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(54) Title: PHOTONIC CRYSTAL STRUCTURE AND METHOD OF FORMATION THEREOF

FIG. 2
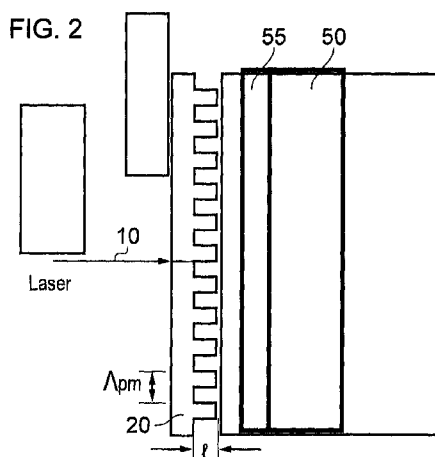
(57) Abstract: The invention provides a method of forming a photonic crystal structure by means of a polymerisable material comprising the steps of: forming a layer of the polymerisable material, the polymerisable material being arranged to experience photoinduced mass transfer upon irradiation with optical radiation; and exposing the polymerisable material to said optical radiation at locations corresponding to a photonic crystal structure to be patterned thereby to form said structure by photoinduced mass transfer.

PHOTONIC CRYSTAL STRUCTURE AND METHOD OF FORMATION THEREOF

Field of the Invention

[0001]   The present invention relates to semiconductor or polymer structures and to
methods of formation thereof.   In particular but not exclusively the invention relates to
nanoscale semiconductor or polymer structures, more particularly but not exclusively
organic and/or light-emitting semiconductor nanostructures. Embodiments of the invention
relate to organic semiconductor liquid crystal structures.

Background to the Invention

[0002]   It is known to fabricate nanometre scale structures in transparent insulating thin
films. Methods of fabricating such structures include lithographic patterning and etching,
for example using electron beam lithographic techniques.   Other techniques include
nanoembossing where a nanostructure is fabricated by embossing a thin film using a
stamp.

[0003]   Photonic crystals (PCs) are structured materials with a periodic variation in
refractive index. The length of the period is of the order of the optical wavelength. This
can allow the creation of photonic band-gaps (PBGs). PBGs are spectral regions over
which light propagation is forbidden.

[0004]   A problem with known techniques for fabricating photonic structures is that they
are typically not compatible with low cost mass-production techniques. The availability of
easily formed nano-photonic structures on light-emitting and semiconducting materials,
which are compatible with roll-to-roll and other large scale manufacturing processing, may
provide the disruptive factor required to deliver next generation photonic materials and
devices to markets in displays, optical communications, quantum information processing,
sensors, etc.

[0005]   2D PCs require high contrast between regions of low and high refractive index
and may be fabricated by etching holes in inorganic semiconductor materials such as
GaAs and silicon. Very high performance devices are obtained but the nanostructures are
fabricated using electron or ion beams, which is expensive and slow. Line defects and
nanocavities are made in the PC by omitting a number of holes, shifting their position or
changing their size. The Purcell effect has been observed with extremely high Q factors
($>10^6$) (S. Noda, Nature Photon., 1 449 (2007). Work on organic material is at a very early
stage: Hybrid organic-inorganic approaches have been introduced with the demonstration

of emission from an organic nanocavity formed by evaporation of an organic layer into a 2D photonic crystal fabricated using a SiO_2 holey membrane. (M. Kitamura, Appl. Phys. Lett. *87* 151119 (2005))

[0006] Holographic lithography has been used to pattern periodic structures in polymer dispersed liquid crystals (LCs) (C. Paquet, Mater. Today, *11*, 48 (2008)). However, although 3D as well as 2D structures are obtained, these materials have a low refractive index contrast and are not light emitting. 1D and 2D photonic structures are commonly used to provide distributed feedback for organic lasers. Substrate etching and mechanical nano-imprinting have been used to pattern the materials.

[0007] Embossing and nanoimprinting techniques have frequently been used to pattern surface features on organic semiconductors. Patterns may be created by mechanical deformation of the organic thin film using a mold with topographic features. Very good resolution is obtained but the masters are expensive. The process relies on displacing polymer in confined spaces, which leads to systematic effects for large-area patterning.

[0008] Hard contact with the stamp may also be detrimental to the yield of devices. Photolithography has been used to pattern photopolymerisable organic semiconductors but involves a wet etching step to develop structures. Organic semiconductors have also been patterned by laser ablation, e.g. to form channels in pentacene thin film transistors.

Summary of the Invention

[0009] In a first aspect of the present invention there is provided a method of forming a photonic crystal structure by means of polymerisable material comprising the steps of:

forming a layer of a polymerisable material, the polymerisable material being arranged to experience photoinduced mass transfer upon irradiation with optical radiation; and

exposing the polymerisable material to said optical radiation at locations corresponding to a photonic crystal structure to be patterned thereby to form said structure by photoinduced mass transfer.

[0010] Embodiments of the invention have the advantage that a patterned light emitting organic structure may be formed in a single step of exposure of the PLC material to light. Consequently, in some embodiments a patterned light emitting organic structure may be formed in a rapid, materials and energy efficient manner and at relatively low cost.

[0011] Embodiments of the invention are useful in telecommunications, quantum information processing and display devices such as emitters including lasers and radiation detectors, OLEDs, backlights and any other suitable devices.

[0012] The period of the periodic variation of refractive index of a PC according to embodiments of the invention may be in the range of from around 120 nm to around 3000 nm, optionally from around 350 nm to around 2000 nm, further optionally from around 400 nm to around 1800 nm.

[0013] Preferably the polymerisable material comprises a polymerisable liquid crystal (PLC) material.

[0014] The polymerisable material may comprise a polymerisable light emitting liquid crystal material.

[0015] The polymerisable material may comprise a polymerisable light emitting nematic liquid crystal material.

[0016] Optionally, the polymerisable material may comprise a semiconducting material.

[0017] Optionally, the polymerisable material may comprise an amorphous material.

[0018] Preferably the method does not require a further step of polymerisation of the polymerisable material thereby to form said photonic crystal structure.

[0019] Preferably the step of exposing the polymerisable material to said optical radiation causes polymerisation of said polymerisable material thereby to form said photonic crystal structure.

[0020] The step of exposing the polymerisable material to said optical radiation may be performed with the polymerisable material at room temperature.

[0021] The step of exposing the polymerisable material to said optical radiation may be performed with the polymerisable material at a temperature in the range from around 15°C to around 100°C, optionally from around 20°C to around 70°C.

[0022] The method may further comprise the step of annealing the structure following irradiation at an elevated temperature, the elevated temperature being optionally in the range from around 15°C to around 100°C, further optionally from around 20°C to around 70°C.

[0023] The photonic crystal structure may comprise a light emitting polymer, the structure having a plurality of laterally spaced apart portions corresponding to said structure to be patterned wherein the light emitting polymer has a thickness different from portions of the structure between the laterally spaced apart portions.

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[0024]   The laterally spaced apart portions may have a thickness greater than the portions of the structure between the laterally spaced apart portions.

[0025]   The portions of the structure between the laterally spaced apart portions may have a thickness of substantially zero.

[0026]   The laterally spaced apart portions may have a thickness lower than the portions of the structure between the laterally spaced apart portions.

[0027]   The laterally spaced apart portions may have a thickness of substantially zero.

[0028]   The laterally spaced apart portions are preferably substantially periodically spaced apart.

[0029]   The structure to be patterned may comprise a plurality of spaced apart ridge members.

[0030]   Other shapes of spaced apart features are also useful.

[0031]   The structure to be patterned may comprise a plurality of spaced apart post members.

[0032]   The post members may be spaced apart in a plurality of non-parallel directions.

[0033]   The structure to be patterned may comprise a plurality of spaced apart wells.

[0034]   The wells may be spaced apart in a plurality of non-parallel directions.

[0035]   The wells may be arranged to provide a periodic structure having a period corresponding to a photonic bandgap whereby optical radiation of a prescribed one or more wavelengths is substantially prevented from propagating laterally through the structure along a direction in which one or more wells are provided.

[0036]   The polymerisable material may comprise a light-emitting material and the one or more wavelength may correspond to one or more wavelengths emitted by the light emitting material.

[0037]   An emission wavelength of the light-emitting material may overlap an edge of the photonic band-gap.

