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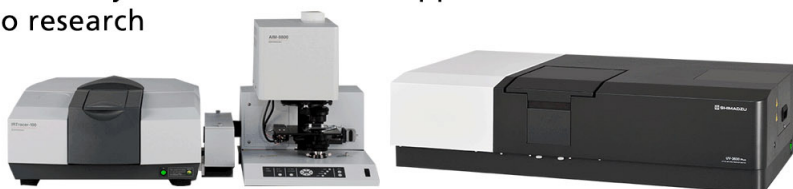
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Nanoimprint lithography of chromophore molecules under high-vacuum conditions

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We report on high-vacuum nanoimprint lithography onto chromophore dye molecules embedded in optically inert polymer matrices. A specifically designed high-vacuum (10^{-5} – 10^{-6} mbar) chamber to perform nanoimprint lithography at temperatures up to 300 °C and pressures up to 10^5 psi on areas of more than 25 cm² allows us to imprint in principle any class of thermoplastic molecules without loss of functionality. We tested our system by imprinting different polymers and polymer/dyes blends, demonstrating that the photoluminescence efficiency of light-emitting molecules is preserved in the lithography process. © 2004 American Vacuum Society.

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I. INTRODUCTION

Nanoimprint lithography (NIL)¹ has been demonstrated to be a powerful and straightforward technique for patterning organic materials, offering low cost, large-area operation, and extremely high resolution.² The NIL is based on a master pattern, realized into a hard mold, which is transferred to the organic film under pressure (10^2 – 10^4 psi). The process temperature is chosen in order to decrease the viscosity of the target compound, allowing the material to be displaced from the protrusions of the mold,³ and the shape to be transferred from the master to the polymer (Fig. 1).

NIL can compete with traditional lithographies for pattern definition into poly(methylmethacrylate) (PMMA) and other resists used for the subsequent etching processes on semiconductors.^{4,5} In addition, it can be employed to directly pattern optically and electrically active molecules for one-step fabrication of organic-based devices. Unlike inert polymers, NIL of active materials has to be carried out under a vacuum,⁶ in order to avoid the degradation of their optical and electrical properties mainly induced by oxygen incorporation and substitution occurring at the high temperature of the imprinting process.⁷ Low-vacuum or nitrogen environments, which have been used to prevent luminescence quenching in light-emitting molecules,⁶ usually require quite a complex setup, such as large vacuum chambers with a controlled atmosphere surrounding the NIL press.⁸ Room-temperature NIL processes on curable monomers have also been proposed to realize patterns on some functional semiconducting polymers.⁹ In order to retain both the very cheap operation and the wide flexibility of the technique, one would need simple add-on components, which should be compatible with most of the precision hydraulic presses available on the market and with different controlled atmospheres.

In this article, we report on NIL experiments carried out

under high-vacuum conditions by means of a suitably designed chamber. Our setup operates up to 300 °C, with pressures as large as 10^5 psi, and areas of more than 25 cm², under a vacuum of 10^{-5} – 10^{-6} mbar. This allows us to perform nanoimprint processes on virtually any organic thermoplastic molecule without degradation of functionality. We tested our system installed on a commercial laboratory press, for imprinting PMMA, which was used as optically inert matrix embedding chromophore dyes. We achieve excellent fidelity of the pattern transfer, with reproducible and easy operation conditions, and, more important, no degradation of the luminescence efficiency of the light-emitting molecules.

II. EXPERIMENT

Two main systems can be envisaged to control the atmosphere while performing NIL, i.e., (i) a large controlled chamber surrounding the whole press environment and (ii) a small component to be placed between the pressing hot plates, which should effectively transmit the high pressure and the temperature to the sample. The latter configuration is undoubtedly more convenient in terms of cost, volume, and flexibility. A photograph of our high-vacuum chamber is shown in Fig. 2. We built it by specifically designed stainless-steel bellows and ultrahigh-vacuum Conflat® flanges (realized by Streas, Italy), with copper gaskets allowing high-temperature operation (up to 450 °C). In order to improve the mechanical stability of the chamber, which is a critical issue during the imprinting process, and to increase the system resistance to compression due to the concomitant application of the high vacuum and of the external pressure, we added four parallel steel springs to the bellows (Fig. 2). Two steel cylinders (diameter=58 mm) extend through the flanges, thus providing the thermal contact with the hot plates of a precision hydraulic press (P/O/Weber, Germany). The cylinders transmit heat and pressure to the sample inside the chamber, moreover assuring a correct contact between the master and the sample during imprinting, by virtue of their parallelism. The overall internal volume of the chamber

