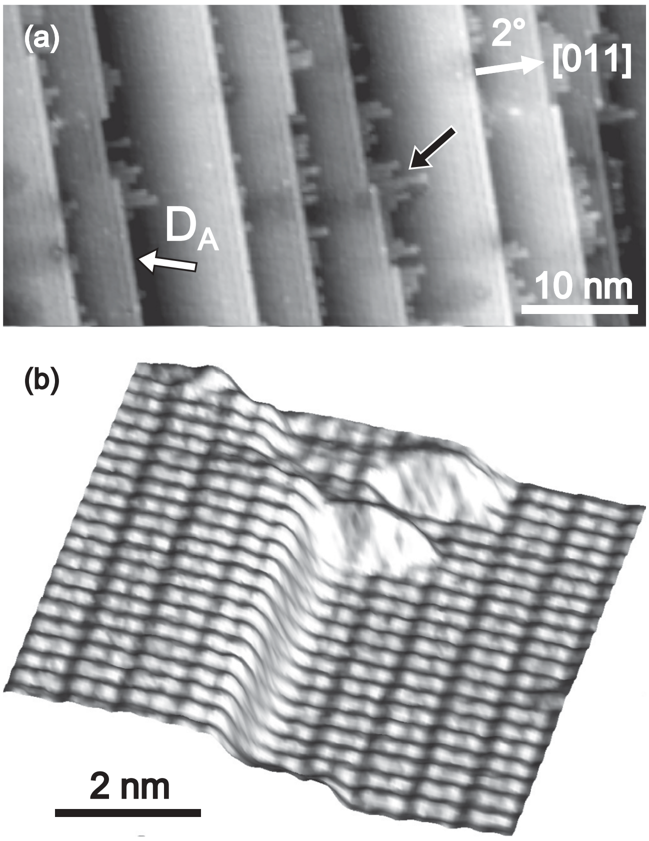

FIG. 2. (a) Empty-state image ($I_t = 170$ pA, $V_t = 1.24$ V) of Si(100) surface misoriented 2° in the [011] direction with D_A-type steps (one example marked by a white arrow). The black arrow indicates dimer rows of the residual B-type domain. (b) Empty-state image ($I_t = 150$ pA, $V_t = 1.24$ V) and atomic resolution detail (smoothed, z-scale $3\times$ magnified) of a double-layer step at the Si(100) surface with 2° misorientation in [011]. Dimer rows parallel to the step edge, without an intermediate terrace, are clearly visible, implying a true D_A-type step.

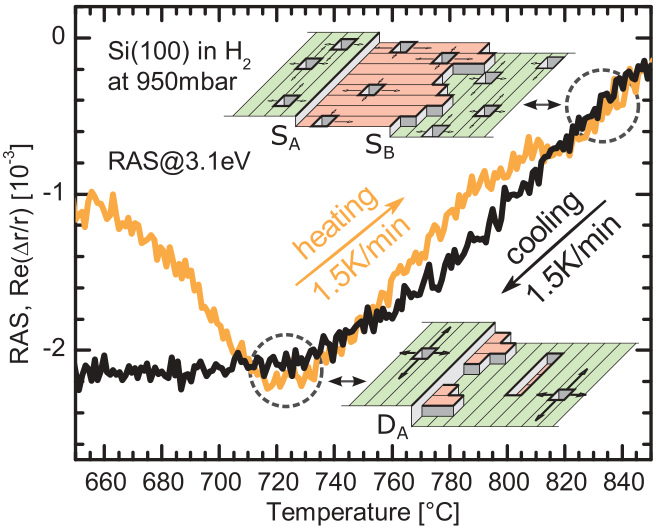

FIG. 3. (Color online) Transient RAS measurements of a Si(100) sample with 2° misorientation at 3.1 eV (corresponding to the characteristic RAS peak at 3.4 eV of Fig. 1 in the given temperature range) during heating (orange line) and cooling (black line) between 650 and 850 °C in H_2 at a constant pressure of 950 mbar. Vacancy generation increases with temperature (upper sketch), whereas vacancy diffusion dominates at temperatures around 720 °C (lower sketch).

of the majority domain during the process, (ii) extract the essential preparation parameters, and (iii) use this information for comparison with our microscopic understanding. Thereby, we found that conditions in the temperature range between 700 and 750 °C appear decisive for the generation of D_A double-layer steps. Crucially, we kept the hydrogen pressure constant at 950 mbar during our preparation process down to temperatures around 500 °C. Previous experiments, where the pressure was reduced above 500 °C, led to the standard two-domain $(2 \times 1)/(1 \times 2)$ reconstruction.[19]

