Optical probing of sample heating in scanning near-field experiments with apertured probes

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We have used the inherent thermochromism of conjugated polymers to investigate substrate heating effects in scanning near-field experiments with metal-coated "apertured" probes. Chemically etched and pulled fibers were used to provide near-field excitation of fully converted films of poly(*p*-phenylene vinylene), PPV, and of poly(4,4′-diphenylene diphenylvinylene). We detect no significant blueshift of the photoluminescence spectra generated with near-field excitation, in comparison to those collected with far-field excitation. We conclude that polymer heating in the region contributing to the luminescence is less than 40 K. We also demonstrate that thermolithography of the PPV precursor is not significant by comparing UV (325 nm) and red (670 nm) illumination. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1842860]

Scanning near-field optical microscopy (SNOM)[1] has recently become a common technique, not only for optical imaging and spectroscopy with sub-diffraction resolution, but also as an instrument for the fabrication of a variety of nanostructures by means of so-called scanning near-field lithography, SNOL.[2,3]

The generation or collection of spatially localized optical fields in scanning near-field microscopes is made possible by the use of specialized probes consisting either of waveguides featuring a subwavelength aperture, for example tapered optical fibers with an opaque metallic coating and a small aperture at the fiber apex (aperture-SNOM), or of sharp metallic tips that can enhance the electromagnetic field at their apex (apertureless-SNOM).[4,5] Aperture-SNOM has been developed first[6,7] and still is the most common implementation.

One of the most significant features of aperture probes is the low optical throughput of the fibers themselves ($10^{-3} - 10^{-4}$ for etched fibers, but 10^{-6} for pulled fibers), which results from the shape of the probes, and the concomitant absorption in the metal coating. Probe heating, especially in proximity of the apex, is thus inevitable, and increased operational temperatures up to several hundred degrees have been reported by several authors.[8,9]

The question arises as to whether such high temperatures can sustain a significant heat transfer from the probe apex to the sample, capable of locally raising the sample temperature by any measurable amount. Various heating mechanisms have been discussed in literature,[10] but the general consensus is that thermal conduction and direct optical and radiative transfer are dominant.

The issue is particularly important for SNOL of the precursor of poly(*p*-phenylene vinylene), PPV, since this is made insoluble by exposure to high temperatures in addition to exposure to UV light. Thermolithographic effects need to be carefully understood and controlled to obtain optimum resolution from the SNOL process, because undesired thermal conversion by a hot probe could degrade lateral resolution.

Here, we used the inherent sensitivity of the optical properties of conjugated polymers (and emission in particular) to changes in temperature (thermochromism)[11] to study the local heating of the sample surface. Conjugated polymer photoluminescence and absorption spectra are blueshifted upon heating, due to the excitation of progressively higher vibrational levels, and the subsequent loss of conjugation along the chains.

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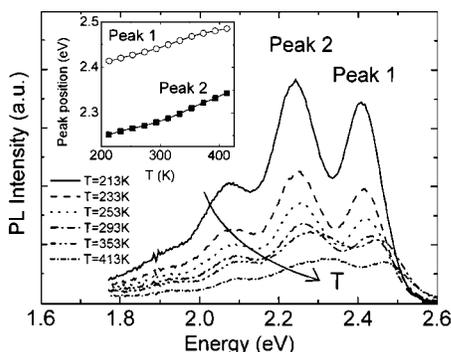
FIG. 1. Temperature dependence of the photoluminescence spectra of a 50-nm-thick PPV film on a spectrosil substrate, in the range 213–413 K. Inset: The temperature evolution of the position of peaks 1 and 2 as determined by fitting the peaks with Gaussian functions.

