Chapter 5

Fabrication and Characterization of Si-Ag Core-Shell Nanowire Resonators

5.1 Introduction

In Chapter 4, we discussed a theoretical investigation of Si-Ag core-shell nanowire resonators (Figure 5.1), and demonstrated that in this geometry, modes can be confined to ultra-small volumes. In this chapter, we address several routes to fabricating these resonators and methods of characterizing their optical properties. Both top-down and bottom-up fabrication are explored, and dark-field optical spectroscopy is used to investigate the properties of these resonators.

5.2 Fabrication of Si-Ag Core-Shell Nanowires

In this section, we describe the two methods employed for fabricating core-shell nanowires. The first is a bottom-up approach that begins with Si nanowires grown by chemical vapor deposition (CVD), and the second uses electron beam lithography (EBL) and reactive ion etching (RIE) to fabricate Si nanowires. In both cases, the Ag coating is deposited by RF-magnetron sputtering.

5.2.1 Bottom-Up Approach

The bottom-up fabrication method is shown schematically in Figure 5.2. The wires are grown using the vapor-liquid-solid (VLS) growth mechanism [74] with Au as a catalyst, following the method developed by Kayes et al. [75]. We begin with a

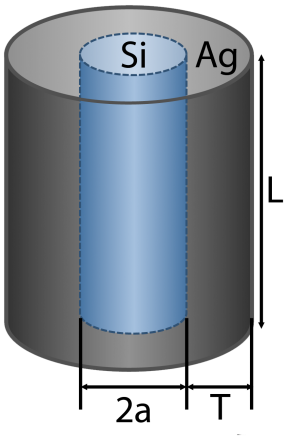

Figure 5.1. Si-Ag core-shell nanowire resonator, consisting of a Si core (radius a), Ag cladding (thickness T), and length L.

Si $\langle 111 \rangle$ substrate with 300 nm thermal oxide. The Au catalyst is patterned using photolithography and a mask consisting of 3 μm holes in a rectangular array with 7 μm center-to-center spacing. After pattern exposure, the SiO_2 in the exposed region is etched away with HF acid, leaving an oxide-free Si surface that will serve as the substrate for wire growth. Au catalyst (100 nm thick) is deposited using thermal evaporation. After liftoff, the Au dots are patterned only on top of the Si $\langle 111 \rangle$ surface and are separated from one another by SiO_2. This prevents Au migration during the high-temperature CVD growth.

After Au patterning, nanowires were grown in a CVD reactor at 1000 °C with $SiCl_4$ and H_2 gas as the precursors. In the VLS method, Si from the $SiCl_4$ is absorbed by the liquid Au, forming a Au-Si alloy. The remaining Cl reacts with H_2 producing HCl gas. The Au-Si alloy at the wire tip passes through the binary eutectic point, upon which the Si solidifies and separates, forming the nanowire. The samples were first annealed in a tube furnace at 1000 °C for 20 min under 1 atm of H_2 at a flow rate of 1000 SCCM. Wires were then grown for 5 min at 1000 °C at 1 atm of H_2 and $SiCl_4$, at flow rates of 1000 and 20 SCCM, respectively. For our purposes, short ($\approx$1 μm) wires are grown. After growth, the Au catalyst tips are etched off using Transene Au etch TFA (KI-I_2 complex) for 3 min.

