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청정소재제품기술

Fabrication of Patchable Organic Lasing Sheets via Soft Lithography

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Abstract

Here, we report a novel fabrication technique for patchable organic lasing sheet based on non-volatile liquid organic semiconductors and freestanding polymeric film with high flexibility and patchability. For this work, we have fabricated the second-order DFB grating structure, which leads to surface emission, embedded in the freestanding polymeric film. Using an ultra-violet (UV) curable polyurethaneacrylate (PUA) mixture, the periodic DFB grating structure can be easily prepared on the freestanding polymeric film via a simple UV curing process. Due to unsaturated acrylate remained in the PUA mixture after UV curing, the freestanding PUA film provides adhesive properties, which enable mounting of the patchable organic lasing sheet onto non-flat surfaces with conformal contact. To achieve laser actions in the freestanding resonator structure, a composite material of liquid 9-(2-ethylhexyl)carbazole (EHCz) and organic laser dyes was used as the laser medium. Since the degraded active materials can be easily refreshed by a simple injection of the liquid composite, such a non-volatile liquid organic semiconducting medium has degradation-free and recyclable characteristics in addition to other strong advantages including tunable optoelectronic responses, solvent-free processing, and ultimate mechanical flexibility and uniformity. Lasing properties of the patchable organic lasing sheet were also investigated after mounting onto non-flat surfaces, showing a mechanical tunability of laser emission under variable surface curvature. It is anticipated that these results will be applied to the development of various patchable optoelectronic applications for light-emitting displays, sensors and data communications.

Keywords : Patchable electronics, Organic devices, Organic lasers, Polyurethaneacrylate, Soft lithography

1. Introduction

Organic electronic and optoelectronic devices have attracted a lot of interest in the past few decades, due to the remarkable properties of light weight, solution-based processing, and mechanical flexibility [1-6]. In particular, non-volatile liquid organic semiconductors are receiving much attention as emerging functional materials for organic optoelectronic applications in recent years, because these fluidic materials present strong advantages including tunable optoelectronic responses, degradation-free characteristics, solvent-free processing, and ultimate mechanical flexibility and uniformity [7-12]. Various organic optoelectronic devices using non-volatile liquid organic semiconductors have been already demonstrated, which include photorefractive devices, organic light-emitting diodes, dye-sensitized solar cells, memories, and optically-pumped lasers [13-18]. In a lasing context, solvent-free liquid organic lasers based on distributed feedback (DFB) resonator structures were recently demonstrated in the blue, green and red regions, using 9-(2-ethylhexyl)carbazole (EHCz) doped with organic dyes [19, 20]. In consideration of unconventional functionalities that can be successfully introduced to organic devices, such as flexibility and patchability, this class of solvent-free liquid organic lasers provides promising opportunities in extending optoelectronic applications, such as light-emitting displays, data communications, highly sensitive bio- and chemical sensors, and portable analytic instruments.

An ultra-violet (UV) curable polyurethaneacrylate (PUA) mixture is a versatile material for soft lithography with sub-100 nm resolution [21, 22]. The surface energy of PUA mixture is sufficiently low (~23 dyn cm^{-1}) after UV curing, which facilitates clean release of the cured PUA film in a freestanding manner from a supporting backbone such as glass or silicon substrate [23-25]. Such freestanding PUA films have high flexible properties, tensile modulus of ~19.8 MPa, and elongation at break

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of ~45% [21, 22]. Unsaturated acrylate remained in the PUA mixture after UV curing provides the freestanding PUA films with adhesive properties, which can lead to remarkably simple fabrication of patchable polymeric substrates with high flexibility.

Here we demonstrate a patchable organic lasing sheet based on non-volatile liquid organic semiconductors, which can be easily mounted onto non-flat surfaces without using any glues or adhesive tapes. For this work, we have fabricated the second-order DFB grating structure, which leads to surface emission (i.e., diffracted light is out-coupled in the perpendicular direction to the waveguide plane), embedded in the freestanding PUA film with high flexibility and patchability. To achieve laser actions in the flexible resonator structure, a composite material of liquid EHCz and organic laser dyes was used as the laser medium. Since the degraded active materials can be easily refreshed by a simple injection of the liquid composite [11, 12], the patchable organic lasing sheet has degradation-free and recyclable characteristics. Lasing properties of the patchable sheet were investigated after mounting onto non-flat surfaces, showing a mechanical tunability of laser emission according to the surface curvature. The results strongly suggest great potential for the development of various patchable applications for light-emitting displays, sensors and data communications.