[0038]   Preferably the wells are periodically spaced apart.

[0039]   A prescribed one or more wells of the structure may not be formed or may be displaced whereby an emitter of optical radiation may be provided.

[0040]   The emitter may correspond to a nanocavity micro-emitter.

[0041] The method may comprise the step of providing a phase mask and exposing the mask to optical radiation thereby to expose the layer of polymerisable material to optical radiation thereby to pattern the photonic crystal structure.

[0042] The step of exposing the polymerisable material to said optical radiation at locations corresponding to a photonic crystal structure to be patterned comprises the step of providing an optical interference pattern using holographic or other methods.

[0043] The photopolymerisable material may comprise a reactive mesogen having the formula B-S-A-S-B, wherein A is a chromophore, S is a spacer, and B is an end group which is susceptible to photopolymerisation.

[0044] Preferably A is a chromophore of general formula $-(Ar-Fl)_n-Ar$ wherein Ar is an aromatic diradical or a heteroaromatic diradical bonded linearly or substantially linearly to adjoining diradicals, or a single bond; Fl is a 9,9-dialkyl substituted fluorene diradical joined to adjoining diradicals at the 2 and 7 positions; the Ar and Fl diradicals may be chosen independently in each of the n subunits of the chromophore; and $1 \leq n \leq 10$; S is a spacer; and B is an endgroup which is susceptible to polymerisation.

[0045] The phonotic crystal structure may comprise a material having a periodic variation in refractive index.

[0046] The variation in refractive index may have a period of from around 120 nm to around 3000 nm.

[0047] The variation in refractive index may have a period of from around 350 nm to around 2000 nm, preferably from around 400 nm to around 1800 nm, more preferably around 400 nm to around 1600 nm, optionally around 400 nm to around 1000 nm, optionally around 1550 nm.

[0048] Other materials are also useful. Any other suitable photopolymerisable material may be used such as a photopolymerisable insulating liquid crystal material or non liquid crystal material of sufficiently high refractive index. For example, a material having a refractive index greater than or substantially equal to 2. Non light emitting and non-semiconducting materials may be useful. Thus, passive photonic crystal materials may be useful.

[0049] In a second aspect of the invention there is provided a photonic crystal structure comprising a photopolymerised material patterned by photoinduced mass transfer.

[0050] There may also be envisaged a method of forming a light emitting and/or semiconducting polymer structure comprising the steps of:

forming a layer of a polymerisable liquid crystal (PLC) material, the PLC material being arranged to experience photoinduced mass transfer upon irradiation with optical radiation;

exposing the PLC material to said optical radiation at locations corresponding to a
5   structure to be patterned thereby to cause said photoinduced mass transfer.

Brief Description of the Drawings

[0051]   Embodiments of the invention are further described hereinafter with reference to the accompanying drawings, in which:

10   Figure 1 shows a chemical structure of a compound used for photoembossing surface structures according to embodiments of the present invention;

Figure 2 shows an arrangement for exposing a layer of material to optical radiation thereby to pattern a nanostructure;

Figure 3 shows (a) a 3D image of a typical grating formed using a 1 micron phase
15   mask and (b) a surface profile of the grating parallel to a direction of the grating wave-vector;

Figure 4 shows a distributed feedback laser device structure;

Figure 5 shows a process of in-situ photopolymerisation of a liquid crystal;

Figure 6 shows a phase mask and the interference pattern produced on
20   transmission through it according to an embodiment of the invention;

Figure 7 shows a relative orientation of a reactive mesogen and stripes of a stripe structure during a course of patterning of the structure; and

Figure 8 shows a photonic bandgap structure containing a defect.

Detailed Description of the Invention
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[0052]   In one embodiment of the invention a semiconducting liquid crystal (LC) shown schematically in Figure 1 is used to form a photonic crystal (PC) structure.

[0053]   The transition temperatures of the material are:

30   **Cr 52°C N 143°C I; Tg 0°C**

[0054] The central core or chromophore is light-emitting and semiconducting. It has diene end-groups, which are crosslinkable by irradiation with ultraviolet light. Different crosslinking groups can be alternately used.

[0055] In one example of the fabrication of a nanostructure, sample preparation and exposure were carried out in a glove box under nitrogen atmosphere with humidity of less than 1 ppm and an oxygen concentration less than 30 ppm. A cleaned 25 x 25 mm^2 glass substrate was used in some examples, optionally covered with a layer of poly(3,4-ethylenedioxythiophene) (PEDOT) around 40 nm thick. The PEDOT layer can be used to improve the film forming quality of the LC.

[0056] PLC films of different thicknesses were applied by spin-coating the compound dissolved in a chlorobenzene solvent. A typical spin speed is 900 rpm for 30 s. The compound concentrations varied between 0.02-0.03 mg/µl and higher concentrations can also be used for thicker films. For example, the thickness of a film prepared with the standard settings 900 rpm, 0.03 mg PV237 in 1 µl chlorobenzene was 80 ± 5 nm. After spin-coating all films were heated at 5°C/min to 65°C, where they were cured for 15 min and then cooled down to RT again at 5°C/min. Next the samples were patterned and crosslinked by irradiation with ultraviolet light from a HeCd laser at 325 nm through a +1/-1 phase mask of period 530 nm or 1 micron.

[0057] An arrangement for patterning and cross-linking according to an embodiment of the invention is shown in Figure 2. A beam of laser radiation 10 is incident upon a phase mask 20.

[0058] A phase mask 20 formed from a material transparent to the laser radiation employed is provided. The mask 20 has a variation in thickness arranged to retard light passing through the mask at periodic locations thereby to form an interference pattern on a layer 55 of PLC material to be patterned. The PLC layer 55 was formed on a substrate 50 oriented in a plane parallel to that of the phase mask 20 and provided in close proximity thereto.

[0059] The phase mask 20 acts as a precision diffraction grating giving an interference pattern of intensity modulated light. The period of the intensity pattern is equal to either the period of the phase mask or half the period.

[0060] Other methods, e.g. holography, can also be used to produce an interference pattern of the required period.

[0061] The phase mask 20 is very delicate and is sensitive to the vibrations or misalignment. The mask alignment with respect to the polarisation direction of the laser was judged by eye with a probable error of ± 3°. Two polarisation configurations were

used: the polarisation of the laser was either parallel or perpendicular to the wave vector of the phase mask 20.

[0062] In one example, the mask 20 was placed directly on top of the PLC layer 55 and the mask 20 and substrate 50 pressed together as they were attached to a hot stage below with several screws, whose heads were pressing the mask down.

[0063] The mask 20 was then exposed to laser radiation thereby to cause photoinduced mass transfer of PLC material of PLC layer 55.

[0064] A laser radiation energy of 600 J/cm^2 was required in order to produce a patterned liquid crystal (LC) film that was insoluble to the solvent used for deposition during subsequent processing.

[0065] The substrate 50 was moved with respect to the mask 20 by means of an xy-stage so than a larger area than that of the laser beam could be irradiated. The speed of travel of the xy-stage was kept between 0.48 and 0.52 mm/s.

[0066] A doughnut shaped laser beam was generated, 4 mm in diameter. The laser power of the beam was measured before the crosslinking was started and varied between 52-53 mW. The mask's attenuation of the initial beam as well as the splitting into two beams were also considered in the fluence calculation. Crosslinking times were adapted accordingly so that all areas were crosslinked with at least 600 J/cm^2 or higher.

[0067] The phase mask 20 was a 530 nm phase mask (by Ibsen Photonics) fabricated to match the wavelength of the HeCd laser. It was formed from fused silica and split the beam in 5 mW for the 0th order and 22 mW for − 1 and +1 order respectively. For the fluence calculations 22 mW was used. In this particular example no higher orders were present.

[0068] A 1 μm mask was also used. The working wavelength was unknown but was also in the ultraviolet region. With 52 mW initial laser power about 32-38 mW were measured for the 0th order and 5 mW for -1 and +1 order. In this case the crosslinking time was calculated with 32 mW as laser power to ensure that the layer would be fully crosslinked. There were also higher orders observable, but these could not be measured singly. They could however not have been strong as the total power measured directly behind the mask lay between 45-47mW.

[0069] The samples were irradiated either at RT or 65°C. At the latter temperature the compound is in a nematic state. No further processing was carried out. A surface grating was spontaneously formed by irradiation with the spatially modulated light from the phase mask.