We have used commercially available fiber probes to illuminate thin films of two prototypical electroluminescent polymers, PPV[12] and poly(4,4′-diphenylene diphenyl vinylene), PDPV,[13] and we have aimed at detecting a blueshift of the photoluminescence (PL) spectra collected in the far-field following near-field illumination, with respect to spectra collected in the far-field with far-field illumination (near-field and far-field spectra, respectively, for brevity). Far-field PL spectra were also collected as a function of temperature to provide a reference for an indirect optical measurement of the local film temperature. Approximately 50-nm-thick films of PPV were prepared on spectrosil substrates by thermal conversion of a spin-coated film of the precursor (Aldrich) at 220 °C for 5 h, at $<10^{-5}$ mbar. PDPV films were spin-coated from a 1% toluene solution so as to give ~50-nm-thick films.

We acquired time-integrated, temperature-dependent far-field PL spectra in a cryostat under a dynamic flow of helium. Excitation and detection was provided by a time-correlated single-photon counting system described elsewhere.[14] Samples were excited with a pulsed diode laser emitting at 407 nm.

For the near-field experiments we used a SNOM of our own design and construction[3] which uses a tuning-fork mechanism with shear force feedback for the probe–sample distance regulation. The apertured probe was brought in shear-force contact and acted as a near-field-excitation source for PL measurements. The PL signal was collected in far-field in transmission mode by means of a long working distance 10× achromatic objective (N.A.=0.25) and then recorded by a spectrometer (Ocean Optics S2000-UV-VIS). We used probes provided by Jasco Inc. (NPU-50D) suitable for UV illumination, which have a flat, circular end of diameter 1.4 μm, as opposed to a traditional taper. The aperture size is in the range of 20–80 nm and the far-field throughput is about 10^{-3}–10^{-4}, similar to those recently used for the fabrication of PPV nanostructures.[3] Near-field PL was excited by launching into the fibers the 325 nm line of a He–Cd laser. To minimize photo-oxidation at the illuminated spot, which may lead to bleaching of the absorption and to a major degradation of the PL efficiency that could also interfere with the observation of a blueshift, we did not keep the probe at a fixed position on the sample, but we scanned the surface at a speed of 0.5 μm s^{-1}. This is comparable with typical SNOL scan speeds.

In Fig. 1 we report the far-field PL spectra of PPV as a
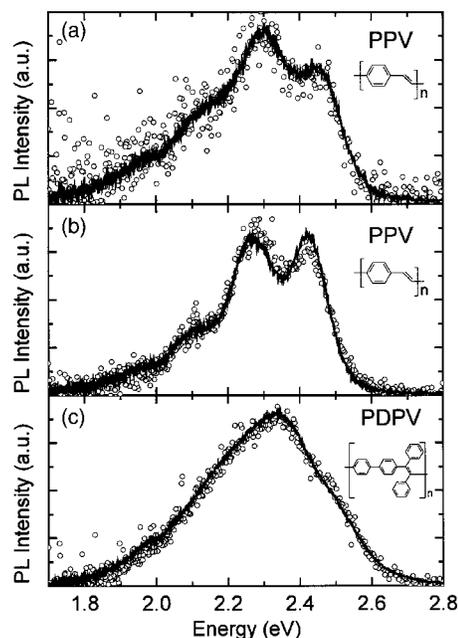
FIG. 2. Room temperature far-field (solid lines) and near-field (circles) PL spectra of different PPV (a), (b) and PDPV (c) films on spectrosil substrates. The materials chemical structures are displayed as inset. Excitation is from a He–Cd laser (325 nm). The power launched into the fiber was 8.2 mW in all cases. The probes certified aperture is 60±5 nm for the experiment of (a), 20±5 nm for the experiment of (b), and 60±5 nm in the case of (c).

function of temperature in the range 213–413 K. The spectra consist of three main peaks whose room temperature maxima occur at approximately 2.44 eV (or 508 nm, peak 1), 2.28 eV (or 544 nm, peak 2) and at 2.09 eV (or 593 nm). When the temperature increases, the spectra show a decrease of the PL intensity, and a blueshift. The decreased intensity is due to the decrease of the PL efficiency, which is most likely connected with a variation of the nonradiative decay rate resulting from higher exciton mobility. We used Gaussian functions to fit the main peaks and extract their evolution as a function of temperature, which is reported in the inset in Fig. 1 for peaks 1 and 2. As expected, we observe a distinct blueshift with increasing temperature, which we estimate to be 0.44 meV/K for peak 1 and 0.50 meV/K for peak 2, in the range 293–373 K.