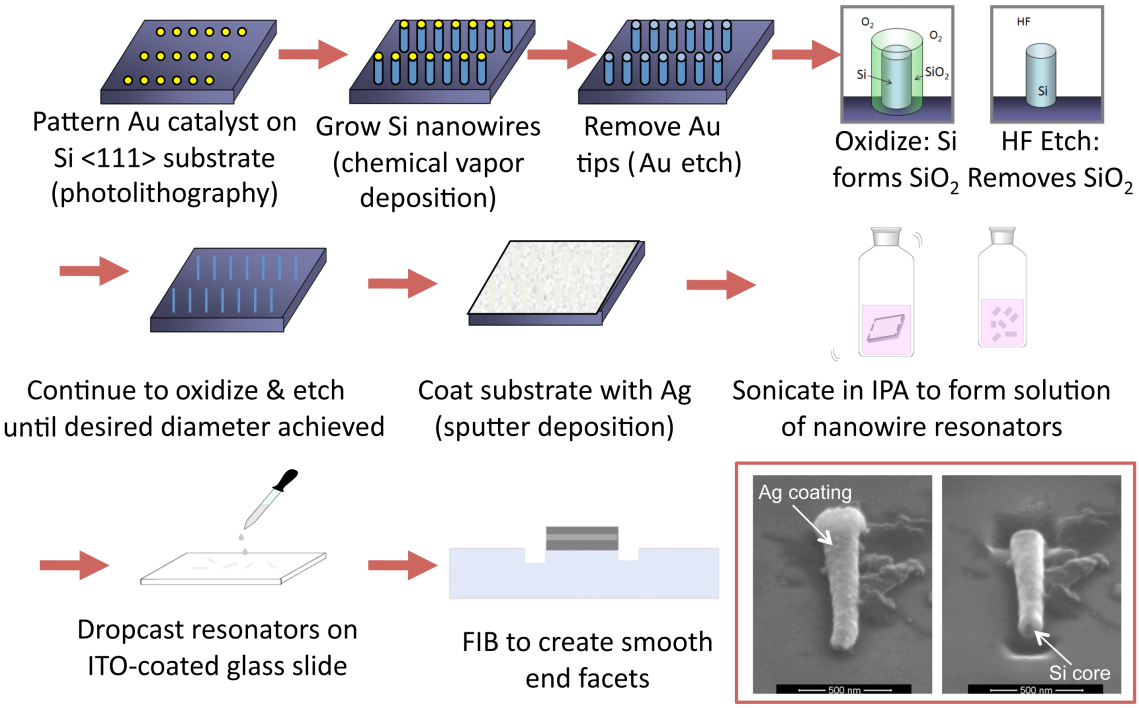

Figure 5.2. Bottom-up fabrication procedure for making Si-Ag core-shell nanowires. Si nanowires grown by Au-catalyzed CVD (VLS procedure) are oxidized and etched to reach a desired diameter of <100 nm, and coated with Ag by sputtering. After sonicating to disperse in IPA, wires are dropcast onto an ITO-coated glass slide and cut by FIB to the desired length and to attain smooth end facets.

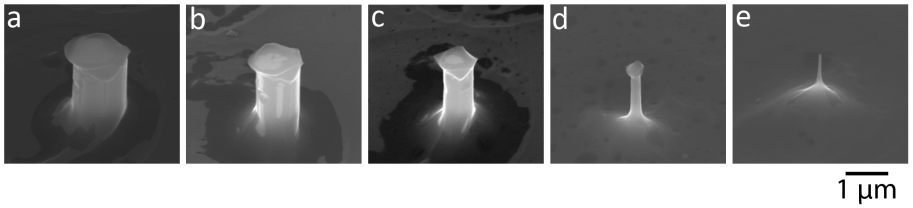

Figure 5.3. (a) A representative wire approximately 1.3 μm in diameter after 3 hr of wet oxidation at 925 °C and 5 min etching in BHF; (b) 900 nm diameter after 1.2 hr oxidation at 925 °C and 2.75 min BHF; (c) 700 nm diameter after 3 hr oxidation at 950 °C and 5 min BHF; (d) 200 nm diameter after 3 hr oxidation at 950 °C and 5 min BHF; (e) 50 nm diameter after 45 min oxidation at 950 °C and 5 min BHF.

The nanowire diameter and spacing are determined by the size and position of the Au catalyst on the growth substrate. Photolithography limits these dimensions to approximately 1 μm, which is much larger than the wire diameters explored in Chapter 4. To achieve smaller wire diameters, a series of wet oxidation and wet chemical etching was employed (Figure 5.3). The wires were oxidized in a tube furnace operating at 925 °C and 950 °C for times varying from $0.75 - 3$ hr, creating a thick SiO_2 layer on the surface of the Si wire and growth substrate. This oxide layer was removed by submersion in buffered HF(aqueous) (BHF) acid for 5 min, after which the oxidation and etching procedure was repeated. Ultimately, the wire diameter was decreased from approximately 1.5 μm to less than 70 nm.

A uniform Ag layer of 60 nm was deposited around the Si nanowire using RF-magnetron sputtering (Figure 5.4). The sample was placed in a cuvette with isopropyl alcohol (IPA) and sonicated for 30 s to form a solution of Ag-coated Si nanowires. Approximately 10 μL of this solution was dropcast onto an indium tin oxide (ITO)-coated SiO_2 substrate in 1 μL increments using a micropipette, and the IPA was allowed to evaporate between each droplet. Afterwards, a FIB with a Ga^+ source operating at 30 keV and 10 pA was used to cut the core-shell nanowires to desired lengths and to create smooth end facets.