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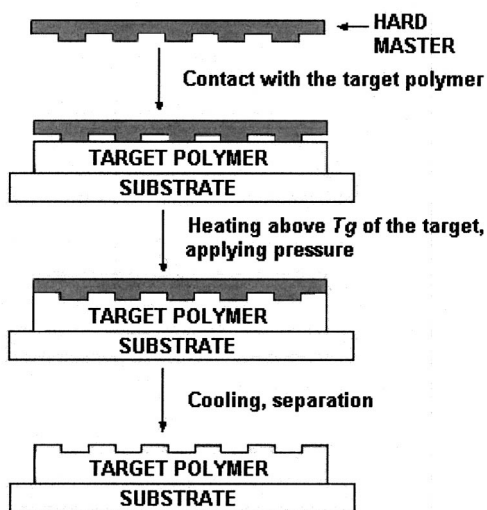


FIG. 1. Schematic diagram of the NIL process (features not in scale).

is less than 650 cm^3 , thus allowing us to apply the vacuum in a few seconds. An analog micrometer between the upper and the lower flanges provides a measure of the chamber compression with an accuracy of $10 \text{ }\mu\text{m}$.

The molds for the NIL were realized by photolithography and by electron-beam lithography by an Elphy Plus pattern generator (Raith, Germany) controlling a Stereoscan 440 scanning electron microscope (Leica, Germany), and subsequent reactive ion etching (CF_4/Ar) onto silicon substrates. The etch depth of the molds was comprised between 200 and 600 nm. We directly used these masters to imprint PMMA (Sigma-Aldrich, $T_g = 120 \text{ }^\circ\text{C}$) films of a thickness around $1 \text{ }\mu\text{m}$. The surface morphology of the masters and of imprinted samples was investigated by optical and scanning electron microscopy [(SEM) Leica Stereoscan 440].

Different dye molecules were embedded in these optically inert polymer films, namely 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) and Coumarin 334 (C334), commonly employed for the realization of optically pumped organic solid-state lasers.¹⁰ The photoluminescence (PL) efficiency, η_{PL} , of spin-cast films of the polymer-dye blends was measured before and after the NIL process by using an integrating sphere. The sphere is hollow and coated with a diffusely reflecting material, thus collecting the average emitted photons per solid angle, independent of their angular distribution, toward a charge coupled device spectrograph (Fig. 4). We excited samples by a He–Cd laser ($\lambda = 325 \text{ nm}$, excitation density = 0.1 W/cm^2), at near-normal incidence and at room temperature. The optical measurements were carried out under nitrogen flux to prevent damage of samples under photoexcitation.

III. RESULTS AND DISCUSSION

As a consequence of the reaction, F , of the bellows and of the springs to compression, x , the pressure actually applied to the sample during NIL is weaker than that applied by the external hot plates. In order to exactly know the applied

