Ultra Sensitive Surface-Enhanced Raman Scattering Detection Using Uniform Sub-5 nm Gap Optical Antennas

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Abstract: Arch-dipole optical antennas with uniform 5nm gaps have been fabricated on Si substrate using deep-UV "spacer" lithography. Strong surface-enhanced Raman scattering (SERS) signals with an enhancement factor of 1.1×10^8 have been measured.
OCIS codes: (240.6695) Surface-enhanced Raman scattering; (350.4238) Nanophotonics and photonic crystals

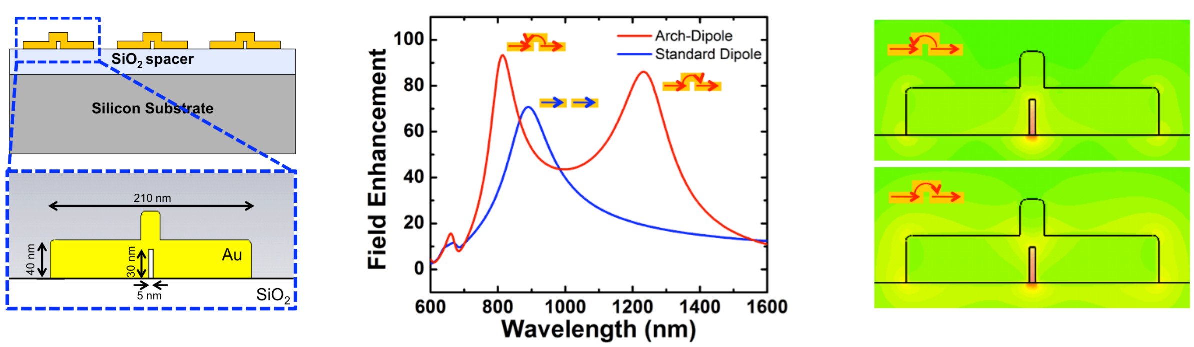
1. Introduction

Optical antennas are widely used in surface-enhanced Ramon spectroscopy (SERS) [1] because of their ability to focus light in sub-diffraction-limited area, resulting in strong field enhancement [2]. The field enhancement depends critically on the gap spacing of optical antennas [3]. Current nanofabrication techniques such as focused ion beam milling and electron beam lithography are limited by poor uniformity and reproducibility as the dimension decreases below 10 nm, making it difficult to fabricate optical antennas with well-defined sub-10 nm gap spacing.

In this paper, we report on the design and demonstration of new optical antennas with uniform sub-5nm gap spacing. Using deep-UV spacer lithography, the antenna gap is defined by a thin dielectric layer whose thickness is precisely controlled by atomic layer deposition (ALD). We have fabricated arch-dipole antennas with 5-nm gap spacing. Strong SERS signals from *trans*-1,2-two (4-pyridyl) ethylene (BPE) molecules have been measured from the antennas, with an enhancement factor of 1.1×10^8. The resonance characteristics and the excitation polarization dependence of the SERS signal confirm the observed SERS enhancement is resulted from the antennas. Since the proposed new antennas can be made by deep UV lithography, uniform SERS substrates with sub-5nm gaps can be mass produced in existing Si CMOS foundries.

2. Optical Antenna Design and Fabrication

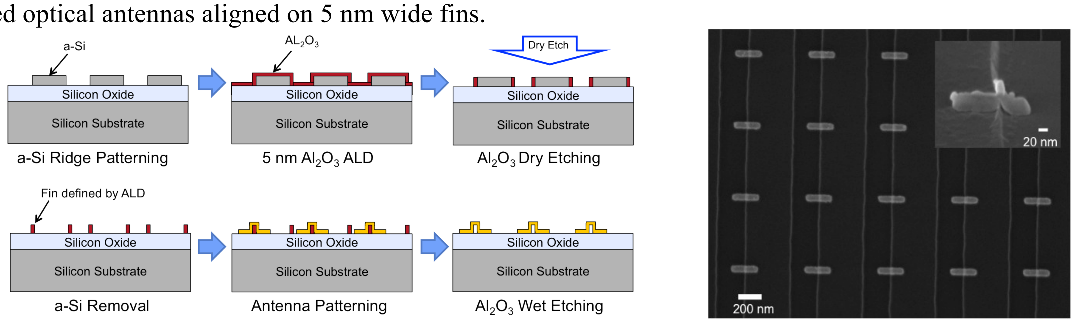
The schematic of the "arch-dipole" antenna is illustrated in Fig. 1(a). Similar optical antennas have been used to enhance spontaneous emissions in semiconductors [4]. The two arms of a dipole are connected by an arch. The resonance frequency of the antenna is mainly defined by the width and height of the arch. As will be shown in the fabrication section, both dimensions are controlled by the thickness of precisely deposited thin films. We have simulated the performance of such antennas using finite integration technique (FIT). Fig. 1(b) and (c) shows the field enhancements and distributions of the antenna modes identified by the current direction in the arch. The field enhancements (85 and 95) are slightly higher than the standard dipole with the same gap spacing (70). We used the high order mode (arch current in opposite direction) because the antenna dimensions are easier to fabricate (larger) and the field enhancement is slightly larger.



