Microelectronic Engineering 129 (2014) 58–64

Contents lists available at ScienceDirect

Microelectronic Engineering

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

On the fabrication and mechanism of pinecone surface structures

Qianqing Jiang [a], Wuxia Li [a,*], Jiajia Mu [a], Wangning Sun [a], Changzhi Gu [a,*]

[a] *Beijing National Lab of Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*

ARTICLE INFO

Article history:
Received 12 May 2014
Accepted 12 July 2014
Available online 22 July 2014

Keywords:
3D metallization
Pinecone structures
Nanocones
Shadow effect

ABSTRACT

Nanostructured metal surfaces, in contrast to their corresponding bulk counterparts, have increased area, redistributed surface potential energy and novel physicochemical properties, thus have great potentials to be applied in a wide range of fields. In the work, different fabrication methods were employed to produce semiconducting and polymer conic structures, to provide three-dimensional frameworks with different surface properties, e.g. morphology, microstructure and chemical composition. Followed by metal deposition, 3D metalized conic structures, e.g. Ag–Si, Au/Ni–Si, Au/Ti–Si and Au/Cr–Si pinecones, were formed. The influence of factors, including the thickness and material type of the deposited metals, the metal deposition method, and the geometry, size and material type of the conic frameworks, on the 3D surface metallization process, were investigated and the related mechanisms were discussed.

1. Introduction

In surface sciences, it is well-known that it is the pre-structured surface of the substrate that has large affection on the related physical and chemical processes taken on it. Structured surfaces have increased area, redistributed surface potential energy and novel physicochemical properties, therefore, have great potential to be applied in many specific conditions [1–3]. Among various surface structures, cone-shaped structures have many unique properties, including large aspect ratio, small tip radius of curvature, high emission current density, superior electrical/thermal conductivity, robust mechanical strength, and good chemical stability [4,5]. It has been demonstrated that such structures have abundant functionalities in a broad range of application fields, e.g. near field optics [6,7], molecular detection by enhanced Raman scattering [8], and metamaterial [9].

Therefore, different methods have been developed by researchers to fabricate single or large area of conic surface structures and the related mechanisms have been proposed [10–18]. Zhang et al. reported the fabrication of ordered Si cone arrays with controllable morphologies and wettability by reactive ion etching system with two-dimensional silica colloidal crystals as masks [10]. Xu et al. reported the fabrication of self-organized vertically aligned single-crystal Si nanostructures with controlled shape and aspect ratio by reactive plasma etching [15]. Seo et al. reported a strategy of combined methods by electrochemical and chemical etching, though which precisely controlled vertical arrays of Si wires and cones have been fabricated [11]. In addition, direct laser writing (DLW), a technique that based on two-photon polymerization (2PP), has been widely used for the realization of arbitrary three-dimensional (3D) micro-/nanostructures [12–14]. However, issues such as how to effectively metalize the structured 3D surface in a controllable method and what the possible mechanisms would be related are required to be addressed.

In this work, we investigated the evolution of the 3D surface morphology during metal deposition on pre-fabricated conic structure. In particular, firstly, Si cones were fabricated in a reactive-ion etching-inductively-coupled-plasma (RIE-ICP) system. Then thin layers of metal were deposited to form Ag–Si, Au/Ni–Si, Au/Ti–Si and Au/Cr–Si surface structures via vacuum evaporation. It was found that for Si cones fabricated by RIE-ICP, the metal deposition resulted surface metallization obeys the mechanism of island growth; on the other hand, for FIB processed Si, diamond cones and IP-L polymer cones, island and layer by layer mixed growth have been observed. In more details, a completely formation of a pinecone structure could be characterized with four stages, namely, the initial metal atom seeding, the particle aggregation/nucleation, the steady shadowing 3D growth and the stacking pile-up growth. Systematic experiments were conducted to explore the trends and mechanism on metallization of 3D surfaces. Our results demonstrate that 3D structure fabrication followed by thin metal film deposition is an effective method for fabrication of metallic 3D surface structures; it potentially can be used to construct 3D devices, especially for SERs [6,7,9] and biosensors [8] due to the large surface area and possible improved surface plasmonic properties at the 3D interfaces [9].

* Corresponding authors.
E-mail addresses: liwuxia@aphy.iphy.ac.cn (W. Li), czgu@aphy.iphy.ac.cn (C. Gu).

