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Double Step Fabrication of Ag Nanowires on Si Template

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Abstract

As Ag does not form any silicide on Si surfaces, Ag wire is a candidate for self-assembled nanowire on the reconstructed and single-domain Si(5 5 12)-2×1. In the present study, various Ag coverages and post-annealing temperatures had been tested to fabricate a Ag nanowire with high aspect ratio. When Ag coverage was less than 0.03 ML and the post-annealing temperature was 500(C, Ag atoms preferentially adsorbed on the tetramer sites resulting in Ag wires with an inter-row spacing of ~5 nm. However, its aspect ratio is relatively small and its height is also not even. On the other hand, the Ag-posited surface completely loses its reconstruction even with the same annealing at 50 0℃ if the initial coverage exceeds 0.05 ML. But the additional subsequent annealing at 700℃ and slow-cooling process recovers the well-ordered Ag chain with relatively high aspect ratio on the same tetramer sites. It can be understood that, in the double step annealing process, the lower temperature annealing is required for cohesion of adsorbed Ag atoms and the higher temperature annealing is for providing Ag atoms to the tetramer sites.

1. Introduction

A few years ago, several high-index surfaces of silicon with stable reconstruction have been discovered by theoretical and experimental characterization [1]. Most notable of these systems is the Si(5 5 12) surface since the clean and reconstructed Si(5 5 12)-2×1 surface has a single-domain and one-dimensional symmetric structure [2]. This surface, unlike the other more familiar low-index surfaces, should offer a much more suitable template for the growth of one-dimensional quantum well wires [3]. As Ag does not form any silicide on Si surfaces, Ag wire is a candidate for self-assembled nanowires on the reconstructed and single-domain Si(5 5 12)-2×1 surface. It is already known that Ag qualified nanowires can be grown on Si(5 5 12)-2×1 in a self-assembly manner [4].

Most of the previous studies on the growth of Ag rows used lower annealing temperature (T<550℃) and annealing for 5～10min just one time [3-5]. An understanding of the effect of higher annealing temperature (T>600℃) and multiple annealing processes is still lacking, even the physics behind these successful technologies of Ag nanowire fabrications is not clear. It has also not been reported that the wide (7 7 17) domains parasitic on Si(5 5 12) and the growth of Ag row on Si(7 7 17). Several questions pertaining to these results can be posed. To answer these questions, we need to know the correlation between the thermal history of the sample and the structure of Ag:Si(5 5 12) in various annealing processes. In order to study the role of annealing temperature in the assembly process, we must observe the sample surfaces following their changes in various processes and at different coverages. In the present study, therefore, we focus on exploring the double step fabrication of Ag nanowires

on Si(5 5 12), especially on the parasitic Si(7 7 17) domains, and the high-index Si(5 5 12) surface has been employed as a template to fabricate such qualified wires in the self-assembled manner.

2. Experimental Details

The experiments were performed in an ultrahigh vacuum (UHV) system composed of a main and preparation chamber at Chonbuk National University, Korea. The main chamber contains a commercial scanning tunneling microscope (STM) with the sample heater and transfer mechanisms for sample and tip exchange. The preparation chamber is equipped with the facility for metal deposition. The bass pressure was 2×10^{-10} mbar. The Si(5 5 12) wafers were cut and mounted on the sample holder for the row direction ([-110]) to be either parallel or perpendicular to the heating current-flowing direction. The mounted sample direction was confirmed by STM. The samples were cleaned by degassing at 700(C for a night and flashing to ~1200℃ for 1s, some 100 times (P<5× 10^{-10}mbar), and then reconstructed by cooling down at 2℃/s from~1000℃ to room temperature (RT). The temperatures were measured with an infrared pyrometer (Minolta TR-630). Ag atoms were evaporated from a Ta basket onto Si substrates at RT, where the deposition rate was calibrated using a thickness monitor. Typical rates were ~0.5 ML/min, with 1 ML equal to the atomic density of a reconstructed Si(5 5 12)-2×1 surface, or 5.84×10^{14} atoms/cm^2.

