Direct and quantitative photothermal absorption spectroscopy of individual particulates


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Photonic structures have provided unparalleled control over the flow of light due to strong light-matter interaction from their sub-wavelength features. In particular, micro/nanoparticulates, such as micro/nanoparticles or micro/nanowires, can exhibit significant absorption enhancement when the length scale is comparable to or smaller than the wavelength of light. This enhancement combined with the inherently low material cost of these structures make them advantageous in applications such as solar cells, light emitting diodes, and photothermal therapy. To characterize this enhancement at the single particulate level, conventional methods have consisted of indirect or qualitative approaches which are often limited to certain sample types. To overcome these limitations, we used a bilayer cantilever to directly and quantitatively measure the spectral absorption efficiency of a single silicon microwire in the visible wavelength range. We demonstrate an absorption enhancement on a per unit volume basis compared to a thin film, which shows good agreement with Mie theory calculations. This approach offers a quantitative approach for broadband absorption measurements on a wide range of photonic structures of different geometric and material compositions. © 2013 AIP Publishing LLC.
highly sensitive thermal sensors. In fact, it has been demonstrated that when lock-in detection is used, these sensors can achieve a temperature resolution of 4 μK and a power resolution of 4 pW. The cantilevers have been used in studies to probe near-field radiative transfer on the order of 100 nW, to measure the thermal conductivity of a single polyethylene nanofiber, to map infrared absorption in thin-films with a spatial resolution of 100 nm, and to detect chemical and biological molecules using mid-IR spectroscopy. Because of the high heat flux sensitivity, the use of a bilayer cantilever is well suited for single particle absorption measurements. To demonstrate the feasibility of this approach, we use this technique to measure the spectral absorption efficiency of an individual silicon microwire in the visible wavelength range.

The choice of a silicon microwire was motivated by its current technological importance in applications such as solar photovoltaics and photo detectors. To assess the enhancement in absorption, we can compare the spectral absorption efficiency to a volumetrically equivalent thin film. Since absorption is dictated by the particles’ cross section, we can consider an equivalent cross section image of a thin film whose width is equal to the diameter of a wire. For the thin film to be volumetrically equivalent, the thickness must equal to t = αD/4. Using the Fresnel coefficients, the absorptance of a thin film was calculated as shown in Fig. 1(a). By taking the ratio of the spectral absorption efficiency of the microwire to the corresponding volumetrically equivalent thin film, an absorption enhancement, R, was obtained as shown in Fig. 1(b). For a diameter D = 1000 nm, the absorption enhancement, as shown in Fig. 1(b), is higher overall compared to the thin film with a peak value of R = 2.621 at a wavelength of 592 nm in the wavelength range considered.

To measure the absorption enhancement of a single silicon microwire, we used a bilayer cantilever to directly measure the absorbed power by the microwire when under illumination from a monochromatic light source. This was accomplished by attaching the microwire directly to the cantilever. Light absorbed by the microwire conducted as heat to the cantilever resulting in a temperature change. The thermal expansion mismatch then caused the bilayer cantilever to bend. Therefore, the bending response of the cantilever was directly correlated to the absorbed power. Following a series of calibrations, we were then able to extract quantitatively the absorption efficiency from the bending response of the bilayer cantilever.

A pyrex nitride gold coated tipless cantilever (Kleindiek, PNP-TR-TL-Au) was used in this work. A silicon microwire is suspended from one end in order to avoid illumination of the cantilever during measurement. As a result, the microwire in this configuration also functions as a pathway for heat to conduct to the cantilever.

In this study, n-type silicon microwires were fabricated using a metal-assisted etching technique. A SEM cross section image of a silicon microwire sample is shown in Fig. 2(a). These nano/microwires typically had a length of 100 μm and a diameter that ranged from 100 to 1000 nm. To attach the microwire to the cantilever, a set of piezoelectric nanomanipulators were used in a dual-column focused ion beam system. An ultrahigh vacuum adhesive (Kleindiek, SemGlu) was applied to glue the microwire to the cantilever. Figure 2(b) shows an image of the silicon microwire used for measurement attached to the cantilever. For this particular microwire, the average diameter was 983 nm and the length was 92.7 μm.

