Nuclear Instruments and Methods in Physics Research B 315 (2013) 248–251

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Surface modification of oxide layer on Si using highly charged ions

M. Sakurai [a,*], S. Liu [a], S. Sakai [a], S. Ohtani [b], T. Terui [c], H.A. Sakaue [d]

[a] Department of Physics, Kobe University, Rokkodai, Nada-ku, Kobe 657-8501, Japan
[b] Institute for Laser Science, University of Electro-Communications, Chofu, Tokyo 182-8585, Japan
[c] National Institute of Information and Communications Technology, Iwaoka, Nishi-ku, Kobe 651-2492, Japan
[d] National Institute for Fusion Science, Oroshi-cho, Toki 509-5292, Japan

ARTICLE INFO

Article history:
Received 29 November 2012
Received in revised form 8 March 2013
Accepted 29 March 2013
Available online 6 April 2013

Keywords:
Highly charged ion
Electron beam ion source
SEM
XPS
HREELS

ABSTRACT

Surface modification using highly charged ions is presented. The surface of a Si wafer which is covered with a native oxide layer is used as a sample. The sample was irradiated with Ar^{11+} ions at a fluence of 10^{13}–10^{14}/cm^2. The Ar^{11+} ions were obtained from an electron beam ion source (Kobe EBIS). The surface was investigated using secondary electron microscopy, X-ray photoelectron spectroscopy and high-resolution electron energy loss spectroscopy. The obtained results suggest that the native oxide layer is sputtered by the irradiation of Ar^{11+} ions and that the structural modification makes the density of the oxide layer lower and the electric conductivity higher.

1. Introduction

Irradiation of solid targets with slow highly charged ions (HCIs) modifies the surface structure. The HCI carries large potential energy as a summation of ionization energy for each promotion step of charge state. When a HCI enters the surface the potential energy is dissipated at a nano-scale region over the surface in a very short time (a few femto-seconds) which leads to the emission of hundreds of secondary electrons, sputtering of many secondary ions, and structural modification of the topmost surface layers [1,2]. The amount of modification such as the size of irradiation traces quantitatively depends on the charge state of the HCI. For highly oriented pyrolytic graphite (HOPG) sample, the Raman spectrum of an irradiated sample shows a D peak observable for deformed lattice and the peak height proportionally increases with the potential energy of the HCI [3].

Single ion implantation (SII) is a technique to implant dopant ions one-by-one into a fine semiconductor device structure in order to avoid inhomogeneity of dopant atoms [4], and also an important approach toward realizing quantum register [5,6]. We have demonstrated that collision event of a HCI with a surface is detectable with almost 100% efficiency, which is an essential requirement in SSI technique, by virtue of advantageous characteristics of HCI that the secondary electron yield is far beyond unity [7]. If SII using HCI is available it is also useful for other processing techniques in nano technology; creation of nano-sized structures such as nano-gaps, cutting a carbon nano tube at an arbitrary position and probing of nano-sized materials for instrumental analysis, utilizing the unique property of HCI that single HCI sputters the atoms over nano-scaled region on a surface.

In order to establish SII technology using HCI, however, there are many technical challenges before reaching the goal. For instance, it is necessary to develop a positioning technique; single HCI must be injected at a desired position with nanometer resolution. For this purpose, we started to establish an observation method to identify the irradiated area in the first place. Scanning tunneling microscopy (STM) can recognize each irradiation trace created by the injection of single HCI, however, it is not useful to quickly discriminate irradiated domains with sizes in the μm range from unirradiated area in the mm range. Since secondary electron microscopy (SEM) is useful for such applications, we have examined the aptitude of SEM for the identification of irradiated areas.