[0070]   An atomic force microscope was used to measure the surface morphology of the thin films after irradiation. The grating was preserved after washing in chlorobenzene solvent, indicating that it had become insoluble.

[0071]   Figure 3 shows (a) a 3D image of a typical grating formed using a 1 micron phase mask and (b) a surface profile of the grating parallel to a direction of the grating wave-vector.

[0072]   The process of photo-embossing described above has the advantage that patterning of a film of a PLC material may be performed by mass transfer upon irradiation with patterned light, such as patterned ultra-violet (UV) light.

[0073]   In the example of Figure 3, surface relief amplitudes of up to 140 nm were obtained even though the as-deposited films (with smooth surface) were only around 80 nm in thickness. Grating periods as small as 260 nm were achieved in some examples.

[0074]   The photo-embossing process may be performed in a single step with no post-annealing or wet etch required, in some embodiments. Thus the method is highly suited to high-throughput manufacturing technologies.

[0075]   In some embodiments the patterned films are cross-linked during the course of exposure to laser irradiation at the patterning stage, providing robust, environmentally stable structures.

[0076]   Photoinduced mass transfer is understood to be due to monomer diffusion from troughs to peaks in intensity of incident optical radiation. It is distinct from laser ablation, where material is physically removed from a surface by laser radiation.

[0077]   In one embodiment, the method may be used to produce an organic laser device by patterning a series of stripes of light emitting semiconductor polymer material. Light-emitting dopants could be incorporated to tailor the wavelength of emission.

[0078]   A spacing between the stripes (or 'grating period') may be selected in order to provide distributed feedback (DFB) along a length of the material, which may provide a laser cavity 170. Two-dimensional structures could also be used to provide distributed feedback in both in-plane directions.

[0079]   The grating period, Λ may be selected according to the equation:

$$m\lambda = 2n_{eff}\Lambda$$

where m is an integer (the 'order' of the DFB structure), λ is the wavelength of light emitted by the light emitting polymer material and n_{eff} is the refractive index of the polymer material at wavelength λ. It is to be understood that n_{eff} is around 2 for the PLC materials discussed herein. Other values of n_{eff} can be obtained by changing the chemical structure of the material or the lasing wavelength.

[0080] It is to be understood that λ may be any suitable wavelength. For example, λ may be in the range from around 400 nm to around 3 microns (μm). In some embodiments λ is in the range from around 400 nm to around 2000 μm. In some embodiments λ is in the range from around 400 nm to around 1600 μm.

[0081] For m = 1 (first order structure) Λ is typically in excess of 120 nm.

[0082] For m = 2 (second order structure) enhanced outcoupling efficiency of light is achieved, overcoming the limit

$$\eta = \frac{0.75}{n^2}$$

where η is the outcoupling efficiency and n is the refractive index.

[0083] This limit occurs because light emitted at a wavelength greater than the critical angle is waveguided in the thin film.

[0084] A suitable DFB laser structure is shown in Figure 4 (not to scale). It can be seen that a structured layer 155 of an organic light emitting LC material has been formed on a glass substrate 150 by photo-induced mass transfer as described above. Optical pumping of the layer 155 with laser irradiation may be used to cause light emission by the layer 155.

[0085] It is to be understood that for m = 1, radiation is primarily emitted by the structure parallel to the x-axis of Figure 4 (i.e. parallel to the grating wavevector). For m = 2, radiation is primarily emitted parallel to the z-axis, i.e. normal to the plane of the layer 155.

[0086] It can be seen that a thickness of the layer 155 varies between t1 at a peak in thickness and t2 at a trough where t1 is greater than t2. In some embodiments t2 is substantially zero. In other words the layer 155 is substantially in the form of a series of pillars or stripes spaced apart along a length of the cavity 170.

[0087] The laser device structure of Figure 4 may be optically pumped. Alternatively or in addition it may electrically pumped.

[0088] The DFB structure can also be incorporated into an OLED to improve the outcoupling efficiency.

[0089] Figure 5 shows a chemical structure of a compound 105 used for photoembossing surface structures according to embodiments of the present invention (a) before exposure to optical radiation and (b) after exposure to optical radiation. Following exposure to optical radiation the reactive mesogens (RMs) 105 crosslink to form a stable polymer structure.

[0090] The RMs 105 each comprise a chromophore group C coupled to and sandwiched between two spacer groups S, each spacer group having a polymerisable group PG at or close to a free end thereof.

[0091] Figure 6(a) is a schematic illustration of a phase mask 20 during a course of exposure to laser radiation. It is to be understood that the two first order beams of optical radiation emerge through the phase mask 20 with zero order ideally completely suppressed.

[0092] Figure 6(b) shows a calculated intensity variation at a surface exposed to optical radiation transmitted through the phase mask of Figure 6(a) under ideal conditions where no zero order beams are transmitted. It can be seen that the optical radiation generates a stripe pattern directly on the exposed surface.

[0093] Figure 6(c) shows a calculated intensity for a 'real' phase mask having some zero order beams. It can be seen that some 3D peaks in light intensity are caused to occur on the exposed surface, leading to a deviation from the ideal exposure conditions of FIG. 6(a) for some embodiments of the invention in which an intensity of optical radiation exposing the surface is substantially uniform along a length of each stripe.

[0094] In some embodiments, polarised laser radiation may be employed to expose the RMs 105. It is found that longitudinal axes of RM molecules tend to become aligned parallel to a direction of electric polarisation of optical radiation incident upon the PLC material. Thus, a direction of orientation of the RM molecules may be controlled by controlling the polarisation of incident laser radiation.

[0095] The RM molecules also show anisotropic viscosity, their viscosity being lower along a direction parallel to the longitudinal axis. Thus, in the case that the electric field is oriented parallel to a wavevector of the stripe pattern as shown in Figure 7(b), i.e. normal to a longitudinal axis of the stripes and in the plane of the stripe pattern, more rapid mass transport occurs along the direction parallel to the wavevector of the stripe pattern compared with the situation in which the electric field is oriented normal to the wavevector, parallel to the longitudinal axis of stripes of the stripe pattern as shown in Figure 7(a).

Thus, stripe patterns are generally deeper when the electric field vector of the laser radiation is oriented parallel to the wavevector.

[0096] Figure 8 shows a structure in which a layer 255 of PLC material has been exposed to optical radiation thereby to form a 2D array of 'holes' in the layer 255. The holes are spaced apart with a period corresponding to that required to form a photonic band gap at a prescribed wavelength. Similar periods are required for the first DFB structure discussed above. For a wavelength of 600 nm and an effective index of 1.8, a spacing of 166 nm is estimated. Finite element modelling is required to obtain the best depth, shape and relative size of hole. It is understood that good results are expected when the film thickness is equal to wavelength/2.

[0097] In the embodiment of Figure 8 it can be seen that the array of holes is 'defective' in that one hole is missing in region 285 of the layer 255.

[0098] Region 285 may be used to generate optical radiation with optical or electrical excitation. It is to be understood that light emitted by region 285 may be prevented from travelling laterally through the layer 255 by the array of holes 282. Thus, a relatively high intensity beam of light is emitted from the region 285 in a direction normal to a plane of the layer 255.

[0099] Such a structure has the advantage that a source of radiation of relatively high finesse may be produced.

[00100] In some embodiments the region 285 is produced by exposing the region 285 to light to cause crosslinking of the PLC material provided in that area. Subsequently, the film is exposed to light to pattern the holes 282 in region 255 in the film by photo-induced mass transport (or mass transfer).

[00101] The region 285 where the holes are missing may also be referred to as a 'nanocavity'.

[00102] It is to be understood that inverse structures may also be formed in order to provide a photonic band gap (PBG) structure. In other words, region 285 may be surrounded by discrete spaced apart pillars instead of a material having holes 282 therein. The pillars may be of a size and spacing corresponding to that of the holes 282.

[00103] Organic 2D photonic crystals (PCs) with full PBGs (with or without nano-cavities) have not been demonstrated previously. Furthermore, conjugated light-emitting/ semiconducting polymers have never been photo-embossed.

