

TWO-PHOTON STEREOLITHOGRAPHY USING PHOTOCURABLE COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefits of U.S. provisional application No. 60/929,972, filed July 20, 2007, the contents of which are incorporated herein by reference.

[0002] This application is related to PCT application entitled "Device and Method for Focusing a Beam of Light with Reduced Focal Plane Distortion", filed by the same applicants concurrently with the present application, the contents of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0003] The present invention relates to methods of two-photon stereolithography, particularly two-photon stereolithography using photocurable compositions.

BACKGROUND OF THE INVENTION

[0004] Two-photon stereolithography is an emerging and promising technology, with many potential applications, such as in the semiconductor industry, for photonics devices, in the wireless industry, for microelectromechanical systems (MEMS) or nanoelectromechanical systems (NEMS), in the rapid prototyping industry, in tissue engineering, and in the chemical and pharmaceutical industries. Two-photon stereolithography (e.g. two-photon polymerization) utilizes localized two-photon absorption/excitation to induce structural changes in a target. However, not all materials are suitable for two-photon stereolithography. Only in certain materials, two-photon absorption induced polymerization can proceed at a sufficient rate to be of practical use for two-photon stereolithography.

SUMMARY OF THE INVENTION

[0005] In accordance with an aspect of the present invention, there is provided a method of processing a material to form a three-dimensional article,

comprising providing a photocurable material comprising a poly(meth)acrylate having a (meth)acrylate functionality of at least 3 and a molecular weight (MW) of at least 650, a urethane(meth)acrylate having a (meth)acrylate functionality of 2 to 4 and a MW of 400 to 10,000, a di(meth)acrylate made from bisphenol A or bisphenol F; and a photoinitiator; focusing a beam of light to a focus region of the material to induce two-photon absorption in the focus region, and thus polymerization of the material in the focus region; and scanning the beam across the material according to a pre-selected pattern so that the beam is focused to different pre-selected regions, to induce polymerization of the material at the pre-selected regions. A wavelength of light is selected to induce two-photon absorption in the material.

[0006] An un-polymerized portion of the material may be removed from a polymerized portion of the material, to form the three-dimensional article. The material may comprise 2 to 20 wt% of the poly(meth)acrylate, 20 to 60 wt% of the urethane(meth)acrylate, 20 to 80 wt% of the di(meth)acrylate, and 0.1 to 10 wt% of the photoinitiator. The poly(meth)acrylate may have a MW in the range of 880 to 1200. The material may comprise 5 to 18 wt% of the poly(meth)acrylate. The material may comprise 20 to 50 wt% of the urethane(meth)acrylate. The material may comprise 35 to 55 % of the di(meth)acrylate. The material may comprise 2 to 8 wt% of the photoinitiator. The material may comprise 8 to 16 wt% of the poly(meth)acrylate, 25 to 45 wt% of the urethane(meth)acrylate, 40 to 50 wt% of the di(meth)acrylate, and 3 to 7 wt% of the photoinitiator. The di(meth)acrylate may be monomeric or oligomeric. The di(meth)acrylate may be a mixture of ethoxylated bisphenol A diacrylate and ethoxylated bisphenol A dimethacrylate. The beam may be scanned according to a first pre-selected pattern to induce polymerization at pre-selected regions within a first layer, and subsequently scanned beam according to a second pre-selected pattern to induce polymerization at pre-selected regions within a second layer. The first pattern and the second pattern may be different or identical. The scanning may be repeated to polymerize selected regions in more than two layers of the material. The beam may have a spot size of about 2 μm or less at the focus region. The focus region may have a volume of about 10^{-12} cm^3 or less.

[0007] Other aspects and features of the present invention will become apparent to those of ordinary skill in the art upon review of the following description

of specific embodiments of the invention in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] In the figures, which illustrate, by way of example only, embodiments of the present invention,

[0009] **FIG. 1** is a schematic diagram of a two-photon stereolithography apparatus;

[0010] **FIG. 2** is a schematic side view of the objective lens, target and support shown in **FIG. 1**;

[0011] **FIG. 3** is a scanning electron microscopy (SEM) image of a top view of an article formed by two-photon polymerization using the apparatus of **FIG. 1** and a composition exemplary of an embodiment of the present invention;

[0012] **FIG. 4** is an SEM image of a perspective view of the article of **FIG. 3** in a different state;

[0013] **FIG. 5** is an SEM image of a perspective view of a second article having an array of unit devices, formed by two-photon polymerization using the apparatus of **FIG. 1** and a composition exemplary of an embodiment of the present invention; and

[0014] **FIG. 6** is an SEM image of a top plan view of a unit device on the article shown in **FIG. 5**.

DETAILED DESCRIPTION

[0015] In exemplary embodiments of the present invention, a liquid composition comprising a poly(meth)acrylate, a urethane(meth)acrylate, a di(meth)acrylate, and a photo-initiator, is used for two-photon stereolithography. The poly(meth)acrylate has a (meth)acrylate functionality of at least 3 and a molecular weight (MW) of at least 650. The urethane(meth)acrylate has a (meth)acrylate functionality of 2 to 4 and a MW of 400 to 10,000. The di(meth)acrylate is made from bisphenol A or bisphenol F; and a photoinitiator.

