Dual-mode sensing platform based on colloidal gold functionalized porous silicon

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We report a dual-mode sensing platform based on a single layer porous silicon (PSi) film impregnated with colloidal gold nanoparticles. This gold-coated PSi film supports both quantification of molecular binding via reflectance measurements and molecular identification via surface enhanced Raman scattering (SERS). A detection sensitivity of approximately 400 nm/RIU was demonstrated through binding of benzenethiol molecules. Identification of the unique SERS peaks was possible with uniform signal intensity across the sample and a detection limit below 1 μM. © 2010 American Institute of Physics. [doi:10.1063/1.3503608]

Porous materials have attracted much attention for label-free sensing due to the large available surface area for molecular binding and their capability of size-selective molecule filtering. Typical sensors based on porous materials only operate in a single mode. For example, molecular binding events can be detected by monitoring thin film interference patterns using spectral reflectance, waveguide resonances using angle-resolved reflectance, or microcavity emission peaks using photoluminescence measurements. Dual-mode sensing platforms based on colloidal gold functionalized porous silicon have also been reported as promising surface enhanced Raman scattering (SERS)-active templates. In this work, we demonstrate a dual-mode sensing platform based on a single layer porous silicon (PSi) film decorated with colloidal gold (Au) NPs. Colloidal Au NPs are a convenient SERS platform due to their strong local field confinement, controllable size, and chemical stability. Our hybrid Au-PSi structure combines the advantages of molecular quantification via reflectance measurements and molecule identification via SERS spectral analysis on a single substrate.

Reflectance spectra of PSi structures in this work were measured by a Cary 5000 spectrophotometer (Varian) at near normal incidence. SERS spectra were measured at normal incidence with an XploRA 730 Raman microscope (Horiba Jobin Yvon) utilizing a 785 nm diode laser (9 mW) and 100× magnification. Data was collected with an integration time of 20 s and averaging of five scans.

Single layer PSi films were fabricated by electrochemical etching of an n-type silicon wafer (100), 0.01 Ω cm) in 5.5% aqueous hydrofluoric acid (HF). A sacrificial layer was first etched with a current density of 40 mA/cm² for 30 s, and removed from the silicon substrate by applying a high current density pulse (250 mA/cm² for 3 s) in a manner similar to what has been reported previously. This electropolishing procedure not only led to wider pore openings (~80 nm) at the top of the PSi layer to facilitate infiltration of Au NPs and target molecules but it also created a rough surface with approximately 40 nm deep silicon corrugations [Fig. 1(a)], which is beneficial for SERS measurements. A 2.3 μm (±20 nm) thick PSi layer with 60 nm (±10 nm) pore openings was subsequently formed on the roughened silicon wafer by applying a current density of 35 mA/cm² for 150 s. The PSi dimensions were estimated based on cross-sectional scanning electron microscopy (SEM) imaging (not shown). The PSi sample was then oxidized at 500°C in air ambient for 5 min (Omegalux LMF-3550 oven).

Two different sizes of Au NPs were prepared using synthetic procedures analogous to those reported elsewhere. Briefly, for synthesis of Au NPs with approximately 4.5 nm size, 1 mL of freshly prepared ice-cold solution of 0.3 M...
NaBH₄ was added to an aqueous solution (100 mL) of HAuCl₄ (0.25 mM) and trisodium citrate (0.25 mM) under vigorous stirring. The solution with formed Au NPs was stirred for 10 min. For synthesis of Au NPs with approximately 14.8 nm size, 1 mL of trisodium citrate (1.2 mM) was injected into 100 mL of boiling aqueous solution of HAuCl₄ (0.3 mM). After 10 min of vigorous boiling, the solution containing Au NPs was removed from the oil bath and left undisturbed for 1 h. Transmission electron microscopy (TEM) imaging was performed to confirm the size of the NPs, as shown in the insets of Figs. 1(b) and 1(c). The Au NPs will be denoted further as small (4.5 nm) and large (14.8 nm) Au NPs, respectively.

In order to attach the colloidal Au NPs on the pore walls and top surface of the PSi sample, 4% 3-aminopropyltriethoxysilane solution in water and methanol was used as a linker molecule. The silanized PSi samples were immersed in solutions containing either the small or large colloidal Au NPs for 24 h. After the infiltration, the PSi samples were rinsed with deionized water and dried with nitrogen.

The dual-mode sensing operation of the Au coated PSi substrate was demonstrated by detection of benzenethiol. Au–PSi samples were immersed in 0.2 mM benzenethiol in ethanol for 1 h, and the samples were subsequently rinsed with ethanol and dried with nitrogen.

