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Monohydride Formation on Vicinal Si(001) Investigated by Reflectance Anisotropy Spectroscopy

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We report reflectance anisotropy spectroscopy (RAS) results for the controlled dosing of atomic hydrogen onto a clean 3° offcut Si(001)-(1 × 2) sample, cut so as to expose a single domain under ultra-high vacuum (UHV) conditions. Upon dosing approximately 0.8 monolayers of atomic hydrogen onto this surface at room temperature, followed by annealing, large changes in the RAS line-shape are observed. These are attributed to terrace disorder, step roughening and to the formation of the monohydride Si(001)-(1 × 2)-H phase, respectively, with increased annealing temperature. However, a (1 × 2) LEED pattern is observed throughout H adsorption and after annealing. We compare the RAS spectrum for the monohydride phase with microscopic calculations of the optical response and interesting agreement is found in the region of 3.2 eV.

1. Introduction

The interaction of hydrogen with semiconductor surfaces has been the subject of widespread interest in recent years owing to its use in chemical vapour deposition (CVD), chemical beam epitaxy (CBE), and in surface passivation. Here we investigate the initial adsorption of atomic hydrogen (H) onto clean Si(001) under well controlled ultra-high vacuum (UHV) conditions. Under these conditions, it is known that atomic H forms an ordered monohydride (1 × 2) phase at 1 monolayer (ML) coverage [1]. A well ordered dihydride (1 × 1) phase, which saturates at the higher coverage of 2 ML (i.e. 2 H atoms for every surface Si atom) cannot be obtained by this method and may only be produced by wet chemical etching [2].

In this paper, we apply the optical probe technique, reflectance anisotropy spectroscopy (RAS), to the formation of the monohydride phase. RAS was developed in its present form by Aspnes and Studna [3] and has proven to be a powerful tool in surface science. The technique derives its surface sensitivity from measurements of the difference in normal incidence reflectance for light polarized along two major orthogonal axes along the surfaces of cubic crystals which have isotropic bulk optical properties. For a (001) surface, the RAS intensity is described by

$$\frac{\Delta R}{R} = 2 \frac{R_{[\bar{1}10]} - R_{[110]}}{R_{[\bar{1}10]} + R_{[110]}} \quad (1)$$

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where $R_{[\bar{1}10]}$ and $R_{[110]}$ are the optical reflectances along the $[\bar{1}10]$ and $[110]$ directions of the sample surface, respectively. For the clean vicinal Si(001) surface, the $[\bar{1}10]$ direction lies parallel to the Si dimer bond direction of the majority domain.

RAS has been used previously to characterise the H/Si(001) system by atomic hydrogen dosing under UHV conditions [4 to 7] but little consensus concerning the actual RAS lineshape for the monohydride phase has been reached. Our results show qualitative agreement with those obtained for the growth of Si on vicinal Si(001) under gas source MBE conditions using disilane (Si_2H_6), but the origin of the features observed was not explained [8]. Here, we fully explain the features observed in the RAS spectrum for the monohydride phase by comparing experimental RAS data with microscopic calculations of the optical response.

2. Experimental

The experiments were performed in a UHV chamber, with a base pressure of 2×10^{-10} mbar. The Si(001) substrates (resistivity 2200 Ωcm , phosphorus doped) were cut 3° off the (001) plane towards the $[110]$ direction. The samples were degassed at 873 K overnight and cleaned by sequential heating cycles up to 1273 K, while keeping the system pressure below 2×10^{-9} mbar. Once the sample cleaning procedure was complete, LEED revealed a (1×2) pattern indicative of a surface consisting of mainly one domain, with energy dependent spot-splitting consistent with a periodic step structure.

