Growth of Ag nanowires on Au-pre-facetted 4° vicinal Si(001)

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Abstract
We studied the self-assembly of wire-shaped Ag islands at high temperature with low energy electron microscopy and photoemission electron microscopy. A Au-faceted vicinal Si(001) surface was used as a substrate. The initial Ag deposit at 600–620 °C induces a surface phase change from the (5 × 3.2) reconstruction of the Au-covered (001) terraces, to a (3 × 2) reconstruction, but leaves the structure of the Au-induced step bunches intact. Subsequent Ag growth produces two distinct types of 3D crystalline islands: compact and wire-like. The total Ag deposit is comprised mostly of compact islands, with only a small minority of wire-like islands. We attribute the wire formation to local step bunches that create the proper quasi-one-dimensional diffusion environment for the Ag islands to grow with a high aspect ratio.

1. Introduction

Metallic nanowires on silicon surfaces are of interest technologically because of their potential application in quantum devices, and scientifically since they provide a subject for the study of the physics of quasi-one-dimensional systems. One way to form nanowires is through self-assembly [1]. In several studies isolated, wire-shaped islands, with relatively large aspect ratios, are observed to form on Si substrates during deposition of metals. The results of these studies generally fall into two categories. In the first category are nanowires that form a silicide during reaction deposition epitaxy, including certain rare earth metals [2–8] and transition metals [9–12]. In the second category are nanowires that grow while maintaining an abrupt interface with the substrate and without intermixing or compound formation. This second category thus far is limited to Pb [13–15] and Ag [16,17].

Several different physical processes have been offered to explain the nanowires' formation for the different epitaxial systems. It was first proposed [16] that anisotropic mismatch strain was responsible for forming the nanowires. There indeed appears to be a correlation between strain and the observation of nanowire growth in different silicide systems [5]. However, He et al. [10] have suggested another mechanism for the formation of silicide nanowires on Si that does not depend on lattice mismatch strain.

In our studies of Ag nanowire growth on vicinal Si(001) [17] strain also does not appear to play a role [18], and we attribute the nanowire growth to anisotropic diffusion caused by step bunching during the Ag deposition. It therefore appears that there is, as yet, no universal model for the formation mechanism of the nanowires, and that the different mechanisms may have different levels of importance for different systems.

Here we evaluate the role of steps and step bunches by creating the optimum kinetically limited environment for the formation of Ag nanowires by pushing the step density to the extreme. We use, as a substrate, a vicinal Si(001) surface that has been faceted by Au adsorption at elevated temperatures [19]. This surface displays a more dramatic hill-and-valley morphology than that induced by Ag adsorption [20]. We observe the growth of Ag nanowires on this surface in situ, in real-time with low energy electron microscopy (LEEM) and photoemission electron microscopy (PEEM). We also present the results of the surface characterization before and after Ag deposition with spot profile analyzing–low energy electron diffraction (SPA–LEED), and verify the nanowires' shapes ex situ with scanning electron microscopy (SEM).

2. Experimental

The experiments were performed in two different ultrahigh vacuum (UHV) systems with a base pressure in the 10−10 mbar regime. The LEEM micrographs were recorded in the IBM LEEM I prototype [21]. The instrument can be operated in LEEM mode, and also in PEEM mode with the electron gun switched off, and the
Sample were cut from custom made Si(001) wafers (Silizium Bearbeitung Andrea Holm), miscut by 4° in the [110] direction. Prior to the experiments, the samples were wiped with ethanol, mounted in the sample holder, and degassed in ultra high vacuum at ≈600°C for several hours. Afterward, the protective oxide was removed by repeated flash annealing to ≈1250°C for several seconds.

After confirming the cleanliness of the surface by LEEM or SPA–LEED, Au was deposited to yield the faceted substrate. During Au deposition at 880°C, the 4° miscut Si(001) surface undergoes a step bunching transition, that ultimately results in an ordered sequence of (5×3.2) Au-reconstructed (001) terraces and (119) facets [19]. The kinetics of this faceting process [19,24], the driving forces [25], and the Au-induced reconstructions involved [19,26] have been extensively studied in the past and were recently reviewed [27,28].

After completed faceting at high temperature, the Au flux was stopped, the sample temperature was lowered below 650°C, and Ag deposition was started. At this lower temperature, the Au-faceted surface is thermally stable and no changes in the step structure could be observed even after annealing of the faceted samples for several hours. During Ag deposition at this temperature, however, there is a small degree of Ag desorption from the surface. The Ag deposition rate, therefore, had to be sufficiently high to overcompensate the desorption.

