Atomic-scale control of the III-V-on-Si formation for solar energy conversion devices

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III-V semiconductor materials are well established in high-performance multi junction solar cells and also constitute a promising absorber material class for solar-driven water splitting due to their tunable electro-optical properties. The concept of III-V based high performance devices on silicon substrates relies on suitable Si(100) preparation prior to III-V-on-Si heteroepitaxy. One of the fundamental problems for III-V-on-Si growth relates to the difference in atomic structure which manifests itself in the polarity of the III-V material as opposed to the non-polar nature of the silicon substrate. As a consequence, the step structure of the substrate is vital for defect-free heteroepitaxy, with single layer steps on the substrate initiating anti-phase disorder in the III-V material, while a double-layer stepped substrate in principle enables anti-phase-free III-V growth [1-3]. While UHV preparation of double-layer stepped Si(100) is well established, less is known about comparable preparation methods in the hydrogen-based MOVPE environment. Considered energetically least favorable on both the clean and the monohydride-terminated Si(100) surface, single domain surfaces with double layer steps in the unusual D_A configuration were recently prepared in MOCVD ambient [4]. The D_A step formation on Si(100) with 2° offcut in CVD ambient is suggested to originate in vacancy generation and diffusion on the terraces accompanied by preferential annihilation at the step edges. Here, we investigate Si removal and vacancy formation on Si(100) substrates with large terraces under CVD preparation conditions. With in situ reflection anisotropy spectroscopy (RAS), we directly observe the domain formation in dependence of the preparation route. Oscillations in transient RA measurements indicate layer-by-layer Si removal during annealing in hydrogen. Based on scanning tunneling microscopy results, we conclude that vacancy island formation and anisotropic expansion preferentially in parallel to the dimer rows of the terraces explains the layer-by-layer Si removal process.

RA spectra of the monohydride-terminated Si(100) surface show a characteristic peak at the E1 transition of silicon which is related to the dimerized surface reconstruction [4]. For Si(100) samples misoriented by 2°, we found that the temperature range around 770 ºC is decisive in order to form stable D_A steps and that annihilation of vacancies at the step edges plays a major role [4-7]. For low-offcut samples the result differs drastically, as can be seen in the transient RA signals measured during annealing at about 770 ºC in 950 mbar H2 (Fig.1).

Since the sign of the dimer-related peak in the RA spectrum (at 3.1 eV at 770ºC) corresponds to the dimer orientation, the transient shows a preferential A-type domain decreasing until the contributions of both domains cancel each other out. The former minority domain then prevails until the opposite development occurs. The prevalence of one domain can be preserved by cooling the sample, the insets in Fig. 1 show corresponding RA spectra. The constant period of the oscillation in the transient indicates a uniform transformation. Consequently, Fig. 1 shows layer-by-layer removal directly via the dimers, which are oriented mutually perpendicular from layer to layer.

Based on STM measurements, we conclude that the formation of vacancy islands on the large terraces and their anisotropic expansion, preferentially in parallel to the dimer rows of the terraces, are the reason for the observed layer-by-layer removal. Removal of the subjacent Si layer 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 layer.

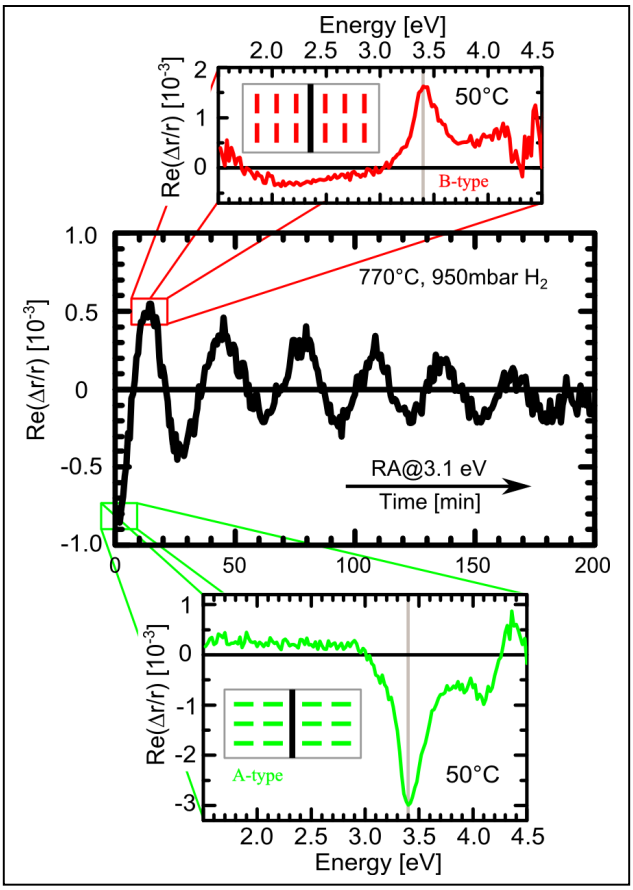

Fig. 1. Transient in situ RA measured at 3.1 eV during annealing of Si(100) 0.1° -> [011] at about 770 K in 950 mbar H_2. The insets show RA spectra of corresponding surfaces after optimized preparation and cooling to 50 ºC. The grey lines indicate the thermal shift relative to 3.1 eV at 770 ºC.

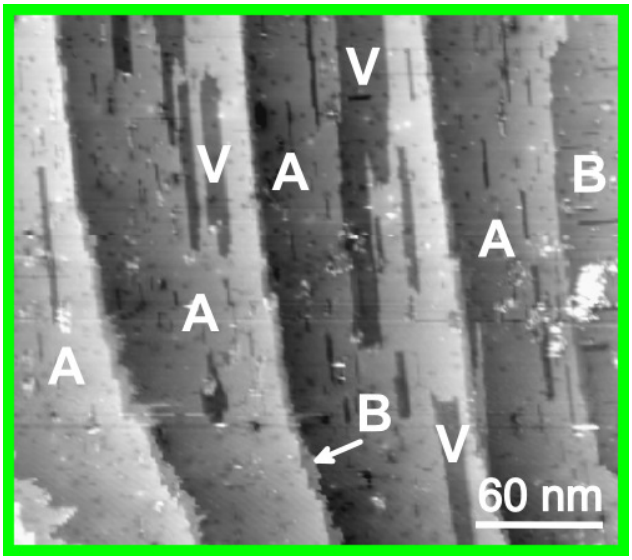

Fig. 2.STM (emtpy state) image of a Si(100) 0.1º sample which was cooled fast after buffer growth and annealing at 1000 ºC. The surface exhibits mainly A-type terraces ("A") and vacancy islands ("V"s) elongated parallel to the dimer rows.

Fig. 2 shows an STM image of a Si(100) 0.1º sample which was cooled fast after buffer growth and annealing at 1000 ºC. The terraces exhibit mainly A-type domains with dimers oriented perpendicular to the step edges. Consequently double-layer steps of the D_A-type prevail. However, we also observe vacancy islands which were elongated parallel to the dimer rows of the terraces (indicated by "V"s). The vacancy islands are likely the result of a Si removal process during the cooling in H_2 ambient.

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