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(21) International Application Number: PCT/US99/05008 (22) International Filing Date: 5 March 1999 (05.03.99) (30) Priority Data: 60/076,908 5 March 1998 (05.03.98) US (71) Applicant (for all designated States except US): FED CORPORATION [US/US]; Hudson Valley Research Park, 1580 Route 52, Hopewell Junction, NY 12533 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): JONES, Gary, W. [US/US]; 8 Taconic View Court, Lagrangeville, NY 12540 (US). CAMPOS, Richard, A. [US/US]; 4 Perry Street, Cortlandt Manor, NY 10566 (US). DESTAFENO, Joseph, J. [US/US]; 18 Oakland Avenue, Chester, NY 10918 (US). (74) Agent: COYNE, Patrick, J.; Colier, Shannon, Rill & Scott, PLLC, Suite 400, 3050 K Street, N.W., Washington, DC 20007 (US).		(81) Designated States: US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: BLUE AND ULTRAVIOLET PHOTOLITHOGRAPHY WITH ORGANIC LIGHT EMITTING DEVICES (57) Abstract A system and method of photolithography. The system of the present invention includes the use of an Organic Light Emitting Device ("OLED") as a light source for photolithography. A programmable matrix of OLEDs may be used to generate blue or ultraviolet light for patterning a layer of photosensitive material. The programmable OLED matrix may be either actively or passively driven.		

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BLUE AND ULTRAVIOLET PHOTOLITHOGRAPHY WITH ORGANIC LIGHT EMITTING DEVICES

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Field of the Invention

The present invention relates to the field of lithography. More particularly, the present invention relates to the use of Organic Light Emitting Devices ("OLEDs") as light sources for photolithography.

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Background of the Invention

Lithography involves the process of forming patterns on a layer of photosensitive material, typically photoresist. Photolithography is a type of lithography in which a light source is used to create the patterns on the photoresist layer. Light may either be projected directly onto the photo
15 resist surface or projected through a mask. The mask is designed so that the light which passes through forms the desired pattern on the surface. Pressurized lamps, lasers, and any other sources of ultraviolet or infrared light may be used to create the patterns on the photoresist. The light sources normally are large and costly.

Current photolithography processes possess certain inefficiencies. For example, many
20 processes do not allow all portions of a large surface to be patterned simultaneously. In laser lithography, a large pattern must be created by either moving the laser beam incrementally over the photoresist surface or by moving the photoresist surface under the laser. Furthermore, current light sources, such as laser generators, are generally very expensive. Similarly, processes which involve the use of a mask between the light source and the layer of photoresist are also inherently inefficient.
25 Typically, multiple masks must be used in order to pattern an entire substrate. The current lithography processes must allow time for switching between the required masks. Also, the masks themselves must be specially produced in an expensive and time consuming process. The production of new semiconductor chips or integrated circuits cannot begin until the masks are produced. The photoresist layer cannot be exposed until the masks have been manufactured. This
30 delay may affect the amount of time it takes for a new semiconductor product to reach the market.

Current processes generally require the use of large machinery and support systems. Most traditional light sources are housed in large immobile equipment.

Accordingly, there is a need for a lithographic process which allows a layer to be patterned quickly and inexpensively. There is also a need for a photolithographic process which does not
5 require the use of multiple masks. Furthermore, there is a need for a lithography process which is capable of producing semiconductor products immediately following the completion of the design phase.

Objects of the Invention

10 It is therefore an object of the present invention to provide an economical system for photolithography.

It is a further object of the present invention to provide a cost effective method of patterning a large area photoresist layer.

It is another object of the present invention to provide a reduced size system for
15 photolithography.

It is yet another object of the present invention to provide a programmable mask system for photolithography.

It is still another object of the present invention to provide a photolithography system which may be rapidly modified in order to produce newly designed patterns.

