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Surface Science 507–510 (2002) 615–618

SURFACE SCIENCE

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Scanning tunneling microscopy study of the stability of nanostructures on Si(1 1 1) at elevated temperature

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Abstract

The creation and local reorganisation of periodically structured Si(1 1 1) substrates is described. A regular hole pattern is produced on vicinal Si(1 1 1) surfaces by lithographic techniques. After heat treatment this pre-structured Si surface transforms into terraced and stepped regions. The resulting terrace size can be controlled by the layout of the hole pattern. The early stage of the structural changes were studied by scanning tunnelling microscopy and secondary electron microscopy as a function of the annealing temperature and for different dimensions of the hole pattern. A simple model is proposed which ascribes the observed morphological changes to an anisotropic surface diffusion on the patterned surface. It is proposed that the variation of the hole diameter and spacing between holes can be employed to control systematically the resulting surface structure after heat treatment. © 2002 Published by Elsevier Science B.V.

Keywords: Silicon; Scanning electron microscopy (SEM); Scanning tunneling microscopy; Step formation and bunching; Surface structure, morphology, roughness, and topography; Vicinal single crystal surfaces

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1. Introduction

The controlled preparation of structured silicon surfaces as potential substrates for the growth of periodic nanostructures is of great technological interest [1]. Many different approaches to structure surfaces have been described: the structural periodicity of reconstructed surfaces has been used to control the growth of adsorbates [2,3], nanofabrication with scanning probe microscopy [4] and focused ion beam patterning [5] have also been proposed. These methods suffer from the limited area (~100 × 100 nm^2) which can be structured. A different approach has been described by Ogino and co-workers [6,7]. They aligned an array of etched holes on a vicinal Si(1 1 1) surface by lithography and were able to show the reorganisation of the silicon surface into very regular atomically flat terraces separated by step bunches after thermal treatment. We combine the lithography approach of Ogino and co-workers with

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0039-6028/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0039-6028(02)01324-9

our prior work on the local atomic rearrangements of concave silicon surfaces [8–10], which were prepared by dimple grinding. Here, we focus on the description of the very early stages of the surface reorganisation. A more detailed study which discusses the influence of the hole diameter and the spacing of the holes on the surface reorganisation upon heat treatment will be published elsewhere [11].

2. Experimental

Regular hole patterns have been created on a slightly misoriented (1.5° along $[1\,1\,\bar{2}]$), two-inch, silicon (1 1 1) wafer by classical optical lithography. A specially designed mask was used. It was composed of 16 distinct areas with rectangular hole-arrays, each characterized by a certain hole diameter and varying hole spacing. The hole diameters vary between 1 and 30 μm for the different hole-arrays, within each array the spacing between the holes was varied. This gives rise to arrays with increasing hole density from one side of the patterned zone to the other. The transfer of the hole pattern from the mask to the silicon surface was done by classical optical lithography followed by either wet chemical etching in HNO_3, HF and CH_3COOH or by reactive ion etching (RIE) with SF_6. The depth of the etched holes could be varied between 200 nm and 1 μm, depending on the etch process. An example for the produced hole pattern on Si(1 1 1) is presented in Fig. 1, where the transition from a hole distance of 27 μm (left side) to 18 μm (right side) for a 9 μm diameter hole array is shown. The cross-sectional profile for each hole is close to rectangular after RIE and close to concave-shaped after chemical etching, as checked by scanning electron microscopy observations of cross-sectional samples. The Si(1 1 1) samples (n-type, resistivity 0.5–1 Ω cm) used for the present experiments are misoriented by 1.5° in the azimuthal $[1\,1\,\bar{2}]$ direction. Samples of 5×15 mm^2, cut within the different patterned areas, were precleaned in methanol prior to being mounted on a Ta holder in the ultra-high vacuum chamber, which was equipped with a scanning tunnelling microscopes (STM). The samples were resistively heated by a DC current; the current direction in the present experiments was perpendicular to the misorientation direction. The samples were first carefully outgassed at 300 °C and then at 600 °C for 12 h and subsequently flashed to 1200 °C in intervals of 15 s. Morphological changes were studied in situ under ultra high vacuum conditions by STM, either after cooling down to room-temperature or in a high temperature STM for a sample temperature between 500 and 900 °C. The experimental methods used for this study are presented in more detail in a different paper [12].

