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Direct nanoimprint of submicron organic light-emitting structures

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We have demonstrated a method to directly pattern organic light-emitting structures with a submicron resolution without any degradation in optical properties. Both small molecules and polymer-based light-emitting structures were patterned by nanoimprint at 150 °C in a vacuum. The comparison of luminescence efficiency before and after patterning shows that nanoimprint did not cause degradation in the optical property of the materials. Nanoimprint offers a low-cost, high-throughput, high-resolution patterning technique that opens a way for realizing novel photonic devices based on organic light-emitting materials. © *1999 American Institute of Physics.* [S0003-6951(99)04144-3]

Organic light-emitting materials and devices, such as organic light-emitting diodes (OLED), organic flat panel displays, and organic lasers have been under intensive investigation for a decade.[1,2] However, direct patterning of organic light-emitting media with high resolution, while essential to the further development of the organic light-emitting devices, is an area virtually unexplored. Because organic light-emitting materials experience deterioration in their optical properties when exposed to water, oxygen, high-energy particles (e.g., photons and electrons), and are also soluble in the solvents used in conventional patterning methods, current technology is unsuitable for patterning, and alternative patterning techniques need to be developed. Previously, several direct patterning methods like vacuum deposition through a shadow mask,[3] laser photoablation,[4] and inkjet printing[5,6] have been widely used. Also, sealing the OLED organics before using conventional patterning environments has been developed.[7,8] However, all of them suffer from limited resolution ($>10\ \mu$m). Considering that submicron patterning is required in many applications, such as ultrahigh resolution OLEDs,[9] distributed feedback organic lasers,[10–13] and organic photonic crystals,[11] new high-resolution techniques for patterning organic light-emitting media are desired. No existing method can be used to pattern light-emitting organics with a submicron resolution that does not cause degradation of the light emission efficiency.

Previously, nanoimprint lithography was demonstrated to be a high-throughput lithography technique with a sub-10 nm resolution capability.[14,15] Direct patterning of poly(methylmethacrylate) (PMMA) resist and thermoplastic (polycarbonate, PVC, etc.)[16] substrates has been demonstrated. Therefore, it is very attractive to use this technique for direct patterning of active organic light-emitting media. However, would the temperature and pressure environment in nanoimprint degrade the optical property of the organic materials? This letter reports the investigation of nanoimprint techniques for high-resolution patterning of both small molecule and some polymer hosted light-emitting media. The comparison of luminescence efficiency before and after patterning shows that nanoimprint did not cause degradation in the optical property of the organics.

Two kinds of light-emitting materials were used in this work. The first material was hosted by Alq_3 (8-hydroxyquinoline aluminum), a widely used electron conducting small-molecule, light-emitting material for highly efficient OLEDs[1] and optically pumped lasers.[11,17] The Alq_3 is doped with 2 wt % DCMII dye molecules to achieve high luminescence efficiency based on Förster energy transfer.[11,17] The organic films were prepared either by thermal evaporation or by spin coating. The thickness of the film was about 200 nm measured by an ellipsometer. The second material used PMMA as the matrix, which was blended with various semiconducting small molecules like Alq_3, and DCMII. This type of blend material was also used in OLEDs and organic lasers previously.[9] The polymer films were prepared by spin coating and the thickness was about 200 nm.

A detailed description of the nanoimprint lithography process can be found in our previous work.[14,15] The SiO_2 grating masks (molds) used in this work were made by interference lithography with a period of 200 or 300 nm and a height of 180 nm. The nanoimprint process in this work was performed in a vacuum of ~ 1 Torr, at a pressure of about 800 psi, and a temperature of 150 °C. The total process time including vacuum, heating up, imprint and cooling down was approximately 15 min.

Figure 1 shows atomic force microscope (AFM) images of the Alq_3/DCMII gratings with a period of 200 and 300 nm, respectively. This is the first time that the high-efficient, small-molecule, light-emitting materials were directly patterned into submicron structures. These structures have a number of applications including distributed feedback (DFB) lasers and photonic crystals.[10–13] In contrast, all previous optically pumped DFB lasers and photonic crystal structures were fabricated by depositing the organic light-emitting molecules onto a prepatterned dielectric (e.g., silicon dioxide) substrate.[10–13] Since the refractive index of the transparent

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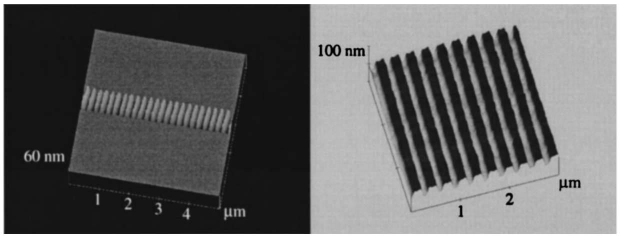

FIG. 1. AFM images of the Alq_3/DCMII gratings with a period of 200 nm (left) and 300 nm (right), respectively, patterned directly by nanoimprint.

dielectric substrate is very close to that of the organic light-emitting material, the dielectric contrast of the gratings is small. With nanoimprint, a large dielectric grating contrast (due to the polymer and air interface) can be obtained, which is critical for DFB lasers, and especially, photonic crystals.