2. Material and methods

2.1. Materials

A UV curable PUA mixture was synthesized in accordance with previous reports [21, 22], and other molecules used in this work were purchased from Sigma-Aldrich. A liquid EHCz host was doped with coumarin 153 (C153) and 4-(dicyanomethylene)-2-methyl-6-julolidyl-9-enyl-4H-pyran (DCM2), of which chemical structures are shown in Figure 1. The dye-doped EHCz blend of EHCz:C153:DCM2 (95.0:3.1:1.9 wt%) was used as an active composite for red-light emission.

2.2. Fabrication of patchable organic lasing sheet

A patchable organic lasing sheet was fabricated as schematically illustrated in Figure 2. The PUA mixture was drop-dispensed onto a master-pattern of polydimethylsiloxane (PDMS) mold,

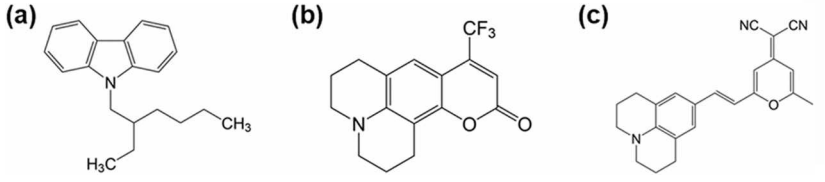

Figure 1. Chemical structures of (a) 9-(2-ethylhexyl)carbazole (ECHZ, liquid host), (b) coumarin 153 (C153, laser dye) and (c) 4-(dicyanomethylene)-2-methyl-6-julolidyl-9-enyl-4H-pyran (DCM2, laser dye).

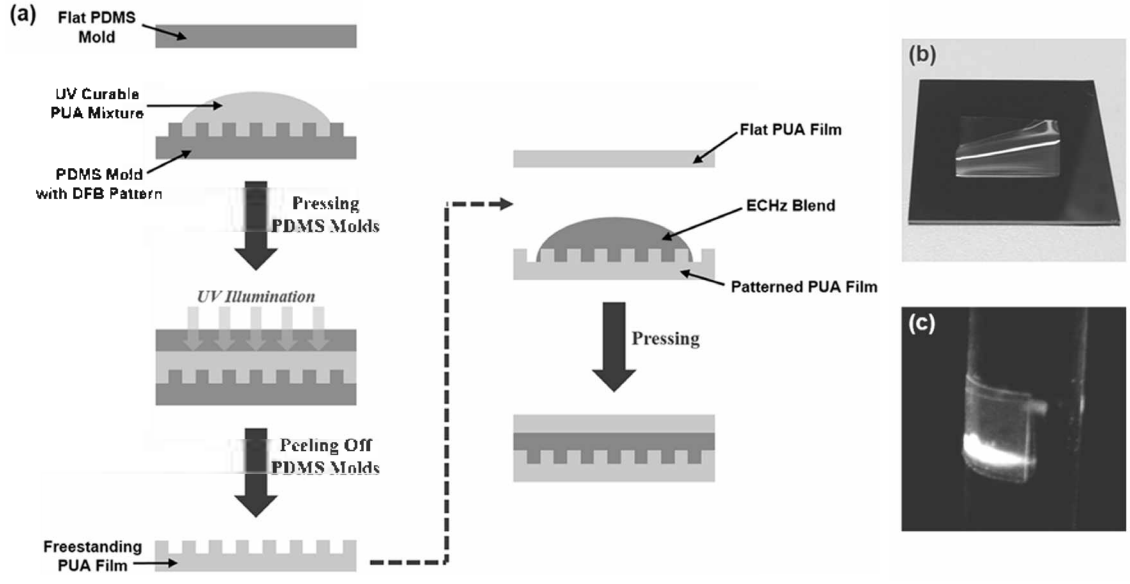

Figure 2. (a) Schematic illustration of the preparation of free-standing PUA film with DFB grating structure, and patchable organic lasing sheet. (b) Photo image of the freestanding PUA film with DFB grating structure. (c) Photo image of the patchable organic lasing sheet mounted on the curved surface, which shows high flexibility and patchability.

