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Sample heating in near-field scanning optical microscopy

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Heating near the aperture of aluminum coated, fiber optic near-field scanning optical microscopy probes was studied as a function of input and output powers. Using the shear-force feedback method, near-field probes were positioned nanometers above a thermochromic polymer and spectra were recorded as the input power was varied. Excitation at 405 nm of a thin polymer film incorporating perylene and N-allyl-N-methylaniline leads to dual emission peaks in the spectra. The relative peak intensity is temperature sensitive leading to a ratiometric measurement, which avoids complications based solely on intensity. Using this method, we find that the proximal end of typical near-field probes modestly increase in temperature to 40–45 °C at output powers of a few nanowatts (input power of ~0.15 mW). This increases to 55–65 °C at higher output powers of 50 nW or greater (input power of ~2–4 mW). Thermal heating of the probe at higher powers leads to probe elongation, which limits the heating experienced by the sample. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2130388]

Near-field scanning optical microscopy (NSOM) is a scanning probe technique that enables high spatial resolution optical measurements through the use of aluminum coated fiber optic probes that deliver light to nanometric dimensions.[1–3] By scanning these probes within nanometers of a sample, high-resolution optical and topographical information is simultaneously recorded. This technique has been applied to a range of samples from solid-state to biological, where correlating the optical signal with sample topography is often extremely informative.[3] One concern, however, especially for applications involving heat sensitive samples, revolves around heating effects that take place near the aperture of the fiber optic NSOM probes. As light travels towards the aperture, a significant portion is lost to reflection and absorption into the aluminum coating, which can cause heating at the tip aperture. This effect eventually results in tip failure as the input power into the probe is increased.

Characterization of NSOM probe heating has been complicated by the small size of the probe aperture and differences in actual probe geometries. Early work explored heating effects using thermocouples positioned tens of microns from the tip aperture, in the taper region of the probe.[4,5] These studies found temperatures as high as 470 °C, before eventual tip failure.[4] With the thermocouple positioned 25 μm from the tip aperture, temperature increases of 60 °C per mW of light coupled into the fiber were measured. Other studies characterized changes in infrared (IR) light throughput to characterize tip heating with visible light.[6–11] Modulation of IR throughput as a function of visible light power suggested the NSOM probe temperature increased from 50 to 390 °C, as input power increased from 0.5 to 4.5 mW.[9] These measurements, however, provide only indirect evidence of what the sample experiences. A more direct measurement of the actual heating experienced by the sample can be investigated using thermochromic samples to sense the heating occurring directly at the NSOM aperture.

Recently, Cacialli and co-workers reported NSOM measurements using a thermochromic polymer, which exhibits a blue shift in its emission spectra with increasing temperature.[12,13] NSOM measurements using commercially available gold-coated chemically etched fiber optic probes revealed no significant blueshift in the emission spectra, suggesting sample heating near the aperture is less than 40 K. Here we extend these measurements using a thermochromic polymer incorporating perylene and N-allyl-N-methylaniline (NA) that exhibits "two-color" emission.[14] As such, ratiometric measurements of the peak intensities enable precise characterization of probe heating directly at the NSOM aperture.

NSOM probes were fabricated from single mode optical fiber (460-HP, Nufern) that is pulled to a fine point using a commercial micropipette puller (P-2000, Sutter Instruments). Once pulled, the probes are coated with ~50–100 nm aluminum in a homebuilt evaporation chamber. Figure 1(a) shows a phase-contrast microscopy image of a typical NSOM probe used in this study, while Fig. 1(b) shows a NSOM fluorescence image of single molecules in a DPPC lipid film. The smallest feature size in the NSOM fluorescence image is approximately ~35 nm, demonstrating the subdiffraction limited spatial resolution of the NSOM probes used in this study. All studies reported here use straight NSOM probe geometries with shear-force feedback for tip-sample distance control. The NSOM microscope is a homebuilt design, the details of which can be found elsewhere.[15]

Figure 2 shows the bulk emission spectra of the perylene-NA polymer revealing two peaks located at ~475 and ~510 nm. Upon heating of the polymer, the ratio between the 475 and 510 nm peaks increases, providing a convenient marker of temperature that is not sensitive to intensity or concentration changes. The NSOM spectra, at various output powers, of the perylene-NA polymer are correlated to temperature using this ratio as a marker as previously reported.[14] This is used to quantify local heating effects of the sample directly below the NSOM aperture.