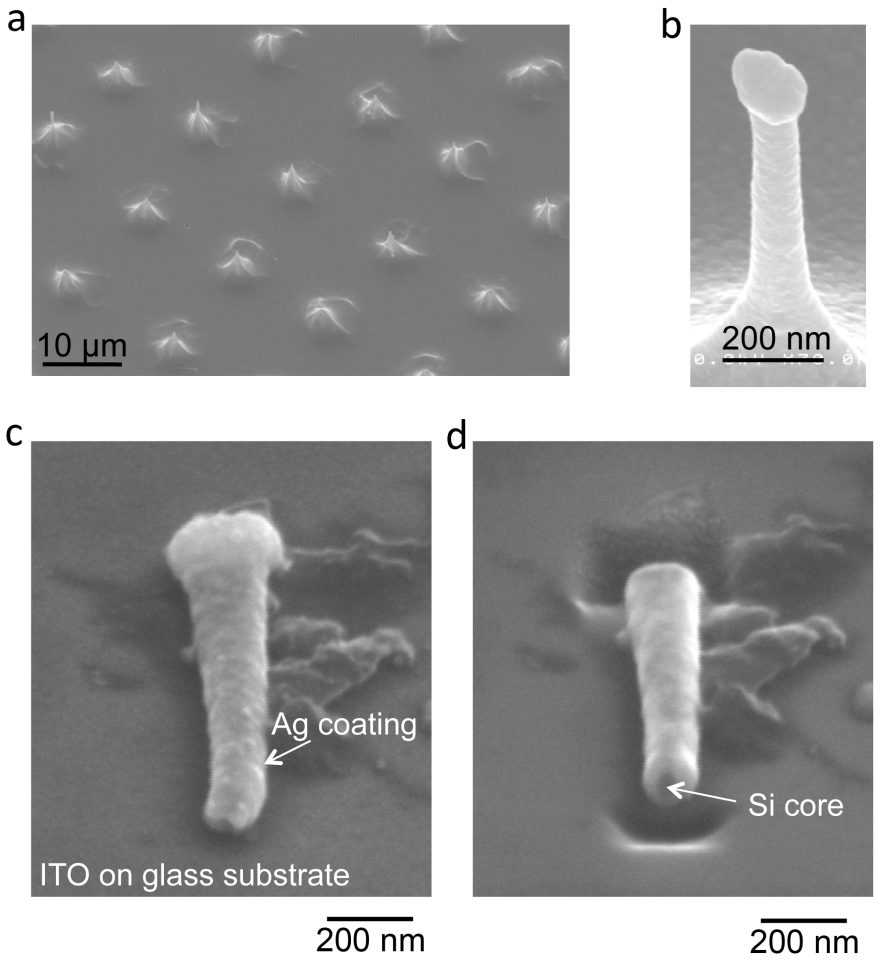

Figure 5.4. (a), (b) SEM images of Ag-coated NWs. (c) Ag-coated NW dropcast on ITO-coated glass substrate and (d) cut with FIB.

5.2.2 Top-Down Approach

We also investigate a top-down approach to fabricating Si-Ag core-shell nanowire resonators using EBL, RIE, and metal sputtering (Figure 5.5). Here, we start with a silicon-on-insulator (SOI) wafer with a 220 nm thick Si ⟨100⟩ device layer on 3 μm of SiO_2 on Si. On top of this, we spin a thin (75 nm) layer of poly(methyl methacrolate) (PMMA). Arrays of small holes 100×100 μm^2, 40–80 nm diameter with spacing from 1–20 μm are patterned in the PMMA using electron beam lithography and developed for 45 s in 1:3 MIBK:IPA. A 30 nm thick layer of Al_2O_3 is deposited by RF-magnetron sputtering. Although this technique results in conformal deposition, the swelling of the PMMA in acetone succeeds in fracturing the thin, brittle layer of of the Al_2O_3. Liftoff is performed by soaking the sample in acetone for 1 hr and then gently wiping the surface with a cloth-tipped swab. This results in small Al_2O_3 dots on the SOI that serve as a mask for RIE.

Arrays of Si nanowires 40–80 nm diameter are created by reactive ion etching through the top Si layer of the SOI wafer with Pseudo-Bosch (SF_6/C_4F_8) etch chemistry [76]. Afterwards, the Al_2O_3 mask is removed by etching the sample in a base-RCA clean with a solution of 5:1:1 H_2O:H_2O_2:NH_4OH at 70 °C for 60 s. This procedure creates uniform Si nanowires 220 nm tall on the 3 μm oxide layer, as seen in Figure 5.6a before removal of the Al_2O_3 etch mask.