[00104] In our case photo-embossing will create a 2D array of nanopillars surrounded by air or the inverse structure. The emission of embedded light-emitters is suppressed in the

PBG but can be substantially enhanced at its edges. Spontaneous emission that is not extracted from the device contributes to losses. Therefore, inhibiting undesirable spontaneous light emission and redistributing the energy into useful forms will have a major impact on display efficiency. 2D PCs require high contrast between regions of low and high refractive index to achieve a *full* PBG. This is a spectral region where light propagation is forbidden in all directions in the plane of the film.

[00105] As a result of their high conjugation, luminescent LCs according to embodiments of the present invention have a high refractive index ($n_{average}$ > 2) at the emission peak of a thiophene-fluorene nematic, (K.L. Woon, Liq. Cryst. *32*, 1191 (2005)). This is significantly bigger than the minimum value of 1.6. predicted to give a TE-like full PBG (opt Express2007). The material is luminescent and emits TE modes only, since the LCs lie in the plane of the thin film. TM modes need not be considered, which lowers the constraints to achieve a full PBG.

[00106] The photoluminescence quantum efficiency (PLQE) of a thin film of the material used in the structure of Figure 3(a) is 0.27. Other nematic LCs with PLQE >0.50 have been synthesised.

[00107] In some embodiments relatively deep nanostructures with a relatively small period are useful. In some embodiments, polymeric LC material emitting in the region 500-600 nm were used, thereby requiring a sub-200 nm grating period.

[00108] A second approach is to use Förster energy transfer to effectively excite the emission of dopants at longer wavelengths. Light-emitting semiconductor nanocrystals may be used as dopants.

[00109] These materials have two advantages: firstly they increase the refractive index of the material in which they are provided; secondly, their narrow band emission is tunable according to the size of particle and so can be matched to the PBG bandedge.

[00110] Defects or nanocavities may be introduced by perturbating the PC lattice locally, e.g. by omitting a hole (which may be an air hole) as discussed above.

[00111] When a nanocavity or defect of volume *V* is placed in a 2D PC, photons can be effectively trapped for a long time with many interesting effects. When the *Q* factor (a measure of the ability to store light) of the cavity is sufficiently large, the emission coupled to the single-cavity mode can be substantially enhanced by a factor of *Q/V*; this is known as the Purcell effect. The nanocavity effectively slows down the speed of light, sometimes by many orders of magnitude.

[00112] For example, quantum information processing requires the quantum state of light to be stored for a sufficiently long time to enable quantum operations. Slowing and

trapping light are ways to achieve this. One of the current limitations of integrated optical signal processing is an easily integrated light source. Lasers generally emit a large amount of undesired spontaneous emission before they start to lase, which degrades their efficiency. Therefore, so-called "thresholdless lasers," that emit almost no spontaneous emission, are feasible in a nanocavity, where emission is suppressed in all modes apart from the cavity mode. Our materials present an extremely simple and unique way to fabricate defects.

[00113] In some embodiments, an area of diffraction-limited size of a thin film layer is cross-linked before irradiation through the phase mask. (The nonlinear response of photopolymerisation may allow an even smaller area to be fixed.)

[00114] Surface relief patterns cannot be formed in these regions because of their high viscosity and they will form nanocavities.

[00115] A further advantage of our materials is that they are easily aligned with very high order parameters (S>0.9). Photoalignment methods can be used where the alignment direction is patternable. The transition dipole moments of the LC emitters are oriented along the rod axis, so that they all emit in a single in-plane direction when they are uniformly aligned. This gives the added advantage that the cavity needs only to apply a 1D rather than 2D PC structure to completely suppress emission in the plane.

[00116] Photo-embossing (i.e. photo-induced mass transfer) is a novel method to optically imprint semiconducting organic materials and its mechanism is not yet evaluated. Similar photoinduced gratings have previously been generated in transparent thin films. These materials are extensively researched for optical filters, holography, antireflection surfaces as well as resonant cavities. They are passive unlike nematic semiconductor structures described herein which show efficient light-emission and semiconducting properties. Unlike grating formation in passive materials, nanostructures described herein may be formed at room temperature with sub-micron periods and do not require heating to develop a latent image. A photoinduced birefringence is obtained during their formation suggesting some similarities with grating formation in azo materials.

[00117] Although embodiments of the invention described herein represent the first direct method to optically imprint semiconducting organic materials, photoinduced gratings have previously been generated in transparent thin films of three different classes of materials. These materials are extensively researched for optical filters, holography, antireflection surfaces as well as resonant cavities. All three classes of materials are passive unlike our nematic semiconductor which show efficient light-emission and semiconducting properties. Photoembossed surface relief structures have been formed in non-semiconducting photopolymers primarily used for holography. The photopolymer layer is irradiated with

spatially modulated UV light, creating radicals in the illuminated areas. The free radicals are captured in the glassy matrix but there is little polymerisation because monomer diffusion to the reactive sites is restricted. After exposure the sample is heated above a threshold temperature, where the sample changes from a solid to a more mobile, liquid-like

5   state. The polymerisation of the monomer in the exposed areas changes the chemical potential and provides a driving force for the monomers to diffuse from the unexposed to the exposed areas. The mass transport creates a volume increase in these regions and, consequently, a surface relief structure. Surface relief gratings can only be made in photopolymers at low spatial frequencies ($<10^6$ m^{-1}).

10   [00118] Typically aspect ratios (feature height to width) are <0.05, although very high aspect ratios have recently been observed. The photoembossing of surface relief structures has also been demonstrated by polymerisation of a nematic liquid crystals monomer blend, which is transparent and insulating. The material was locally irradiated in the nematic phase to produce a latent image which developed into a topological feature by

15   annealing above the clearing point. Surface structures can also be reversibly formed in materials containing azobenzene moieties or other photoisomerisable groups. In this case gratings are formed by mass transport even in the glassy state. The formation of gratings has also some unusual polarisation effects; large amplitudes are obtained by interference of two orthogonal circularly polarised beams even though there is no intensity modulation.

20   Several mechanisms for photoinduced mass migration of azobenzene molecules have been suggested e.g. the gradient force of the optical electric field, isomerisation-driven free volume expansion, the mean field theory of anisotropic intermolecular interaction etc.

[00119] In some embodiments of the invention a 2D phase is used to create a 2D array of nanopillars surrounded by air or the inverse structure described above with reference to

25   Figure 8. Pillars of relatively large amplitude are preferred in some embodiments and therefore almost complete transfer of material from the un-irradiated regions to the exposed regions of the film is preferred.

[00120] PLC materials suitable for use in embodiments of the invention include, for example, a light emitting or charge transporting polymer comprising a polymer formed from

30   reactive mesogens having the formula:

B-S-A-S-B

wherein A is a chromophore of general formula –(Ar-Fl)$_n$-Ar- wherein Ar is an aromatic diradical or a heteroaromatic diradical bonded linearly or substantially linearly to adjoining diradicals, or a single bond; Fl is a 9,9-dialkyl substituted fluorene diradical joined to

35   adjoining diradicals at the 2 and 7 positions; the Ar and Fl diradicals may be chosen

independently in each of the n subunits of the chromophore; and 1 ≤ n ≤ 10; S is a spacer; and B is an endgroup which is susceptible to polymerisation.

[00121] Optionally, the endgroup B may be susceptible to photopolymerisation.

[00122] Optionally, the polymer may be formed by photopolymerisation.

[00123] Optionally, the endgroup (B) comprises a diene and the diene may be selected from the group consisting of 1,4 dienes, 1,5 dienes and 1,6 dienes. Optionally, the diene functionalities are separated by an aliphatic linkage. Alternatively, the diene functionalities may be separated by an inert linkage, which is optionally selected from the group consisting of ether and amine linkages.

[00124] Optionally, the light emitting or charge transporting polymer is a light emitting electroluminescent polymer.

[00125] Optionally, the light emitting or charge transporting polymer is a hole transporting polymer.

[00126] Optionally, the light emitting or charge transporting polymer is an electron transporting polymer.

[00127] Optionally, the light emitting or charge transporting polymer is substantially photoinititor free.

[00128] In one embodiment of the polymer of the above formula, 2 ≤ n ≤ 7.