Lower annealing temperatures result in shorter rows due to limited surface diffusion, whereas higher temperatures result in wider structures that disrupt all of the underlying Si structures. To improve Ag row growth on Si(5 5 12) surface, we used a new method, that is the double step fabrication to make Ag nanowires. The method includes two post-annealing process for Ag:Si systems, the first annealing was performed at lower temperature around 500℃ for 10~15min, the second annealing at 600~750℃ for 30min and slow-cooling down to RT. The samples here were heated directly by passing direct current (DC) through Si wafer.

STM images of the filled electronic states were acquired at RT with a constant current of 0.5-0.8nA

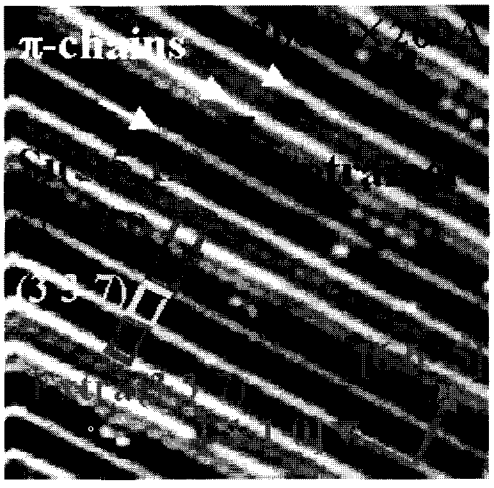

Fig. 1. Filled-state STM images of the clean Si(5 5 12)-2×1 surface. The 2×1 unit cell is outlined and consists of one (7 7 17) subunitcell(wider) and one (3 3 7) subunit

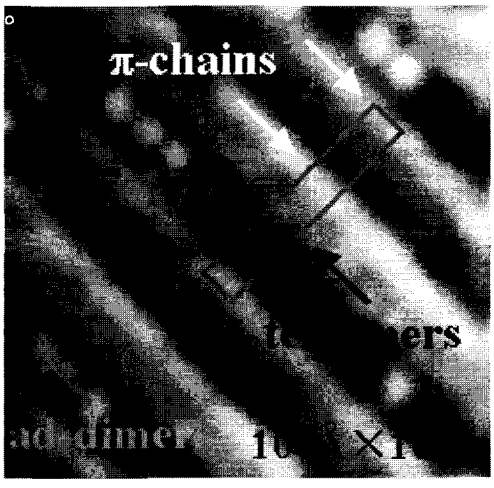

Fig. 2. Si(5 5 12)-2×1 unit cells missed (3 3 7) units, resulting in two adjacent (7 7 17) units

and bias voltages between 1.5V and 3V. All images presented here are rendered topographies or error singles of the filled states.

3. Results and Discussion

Figure 1 shows STM images for the morphology of the clean Si(5 5 12)-2×1 surface consists of single-domain row structures. These rows are oriented along the [-1 1 0] direction and have a periodicity of 5.35nm in the [6 6 -5] direction. The 2×1 unit cell of (5 5 12) includes three (-chains and two tetramers rows, where the tatramer rows are the most reactive structures on the surface. The structure often incorporates a number of subunits already known to exist on the low-index Si surfaces such as (7 7 17) and (3 3 7). The (5 5 12) unit cell can be divided into two subunit cells: (7 7 17) (wider) and (3 3 7) (narrower). The role of surface stress has already been suggested as a mechanism for the incorporation of extra or missing (3 3 7) unit cells on vicinal (5 5 12) sample. Adsorbed dimers are located along the dark rows. Both ad-dimers and the case of an extra (3 3 7) are types of defect appearing in the (5 5 12)-2×1 reconstruction. These defect structures on the surface do not appear to influence the noble metal overlayer growth [6].

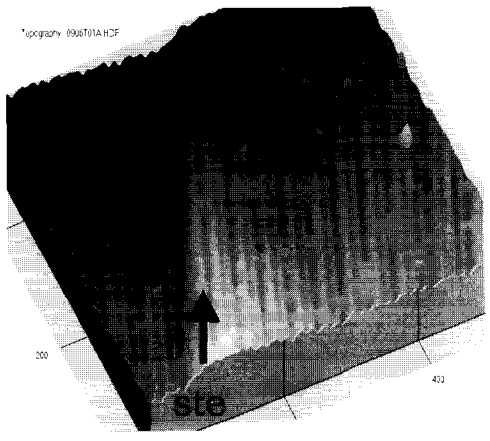

Fig. 3. Si (7 7 17) domain parasitic on Si(5 5 12) -2 ×1surface.