The metal cladding is formed by sputtering a 60 nm Ag layer over the sample, coating the Si nanowires. As shown in Figure 5.6b, this results in conformal coating of the sidewalls and substrate below, as well as creating a larger ball of Ag atop the nanowire. To perform experiments, we must obtain optical access to the Si core. The removal of excess Ag is achieved by sputtering in an Ar plasma. We find that after 3 separate sputtering steps of 5 min, 5 min, and 2 min, the excess Ag atop the nanowire, as well as the Ag on top of the SiO_2/Si substrate below, has been removed. Although primarily isotropic, the Ar plasma etch is just directional enough that the Ag removed from the sample is redeposited on the Si nanowire sidewalls to protect the cylindrical Ag coating during the etch. The resulting structure is shown in Figure 5.7.

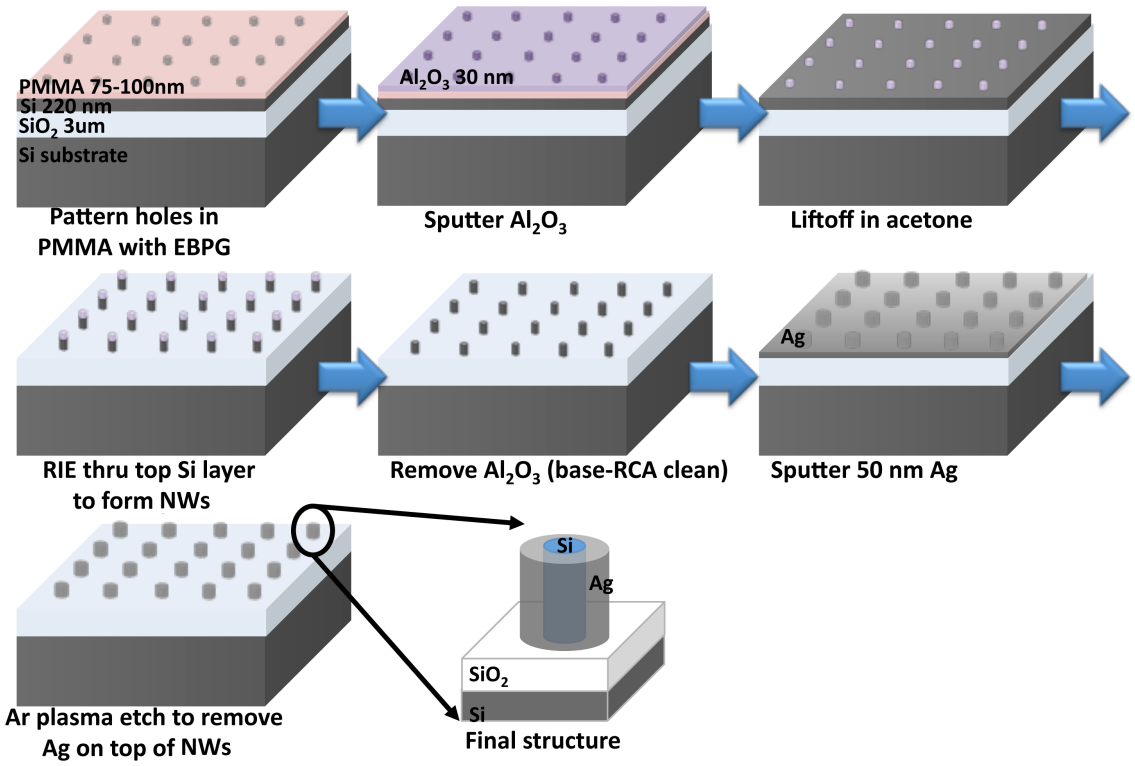

Figure 5.5. Top-down fabrication steps for Si-Ag core-shell nanowire resonators. Small dots of Al_2O_3 are patterned using electron beam lithography and liftoff, and used as an etch mask for RIE. Ag is deposited by sputtering and optical access to the nanoresonators is achieved by etching in Ar plasma.