20 It is a further object of the present invention to provide a portable system for photolithography.

Summary of the Invention

A method of patterning a photosensitive surface comprising the steps of: providing a
25 photosensitive surface to be patterned; and exposing the photosensitive surface to light emitted from a light source comprising an organic light emitting device. The photosensitive surface may comprise photoresist material. The light source may comprise either an actively or passively driven matrix of organic light emitting devices. The light source may emit ultraviolet or blue light. The OLED matrix may overlie a silicon substrate comprising integrated circuitry. The matrix may be
30 programmed to emit various patterns of light. The matrix may be one-dimensional or two-dimensional. The position of the photosensitive surface relative to the light source may be varied in order to pattern the surface during the step of exposing the photosensitive surface to light. The

step of exposing may include employing a plurality of the OLED matrices simultaneously. The present invention includes a light source for patterning a photosensitive surface comprising: a matrix of organic light emitting devices; a silicon substrate underlying the matrix of organic light emitting devices, wherein the substrate comprises integrated circuitry capable of being programmed to provide different patterns of light emissions from the matrix. The light source may include an actively or passively driven matrix. The matrix may include microcavity forming structural elements. The matrix may also comprise organic light emitting devices with polarizing elements and/or focusing elements. The light source may include a matrix with frequency doubling materials for converting the light generated by organic material in the organic light emitting devices to blue or ultraviolet light. The matrix may emit blue or ultraviolet light.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only, and are not restrictive of the invention as claimed. The accompanying drawings, which are incorporated herein by reference, and which constitute a part of the specification, illustrates certain embodiments of the invention, and together with the detailed description serve to explain the principles of the present invention.

Brief Description of the Drawings

Figure 1 depicts a photolithographic system according to the present invention with an OLED light source.

Figure 2 depicts an alternative embodiment of a photolithographic system according to the present invention.

Figure 3 is a top view of a portion of the OLED matrix.

Detailed Description of the Invention

Referring first to Fig. 1, which discloses the photolithographic system **10** according to the present invention. The system **10** comprises an OLED matrix **20**; and photosensitive material to be patterned **40**. The OLED matrix **20** emits light downward onto the photosensitive material surface **44** developing away the photosensitive material. The pattern emitted by the OLED matrix is duplicated on the photosensitive material **40**.

Fig. 2 discloses an alternative embodiment of the present invention, which further includes a lens assembly **30**. The lens assembly functions to reduce the size of the emitted light image in order to increase the pattern density on the surface **44**. For example, the lens assembly **30** may

provide a factor of ten reduction. The material **40** may comprise a silicon wafer **42** coated with a layer **41** of photosensitive material such as photoresist. The photoresist layer **41** may be sensitive to light from any portion of the spectrum, however materials sensitive to blue or ultraviolet light are preferred. The system **10** shown in Fig. 2 includes the movement of the material **40** as shown by
5 arrow **50**. The material **40** is translated in the appropriate direction by a suitable mechanical system (not shown). The system **10** may serve as one station in the larger assembly process for a semiconductor device. In that case, the material **40** may be moved away from the OLED matrix **20** to the next station. Alternatively, following an exposure to the OLED matrix **20** the material **40** may be re-oriented in place to allow for patterning of another section of the material **40**.

10 Fig. 3 discloses a matrix section **22** of the OLED matrix **20**. The matrix section **22**, when illuminated, defines the letter "F". The illumination is provided by pixels **221**, which contain organic light emitting material.

OLEDs are typically used in the area of flat panel displays. However, this same technology has the ability to deliver, through the inclusion of microcavity structures, a bright directed beam of
15 visible light. This light can be generated by utilizing relatively simple and inexpensive vacuum evaporation techniques (for molecular crystal systems) or spin coating techniques (for polymeric systems). The use of OLEDs to produce blue and ultraviolet light provides significant reductions in cost and size of photolithographic tools. The system of the present invention may also be used to fabricate the masks required for current lithography processes.