The hydrogen source consisted of a differentially pumped gas line linked to a sensitive gas-inlet valve. After several hydrogen flushing cycles of the gas-line, H_2 gas was allowed into the vacuum chamber until a pressure of 5×10^{-7} mbar was reached. To crack the H_2 bond and form atomic hydrogen, a W filament operating at approximately 1800 K was positioned <4 cm from the sample. Sample contamination arising from out-gassing of the W filament at 1800 K was ruled out through observation of no variation in the RAS amplitude or lineshape of the clean Si(001) sample over a period of at least 10 min. This also ruled out any significant filament-induced sample heating, which is known to affect the RAS signal [9].

A split-spot (1×2) LEED pattern was still observed after H dosing and annealing despite large changes in the RAS response. All RAS and LEED experiments were carried out with the sample cooled to room temperature after annealing. After several H doses, a deterioration of the UHV chamber base pressure occurred due to the low efficiency of the chamber ion- and turbo-pumps in pumping hydrogen.

The RAS spectrometer used in this work is described elsewhere [10]. The central part of a large diameter strain free optical viewport was used so that the RAS spectrometer could access the sample in UHV. The strain in this viewport was essentially zero meaning that azimuthal rotation of the sample about its surface normal to an equivalent position to correct for strain within the viewport was unnecessary. This was confirmed by measurement of a clean vicinal Si(001) RAS spectrum which was in agreement with previous works [11 to 13].

3. Calculation

The calculation was performed within the local density approximation of density functional theory (LDA-DFT) using a plane-wave basis set and norm-conserving pseudopo-

tentials. The fully relaxed atomic positions were obtained by Car-Parrinello molecular dynamics simulation [14] and the Si(001) surface was represented by a repeated slab geometry with 12 atomic layers and 4 empty layers. The wavefunctions were expanded in a set of plane waves corresponding to a cut-off of 15 Ry. Four special k -points in the irreducible Brillouin zone (IBZ) were used for the determination of the equilibrium geometry, while a set of 64 special k -points was enough to achieve a good convergence in calculating the optical properties. All the optical spectra were calculated using a reduced kinetic energy cut-off of 10 Ry.

Within the slab geometry, the RAS response can be written as

$$\frac{\Delta R}{R} = \frac{16\pi\omega d}{c} \operatorname{Im} \left| \frac{\alpha_x(\omega) - \alpha_y(\omega)}{\epsilon_b - 1} \right|, \quad (2)$$

where α is the half-slab polarizability, x and y correspond to the $[\bar{1}10]$ and $[110]$ directions, respectively, ϵ_b is the bulk dielectric function and d is the half-slab thickness [15]. The calculation of α and ϵ_b involved determination of the matrix elements of the momentum operator between valence and conduction states. In order to compare the theoretical spectra with the experimental results, a scissors operator of 0.5 eV was applied.

4. Results and Discussion

In the following discussion, we interpret the RAS results in terms of surface structure changes that occur when H is adsorbed onto clean Si(001)-(1 × 2) at room temperature followed by annealing. Increasing the annealing temperature results in the formation, and subsequently, the desorption of the monohydride phase producing significant changes in the RAS lineshape. Then we compare the RAS spectrum for the monohydride surface with microscopic calculations of the optical response.

Fig. 1 shows the clean 3° offcut vicinal Si(001)-(1 × 2) RAS spectrum and the changes in this spectrum induced by room temperature H-adsorption followed by annealing up to the formation of the monohydride (1 × 2)-H surface. As outlined above, the RAS spectrum for the clean vicinal Si(001) surface is in good agreement with previous works [11 to 13]. In absence of Auger electron spectroscopy (AES), this RAS spectral lineshape confirms sample cleanliness, as such an RAS spectrum was obtained previously when AES was present to confirm sample cleanliness [11].