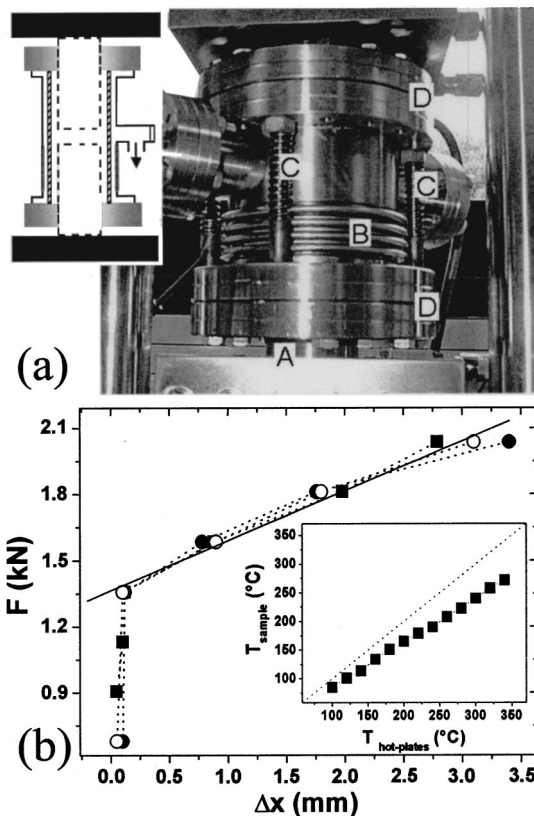


FIG. 2. (a) Photograph of the add-on high-vacuum chamber. Inset: chamber scheme. The arrow indicates the vacuum line. (A) Pressing cylinders (external part leaning out). (B) Main bellows. (C) Additional external springs. (D) Conflat® flanges. (b) Calibration of the applied force vs the chamber compression at different operation temperature: room temperature (solid circles), $200 \text{ }^\circ\text{C}$ (open circles), and $230 \text{ }^\circ\text{C}$ (solid squares). Dotted lines are guides for the eye. The continuous line is a linear fit of the elastic regime for $T = 200 \text{ }^\circ\text{C}$. Inset: Sample temperature vs temperature of the press hot plates. The maximum measured temperature difference between hot plates and sample is $70 \text{ }^\circ\text{C}$ at $T = 340 \text{ }^\circ\text{C}$.

force, we determined the dependence of F on x , finding a roughly linear elastic behavior ($F \propto x$) with elastic constant $\cong 0.23 \text{ kN/mm}$, exhibiting variations of less than 10% at different temperatures (Fig. 2). Instead, a small temperature offset between the hot plates and the samples (i.e., along the pressing cylinders) is measured, ranging between 15 and $70 \text{ }^\circ\text{C}$ in the range $100\text{--}300 \text{ }^\circ\text{C}$ (inset of Fig. 2). We tested our setup with a vacuum up to 10^{-6} mbar .

Master structures were used to imprint PMMA in the high-vacuum chamber. NIL was carried out both by using these masters directly as molds and after a treatment with a solution of octadecyltrichlorosilane in 2,2,4-trimethylpentane (4:1000 volume/volume, spin cast at 6000 rpm for 40 in.), to inhibit the possible adhesion between the mold and the polymer during NIL. No substantial difference was observed in the patterns printed by the two procedures. The imprinting process on PMMA on different substrates was performed at about $160 \text{ }^\circ\text{C}$ with an applied pressure of 10^4 psi . A vacuum of 10^{-5} mbar was applied for NIL on films of polymers/dyes blends.

Figures 3(a)–3(b) and 3(c)–3(d) show an example master

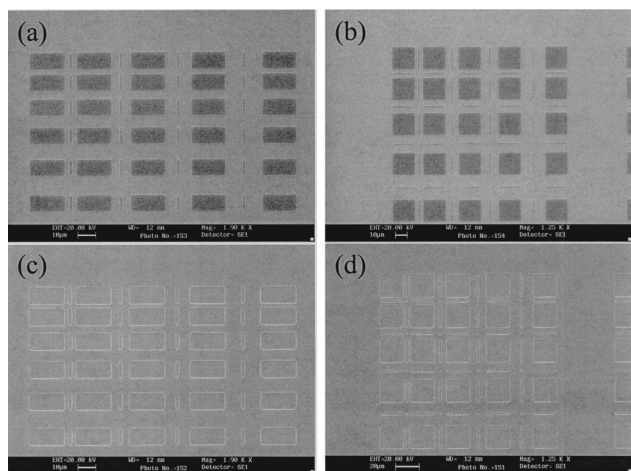


Fig. 3. SEM two-dimensional view of master patterns [(a) and (b)] and of the corresponding transfers into PMMA [(c) and (d)].

and the final patterns obtained on PMMA, respectively, imaged by SEM, demonstrating the excellent fidelity achieved with the replication procedure. Features having size comprised between 300 nm and 100 μm were imprinted by us with the same fidelity onto areas up to several cm^2 . We believe that these limits are due to the employed molds, and that by using proper master structures it would be possible to achieve the very high resolution allowed by NIL.² The high quality of the large-area pattern transfer also demonstrates the good parallelisms between the two internal surfaces of the pressing cylinders of the chamber.