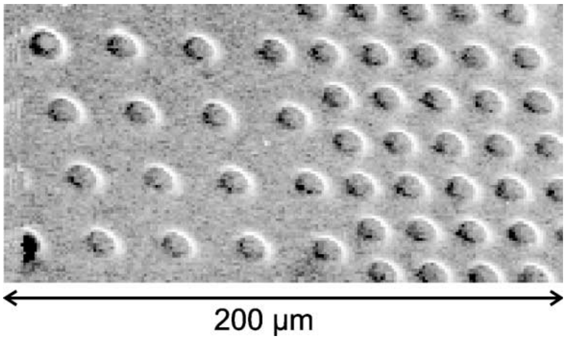

Fig. 1. SEM-image of the etched hole pattern before heat treatment of the sample. Holes with 9 μm diameter and two different spacings have been etched into the Si(1 1 1) substrate. Imaged area 200×100 μm^2.

3. Results and discussion

During heat treatment at 1200 °C, the global morphology of each hole changes as a function of time, as indicated by the scanning tunneling microscopy images of Fig. 2. Fig. 2(a) indicates that already after 5 min at 1200 °C, the former cylindrical hole exhibits a wider upper diameter, and the side walls show a gradually increasing slope for decreasing distances from the center of the hole. The former flat sections in between the holes, see Fig. 1, exhibit now a saddle-like height variation. The step bands surrounding the hole evidence this, which indicate lines of equal height. The bottom of the hole is flat and resembles a Si(1 1 1) surface. The sidewalls of the hole exhibit flat sections for every 120° azimuthal rotation, as indicated by the white arrows in Fig. 2(a). These directions correspond to the $\langle \bar{1}\bar{1}2\rangle$ directions, along which single- and triple-layer steps are found [9]. In contrast to these flat sections, the adjacent surface area is rough, as shown by the zoom-in STM image in Fig. 2(b) of an etched hole after anneal. Step bunches are observed along $[1\,\bar{2}\,1]$ and $[\bar{2}\,1\,1]$, whereas the smooth area in-between along $[\bar{1}\,\bar{1}\,2]$ is a region of single- and triple-layer steps [9]. Fig. 2(c) presents a schematic view of the initial pattern, where the holes are located at the grey areas, and the vertical contour lines, which are formed by steps due to the thermal treatment, are sketched as circles surrounding the holes. The image area of Fig. 2(a) is indicated by the rectangle. The broken lines indicate where finally step edges are located on the patterned surface, as shown in Fig. 3.

Fig. 2 characterises the onset of the morphology changes after annealing for 5 min at 1200 °C. For longer annealing times, a stepped surface evolves, as presented in Fig. 3 for an annealing time of 60 min. This atomic force microscopy (AFM) image shows a stepped surface with parallel step edges separated by 7.5 μm along $[1\,1\,\bar{2}]$. The step separation is determined by the spacing of the holes in the original hole pattern, as sketched in Fig. 2(c). The step-down direction is determined by the misorientation along $[1\,1\,\bar{2}]$ of the Si substrate. The single step height of the structure shown in Fig. 3 is