We have analyzed SEM images of HOPG and Si with a native oxide layer irradiated with Ar^{11+} ions at a fluence of 10^{13-14}/cm^2, and the remarkable difference of tone in the SEM images between the irradiated and unirradiated domains [8]. In a similar irradiation experiment with Ar^{+} ions, a fluence of 10^{15}–10^{16} was necessary to obtain enough tone contrast between irradiated and unirradiated area. The reason for the SEM contrast in the Si sample is assumed to be a charging effect; the irradiated domain has a higher conductivity than the unirradiated one. In the present paper, we present additional proof for this proposed mechanism and discuss the characteristics of modification induced by the irradiation with HCIs.

* Corresponding author.
E-mail address: msakurai@kobe-u.ac.jp (M. Sakurai).

0168-583X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.nimb.2013.03.040

2. Experimental

We used an electron beam ion source (EBIS) installed at the Kobe University (Kobe EBIS) for the production of HCIs [9]. The Kobe EBIS produces a continuous ion beam of Ar HCI in the charge state up to 17+ in the 100 pA range, operating the EBIS in 'pulse mode' where the electron beam is periodically intermitted for short time (~1 ms) with a period of 0.1–1 s [10]. The charge state distribution for higher charge states is improved over the conventional operation provided the ultimate pressure of residual gases is in the 10^{-9} Pa range and the pressure of introduced Ar gas is limited in the 10^{-8} Pa range. In the present experiment, 0.5 nA of Ar^{11+} is used for the irradiation at the accelerating voltage of 3 kV. The Si sample with a natural oxide layer was irradiated with Ar^{11+} at a fluence of $10^{13}/cm^2$ using a mask, i.e., a cantilever with a hole near the tip. The purpose of using a cantilever with a hole is to develop a positioning technology in HCI injection. The hole in the size of 10×10 μm is made using a focused ion beam (FIB) apparatus. The SEM image of the cantilever after the FIB process is shown in Fig. 1. The cantilever was mounted parallel to the sample as shown in Fig. 2. The distance between the hole and the sample is 0.3 mm. After the irradiation, the SEM image of the sample was observed around the area beneath the hole. We used a high-resolution SEM (JSM-6700F, JEOL) installed at the National Institute of Information and Communications Technology, Japan. The acceleration voltage of the primary electron beam is as low as 1 kV in order to emphasize the information from topmost surface layers. X-ray photoelectron spectroscopy (XPS, ESCA-3400, Shimadzu) and high-resolution electron energy loss spectroscopy (HREELS, ELS5000, LK Technologies) were also employed to measure for irradiated (without any mask) and unirradiated samples. The fluence of HCIs at the samples used for these measurements is in the order of $10^{14}/cm^2$.

3. Results and discussion

The SEM image of Si irradiated with Ar^{11+} ions revealing the shadow of the cantilever is shown in Fig. 3. The unirradiated area which is covered with the cantilever shows a brighter contrast compared to the irradiated area. The trace of the hole on the cantilever is clearly observable. The size of the square on the SEM image is expanded from the real size, which indicates that the HCI beam has a divergence and hits a wider area on the sample. Taking into account the distance between the cantilever and sample, the divergence of HCI is roughly estimated at ~15 mrad in horizontal direction and ~5 mrad in vertical direction. Since the spot size is ~1 mm, the beam emittance would be estimated at ~5 mm mrad in vertical direction. The horizontal divergence is larger than the vertical one, since the bending magnet for charge separation diverts the beam horizontally. If we use a cantilever with a hole with smaller size (10–100 nm) to limit the HCI beam and put the tip of the cantilever on the sample surface, a positioning of the HCI beam with an accuracy in the nanometer range would be possible. The previous SEM observation for Si covered with a native oxide layer, which was irradiated with Ar^{11+} ions at a kinetic energy of 33 keV, indicated a tone contrast between irradiated and unirradiated areas, and it was ascribed to a charging effect; regions with charge accumulation on the sample brought by the incident electron reflect more incident electrons and show a brighter contrast [8]. A previous atomic force microscopy (AFM) observation for the same sample described above showed a swelling effect

