Surface Science 652 (2016) 334–343

Contents lists available at ScienceDirect

Surface Science

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

Metal impurity-assisted formation of nanocone arrays on Si by low energy ion-beam irradiation

Kayla Steeves Lloyd [a], Igor L. Bolotin [a], Martina Schmeling [b], Luke Hanley [a], Igor V. Veryovkin [a,*]

[a] Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60607, United States
[b] Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, IL 60626, United States

ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form 7 March 2016
Accepted 14 March 2016
Available online 17 March 2016

Keywords:
Ion beam sputtering
Nanoscale morphology evolution
Self-organization Atomic Force Microscopy
Total Reflection X-ray Spectrometry

ABSTRACT

Fabrication of nanocone arrays on Si surfaces was demonstrated using grazing incidence irradiation with 1 keV Ar^+ ions concurrently sputtering the surface and depositing metal impurity atoms on it. Among three materials compared as co-sputtering targets Si, Cu and stainless steel, only steel was found to assist the growth of dense arrays of nanocones at ion fluences between 10^{18} and 10^{19} ions/cm^2. The structural characterization of samples irradiated with these ion fluences using Scanning Electron Microscopy and Atomic Force Microscopy revealed that regions far away from co-sputtering targets are covered with nanoripples, and that nanocones popped-up out of the rippled surfaces when moving closer to co-sputtering targets, with their density gradually increasing and reaching saturation in the regions close to these targets. The characterization of the samples' chemical composition with Total Reflection X-ray Fluorescence Spectrometry and X-ray Photoelectron Spectroscopy revealed that the concentration of metal impurities originating from stainless steel (Fe, Cr and Ni) was relatively high in the regions with high density of nanocones (Fe reaching a few atomic percent) and much lower (factor of 10 or so) in the region of nanoripples. Total Reflection X-ray Fluorescence Spectrometry measurements showed that higher concentrations of these impurities are accumulated under the surface in both regions. X-ray Photoelectron Spectroscopy experiments showed no direct evidence of metal silicide formation occurring on one region only (nanocones or nanoripples) and thus showed that this process could not be the driver of nanocone array formation. Also, these measurements indicated enhancement in oxide formation on regions covered by nanocones. Overall, the results of this study suggest that the difference in concentration of metal impurities in the thin near-surface layer forming under ion irradiation might be responsible for the differences in surface structures.

1. Introduction

Interest in using low-energy ion-beam irradiation as a tool for nanostructuring and functionalization of the surfaces of various materials has steadily increased over the last four decades [1–10]. This interest stems in large part from the simplicity and versatility of this technique and its ability to facilitate the fabrication of a rich variety of patterns on solid surfaces [11]. These patterns include ordered arrays of nanoripples [8,12–15], nanodots [16], nanocones [17], nanoparticles [18,19] and nanowires [19–21]. Another valuable asset of this technique is the potential to fabricate homogenously ordered nanopatterns over large areas while still maintaining a high degree of control over surface morphology and chemistry [3]. It is widely agreed that the formation of nanopatterns under low-energy ion-beam irradiation occurs via self-organization of the irradiated surface [4,5,10,22–24]. This self-organization phenomenon allows for an effective "bottom-up" approach for nanofabrication [9,25]. Additionally, by varying the ion irradiation parameters and target temperature, one can control the complex process of surface self-organization and thus enable programmable functionality in materials [9]. This programmable functionality has helped identify numerous applications for such nanostructures, including optimizing the performance of thermoelectric generators, nanosensors, field emitter arrays, and optoelectronic devices [26–28].