[0016] In different embodiments, the composition may comprise 2 to 20 wt% (weight percent) of poly(meth)acrylate, 20 to 60 wt% of urethane(meth)acrylate, 20 to 80 wt% of di(meth)acrylate, and 0.1 to 10 wt% of photoinitiator.

[0017] In one embodiment, the poly(meth)acrylate may have a MW in the range of 880 to 1200.

[0018] In some embodiments, the composition material may include 5 to 18 wt% of poly(meth)acrylate, 20 to 50 wt% of urethane(meth)acrylate, 35 to 55 wt% of di(meth)acrylate, or 2 to 8 wt% of photoinitiator. In one embodiment, the material comprises 8 to 16 wt% of poly(meth)acrylate, 25 to 45 wt% of urethane(meth)acrylate, 40 to 50 wt% of di(meth)acrylate, and 3 to 7 wt% of photoinitiator.

[0019] The poly(meth)acrylate may include a tri-, tetra-, or penta-(meth)acrylate. The di(meth)acrylate may be monomeric or oligomeric, and may be a mixture of ethoxylated bisphenol A diacrylate and ethoxylated bisphenol A dimethacrylate.

[0020] The composition may also include a surfactant.

[0021] The composition may include a photocurable composition described in US Patent No. 6,025,114, the contents of which are incorporated herein by reference.

[0022] In an exemplary embodiment of the present invention, the composition may contain a selective combination of the following commercially available materials, where the texts in parentheses indicate exemplary product names and suppliers:

- ethoxylated bisphenol A dimethacrylate (SR-348, Sartomer™);
- ethoxylated bisphenol A diacrylate (SR-349, Sartomer);
- ethoxylated 1,1,1-trimethylpropane triacrylate (SR-9035, Sartomer);
- UV photoinitiator DAR1173 with a formula of $\text{Ph-CO-C}(\text{CH}_3)_2\text{OH}$

- 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba Geigy™, referred to herein as IRG);
- aliphatic urethane acrylate (EB-270, UCB Chemicals™);
- silicone surfactant (DC190, Dow Corning™);
- Urethane acrylate (NR-2720, Zeneca Resins™).

[0023] In some embodiments of the present invention, the composition may include a mixture listed in **Tables I** and **II**.

Table I. Mixtures for two-photon lithography

Mixture	SR-349	SR-348	NR-2720	SR-9035	DAR-1173	DC190	IRG
1	8.0	42.0	34.5	10.0	5.5	—	—
2	—	45.0	34.5	15.0	5.5	—	—
3	8.0	42.0	34.5	10.0	5.5	0.2	—
4	—	45.0	34.5	15.0	5.5	0.2	—
5	20.0	35.0	29.0	10.5	5.5	—	—
6	20.5	35.9	29.8	10.8	5.5	—	3.0

Table II. Mixtures for two-photon lithography

Mixture	SR-349	SR-348	NR-2720	SR-9035	DAR-1173	IRG	EB-270
7	15.0	46.0	24.0	9.5	5.5	—	—
8	10.0	40.0	25.0	19.5	5.5	—	—
9	19.0	44.0	21.0	11.0	5.0	—	—
10	4.5	40.0	40.0	10.0	5.5	—	—
11	—	42.0	42.0	10.5	5.5	—	—
12	—	49.9	30.2	14.4	5.6	—	—
13	—	45.5	34.5	15.0	5.0	—	—
14	55.0	—	29.0	10.5	5.5	—	—
15	55.0	—	29.0	10.5	—	5.5	—
16	56.6	—	29.8	10.8	—	2.8	—
17	20.5	35.9	29.8	10.8	—	3.0	—
18	10.9	36.6	—	12.5	5.5	—	34.5
19	—	50.0	—	19.5	5.5	—	25.0

[0024] While not all photocurable materials are suitable for fabricating articles by two-photon stereolithography, the compositions described above may be formed into 3D articles according to a two-photon stereolithography process described next.

[0025] In one embodiment, a material formed of the composition described above can be processed to form 3D particles by focusing a beam of light to a focus region in the material to induce two-photon absorption in the focus region, and thus polymerization of the material in the focus region. As two-photon absorption is limited to a small region, the material in the areas outside the focus region will not be polymerized. The light beam is scanned across the material according to a pre-selected pattern so that the beam is focused to different pre-selected regions in the material to induce polymerization of the material at the pre-selected regions. The beam may be scanned across a transversal plane that is perpendicular to an axis, such as the optical axis of the focusing device that focuses the beam onto the material. Once the scan in one layer of the material is completed, the target material may be moved relative to the focusing device to scan another layer according to a pre-selected pattern which may be different from or the same as the pattern for the previous layer. The scanning may be repeated to polymerize selected regions of the material in more than two layers, layer-by-layer. Thus, different regions in the material are polymerized according to a pre-selected design. The material in the polymerized region may be hardened and solidified. Thus, in one embodiment, the un-polymerized portions of the material may be removed from the polymerized portion of the material and the polymerized portion of the material forms a 3-D article. Depending on the application and the material used, in some embodiments, the polymerized portions may be removed from the un-polymerized portions and the un-polymerized portion forms the product article. The removed portions can be removed after completion of the scanning of a layer and before scanning the next layer, or after all layers have been scanned.