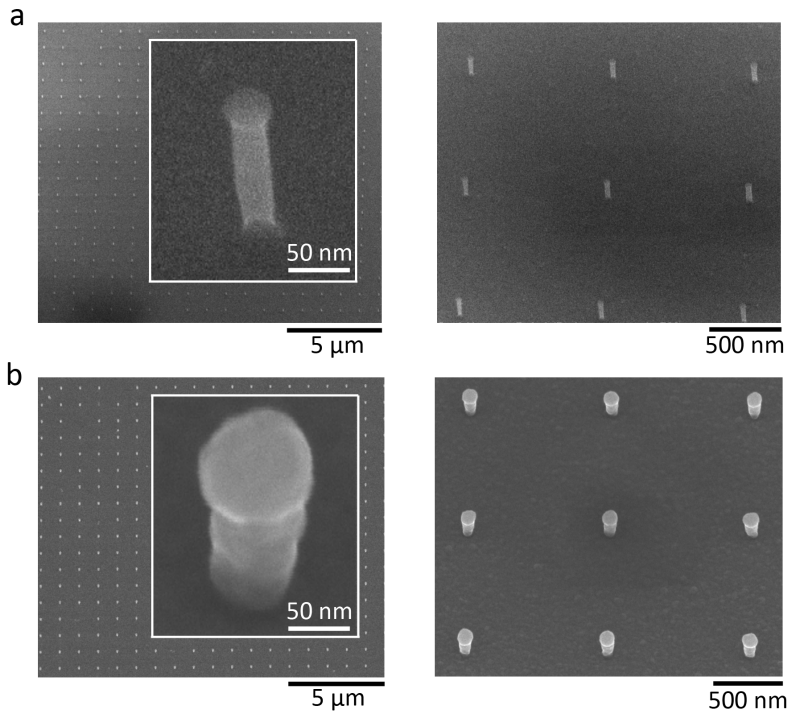

Figure 5.6. SEM micrographs taken at 30° tilt of (a) Si nanowires fabricated by electron beam lithography and reactive ion etching, and (b) Si nanowires coated with Ag by sputtering.

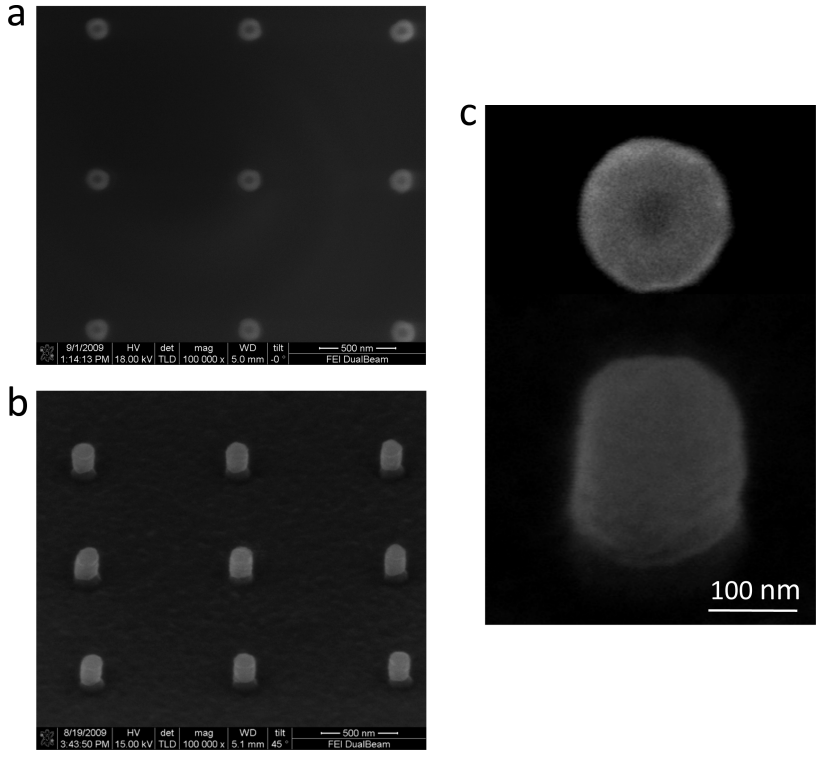

Figure 5.7. SEM images of fully-fabricated Si-Ag core-shell nanowire resonators after Ar sputtering to remove excess Ag taken at (a) 0° and (b) 45° tilt. Higher-magnification images are seen in (c).

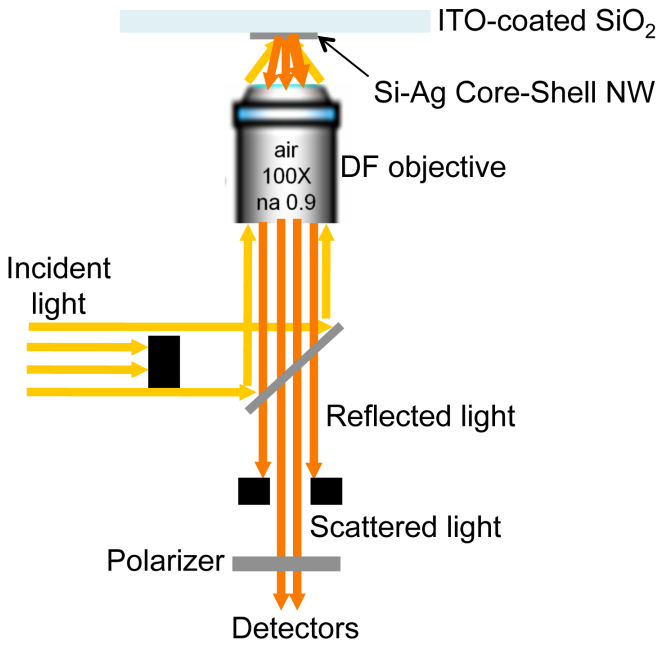

Figure 5.8. Schematic illustration of DF spectroscopy and imaging in an inverted optical microscope. This setup collects the scattered light from the sample, illustrated here as a Si-Ag core-shell nanowire on ITO-coated SiO_2.