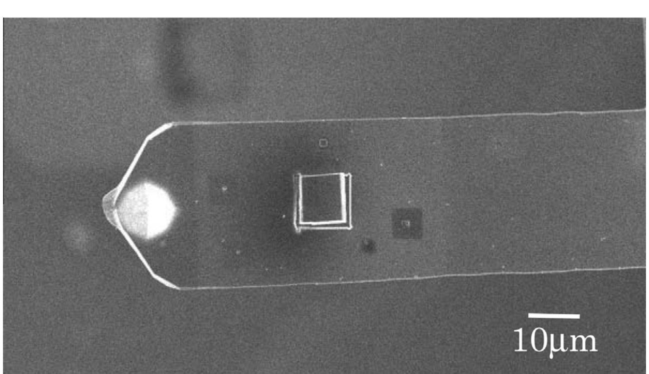

Fig. 1. SEM image of the cantilever after FIB process. The size of sides of square is 10 μm.

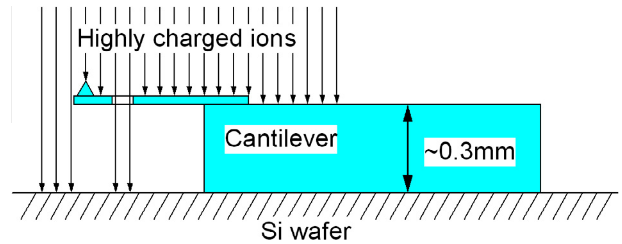

Fig. 2. Geometry of irradiation of the Si wafer covered with the cantilever which is FIB processed as shown in Fig. 1.

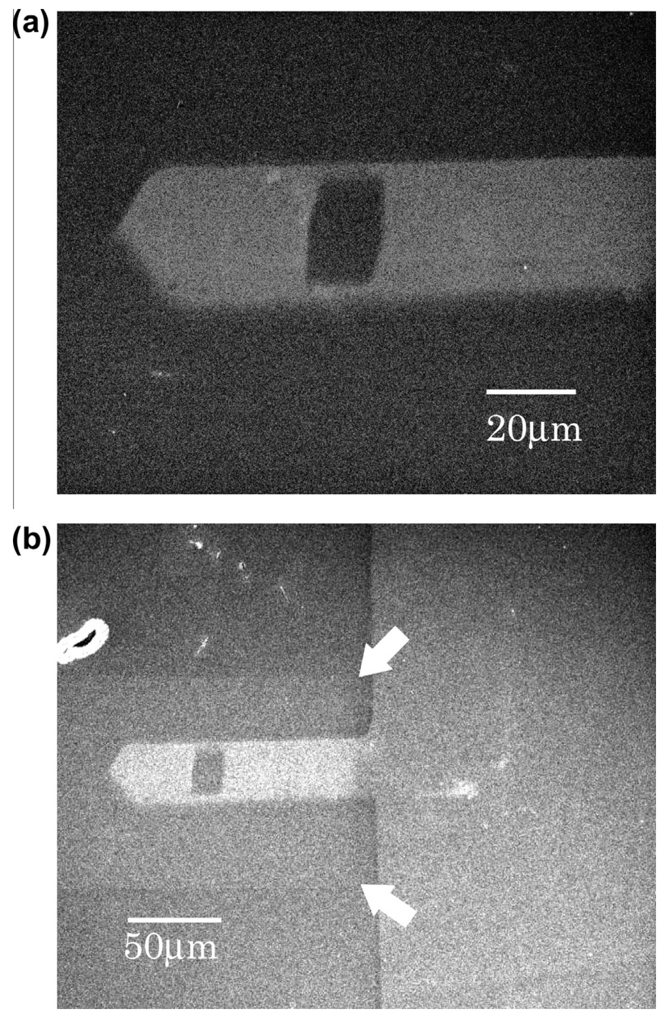

Fig. 3. SEM image of Si irradiated with Ar^{11+} revealing the shadow of the cantilever. The fluence of ions is in the order of $10^{13}/cm^2$, (a) Is an enlarged image of cantilever. For (b) Wider area was observed including base plate of cantilever, (b) was recorded after (a).