

Silicon Nanowire Vertical Arrays with Porous Top Electrodes for Trace Vapor Preconcentration and Partial Separation

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ABSTRACT

Silicon nanowire (SiNW) arrays are demonstrated as a suitable substrate for the preconcentration of trace nitroaromatic compounds and subsequent desorption via Joule heating of the array. Arrays are fabricated from Si wafers containing epitaxially grown layers of high conductivity p-type Si, with a relatively low conductivity intrinsic Si layer. Arrays are fabricated using a combination of nanosphere lithography (NSL) and metal-assisted chemical etching (MACE). The resulting arrays consist of ordered Si nanowires. The individual wires have a diameter of approximately 350 nm (center-to-center spacing of 500 nm) and lengths of ~ 5 μm . Each SiNW array chip has approximately 10^8 individual wires. The temperature-dependent shift of the crystalline Si Raman single phonon line was used to estimate the temperature of the array during desorption, with temperatures in excess of 200°C observed. The effectiveness of the adsorption and desorption of trace nitroaromatics, including TNT, was evaluated by coupling the array to a mass spectrometer.

Keywords: Preconcentrator, silicon nanowire array, Joule heating, explosives

1 INTRODUCTION

Traditional chemical detection using analytical instrumentation (i.e. gas chromatography-mass spectrometry (GC-MS)) offers robust capabilities, but at the cost of instrument size and hardware complexity. For example, current state of the art instruments incorporate vapor sampling onto a sorbent material followed by thermal desorption to a programmable temperature vaporization (PTV) inlet to focus the desorbed vapor for subsequent introduction to a GC for separation [1, 2]. This methodology achieves detection at environmentally relevant levels, however, analysis time can be long (minutes to hours) due to a combination of sampling time (limited by sample flow rate through the stationary phase media) and instrument duty cycle (limited by the time necessary to desorb and refocus vapor on the PTV inlet). One modification of this approach to vapor detection is the direct delivery of materials desorbed from a reduced stationary phase volume contained within the PTV inlet to the head of a GC column [3]. Two advantageous consequences of this modification are

increased sampling flow rates and more rapid desorption due to the reduction in stationary phase volume.

The reduction in total analysis time afforded by increased sampling rate and direct desorption onto a GC column sacrifices selectivity and sensitivity, specifically associated with measurement precision and vapor concentration at the detector. The primary reason for this is the contribution of eddy diffusion to broadening of the desorbed analyte vapor cut. Eddy or multipath diffusion results from random analyte movements as it migrates through the packed sorbent bed. The broadening is exacerbated by radial temperature gradients during the heating of the sorbent bed. Together, these phenomena can reduce the apparent signal to noise for a desorbed zone of analyte by several orders of magnitude and cause significant errors in elution/migration time.

A highly ordered SiNW array provides significant surface area for analyte adsorption and reduces the effects of temperature gradients, as the array can be resistively heated for rapid and uniform desorption. This work focuses on developing and characterizing SiNW arrays for adsorption/desorption of trace vapors and demonstrates their capabilities to concentrate trace nitroaromatic vapors.

2 DEVICE FABRICATION AND EVALUATION

A self-assembled layer of polystyrene beads is spin coated onto the silicon substrate, and reactive ion etching is used to reduce the bead size, defining the final nanowire diameter and spacing. A 25 nm gold metal layer is deposited, and the beads are then removed via solvent. The polystyrene beads act as a nanomask, leaving the gold film pierced by an array of holes equal in size to the beads. Next, metal-assisted chemical etching (MACE) is used to create the highly ordered nanowire array. Briefly, the sample is immersed in a solution of hydrofluoric acid (HF) and hydrogen peroxide, whereupon a redox reaction occurs at the interface between the gold and the silicon. The silicon oxidizes and the oxide is removed by the HF. As a result, the gold film effectively “sinks” into the Si wafer; wherever there is a hole in the film, a Si nanowire is formed. Fabrication is completed by the deposition of a 2nd porous gold electrode on top of the array which allows vapor to penetrate into the array in a top down fashion. The porous top electrode allows one to pass a current and heat the SiNWs while also allowing analytes to