As described earlier, an important issue in patterning organic light-emitting materials is how to avoid degradation of light emitting efficiency caused by the patterning process. Since oxygen, water, and high-energy particles (photons) are the killers of the light-emitting efficiency of the organics, the nanoimprint patterning process needs to be performed in a low vacuum or nitrogen environment. To study the influence of the imprint environment (i.e., high pressure and temperature) on the optical property of the organic light-emitting material, we measured the luminescence efficiency of the sample before and after imprint patterning. Figure 2 shows the measured luminescence spectral intensity of the sample before and after patterning, respectively, excited by an argon ion laser (488 nm) with a power density of $\sim 10\,\mathrm{mW/cm^2}$. The photoluminescence was measured by a 3/4 monochromator with a photomultiplier. From Fig. 2, it is concluded that virtually no degradation is caused by the nanoimprint patterning process. To study possible influences of the sample substrate, both silicon and glass substrates were used in this work. The same conclusion was drawn for both types of substrates. In contrast, the sample patterned by nanoimprinting in air had much lower photoluminescence efficiency, i.e., about one order smaller than that imprinted in vacuum.

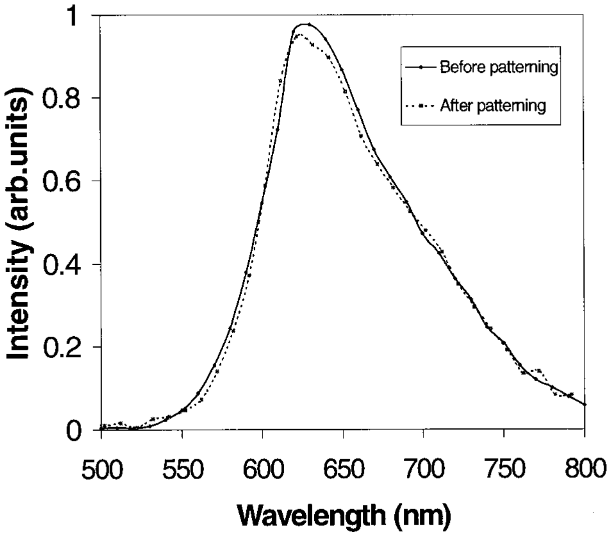

FIG. 2. The measured luminescence spectral intensity before (solid) and after (dashed) nanoimprint, respectively. An argon ion laser (488 nm) was used for excitation. It shows that the nanoimprint process did not degrade the optical property of the organics.

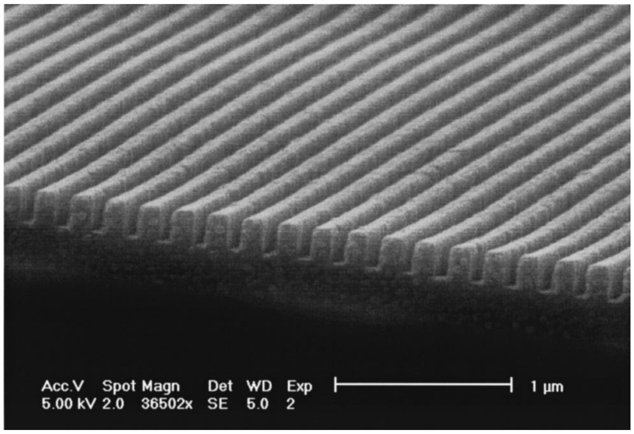

FIG. 3. SEM image of the patterned grating of PMMA/Alq_3/DCMII with a period of 200 nm by nanoimprint.

The polymer (PMMA) based light-emitting media was also fabricated using nanoimprint and investigated in the same manner described earlier. Figure 3 shows the scanning electron microscope (SEM) images of the patterned gratings of PMMA/Alq_3/DCMII by the nanoimprint process. We should indicate that, the resolution obtained so far is limited by the smallest feature size on our mold. In principle, the nanoimprint process can give a much higher resolution down to 10 nm.[14,15] The experimental results of the luminescence efficiency measurement gave the same conclusion as that of the small molecule organics, i.e., no degradation caused by nanoimprint.

In summary, nanoimprint is used to pattern both small-molecule and polymer-based light-emitting media with an ultrahigh resolution (down to sub-200 nm). The luminescence efficiency comparison shows that the nanoimprint process did not degrade the optical property of the organics. The low-cost, high-throughput, high-resolution patterning technique opens a way for realizing novel photonic devices based on organic light-emitting materials.

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