and then covered with a flat glass substrate. The master-pattern of PDMS mold was chosen for the second-order DFB operation according to the Bragg condition, which has a period of ~420 nm and a height of ~110 nm. Square PDMS pillars with a height of 50 μm were used for a fixed gap distance between the PDMS mold and the glass substrate, and the excess amount of the PUA mixture was squeezed out by applying pressure from one end of the sample toward the other end using a roller. Subsequently, the PUA mixture was exposed to UV light (~365 nm) for several minutes through the glass substrate. After this UV curing process, both PDMS mold and glass substrate were easily peeled off from the cured PUA film owing to the low surface energy of PUA (~23 dyn cm^{-1}), and a freestanding PUA film with the replicated DFB pattern was prepared. The dye-doped EC1Iz blend was then drop-dispensed onto the DFB pattern of the freestanding PUA film. To complete the structure of lasing sheet, another freestanding PUA film without any pattern was separately prepared using a flat PDMS mold with the same procedure as described above. The patternless freestanding PUA film was brought onto the drop-dispensed EC1IZ blend for covering the sample, and excess active composite was also squeezed out by applying pressure. It is worth noting that the cured PUA films are transparent in the visible range (i.e., ~90% transmissivity in the range from 300 to 1,100 nm) [24], and thus the outstanding properties of PUA can be successfully introduced to optical and optoelectronic applications.

2.3. Measurements

For the characterization of the lasing properties, the patchable organic lasing sheet was excited using a pulsed-N_2 laser at 337 nm (with pulse duration of 800 ps and a repetition rate of 8 Hz). The excitation beam was focused into a stripe (0.5 cm × 0.08 cm), and the energy of the excitation pulses was controlled using a set of neutral density filters. The emission spectra were measured in the normal direction to the sample surface using an optical fiber coupled to a charge coupled device spectrometer.

3. Results and Discussion

3.1. Lasing properties of patchable organic lasing sheet in a planar geometry

To investigate the lasing properties of the patchable organic lasing sheet, the sample was firstly mounted onto the glass substrate and maintained in a planar geometry during the emission measurement. Figure 3 shows the emission spectra of the patchable organic lasing sheet at excitation energies below and above the lasing threshold. Since the optical spectra of ECHz, C153, and DCM2 are efficiently overlapped for Förster-type energy transfer scheme [19, 20], the light emission from the ECHz blend was effectively tuned and mainly observed in the red region below the lasing threshold via cascade energy transfer from ECHz to C153 and DCM2. On the periodic DFB corrugation, the emitted light from the medium propagates in the waveguide plane and is scatted according to the Bragg condition:

$$m \lambda_{Bragg} = 2 n_{eff} \times \Lambda \quad (1)$$

where λ_{Bragg} is the wavelength of the emitted light, Λ is the period of the DFB structure, n_{eff} is the effective refractive index of the waveguide plane, and m is the order of the diffraction process. Because the period of the DFB structure was selected for the second-order operation (i.e., surface emission), the red laser emission peak in the normal direction to the sample surface was emerged at ~619.5 nm above the lasing threshold. The output emission intensity and the full width at half maximum (FWHM) corresponding to the pumping intensity for the patchable lasing sheet is also shown in Figure 3. The FWHM of the

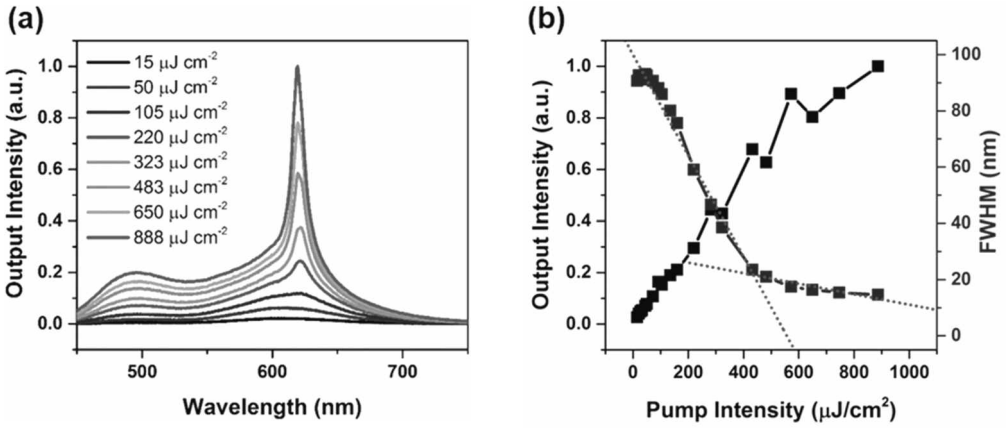

Figure 3. (a) Laser emission spectra under variable pumping intensity, and (b) output intensity (black squares) and FWHM (blue squares) of laser emission corresponding to the pumping intensity. Red dot lines indicate the abrupt change in the FWHM.