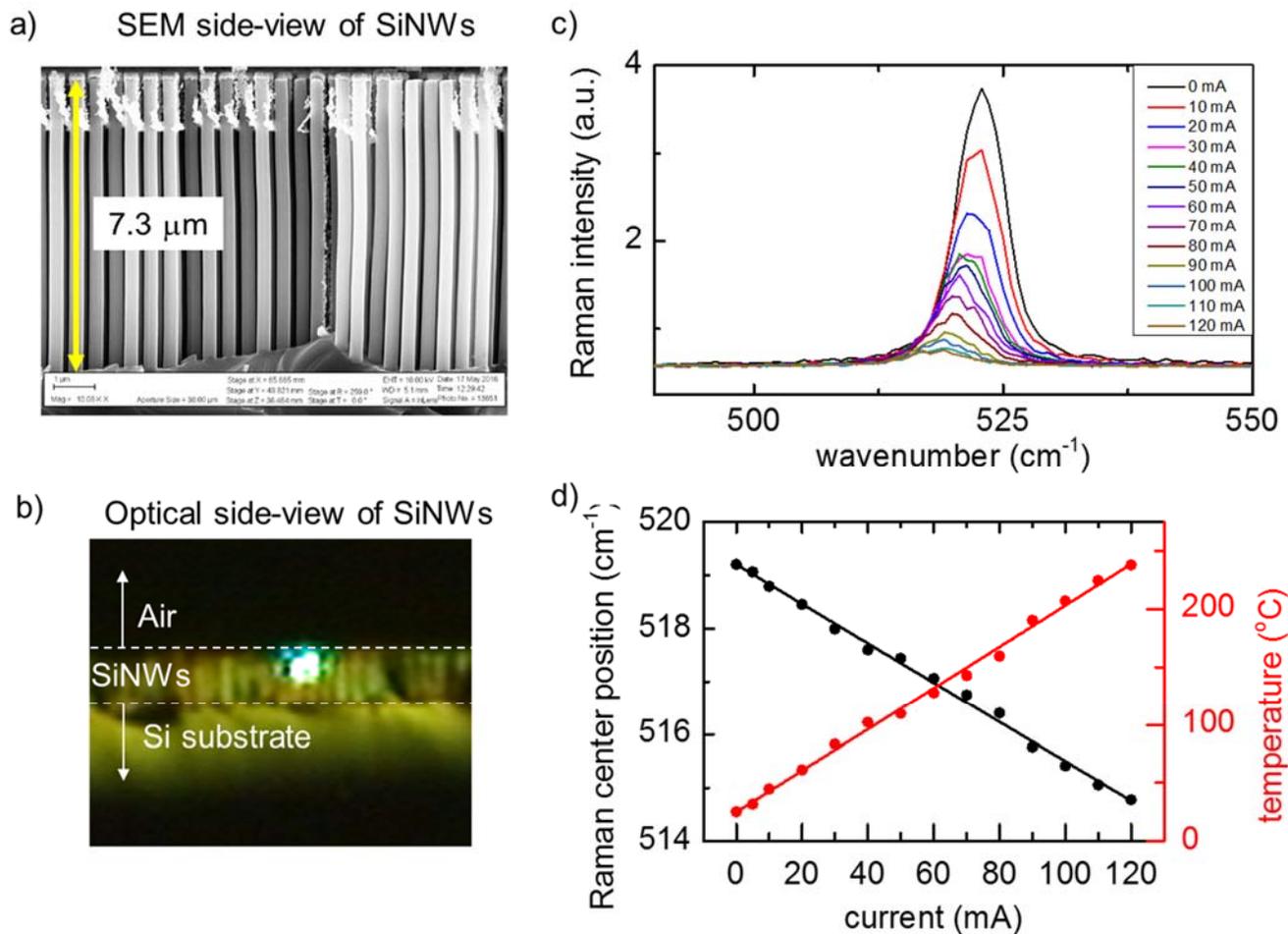


Figure 1. a) SEM side view of SiNW array. b) Optical side view of array. Bright green spot indicates the Raman laser. c) Raman spectra as a function of applied current. d) Temperature versus current relationship

pass quickly into the array during sampling and out of the array during desorption.

