Fabrication and thermal annealing behavior of nanoscale ripple fabricated by focused ion beam

D.Z. Xie*, B.K.A. Ngoi, W. Zhou, Y.Q. Fu

Precision Engineering and Nanotechnology Center, School of Mechanical and Production Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

Received 25 October 2003; received in revised form 28 November 2003; accepted 28 November 2003

Abstract

The development, during annealing, of periodic one-dimensional ripple structure has been investigated. The nanoscale ripple array was fabricated on silicon(0 0 1) crystal surface using focused ion beam (FIB). Annealing was performed isothermally in a flowing argon gas ambient at 670 °C. The morphology of the ripple before and after annealing was analyzed by use of atomic force microscope. The height of the ripple decreased after thermal annealing. Furthermore, after annealing, spikes of gallium and/or gallium-rich precipitate were also observed on the surface of the ripples and the FIB milled areas.

© 2003 Elsevier B.V. All rights reserved.

PACS: 68.35Bs; 79.20Rf

Keywords: Focused ion beam; Sputtering; Micromachining; Surface diffusion

1. Introduction

Nanostructuring and nanofabrication is continuously growing in many areas [1–3]. As the feature size of devices has been reduced to a submicrometer or nanometer scale, e.g., the feature size of Si IC chip has been shrunk to a point less than 100 nm, the thermal stability of the nanoscale structure has been a great concern [4–8]. Keeffe et al. (KUB) [6] studied the annealing behavior of periodic atomic step arrays associated with etched sinusoidal grating structures on Si(0 0 1). In their experiments the grating wavelengths (4–6 μm) are in micrometer scale, and the amplitudes (∼100 nm) are in the nanoscale. They used lithographic technique to produce these sinusoidal patterns and used STM to monitor the development of the periodic grating. They found that the grating amplitudes decay exponentially with time in the temperature range from 800 to 1100 °C. Erlebacher et al. [4] studied nanometer scale ripples (both period and amplitude are in nanometer scale) and observed a nonexponential decay for the time evolution of the ripple amplitude during anneals over the temperature range 650–750 °C. In their experiment the periodic ripple structures were made on Si(0 0 1) by sputter rippling, i.e. the ripple self assembled during low energy Ar⁺ ion bombardment at glancing angles and elevated temperatures.

The focused ion beam (FIB) is now an indispensable tool in both nanoscale characterization and fabrication of electronic materials and devices [1,9–11]. FIBs have had a great impact on the technology of...
integrated circuit fabrication. It is one of main tools for failure analysis of integrated circuit by cutting of wires to isolate elements of a circuit or connecting electrically isolated elements with wires created by the deposition of metals [12]. It has also been used to fabricate high density optical storage [13] and high density magnetic storage [14]. FIB deposition of nanointerconnects (NIs) is an attractive approach to the formation of electrical contacts to structures such as carbon nanotubes and single molecules [15]. In recent years, FIBs have been used to investigate the ripple formation [16,17]. It has the advantage to observe in situ the formation progress of ripple structure by detecting the secondary electrons emitted from the surface during FIB etching.

In this paper we report the experimental observation of morphology of nanoscale rippled surface before and after thermal annealing. In our research, we used FIB to fabricate the one-dimensional periodic nanoscale ripple grating on Si(0 0 1) surface. Using of FIB direct writing methods the period of the grating can be very easily controlled.

2. Experiment

In this work, the fabrication of ripple was accomplished by using a Micrion Workstation 9500EX. This FIB system uses gallium ions (Ga\(^{+}\)) which can be accelerated up to a highest energy of 50 keV after their extraction from a liquid metal ion source (LIMS). The ion beam energy used in this work was 45 keV, the extraction current was about 2.5\(^{-}\)\(\mu\)A. The limiting aperture size was 25\(\mu\)m and the focused ion beam current was 10\(^{-}\)20 pA, yielding a beam diameter of approximately 20–25 nm (full width at half maximum, i.e., FWHM). The chamber pressure was 1\(\times\)10\(^{-}\)6 Torr during etching process. The ion beam is normally incident on the sample surface. Each periodic grating is defined in a 5\(\mu\)m \(	imes\) 6\(\mu\)m area including 10 ripples that were fabricated one by one. The grating period is designed to be 600 nm. The amplitude of the ripple ranges from 20 to 100 nm. And the width of the ripple ranges from 40 to 140 nm. After FIB etching and subsequently isothermal annealing, the ripple gratings were measured using a Digital Instruments Nanoscopy III multitmode atomic force microscopy (AFM) in tapping mode.

The isothermal annealing was performed in flowing high purity argon (Ar) gas at 670 \(^\circ\)C for 3000 s using Nabertherm R40/250/12-C6 furnace. Prior to annealing the sample, a flow of 45 sccm Ar gas was introduced into the furnace for 10 min to blow away the air. During annealing the flow rate of Ar gas was kept 10 sccm.

3. Result and discussion

In our experiments three groups of ripple gratings have fabricated. Each ripple grating consists of 10 ripples in a 5\(\mu\)m \(	imes\) 6.6\(\mu\)m area. The 10 ripples were defined by etching 11 box one by one with a pitch of 0.6\(\mu\)m. The details of the designed parameters are listed in Table 1. Fig. 1 shows the AFM image of ripple grating A(1). According to the AFM results the height of the ripple, after milling, depends to the ripple width by detecting the secondary electrons emitted from the surface during FIB etching. Fig. 2 shows the dependence of the ripple height on its width. From Fig. 2 it can be seen that for 40 nm width ripple grating A(1) the residue height (8.9 nm) is much smaller than the designed height (20 nm) due to milling down of the whole area. For the 140 nm width ripple grating C(1) the experimental ripple height (21.3 nm) is a little higher than the designed height (20 nm), i.e. the apex of the ripple is a little higher than the unetched surface. It can be seen from Figs. 1 and 2 that the edges of the grating are also higher than the unetched area. Two factors are contributed to this extruding. The first is due to the beam tail effects. Since the distribution of the ion beam intensity is Gaussian shape. The low intensity of beam tail will cause the substrate damaged or amorphization at the defined box edges [18]. As the damaged and amorphous material has a lower density than the crystalline one, a swelling of the sample surface at the box rim edges.