Despite the empirical success of nanopattern fabrication, the fundamental understanding of the mechanisms governing pattern selection under ion beam irradiation is still lacking. Existing theoretical models account for early stages of the pattern formation, but these theories do not extend to later stages and therefore require further exploration [29–32]. Additionally, these same theories fail to predict, for instance, differences in patterns observed for different materials, particularly for chemical compounds [1,9,10,24,33]. This limitation may have arisen from a focus on surface morphology rather than on surface chemical composition [34]. Recently, interest in surface chemistry has been renewed through the revelation that metal impurities might play a major role in the nanoripple pattern formation [35]. This interest has further grown with the development of so-called surfactant sputtering as evidenced by recent studies of the role of metal impurities in

* Corresponding author.

http://dx.doi.org/10.1016/j.susc.2016.03.016
0039-6028/

nanopatterns formation [7,26,36–38]. Surfactant sputtering, based on the co-deposition of surfactant atoms from a nearby metal target during ion irradiation, can form a variety of the aforementioned patterns on Si surfaces [2,3,5,27,36,37,39]. As a result, a hypothesis that formation of silicides is a necessary condition for pattern formation on silicon recently started to gain broad support [40]. This hypothesis has inspired new studies exploring surface silicide formation during ion irradiation [9, 25,40–43].

In view of this growing interest in the role of surface impurities in nanopattern formation under low-energy ion irradiation, we report here experimental results of our study of surface nanopattern formation on silicon irradiated by low-energy argon ions that co-sputtered stainless steel targets. Instead of focusing on previously well-studied fine nanoripple and nanodot patterns, this work concentrates on coarser nanostructures, often called arrays of nanocones (sometimes alternatively referred to as nanotips, nanofibers, or nanograss) [44–46]. Nanocones are commonly seen structures obtained with low-energy ion irradiation [9,17,26,46–52]. Moreover, nanostructures with very similar morphology and dimensions can also be produced by plasma-based methods [45,53,54]. Nanocones are not exclusive to silicon: metals [47,48,50], carbon and other carbonaceous materials [46,49] including diamond [55], as well as GaSb [56] have also been reported as surfaces where such structures could be fabricated by ion irradiation. Interestingly, the observations that formation of nanocones on ion-irradiated surface can be aided by co-deposition of impurity atoms were made already in the 1970s [47–49]. As a possible explanation for this phenomenon, a formation of seed clusters on the surface from impurity atoms due to their surface diffusion was proposed [57], and the apparent consensus in the 1970s literature was that such clusters could locally alter sputtering yield and act as surface masks initiating nanocone formation [47–50].

In this paper we specifically describe ion-irradiated nanostructured samples that have been comprehensively characterized by structure-sensitive (Scanning Electron Microscopy, SEM and Atomic Force Microscopy, AFM) and chemical composition-sensitive (X-ray Photoelectron Spectrometry, XPS and Total Reflection X-ray Fluorescence Spectrometry, TXRF) surface characterization techniques in order to better understand the interplay between the chemical composition of these materials and the structure of their surfaces. One of the key questions we asked was whether the silicide formation was indeed the primary driver of the surface self-organization in this case, especially in view of others reporting the same structures forming on diamond and other materials irradiated by low energy ions [40,46,56].

2. Experimental details

The instrumentation used in this work for ion bombardment and X-ray photoelectron analysis has been previously described [58–60]. The ion irradiation layout can be seen in Fig. 1. Briefly, a commercial Kaufman ion source (Fig. 1a) using electron impact ionization (Model 3 cm Ion Source, Veeco-CS) produced 1 keV Ar^+ ions, with working pressure of Ar gas (99.99% purity) maintained by a mass flow controller (Type 246, MKS). Si wafers (Wafer World, Inc., Si (100) p-type, boron doped) were used as irradiation targets for all experiments (Fig. 1b). The irradiation chamber had a base pressure of 4×10^{-9} Torr and working pressure of 3×10^{-5} Torr. The sample fabrication was carried out at an ion incident angle of 75° off normal with near-grazing incidence, with a distance between ion source and the target of ~200 mm. The typical average ion current density was 1 μA/mm^2 for the beam profile with FWHM of approximately 20 mm. The samples discussed here were irradiated at room temperature for periods of time between 40 and 120 min corresponding to ion fluences of ~3×10^{18} ions/cm^2 and 9×10^{18} ions/cm^2, respectively. Before and after each sample irradiation, a Faraday cup was utilized to measure ion beam profile by scanning across the beam. Although generally stable, the primary ion current exhibited a slow drift during a given measurement.