A schematic of the measurement platform is shown in Fig. 2(c). This platform is based on the previous studies. The cantilever was mounted onto a copper plate using silver epoxy. The copper plate served as both a heat reservoir and an electrical conductor in order to electrically ground the sample. To measure the bending response, a 635 nm continuous-wave (CW) laser is reflected off the tip of the cantilever onto a position sensitive detector (PSD). A 670 nm transistor-transistor-logic (TTL) modulated laser was used for the lock-in detection.
The thermal conductivity of the microwire was estimated to account for size effects. This was necessary to calculate the thermal time constant of the cantilever and the silicon microwire. The thermal time constant is related to the geometry and properties of the cantilever, the microwire, and the environment. The thermal time constant is given by 

$$\tau = \frac{1}{2\pi f}$$

where $$f$$ is the modulation frequency. The choice of the modulation frequency was dictated by the power line frequency at 60 Hz and integer multiples of this frequency. For the silicon microwire, a modulation frequency of 160 Hz was used.

The spectral absorption efficiency of the silicon microwire is defined as

$$Q_{abs}(\lambda) = \frac{P_{abs}(\lambda)}{P_{inc}(\lambda)} = \frac{|X(\lambda)/(|\beta S_p|)|}{P_{tot}(\lambda)f_{inc}}$$

where $$X(\lambda)$$ is the spectral bending response of the cantilever, $$P_{tot}(\lambda)$$ is the total output power from the optical fiber, $$f_{inc}$$ is the fraction of the input power that is incident on the sample, and $$S_p$$ is the power sensitivity.

The total output power from the optical fiber, $$P_{tot}(\lambda)$$, was measured using a photodiode. To measure the power of the CW detector laser, the beam intensity exhibited a Gaussian distribution, and the area within the beam spot must be precisely known. Furthermore, the beam intensity was measured on the vacuum chamber and illuminating the silicon microwire with monochromatic light in the wavelength range of 420 to 600 nm in increments of 10 nm. Lock-in detection was required to provide the necessary sensitivity in this system. The attenuation factor was measured to be $$\beta = 0.4032$$.

In order to extract quantitative data from the bending response, a power calibration was required. This calibration correlates the bending response to a known heat input. The total output power from the optical fiber, $$P_{tot}(\lambda)$$, was measured using a photodiode. To measure the power of the CW detector laser, the beam intensity exhibited a Gaussian distribution. The attenuation factor was measured to be $$\beta = 0.4032$$.
interval with an average uncertainty of 12.5%. This uncertainty is primarily due to the high sensitivity of the parameter, $f_{\text{inc}}$, to the position of the microwire and the measurement of absorbed power for the power calibration. The theoretical spectral absorption efficiency for a uniform microwire with an average diameter of 983 nm and a volumetrically equivalent thin film are also shown in Fig. 3. Compared to the theory, the experimental results exhibit moderate agreement with an average percent error of 9.2%. The maximum percent error was found to be 24.6% at a wavelength of 580 nm.

To assess the significance of the discrepancy between Mie theory and our experiment, several corrections were applied to the theoretical results to better coincide with experimental conditions. First, a size average was performed to account for non-uniformity in the microwire. The standard deviation of this non-uniformity was 28 nm for the section of the microwire illuminated. As a simple approximation, a weighted average was applied to the spectral absorption efficiency by superimposing theoretical solutions calculated at different diameters as measured at different points in the SEM image. Second, a wavelength average was performed to account for the finite bandwidth of the incoming light. The full-width half-maximum was measured to be 7–8 nm for all wavelengths. As a simple approximation, a linear fit is applied to the light input and used as a weighting function. In addition, the angle of incidence, taken perpendicular to the axis of the microwire, and the polarization of the incoming light were also investigated and determined to be approximately normally incident and unpolarized, respectively.

These corrections were applied to the theoretical results as shown in Fig. 4(a). It can be observed that size averaging smeared the interference peaks resulting in smaller amplitude oscillations. The addition of wavelength averaging did not alter the results significantly. Overall, the experimental results exhibit a much better agreement with the modified theoretical curve. The average percent error decreased to 4.7%. The maximum percent error also decreased to 14.2% at 580 nm. The absorption enhancement was obtained by normalizing the experimental results to the theoretical spectral absorptance for a volumetrically equivalent thin film with a thickness of $t = 983\pi/4$ nm. The results are shown in Fig. 4(b). The experimental results indicate an overall
absorption enhancement compared to the thin film across the measured wavelength range.

In summary, we utilized a bilayer cantilever as a photothermal sensor to directly and quantitatively measure the spectral absorption efficiency of a single silicon microwire. We demonstrated an absorption enhancement on a per unit volume basis compared to a thin film, which exhibited good agreement with theoretical predictions. We envision the excellent sensitivity and broad applicability of the method developed in this work can be applied to the measurement of nanoparticulates and photonic nanostructures with different geometric and material compositions. Recent studies have also introduced greater functionality to the cantilever platform and absolute absorption measurements in the infrared wavelength range. The approach developed in this work therefore has the potential to enable broadband absorption measurements in the optical wavelength range to an extent previously unattainable.

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