[00129] The invention also envisages a process for forming a light emitting or charge transporting polymer comprising photopolymerisation of a reactive mesogen having the formula:
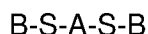
B-S-A-S-B

wherein A is a chromophore of general formula-$(Ar-Fl)_n$-Ar- wherein Ar is an aromatic diradical or a heteroaromatic diradical bonded linearly or substantially linearly to adjoining diradicals, or a single bond; Fl is a 9,9-dialkyl substituted fluorene diradical joined to adjoining diradicals at the 2 and 7 positions; the Ar and Fl diradicals may be chosen independently in each of the n subunits of the chromophore; and 1 ≤ n ≤ 10; S is a spacer; and B is an endgroup which is susceptible to photopolymerisation.

[00130] In said process, the endgroup (B) optionally comprises a diene, and the diene may be selected from the group consisting of 1,4 dienes, 1,5 dienes and 1,6 dienes. Optionally, the diene functionalities are separated by an aliphatic linkage. Alternatively, the diene functionalities may be separated by an inert linkage, which is optionally selected from the group consisting of ether and amine linkages.

[00131] In said process, the photopolymerisation of the reactive mesogen optionally results in a light emitting electroluminescent polymer, a charge transporting polymer or an electron transporting polymer.

[00132] Optionally, said photopolymerisation substantially occurs without a photoinitiator.

[00133] The invention also envisages a device comprising a polymer layer comprising a light emitting or charge transporting polymer comprising a polymer formed from reactive mesogens, as hereinbefore defined. Optionally, said device is one of an electronic device, a light emitting device, a display device, an organic light emitting device, a lighting element, a backlight and a laser.

[00134] The invention also provides a material for forming a light emitting or charge transporting polymer comprising a reactive mesogen having the formula:
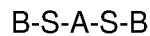
B-S-A-S-B

wherein A is a chromophore of general formula $-(Ar-Fl)_n-Ar-$ wherein Ar is an aromatic diradical or a heteroaromatic diradical bonded linearly or substantially linearly to adjoining diradicals, or a single bond; Fl is a 9,9-dialkyl substituted fluorene diradical joined to adjoining diradicals at the 2 and 7 positions; the Ar and Fl diradicals may be chosen independently in each of the n subunits of the chromophore; and $1 \leq n \leq 10$; S is a spacer; and B is an endgroup which is susceptible to polymerisation.

[00135] Optionally, in said material, the endgroup B may be susceptible to photopolymerisation.

[00136] Optionally, said material may be formed by photopolymerisation.

[00137] Optionally, in said material, the endgroup (B) comprises a diene and the diene may be selected from the group consisting of 1,4 dienes, 1,5 dienes and 1,6 dienes. Optionally, the diene functionalities are separated by an aliphatic linkage. Alternatively, the diene functionalities may be separated by an inert linkage, which is optionally selected from the group consisting of ether and amine linkages.

[00138] Optionally, in said material, the light emitting or charge transporting polymer is a light emitting electroluminescent polymer, a hole transporting polymer or an electron transporting polymer.

[00139] Optionally, in said material, the light emitting or charge transporting polymer is substantially photoinititor free.

[00140] With reference to the above formula, in one embodiment of said material, $2 \leq n \leq 7$.

[00141] The invention also envisages a backlight or display which includes a polymer formed from reactive mesogens having the formula:
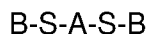
B-S-A-S-B

wherein A is a chromophore of general formula $-(Ar-Fl)_n-Ar-$ wherein Ar is an aromatic diradical or a heteroaromatic diradical bonded linearly or substantially linearly to adjoining diradicals, or a single bond; Fl is a 9,9-dialkyl substituted fluorene diradical joined to adjoining diradicals at the 2 and 7 positions; the Ar and Fl diradicals may be chosen independently in each of the n subunits of the chromophore; and $1 \leq n \leq 10$; S is a spacer; and B is an endgroup which is susceptible to polymerisation. In said backlight or display, optionally said polymer has $2 \leq n \leq 7$.

[00142] Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of them mean "including but not limited to", and they are not intended to (and do not) exclude other moieties, additives, components, integers or steps. Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

[00143] Features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

[00144] The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

CLAIMS

1.   A method of forming a photonic crystal structure by means of a polymerisable material comprising the steps of:

       forming a layer of a polymerisable material, the polymerisable material being arranged to experience photoinduced mass transfer upon irradiation with optical radiation; and

       exposing the polymerisable material to said optical radiation at locations corresponding to a photonic crystal structure to be patterned thereby to form said photoinduced mass transfer.

2.   A method as claimed in claim 1 wherein the polymerisable material comprises a polymerisable liquid crystal (PLC) material.

3.   A method as claimed in claim 1 or 2 wherein the polymerisable material comprises a polymerisable light emitting liquid crystal material.

4.   A method as claimed in claim 1, 2 or 3 wherein the polymerisable material comprises a polymerisable light emitting nematic liquid crystal material.

5.   A method as claimed in any one of claims 1 to 4 wherein the polymerisable material comprises a semiconducting material.

6.   A method as claimed in any preceding claim wherein the polymerisable material comprises an amorphous material.

7.   A method as claimed in any preceding claim wherein the method does not require a further step of polymerisation of the polymerisable material thereby to form said photonic crystal structure.

8.   A method as claimed in any preceding claim wherein the step of exposing the polymerisable material to said optical radiation causes polymerisation of said polymerisable material thereby to form said photonic crystal structure.

9.   A method as claimed in any preceding claim wherein the step of exposing the polymerisable material to said optical radiation is performed with the polymerisable material at room temperature.

10.   A method as claimed in any one of claims 1 to 8 wherein the step of exposing the polymerisable material to said optical radiation is performed with the polymerisable material at a temperature in the range from around 15°C to around 100°C, optionally from around 20°C to around 70°C.

11.   A method as claimed in any preceding claim further comprising the step of annealing the structure following irradiation at an elevated temperature, the elevated temperature being optionally in the range from around 15°C to around 100°C, further optionally from around 20°C to around 70°C.

12.   A method as claimed in any preceding claim wherein the photonic crystal structure comprises a light emitting polymer, the structure having a plurality of laterally spaced apart portions corresponding to said structure to be patterned wherein the light emitting polymer has a thickness different from portions of the structure between the laterally spaced apart portions.

13.   A method as claimed in claim 12 wherein the laterally spaced apart portions have a thickness greater than the portions of the structure between the laterally spaced apart portions.

14.   A method as claimed in claim 13 wherein the portions of the structure between the laterally spaced apart portions have a thickness of substantially zero.

15.   A method as claimed in claim 6 wherein the laterally spaced apart portions have a thickness lower than the portions of the structure between the laterally spaced apart portions.

5   16.   A method as claimed in claim 9 wherein the laterally spaced apart portions have a thickness of substantially zero.

17.   A method as claimed in any one of claims 12 to 16 wherein the laterally spaced apart portions are substantially periodically spaced apart.

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18.   A method as claimed in any preceding claim wherein the structure to be patterned comprises a plurality of spaced apart ridge members.

19.   A method as claimed in any preceding claim wherein the structure to be patterned
15   comprises a plurality of spaced apart post members.

20.   A method as claimed in claim 19 wherein the post members are spaced apart in a plurality of non-parallel directions.

20   21.   A method as claimed in any preceding claim wherein the structure to be patterned comprises a plurality of spaced apart wells.

22.   A method as claimed in claim 21 wherein the wells are spaced apart in a plurality of non-parallel directions.

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23.   A method are claimed in claim 21 or 22 wherein the wells are arranged to provide a periodic structure having a period corresponding to a photonic bandgap whereby optical radiation of a prescribed one or more wavelengths is substantially prevented from propagating laterally through the structure along a direction in which one or more wells are
30   provided.

24.   A method as claimed in claim 23 wherein the polymerisable material comprises a light-emitting material and the one or more wavelengths correspond to one or more wavelengths emitted by the light emitting material.

25.   A method as claimed in claim 24 wherein an emission wavelength of the light-emitting material overlaps an edge of the photonic band-gap.

26.   A method as claimed in any one of claims 21 to 25 wherein the wells are periodically spaced apart.

27.   A method as claimed in claim 26 wherein a prescribed one or more wells of the structure are not formed or are displaced whereby an emitter of optical radiation may be provided.

28.   A method as claimed in claim 27 wherein the emitter corresponds to a nanocavity micro-emitter.

29.   A method as claimed in any preceding claim comprising the step of providing a phase mask and exposing the mask to optical radiation thereby to expose the layer of polymerisable material to optical radiation thereby to pattern the photonic crystal structure.