Prior to irradiation with Ar^+ ions, samples were mounted onto a custom-built sample holder as seen in Fig. 1b. In the diagram provided, ions are approaching the target downwards from the right. The ridges on the sample plate were made such that co-sputtering targets could be interchanged for different materials (stainless steel, Cu, Si, etc.) or, alternatively, the ridges themselves could serve as targets. The angle between the ridge and sample surface was approximately 45°. The material used to fabricate the ridges was 302 stainless steel shim stock with thickness ~130 μm, which after bending to the desired angle was spot-welded on the main sample holder plate. The ion beam simultaneously irradiated both the sample and the co-sputtering target, thereby allowing for irradiation and concurrent metal deposition onto the Si sample, as seen in Fig. 1a and b. As shown in Fig. 1b, we used "sacrificial" Si wafers to shield our samples from material sputtered from the main sample holder: the samples were mounted on top of such wafers, and a separate wafer was installed on the side from which ions approached the samples.

After ion irradiation, the sample has prominent matte areas, which correspond to areas that were nanostructured (Fig. 1c). These areas appear asymmetric because the matte region A was closer to the central ridge where ion current was higher and the ion beam incidence was not perfectly parallel to the ridges so that part of the matte region opposite to region A was in the shade of the ridge (see Fig. 1b). Furthermore, the indicated points A and B correspond to the approximate regions characterized by SEM, AFM, TXRF and XPS.

The surface morphology was analyzed by scanning electron microscope (SEM, JEOL JSM-6320F) and atomic force microscope (AFM, Bruker-Nano Dimension Icon). AFM was utilized in contact mode, in air, with a resolution of 512 × 512 pixels. Cantilevers comprised of silicon nitride and a nominal tip radius of 2 nm were used. The sample was traversed from edge to edge with scans roughly 2 mm apart. For SEM, the samples were examined at 3.2 kV with the same scanning pattern.

Surface elemental concentrations were quantified by Total Reflection X-ray Fluorescence spectrometry, (TXRF, S2PicoFox, Bruker Nano, Berlin) with the aid of calibration curves for each element of interest. To our knowledge, the technique of TXRF has not been applied yet to characterization of surfaces nanostructured by ion beams. Its basic X-ray probe layout is similar to another technique, which has been frequently applied to such samples, Grazing Incidence X-ray Scattering (GISAX) [7,34,35,37,61,62]. The difference between these two methods lies in the type and nature of X-ray detectors used. We chose laboratory-based TXRF because this technique is capable of (1) quantitatively measuring the surface composition and (2) semi-quantitatively probing the elemental composition under the sample surface [63–65]. In TXRF, a primary X-ray beam (Mo-Anode, 50 kV, 600 μA) strikes a highly reflective surface at very low incident angles and is totally reflected within the upper few atomic layers of the material. Material deposited on top of the reflective surface or embedded within a few atomic layers below the surface is excited fluorescence and analyzed. Detection limits as low as 10^9 atoms/cm^2 can be achieved with TXRF for heavier elements [63–65]. Analysis time was 2000 s for both sample and calibration standards. For quantifying the elemental composition, a multistandard (Cr, Mn, Fe, Ni and Cu — 10 μl of each) solution pipetted on a SiO_2 sample was used, and a special calibration curve was constructed for each element on a Si sample. In order to probe different sample regions, the sample was moved laterally with respect to the fixed position of the X-ray probe, which had a footprint of ~2 mm × 5 mm on the sample surface. In order to perform angular scans of the X-ray beam incidence, the sample was tilted in the beam incidence plane around the center of the X-ray beam spot.

Chemical states of the elements detected on sample surfaces were characterized by high-resolution monochromatic X-ray photoelectron spectroscopy (XPS), using a previously described instrument [59]. A high-resolution monochromatic Al Kα X-ray source (15 keV, 20 mA emission current, model VSW MX10 with a 700 mm Rowland circle monochromator, VSW Ltd., Macclesfield, U.K.) and a 150-mm concentric