5.3 Optical Characterization

The Si-Ag nanowire resonators are characterized optically using a combination of bright- and dark-field spectroscopy. The experimental setup is seen in Figure 5.8. Incident light from an unpolarized halogen lamp is sent through a dark-field (DF) objective (100×, 0.9 NA) that collects only scattered light from the sample. The light is focused into a monochromator and CCD spectrometer that allows spectroscopy to be performed on single nanowires, as well as arrays. A rotatable polarizer on a flip-mount in the detection path permits collection of polarization-resolved scattering spectra.

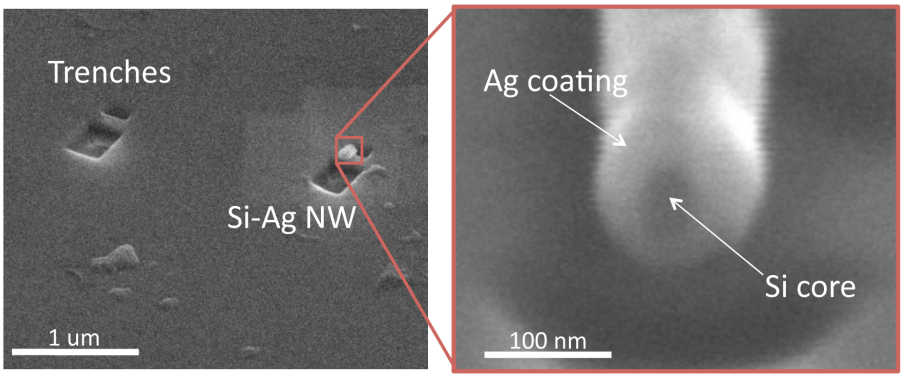

Figure 5.9. Left: SEM image of a FIB-cut Ag-coated Si NW and corresponding trenches used for normalization. Right: Close-up SEM image of Ag-coated Si NW.

5.3.1 Dark-Field Spectroscopy of Bottom-Up Fabricated Si-Ag Core-Shell Nanowires

We perform optical measurements on single nanowires fabricated by the bottom-up technique described in Section 5.2.1. As this technique measures scattered light, and the FIB-cut process creates subwavelength trenches that scatter the incident light, we also fabricated trenches near the core-shell nanowire as shown in Figure 5.9. Dark-field spectra are collected from both the wire and the corresponding trenches, and we ultimately report spectra corrected as

$$DF_{\text{corrected}} = \frac{DF_{\text{wire}}}{DF_{\text{trenches}}}. \tag{5.1}$$

As the close-up SEM in Figure 5.9 shows, this wire 250 nm in length has clean end facets, a Si core diameter of 50 nm, and Ag coating 50 nm thick.

Polarization-resolved dark-field scattering spectra of this core-shell nanowire are shown in Figure 5.10a. Here, the longitudinal axis of the nanowire is oriented along 0°–180°. Several peaks are observed, the brightest at $\lambda = 450$ nm and $\lambda = 700$ nm. Maximum DF intensity is observed for 90° polarization, decreasing to a minimum at 0° and 180°. Calculations of the FF emission for plane wave excitation incident at $\theta = 45°$ from the surface normal are also plotted in Figure 5.10a. We find good

agreement between the spectral peaks in the calculated emission spectrum and the experimental DF scattering spectrum at $\theta = 90°$. Polar plots of the DF scattering intensity at several wavelengths are seen in Figure 5.10b. For all wavelengths, emission is oriented perpendicular to the longitudinal axis of the wire. Highest intensity is observed at $\lambda = 450$ nm.

5.3.2 Dark-Field Spectroscopy of Top-Down Fabricated Si-Ag Core-Shell Nanowires

We also performed dark-field spectroscopy measurements on the top-down fabricated Si-Ag core-shell nanowire resonators. These samples have arrays with varying Si core diameters and spacing between the resonators, allowing investigation of both individual resonators and collections of several resonators. A DF image is seen in Figure 5.11 for a 100×100 μm^2 array with 5 μm spacing between the wires, which shows significant response in the blue end of the spectrum.