[0026] Removal or separation of one portion of the material from the other may be performed using any suitable technique, depending on the particular application. In one embodiment, two-photon absorption will induce certain chemical reactions in the selected regions of the material. The chemical reactions

result in a new material. The new material and the original material will have different chemical or physical properties. Thus, the removal or separation of the materials may be performed based on the differences. For example, if one material is a liquid and the other is a solid, they may be readily separated. In other cases, one material may be soluble and the other may be insoluble in a particular solvent. Thus, the soluble one may be removed by washing using the solvent. In some cases, one material may also be easily removed by another technique, while the other material is substantially unaffected by that technique.

[0027] With two-photon lithography, a liquid target material can be formed into a 3D article by scanning the liquid material contained in a container. It is not necessary to form the article by scanning an initial layer of liquid to first form a solid bottom layer and then add more liquid on top of the solid layer to form the next layer, which would be necessary if the material is to be cured by single-photon lithography. As two-photon absorption can occur only within a limited portion of the beam path at a selected depth in the target material, the target material may be formed layer-by-layer without having to add new liquid material during the scan. Thus, production rate can be much higher.

[0028] Further, with two-photon stereolithography, some potential problems arising from adding new liquid to a solid substrate, such as insufficient cross-linking between the adjacent layers may be avoided.

[0029] **FIG. 1** is a schematic diagram illustrating a system **10** for two-photon stereolithography, which can be used to treat the above compositions according an exemplary embodiment of the present invention.

[0030] System **10** includes a light source for emitting a beam of photons, such as laser source **12**. In this embodiment, laser source **12** is a pulsed tunable near-infrared laser, such as a Ti-sapphire laser. A commercially available laser source, such as the Spectra Physics Mai Tai™ broadband Ti-sapphire laser may be used. The pulse rate may be of the order of femtosecond. Other suitable lasers may be used in other embodiments.

[0031] Laser source **12** is used to produce a beam **14A** of laser light. The wavelength of the laser light (photons) is selected to induce two-photon absorption in the particular target material. For example, if a single-photon absorption wavelength for the particular material is L_1 , the wavelength for two-photon absorption may be $2L_1$. In order to work with different materials, laser source **12** can be tuned in wavelength within a given range. For example, to use two-photon absorption to activate UV polymerization in a material where the required absorption energy quantum is about 355 nm, the spectrum of the light may have a peak at about 710 nm.

[0032] In this embodiment, the laser wavelength is tunable between about 700 to about 1020 nm. The output beam diameter from laser source **12** is less than 2 mm with a focusing diameter of $1/e^2$. The full far field divergence angle of the beam is less than about 1 mrad. In the pulsed mode, the average output power of laser source **12** is larger than 2.5 W, and the peak power is larger than 310 kW. In different embodiments, the average laser output power may be from about 50 mW to about 4 W. A higher laser power may be used with a dry objective lens and may be desirable as it can provide higher scanning speed and throughput. In the present embodiment, the pulse repetition rate may be about 80 MHz, and the pulse width may be about 100 fs.

[0033] In another embodiment, beam **14A** emitted from laser source **12** may have a beam width of less than about 1.2 mm with a focusing diameter of $1/e^2$. In some embodiments, a smaller beam diameter may be advantageous as it can provide a higher resolution.

[0034] An isolator **16** is positioned adjacent to laser source **12** in the path of the beam **14A** to isolate laser source **12** from reflected laser light. That is, isolator **16** is configured and positioned to prevent reflected laser light to re-enter laser source **12**, as reflected light may disrupt the mode locking operation of the laser. In this embodiment, isolator **16** is a broadband isolator. For example, a 10-5-NIR-HP™ isolator from Optics For Research™ (OFR) may be used. In other embodiments, other suitable laser light isolator may be used.

[0035] A shutter **18** is positioned downstream of isolator **16** for selectively transmitting beam **14A** therethrough. Shutter **18** is an Acousto-Optic Modulator (AOM) in this embodiment, which provides fast-shutter operation. For example, an AA MOD 110 shutter from AA Opto-Electronic™ may be used.

[0036] In other embodiments, shutter **18** may be placed elsewhere, such as further downstream, and may be any other suitable high-speed shutter for the specific application. For example, the shutter speed may be on the order of about 100 MHz.

[0037] An optical beam expander **20** is positioned downstream of shutter **18**, and is configured to expand beam **14A** and produce a collimated beam **14B** with an increased beam width (beams **14A** and **14B**, as well as **14C** shown **FIG. 2**, are also collectively referred to as beam **14**). As used herein, a collimated beam refers to a beam that has a low divergence. For example, in some embodiments, the divergence of the collimated beam **14B** may be less than about 7.6 mrad. As can be appreciated, a perfectly collimated beam of light (with divergence of zero) is difficult or impossible to obtain in practice. Further, the divergence of the collimated beam **14B** is varied during use and may deviate from the lowest divergence achievable for a given optical setup.

[0038] A dichroic mirror **22** may be provided to reflect beam **14A** into expander **20**.

[0039] Expander **20** includes an expansion lens **21** for expanding the beam diameter to a large enough size so that the beam diameter is larger than the input aperture (not separately shown) of the focusing device such as microscope **28**, so that the back of the objective lens **30** (see below) is overfilled to make full use of the objective aperture. Expansion lens **21** is a diverging lens, also referred to as a negative, concave or dispersing lens. For expansion lens **21**, the lens surfaces may be plano-concave, double (bi) concave or concavo-convex.