20 The use of OLED technology in matrix form allows large-area patternability onto rigid or flexible substrates. The OLED matrices which include blue or UV light generating organic materials are preferred for use as the matrix **20**. The wavelength of the emitted light allows for accurate patterning on the photoresist surface. OLED matrices which include visible or infrared light emitting organic materials may be used in conjunction with frequency doubling or upconversion
25 materials such as inorganic nonlinear crystals, or nonlinear polymers, to produce blue or ultraviolet light.

The OLED matrix **20** is normally constructed over a silicon substrate containing integrated circuitry. As a result, the OLED matrix **20** may be programmed. Programming may be used to project different patterns onto the photosensitive surface **44**. As the projected light patterns change,
30 the material **40** may be translated in order to rapidly pattern a large area. The capability of programming the OLED matrix eliminates the need for a mask, since the OLED matrix effectively functions as a programmable mask. The matrix **20** may be either passively or actively driven.

Typically, the matrix **20** includes matrix lines which are capable of carrying current or voltage pulses of selected magnitudes. The pulses are provided to the matrix lines by drivers. The signals from the drivers pass to the OLED conductors through one of the matrix lines and the integrated circuitry located within the substrate. The signal from the driver provides current of varying magnitude to the conductors thereby determining whether or not each OLED or pixel cell is on, off, or at some intermediate gray level. The integrated circuitry may be programmed in order to control the pattern of emitted light.

The matrix **20** may be either a one or two dimensional matrix. Use of a linear matrix or array requires moving or stepping either the material **40** or the matrix **20** in order to construct the pattern one line at a time. Multiple OLED matrices and multiple steppers may be used in order to rapidly pattern the photosensitive surface **40**. The use of multiple OLED matrices will increase printing and patterning speed. The present invention may also include the use of reduction stepper technology to generate printed designs.

At the pixel level, the present invention may include an OLED matrix of the type disclosed in U.S. Patent Application Serial No. 09/074,424, filed on May 8, 1998, and incorporated herein by reference. The OLED matrix designs may include microcavity-forming structural elements, such as a reflective quarter-wave mirror stack of alternating oxide and nitride layers (e.g. $\text{SiO}_2/\text{Si}_x\text{N}_y$ and $\text{SiO}_2/\text{TiO}_2$), which provide improved color purity and optical directionality. The microcavity structure promotes harmonic generation by narrowing the spread of light. The use of an OLED matrix with narrow light emissions may reduce the cost of any lensing system required for high resolution applications.

The OLED matrix **20** may further include polarizing elements at the pixel level. These polarizing elements may include polarized solid-state organic emissive layers, which further promote harmonic generation and reduce power waste. The OLED matrix **20** may also include focusing elements at the pixel level, such as microlenses.

Direct UV light may also be generated for photolithography by using an efficient green-emitting OLED produced by Kodak Corp. The OLED structure may comprise the following layers: an indium-tin-oxide, or ITO, electrode on a suitable substrate such as glass; followed by vacuum depositions of a buffer layer of copper Phthalocyanine, CuPC; a hole transport layer comprising the diamine molecule NPB; a doped organic layer comprising of aluminum quinoline, or ALQ, host with Coumarin 6 dye; an electron-transporting pure ALQ layer; and a Mg:Ag cathode layer. A nonlinear frequency conversion crystal may be bonded to the glass substrate on the viewing side of the OLED

device. The optical emission exits through the semitransparent ITO electrode, and penetrates the frequency conversion layer which doubles the green emission at 500 nm into ultraviolet emission at 250 nm. A polymer film capable of frequency upconversion may be spun on the glass viewing side in place of the nonlinear crystal. A reflective multilayer stack may be deposited on the glass substrate prior to the ITO coating to provide microcavity effects.

When generating near UV light for i-line lithography, the OLED matrix may include butyl-PBD or p-terphenyl to emit light with a wavelength near 365 nm. Poly-(methylphenylsilane) may be used to emit light with a wavelength near 351 nm.

