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Observation of tip-to-sample heat transfer in near-field optical microscopy using metal-coated fiber probes

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Metal-coated scanning near-field optical microscopy fiber probes can undergo significant heating due to partial absorption of the coupled light by the metallic film covering the apical zone. In this letter we report experimental evidence of tip-to-sample heat transfer on a 7,7′,8,8′-tetracyanoquinodimethane molecular crystal. Local melting is observed at nanometric tip–sample distances, when increasing the laser power injected into the fiber above a threshold of 8.8 mW. Hole formation and material displacement are observed, as well as failure of the shear-force-based imaging process, due to partial sticking of the melted material to the probe. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1929877]

Scanning near-field optical microscopy (NSOM)[1] has shown imaging capabilities well beyond the diffraction limit. The so-called "aperture-NSOM" exploits sensors based on tapered optical fibers, ending with a nanoscopic aperture (30–100 nm).[2] The aperture diameter is defined by a lateral metallization with a thin film (typically Au or Cr–Al ~100 nm thick) deposited by thermal evaporation or sputtering techniques. Multiple reflections at the metallized sides[3] confine the light towards the apical aperture. Such reflections have a twofold effect: they reduce the throughput of the probes (to 10^{-6}–10^{-3}), and increase the total amount of light absorbed by the metal coating (20%–30% of the coupled power, to be compared to the 8% of the aluminum absorption at normal incidence). As a result, the metallic film can heat up to several hundreds of degrees[4] and undergo thermal expansion phenomena.[5,6] The issue of heat transfer (HT) at the nanoscale has profound implications from both the theoretical[7] and the technological[8] point of view. New physical phenomena take place when structure sizes and distances become comparable with the thermal radiation wavelength.[9] Concerning NSOM, the question arises as to whether HT occurring when the nanoscopic hot tip[15] is placed in close proximity (1–10 nm) of a surface can yield a detectable increase of the sample temperature. NSOM fluorescence experiments on semiconductors,[10] and on biological membranes in liquid[11] have ruled out modifications of the thermal distribution of charge carriers and the occurrence of sample damages, indicating negligible sample heating. The issue is more controversial and still debated in NSOM lithography (SNOL). Although light absorption is intended to play the major role in changing the local sample properties (solubility,[12] crystalline structure,[13] molecular alignment[14]), exposure to high temperatures can strongly influence the physical-chemical processes. Moreover, theoretical calculations[15] suggest that tip-sample HT can prevail against the heating induced by light absorption, raising the sample temperature up to several hundreds of °C. In this letter we provide unambiguous evidence of sample heating induced by HT in NSOM.

We use an upgraded version of a homemade aperture-NSOM.[16] Illumination at 514.5 nm is provided by an Ar^+ laser. Nonoptical shear-force detection[17] is implemented to control the tip–sample distance. Commercially available Cr–Al coated probes (Nanonics, aperture 100 nm), based on multimode optical fibers (core 100 μm, optimized for UV light transmission) are exploited. Connectorized fiber-coupling packages (Thorlabs, F220FC-A) permit to couple 80% at least of the laser light into such sensors. Samples consist of 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) single crystals grown by precipitation from solution. TCNQ and its charge-transfer complexes, similar to other organic semiconductors and conducting polymers, feature a low thermal conductivity, similar to the one assumed in the theoretical simulations in reference.[15] TCNQ conductivity (λ_{TCNQ}) has not been reported in the literature so far. However, crystalline $\mathrm{TEA(TCNQ)_2}$, a conducting charge-transfer complex,[18] has a conductivity of 0.4 W/mK at room temperature. For crystalline TTF-TCNQ, a different charge-transfer complex, we can extrapolate a value ~1.8 W/mK from the T^{-1} temperature dependence observed by Salamon *et al.*[19] Amorphous TTF-TCNQ pressed at 10^8 Pa shows values ~0.15 W/mK.[20] In a similar way, conducting polymers

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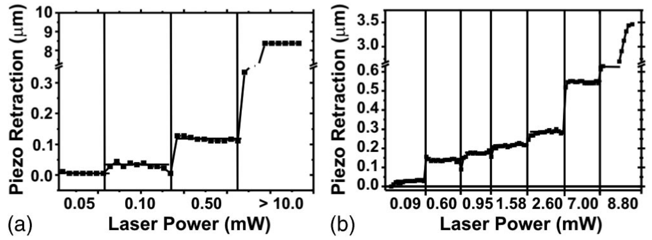

FIG. 1. Plots of the piezo retraction, corresponding to the tip thermal expansion, as a function of the laser light power. Increasing the power to values higher than 10 mW leads to a complete retraction of the piezo (a). The onset of the sample melting can be estimated (b) at 8.8 mW.

such as (AsF_5)-doped polyacetylene,[21] or metal-doped polyaniline[22] have conductivities of 0.4–0.7 W/mK, while for undoped polyacetylene,[21] poly(methyl-methacrylate),[23] or polycarbonate[24] the conductivity drops to ~0.2 W/mK. We thus expect λ_{TCNQ} to be of the order of $\sim 10^{-1}$ W/mK. The TCNQ bulk melting point is known to be around 290 °C (Sigma Aldrich data sheet, http://www.sigmaaldrich.com).

