Nanopattern-Assisted Growth of Organic Materials for Device Applications

Personnel

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The goal of this work is to use nanopatterning to improve the performance of organic optoelectronic and electronic devices such as Organic Light Emitting Diodes (OLEDs) and Organic Field Effect Transistors (OFETs). OLEDs and OFETs are devices in which thin films of organic small molecules serve as light emitting or charge transporting materials. The organic thin films are typically prepared by thermal evaporation onto unpatterned SiO_2 or Indium Tin Oxide (ITO)-coated SiO_2 substrates. We have evaporated organic materials onto nanopatterned substrates in order to (1) improve light extraction from OLEDs and (2) promote molecular ordering in OFET thin films. The nanopatterning is accomplished by interference lithography, and results in features that are on the order of hundreds of nanometers in size.

Nanopatterning by Interference Lithography
In interference lithography, photoresist is exposed by the optical standing wave generated by the interference of two coherent beams of light. For a single exposure, the resulting pattern is a linear grating as shown in Figure 19. The grating period (P) is determined both by the wavelength (λ) of light used and by the angle (θ) of the beam with respect to the substrate normal, and is given by $P = l / 2 \sin q$. Typically a trilayer resist stack is used, which consists of an anti-reflection coating (ARC) to prevent back reflections from the Si substrate, an SiO_x interlayer to serve as an etch mask, and finally the photoresist (see Figure 19).

For this work, all interference lithography was performed in the Nanostructures Laboratory (NSL) at MIT using a Lloyd's Mirror configuration. In this configuration, part of the light from a HeCd laser (λ=325 nm) is directly incident on the substrate while part of the light is reflected onto the substrate by a mirror oriented perpendicular to the substrate. Accessible periods using this setup are 170 nm up to 1 μm.

After two exposures, with the substrate rotated by some angle for the second exposure, we can generate a two dimensional pattern. For a 90 degree rotation the resulting pattern is a square array of posts or holes if positive or negative resist is used, respectively. The typical dose used for the each of the two exposures is 65 percent of that needed to clear the resist in a single exposure. Figure 20 show SEM micrographs of a square array of posts in a positive photoresist. When the substrate is rotated by 60 degrees for the second exposure, a hexagonal pattern is generated.

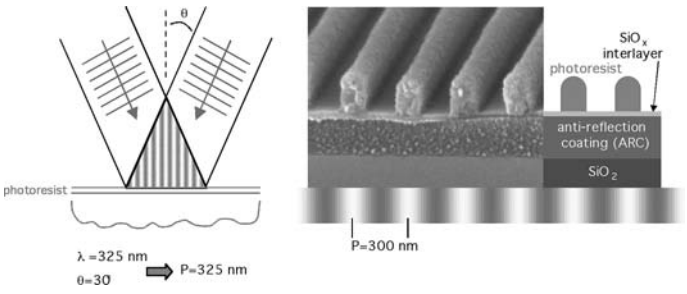

Fig. 19: Schematic representation of the interference lithography process (left) and its application to generating a periodic pattern in the photoresist layer (right).

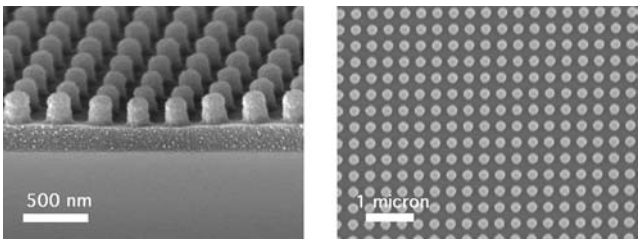

Fig. 20: Photoresist pillars generated after two exposures of the photoresist to the light interference pattern.

Application of Nanopatterning to Organic Light Emitting Devices–Light Extraction

A typical OLED is fabricated by first evaporating organic layers on top of an ITO-coated glass substrate, and then evaporating a metal cathode on top of the organic layers. The weak microcavity that is formed by the reflective electrode and reflection at the glass/ITO interface can sustain highly-lossy waiveguided modes. The waveguided light dissipates most of its energy to the metal electrode after a very short propagation (sub-micron path length). Furthermore, light in the radiative modes of the OLED, emitted at shallow angles can also be absorbed by the structure after multiple total internal reflections. Such losses in OLED efficiency can account for more than 60% of all the internally generated radiation. In order to improve the OLED efficiency it is, therefore, desirable to devise a device structure that redirects the light into vertically-emitted radiative modes.