In Fig. 2(a) we report the near- and far-field spectra of the same PPV sample used in the above-described temperature-dependent experiment, and in Fig. 2(b) analogous spectra obtained on a different PPV sample. Although the near-field spectra are significantly noisier than the far-field ones, owing to the smaller signals achievable with near-field excitation, they are sufficiently well resolved to allow comparison with the far-field spectra, from which we conclude that there is no significant blueshift. More precisely, by comparing the far-field temperature calibration with the most blueshifted data points of the blue-edge of the near-field spectra in Fig. 2(a) in the range 2.5–2.55 eV, we can conservatively estimate that any local heating of the PPV film, if present, should not be greater than 40 K. Even smaller values of the higher bound for the local heating would result from considering Gaussian best fits of the various peaks (10 K or so), but the near-field spectra are too noisy to allow good-quality fits. The absence of a significant blueshift in near-field PL spectra on PPV is in agreement with the results that we obtained when we conducted an analogous experi-

Intended patterns

325 nm
0.75 mW

670 nm
4 mW

(a)

SNOL results

50 µm

(b)
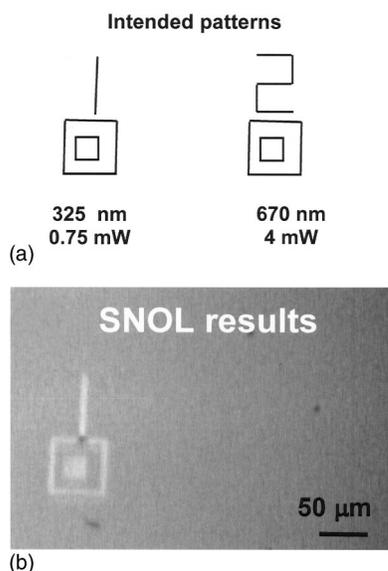
FIG. 3. Intended patterns (a), and optical microphotograph (b) of the PPV structures obtained by SNOL with irradiation of the PPV precursor at 325 nm (left) and 670 nm (right). No structure is observed with red near-field illumination thereby confirming the absence of thermolithographic effects in UV SNOL of PPV precursor. The power launched into the fiber was 0.75 mW for UV light and 4 mW for visible light. We used a gold-coated fiber probe (Jasco Inc.) with a certified aperture of 80±5 nm.

ment using pulled Cr–Al metal coated fibers provided by Nanonics Ltd.

Essentially identical results were obtained when measuring the near- and far-field spectra of PDPV, reported in Fig. 2(c). Again, no significant blueshift between far- and near-field spectra is found, thus corroborating the conclusion that the polymer samples do not suffer from significant local heating as a result of interaction with the SNOM probe, in the region from which the luminescence originates.

Such a weak sample heating should ensure the feasibility of SNOL on thermally sensitive specimens, such as PPV precursor films. We also investigated the possibility of patterning the PPV precursor by pure thermolithographic effects, by using 670 nm radiation, which is not absorbed by the polymer sample, but which contributes to heating of the probes due to optical absorption in the metal. To ensure that probe heating is comparable or greater than with UV illumination (Au reflection coefficient at normal incidence[15] is ~0.9 for λ=670 nm and ~0.25 for λ=325 nm, whereas the

fiber transmission of 670 nm light is greater than transmission of 325 nm radiation by a factor of 1.5), we launched 0.75 mW UV and 4 mW red radiation into the optical fiber.

The intended patterns are shown in Fig. 3(a), whereas Fig. 3(b) is an optical microscope photograph showing the final result after development and thermal conversion. We observe a fully converted PPV structure where UV light was used, but a complete absence of any lithographic feature where visible light was used. The absence of lithographic features in the case of visible light, which is not absorbed by the PPV precursor, confirms that the photolithographic process is not affected by the close proximity of the hot SNOM tip to the sample surface.

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