Upon the adsorption of 8 s of atomic hydrogen (approximately 0.8 ML) at 5×10^{-7} mbar onto the clean vicinal Si(001)-(1 × 2) surface at room temperature, a significant reduction in anisotropy is observed (see Fig. 1). From the figure, it can be seen that although adsorption of H causes the RAS intensity to decrease, the overall RAS lineshape still resembles that of the clean Si(001) surface. Hence, the effect of H adsorption has been to remove some of the step and terrace optical anisotropies which are both known to contribute significantly to the overall RAS response for a vicinally cut Si(001) sample with an offcut $>1^\circ$ towards the $[110]$ direction [16]. As the RAS lineshape resembles that of the clean surface, the RAS signal must arise from areas of clean surface, both steps and terraces not covered by H. From the STM work of Bolland [17], the terrace H randomly occupies Si dimer dangling bond sites, while on the steps H most likely bonds to dangling bonds associated with the re-bonded step geometry [18]. Upon annealing the as-deposited sample to 400 K (see Fig. 1), a small peak is observed in the region of 3.5 eV which we discuss later.

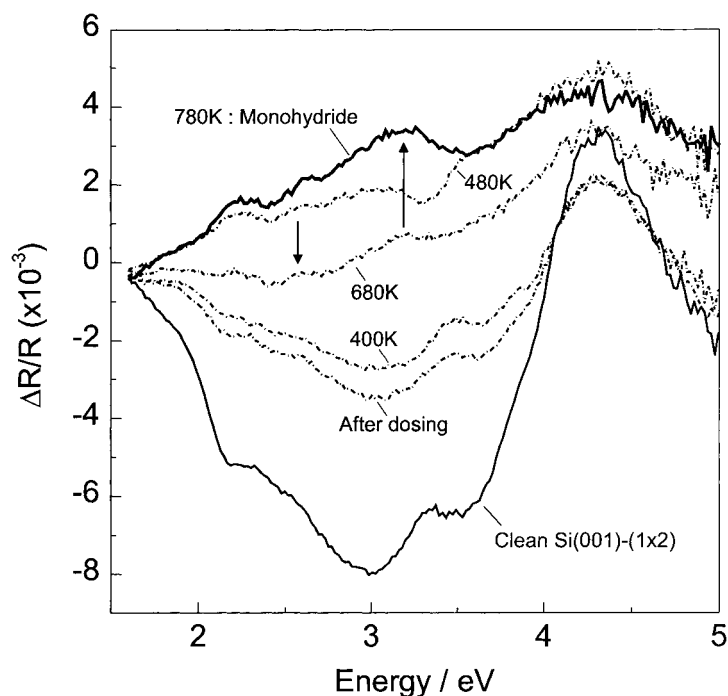


Fig. 1. Initial adsorption of approximately 0.8 ML of H onto the clean 3° offcut Si(001) surface. The samples were annealed for 5 min and each spectrum was taken with the sample cooled down to room temperature after annealing

Annealing to 480 K produces large changes in the RAS lineshape and the whole spectrum becomes positive in sign. It appears from this large change that the increase in annealing temperature causes a re-distribution of H on the Si(001) terraces and steps, removing both the clean surface step and Si dimer dangling bond terrace contributions to the RAS response [16]. We propose that the step contribution is removed through H saturation of the re-bonded step edge dangling bonds [18] while the Si dimer related terrace response is now removed through random occupation of H on Si dimer dangling bond sites over the whole terrace region [17]. This random occupation of H changes the terrace electronic structure, and hence the RAS lineshape, although structurally, the Si dimer rows still exist yielding a (1×2) LEED pattern. A sharp structure is observed in the RAS spectrum in the region of the E_1 gap of bulk Si at 3.4 eV. We associate this feature with an off-resonant step contribution to the surface-induced optical anisotropy in agreement with previous authors [5, 6].

