



Sensitive and selective detection of hydrocarbon/water vapor mixtures with a nanoporous silicon microcantilever



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ABSTRACT

We have developed a sensitive and selective sensor for hydrocarbon/water vapor mixtures using nanomechanical infrared (IR) spectroscopy with a porous silicon (P-Si) microcantilever. Facile and direct anodization process is utilized to fabricate vertically aligned nanopores of 20–50 nm diameters on a plain silicon microcantilever. The effective Young's modulus and surface area of a P-Si microcantilever can be easily controlled by the thickness of the anodized P-Si layer. Here we demonstrate the detection of 1 wt% naphtha/water vapor mixtures using nanoporous cantilever IR spectroscopy. Nanoporous nature of the cantilever surface enhances its thermomechanical sensitivity. In addition, trapping the volatile hydrocarbon molecules in the nanowells increases the analyte concentration on the surface. Nanomechanical IR spectra of adsorbed vapors were obtained by plotting the deflection amplitudes of the microcantilever as a function of the illuminating IR wavenumber. The mass of the adsorbed vapors was determined from variations in the resonance frequency of the cantilever.

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1. Introduction

Sensitive and selective detection of volatile organic compound vapor mixtures is a challenge because of their highly volatile nature, non-specific interactions with sensor surfaces, and the potential interference from identical chemical groups [1–3]. This selectivity challenge is addressed in miniature array sensors by depositing functionally different polymers on individual sensor surfaces in the array to interact with volatile vapor molecules and subsequent response analysis by intelligent pattern recognition algorithms [4–6]. However, chemoselective interfaces of polymer layers can provide only partial selectivity [7–9]. Chemical vapor sensors for industrial applications often show false-positive signals due to environmental interference, for example, humidity, which degrades the performance of the chemoselective layers [3,10]. Complex mixture of hydrocarbons such as naphtha is industrially relevant since it has been used as a diluent in extraction of bitumen from oil sands [11]. Therefore, developing a real-time

sensor with selectivity and sensitivity for detection of naphtha in a water–naphtha mixture is of great interest.

Recently, nanomechanical infrared (IR) spectroscopy has been developed and widely applied in order to overcome chemical selectivity issues in chemical vapor detection [12–17]. This technique is a calorimetric method that exploits the high thermomechanical sensitivity of a bi-material microcantilever for speciation of surface adsorbed molecules. Despite its very high chemical selectivity, its poor sensitivity has limited the application of this technology for detection and recognition of volatile organic vapors at very low concentrations. The flat surface of a plain bi-material cantilever imposes a severe limitation on detection sensitivity due to the limited number of adsorption sites. Although the thermomechanical sensitivity of a cantilever could be enhanced by depositing a thin layer of metal on the cantilever, the metal deposition process introduces many challenges such as inducing residual tensile stress and increased stiffness of the cantilever [18,19].

To overcome these sensitivity challenges, various nanostructured microcantilever have been fabricated using self-assembly techniques, electrochemical etching, and sol–gel methods to increase the interfacial surface area for molecular adsorption [20–26]. However, it is difficult to enhance both the thermomechanical sensitivity and cantilever surface area without resorting to time-consuming and complicated fabrication processes [21–26]. In this article, we demonstrate facile and rapid fabrication of porous

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silicon (P-Si) microcantilever from conventional plain Si cantilevers using electrochemical etching. Successful detection, recognition, and quantification of complex hydrocarbon/water vapor mixture were demonstrated using nanomechanical IR spectroscopy with a P-Si microcantilever. The selectivity of detection of complex hydrocarbons was not affected by presence of fully saturated water vapor.

2. Experimental

2.1. Fabrication of nanoporous Si microcantilevers

A rectangular, highly doped n-type silicon cantilever array with a triangular free end was purchased from Nanoworld (Neuchatel, Switzerland). Each microcantilever in the array is approximately 500 μm long, 100 μm wide and 1 μm thick and has a spring constant of ~ 0.03 N/m. To fabricate the P-Si layer on the cantilever, a direct anodization method was adopted. Dodecanethiol, ethanol, hydrofluoric acid were purchased from Sigma–Aldrich and used without further purification. A 75 nm-gold with 5 nm-chromium adhesion layer was coated on one side of the Si cantilever using e-beam evaporation, and dodecanethiol was coated on the gold surface in order to reduce the damage to the gold layer during the anodization. The anodization process was carried out in 5 wt% of hydrofluoric acid with a 50 vol.% of ethanol solution under 1.5 V using a DC power supply. The various thicknesses of the P-Si layers were obtained using different anodization times: 20 s (P-Si20), 60 s (P-Si60), and 90 s (P-Si90).

Fig. 1(a) shows cross-sectional scanning electron microscopy (SEM) images of 1 μm -thick P-Si cantilevers with three different

P-Si layer thicknesses. The nanopores are vertically aligned, indicating that highly doped n-type Si is oriented in (1 0 0) direction. Fig. 1(b) shows the thickness of P-Si layer as a function of the anodization time and the straight line is a linear fit of the P-Si layer thickness. The growth rate from the slope is determined to be ~ 7.8 nm/s. The pore diameter is around 20–50 nm as shown in the SEM image of Fig. 1(c). Fig. 1(d) shows the optical image of a P-Si cantilever array, showing the color change after anodization because of the interference in visible light.

