Femtogram mass measurement of airborne engineered nanoparticles using silicon nanopillar resonators

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Abstract

Silicon nanopillar resonators were fabricated and used for sensing airborne engineered nanoparticles (ENPs) by monitoring resonant frequency shifts induced by the mass of trapped ENPs. Inductively coupled plasma (ICP) cryogenic dry etching and thermal oxidation were utilized in sensor fabrication. An electrostatic aerosol sampler and piezo shear actuator were used to collect the flowing ENPs and excite the nanopillars in resonant mode, respectively. By using the fundamental bending frequency, the sensor can achieve a mass sensitivity of 7.41 Hz/fg, which enables its application to a nanobalance to detect airborne ENPs in the femtogram regime. A simple cleaning method of polluted nanopillars was also performed to remove the adhered ENPs, thus efficiently extend the operating life of the sensor. This developed sensor is targeted for use in airborne ENP sensing applications.

Keywords: nanopillar resonators; ICP cryogenic dry etching; airborne nanoparticles; mass sensitivity

1. Introduction

Personal monitoring of exposure to airborne ENPs requires small, low weight, and low-cost sensors, e.g., based on MEMS/NEMS resonators. Such sensors can count the tiny mass of ENPs deposited on their surfaces as a shift in their resonance frequencies with high measuring precision, i.e. a mass sensitivity of 8.33 Hz/ng found with a self-sensing silicon cantilever in an air pollution sampling of ~20 nm carbon ENPs [1, 2]. Nevertheless, further device miniaturization and surface enhancement are needed to improve

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the detection limit of the airborne ENPs. Nanopillar resonators offer the potential for both resonant operation under workplace conditions and largest surface area [3, 4]. This work presents a characterization of silicon nanopillar resonators which are capable of detection and measurement of airborne TiO$_2$ ENP mass in a few femtogram regimes.

2. Fabrication and Characterization of Silicon Nanopillar Resonators

In order to fabricate the nanopillars in silicon, two main processes were used, i.e., ICP cryogenic dry etching and sacrificial thermal oxidation [5]. Firstly, a silicon wafer of 300 μm thick was covered by photoresist mask (AZ 726 MIF) of 0.6 μm which was then patterned using UV lithography resulting in a round shaped structure. By using an SI 500 C cryogenic dry etcher (Sentech Instruments), the patterned silicon probe was etched with an etch rate of ~4 μm/min. After ICP cryo dry etching, the photoresist layer was washed off in a solution mixture of H$_2$O$_2$ and H$_2$SO$_4$. In this step, the observed pillars have an aspect ratio of >10 and a diameter of ~3.5 μm. To further reduce the diameter of the pillars, a thermal oxidation of the dry-etched pillars was performed. After being oxidized three-times, the pillar diameter was reduced down to ~650 nm with an aspect ratio of 20 (Fig. 1(a, b)). By reducing the pillar diameter, an increase of displacement and a decrease of pillar mass can be expected which then cause an increase of mass sensitivity and quality factor of the device.

For dynamic operation, the nanopillars were mounted on an external shear-force piezoactuator supplied by AC sinus voltage of 10 V and operated in a scanning electron microscope (SEM) revealing resonant frequencies of the pillars in the range of 434.63 kHz to 458.21 kHz with quality factor of 1700 (Fig. 1(c)). These varied resonant frequencies can be attributed to the shapes and dimensions of the nanopillars which are not perfectly uniform and tube-shaped structures. Affected by thermal oxidation process, the pillars may not have planar surfaces of the pillar tips, conical shapes are yielded instead.

3. Engineered Airborne Nanoparticle Experiment and Analysis

An assessment using TiO$_2$-based ENPs and electrostatic aerosol sampler was performed in a test chamber under typical workplace condition ($V = 1 \text{ m}^3$, $T = 23 ^\circ \text{C}$, $rH = 30 \%$, $p = 1 \text{ atm}$) to examine the silicon nanopillar resonators (diameter $d = 650 \text{ nm}$, length $l = 40 \text{ μm}$, pitch $a = 10 \text{ μm}$) (Fig. 2(a)). A fast
mobility particle sizer (FMPS, TSI 3091) with a time resolution of 1 Hz was utilized for measuring the size distribution of ENPs in the diameter range from 6 to 523 nm. After 30-min ENP sampling with total concentration of ~8000 particle/cm³ maintained by constant output atomizer (TSI 3076) and applied sampler voltage (TSI 3089) of -9.5 kV, some ENPs are randomly stuck on the pillars (Fig. 2(b, c)). As expected [6], particles on the top parts of the pillars are more in number due to the higher electric fields in those areas. Furthermore, the aerosol flow direction which is perpendicular to the pillar probe may affect the preferable ENP deposition on the pillar tips which then induces resonant frequency shifts (Fig. 3(a)). To obtain a quantitative analysis of deposited ENPs, seven nanopillars which are located close to each other on the substrate were observed. As expected, pillar with more collected ENPs has a larger resonant frequency shift $\Delta f$ (Fig. 3(b)), i.e., pillar 7 with $\Delta f_{P7} = 14.39$ kHz. For pillar 2, with a single pillar weight $m_{P2} = 30.9$ pg, unloaded resonant frequency $f_{P2} = 458.21$ kHz, and resonant frequency shift $\Delta f_{P2} = 2.16$ kHz, a total deposited ENP mass $\Delta m_{P2} = 2 \times m_{P2} \times \Delta f_{P2} / f_{P2} = 291.58$ fg can be calculated. A mass sensitivity of 7.41 Hz/fg was then yielded from the experiment. This Si nanopillar has improved the mass sensitivity of the sensor by a factor of ~0.7 million compared to the Si cantilever [1].

To extend its operating life, recycling of the pillar sensor was performed using an ultrasonic cleaning method (Fig. 4(a)). During the high pressure stage of cleaning process, the formed bubbles imploded releasing enormous amounts of energy attacking every surface, hence after 1-2 min the TiO₂ NPs were removed from the pillar surface (Fig. 4(b)). Therefore, the sensor can be reused for other measurements.

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**Fig. 2.** (a) Airborne titanium dioxide (TiO₂) nanoparticle sampling setup; (b) silicon nanopillars loaded by TiO₂ ENPs during 30-min aerosol sampling and (c) the magnified view of a single loaded nanopillar.

**Fig. 3.** (a) Measured shift of the fundamental resonant frequency of a nanopillar induced by the mass of TiO₂ ENPs adhered to it within 30 min (pillar 1); (b) distribution of resonant frequency shifts of seven nanopillars.
Fig. 4. (a) Schematic of ultrasonic process for removing the attached ENPs from silicon nanopillars; (b) the SEM images of nanopillars before and (c) after ultrasonic cleaning.

4. Conclusion

Femtogram mass measurement of airborne ENPs has been conducted using silicon nanopillar resonators by monitoring their resonant frequency shifts. Sensors were fabricated mainly utilizing inductively coupled plasma (ICP) cryogenic dry etching and thermal oxidation. Recycling of the sensors was successfully tested with a simple ultrasonic cleaning method. A miniaturized electrostatic aerosol sampler and an optical detection method need to be integrated for being implemented as a handheld device and operated in real workplace condition.

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