[0040] Expander **20** also includes an expander objective lens **23** positioned downstream of expansion lens **21**. Expander objective lens **23** is a converging lens, also referred to as a positive, convex lens. The lens surfaces of a converging

lens may be plano-convex, bi-convex or meniscus. The beam size of beam **14** can be increased after passing through expander **20**.

[0041] Expander **20** is electronically controlled to expand and collimate beam **14**. Expander **20** increases the beam diameter to a desired size and is also configured to automatically adjust the divergence (collimation) of beam **14B** for correcting focal plane distortion, which is mainly due to field curvature effect, as will be further explained below.

[0042] In this embodiment, expansion lens **21** is axially moved/adjusted by a motorized translator (not separately shown) to vary or adjust the distance between expansion lens **21** and expander objective lens **23**. The distance adjustment is automated. As such, beam expander **20** also acts as an on-the-fly focusing module to automatically correct for any focal plane distortion, which may occur such as when large lens elements that do not correct for plane distortion are used. The physical distance between expansion lens **21** and expander objective lens **23** may be increased or decreased from a balanced distance, such as 90 mm, to change the beam size/diameter, or to reduce plane distortion. For example, one of the lenses **21** and **23** may be repositionable. The movement of the movable lens may be driven by a motor. Distance adjustment may also be made by changing the optical distance between the two lenses without changing the physical distance therebetween in a different embodiment.

[0043] In one embodiment, the diameter of the collimated beam **14B** may be about 10 mm, and the distance between lenses **21** and **23** (thus divergence of beam **14B**) may be adjusted so that the diameter of beam **14B** may be varied to a few mm above or below 10 mm at the input aperture of microscope **28**.

[0044] In system **10**, expander **20** includes a varioSCAN 20™, provided by Scanlab AG™. This device may be controlled using an RTC™ control board and control software provided by the same company. Details of construction and operation of varioSCAN 20™ can be obtained from Scanlab, such as from its website: www.scanlab.de/. In other embodiments, varioSCAN 20™ may be replaced with another suitable expander and dynamic focusing device.

[0045] A mirror **24** is placed downstream of expander **20** to direct expanded collimated beam **14B** into a scanner **26**.

[0046] Scanner **26** re-directs beam **14B** to scan beam **14B** over a desired target region. A galvanometer scanner may be used as scanner **26**. For example, the scanner may be a ScanCube7™ scanner provided by Scanlab. In a typical galvanometer scanner, two scan mirrors (not separately shown) may be provided, each driven by a galvanometer. Each scan mirror is independently adjusted (turned) to redirect the beam in one dimension. Thus, the two scan mirrors in combination can scan the beam across a two-dimensional plane.

[0047] A focusing device, such as a microscope **28**, is placed downstream of scanner **26**. Except the features expressly described herein, microscope **28** is otherwise a conventional microscope and can be constructed using conventional technology. Microscope **28** is positioned and configured to focus beam **14B** onto a focal plane in a focus region of a target material.

[0048] Microscope **28** has a dry objective lens **30**. A dry objective lens does not need to be immersed in oil or water to function properly. A dry objective lens can properly function when it is immersed in air or another gas environment. In this embodiment, a Nikon™ ELWD air objective is used. In other embodiments, other types of dry objectives may be used. Suitable Nikon ELWD air objectives include objectives that have magnification factors of 20x to 100x, such as 20x, 50x, and 100x. The numerical apertures (NA) of these objective lens are 0.4, 0.55, and 0.8, respectively. The 3-D resolution of these objective lens are respectively 1x1x7, 0.5x0.5x1, and 0.1x0.1x1, respectively (all in micron). The NA in dry objective lens **30** may vary from about 0.4 to about 0.9.

[0049] Objective lens **30** focuses beam **14B** onto a focal point (focus region) in target **32**.

[0050] Target **32** is supported by a support **34**, which includes an adjustment mechanism, such as a high-resolution stage or a galvanometer.

[0051] Support **34** may move and adjust the position of target **32** in three (3) dimensions. Support **34** may be motorized for moving the target. Support **34** can

move target **32** at least along the axial direction of beam **14**. Optionally, support **34** may be configured to also move target **32** in transversal directions. In some embodiments, support may be configured to provide both translational and rotational movement of target **32**.

[0052] A camera **36** such as a CCD (charge-coupled device) camera is provided for taking images of the processed target and monitoring the operation of apparatus **10**. Camera **36** may be positioned to receive light from mirror **22**.

[0053] A controller **38** may be provided for controlling the operation of apparatus **10**. Controller **38** is in communication with expander **20** for controlling the automatic adjustment of the distance between expansion lens **21** and expander objective lens **23** to reduce distortion (curvature) of the focal plane of microscope **28**. Controller **38** may also be in communication with one or more of laser source **12**, shutter **18**, scanner **26**, support **34**, and camera **36**, to receive input therefrom, and may optionally control the operation thereof. The distance adjustment may be controlled based, at least in part, on the position or location of the current beam waist, or on the position/angles of the scan mirrors in the scanner which determines the direction of the beam axis. For each given beam direction, a length value may be stored in a memory in association with the beam direction or the expected coordinates of the location of the beam waist. The distance between lenses **21** and **23** is set to the corresponding length associated with that location when the beam is scanned toward that location. In this regard, controller **38** may be in communication with both expander **20** and scanner **26** to synchronize the movement of the motorized lens in expander **20** and the scan mirrors in scanner **26**.