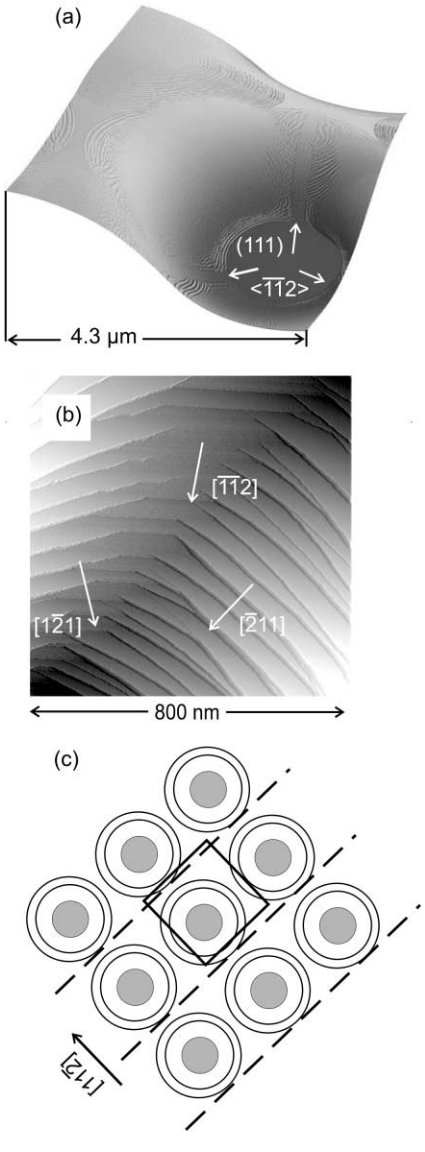

Fig. 2. (a) STM-image of one hole after annealing at 1200 °C for 5 min. The upper diameter of the hole has increased, and smooth areas of the side walls of the hole along $\langle \bar{1}\bar{1}2\rangle$ are formed. The bottom of the hole is a flat Si(1 1 1) surface. Imaged area 4.3 × 4.3 μm^2. (b) Zoom into one smooth section of the sidewall showing the transition from the smooth one and three-layer-high stepped region along $\langle \bar{1}\bar{1}2\rangle$ to the adjacent step bunch regions. STM-image, 800 × 800 nm^2. (c) Schematic of the imaged area of (a), shown as a rectangle. The original hole positions are shown in grey. The upper hole diameter increases, and circles indicate a simplified view of the contour lines to be seen as steps in (a). The dashed lines indicate the position of the step edges, which are observed after a longer anneal, see Fig. 3.

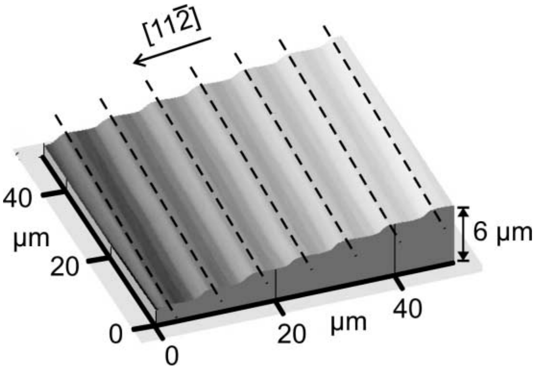

Fig. 3. AFM-image of the resulting surface morphology after annealing at 1200 °C for 60 min. Straight steps, regularly spaced along $\langle 1\,1\,\bar{2}\rangle$ separate flat terraces. The initial hole distance determines the step separation. The dashed lines indicate the step edges.

0.6 μm. This is less than the original hole depth of order 1 μm.

At the heating temperatures used in our experiments of 1200 °C, adatom evaporation and surface diffusion are the main reorganisation processes. The two basic morphologies, smooth surfaces with an azimuthal orientation along $[\bar{1}\,\bar{1}\,2]$ and the rougher regions of the step bunches along $[1\,1\,\bar{2}]$ created on our substrates are expected to represent very different conditions for atom evaporation and surface diffusion. It seems very likely that the smoother regions formed by mono- and triple-layer-high steps and small terraces act as a sort of channel for the reorganisation process. A model of the relevant restructuring processes on an atomic scale should take the correlation between structure, atomic mobility and surface energetics into account, and this work is under way.

On a mesoscopic scale, the pinning of step bunches, which are thermally driven to move over the surface due to the annealing treatment, at the upper periphery of the holes within each hole array gives rise to the terrace formation. This model, initially proposed by Ogino et al. [6], identifies the step edges of the resulting terrace structure shown in Fig. 3 as step bands made of many step bunches.

4. Summary

We describe the early stages of the reorganisation of a hole pattern on vicinal Si(1 1 1) due to thermal treatment. A simple model is proposed which offers a tentative explanation for the existence of preferential surface diffusion directions on a patterned surface. The understanding of the underlying principles, which govern the restructurization, will allow the controlled tuning of the structure of pre-patterned silicon substrates during thermal treatments.

Acknowledgements

The authors would like to thank Franck Carsenac, LAAS, Toulouse for the RIE experiments. HN and DS acknowledge the continuous financial support of ESIL, Marseille and of the Université de la Méditerranée, Marseille. This work was supported by the French CNRS program "Matériaux".

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