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(54) **METHOD FOR LASER-ASSISTED MANUFACTURING**

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B22F 12/00 (2021.01)
B33Y 10/00 (2015.01)
(Continued)

(52) **U.S. Cl.**
CPC ***B22F 12/00*** (2021.01); ***B05B 5/025*** (2013.01); ***B22F 1/054*** (2022.01); ***B29C 64/00*** (2017.08);
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(58) **Field of Classification Search**
CPC B22F 12/00; B22F 1/054; B22F 10/10; B22F 12/55; B22F 10/25; B22F 10/28;
(Continued)

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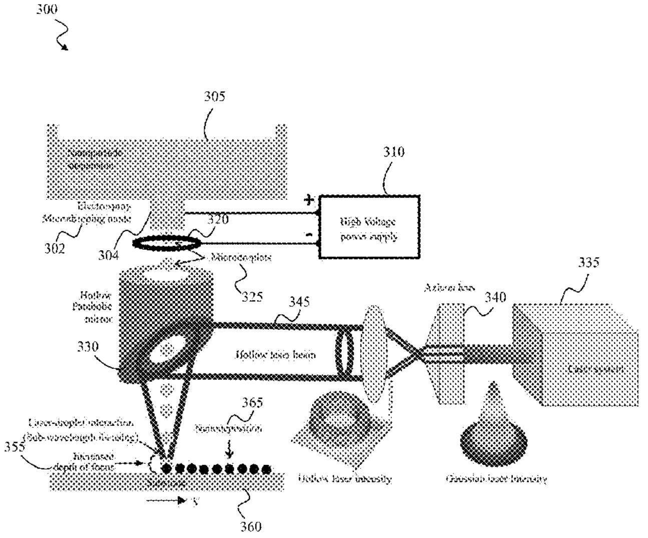
(57) **ABSTRACT**

A laser-assisted microfluidics manufacturing process has been developed for the fabrication of additively manufactured structures. Roll-to-roll manufacturing is enhanced by the use of a laser-assisted electrospray printhead positioned above the flexible substrate. The laser electrospray printhead sprays microdroplets containing nanoparticles onto the substrate to form both thin-film and structural layers. As the substrate moves, the nanoparticles are sintered using a laser beam directed by the laser electrospray printhead onto the substrate.

10 Claims, 9 Drawing Sheets



Related U.S. Application Data

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(51) **Int. Cl.**

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B33Y 70/00	(2020.01)
H01L 31/0352	(2006.01)
H01L 31/0312	(2006.01)
H01L 31/0745	(2012.01)
H01L 31/18	(2006.01)
B29C 64/00	(2017.01)
H01L 31/06	(2012.01)
H01L 31/075	(2012.01)
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B05D 1/04	(2006.01)
B05D 3/06	(2006.01)
C03B 19/01	(2006.01)
C03B 19/06	(2006.01)
B22F 10/10	(2021.01)

(52) **U.S. Cl.**

CPC ***B33Y 10/00*** (2014.12); ***B33Y 30/00*** (2014.12); ***B33Y 70/00*** (2014.12); ***H01L 31/0312*** (2013.01); ***H01L 31/035218*** (2013.01); ***H01L 31/035254*** (2013.01); ***H01L 31/06*** (2013.01); ***H01L 31/075*** (2013.01); ***H01L 31/0745*** (2013.01); ***H01L 31/1812*** (2013.01); *B05D 1/04* (2013.01); *B05D 3/06* (2013.01); *B22F 10/10* (2021.01); *C03B 19/01* (2013.01); *C03B 19/06* (2013.01)

(58) **Field of Classification Search**

CPC B22F 12/33; B22F 12/44; B22F 12/53; B05B 5/025; B29C 64/00; B33Y 10/00; B33Y 30/00; B33Y 70/00; H01L 31/0312; H01L 31/035218; H01L 31/035254; H01L 31/06; H01L 31/0745; H01L 31/075; H01L 31/1812; B05D 1/04; B05D 3/06; C03B 19/01; C03B 19/06; Y02E 10/548; Y02P 10/02

See application file for complete search history.