[0054] Controller **38** may include a computer or other computing devices and may also include software for controlling the operation of apparatus **10**. The control software may include a modified SCAPS program. This program can synchronize the motion of a support stage and the beam scanning and can perform slide by slide scanning.

[0055] Controller **38** may be an integrated device or be provided as multiple separated units.

[0056] In this embodiment, system **10** has a scan speed of up to 30 mm/s and a scan height of up to 30 mm. The scan speed and scan height may be higher in other embodiments depending on the components used.

[0057] **FIG. 2** schematically shows objective lens **30** and target **32**, in more detail. In this embodiment, target **32** includes a target material **40** sandwiched between a top plate **42** and a bottom plate (or substrate) **44**. Top plate **42** and bottom plate **44** are spaced apart by spacers **46**.

[0058] As illustrated in **FIG. 2**, at the focal point of the focused beam **14C**, the beam radius/diameter or width of beam **14C** is at the minimum (referred to as the beam's spot size). This portion of beam **14C** is referred to as its beam waist. In an embodiment of the present invention, when the incident angle of beam **14B** at microscope **28** is varied by scanner **26**, the focal point or beam waist of focused beam **14C** also moves within or close to a focal plane **48**, which is perpendicular to the optical axis **50** of objective lens **30**, due to automatic correction of the focal plane distortion provided by the dynamic adjustment of the distance between lenses **21** and **23**.

[0059] In an embodiment of the present invention, the distance between lenses **21** and **23** is dynamically adjusted to keep the beam waist of focused beam **14C** remain substantially in focal plane **48**, as will be further described below.

[0060] In use, system **10** is operated as follows.

[0061] A beam of laser **14** is produced by laser source **12**. The beam has a sufficiently high peak and average power, such as larger than 310 kW and 2.5 W respectively. Beam **14** has no wavelength that will cause single photon photochemical reaction in the target material **40**, and includes a wavelength that is suitable for triggering or inducing two-photon photochemical reaction in target material **40**. Thus, the spectrum of beam **14** may be a narrow band centered at a desired wavelength or may have a single wavelength. The central wavelength may be in the range of about 700 to about 1020 nm depending on the target material and the reactions that are to be photo-initiated.

[0062] Beam **14A** passes through isolator **16** and then shutter **18**. Isolator **16** prevents any reflected light from getting into laser source **12**, and can thus prolong the lifetime of laser source **12**. Shutter **18** is controlled by controller **38** to selectively stop passage of beam **14** therethrough. The maximum shutter speed may be below 110 MHz in some applications.

[0063] Beam **14A** is directed by mirror **22** to expander **20**. Expander **20** produces an expanded and collimated beam **14B**. The beam width of beam **14B** is larger than the beam width of beam **14A**, for example, by about 4 to about 10 times. The beam width of beam **14B** may be selected to balance a number of factors and considerations. For example, higher expansion may be advantageous for reducing the moving distance of motorized lens in expander **20**. On the other hand, a larger expansion may result in a larger power loss, such as when the beam width is wider than the diameter of the input aperture in microscope **28**. Beam **14** passes through, in order, expansion lens **21** and focusing lens **23**.

[0064] The expanded beam **14B** is directed to scanner **26** by mirror **24**.

[0065] Scanner **26** re-directs and scans beam **14B** onto target **32** through microscope **28** and objective lens **30**. Beam **14B** is focused by objective lens **30** onto a confined volume, the focus region, in target material **40** which is held in position by plates **42** and **44** and support **34**. Dry objective lens **30** is not immersed in any liquid during use but is exposed to air (or another gas).

[0066] The objective lens **30** focuses expanded and collimated beam **14B** into a focus region in the target material **40**. When large optical elements are used, the beam waist of focused beam **14C** can significantly deviate from the focal plane **48** of objective lens **30**. That is, the focal plane distortion at off-axis locations can be significant so as to substantially affect the shape of the product formed. Ideally, beam **14** should be focused onto focal plane **48** regardless of whether its path is near or away from optical axis **50** of objective lens **30**. In practice, it may be acceptable that the beam waist is kept sufficiently close to a plane **48** (i.e. substantially in the plane) as beam **14** is scanned.

[0067] Thus, to improve production quality, focal plane distortion may need to be reduced or eliminated. Without such correction, the focus region would need to be sufficiently small and the resolution of the objective lens would need to be sufficiently high to ensure quality production. With the automatic, real-time reduction or correction of focal plane distortion as described herein, an objective lens with a relatively low resolution, such as a dry objection lens, can be used for two-photon stereolithography.

[0068] In an exemplary embodiment of the present invention, potential focal plane distortion is reduced or corrected by dynamically adjusting the distance between the expansion lens **21** and the focusing lens **23** in expander **20**. This adjustment is automatically controlled by controller **38**. The divergence of collimated beam **14B** produced by expander **20** is dependent on the distance between lenses **21** and **23**. The divergence of collimated beam **14B** can thus be varied by adjusting this distance. The divergence of collimated beam **14B** in turn affects the focal distance of the focal point from objective lens **30**. Thus, by adjusting the distance between lenses **21** and **23** the focal distance can be varied to offset the effect of field curvature, and any other effects that cause focal plane distortion, so that the beam wais of focused beam **14C** (or focal point) remains substantially in the focal plane **48** as beam **14C** is scanned to successive scan positions. Generally, when beam **14** is scanned to a scan position where the beam waist is away from optical axis **50** of objective lens **30**, the focal distance will need to be increased by a suitable amount to offset the effect of field curvature and to keep the beam waist remain in focal plane **48**. The focal distance can be increased by increasing the divergence of the incident beam, collimated beam **14B**.