Dark-field scattering spectra of approximately 15 resonators with 1 μm spacing between the wires is shown in Figure 5.12a, for resonators with 60 nm, 50 nm, and 40 nm Si core diameters, 60 nm of Ag coating, and 220 nm tall. The spectra reported here are corrected to a background spectrum from another region of the sample by

$$DF_{\text{corrected}} = \frac{DF_{\text{wire}}}{DF_{\text{background}}}. \tag{5.2}$$

A number of peaks are observed in the DF spectra for the three different sizes, and the spectral positions of these peaks appear to be independent of the Si core diameter. However, the intensity of the peaks does depend on this dimension. If the spectral features were due to longitudinal modes of the resonator, one would expect the peak position to vary with the Si core diameter. Instead, these peaks originate from Fabry-Pérot oscillations in the SiO_2 film that couple to free space through the Si-Ag core-shell resonators. The DF spectrum in Figure 5.12b is from a single resonator with 50 nm Si core diameter, 60 nm Ag coating thickness, and 220 nm tall, and the same spectral features can be observed. Essentially, these resonators act as antennas that

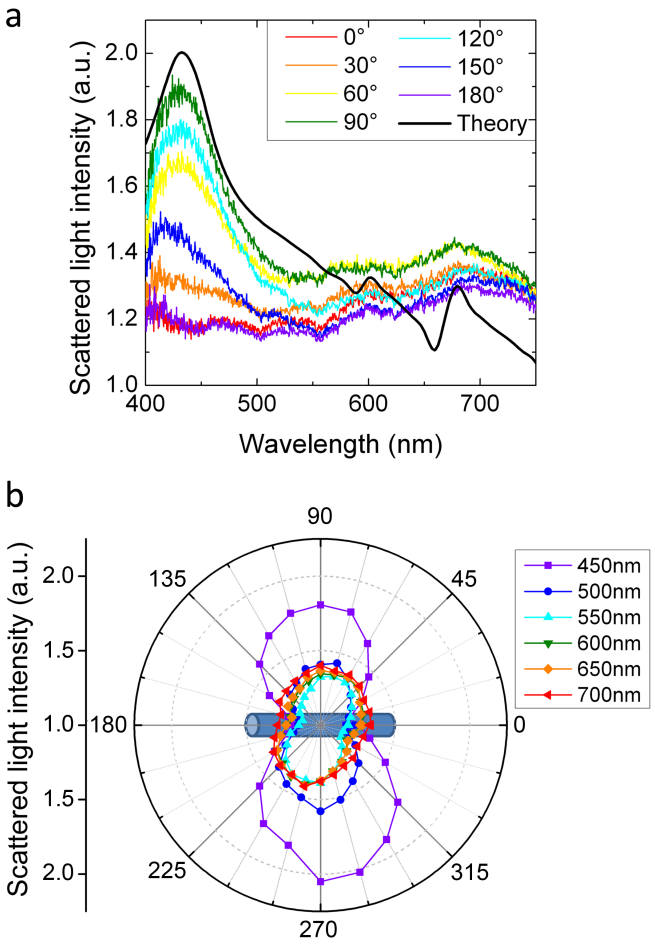

Figure 5.10. (a) Polarization-dependent DF scattering spectra from the NW in Figure 5.9. In black, theoretical results for BEM calculations of integrated FF intensity for plane-wave excitation at $\theta = 45°$. (b) Polar plots of DF scattering intensity at wavelengths of $\lambda = 450, 500, 550, 600, 650$, and 700 nm. DF intensity is oriented along the transverse axis of the nanowire.