30.   A method as claimed in any preceding claim wherein the step of exposing the polymerisable material to said optical radiation at locations corresponding to a photonic crystal structure to be patterned comprises the step of providing an optical interference pattern using holographic or other methods.

31.   A method as claimed in any preceding claim wherein the photopolymerisable material comprises a reactive mesogen having the formula B-S-A-S-B, wherein A is a chromophore, S is a spacer and B is an end group which is susceptible to photopolymerisation.

32.   A method as claimed in claim 31 wherein A is a chromophore of general formula –
(Ar-Fl)$_n$-Ar- wherein Ar is an aromatic diradical or a heteroaromatic diradical bonded
linearly or substantially linearly to adjoining diradicals, or a single bond; Fl is a 9,9-dialkyl
substituted fluorene diradical joined to adjoining diradicals at the 2 and 7 positions; the Ar
and Fl diradicals may be chosen independently in each of the n subunits of the
chromophore; and $1 \leq n \leq 10$; S is a spacer; and B is an end group which is susceptible to
polymerisation.

33.   A method as claimed in any preceding claim wherein the photonic crystal structure
comprises a material having a periodic variation in refractive index.

34.   A method as claimed in claim 33 wherein the periodic variation in refractive index
has a period of from around 120 nm to around 3000 nm.

35.   A photonic crystal structure comprising a photopolymerised material patterned by
photoinduced mass transfer.
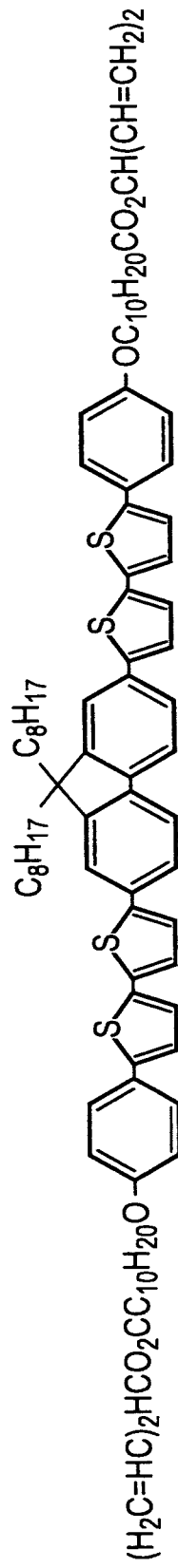
Chemical structure of compound used for photoembossing surface structures