http://dx.doi.org/10.1016/j.mee.2014.07.013
0167-9317/

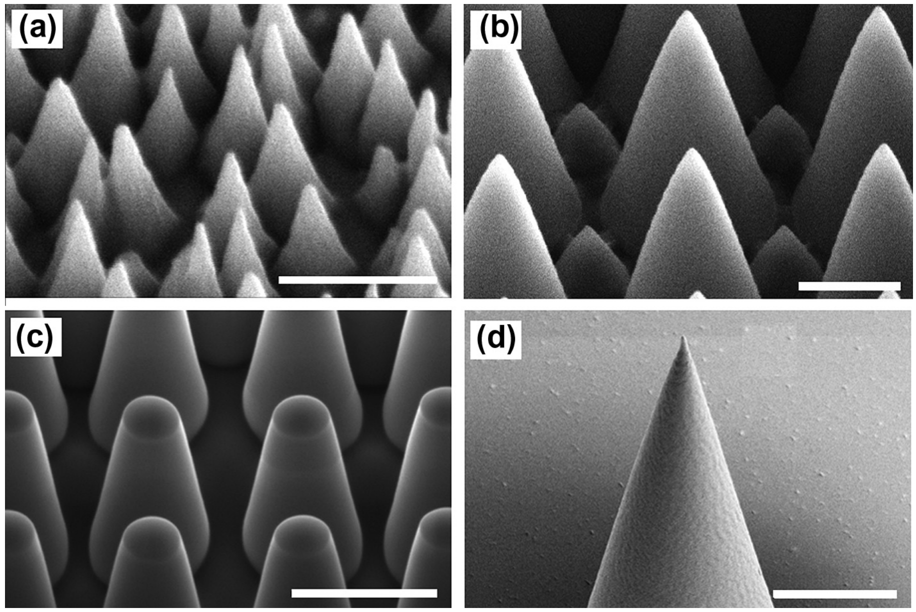

Fig. 1. Scanning electron microscope (SEM) images of arrays of: (a) random Si cones; (b) ordered Si cones; (c) ordered diamond cones; and (d) IP-L cones. The scale bar is 1 μm for (a–c) and it is 10 μm for (d).

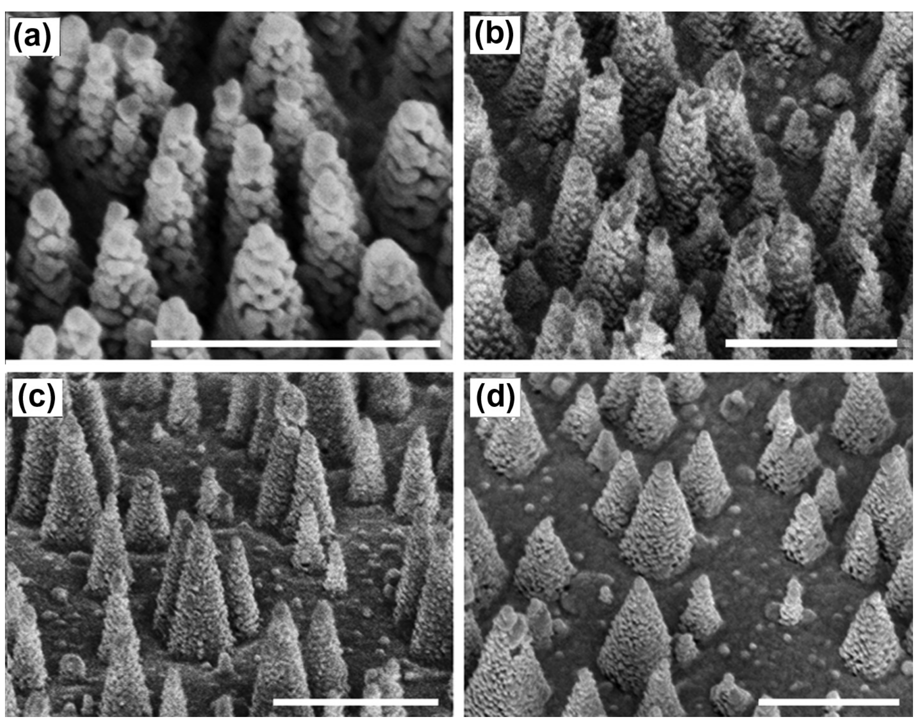

Fig. 2. SEM images of random distributed metal/Si pinecone structures with thermal evaporation of metal layers of: (a) Ag (70 nm); (b) Ni (5 nm)/Au (100 nm); (c) Ti (10 nm)/Au (80 nm); and (d) Cr (20 nm)/Au (100 nm). The scale bar is 500 nm.

2. Experimental

In this work, Si, diamond and IP-L cones were fabricated to serve as the pre-patterned 3D frameworks for 3D metallic surface structure fabrication. Silicon cones were obtained through a maskless etching with a reactive-ion etching-inductively-coupled-plasma (RIE-ICP) system. The reactive gas used was a mixture of O_2 and SF_6. After 7 min dry etching at −120 °C, large area of Si cones were obtained. The addition of O_2 was to form localized micro-/nano SiO_2 on the Si substrate, which could further serve as masks for Si etching. Mechanism of such self-organization process has been reported previously [17]. Diamond and Si cone arrays that with designable size, shape and distribution were fabricated through a commercially available SEM/FIB system utilizing a beam of 30 keV singly charged Ga^+ ions. During focused-ion milling, the base pressure was 2.4×10^{-6} mbar. The system was equipped with an advanced pattern generator (NanoBuilder), which offers flexibility for controlling the geometry, size, and distribution of patterns, potentially could be used to fabricate micro-/nano structure in sufficiently large area. For instance, to produce Si nanocones with