Annealing to 680 K results in a loss of optical anisotropy below 3.0 eV, and in the removal of the sharp 3.4 eV feature (see Fig. 1). As this feature is step-related, its removal must be associated with H roughening of the step edges. This roughening may be caused by extra H at the step edge, promoted through diffusion of terrace H. This is conceivable by analogy to the above saturation coverage of the Si terraces with H, where extra H is known to cause terrace roughening [19]. Evidence for such diffusion is provided by the scanning tunnelling microscopy (STM) work of Boland [17]. This diffusion inevitably supplies the steps with more H. The result is that after this anneal, the

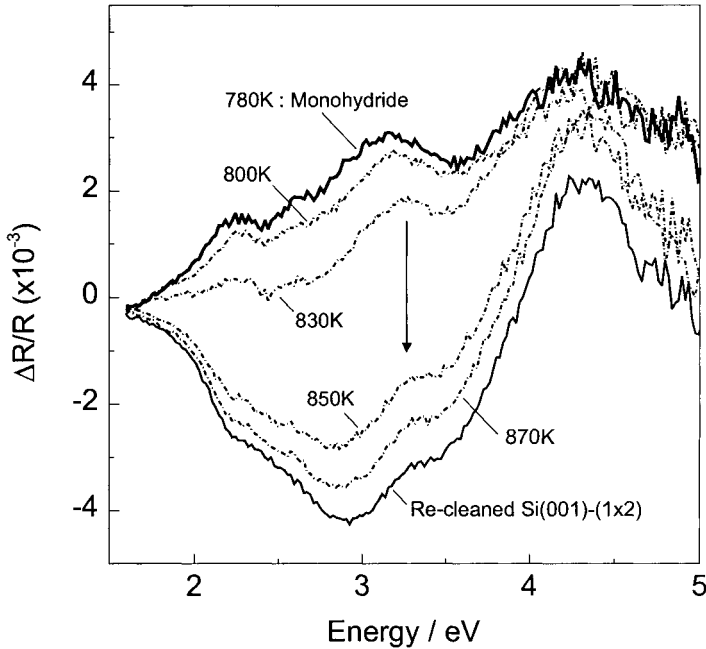


Fig. 2. Desorption of submonolayer H coverage from the 3° offcut Si(001) surface. Each spectrum was taken with the sample cooled down to room temperature after annealing

surface terraces have locally begun to order but can still be regarded as disordered while the surface steps have been roughened by excess H.

Annealing beyond 680 K causes a gradual increase in RAS amplitude, particularly in the region of 3.2 eV, which saturates upon annealing to 780 K (see Fig. 1). We associate this ordering with the formation of the monohydride phase in light of three arguments. Firstly, a (1×2) LEED pattern is observed. Secondly, no change in RAS lineshape or amplitude is observed over a 12 hour period. This implies a surface consisting of no reactive dangling bonds ruling out any desorption arguments from surface steps. Finally, upon annealing the sample to 800 K, a reduction in anisotropy is observed (see Fig. 2). This is expected for the monohydride surface as H is known to desorb from Si(001) at approximately 795 K [20]. Desorption is largely complete after annealing to 850 K. We note that, once re-cleaned, the Si(001)- (1×2) surface RAS amplitude has decreased by approximately 50%. This is consistent with H-induced roughening of the surface steps.

Next, we compare the experimental lineshape of the monohydride surface with microscopic calculations of the RAS response for different H covered Si(001) surface structures, shown in Fig. 3. Such calculations have already been successful in determining the RAS response for clean Si(001), where interesting agreement was found upon comparing experimental RAS data arising from surface Si(001) terraces with calculations of the RAS response for $c(2 \times 4)$ and $p(2 \times 2)$ reconstructed surfaces [21]. From Fig. 3, it can be seen that significant agreement exists for the monohydride surface, particularly below 4.0 eV where both calculated and experimental results show a positive sign, and a strong positive feature in the 3 to 4 eV energy region. We associate the experimental feature observed at 3.2 eV to the calculated peak which occurs at 3.4 to