[0069] The amount of increase of the divergence for a given location, and thus the required length of distance between lenses **21** and **23**, can be initially estimated by calculation based on optics theory for the particular optical setup. The calculated lengths can be further fine tuned or verified by calibration. For example, the calibration may be carried out by visually inspecting an article produced using system **10**, such as with an SEM imaging technique. When the distance is adjusted correctly during beam scanning, the produced article should have a shape closely resembling the input drawing. If the shape of the produced article is deformed in

regions away from axis **50**, the distance data will need to be further modified. The selected length values for different scan positions may be stored, such as in a memory (not separately shown) in controller **38**, in association with the respective scan positions for later retrieval and use. The memory may also be separate from, but in communication with, controller **38**, so that controller **38** can access the stored distance data during operation. In either case, controller **38** can control the adjustment of the distance in synchronization with the movement of scanner **26** based on the stored distance data and the current scan position.

[0070] For example, the distance data and the associated scan positions may be stored in a table format. The distance data may be presented as absolute length values or as differences from an initial distance. For instance, the initial distance may be a distance for producing an optimally collimated beam. The scan position may be defined or represented/expressed in different manners. For example, in some embodiments, the scan position may be defined by the scanner mirror positions. In other embodiments, the scan position may be defined by the direction of beam **14B** such as relative to the optical axis of microscope **28** or objective lens **30**. The scan positions may also be defined by the two-dimensional coordinates of the intercept of the beam axis and the focal plane **48**. For example, if the direction of optical axis **50** is defined as the z-axis, the x-y coordinates of the intercept may be used to define the scan position of beam **14**.

[0071] In one embodiment, to produce a 3D structure in a target material, a 3D drawing of the structure to be produced is broken down into component slices, lines and dots. The target material is first fixed in position to form a slice of the structure by scanning beam **14** using scanner **26** according to the input slice image and by synchronized adjustment of the distance between lenses **21** and **23** to maintain the beam waist within a plane that overlaps the desired slice during scanning. The target material is then repositioned to form the next slice of structure. This process can continue until the entire 3D structure is formed.

[0072] In one embodiment, the wavelength of beam **14** may be about 740 nm. The dry objective lens **30** may have a magnification factor of 20 and the microscope **28** may have a field of view of 400 μm by 400 μm . The spot size of the

beam waist at the focal point may be about 2 μm or less. The depth of focus may be about 10 μm .

[0073] Target material **40** may be any suitable material selected for the particular application, as discussed herein.

[0074] Support **34** is controlled by controller **38** or another controller (not shown) to adjust the position of target **32** as appropriate. The positions may be adjusted based on user input or automatically according to a pre-programmed procedure and based on dynamic input received by controller **38**.

[0075] The process can be monitored in real-time with camera **36**. The images captured by camera **36** may be communicated to controller **38** for processing or analysis and may be used as input for controlling other components in the system.

[0076] The speed of beam scan across target **32** can be as high as 30 mm/s.

[0077] The scan height (along axial direction of the beam) can be as high as 30 mm.

[0078] The scan resolution of system **10** can be varied using different objective lenses and can be as high as 0.1x0.1x0.1 (in micron) with 100x magnification.

[0079] When beam **14** with a sufficient power (beam intensity) and suitable wavelength or spectrum is focused into the focus region of target material **40**, two-photon absorption occurs with a high frequency and photochemical reactions such as photo-induced polymerization will proceed with a sufficiently high rate.

[0080] For instance, in a typical two-photon polymerization process, near-infrared (NIR) light with high peak power is focused on a photopolymer. The photopolymer includes photo-initiators that can form a radical when a single UV photon is absorbed and the absorbed photon energy excites an electron to initiate photo-chemical reaction. The resulting radical will cleave the double bonds of the unsaturated carbon bonds in the acryl groups of the monomers and oligomers,

successively creating new radicals. This chain reaction is terminated when two chain radicals meet and react with each other. The same initiator can simultaneously absorb two coherent NIR photons and form the radical, as the combined photon energy from the two photons can also excite the electron to initiate the same photo-chemical reaction. The probability of two-photon absorption can be approximated by the following equation,

$$n_a \propto \frac{\delta_2 P_{ave}^2}{\tau_p f_p^2} \left(\frac{NA^2}{2\eta c \lambda} \right)^2, \quad \text{Equation (1)}$$

where n_a is the probability that a certain fluorophore in the target material **40** simultaneously absorbs two photons during a single laser pulse, P_{ave} is the time average power of laser beam **14**, δ_2 is the molecular cross-section of the fluorophore molecules in the target material **40**, τ_p is the duration of each laser pulse, f_p is the repetition rate of the laser, $\eta = \frac{h}{2\pi}$ (h being the Plank constant), λ is the excitation wavelength (or the single-photon absorption wavelength), c is the speed of light, and NA is the numerical aperture of objective lens **30**.