In our experiment, we have often detected the wide (7 7 17) domains parasitic on Si(5 5 12), as shown in Fig.2. It reveals that (5 5 12) unit cells missed (3 3 7) units, resulting in two adjacent (7 7 17) units. The Si(7 7 17) plane has similar to the orientation of Si(5 5 12) only 0.3 degree off. Most of wide (7 7 17) domains appear in the terrace adjacent to the step parallel to [-1 1 0] row direction. In a single terrace, the (7 7 17) domain extends to a few hundreds A from the step, then transforms to (5 5 12) [see Fig. 3]. Some (7 7 17) domains are also detected from the bent surface without steps. There wide and pure (7 7 17) domains, appearing near the step or on the bent surfaces, are experiencing the compressed stresses, and these excessive stresses replace the compressed stress originating from a (3 3 7) section in (5 5 12). Hence, the extra (3 3 7) section is not required in a (5 5 12) plane under such stresses, which results in (7 7 17) domain until such local compressed stresses are released.

Frequently, Ag row growth also occurs on Si(7 7 17)-2×1 domains parasitic on Si(5 5 12)-2×1 surface. Fig. 4 shows that Ag monoatomic chains uniformly grow on Si(7 7 17) by the double step fabrication. The 2× periodicity of the Si(7 7 17)-2×1 reconstruction is parallel to the row direction and a stronger 3× periodicity forms along their length, and the (-chains of the underlying Si reconstruction remains on this surface. To distinguish Ag rows from Si rows, here we make a comparison between clean Si(7 7 17) [see Fig.5] and Ag:Si(7 7 17) system [see Fig.4], Ag rows obviously grow along only one of two tetramers within each unit cell of Si(7 7 17) and form Ag monatomic chains with strongly periodic corrugations(3× and 2×) along their length. These rows are the most ordered structures induced by Ag at around 0.1ML coverage. In addition, we can find out that the well-ordered Ag chains with relatively high aspect ratio were made by double step fabrication. On the basis of our understanding, the mechanism of double step fabrication to make Ag nanowires by

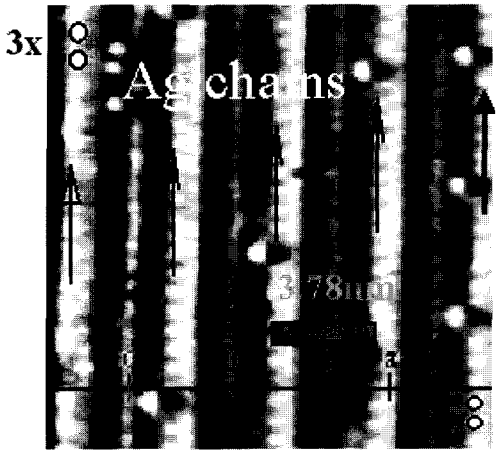

Fig. 4. Ag nanowires grown on Si(7 7 17)-2×1 domain by double step fabrication.

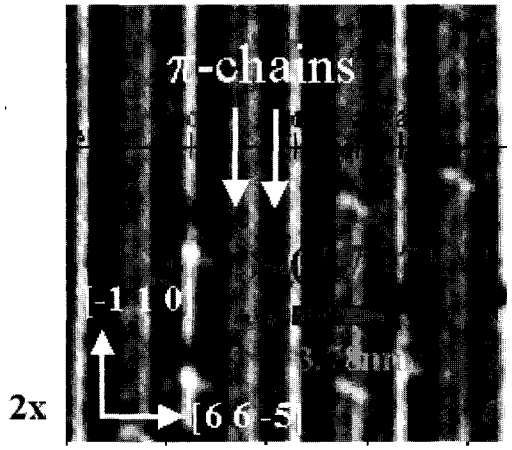

Fig. 5. Error single of clean Si(7 7 17)-2×1 domain by double step fabrication.

self-assembly can be explained as follows:

Ag atoms were deposited onto Si(5 5 12)-2×1 surface at RT and able to find a stable binding site that acts as a trap and/or diffuse along the substrate rows. The Ag atoms captured by traps were usually bound by van der Waals forces with Si surface. In the description of molecular-dynamics (MD) for the diffusion of an atom by hopping, the Ag atoms mainly oscillated at the pico-second scale in the bottom of their potential wells, only rarely at this time scale will the Ag atoms jump from site to site [7].