Both Au and Ag were deposited from home-built evaporation sources [29], using 5 N purity material. In both chambers, Au was deposited by electron beam evaporation from a graphite crucible. Ag was deposited either by electron beam evaporation from a Mo crucible (SPA–LEED chamber) or from a resistively heated ceramic crucible (LEEM chamber). All depositions were monitored in situ. As the experiments crucially depend on the facet structure that is formed during the Au adsorption, samples were exchanged on a daily basis to avoid kinetic limitations caused by irregularities in the step structure of the substrate (e.g. pinning of steps due to the accumulation of defects and dislocations caused by repeated flash-anneal cycles between the Ag depositions). Ex situ SEM images and cross-sections were obtained in a LEO 440 SEM after removal of the samples from the vacuum.

3. Results and discussion

3.1. Impact of Ag deposition on step structure

The suspected mechanisms that tailor the formation of the quasi-one-dimensional Ag nanowires in this study depend on the specific step structure at the surface. We therefore begin with a thorough inspection of the modification of the Au-faceted Si(001) template that takes place during Ag adsorption. Fig. 1a shows a map of the well-known reciprocal space of the vicinal Si(001) surface, along the [110] direction, after Au-induced facetting at 880°C, before the deposition of Ag. The surface consists of large reconstructed (001) terraces with their characteristic 5-fold periodicity perpendicular to the step edges, indicative of the (5×3.2) reconstruction on the terraces [19]. The lattice rods displaying this 5-fold periodicity have been labeled A–F at the top of Fig. 1a. In addition, a system of well-defined (119) facet rods is visible in the figure, indicative of large, reconstructed (119) facets, as expected for such a high faceting temperature. Fig. 1b shows the same surface after Ag deposition at 620°C. Clearly, the surface structure has been modified. First, the 5-fold periodicity on the terraces has been replaced with reciprocal lattice rods at 33%, 50%, and 66% of the surface Brillouin zone. These lattice rods are labeled...
A–C in Fig. 1b, respectively. Secondly, the system of facet rods remains mostly unaltered and the (119) facets are preserved. In addition to the (119) facets, however, weak (117) and (115) rods become visible. These are most easily seen in the vicinity of the (119) and (119) Bragg conditions. This suggests that during the Ag deposition, Ag displaces Au atoms, and in the process, some of the (119) facets are converted into facets with a higher inclination angle.

Fig. 2 shows a LEED pattern of the surface for which the reciprocal space map is displayed in Fig. 1b. The inset marks the relevant spot positions. The SPA–LEED image of Fig. 2 shows a segment of the Brillouin Zone of ±70% around the (00) spot in the center of the image. The horizontal rows of well-defined spots (sketched as dashed-lines in the inset) correspond to the facet rods of the (119), (117), and (115) facets. A sequence of elongated spots along the [110] direction at 33% BZ and 66% BZ (marked as × in the inset) suggests that an Ag-induced (3 × 2) reconstruction is present on the surface. This reconstruction is known [30] to form during deposition of Ag on Si(001). The (3 × 2) spots correspond to the vertical reciprocal lattice rods A and C in Fig. 1b, showing that this reconstruction is present on (001) oriented areas. Indeed, the (001) terraces have been converted from (5 × 3.2)-Au to (3 × 2)-Ag. Interestingly, the (3 × 2) reconstruction also exists in a domain that is rotated by 90° (represented by the (+) symbols in the inset). As the rotational orientation of the (2 × 3)-Ag reconstruction is coupled to the binding geometry of the underlying Si lattice, this indicates that now single steps are present on the initially double-stepped surface. This is also reflected in the existence of the vertical lattice rod B in Fig. 1b. The creation of facets of higher inclination, such as (117) and (115), leads to an increase of the total (001) surface area in order to preserve the overall miscut angle relative to the (001) plane. Thus, the formation of single steps, stabilized by the Ag, is not unexpected. This formation of single steps has also been observed as an intermediate phase during Au-induced faceting [19]. From the relative intensities of the LEED spots of the two rotated (3 × 2) domains in Fig. 2 it is clear that the rotated domains represent a minority.

For Ag wire formation on top of such a surface, several issues need to be addressed. The adsorption of Ag on a Au-covered Si(001) surface results in a complicated combination of materials, that has thus far not been thoroughly investigated. Most likely, some ternary alloy is formed at the surface that includes both Ag and Au, but also contains Si atoms from the substrate. In earlier studies, however, it was found that Ag deposited on top of alloyed Au–Si layers, of various thicknesses on Si(111), produced pure Ag films [31], probably because the submonolayer amount of Au available for alloying is limited, compared to the large amount of Ag deposited. Accordingly, the wires and compact islands that form at higher coverages and temperatures (described in Section 3.2) most likely consist of pure Ag.