<table>
<thead>
<tr>
<th>Width (nm)</th>
<th>Height (nm) (i = 1–5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group A (40)</td>
<td>20 40 60 80 100</td>
</tr>
<tr>
<td>Group B (90)</td>
<td>20 40 60 80 100</td>
</tr>
<tr>
<td>Group C (140)</td>
<td>20 40 60 80 100</td>
</tr>
</tbody>
</table>

The period is 0.6\(\mu\)m for all gratings. The designed height is expected to equal the depth estimated by the dose dependence of etched depth, i.e., 3.6 nC/\(\mu\)m\(^2\) ion dose corresponds to 1\(\mu\)m etched depth.
can be expected [19]. The second is the redeposition. When the ion beam was scanning at the defined box edge, some of the sputtered substrate atoms would redeposit on the surface most nearby the defined box.

Fig. 3 displays the dependence of experimental height on the designed width of ripple. It can be seen that the narrower the ripple is, the larger the difference between designed height and experimental height. For grating group A, after reaching about 31 nm, the ripple height will not increase as the etched depth increases. For group C, the experimental heights are nearly equal to the designed values. On the other hand, the experimental width (full width at half maximum, i.e., FWHM) of the ripple increases as the etched depth increases, except for group A. For group A, the average width of the ripples in all five gratings are 205 nm. In groups B and C the width of the ripple increases as the ripple height increases. Fig. 4 is the experimental results of group C, the line is used as a guide to eyes.

In order to investigate the annealing behavior of the nanoscale ripple, the sample with ripple gratings was annealed in flowing Ar gas at 670 °C. Smoothening of the ripples has been observed after 3000 s annealing. Figs. 5 and 6 show two AFM images of annealed grating. From these two images it can be seen that the ripples do not obviously emerge. At some places the ripple almost completely vanished. The average height of ripples after annealing depends on the ripple width before annealing. For annealed gratings the height of ripples was measured at the place where there is no spike. \( R_{ave} \) (defined as the ratio of average height of the ripples in a grating after annealing to the average height of that ripples before annealing) is 0.63 for all of the five gratings in group A. For gratings in
groups B and C, the $R_{ave}$ ranges between 0.64–0.78 and 0.64–0.85, respectively.

From Figs. 5 and 6, it can be seen that there are many granular spikes in the grating area. Fig. 5B clearly shows that some of the spikes are even much higher than the milled depth. These granular spikes can be assumed to be gallium and/or Ga-rich precipitates formed during annealing due to precipitation of the implanted gallium [20]. During FIB milling the gallium ions were implanted into the subsurface of the substrate. The surface layer became amorphous due to the Ga ion implantation and some of the surface material were sputtered off. As a result of sputtering and implantation, the Ga concentration in the surface region increases with the milled depth. According to

Fig. 2. Height profile (from AFM image) of grating A(1) and C(1) to display effect of ripple width to its height. Ripple heights in both gratings are designed to be 20 nm.

Fig. 3. Comparison of designed heights and experimental heights for different width ripples.

Fig. 4. Relation between ripple width and height for group C gratings.

Fig. 5. Three-dimensional AFM images to reveal the morphology of the ripple grating A(1) after annealing in flowing of Ar gas at 670 °C for 3000 s.
TRIM 2000 code simulation the project range is 36.6 nm with 13.1 nm straggle for 45 keV gallium ions. This means the maximum concentration lies at a depth of approximately 36.6 nm for low dose. After removing of about 20 nm material, the surface Ga concentration reaches a saturation value of about 12% of Si atom density in substrate [18]. During thermal annealing the amorphous layer of the sample recrystallized from the interface of crystalline substrate and amorphous surface layer toward the surface. The crystallization front will drive the implanted gallium atoms out of solution. The implanted Ga moved toward the surface, precipitated and assembled into spikes at the surface [21]. Meanwhile some gallium evaporated from the surface into the flowing Ar atmosphere. Most of the gallium and/or Ga-rich precipitates are located at surface of the ripple or nearby the ripples, as shown in Figs. 5 and 6. This means that the convex maybe a preferential site for the aggregation of gallium. The precipitation of gallium during heat treatment should be a significant factor of concerns for micro device fabrication processes which including FIB micromachining or deposition using gallium as ion source and high temperature heat treatment.

In Erlebacher’s experiments [4] for the ripples with average height = 20 nm and period = 565 nm (this period is close to our grating period 600 nm) created by Ar ion beam etching, the $R_{ave}$ was about 0.31 after annealing at 672 °C for 3000 s in a clean ultrahigh vacuum. This value is much smaller than ours. Since implanted Ga has a remarkable influence on the diffusion of impurities in Si during annealing [21]. Therefore we assume that the gallium would also has an influence on the surface diffusion of Si atoms due to the precipitation of implanted gallium at the surface during the annealing.

4. Conclusion

The following main conclusion may be made. Smoothening of nanoscale ripple fabricated by FIB has been observed after annealing. The implanted gallium diffuses toward the surface and precipitates at the surface during annealing. The convex is a preferential site for aggregation of gallium.

References