Thermal expansion is a clear fingerprint of the NSOM probe heating,[6] and can thus be used to study such phenomenon as a function of the laser power P_{las}. After approaching the tip to the sample, a set of line scans has been acquired on a flat portion of the surface, increasing P_{las} at discrete steps. Figure 1(a) shows the tip elongation vs P_{las}. For $P_{\mathrm{las}} < 1$ mW the feedback circuit retracts the piezo holding the sample at discrete steps, as a response to the probe expansion,[6] in order to keep the tip–sample distance constant. When increasing P_{las} just beyond 10 mW the feedback becomes unstable and retracts the piezo completely, by more than 8μm. Such an anomalous behavior cannot be ascribed to thermal expansion phenomena for several reasons. First, it is unlikely that the coating can slide by 8 μm over the fiber taper. A noticeable thermal expansion of the latter has to be excluded as well, since the fused silica thermal expansion coefficient (0.54×10^{-6} °C^{-1}) is much smaller than the aluminum one (2.35×10^{-5} °C^{-1}). Second, a 100% absorption of the laser light by the coating would be needed to produce such an expansion of the metal coating.[6] As a result the average temperature should become higher than the aluminum melting point. However, this is not the case in our experiment because we have not observed any damage of the probe. We interpret such a phenomenon as a signature of sample heating induced by HT. In particular, we consider that in our case overheating produces the local melting of the surface material, which partly sticks onto the NSOM probe. The tip oscillation gets thus damped, inducing the feedback loop to retract the tip.

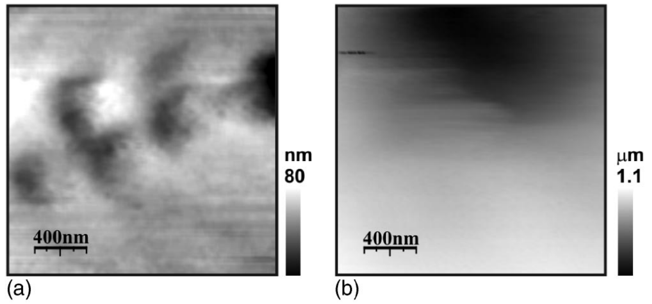

FIG. 3. Topography images (2.0×2.0 μm^2) carried out with a metal coated NSOM probe on the same portion of the sample with laser off (a) and with laser on. (b) In the second case the power injected was just higher than the melting threshold.

To determine the onset of the melting we have increased P_{las} more finely. In Fig. 1(b) we observe the usual thermal expansion behavior[6] up to $P_{\mathrm{las}} = 7.0$ mW. This indicates that the sample surface is not undergoing any relevant morphological change at this stage.[25] At 8.8 mW the probe initially remains in contact with the sample, but soon after the feedback starts retracting by several microns. Differently from what was previously observed, an equilibrium is reached after a retraction of ~3.5 μm. To investigate the effects of such actions on the sample morphology, we have carried out a topography scan on the same zone after switching off the laser. Figure 2(a) shows that the flat surface on the left-hand side of the map, appears strongly modified at the center. A hole has been created [Fig. 2(b)], (depth ~550 nm, width ~250 nm), and some material has accumulated at its boundaries. Hole formation is a phenomenon we sometimes observe when approaching the tip to a soft surface, such as biomembranes,[26] or as in our case, to hot surface. The two bumps are probably due to the formation of droplets of melted material. A further experiment confirming the melt-and-stick model has been carried out. In Figs. 3(a) and 3(b) we compare two consecutive topography maps, acquired on the same sample area, with the laser switched off (a) and subsequently (b) injecting into the fiber a power slightly higher than the melting threshold (preventing the complete retraction of the piezo). In the first case we recover the quite flat sample topography (the roughness is of a few tens of nm). The map in Fig. 3(b) is completely different: it is blurred, lacking in details and showing a vertical excursion of ~1 μm. We conclude that in the melting regime, material sticking leads to the failure of the shear-force-based imaging process. Finally, to rule out that sample heating is due to direct light absorption, we have replaced the metallized tip with an uncoated one. Now, the two consecutive scans of the