The deep blue light required for g-line lithography may be generated by including metal-free phthalocyanine (H₂PC) with the OLED matrix. The light emitted generally exhibits broad Q-band electroluminescence above 800 nm, peaking around 930 nm. Fullerene crystals may also be used to emit light near the same wavelength region. Other blue emitter material and structures are also acceptable. The frequency of the light may be doubled into the g-line wavelength at 436 nm using the innovations described above for direct UV light generation.

There have been many recent developments in the area of OLEDs, which allow this innovative photolithographic process to be utilized. The references discussed below are representative of recent developments in OLED technology.

The methodology to build efficient and bright monochrome OLED devices is disclosed in J. Shi and C.W. Tang, "Doped organic electroluminescent devices with improved stability," Appl. Phys. Lett. 70 (1970), 16650-1667, which is incorporated herein by reference.

Van Slyke et al. U.S. Patent Nos. 5,150,006 and 5,151,629, both incorporated herein by reference, disclose improved blue emitting OLED devices exhibiting greater efficiency and higher levels of stability as compared to conventional blue emitting OLED devices. The OLED devices disclosed in the Van Slyke patents utilize substituted metal oxinoid compounds as emitters. Matsuura et al. U.S. Patent No. 5,503,910, incorporated herein by reference, also discloses improved efficiency and stable blue emitting OLED devices.

Parahexaphenyl may be used as a blue light emitting material in organic EL devices as discussed by A. Niko, S. Tasch, F. Meghdadi, C. Brandstatter and G. Leising, "Red-green-blue emission of parahexaphenyl devices with color-converting media," J. Appl. Phys. 82 (1997), 4177-4182, which is incorporated herein by reference. Ultraviolet-emitting OLEDs are reported in Akihito Fujii, Kenji Yoshimoto, Masayoshi Yoshida, Yutaka Ohmori and Katsumi Yoshino, "Ultraviolet electroluminescent diode utilizing poly(methylphenylsilane)," Jpn. J. Appl. Phys. 34 (1995), L1365-

L1367, which is incorporated herein by reference. An infrared emitting OLED may be produced by using films of metal-free phthalocyanine (H_2Pc). Akihiko Fujii, Yutaka Ohmori, and Katsumi Yoshino. "An organic infrared electroluminescent diode utilizing a phthalocyanine film," IEEE Trans. on Electron. Dev. 44 (1997), 1204-1207, incorporated herein by reference.

5 The use of films of vacuum-sublimed fullerene (carbon 60) crystals is disclosed in A. Werner, H. Byrne, D. O'Brien and S. Roth, "Electroluminescence in fullerene crystals," Molec. Cryst. Liq. Cryst. 256 (1994), 795-800, incorporated herein by reference. The OLEDs disclosed produce emissions at 900 nm under liquid nitrogen.

Discrete OLEDs may be arranged in matrix architectures. For example, in 1995 the Idemitsu
10 group demonstrated a low-resolution, 72x72 mm, 16x16 pixel color display using the broad blue emission from the organic molecule DPVBi together with color-changing media ("CCM") as reported in M. Matsuura, H. Tokailin, M. Eida, C. Hosokawa, Y. Hironata and T. Kusumoto, "Performance of RGB multicolor organic EL display," in Asia Display '95, p. 269, incorporated herein by reference.

15 In late 1996, a passive polymeric display array of 20 μm x 20 μm pixels was fabricated using 193 nm excimer laser photoablation, S. Noach, E.Z. Faraggi, G. Cohen, Y. Avny, R. Neumann, D. Davidov and A. Lewis, "Microfabrication of an electroluminescent polymer light emitting diode pixel array," Appl. Phys. Lett. 69 (1996), 3650, which is incorporated herein by reference. Kodak Corp. has announced experimental results for a polysilicon TFT active matrix
20 OLED array of 320 x 240 pixels 60 μm in size on quartz: M.K. Hatalis, M. Stewart, C. Tang and J. Burtis, "Polysilicon TFT active matrix organic EL displays," in SPIE 3057, Cockpit Displays IV: Flat Panel Displays for Defense Applications, p. 277, incorporated herein by reference.

