Precision Engineering xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Precision Engineering

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

Localized etching of silicon in water using a catalytically active platinum-coated atomic force microscopy probe

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ARTICLE INFO

Article history:
Received 11 March 2017
Received in revised form 20 May 2017
Accepted 31 May 2017
Available online xxx

Keywords:
Atomic force microscopy (AFM)
Catalytic chemical etching
Catalytically active platinum-coated probe
Single-crystal silicon
Nanofabrication

ABSTRACT

This paper presents a novel atomic force microscopy (AFM)-based nanofabrication technique for Si in water that is based on highly localized catalytic etching with a Pt-coated AFM probe. It has been shown that nanoscale grooves can be fabricated on the Si surface at room temperature via Pt-assisted catalytic chemical etching in water without the addition of any chemicals. Furthermore, dissolved oxygen (O_2) in water has been found to be a key element for driving the chemical reaction of Si with water in the Si removal process. Experimental results have also suggested that an oscillating cantilever of the Pt-coated AFM probe for the stirring of water is essential in order to overcome the oxygen mass-transfer limitations and enhance the Si removal rate. The elementary chemical reactions taking place during the etching of Si has been estimated on the basis of electrochemical theory. It is proposed that in the first step, dissolved oxygen is reduced and forms hydroxide ions (OH^-) with water molecules (H_2O) on the surface of the Pt-coated tip. In the second step, Si atoms are oxidized on reaction with OH^- ions and water soluble silicates are formed. The catalytic reaction taking place on the surface of a Pt-coated tip can be enhanced by the application of an anodic potential to an additional Pt wire electrode, resulting in a dramatic fifty-fold increase in the Si removal rate.

1. Introduction

A number of useful techniques for nanolithography and nanostructure fabrication based on atomic force microscopy (AFM) have been studied and developed in recent years [1–4]. The AFM-based nanofabrication technique features a high spatial resolution at the nanoscale and flexibility in both two-dimensional (2D) pattern and three-dimensional (3D) structure generation with the advantages of relatively easy operation at a potentially low cost. Furthermore, this technique is extremely useful for reliable process control in the precise positioning on the patterned surface to be modified, surface topography measurements after the fabrication process with simultaneous force measurements and control with piconewton resolution during the process, and localized surface characterization (mechanical, electrical, and thermal properties) at the nanometer scale. To date, several different methods have been developed for both subtractive processes such as direct mechanical modification of a wide range of materials [5,6] and thermomechanical writing of polymer surfaces [7,8], and additive processes such as local anodic oxidation (LAO) [9–12] and dip pen nanolithography (DPN) [13,14]. There have also been several attempts to perform nanofabrication of self-assembled monolayers (SAMs) by using catalyst-functionalized AFM tips [15]. For example, the penetration of the cell membranes of living cells by photocatalytic titanium dioxide (TiO_2)-coated AFM probes has been demonstrated to take place under UV irradiation in a physiological saline solution based on a highly localized photochemical oxidation reaction [16]. Thus, AFM-based nanofabrication is a promising technology for future advances in nanotechnology.

One of the most important and urgent technological challenges is to achieve single-crystal Si nanostructuring, which can be potentially used for a wide range of applications in microelectronic and optoelectronic devices. The most straightforward approach towards this objective is the mechanical scratching of Si surfaces with either a diamond AFM tip [6,17], a diamond-coated Si tip [18,19], or a diamond-like carbon (DLC)-coated Si tip [20]. Grooves with a depth of ~100 nm may be obtained by scratching at an extremely high nominal load of ~500 μN by using a pyramidal diamond tip integrated with a very stiff Si cantilever (spring constant: ~500 N/m) [17]. However, the AFM-based mechanical scratching of a hard Si surface has been generally limited to the fabrication of shallow grooves with a depth of several nanometers at a nominal load of ~10 μN [18–20]. In order to fabricate Si nanostructures with a high aspect ratio, a friction-induced oxide layer (pattern) formed

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http://dx.doi.org/10.1016/j.precisioneng.2017.06.008
0141-6359/

by scratching the Si surface has been used as an etching mask for the subsequent anisotropic wet-etching process in a potassium hydroxide (KOH) solution, thus allowing the fabrication of protrusive nanostructures [6,21]. Alternatively, the formed oxide layer may also be selectively dissolved in hydrofluoric acid (HF) to fabricate nanotrenches in the Si surface [21]. However, these mechanical scratching processes suffer from the intrinsic problems of tip wear and scratch-induced surface damage.

LAO involves a selective area oxidation of Si surfaces. When a negative bias voltage (ca. 5–20 V) is applied to a conductive AFM tip under relatively high humidity conditions, an anodic oxidation reaction takes place between the AFM tip (cathode) and the Si surface (anode). In this process, hydroxide ions (OH^-) are generated by the ionization of water molecules (H_2O) at a high electric field ($>10^9$ V/m) which subsequently act as an oxidant for the electrochemical reaction [3,10–12]. For instance, Si nanowire field-effect transistors with a width of 60–80 nm have been successfully fabricated by employing AFM-tip-induced local oxidation technique [22]. In this process, the oxide patterns formed on the Si surface served as a mask for the subsequent reactive ion etching (RIE) process. A modified fabrication process has also been proposed for the fabrication of hierarchical Si micro/nanostructures by alternately repeating the AFM-tip-induced local oxidation and wet chemical etching processes [23].