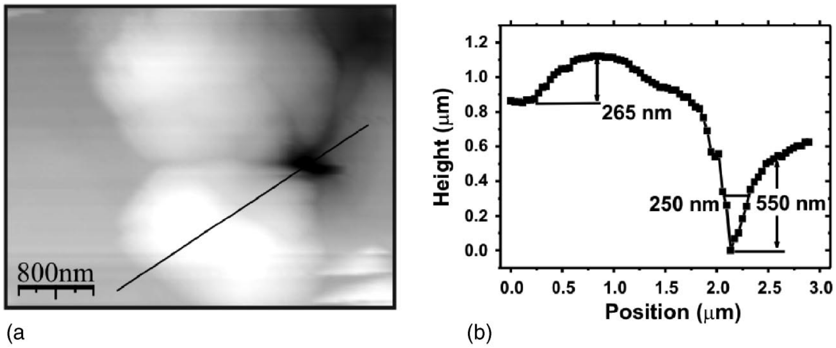

FIG. 2. (a) Topography image (4.0×3.1 μm^2) showing the surface modification induced by the contact with the hot tip ($P_{\mathrm{las}} = 10$ mW). The laser was switched off during the scan. The line profile (b) displays the presence of a hole ~550 nm deep and 250 nm large, surrounded by two bumps ~265 nm high.

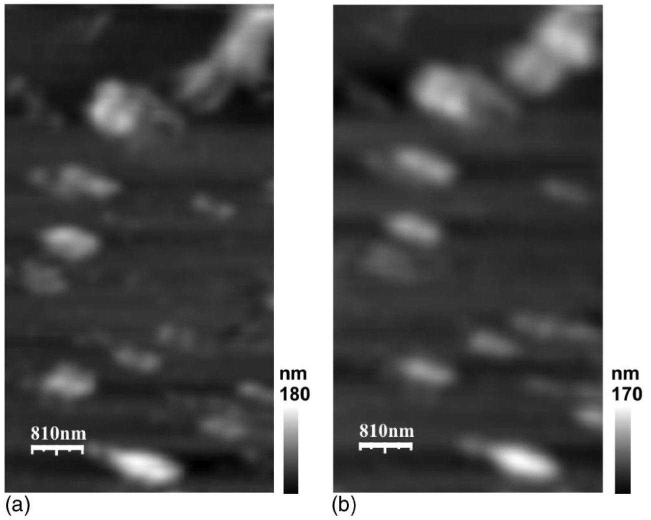

FIG. 4. Topography images ($4.1 \times 7.3\ \mu\mathrm{m}^2$) carried out with an uncoated NSOM probe on the same portion of the sample with laser off (a) and with laser on (b). In the second case the power injected was of 10.6 mW.

same area (Fig. 4) show identical topography features, no matter what the power injected into the fiber is [(a): laser off, (b): $P_{\mathrm{las}}=10.6$ mW].

The observation of sample heating induced by HT strongly depends on the experimental conditions, and especially on materials, power regimes, and shape of the probe. The combination of small aperture probes, high injected powers, and TCNQ as a sample, leads to a clear evidence of tip-sample heat transfer. In particular, the notable depth of the hole observed in Fig. 2(b), up to 0.5 μm, indicates that the sample heating is not confined to the surface region, but extends well into the bulk. This suggests that the local temperature under the tip is comparable to the TCNQ bulk melting temperature, and that any effect of suppression of the melting temperature at the surface,[27] even if present, is not relevant in our case. Moreover, we find that this phenomenon is in fair quantitative agreement with the theoretical simulations carried out by Miyamoto *et al.*[15] Sample temperatures ~300 °C are in fact predicted for $P_{\mathrm{las}} \sim 9$ mW, at tip–sample distances ~10 nm. Such result originates from a numerical solution of the thermal diffusion equation for a system in which the sample consists of a GeSbTe thin film ($\lambda = 0.58$ W/mK), sandwiched between two $\mathrm{ZnS} \cdot \mathrm{SiO_2}$ slabs ($\lambda = 0.66$ W/mK), superposed to a polycarbonate ($\lambda = 0.22$ W/mK) substrate. In particular, this is an indirect confirmation of our estimate on λ_{TCNQ}. Due to its poor thermal conductivity, TCNQ retains the heat, allowing the temperature to raise. Conversely semiconductors, featuring higher thermal conductivities (several tens of W/mK), as well as liquid environments, act as virtually infinite thermal reservoirs, preventing the sample to locally heat up.[10,11] The absence of sample heating we have observed on conjugated polymers[25] is instead due to the low power used, in combination with insertion losses at 325 nm greater than 90% ($P_{\mathrm{coupled}} < 0.5$ mW). Such a regime, while being particularly suited for SNOL, is insufficient to provide any detectable sample temperature increase. A further issue regards the actual shape of the probe. Large apertures allow the coupled light to be transmitted instead of absorbed by the metal coating. We were not able to observe any thermal effect, neither a tip expansion nor any sample melting or spectral emission shift on thermochromic conjugated electroluminescent polymers, when coupling up to several tens of mW to broken probes having apertures much larger than their nominal size.

In summary we have shown that relevant sample heating can occur due to heat transfer from a metallized NSOM tip. We suggest that temperatures higher than the TCNQ bulk melting point are reached at the probe apex, provoking the local melting of the sample. The shear-force imaging process has been observed to fail when launching a laser power greater than ~9 mW into metallized fiber probes, and we propose that this is due to material from the sample sticking to the probe.

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