Standard OLED structures, wherein the organic media are sandwiched between a transparent anode like indium-tin-oxide (ITO) and a reflective cathode such as Mg:Ag in a prescribed ratio, are
25 capable of generating a broad angular distribution of light. This type of distribution is characteristic of a Lambertian source (i.e., emitting light at all forward angles). It is also possible to promote greater directionality of light emission in the direction of the photosensitive surface by the creation of a microcavity structure through the inclusion of a second, highly reflective surface, near the transparent anode. Use of a microcavity structure is described in the following publications, all of
30 which are incorporated herein by reference: A. Dodabalapur, L.J. Rothberg, R.H. Jordan, T.M. Miller, R.E. Slusher and J.M. Phillips, "Physics and applications of organic microcavity light

emitting diodes," J. Appl. Phys. 80 (1996) 6954; and U.S. Patent Nos. 5,405,710 and 5,478,858 issued to A. Dodabalapur, T.M. Miller and L.J. Rotherberg.

Organic material may be assembled in structurally ordered films capable of generating polarized light, thereby realizing power economy in polarization-sensitive applications such as nonlinear frequency conversion. The following references disclose the generation of polarized organic electroluminescence by using short-chain oligomers of well-known polymers: R.N. Marks, F. Biscarini, R. Zamboni and C. Taliani, "Polarized electroluminescence from vacuum-grown organic light-emitting diodes," Europhys. Lett. 32 (1995) 523; and M. Era, T. Tsutsui and S. Saito, "Polarized electroluminescence from oriented p-sexiphenyl vacuum-deposited film," Appl. Phys. Lett. 67 (1995) 2436-2438, both of which are incorporated herein by reference.

Inorganic crystals such as KTP, KDP, and LiNbO₃ are well-known materials used to promote frequency upconversion, or harmonic generation, due to their nonlinear optical coefficients. In some cases, poled polymers may equal or surpass the performance of the best inorganic crystalline materials: D.R. Ulrich, "Nonlinear optical polymer systems and devices," Mol. Cryst. Liq. Cryst. 160 (1988) 1-31, incorporated herein by reference. Polymeric materials provide certain processing advantages which cannot be obtained from commercial inorganic materials.

The present invention employs the latest developments in OLED technology to photolithography. It will be apparent to those skilled in the art that various modifications and variations can be made in the construction, configuration, and/or operation of the present invention without departing from the scope or spirit of the invention. For example, various OLED and matrix designs may be employed as the light source without departing from the scope of the invention. Thus it is intended that the present invention covers modifications and variations of the invention provided they come within the scope of the appended claims and their equivalents.

WE CLAIM:

1. A method of patterning a photosensitive surface comprising the steps of:
providing a photosensitive surface to be patterned; and
exposing the photosensitive surface to light emitted from a light source comprising an organic light emitting device.
2. The method of claim 1, wherein said photosensitive surface comprises photoresist material.
3. The method of claim 1, wherein said light source comprises a matrix of organic light emitting devices.
4. The method of claim 3, wherein said matrix is actively driven.
5. The method of claim 3, wherein said matrix is passively driven.
6. The method of claim 1, wherein said light source emits ultraviolet light.
7. The method of claim 1, wherein said light source emits blue light.
8. The method of claim 3, wherein said matrix overlies a silicon substrate comprising integrated circuitry.
9. The method of claim 8, wherein said matrix may be programmed to emit various patterns of light.
10. The method of claim 3, wherein said matrix is one-dimensional.
11. The method of claim 3, wherein said matrix is two-dimensional.