2.2. Experimental setup

Fig. 2 shows a schematic illustration of the experimental setup. For nanomechanical IR spectroscopy, the P-Si cantilever is mounted in a gas flow cell with a ZnSe window. IR radiation from the monochromator (Foxboro Miran 1A-CVF) was focused onto the P-Si surface of the cantilever using a spherical mirror. The IR light was chopped at a frequency of 80 Hz. The IR wavelength is scanned from 2.5 μm to 14.5 μm (4000 cm^{-1} to 690 cm^{-1} in wavenumbers) with a spectral resolution of approximately 0.05 μm at 3 μm , 0.12 μm at 6 μm , and 0.25 μm at 11 μm according to the manufacturer. The nanomechanical IR spectra from variations in the deflection amplitude of the cantilever were taken using a SR850 lock-in amplifier (Stanford Research Systems, Sunnyvale, CA), and the resonance frequencies of the P-Si microcantilever were measured using a SR760 spectrum analyzer (Stanford Research Systems, Sunnyvale, CA). Dry air was used as a carrier gas and was passed through a gas bubbler containing 1 wt% naphtha/water mixture. The total flow rate was regulated at 100 mL/min, using mass flow controllers.

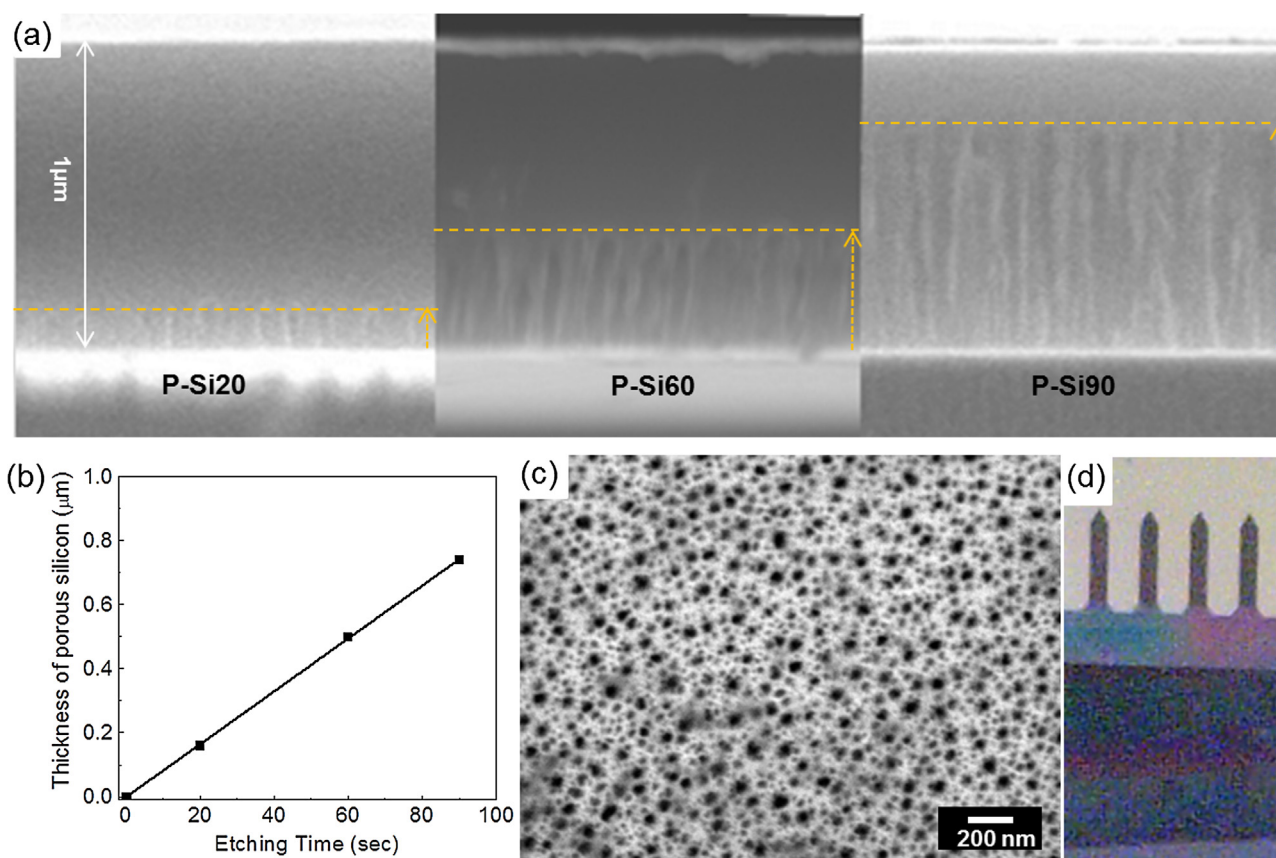


Fig. 1. (a) Cross-sectional scanning electron microscopy (SEM) images of the nanoporous Si microcantilever beams with different anodization time: 20 s (P-Si20), 60 s (P-Si60), and 90 s (P-Si90). Yellow-dashed lines and arrow indicate the average thickness of each P-Si layer and the direction of P-Si formation, respectively. (b) P-Si layer thickness as a function of anodization time. The straight line is the linear fit of thickness. (c) Top view of an SEM image on a P-Si90 microcantilever. (d) Optical image of P-Si cantilevers array.

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