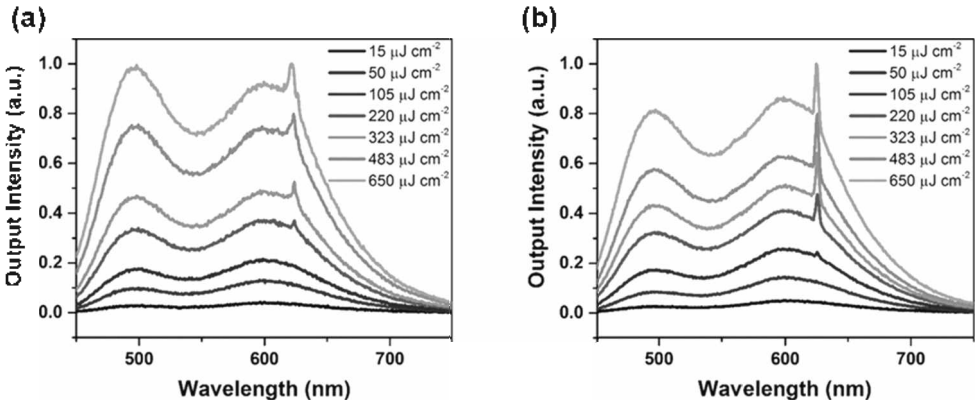

Figure 4. Laser emission spectra of the patchable organic lasing sheet mounted on the curved surfaces with bending radii of (a) 14 mm and (b) 4 mm.

patchable lasing sheet drops from ~90 to ~15 nm as the pumping intensity increases. The lasing threshold is deduced from the abrupt change in the FWHM, which is found to be ~430 μJ cm^{-2}.

3.2. Mechanical tunability of laser emission

To examine mechanical tunability of the patchable organic lasing sheet, the sample was mounted onto the cylindrical bottles with curvatures of 0.07 and 0.25 mm^{-1} as shown in Figure 4. The corresponding laser emission was measured on each curved surface, of which the emission spectra below and above the lasing threshold are shown in Figure 4. As the curvature increases up to 0.25 mm^{-1}, the laser emission peak above the lasing threshold is gradually red-shifted from ~619.5 to ~624.7 nm (see Figure 5). This behavior is consistent with previous works reporting mechanically tunable DFB lasers based on polymer and small organic molecules [20, 26]. In this context, our demonstration of the patchable organic lasing sheet suggests a wide range of possibilities for various patchable optoelectronic applications with mechanical tunability, even though optimizing the fabrication process, device design and selection of device components would be further improved.

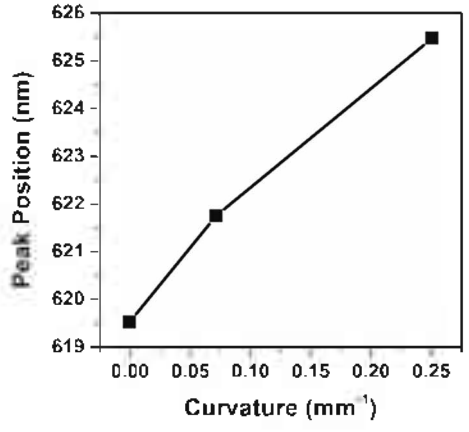

Figure 5. A change in peak position of the patchable organic lasing sheet under variable surface curvature.

4. Conclusions

In conclusion, we have introduced a novel fabrication process for patchable organic lasing sheet based on non-volatile liquid organic semiconductors and freestanding polymeric film with high flexibility and patchability. The freestanding polymeric film providing adhesive properties is easily patterned using a soft PUA mixture, and thus the resonator structure such as periodic DFB grating corrugation can be embedded in the film via a simplified preparation procedure. The patchable organic lasing sheet can be easily mounted onto non-flat surfaces without using any glues or adhesive tapes, and also has degradation-free and recyclable characteristics due to its fluidic laser medium. In addition, lasing properties of the patchable sheet show a mechanical tenability of laser emission according to the surface curvature of non-flat surface. We anticipate that these results will contribute to the development of various patchable optoelectronic applications for light-emitting displays, sensors and data communications.

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