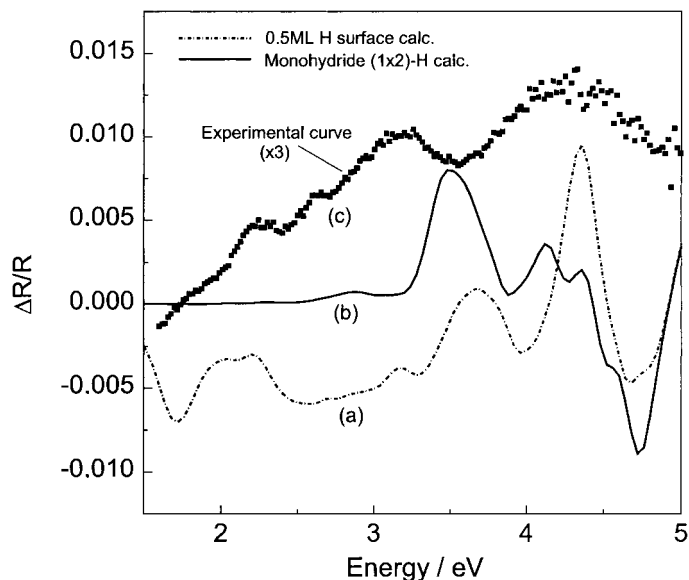


Fig. 3. LDA-DFT calculations of the RAS response for (a) the 0.5 ML H covered surface (1H per Si dimer) where each H is positioned on the same dangling bond site on each dimer and (b) the monohydride phase (2H per Si dimer). The RAS experimental data for the monohydride phase, magnified ($\times 3$), is also shown (labelled (c) in the figure)

3.5 eV. Such discrepancies in the energy position are considered within calculational uncertainty for calculations of this kind, despite the application of a 0.5 eV scissors operator, and may arise due to excitonic and local-field effects which are ignored in the calculation. The 3.4 to 3.5 eV peak arises due to a non-resonant effect involving monohydride perturbation of the bulk E_1 structure. Transitions from the Si–H bond to its antibond can be excluded, since they occur close to 7 eV [22].

The RA amplitude of the calculated peak at 3.4 to 3.5 eV is five times larger than the experimental peak. The calculated spectra assume a flat surface with no steps containing a 100% domain imbalance whereas for our vicinal sample, the clean Si(001)–(1 \times 2) domain ratio is 4:1 for (1 \times 2):(2 \times 1) yielding at best, a 60% domain imbalance. The effect of H roughening of the step edges which cover essentially 20% of the surface, which is also expected to reduce the domain ratio further reconciles the differences in the RAS amplitude observed.

Other agreement exists on comparing experiment with calculation. The RAS spectra for initial adsorption of H and also after gentle annealing to 400 K reveal a small feature centred at 3.5 eV (see Fig. 1). This feature is also present in the calculated data for the 0.5 ML H covered surface, but centred at 3.7 eV. The calculated 0.5 ML H model surface possesses one H attached to the same dangling bond site on each of the Si dimers. Hence, this agreement is consistent with the existence of some ordering of H on the terraces, even before annealing. With regard to the experimental RAS data, the 3.5 eV feature is not re-established during desorption of the monohydride phase. This suggests that H desorbs from the monohydride phase in pairs from each dimer rather than individually, in agreement with the STM results of Boland [17].

The experimental peak at 4.2 eV obtained for the monohydride phase may also correspond to the weak structures observed in the calculation of the monohydride surface between 4.0 and 4.5 eV (see Fig. 3). However, this feature could also be related to small regions of the monohydride surface containing only one H per Si dimer on consideration of the calculated RAS response for the 0.5 ML H covered surface (see Fig. 3) where a large positive feature exists in the region of 4.3 eV.

5. Conclusion

We have studied the initial adsorption of atomic H on the clean Si(001)-(1 × 2) surface under well-controlled UHV conditions. Comparing the experimental RAS results with calculated data of the RAS response, good agreement is found for the Si(001) monohydride surface. Despite a (1 × 2) LEED pattern being observed throughout H adsorption and desorption, RAS displays a large dependence on annealing temperature. This result highlights the importance of electronic structure probes such as RAS over geometrical structure probes, such as LEED, in generating reproducible surface structures.

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