To the best of our knowledge, AFM-based nanofabrication as a chemical etching strategy has not been utilized for the direct removal of Si to date. In another novel approach to the chemical etching of Si, an abrasive-free chemical polishing method called catalyst-referred etching (CARE) has been developed [24–26]. This process is based on a catalytic chemical reaction at the contact points of a wafer surface with a Pt catalyst. A Si (100) wafer is atomically planarized by using a Pt rod and an aqueous solution of HF as the catalyst and etchant, respectively [24]. This technique has been successfully applied to the planarization of the 4H polytype of silicon carbide (4H-SiC) (0001) [25] and gallium nitride (GaN) (0001) [26] wafers in just water with a catalytic Pt plate. In recent years, metal-assisted chemical etching (MACE) has been attracted increasing attention as another nanofabrication method for the preparation of Si nanostructures with a high aspect ratio (e.g., nanowires and nanopores) due to its simplicity and relatively low cost [27–30]. In this process, the catalytic activity of the noble metals (e.g., Ag, Au, or Pt) that are patterned on the Si surface plays a key role in promoting the selective etching of Si. The MACE technique is based on the principle of a local galvanic cell mechanism. In a widely accepted model, the local cathodic reduction of the oxidizing agents such as hydrogen peroxide (H_2O_2) or dissolved oxygen (O_2) is enhanced on the noble metal, consequently generating holes (h^+), whereas the Si undergoes etching via local anode oxidation by the injection of holes into its valence band. However, the strongly corrosive and highly toxic solution of HF must be used as an etchant for the direct dissolution of Si and/or the dissolution of the formed silicon dioxide (SiO_2) in this process. Based on the same principle, it has been made possible to perform an AFM-based nanofabrication of Ge by using a Pt-coated AFM probe in water because its oxide (GeO_2) is soluble in water [31]. In this work, a novel AFM-based nanofabrication technique for Si surfaces has been developed which involves highly localized Pt-assisted catalytic chemical etching in water at room temperature. Initially, it has been experimentally demonstrated that nanoscale grooves can be fabricated on the Si surface by using a Pt-coated AFM probe in water. Subsequently, the elementary chemical reactions taking place during the etching of Si have been discussed based on the principles of electrochemistry. The effect of the applied potential in enhancing the Si removal rate has also been examined.

2. Experimental methods

Nanofabrication was carried out with a commercially available AFM system (Asylum Research MFP-3D-BIO) that was placed on an inverted microscope (Nikon Ti-U). Si-based AFM probes (Olympus AC200TN, nominal spring constant: 9 N/m, nominal tip radius: ~7 nm) were used as a tool. The Si probes were thermally oxidized to obtain a protective layer (thickness: 80 nm) in a muffle furnace in an atmosphere at 950 °C for 150 min and then coated with a Pt thin film (thickness: 100 nm) and Ti adhesive layer (thickness: 10 nm) by using a sputtering method (Fig. 1(a)). For comparative experiments, a Au thin film (thickness: 100 nm) was also deposited instead of the Pt thin film. After depositing either Pt or Au layer, the radius of the

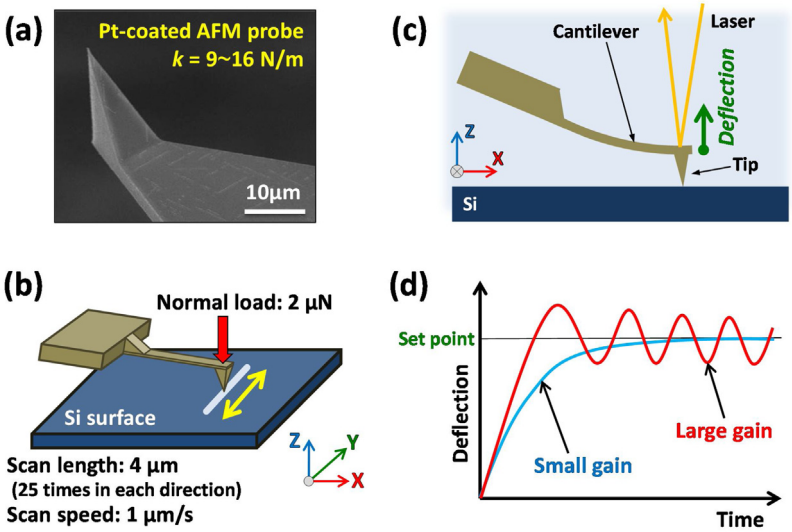

Fig. 1. Experimental procedure for Si nanofabrication. (a) Scanning electron microscopy (SEM) image of a Pt-coated AFM probe. (b) Schematics of the fabrication process, in which an AFM probe transverses laterally along the same line (25 times in each direction) on the Si surface repeatedly over a scan length of 4 μm in water in the contact mode with a normal load of 2 μN and scan speed of 1 μm/s. (c) Schematics of the vertical deflection control of the Si cantilever by using the optical lever technique. (d) Schematics of the change in the cantilever deflection as a function of time for a small (blue line) and large (red line) feedback gain. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Please cite this article in press as: Yamamoto K, et al. Localized etching of silicon in water using a catalytically active platinum-coated atomic force microscopy probe. Precis Eng (2017), http://dx.doi.org/10.1016/j.precisioneng.2017.06.008