We used the temperature-dependent shift in the Si Raman single phonon line to estimate the temperature of the SiNWs as a function of applied current. The relationship between the one-phonon Raman peak location and temperature rise in Si is approximately linear from room temperature to 600K [4]. At room temperature, the one-phonon Raman peak occurs at $\sim 520 \text{ cm}^{-1}$. For every 1 K increase in temperature, the Raman peak shift decreases by about 0.02 cm^{-1} . It should also be noted the Raman peak broadens with temperature.

In panel a) an SEM side view of the SiNW array is shown. In panel b), we show an optical image of the array. The Si substrate is located at the bottom of the image, and the SiNWs are located between the white dashed lines. The Raman spectrum as a function of current was collected from a few SiNWs located in the laser focus spot (bright green spot in the middle of the image). Current was run through the SiNWs by applying a voltage between the porous top electrode and the Si substrate. The Raman spectrum for

applied currents ranging from 0 mA up to 120 mA is shown in panel c). Note that as the current increased, the Raman peak red-shifted and broadened, indicating a rise in the SiNW temperature. The spectral intensity also decreased with increasing current. It is known that the Raman peak intensity decreases with temperature, but part of the decrease we observed may also be due to thermal drift.

Each Raman peak in c) was fitted with a Gaussian line shape. The center wavenumber of the Gaussian fit is plotted in d) as a function of applied current. A linear fit of the Raman peak center wavenumber vs. current yields a slope of $-0.037 \text{ cm}^{-1}/\text{mA}$. To convert the Raman center position to SiNW temperature, we used the following equation:

$$\text{temperature} = (R_{RT} - R(I))/0.02 \text{ cm}^{-1}/^{\circ}\text{C} + 22 \text{ }^{\circ}\text{C}$$

where R_{RT} is the Raman center position at room temperature (i.e., applied current = 0 mA) and $R(I)$ is the Raman center position at an applied current of I . We assumed a room

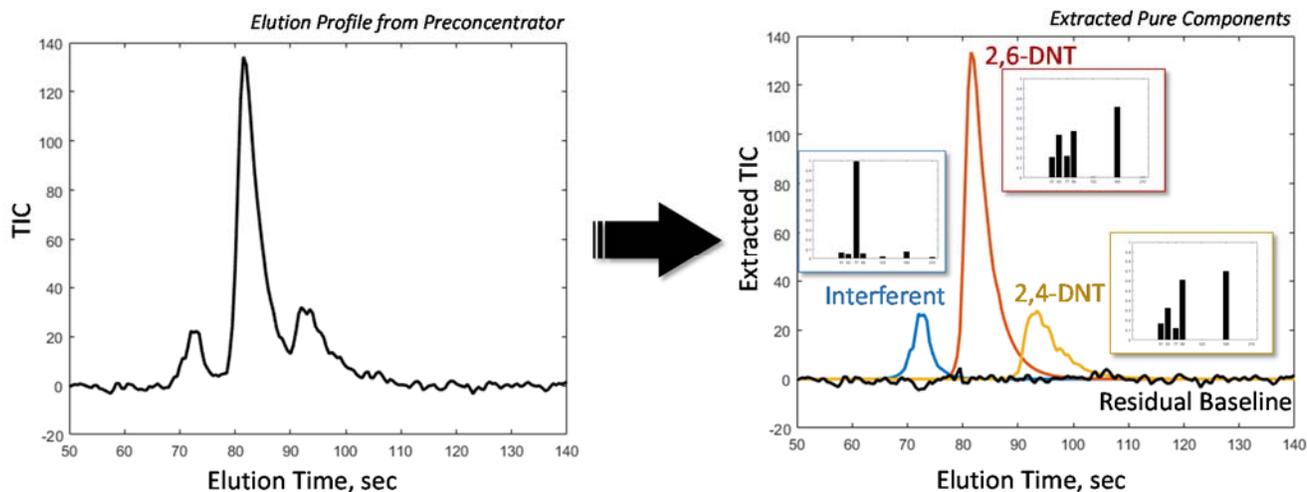


Figure 2. (Left) – Total ion chromatogram for the separation of a two component mixture of 2,6-DNT and 2,4-DNT. (Right) – Results of chemometric deconvolution of data identifying the number of unique peaks and identifying the two analytes of interested based upon pure component spectra.

temperature of 22 °C. A linear fit of the temperature vs. current yields a slope of 1.78 °C/mA

3 ADSORPTION/DESORPTION CAPABILITIES

Arrays were evaluated by delivering mixtures of trace TNT, DNT, and other vapors to SiNW arrays using a custom vapor handling system, at a fixed concentration, flow rate, and duration. Briefly, test vapors were delivered to the array using a custom trace explosives sensor testbed (TESTbed) [5]. After adsorption, the analyte was desorbed using a custom LabVIEW program and Keithley 2602A SourceMeter.