[0081] As can be determined from the above equation, a consequence of two-photon absorption initiated photochemical reaction is that sufficient photo-chemical reaction can occur within a confined region, the focus region around the beam waist, to cause structural change within the focus region, but not outside the focus region because the probability of two-photon absorption outside the focus region is too low to cause significant structural change. The focus region in two-photon absorption is axially confined. That is, the focus region only extends along a small portion of the axis of the objective lens. Practically speaking, the probability of two-photon absorption/excitation falls off as the fourth power of the distance from the focal point of the objective lens, as the laser intensity itself has a quadratic dependence on axial distance. Typically, the volume of the focus region in two-photon absorption can be about 10^{-12} cm^3 or less. In contrast, the probability of single-photon absorption remains more stable over a large portion of the axis of the objective lens, as it is only a function of the laser intensity which is in turn linearly dependent on axial distance.

[0082] As a result of the two-photon absorption/excitation initiated photochemical reactions, a desired structural change will occur within the focus region of target material **40**. The structural change can include chemical structural change, physical structural change, or both. The structural change can be visible or invisible to human eye. Because two-photon absorption only occurs with high probability in the focus region, no significant structural change will occur outside the focus region. By controlling the incidence direction of beam **14B** relative to the target material **40**, and thus the focus region in target material **40**, 3-D structures can be produced. This process may be controlled by controller **38**.

[0083] The axial movement of the focus region within target material **40** is accomplished by axially moving support **34** along the axial direction of the optical axis **50** of objective lens **30**. The transversal movement of the focus region within target material **40** is accomplished by re-directing beam **14B** using scanner **26** to scan the beam to successive scan positions. Additional transversal movement may be achieved by translational or rotational movement of support **34** in the plane transversal to the optical axis **50** of objective lens **30**. In different embodiments, these movements may be effected differently. For example, axial movement may be effected by changing the focal plane of the beam, such as by adjusting or moving one or more optical focusing elements (e.g. microscope **28**).

[0084] As now can be appreciated, system **10** can conveniently provide certain benefits. As no immersion liquid such as oil is needed to immerse the objective lens, the chance for contamination of focusing elements and the target material is reduced or minimized. As plane distortion is corrected dynamically, larger optical elements can be used thus increasing the sizes of devices that can be fabricated using system **10**. The operation of system **10** is more flexible and easier as compared to some conventional devices. The scan speed and scan height are relative high in system **10**, as compared to conventional two-photon lithography techniques where the objective lens are immersed in oil or water. The scan height in these conventional techniques is limited by the size of the oil droplets and the focal diameter of the objective lens and is typically less than about 1 mm. In system **10**, the requirements for objective lens **30** are not as strict as for oil immersed objective lenses used in the conventional techniques. Thus, a wider

selection of objective lenses may be used in system **10**. When an AOM is used as the shutter, the shutter speed is faster. As expander **20** can provide automatic slice planarity control, relatively high magnification and resolution can be achieved without an oil immersion objective lens in two-photon lithography applications.

[0085] In addition, system **10** may be provided with laser focus wobble function, device stitching function, and device arraying. These functions make it possible to produce larger target devices by moving the support stage in the transversal directions.

[0086] System **10** can provide relatively high production throughput as compared to oil or water immersion based two-photon techniques.

[0087] System **10** may be modified while still retaining one or more of the benefits described herein. For example, laser beam properties may be varied in different embodiments and for different applications; and some components or devices may be located at an alternative position and still serve the same functional purposes. For instance, in different embodiments, camera **36** may be placed elsewhere and may receive reflected light from another point in the optical path of beam **14**. Isolator **16** may be integrated with laser source **12**. Shutter **18** may also be integrated with another optical component, such as laser source **12** or expander **20**, or placed downstream of expander **20**. Expander **20** may be provided as an integral unit or as an assembly of multiple units. Other suitable expander devices such as other suitable devices provide by Scanlab AG may be used as expander **20**. Different optical path of beam **14** may be selected, using more or less mirrors and by placing mirrors or other deflecting or reflecting elements at different locations in the beam path. In different embodiments, the objective lens of the microscope may face different directions. As the objective lens is not immersed in a liquid such oil, the optical axis of the objective lens may be substantially aligned with the vertical direction, or a horizontal direction, or any other direction.

[0088] In a further example, system **10** may be operated in a manner different from the process described above.

[0089] Laser source **12** may also be replaced with another type of light source which can provide a beam of photons of suitable properties.

[0090] In different embodiments, any optical element of system **10**, such as a lens, may be implemented in different manners. For example, each lens may be provided as a single lens, a compound lens, or a group of lenses integrated or combined to provide the desired function.

[0091] Additional optical elements, which may direct, focus or otherwise modify the beam properties or travel direction, may be placed in or along the beam path to perform a function desired for a given application. The additional optical elements may be placed at any suitable point of the beam path, and may be integrated with an element already shown in **FIG. 1**. For example, additional optical elements or features may be provided to improve the performance of the system, including aberration reduction or correction, where the aberration may be spherical, coma, or chromatic, or the like.