In order to assess the retained optical functionality of light-emitting organic compounds after high-vacuum NIL, we measured the luminescence absolute quantum efficiency, η_{PL} , of dye chromophores embedded in polymers matrices before and after the lithography process. The number of photons emitted in PL per absorbed photon by the untextured and the patterned films was determined by accounting for those photons which are not absorbed by the sample at their first incidence, and are absorbed after the successive reflections on the surface of the integrating sphere:¹¹

$$\eta_{\text{PL}} = \frac{P_1 - (R+T)P_2}{(1-R-T)X_L}, \quad (1)$$

where R and T indicate the reflectance and the transmittance of the system, respectively. P_1 and P_2 are the PL signals measured with the laser beam incident on the sample and on the integrating sphere, respectively, and X_L stands for the excitation signal, measured with the laser incident on the sphere and without sample. After placing the sample in the sphere, we measured P_2 , by directing the excitation beam on the sphere wall, and P_1 , by directing the laser on the film. Finally, we removed the sample and measured X_L by the laser signal. All of the signals were normalized by the spectral response of the experimental setup (see Fig. 4). The NIL process was carried out on polymer/dye films spin cast onto Spectrosil substrates, whose absorption at 325 nm can be neglected, as in Eq. (1). We found for our samples a PL spectral range comprised of between 490 and 710 nm, and

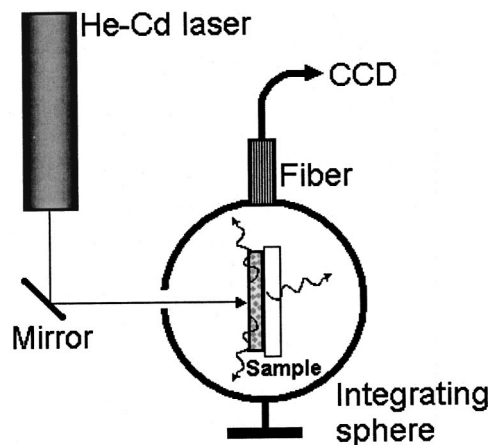


Fig. 4. Schematic diagram of the experimental setup employed for the measurements of the PL absolute quantum efficiency (elements not in scale).

between 450 and 700 nm, and peak wavelengths of 580 nm and of 507 nm, for DCM and Coumarin blends, respectively. The PL quantum yield of DCM/PMMA blends was found to be almost constant (slightly increasing) around a value of 20%, whereas an appreciable increasing of η_{PL} was measured for Coumarin/PMMA blends, varying from 9% to more than 14% after patterning. This increase can be ascribed to the diffusion of chromophores^{12–14} inside the PMMA film at the temperature above T_g needed to imprint, leading to more uniform dye distributions within the polymer slab and consequently reducing the intermolecular decay channels responsible for the concentration quenching of PL usually observed in dye molecules. Another element which can contribute to the increase of the PL yield is the wavelength-scale structures patterned onto the film. This enhances the emission in the forward direction, thus reducing the self-absorption of the radiation inside the polymer slab.¹⁵ The effect is indeed better appreciated with high-density 300 nm-sized imprinted features, which were the higher-resolution features that we transferred in our experiments. A further discussion of the possible mechanisms at the basis of the increase of η_{PL} will be presented in a forthcoming article. More in general, the fact that η_{PL} does not show any degradation demonstrates that high-vacuum NIL can be applied without deterioration of the functionality of the target materials, even if a quantitative comparison with previous studies⁶ of NIL on light-emitting molecules in controlled atmosphere is not possible, as the η_{PL} values were not previously reported.

IV. CONCLUSION

In this article, we reported on NIL experiments on polymers and polymers/dyes blends under high-vacuum conditions (10^{-5} mbar) by means of a specifically designed imprint chamber. Our system in principle allows us to carry out nanoimprinting on large areas (up to 25 cm^2) on optically and electrically active compounds, without any degradation of the luminescence performances of organic molecules, as confirmed by measuring the PL efficiency of laser dye chro-

mophores embedded in the imprinted polymer before and after the lithography process. By this method, both the low cost operation and the wide chemical flexibility of mechanical lithography can be exploited easily on any organic compound, with great impact on plastic electronics and photonics.

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⁸For an example of presently available commercial system, one can see: http://www.obducat.com/sida_78.asp

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