Desorption from the array was detected using an Agilent 5976 mass selective detector (MSD). Briefly, the sample chamber contained a stainless steel base and a ZIF socket to which the SiNW array, mounted on a pin grid array chip, was connected. A Plexiglas or stainless steel top was sealed directly to the pin grid array chip. Multiple access ports allowed the introduction and exit of vapor, and access to the MSD by a heated capillary transfer line.

When coupled to a multichannel detector such as a mass spectrometer, it was possible to resolve multiple components by leveraging unique detector responses and the partial separation afforded by the vapor pressure of the analyte and its affinity for the array substrate. Trace vapors were detected at two orders of magnitude below their saturated vapor concentration.

Figure 2 shows a representative desorption “chromatogram” of a mixture of 10 ppb_v 2,6-DNT and 3.4 ppb_v 2,4-DNT. The first peak is a highly volatile interferent associated with thermal degradation of the analytes. The nominal load of 2,6-DNT on the array is approximately 15

ng, and the nominal load of 2,4-DNT is approximately 5 ng. A combination of evolving factor analysis and spectral similarity measurements allow for the spectral response of individual components to be identified sequential. The pure component spectra are used to extract and estimate the pure component profile, which is in turn fitted to an exponential.

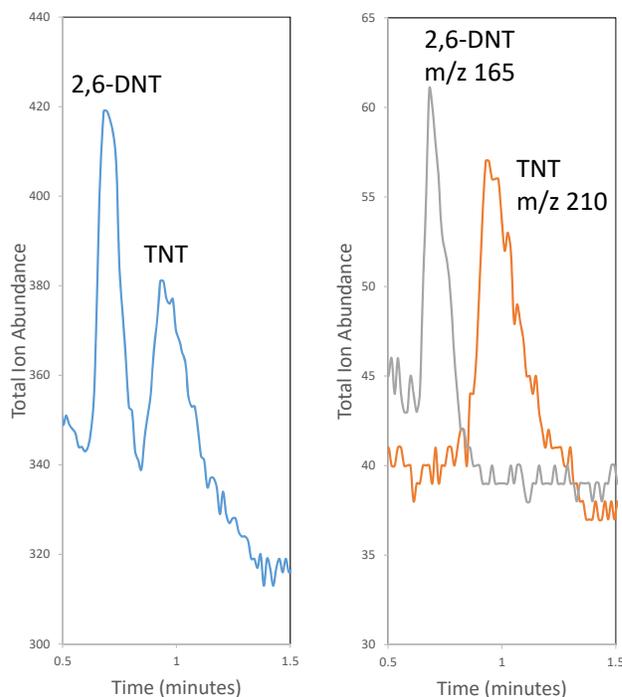


Figure 3. (Left) - Desorption of a mixture of 2,6-DNT and TNT. (Right) Selective ion traces for the analytes. Vapor concentrations were 10 ppb_v for 2,6-DNT and 8 ppb_v for TNT. Nominal sample loads were 30 ng for both analytes.

This allows us to iteratively extract and preset the desorption profiles for each component desorbed from the array.

Separation of less volatile explosives are possible as demonstrate with the adsorption and desorption of 2,6-DNT and TNT as shown in Figure 3. The quality of the separation is better realized by looking at select ions for 2,6-DNT and TNT. The two components are nearly baseline resolved.

4 CONCLUSIONS

This work demonstrates preconcentration and desorption of trace explosives vapors from SiNW arrays. The array's large surface area enables analyte adsorption without a stationary phase. Analyte is rapidly desorbed by Joule-heating the nanowires, suggesting the arrays can be used as an integrated preconcentration stage for portable analytical devices.

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