The first sensing operation was probed by reflectance measurements. Thin film interference fringes undergo a spectral shift based on the Au NP and benzenethiol molecule-induced overall refractive index change of the PSi film. Figure 2 shows the reflectance spectra after each process step: after silanization, after attachment of Au NPs, and after adsorption of benzenethiol on the Au NPs. Figure 2(a) shows an approximately 85 nm blueshift of the spectrum upon the infiltration of small Au NPs, since the refractive index of Au is less than air. A smaller blueshift of approximately 60 nm was observed after exposure of the PSi film to large Au NPs, as shown in Fig. 2(b). We note that the reflectance intensity in both cases is low due to scattering from the rough PSi surface. An approximately 8 nm redshift was observed after benzenethiol adsorption on the small Au NPs while negligible reflectance shift was observed for the PSi sample with large Au NPs. Benzenethiol naturally forms a monolayer on gold surfaces. Control experiments performed by exposing PSi samples without Au NPs to benzenethiol showed no measurable fringe shift.

Based on these reflectance measurements, we estimated the coverage and distribution of Au NPs and benzenethiol in both samples using the transfer matrix method and effective medium theory. Following our prior work, we fit the measured “silanized” interference fringes with a simulated spectrum: we assumed a PSi film thickness of 2.3 μm and then determined that the refractive index of silanized PSi was 1.88, which corresponds to a porosity of 64%. In a similar manner, we determined the refractive index change of the PSi film after Au NPs decorated the surfaces and benzenethiol was attached to the Au NPs. To provide insight on the distribution of NPs, we considered the PSi film as consisting of three zones. Based on the size of Au NPs, we assumed the top zone was a 4.5 or 14.8 nm thick, 66% porosity Au layer to model the complete coverage of the respective Au NPs on the available top surface area of the PSi. The middle zone, representing the triangular roughened surface, was assumed to be a 40 nm thick, 65% porosity PSi layer with 50% Au coverage. The bottom zone consisted of the 2.3 μm thick, 64% porosity PSi layer with partial coverage of Au NPs. In order to fit our simulated spectra to the measured reflectance curves, we found that the effective overall refractive index changes upon the infiltration of small Au NPs and subsequent adsorption of benzenethiol molecules on the NPs were 0.08 and 0.02, respectively, which suggests nearly 30% (±5%) Au NPs coverage inside the pores and approximately 60% benzenethiol coverage on the surface of the small Au NPs. Given the 8 nm (±1 nm) spectral shift after benzenethiol attachment, we estimate the detection sensitivity of a sensor based on a PSi film with small Au NPs is 400 (±50) nm/RIU. For the larger Au NPs, simulations suggested that the 60 nm blueshift measured after infiltration was almost entirely due to complete Au NP coverage on top of the PSi film. With few large Au NP infiltrated deep inside the pores, we expect negligible reflectance fringe shift after benzenethiol attachment, which is consistent with the measured result. The fringe shift is much more sensitive to small refractive index changes occurring inside the PSi film as opposed to on top of the film. Hence, the large Au NPs cannot be used for dual-mode sensing.

The second mode of sensing was investigated by SERS measurements to provide unique molecule identification. Figure 3 shows the experimental SERS spectra after adsorption of benzenethiol molecules on both the small and large Au NPs coated PSi substrates. As expected, higher SERS signal strength was observed from the large Au NPs coated PSi substrate. We believe the majority of the SERS signal originates from NPs on the top region of the PSi film because the SERS signal strength measured from separately prepared 100 nm thick PSi films infiltrated with Au NPs and benzenethiol was the same as the SERS signal strength from equivalent sized benzenethiol-coated Au NPs that impregnated the 2.3 μm thick PSi film. Moreover, by preparing an additional sample with only a roughened silicon surface, we...
found that only about 10% of the SERS signal was due to NPs on the surface. For each sample that was prepared, five different spots were measured across the surface area. Similar SERS signal strengths were collected from all spots, indicating the uniformity of the functionalized surface of our SERS-active substrate. To examine the sensitivity of the SERS measurement, we exposed a small Au NPs coated PSI film to 1 μM benzenethiol in ethanol for 1 h. A clear SERS signal was observed, which suggests that a detection limit below 1 μM is possible. We note that lower detection levels could be obtained by exposing the substrate to benzenethiol for a longer duration. Additionally, higher detection sensitivity and enhanced SERS signal may be achieved through further optimization of the ratio of Au NPs size and PSI pore size.

In summary, a dual-mode sensor based on a Au NPs coated PSI film has been presented. Measurements of the reflectance fringe pattern and SERS spectrum enabled both molecular quantification and identification. A detection sensitivity of 400 nm/RIU was reported based on reflectance measurements after benzenethiol adsorption. Higher detection sensitivity may be achieved through utilizing resonant PSI structures such as microcavities and waveguides. The SERS spectrum showed that benzenethiol could be identified with a detection limit below 1 μM and large area uniform intensity. The ease and low cost of fabrication, high detection sensitivity for small molecules, and integration of dual-modes of sensing using one substrate make the Au NPs coated PSI substrate attractive for use in a variety of sensing applications.

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