Furthermore, it is important to consider that the behavior of Ag adatoms diffusing on bare Si(001) [17] and on Au predeposited Si(001) might be quite different, and might, in addition to the influence of steps, affect wire formation. In a recent study [32] the diffusion of Ag on various Au-induced reconstructions on Si(111) was investigated in electromigration experiments [33]. The results show that the speed of the diffusive spreading-out of a defined patch of Ag depends, in a complicated manner, on the initial interfacial Au reconstruction. Nevertheless, the general behavior of the Ag spreading on the different reconstructions was not significantly different. In particular, the presence of steps did, in all cases, affect the outcome more than the reconstruction. Assuming that similar behavior holds for Ag diffusion on the Au-induced reconstructions on the Si(001) surface, it is likely that the specific adatom diffusion processes, associated with different reconstructions, affect the nanowires only in a minor way. The initial Au reconstruction, encountered by diffusing Ag adatoms, might only be relevant for the ultimate aspect ratio attained by the growing nanowire, but not decisive in determining whether or not a wire is formed.

In summary, the adsorption of Ag on the faceted Au surface at 620 °C affects the overall surface topography of the faceted surface only in a way, that is most likely irrelevant for the wire formation. The reconstruction on the (001) terraces is changed from (5 × 3.2)-Au to (3 × 2)-Ag and the (119) facets are locally modified. During this transformation, a small number of single steps is created. We would like to emphasize that adsorption of Ag at lower temperatures results in LEED patterns that are different from that

**Fig. 2.** SPA–LEED pattern after Ag deposition on the Au-faceted 4° vicinal Si(001) surface. The inset shows a sketch of the LEED pattern. The horizontal gray dotted lines correspond to the facet rods. The features represented by (×) are identified as spots resulting from the (3 × 2)-Ag reconstruction, and the features represented by (+) denote spots resulting from a rotated (2 × 3)-Ag reconstruction domain.

**Fig. 3.** Bright field LEEM image of a Ag wire during growth on a Au-faceted 4° vicinal Si(001) surface. The wire appears bright. The gray-scale modulation of the background reflects the faceted topography of the surface. The wire grows along the step bunches in the (110) direction while preserving its width.
in Fig. 2, and that a systematic investigation of the temperature dependent surface phase diagram of the Au/Ag/Si(001) system has yet to be done. It is important to note, however, that at all temperatures the step structure of the substrate after Au-induced faceting is mostly preserved during the Ag adsorption. The intended anisotropy of the surface, that was created during the Au-induced faceting, thus remains.

3.2. Wire formation

After the completion of the (3 x 2)-Ag reconstructed overlayer, subsequent deposition of Ag produces single crystal compact and wire-shaped islands on top of the reconstruction. Several aspects of the Ag nanowire growth are noteworthy. Fig. 3 shows a LEEM image of one end of a bright Ag nanowire grown at 605 °C on a Au-faceted vicinal Si(001) surface. The faint modulation in the gray-scale around the wire is caused by the large-scale Au-induced faceting that occurred during the initial sample preparation. The wire grows in the [110] direction along the edges of the facets.

Shown in Fig. 4 is a sequence of PEEM images that were recorded at different times during growth of a Ag wire. The wire appears bright and the slight modulation in the background is again caused by the faceted structure of the surface. The wire’s length increases with an average growth rate of ~600 nm/min. Interestingly, the wire’s width remains constant as it grows longer. Fig. 4e shows the wire at a later time, when the wire has a length of 38 μm. We have routinely observed such wires to grow lengthwise without bound (>100 μm) during the duration of our growth experiments.

In addition to the wire, two compact islands (labeled A and B in Fig. 4) are also observed in the figure, and their growth during the observation time is far less significant than the striking increase of the wire’s length. Such compact islands typically grow in a three-dimensional fashion which accounts for their apparent slower lateral growth rate in PEEM.

We grow the wires at a high temperature (well above 600 °C) in an attempt to minimize kinetic limitations. Growing the nanowires at these high temperatures also produces low nucleation densities, and allows us to avoid the interaction of a growing wire with a compact island. At the used temperatures most of the islands are compact as can be seen in Fig. 5, wherein the large field-of-view PEEM image shows a Ag deposit consisting predominantly of compact islands. The vast majority of islands we observe are compact and they remain compact and grow 3-dimensionally throughout the entirety of the subsequent growth. We do not observe the shape transition from compact to elongated islands predicted for strained systems [16] and observed [34] for CoSi2. For the Ag/Si(001) system it has been demonstrated [35] that the Ag islands grow in cube-on-cube manner; that is, Ag(001) planes grow epitaxially parallel to the Si(001) planes of the substrate [36]. Therefore, as can be seen from a coincident site lattice of Ag(001) on Si(001), there are almost exactly four Ag lattice spacings for every three Si lattice spacings, implying negligible mismatch strain of 0.32% in this system [18]. If there is similar negligible strain for Ag on the Au-faceted Si(001) then any shape transition should not be expected. Since only a minority of the islands have the elongated wire shape, we conclude that local kinetic limitation is driving the wires’ formation.