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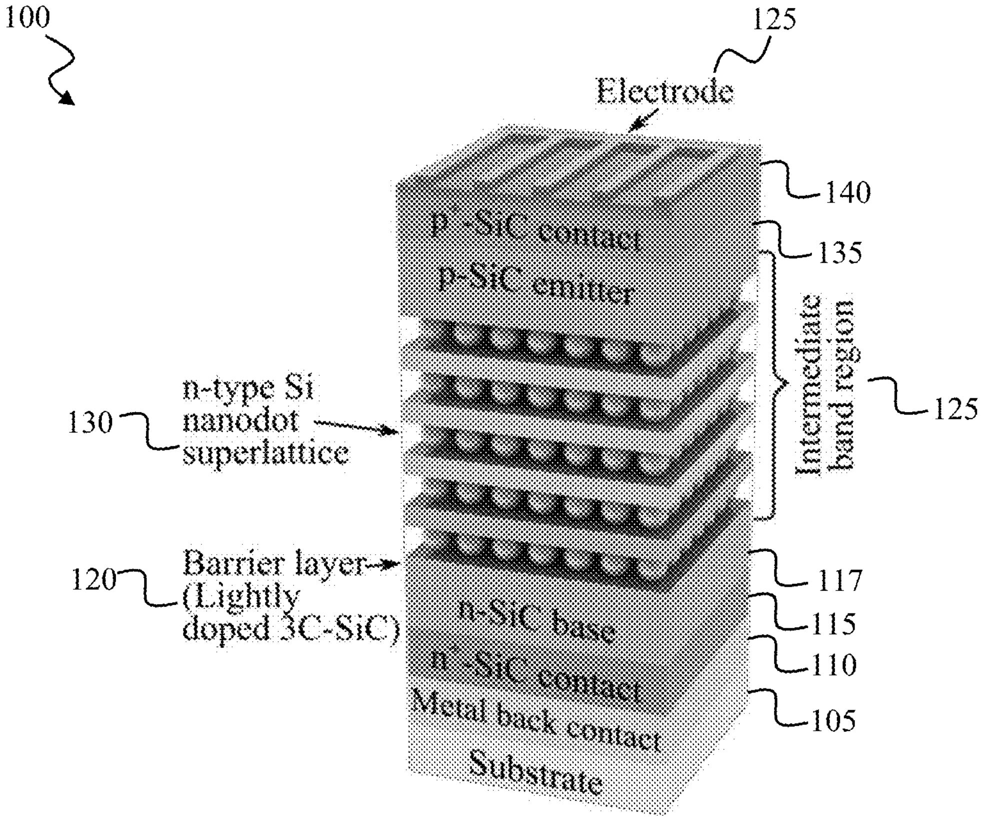

100
125
Electrode
140
p^+-SiC contact
135
p-SiC emitter
Intermediate band region
125
130
n-type Si nanodot superlattice
120
Barrier layer (Lightly doped 3C-SiC)
117
n-SiC base
115
n^+-SiC contact
110
Metal back contact
105
Substrate