FIG. 1
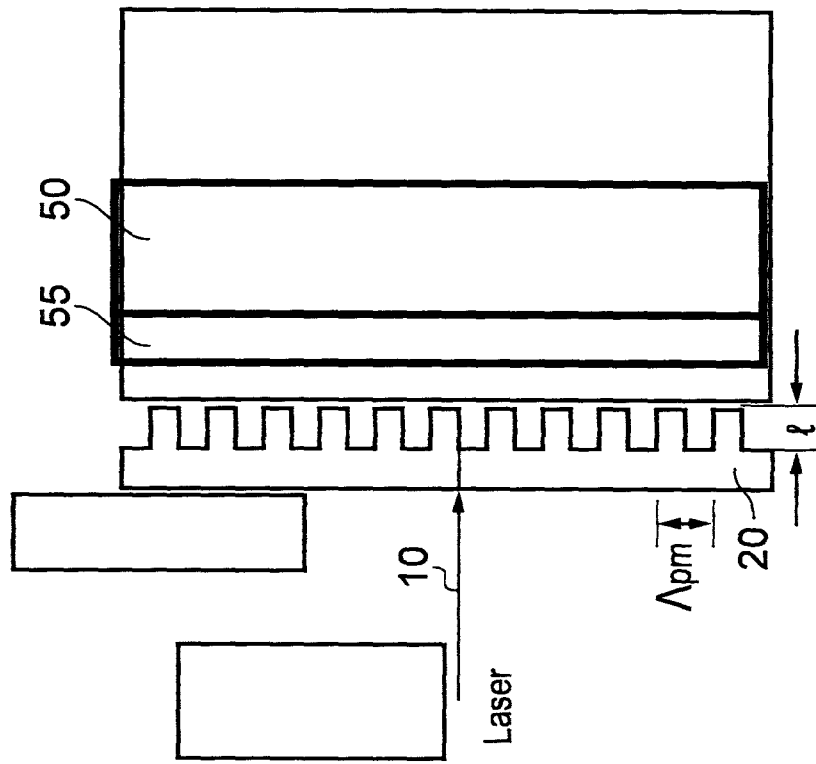
FIG. 2
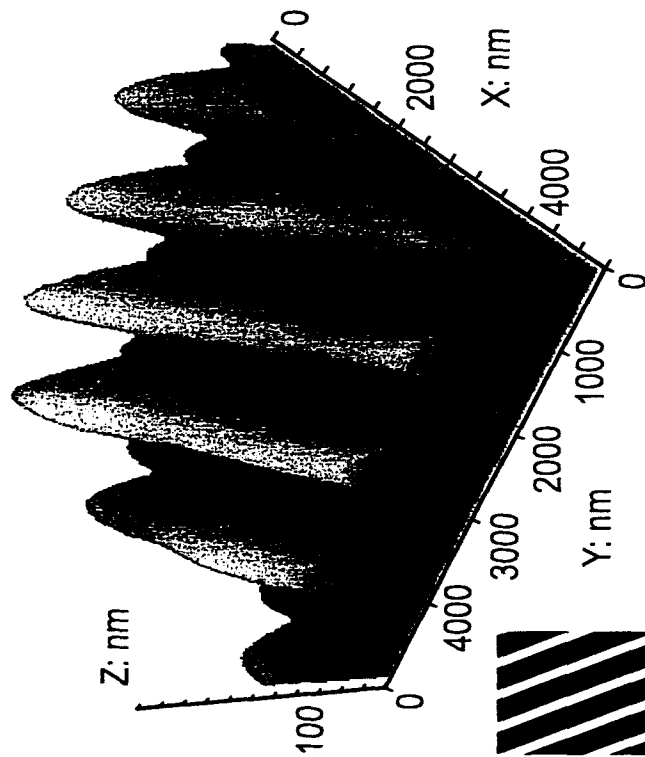
FIG. 3b
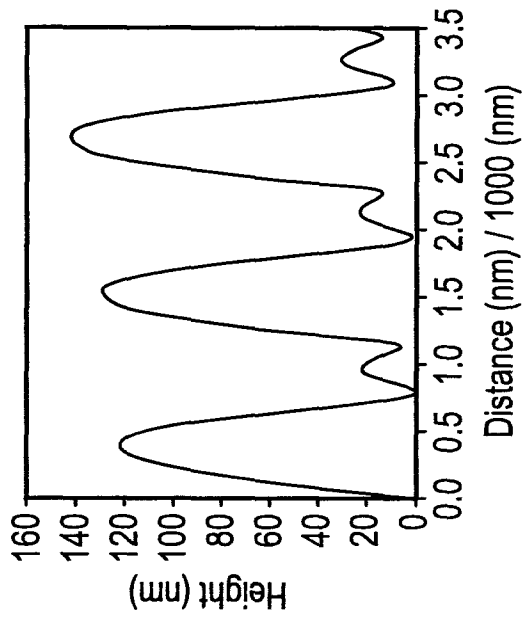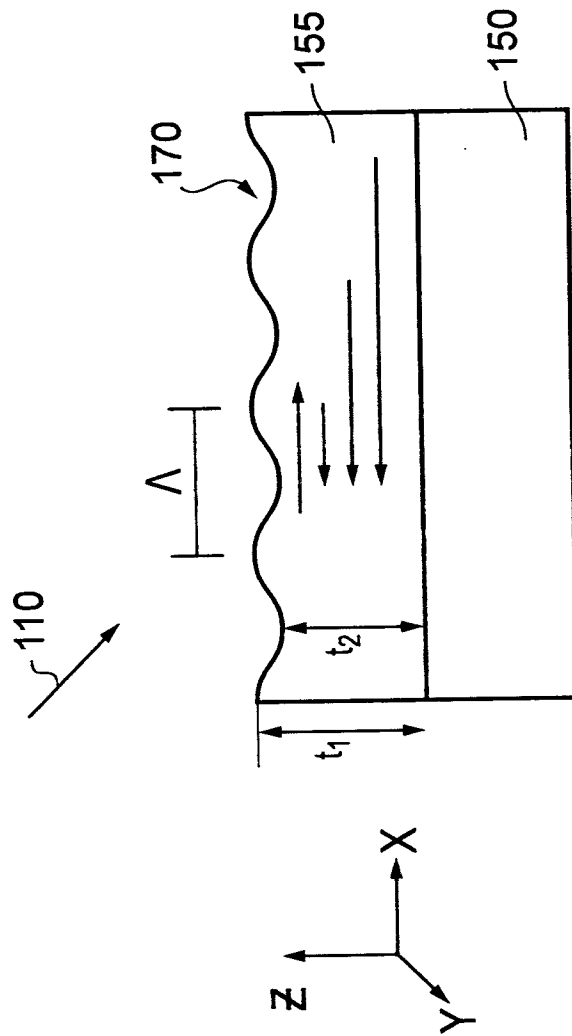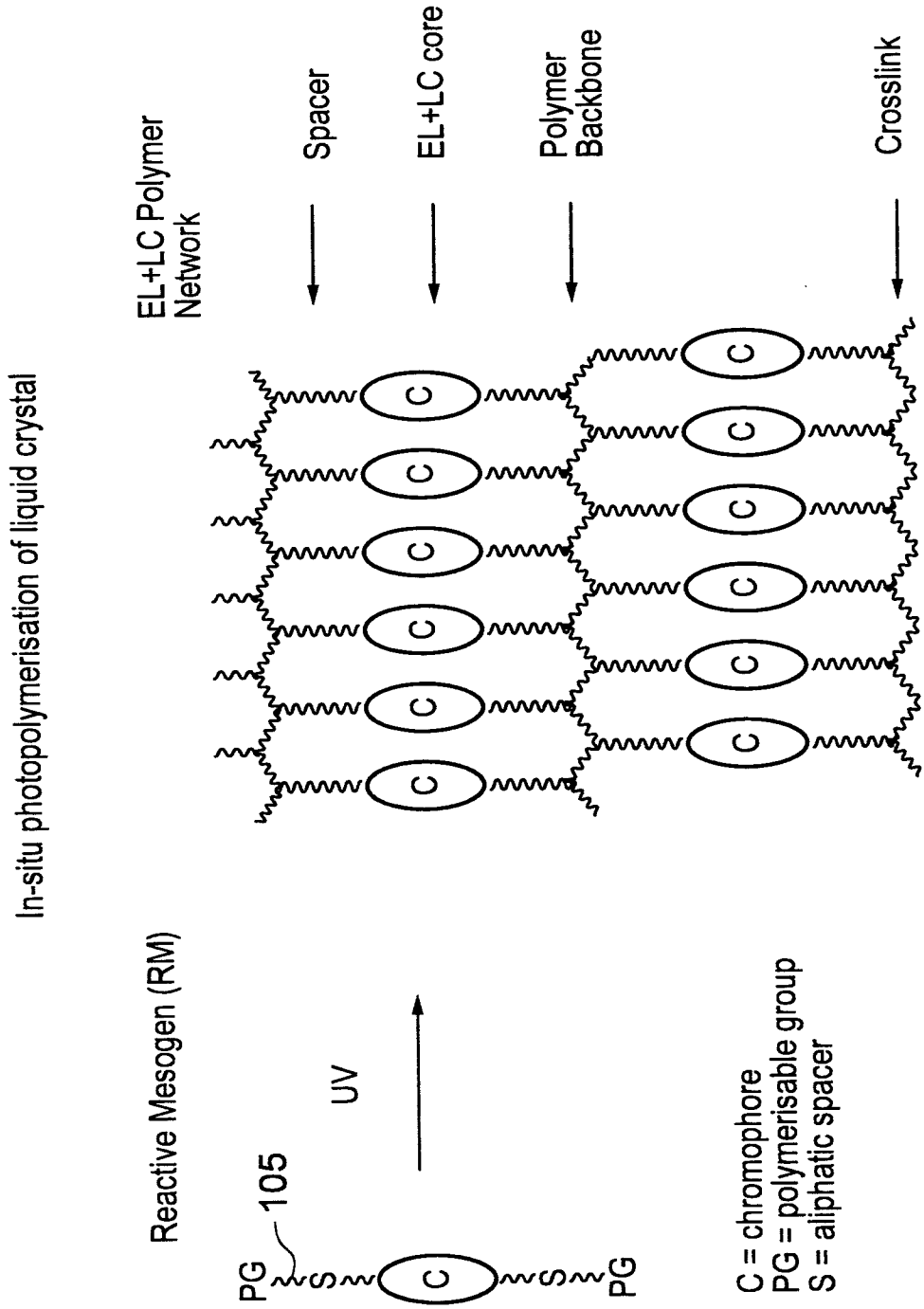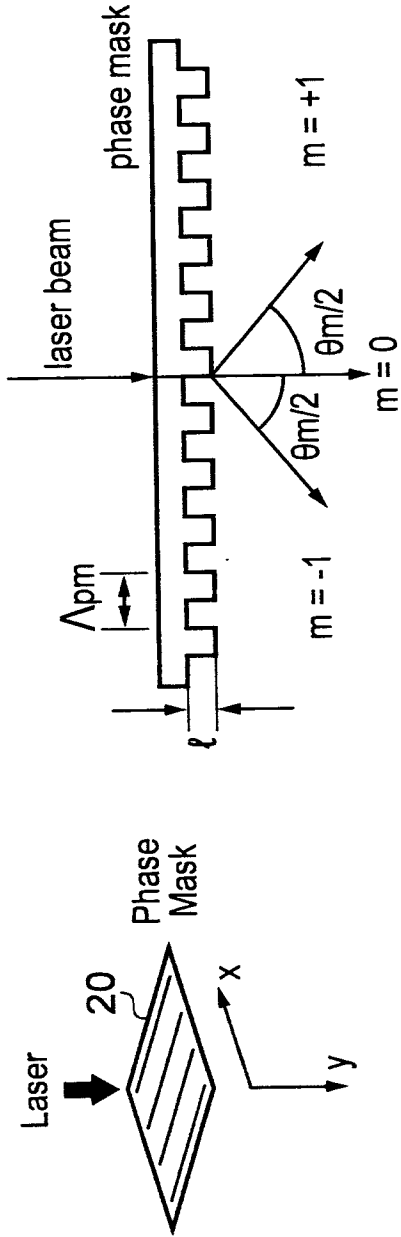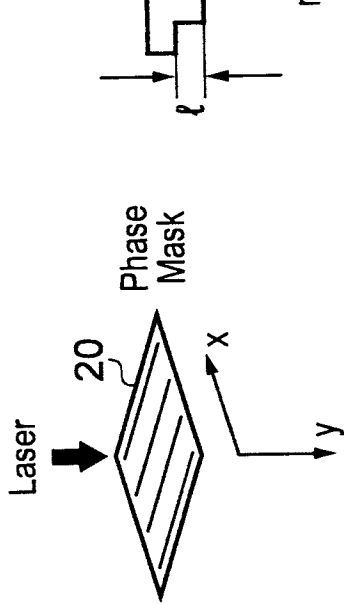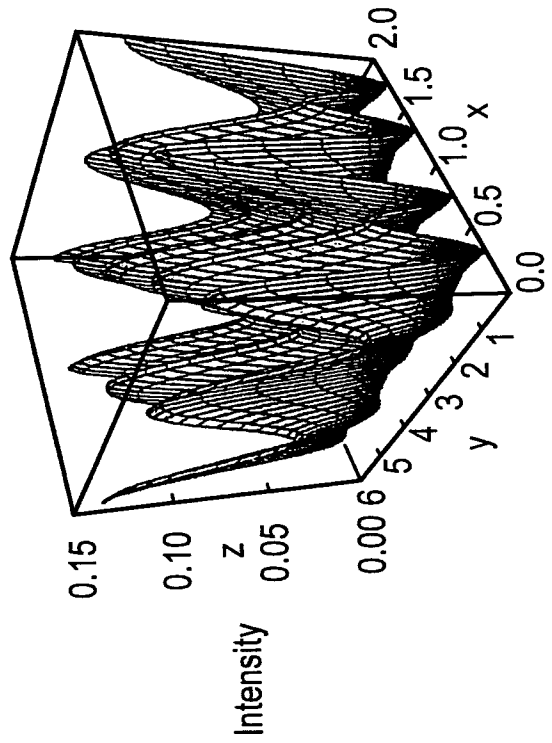
FIG. 3a