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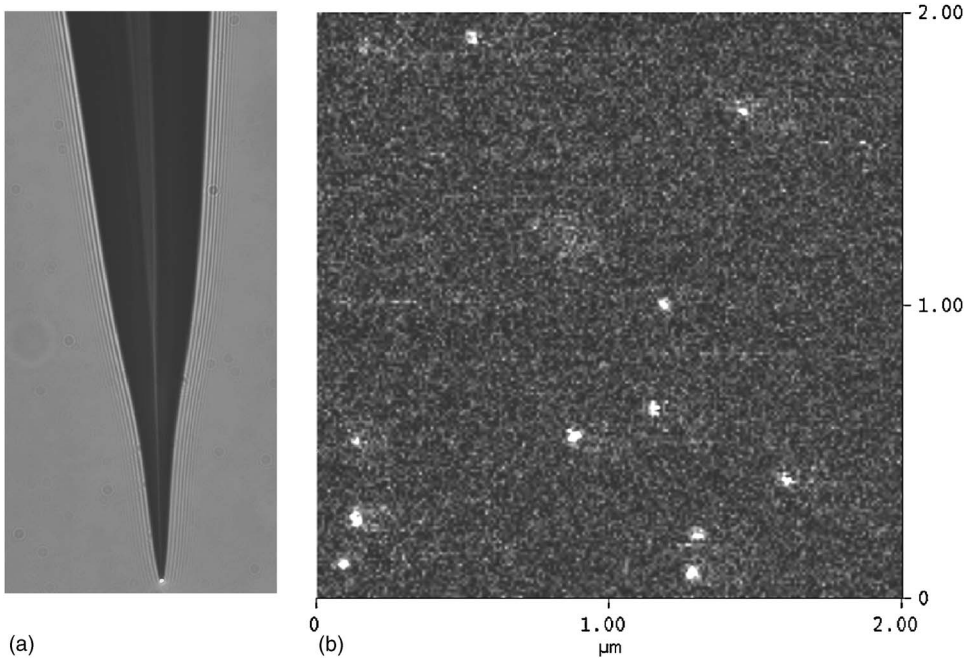

FIG. 1. (a) Phase contrast image of a typical NSOM probe used in the study with a single spot of light emerging from the aperture. (b) NSOM fluorescence image (2 μm$\times$2 μm) of a lipid monolayer doped with fluorescent $diIC_{18}$ probe molecules. Each bright feature in the image is the fluorescence from a single $diIC_{18}$ molecule and has a full width at half maximum of $\sim$35 nm, demonstrating the high spatial resolution obtained with the NSOM probes.

The thermochromic polymer was synthesized using published methods and a thin film was formed on a glass coverslip.[14] Excitation light was provided from a 405 nm diode laser (Power Technology) coupled into the NSOM fiber optic probe. It should be noted that at this wavelength, the optical fiber has losses of greater than 30 dB/km. Minimizing the length of fiber used to less than a meter reduced this effect, but input power values reported are not corrected for this loss. Fluorescence collected following NSOM excitation was dispersed (SpectaPro 300i spectrograph, Acton Research Corporation) and imaged onto a cooled charge coupled device camera (DU420-BV, Andor Technology). Sample heating was determined for each NSOM probe by measuring peak ratios ($\sim$475 and $\sim$510 nm) in the spectra as a function of output power of the probe. Sample heating as a function of output power from a number of NSOM probes is plotted in Fig. 3(a). In all, $\sim$20 NSOM probes were studied and the results shown in Fig. 3(a) are representative of the range of profiles observed. An expanded view of the initial heating is shown in Fig. 3(b). Slight variations in tip aperture size and taper geometry contribute to the range of heating results observed.

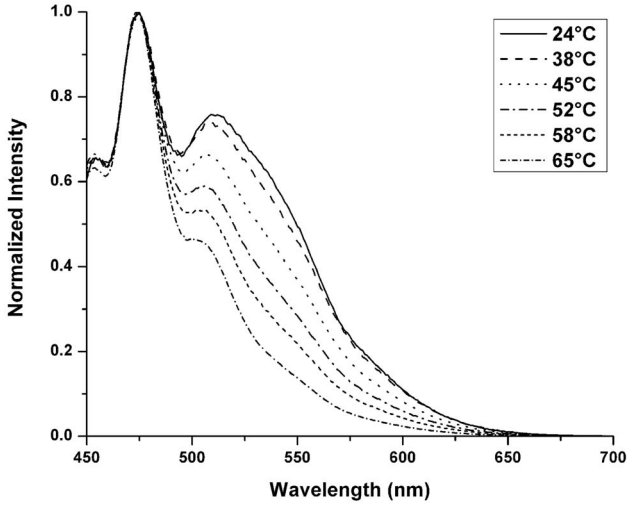

FIG. 2. Bulk emission spectra of perylene-NA polymer as a function of temperature following excitation at 405 nm. The spectra have been normalized to the peak at 475 nm. As temperature increases the ratio between the peaks at 475 and 510 nm increases and there is a slight blueshift in the 510 nm peak.