(a) (b) (c)

Fig. 1 (a) Schematic of the arch dipole antennas. The dimensions of the antenna is shown in the inset. (b) E-field enhancement simulation. The field is measured at the center of the gap. The current distribution of the antenna is shown next to each resonance peak. (c) E-field distribution of two arch-dipole antenna modes.

We use deep-UV "spacer lithography" to define the width and height of the arch, as shown in Fig. 2(a). First, a 30 nm-thick amorphous Si (a-Si) film, which defines the arch height, is deposited on top of a 100 nm thermal oxide-coated Si wafer. After patterning the a-Si into 600 nm pitch grating (by deep UV lithography and dry etching), a 5nm-thick aluminum oxide (Al_2O_3) is deposited conformally by ALD. The flat part of the Al_2O_3 is removed by a blanket reactive ion etching (RIE), leaving only Al_2O_3 film on the sidewalls of a-Si. Upon selective removal of a-Si, they become free-standing fins with 5 nm width and 30 nm height. By depositing metals around the fin, arch dipole antennas with uniform arch spacing and height can be realized. Arch-dipole antenna arrays with 50 nm width and various lengths (120, 150, 180, 210, and 240 nm) are fabricated using this process. Here, we use electron-beam lithography to pattern the antenna around the fins. The antenna metal consists of 40nm gold and 2nm Ge (for adhesion). Finally, aluminum oxide fins are etched away by phosphoric acid. The SEM image in Fig. 2(b) shows the fabricated optical antennas aligned on 5 nm wide fins.

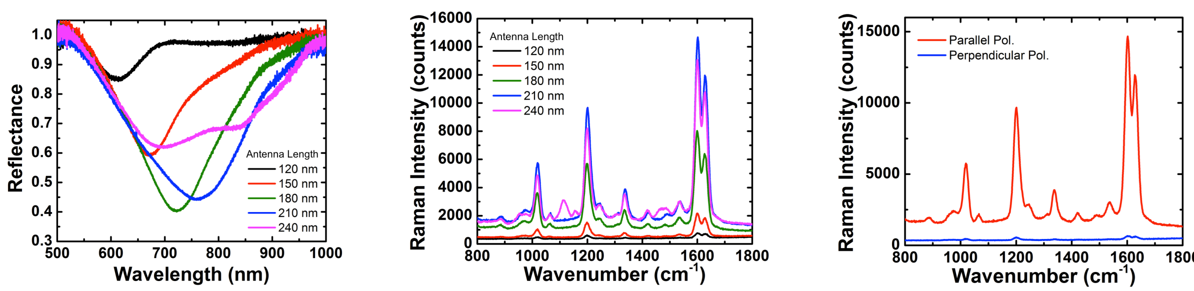


(a) (b)

Fig. 2 (a) Fabrication process. (b) SEM images of optical antenna array aligned on 5 nm fins. Inset shows perspective view of a single antenna.

3. Experiments and Results

The antenna resonance is characterized by the reflectance spectrum of broadband light via a 50x objective lens. Fig. 3(a) shows that the reflection spectra of the antenna arrays. The resonance dip exhibits a red shift with increasing antenna length, as expected. For SERS measurement, we used *trans*-1,2-two (4-pyridyl) ethylene (BPE) as the target molecule. The fabricated samples were immersed in a 6mM solution of BPE in methanol for 2 hours and then rinsed in methanol, followed by blow drying with nitrogen. A 10x objective lens was used to focus the excitation laser (785 nm, 30mW) and to collect the Raman signal for 100 ms. Fig. 3(b) shows the SERS spectra from antenna arrays with various lengths. The strongest Raman signals are observed from the 210 nm and 240 nm long antenna arrays, which have resonances near the excitation and Stokes shifted wavelength, respectively. The calculated enhancement factor for 1200 cm^{-1} peak from the strongest SERS signal is 1.1×10^8 (assuming monolayer coating of BPE molecules on all gold surfaces). This is comparable to the previous reported results [3]. The strong dependence on the excitation polarization (Fig. 3(c)) confirms the SERS signals are from the optical antennas.



(a) (b) (c)

Fig. 3 (a) Reflectance measurement of fabricated optical antenna arrays with antenna length variations. (b) Measured BPE SERS spectra. (c) SERS comparison with two different excitation polarizations.

4. References

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