FIG. 4

(not to scale)

FIG. 5

FIG. 6a

FIG. 6b

FIG. 7a

FIG. 7b

Laser
Polarisation
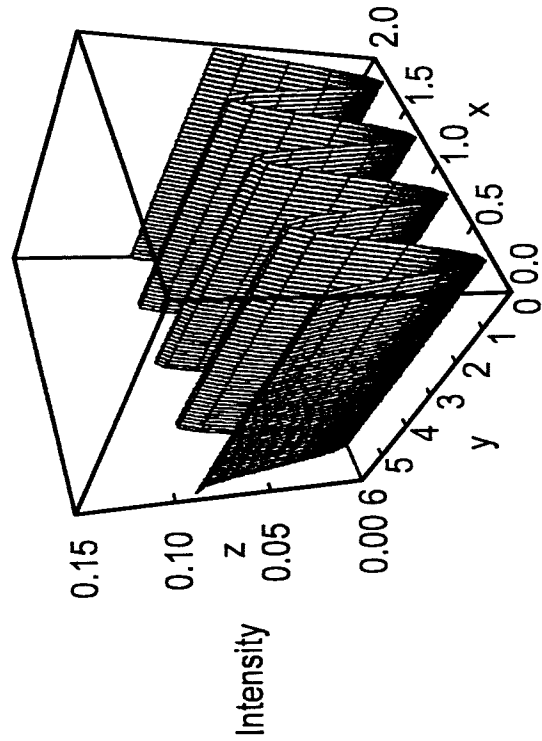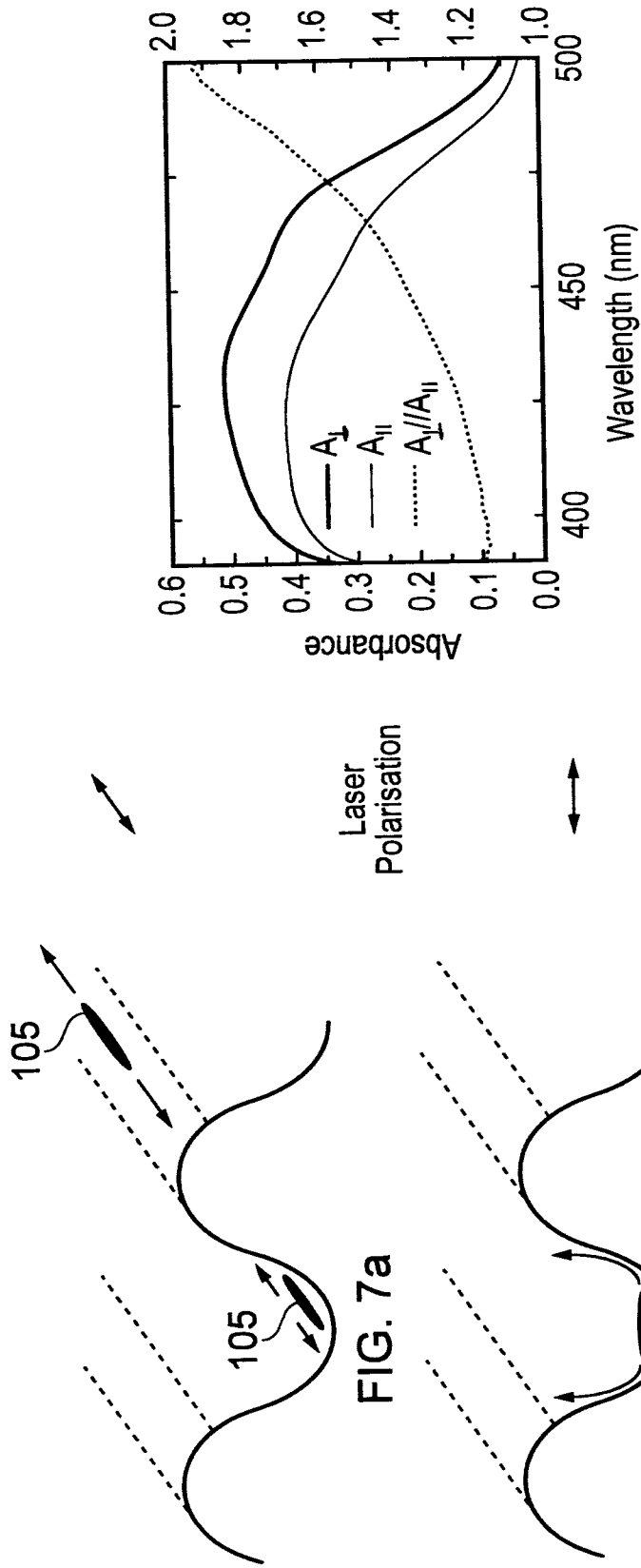
Shear viscosity is anisotropic
Lower for transport parallel to director as obtained with B

Enhanced mass transport

FIG. 7

FIG. 8

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. G02B6/122   G02B6/138
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CAPUTO R ET AL: "FORMATION OF A GRATING OF SUBMICRON NEMATIC LAYERS BY PHOTOPOLYMERIZATION OF NEMATIC-CONTAINING MIXTURES" JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS, PLEIADES PUBLISHING / AIP, MELVILLE, NY, US LNKD-DOI:10.1134/1.1342885, vol. 91, no. 6, 1 December 2000 (2000-12-01), pages 1190-1197, XP001038837 ISSN: 1063-7761	1-3,6-8, 10,11, 18-30, 33-35
Y	the whole document	2-6, 12-17, 31,32

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X Further documents are listed in the continuation of Box C.   X See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 August 2010	13/08/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Riblet, Philippe

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C(Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	* abstract; figures page 3 - page 5	2-6, 12-17, 31,32
X	US 2003/219204 A1 (YERALAN SERDAR [US] ET AL) 27 November 2003 (2003-11-27)	1-3,6-8, 10,11, 18-30, 33-35
Y	paragraphs [0007], [0024]; figure 1	2-6, 12-17, 31,32
X	ROCHON P ET AL: "GUIDED MODE RESONANCE FILTERS USING POLYMER FILMS" APPLIED PHYSICS LETTERS, AIP, AMERICAN INSTITUTE OF PHYSICS, MELVILLE, NY, US LNKD- DOI:10.1063/1.119710, vol. 71, no. 8, 25 August 1997 (1997-08-25), pages 1008-1010, XP000720203 ISSN: 0003-6951 the whole document	1,7-11, 18-30, 33-35
X	FUJISAWA K ET AL: "GRATING OPTICAL LOW-PASS FILTER" JAPANESE JOURNAL OF APPLIED PHYSICS, JAPAN SOCIETY OF APPLIED PHYSICS, JP LNKD-DOI:10.1143/JJAP.35.1768, vol. 35, PART 01, no. 3, 1 March 1996 (1996-03-01), pages 1768-1776, XP000730605 ISSN: 0021-4922 Section 2.2	1,9-11, 18-30, 33-35
X	US 4 877 717 A (SUZUKI TOSHIHIRO [JP] ET AL) 31 October 1989 (1989-10-31)	1,6-11, 18-30, 33-35
	column 7, lines 53-67; figures 3,23 column 8, lines 28-55 column 9, lines 24-44 column 18, lines 46-48	
Y	US 6 613 245 B1 (OHLEMACHER ANGELA [DE] ET AL) 2 September 2003 (2003-09-02)	2-6, 12-17, 31,32
	the whole document	

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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	ALDRED M P ET AL: "ELECTROLUMINESCENT SEGMENTED LIQUID CRYSTALLINE TRIMERS" LIQUID CRYSTALS: AN INTERNATIONAL JOURNAL OF SCIENCE AND TECHNOLOGY, TAYLOR & FRANCIS, GB LNKD-DOI:10.1080/02678290801924931, vol. 35, no. 4, 1 April 2008 (2008-04-01), pages 413-427, XP001513249 ISSN: 0267-8292 page 413	3-6, 12-17, 31,32

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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			JP	2002521354 T	16-07-2002