In general, we find an initial rapid rise in sample heating as output power is increased. At output powers of a few nanowatts, heating at the sample ranged from $\sim$40 to 45 °C. We find that the rise in sample heating begins to slow at higher output powers until a maximum of approximately 65 °C is reached with output powers ranging from 50 to 100 nW. Increasing the output power beyond this point has little effect on sample heating.

The leveling of the sample heating observed at high powers likely arises from thermal expansion of the NSOM probe that effectively increases the distance between the aperture and the sample. As power into the aluminum coated fiber optic probe is increased, thermal expansion of NSOM probes is observed and can be as high as hundreds of nanometers. The amount of thermal elongation depends on the particular probe and is sensitive to differences in aperture diameter, probe shape, and the aluminum coating. In general, at output powers of $\sim$100 nW we observe NSOM probe elongation of approximately 150–375 nm. The large difference between the thermal expansion coefficients of the fiber optic and surrounding aluminum coating ($\alpha_{Al}=2.34\times10^{-5}$ °C^{-1}

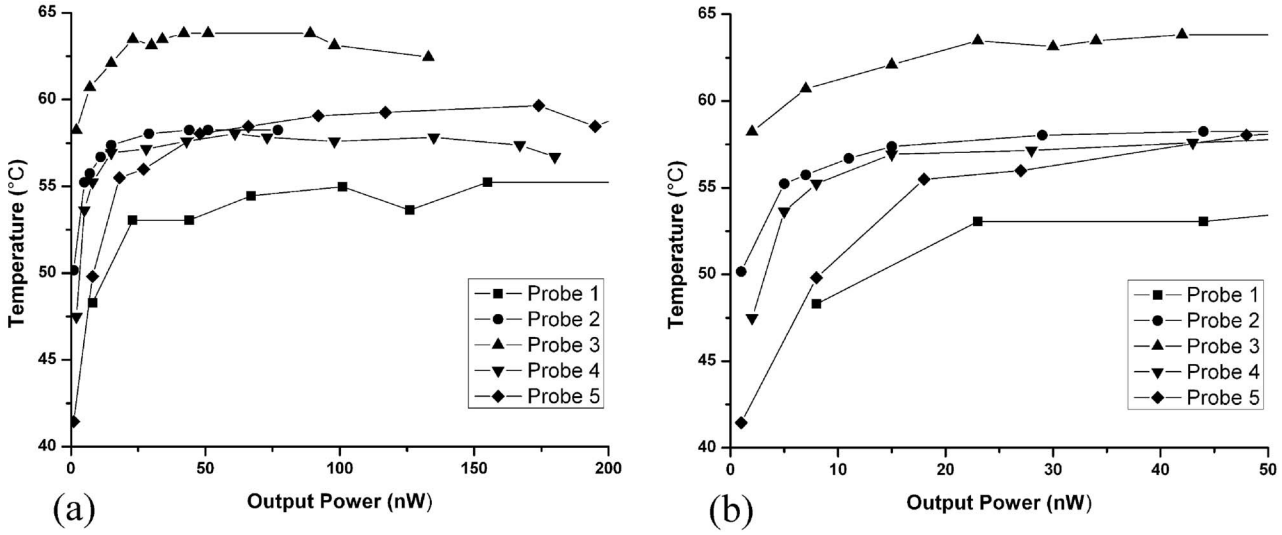

FIG. 3. (a) Representative plots of sample heating as a function of output power for 5 NSOM probes and (b) an expanded view of the initial heating. In all, approximately 20 NSOM probes were studied and these plots demonstrate the range of heating observed. At low output powers, sample heating rises quickly with output power before leveling off between 55 and 65 °C with output powers above ~50 nW.

and $\alpha_{\text{quartz}}=0.5\times10^{-6}\ ^{\circ}\text{C}^{-1}$) lead to differential elongation as the power increases. Eventually, NSOM probes fail as the shear forces developed as a result of the large difference in thermal expansions disrupt the coating.

The thermal elongation of NSOM probes may also lead to the leveling off in sample heating observed in Fig. 3(a). The force feedback implemented in NSOM to control the tip-sample distance senses interactions between the tip and the sample surface. These interactions usually take place between the metal coating of the tip and the surface, since the grains in the aluminum coating usually extend beyond the aperture of the probe. As power is increased which heats the probe, the aluminum coating is expected to elongate greater than the fiber thus increasing the distance between the aperture and the surface. This appears to lead to the leveling off in sample heating at elevated powers. While the heating at the aperture must still be increasing with power, the increasing distance between the aperture and the surface leads to the leveling in the temperature actually experienced by the sample. This provides an interesting self-regulating control that limits the amount of heat the sample is actually exposed to during an NSOM experiment. We are currently characterizing the reduction in sample heating using chemically etched tips and for NSOM experiments in aqueous environments, important for biological applications.

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