FIG. 1

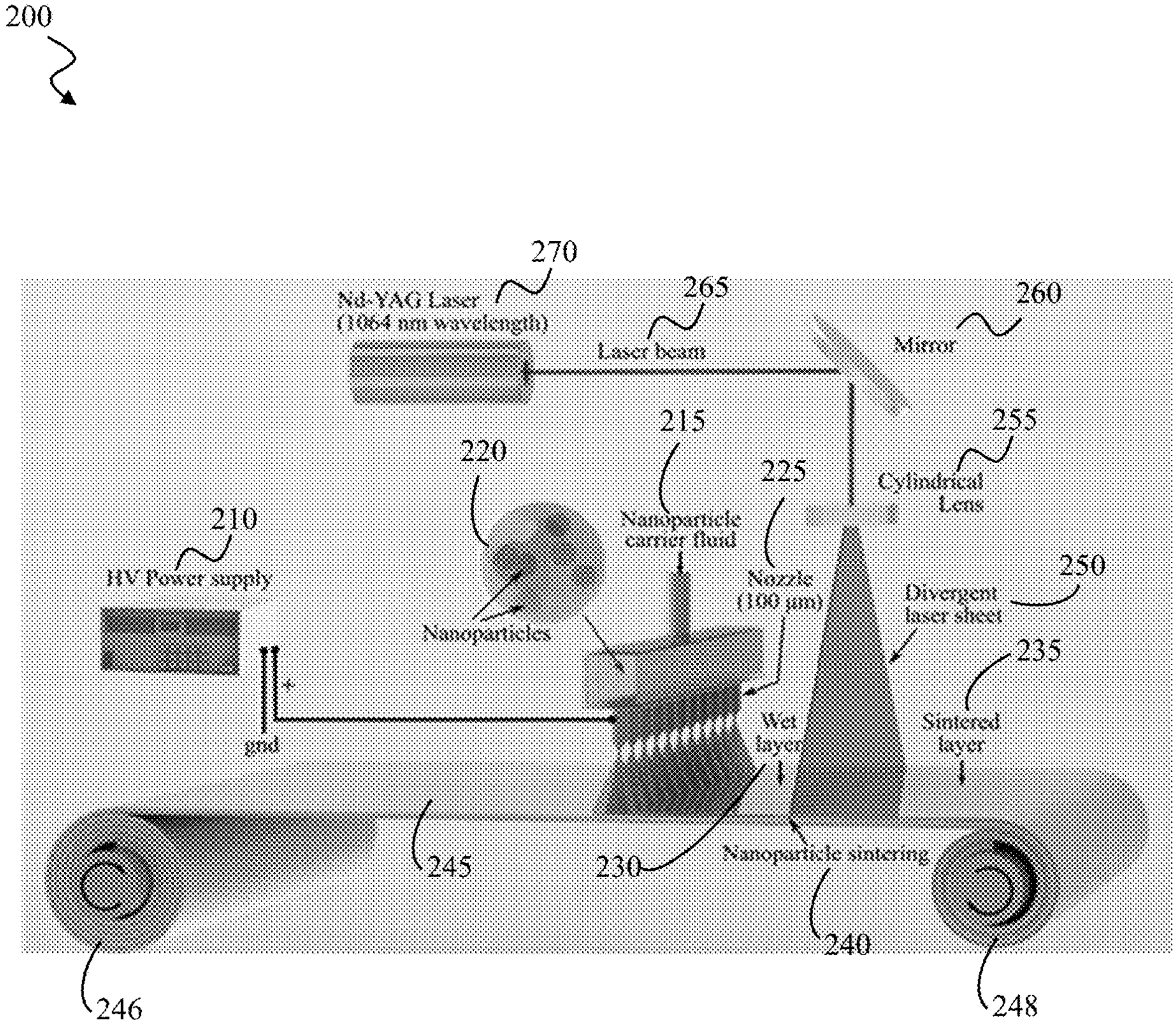

200
270
Nd-YAG Laser
(1064 nm wavelength)
265
Laser beam
260
Mirror
255
Cylindrical
Lens
215
Nanoparticle
carrier fluid
220
225
Nozzle
(100 μm)
210
HV Power supply
Nanoparticles
250
Divergent
laser sheet
235
+
gnd
Wet
layer
Sintered
layer
245
230
Nanoparticle sintering
240
246
248

