Vacuum xxx (2016) 1–6

Contents lists available at ScienceDirect

Vacuum

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

Study of the formation mechanism of hierarchical silicon structures produced by sequential ion beam irradiation and anodic etching

Esther Punzón-Quijorna [a, b], Sarah Kajari-Shröder [c], Fernando Agulló-Rueda [d], Miguel Manso Silván [a, *], Raul José Martín-Palma [a], Pilar Herrero Fernández [d], Vicente Torres-Costa [a, b], Aurelio Climent-Font [a, b]

[a] Departamento de Física Aplicada e Instituto de Ciencia de Materiales Nicolás Cabrera, Universidad Autónoma de Madrid, 28049 Madrid, Spain
[b] Centro de Microanálisis de Materiales (CMAM), Universidad Autónoma de Madrid, 28049 Madrid, Spain
[c] Institut für Solarenergieforschung Hameln (ISFH), 31860, Emmerthal, Germany
[d] Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), 28049 Madrid, Spain

ARTICLE INFO

Article history:
Received 13 July 2016
Received in revised form
23 September 2016
Accepted 9 October 2016
Available online xxx

Keywords:
Nanostructured silicon
High energy ion irradiation
Anodization
Hierarchical structures
Charge carrier deactivation

ABSTRACT

The formation of micropatterns combining nanostructured (porous) Si (NPSi) and bulk Si is induced by a sequential process of selective high energy ion irradiation and anodic etching. In this work, we investigate the microstructural origin of the increase of Si resistivity on irradiated areas, which is responsible for the inhibition of NPSi formation upon anodization. The increase of Si resistivity after irradiation at variable fluence has been evidenced from current voltage (I-V) characteristics. Microstructural aspects of the Si interfaces irradiated with 1.5–20 MeV Si ions have been revealed by elastic backscattering experiments in channeling configuration, Raman spectroscopy and high resolution transmission electron microscopy. It is concluded that inhibition of NPSi formation is induced at fluences that do not imply amorphization. In fact, the analysis of electrochemical capacitance-voltage measurements suggests that, at fluences well below the threshold for lattice disruption, the concentration of holes suffers from a drastic decrease at depths that match the location of maximum damage yield of the implanted Si ions. These results suggest that the mechanism responsible of formation of hierarchical Si structures is the local B dopant deactivation in the irradiated areas.

1. Introduction

The technological dimension of Si experienced a great potential of expansion upon the discovery of efficient visible photoluminescence from nanostructured (porous) Si (NPSi), which broke the limits imposed by the band structure (indirect band-gap) of this semiconductor [1]. The material was intensively studied during the 1990s to evaluate the optoelectronics dimension in terms of emission range and integration with Si based microelectronics. The properties of NPSi greatly expanded into the biocatalysis and biomedical fields as a consequence of its high specific surface area (yielding 500 m^2/g) [2] and its bioactivity in physiological environments [3]. From the biocatalytic point of view, the immobilization of enzymes in NPSi is pointed out as a route for the synthesis of chiral products [4]. With regards to the biomedical field, the applications of NPSi in both biomolecular [2], pharmacological [5] and cellular (tissue) [6] devices have been already outlined.

The control over NPSi fabrication parameters, mainly through electrochemical and optical variables, has allowed the fabrication of anisotropic NPSi structures, such as multilayers, which emphasized the biosensing dimension of the material [7]. Furthermore, 2D structuring has been also induced by using optical [8] and ion beam irradiation techniques [9]. With regards to the latter route, ions with initial energies in the MeV range are known to induce drastic modifications of materials properties upon implantation. In particular, Polesello et al. demonstrated a drastic reduction of the electrochemical susceptibility of Si upon implantation [10]. Taking profit of the good directionality of high energy ions and the possibility to electromagnetically scan the beam, NPSi surface structures were prepared by direct proton beam writing [11]. Alternatively, the use masks to induce selective irradiation from defocused ion beams, identically leads to the inhibition of NPSi

* Corresponding author.
E-mail address: miguel.manso@uam.es (M. Manso Silván).

http://dx.doi.org/10.1016/j.vacuum.2016.10.011
0042-207X/

formation on irradiated areas, which give rise to hierarchical structures. These structures combine NPSi regions supported by Si regions resulting in more stable structures under physiological media than bare NPSi, which holds a great potential for tissue engineering applications [12].

Independently of the selected process for the formation of NPSi surface features, it is known that its porosity strongly depends on the availability of holes at the HF-electrolyte/Si interface, so that the promotion or depletion of these carriers plays a key role in the structuring process [13]. In this work, Si ions in the MeV range have been implanted in p-type Si through micro masks for the subsequent formation of NPSi surface by electrochemical etching. A wide set of techniques are proposed to characterize the materials properties at different stages of preparation of the micropatterns. In fact, the sensitivity of Raman spectroscopy towards changes in semiconductors irradiated at high energies has been already outlined allowing to describe induced strain [14] or partial amorphization [15]. In fact, Mishra et al. compared the Raman detection capability with an analysis by channeling Elastic Backscattering (c-EBS), which had been previously suggested as a fruitful ion probe to investigate ion induced damage in semiconductors [15]. Along with c-EBS analysis, we incorporate in our study the use of a direct local microstructural technique such as transmission electron microscopy, which appears as a robust standardized technique for the characterization of ion irradiated semiconductors [16,17]. We aim at merging all the microstructural information obtained from these techniques and correlate with measurements of electrical/electronic properties, so as to focus on the microstructural basis of the mechanism of inhibition of NPSi formation on irradiated areas.