12. The method of claim 1, further comprising the step of varying the position of said photosensitive surface relative to said light source in order to completely pattern said surface during the step of exposing said photosensitive surface to light.

13. The method of claim 3, wherein said exposing step includes employing a plurality of said matrices simultaneously.

14. A light source for patterning a photosensitive surface comprising:
a matrix of organic light emitting devices;
a silicon substrate underlying said matrix of organic light emitting devices, wherein said substrate comprises integrated circuitry capable of being programmed to provide different
5 patterns of light emissions from said matrix.

15. The light source of claim 14, wherein said matrix is actively driven.

16. The light source of claim 14, wherein said matrix is passively driven.

17. The light source of claim 14, wherein said matrix includes microcavity forming structural elements.

18. The light source of claim 14, wherein said matrix comprises organic light emitting devices with polarizing elements.

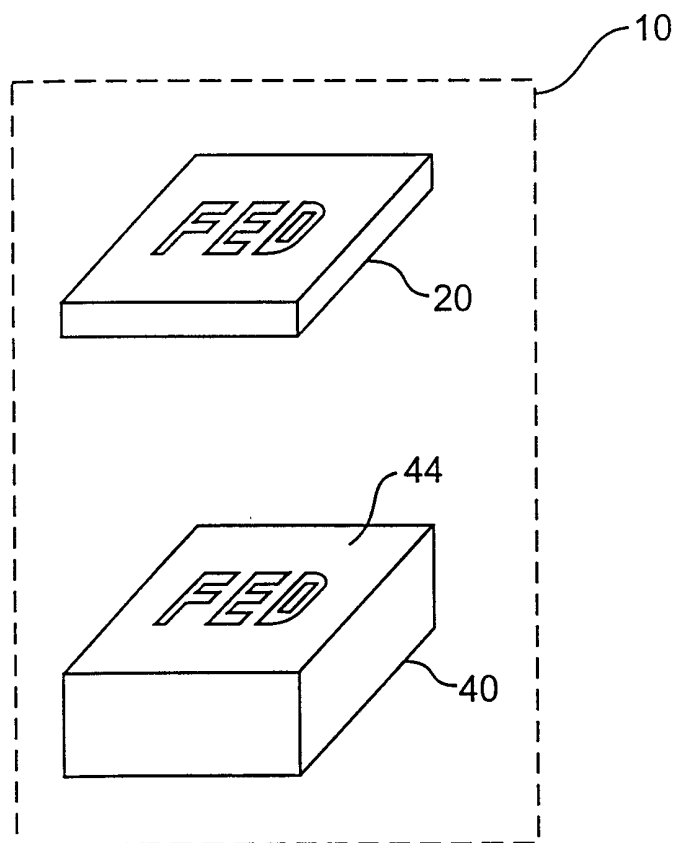
19. The light course of claim 14, wherein said matrix comprises organic light emitting devices with focusing elements.

20. The light source of claim 14, wherein said matrix includes frequency doubling materials for converting the light generated by organic material in the organic light emitting devices to blue or ultraviolet light.