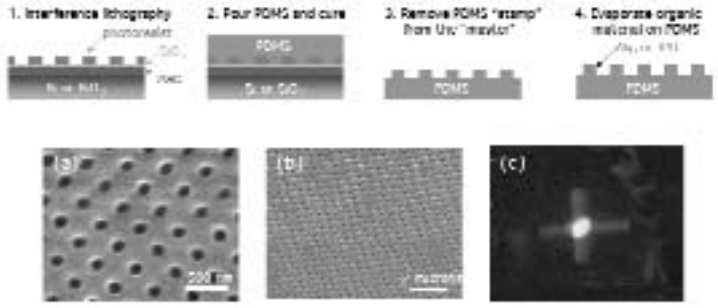

Fig. 21: Sequence of steps for generating a PDMS PBG structure with an organic luminescent layer on top. (a) and (b) Different magnifications of the patterned PDMS structure. (c) Directionally guided light in a cm2 PDMS substrate. The excitation beam impinges the substrate at the bright center spot.

Following earlier studies in III-V materials we propose to redirect the in-plane-emitted light by incorporating a two-dimensional photonic band gap (PBG) structure into the design of our OLED active layers. One possible PBG structure is simply a hexagonal lattice of air holes in a high-dielectric semiconductor. By varying the period and size of the PBG features, or the index of the semiconducting material, this design can be tuned to prevent in-plane propagation of a specific band of emission wavelengths.

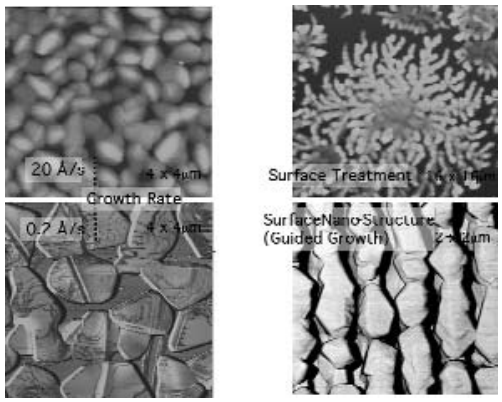

Fig. 22: Effects of growth rate, surface treatment, and nano-patterns on the growth of tetracene thin films.

We generated a PBG structure in PDMS (silicone rubber) substrates by making a "master" in a photoresist layer on Si and then transferring that pattern to PDMS (see Fig. 21). Top view SEM micrographs of a PDMS stamp made from a square lattice of posts are also shown in Figs. 10a and 10b. The period was 340 nm, and the thickness of the photoresist was 200 nm, resulting in 200 nm deep holes in the PDMS. In the final processing step we evaporated a 100 nm thick luminescent organic layer of TPD on top of our PDMS stamp.

We investigated photoluminescence of the TPD film (peak luminescence wavelength, λ_{max}= 415 nm) excited by a mm2 beam of UV light. We observed directed in-plane guiding of light, consistent with the square pattern of the PBG structure (Fig. 21c). This initial study demonstrates the effectiveness of PBG structures in redirecting luminescence in organic devices. In the next step we will use the same method to fabricate PBG patterns in active OLED structures.

Application of Nanopatterning to Organic Field Effect Transistors–Molecular Ordering

Unlike the amorphous organic films used in OLEDs, organic thin films used in organic FETs are typically polycrystalline. As in a conventional FET, the amount of current that flows between the source and the drain electrodes is modulated by the field applied across the metal (gate)-insulator-semiconductor sandwich. The charge carrier mobility through the organic thin film is strongly dependent on the molecular ordering within the film, where the mobilities can be as much as eight orders of magnitude larger for single-phase polycrystalline films as compared with amorphous films of the same material. Our goal is to improve molecular ordering within polycrystalline organic films in order to achieve larger grain sizes and lower defect densities, and ultimately enhance the charge carrier mobility.

A common approach to improving molecular ordering is by modifying the insulating surface onto which the organic semiconductor is deposited. For example, SiO_2 can be treated with silanes such as octadecyltrichlorosilane to create a hydrophobic Self-Assembled Monolayer (SAM). Mechanical modification, such as rubbing a polymeric insulator or a thin pre-film of the organic semiconductor itself, is another possibility. Our approach is similar to this mechanical modification, but more controlled. We use interference lithography to pattern surface relief gratings into an SiO_2 substrate, and then evaporate an organic semiconductor such as pentacene onto this substrate. We expect to observe either graphoepitaxy, by which the molecules are aligned by the artificial surface pattern, or confinement effects, by which defects segregate to the boundaries of the confined grains.

Our initial investigations of deposited film morphology have been done using both Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Figure 22 shows the morphology of four tetracene thin films grown on differently treated SiO_2 substrates. For all films the deposition pressure was 5×10^{-6} Torr, and the substrate was held at room temperature during deposition. Both surface treatment and the growth rate are seen to strongly influence the morphology of films. Significant order is observed for the nano-patterned substrates, where the grains on the plateaus appear to be larger for the deeper gratings. At this time we are also pursuing electron diffraction, X-ray diffraction and polarized fluorescence microscopy measurements in order to further understand the effect of the gratings on the molecular order within the film.