2. Experimental

2.1. Fabrication of hierarchical silicon structures

NPSi/Si micropatterns were prepared according to previously reported processes [18]. Low resistivity (0.05–0.1 Ω cm), boron doped p-type <100> silicon substrates were coated on the back surface with aluminum and annealed at 400 °C during 5 min to provide low resistance ohmic contacts. The irradiation process was carried out with 1.5–20 MeV Si ions at fluences ranging from $5\cdot10^{13}$ to $5\cdot10^{16}$ ion·cm^{-2} (Cockcroft-Walton tandetron accelerator, High Voltage Engineering Europa BV). Such large range of experimental parameters was necessary to individuate conditions well below the amorphization (low fluence) or presenting clear crystalline damage (high fluence), varying the energy of the ions so as to adapt the yield to the different experimental analyses performed (i.e. high yield made I-V measurements more sensitive, low yield was required to shorten capacitance measurements time). For the formation of NPSi/Si hierarchical structures a selective irradiation step was performed through a 40 μm thick Cu mask. After mask removal, samples were electrochemically etched in a 1:1 HF (49%): EtOH solution, with a current of 12 mA (NPSi area equivalent to 45 mA cm^{-2}) for 60 s.

2.2. Electrical and electrochemical characterization

The current voltage (I-V) curves of Si substrates, irradiated with 20 MeV Si ions at different fluences, were obtained in a Faraday box in anodic transversal configuration (positive terminal on the back Al contact of the Si wafer) by using a HP 4140B pico-ammeter. In depth electrochemical capacitance-voltage (ECV) measurements were performed in NH_4HF_2 etching electrolytes with electrolyte-Si contact areas of 0.1 cm^2. Measurements were obtained with a CVP21 electrochemical CV wafer profiler (WEP, Germany). In order to reduce the experiment time, the irradiation energy was reduced to 1.5 MeV, inducing a maximum peak of radiation damage at depths of around 1.7 μm.

2.3. Microstructural characterization

The c-EBS measurements were performed at CMAM in a scattering chamber equipped with a goniometer with three axis (Phi, Theta and Tilt), and variable height (Panmure Instruments), which allows the sample positioning in channeling configuration. The silicon surface barrier detector is fixed defining a scattering angle of 170°. Channeling configuration was achieved by collecting spectra (400 of 0.025 μC each) varying polar and azimuth angles and analyzing them, by the comparison of the integral values below each spectrum. The random spectrum is obtained by adding the 400 spectra, such that the total charge is 10 μC. The same accumulated charge was used to obtain the spectra in channeling configuration, for the sake of comparability. Random and channeling measurements were fitted by using the software RBX [16].

Raman spectra were obtained at room temperature with a Renishaw Ramascope 2000 microspectrometer. The excitation light source was argon ion laser with a 514.5 nm emission wavelength. The light was focused on the sample surface with a 100× microscope objective. Laser power on the sample was below 3 mW. The spatial resolution was around 0.7 μm. The spectral resolution and precision were about 3 and 1 cm^{-1}, respectively.

Cross-sections of NPSi/Si structures were prepared for observation by transmission electron microscopy (TEM). Preparation implied grinding with a Gatan 656 dimpler and ion-milling with a Fischione 1010 as previously described [19]. A JEOL JEM-3000F HSTEM operating at 300 kV accelerating voltage was used to analyze the specimens. Image processing of the high-resolution images was carried out using Gatan Digital Micrograph and ImageJ software packages.

3. Results and discussion

3.1. Electrical properties of irradiated Si

The overall electrical modification of the Si substrate upon irradiation was studied by the homogeneous exposure of the Si substrates to 20 MeV Si ions at fluences ranging from 10^{12} to 10^{14} ions cm^{-2} and subsequent measurement of the I-V characteristics (Fig. 1). The measurements show rectifying I-V characteristics from the reference and irradiated Si/Al structures with a considerable

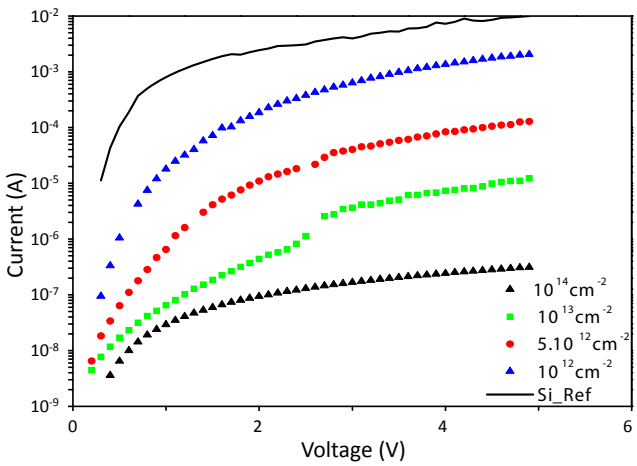

Fig. 1. I-V curves obtained from the reference sample and samples irradiated with 20 MeV Si ions and variable fluence.

Please cite this article in press as: E. Punzón-Quijorna, et al., Study of the formation mechanism of hierarchical silicon structures produced by sequential ion beam irradiation and anodic etching, Vacuum (2016), http://dx.doi.org/10.1016/j.vacuum.2016.10.011