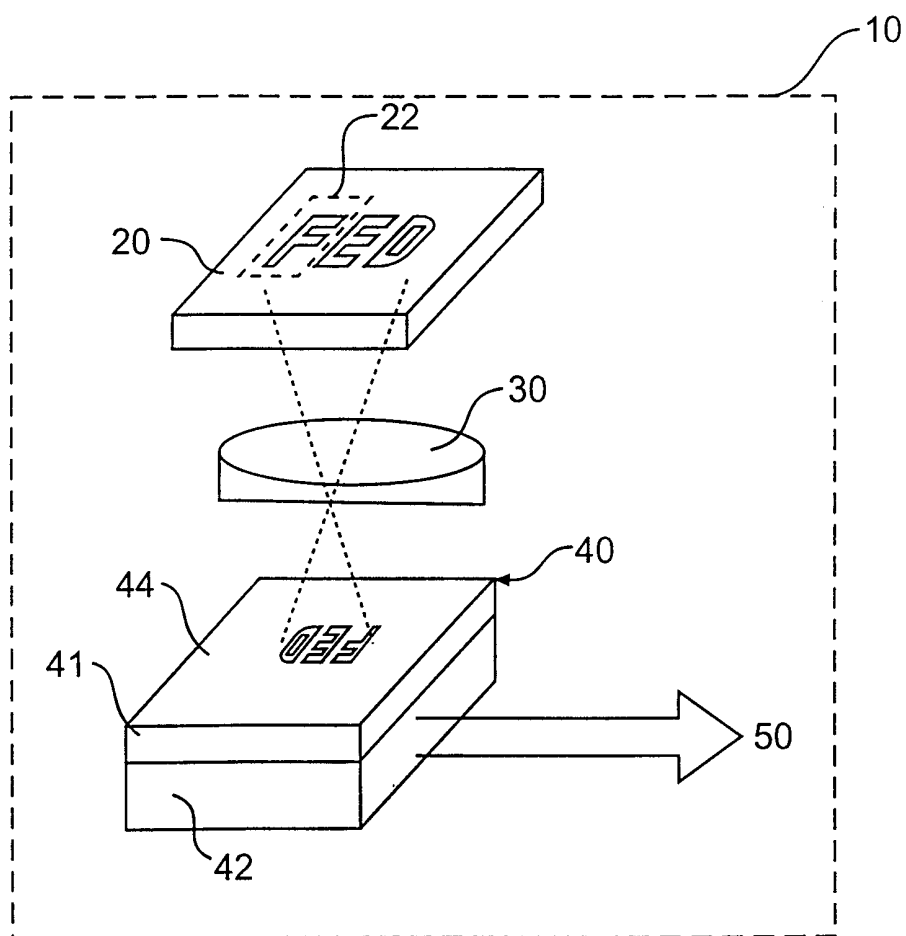
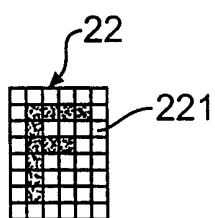
21. The light source of claim 14, wherein said matrix emits blue light.

22. The light source of claim 14, wherein said matrix emits ultraviolet light.

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**FIG. 1**

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**FIG. 2****FIG. 3**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/05008

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01J 1/63; G03F 9/00

US CL : 430/311, 313, 322; 313/504, 505, 510;

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)

U.S. : 430/311, 313, 322; 313/504, 505, 510;

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 practicable, search terms used)

APS, DERWENT

search terms: photoresist, resist, light emitting, electroluminescent, organic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
NONE	NONE	NONE
Y,P	US 5,840,451 A (MOORE et al) 24 November 1998, col. 8, lines 26-45.	1-22
Y,P	US 5,773,194 A (HATTORI et al) 30 June 1998, col. 20, lines 1-3, col 26, lines 9-12.	1-13
Y	US 4,928,122 A (DOI et al) 22 May 1990, col. 2, lines 20-61.	1-13
Y	US 5,543,830 A (LEA) 06 August 1996, col. 1, lines 11-46.	1-13
Y,P	US 5,739,896 A (PATTON et al) 14 April 1998, col. 3, lines 4-41.	1-13

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

* Special categories of cited documents:	*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
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/05008

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,150,006 A (VAN SLYKE et al) 22 September 1992, abstract.	1-22
Y	US 5,503,910 A (MATSUURA et al) 02 APRIL 1996	1-22
Y,P	US 5,866,922 A (HUANG et al.) 02 February 1999, col. 7, lines 11-46.	1-22
Y	US 5,684,368 A (WEI et al) 04 November 1997, col. 4, lines 17-52.	4-5, 15-16
X,P	Organic Light-Emitting Devices for Photolithographic Applications. IBM Research Disclosure 408183. April 1998.	1-22