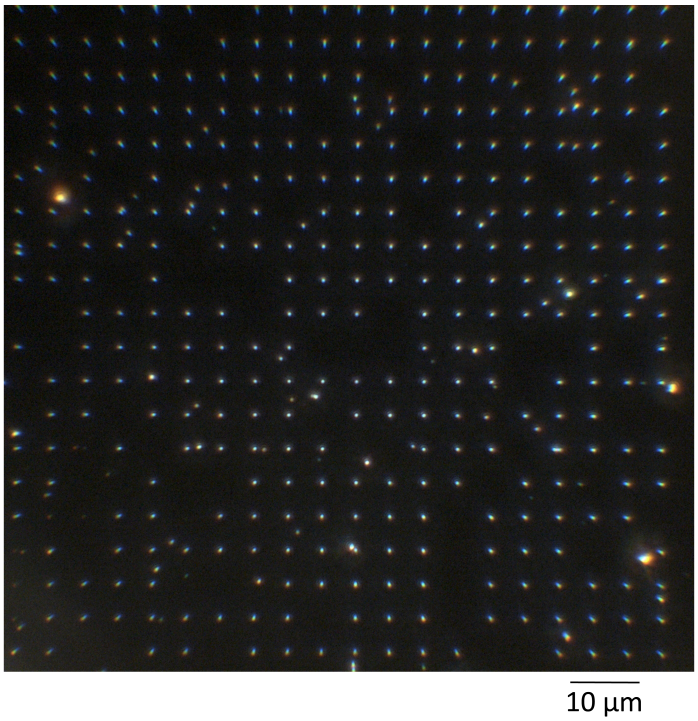

Figure 5.11. DF scattering image of Si-Ag core-shell NWs fabricated by EBL and RIE. By looking at arrays with different spacing, we can collect spectra from multiple and single nanowires.

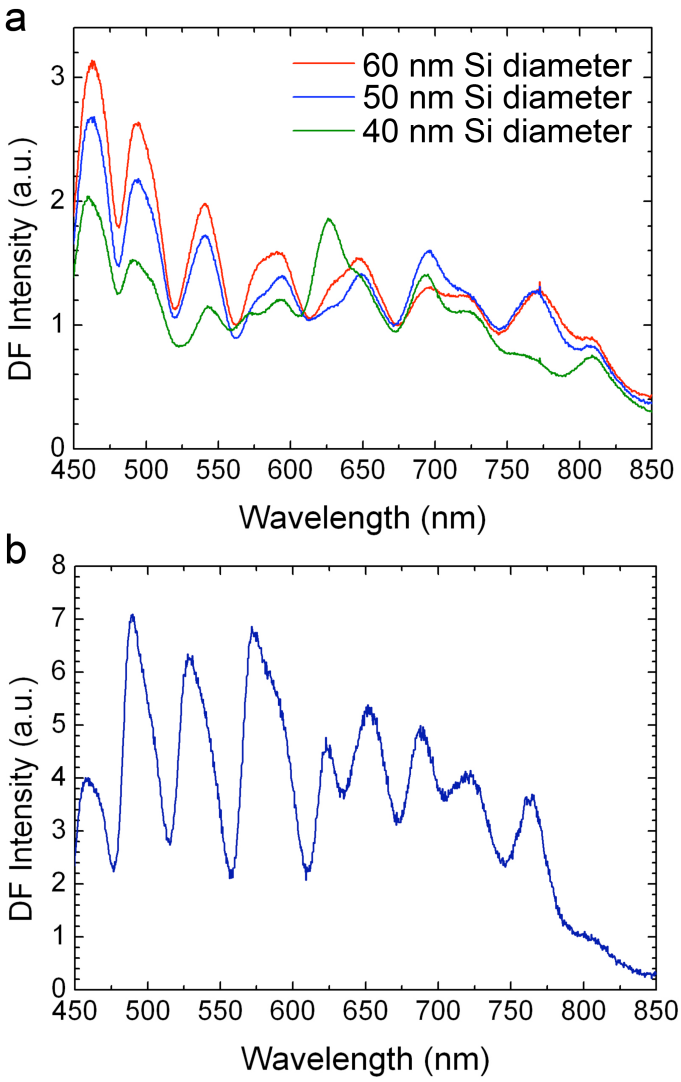

Figure 5.12. (a) DF scattering spectra of 15 nanowires in arrays with different core diameters, 60 nm, 50 nm, and 40 nm. (b) DF scattering spectrum of a single Si-Ag core-shell nanowire with 50 nm Si core diameter.

couple the Fabry-Pérot resonances to the far field. Determining the modes of the Si-Ag resonators uncoupled from the SiO_2 film on Si is not possible in this configuration, but will require removing the thick Si substrate.

5.4 Chapter Summary

In this chapter, we have described how to fabricate Si-Ag core-shell nanowire resonators by two methods. In the first, CVD is used to grow Si nanowires using the VLS process, and a series of oxidation and etching steps are used to create wires of the desired diameter. The Ag coating is deposited by sputtering. After sonication in IPA and dropcasting on ITO-coated SiO_2, the wires are cut to a desired length using FIB. We also used a series of EBL and RIE to fabricate Si nanowires in the top device layer of an SOI wafer, and fabricated the Ag coating by sputtering. Both approaches succeed in fabricating Si-Ag core-shell nanowires with <50 nm Si cire diameter and <300 nm length. Optical characterization is performed in an inverted microscope in a dark-field configuration, and resonances are determined from the scattering spectra. As we showed in Chapter 4, these structures could be useful for sensing applications and, when incorporating light emitters into the Si core, for enhancing the rate of spontaneous emission.