After the 1st annealing of Ag: Si(5 5 12) at lower temperature, the trapped Ag atoms can escape from their traps at elevated temperature when the Ag:Si(5 5 12) was annealed. Once Ag atoms escape, it rapidly diffuses along Si rows until it finds another unoccupied trap or it returns to the initial trap. Since the number of dangling bonds on the top of tetramer rows is the most one in the structure, tetramer rows are the most reactive structure of Si(5 5 12)-2×1 surface and the binding energy in tetramer sites is also the lowest in the surface. So most of Ag atoms diffuse to top of tetramers and nucleate along the more reactive underlying Si tetramer rows. During this process, a part of Ag atoms modify their adsorption energies to rebind with Si substrate in chemisorption that is comparable or more strongly adhering than precursor-mediated physisorption.

At lower coverages, Ag atoms deposited can escape from their traps and diffuse uniformly to tetramer sites by 1st Ag: Si(5 5 12) annealing. They form an overlayer array along the tetramer rows, leading to the growth of one-dimensional Ag nanowires, and only partially disrupt the Si(5 5 12)-2×1 surface reconstruction. For higher coverages, Ag rows widen and remove the π chains, even decay Si substrate steps after Ag: Si(5 5 12) annealing. In this case, Ag covered surface becomes disordered and generates many larger clusters due to cluster-cluster coalescence by atomic motion [8].

As a way of solving the problem that Si substrate reconstruction was disrupted or removed during the growth of Ag rows, Ag: Si(5 5 12) system with higher coverage (> 0.25 ML) was again annealed at 600~700℃ for 30 min then slowly cooled down to RT in around 30min. This process reconstructed by Ag induced a new well-ordered Si(5 5 12)-2×1 surface that appeared very long monatomic chains of Ag, atop one of the tetramer rows of Si(5 5 12) with 2× and 3× structures coexisting along their length. In this method, the quality of Ag growth was obviously enhanced if the distribution of Ag deposited

onto the surface was relatively uniform and their aspect ratio might up to 150:1, and the reconstruction of Si substrate was rarely disrupted.

4. Conclusions

It was experimentally shown that wide Si(7 7 17) -2×1 domains parasitic on Si(5 5 12)-2×1 appeared usually near the step or on the bent surfaces. When Ag coverage was 0.1 ML and the post-annealing temperature was around 500℃, the additional subsequent annealing at 600~700℃ and slow-cooling process, the well-ordered Ag chains preferentially adsorbed on the tetramer sites, resulting in Ag wires with relatively high aspect ratio and an inter-row spacing of ~3.8nm on Si(7 7 17). It can be understood that, in the double step annealing process, the lower temperature annealing is required for cohesion of adsorbed Ag atoms and the higher temperature annealing is for providing Ag atoms to the tetramer sites.

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References

[1] A. A. Baski, S. C. Erwin, and L. J. Whitman, Surf. Sci. **392**, 69 (1997).

[2] A. A. Baski, S. C. Erwin, and L. J. Whitman, Science **269**, 1556 (1995).

[3] S. R. Blankenship, H. H. Song, A. A. Baski, and J. A. Carlisle, J. Vac. Sci. Technol. A **17**, 1615 (1998).

[4] H. H. Song, K. M. Jones, and A. A. Baski, J. Vac. Sci. Technol. A **17**, 1696 (1998).

[5] A. A. Baski, K. M.J Ones, K. M. Saoud, Ultra-microscopy **86**, 23 (2001).

[6] S. C. Erwin, A. A. Baski, L. J. Whitman, Phys. Rev. Lett. **77**, 687 (1996).

[7] F. Schreiber, Prog. Surf. Sci. **65**, 151 (2000).

[8] P. Jensen, Rev. Mod. Phys. **71**, 1695 (1999).