To study the step formation in dependence on temperature, we observed the development of the peak around 3.4 eV in the RA spectrum of Fig. 1 during cooling and heating between 650 and 850 °C (1.5 K/min). The resulting transients at 3.1 eV (RAS peak thermally shifted) in Fig. 3 provides information on step structure formation. While cooling identifies the temperature for step formation, a comparison between the transients during cooling and heating at higher temperatures narrows down the possible mechanisms for this process. Starting from a surface with a small preference of the type-A domain, during heating (orange line), the magnitude of the signal first increases at temperatures up to 720 °C and then steadily decreases to a value close to zero at 850 °C. During cooling from 850 °C down to 720 °C (black line), the magnitude of the RAS signal increases, following a trajectory close to the one during heating. When cooling below 720 °C, the RA signal roughly remains constant. Based on these data, we conclude that the temperature range around 720 °C is decisive in the formation of the D_A step structure. Above 720 °C, the same trend is observed between heating and cooling and the two trajectories are closely aligned, although we observed some hysteresis between cooling and heating in the temperature range between 810 and 760 °C. The close match between the curves suggests that the surface is close to a dynamic equilibrium in this temperature range. In principle, changes of the RA signal intensity may be related to (i) thermal shifts,[34] (ii) hydrogen termination,[12,26,33] or (iii) the surface domain ratio.[32] Since we estimated the hydrogen coverage of Si(100) to about 80% at $T = 850$ °C and $P = 950$ mbar,[17,26] the RA signal at this temperature and below mainly reflects the surface domain ratio.

In Ref. 26, we provided evidence of the strong interaction of the hydrogen ambient with the Si(100) surface under standard CVD preparation conditions. At elevated temperatures, adsorption and desorption of hydrogen take place continuously at the surface,[17] providing for highly reactive conditions. The present domain ratio is determined by the interplay of several processes: hydrogen adsorption and desorption, Si removal (etching) or growth, diffusion of Si adatoms or vacancies, annihilation of vacancies, or attachment of adatoms at step edges. These processes depend on major preparation parameters such as substrate temperature, hydrogen partial pressure, and silane supply. While direct Si removal from the B-type step edge might explain the reduction of the B-type terrace, and consequently the formation of an A-type majority domain, step energetics[14,15] disfavor A-type double-layer steps over a broad range of the hydrogen chemical potential. Hence, a model relying not merely on processes at the step edges should be considered. We therefore propose to adapt a model by Bedrossian and Klitsner[9] and Swartzentruber[10] based on Si removal on the terraces. They investigated experimentally the step structure resulting from Xe-ion bombardment and annealing. Under certain conditions, they found the formation of a majority domain and of D_A steps, which depended crucially on the preferential annihilation of the vacancies at the B-type step edge. We propose that a similar process occurs in our case, where the reactive process environment at 950 mbar H_2 pressure induces vacancy generation: The domain ratio at temperatures between 720 and 850 °C varies continuously, depending mostly on Si vacancy generation, diffusion, and annihilation. If the rate of vacancy generation at 720 °C is finite, but relatively small, the generated vacancies diffuse and reach B-type step edges where they annihilate,[9] resulting in a retreat of the B-type terrace and near-perfect A-type terraces (see Fig. 3, lower sketch). As the temperature increases and the rate of vacancy generation increases more strongly with temperature than the diffusion rate,[14,21] diffusion to the B-type step edges is too slow to remove vacancies from the terraces (see Fig. 3, upper sketch). Since vacancy generation will not differ significantly on A- and B-type terraces, a more balanced domain ratio results, leading to a reduced RAS signature at higher temperature.

In principle, the resulting anomalous D_A step structure is thought to be thermodynamically unstable and should depend on the continuous removal of Si surface atoms, diffusion, and annihilation at the step edge. However, cooling below 720 °C goes along with the formation of a stable monohydride termination.[26] Thus, Si surface atom removal does not occur anymore and hydrogen termination leads at the same time to a significant reduction of the Si adatom diffusion rate[35] and to a passivation of the Si(100) surface.[17] In analogy, vacancy diffusion rates may also be reduced, resulting in a stabilization of the anomalous surface step structure. This accounts for the difference in the two transients of Fig. 3 in the temperature range below 720 °C.

In conclusion, we have obtained double-layer steps of the energetically unfavorable D_A type on monohydride terminated, 2° misoriented Si(100) by CVD processing in hydrogen ambient. We apply a model for the underlying step formation consisting of surface vacancy generation, diffusion, and annihilation at the step edges with subsequent hydrogen passivation, leading to the anomalous step structure with D_A-type double-layer steps. Currently, we are investigating the control of the formation of anomalous D_A-type step structure by fine tuning the crucial process parameters such as T, p, t, etc., and utilizing the variation of step density and terrace width with the degree of misorientation for our characterization. Since we observed a tendency toward conventional D_B steps for vicinal 6° Si(100) substrates,[19] we expect competition between the kinetically driven D_A and the energetically governed D_B double-layer step formation mechanisms when applying the process described above. On nearly exact Si(100), the probability of step edge annihilation processes for vacancies on A-type terraces decreases in comparison to mutual interaction of vacancies possibly resulting in nucleation and growth of vacancy islands.

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