[0092] When reference is made to a plane such as a focal plane, it should be understood that in practical application, slight displacement of the beam waist from the focal plane at certain locations may be inevitable and may be permissible. For example, if the slight displacement does not result in unacceptable structural defects in the finished product, it may be tolerable. As can be understood, for practical purposes when the beam waist is sufficiently close to the focal plane, the structure formed by two-photon absorption induced polymerization may be substantially the same as, or even indistinguishable from, a structure produced with the beam waist strictly moved within the focal plane, due to the depth of focus for the particular optical setup. Thus, it should be understood that it is not necessary that the distance data be selected to restrict the movement of the beam waist to within a geometrical plane. Further, due to many practical limitations, it may not be possible to select distance data such that the beam waist always remains strictly within a geometrical plane. It therefore should be understood that, when a distance is selected to offset the field curvature effect at a given location to focus the beam at a location within the focal plane, it is sufficient that with the selected distance, the beam is focused such that the beam waist is within a tolerable distance from the ideal focal plane. Therefore, for the purposes of this invention, it should be

understood that the locations of the beam waist are considered to be within a plane when they are generally within a plane or when they are sufficiently close to a plane so that their displacement from the plane has no material effect on the finished product.

[0093] An embodiment of the present invention such as a composition described herein may have various applications in many different fields. For instance, the compositions may be used for fabrication of 3D nanometer-scale (> 100 nm) devices, and may be used in semiconductor industry (e.g. as direct-write lithography machine, for producing phase mask, for direct fabrication of optical components onto IC (integrated circuit) devices, for fabrication of sensors); in photonics (e.g. for processing photonic crystals and other optical structures, and quantum electronics); in wireless industry (e.g. for fabrication of resonators, waveguides, all-optics micro-transceiver devices); for fabrication of 3D nanometer-scale microelectromechanical system (MEMS) and nanoelectromechanical system (NEMS) devices; in rapid prototyping industry (e.g. for use in rapid prototyping systems and devices); in tissue engineering (e.g. for fabrication of tissue scaffold, for organ regeneration); in chemical and pharmaceutical industries (e.g. fabrication of substrates for the synthesis of chiral compounds), and the like.

[0094] Sample articles and devices were fabricated by two-photon stereolithography using exemplary compositions described herein. SEM images of two sample products are shown in **FIGS. 3, 4, 5** and **6**. The sample products were formed with a laser light with a wavelength of about 710 nm and an average laser power of about 1W.

[0095] Other features, benefits and advantages of the embodiments described herein not expressly mentioned above can be understood from this description and the drawings by those skilled in the art.

[0096] Of course, the above described embodiments are intended to be illustrative only and in no way limiting. The described embodiments are susceptible to many modifications of form, arrangement of parts, details and order of operation. The invention, rather, is intended to encompass all such modification within its scope, as defined by the claims.

WHAT IS CLAIMED IS:

1. A method of processing a material to form a three-dimensional article, comprising:

providing a photocurable material comprising a poly(meth)acrylate having a (meth)acrylate functionality of at least 3 and a molecular weight (MW) of at least 650, a urethane(meth)acrylate having a (meth)acrylate functionality of 2 to 4 and a MW of 400 to 10,000, a di(meth)acrylate made from bisphenol A or bisphenol F; and a photoinitiator;

focusing a beam of light to a focus region of said material to induce two-photon absorption in said focus region, and thus polymerization of said material in said focus region, a wavelength of said light being selected to induce said two-photon absorption in said material; and

scanning said beam across said material according to a pre-selected pattern so that said beam is focused to different pre-selected regions, to induce polymerization of said material at said pre-selected regions.
2. The method of claim 1, comprising removing a un-polymerized portion of said material from a polymerized portion of said material, thus forming said three-dimensional article.
3. The method of claim 1 or claim 2, wherein said material comprises 2 to 20 wt% of said poly(meth)acrylate, 20 to 60 wt% of said urethane(meth)acrylate, 20 to 80 wt% of said di(meth)acrylate, and 0.1 to 10 wt% of said photoinitiator.
4. The method of claim 3, wherein said poly(meth)acrylate has a MW in the range of 880 to 1200.
5. The method of any one of claims 1 to 4, wherein said material comprises 5 to 18 wt% of said poly(meth)acrylate.
6. The method of any one of claims 1 to 5, wherein said material comprises 20 to 50 wt% of said urethane(meth)acrylate.
7. The method of any one of claims 1 to 6, wherein said material comprises 35 to 55 % of said di(meth)acrylate.

8. The method of any one of claims 1 to 7, wherein said material comprises 2 to 8 wt% of said photoinitiator.
9. The method of claim 1 or claim 2, wherein said material comprises 8 to 16 wt% of said poly(meth)acrylate, 25 to 45 wt% of said urethane(meth)acrylate, 40 to 50 wt% of said di(meth)acrylate, and 3 to 7 wt% of said photoinitiator.
10. The method of any one of claims 1 to 9, wherein said di(meth)acrylate is monomeric or oligomeric.
11. The method of claim 10, wherein said di(meth)acrylate is a mixture of ethoxylated bisphenol A diacrylate and ethoxylated bisphenol A dimethacrylate.
12. The method of any one of claims 1 to 11, wherein said scanning comprises scanning said beam according to a first pre-selected pattern to induce polymerization at pre-selected regions within a first layer, and subsequently scanning said beam according to a second pre-selected pattern to induce polymerization at pre-selected regions within a second layer.
13. The method of claim 12, wherein said first pattern and said second pattern are different.
14. The method of claim 12, wherein said first pattern and said second pattern are identical.
15. The method of any one of claims 12 to 14, wherein said scanning is repeated to polymerize selected regions in more than two layers of said material.
16. The method of any one of claims 1 to 15, wherein said beam has a spot size of about 2 μm or less at said focus region.
17. The method of any one of claims 1 to 16, wherein said focus region has a volume of about 10^{-12} cm^3 or less.