Fig. 4. PEEM images during Ag growth at T = 630 °C on a Au-faceted 4° vicinal Si(001) surface. The Ag islands and wires appear bright, while the ripple-like modulation of the background is due to the Au-induced faceting. The images were recorded at different times during wire growth: (a) t = 27 min, (b) t = 36 min, (c) t = 40 min, (d) t = 45 min, (e) t = 73 min. The scale of panels (a)-(d) is different from the scale of panel (e).

Fig. 5. PEEM image of a larger area of the surface after Ag growth on a Au-faceted 4° vicinal Si(001) substrate. The Ag islands and wires appear bright, while the ripple-like modulation of the background is due to the Au-induced faceting. The wires grow alongside compact islands, along the step bunches of the faceted substrate.

Fig. 6. SEM image of Ag wires (bright) deposited on a Au-faceted 4° vicinal Si(001) surface (dark). All wires have different side facets and widths.
The effect of Ag nanowire growth at a lower temperature ($T = 570^\circ$C) is illustrated in the SEM image in Fig. 6. The island density is increased, relative to that for growth at higher temperatures, for both compact and wire-like islands, with an increased ratio of the number of wires to compact islands. The wires have well-defined side facets, indicating a high degree of crystallinity. It has been independently confirmed by magnetotransport measurements [37], that the wires are indeed single-crystalline with very few defects. It is surprising, though, that the specific shape appears to differ from wire to wire. The cross-section SEM image of Fig. 7 further illustrates that some of the wires are symmetrical, while others consist of a steep side facet coupled with one of a smaller inclination angle on the other side. All wires also show small inclined side facets at their ends.

As the wires only cover a small area of the surface and each wire has different side facets, it is impossible to quantitatively determine the side facet orientation of the wires in a reciprocal space map of a larger surface area with SPA–LEED. Using microdiffraction in the LEEM at different energies, however, allows the determination of the inclination angle of single wires [17], although with less accuracy than is possible with SPA–LEED. There does not appear to be a preferred orientation for the side facets of the wires, and they evolve into (11T).

4. Conclusion

For applications in nanotechnology, well-defined structures are required that can easily be controlled, i.e. that can be formed with specific dimensions at selected locations on the surface. In the case of the Ag wires on Au-faceted vicinal Si(001), only the lateral dimension of the structures can somewhat be adjusted. The extremely long Ag wires form along with compact islands on the faceted surface, and their shape is defined by (11x) side facets of almost arbitrary steepness. The finding of wire growth on the Au-faceted vicinal Si(001) surface is surprisingly similar to recent studies of Ag nanowire formation on bare 4° vicinal Si(001) surfaces [17]. There, the wire formation was attributed to anisotropic diffusion of Ag adatoms, caused by the steps on the surface. During the Ag deposition on vicinal Si(001), the surface forms flat (001) terraces that are separated by multistep bunches [20,17]. Apparently, the Ag forms by multistep formation (on a smaller scale than can be achieved by the Au faceting) a surface with a viscosity similar to the extreme case of the Au-facetted 4° vicinal Si(001) surface. We believe that the wire growth on the Au-covered surface is controlled by effective one-dimensional diffusion, similar to the formation of Ag nanowires on the bare vicinal Si(001) surface. Naturally, as the step bunches get steeper, the anisotropic character of the diffusion is expected to increase. In this respect it is surprising that the wires are – even in the case of the pre-faceted surface – still formed alongside compact islands. Desorption experiments of Ag deposits on both the Au-faceted as well as the bare vicinal Si(001) surface suggest, that the compact islands correspond to the thermodynamic equilibrium shape of the Ag islands, and that the wires are stabilized by growth kinetics. During desorption the wires grow shorter (the time-reversed version of Fig. 4) and vanish before the compact islands desorb, indicating that the compact islands are indeed more thermodynamically stable.

We conclude that steps play an important role for the formation of the Ag nanowires, independently of how the steps were created. The steps introduce an additional component of anisotropy into the surface, and the resulting kinetic limitation leads to anisotropic diffusion and wire formation. Accordingly, if Ag is grown on flat Si(001) surfaces, usually no wire growth is observed. Only in the pathological cases where the step structure of the surface was disturbed during the high temperature sample preparation due to the presence of contaminations that only desorb from the surface at temperatures close to the melting point, we observe wire growth in both of the equivalent [011] directions, i.e. wires that are perpendicular to each other. The implications of our findings address the second concern with self-assembled nanowires, i.e. how to place wires at desired locations. Our experiments suggest that, since wires are only formed on the stepped surfaces, alteration of the local step density ultimately provides control over the nucleation of a wire and its subsequent growth. Such step density variations could easily be achieved, for example, by anisotropic etching, or by deposition of Au patches and subsequent annealing in order to generate step bunches by localized Au-induced faceting.

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