FIG. 2

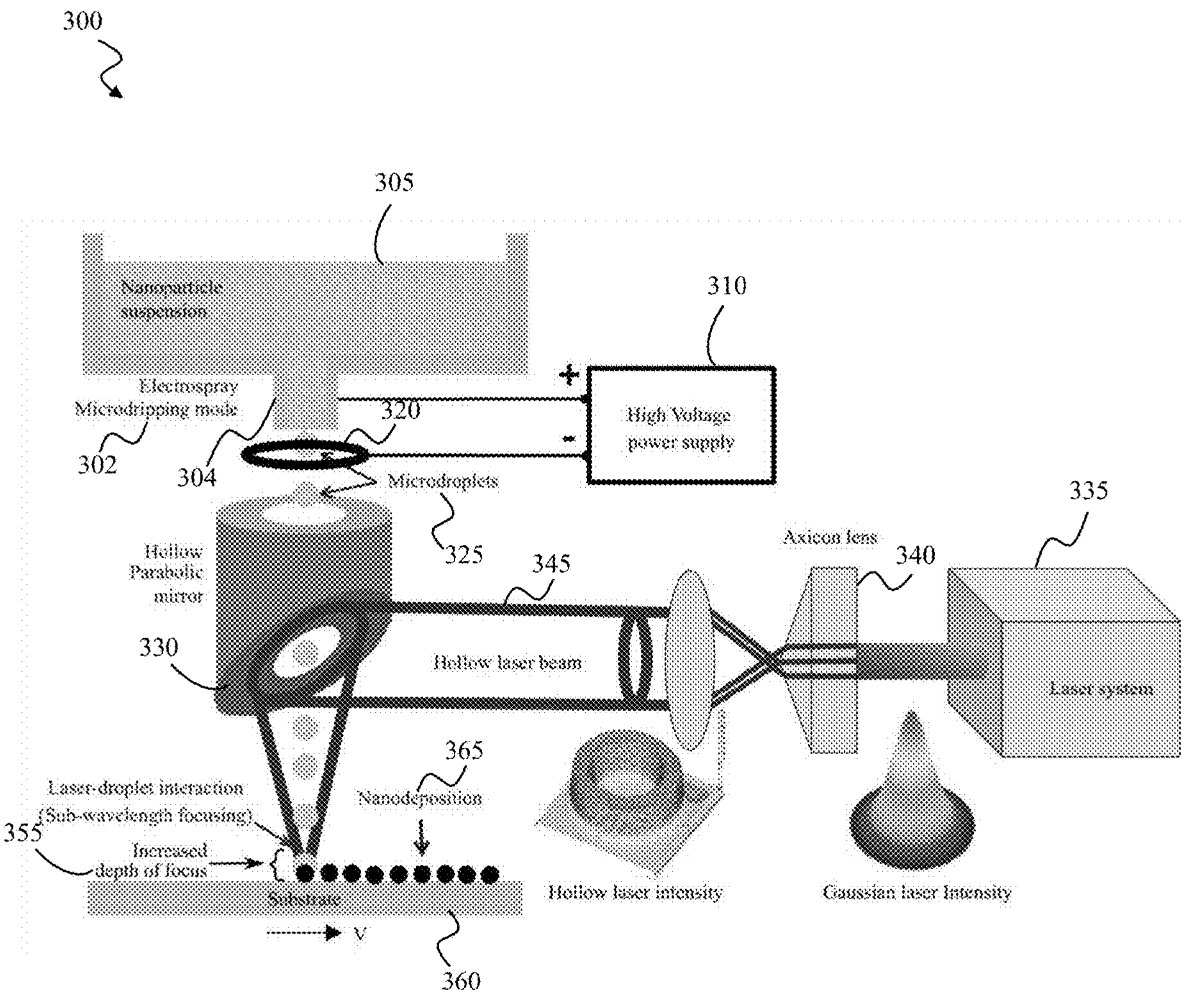
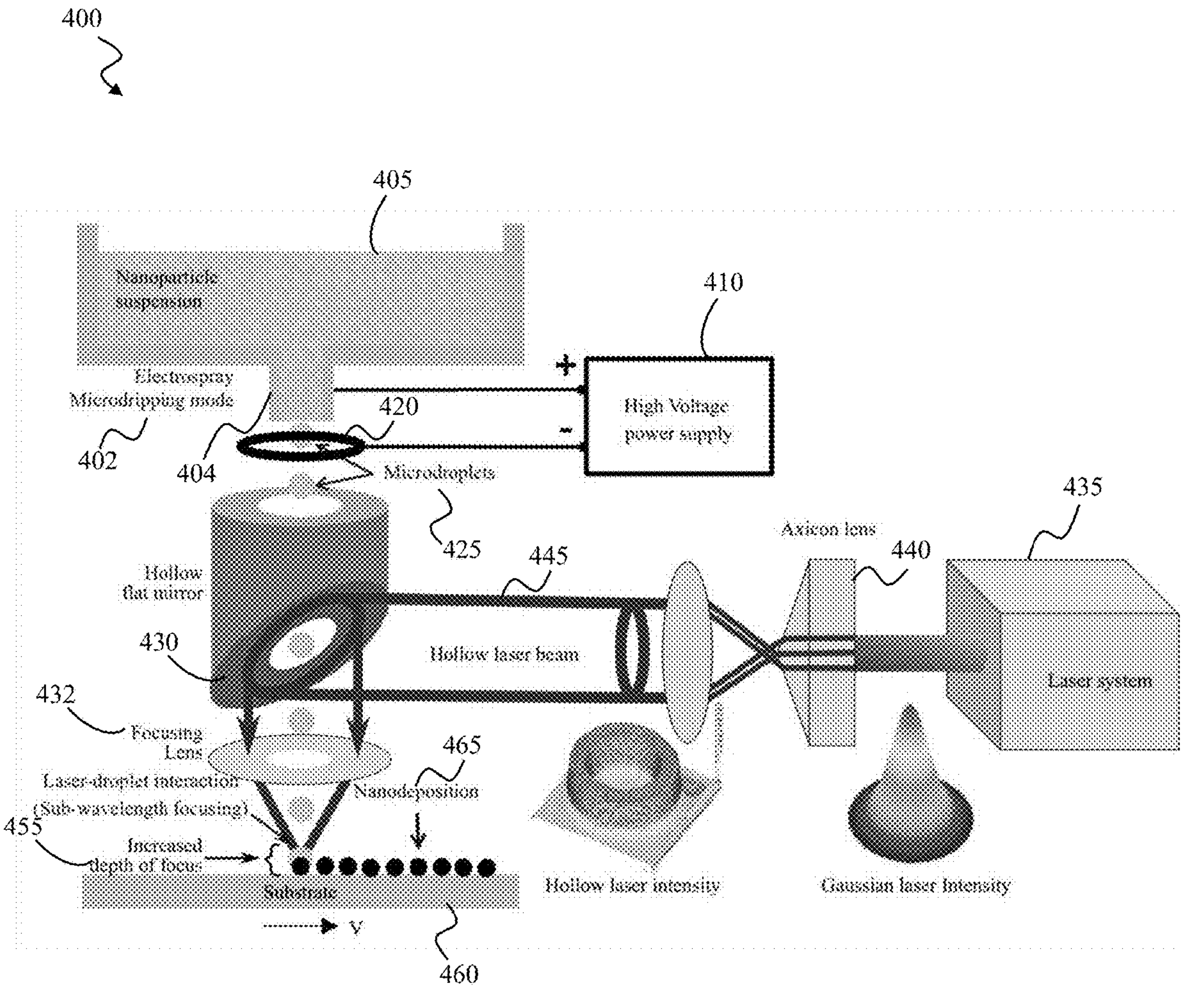

300
305
Nanoparticle suspension
310
High Voltage power supply
+
-
Electrospray Microdripping mode
302
304
320
Microdroplets
325
Hollow Parabolic mirror
330
345
Hollow laser beam
Axicon lens
340
335
Laser system
365
Nanodeposition
Laser-droplet interaction (Sub-wavelength focusing)
355
Increased depth of focus
Substrate
V
360
Hollow laser intensity
Gaussian laser Intensity

FIG. 3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405
Nanoparticle suspension
410
+
-
High Voltage power supply
Electrospray Microdripping mode
402
404
420
Microdroplets
425
435
Axicon lens
440
445
Hollow flat mirror
430
Hollow laser beam
Laser system
432
Focusing Lens
465
Laser-droplet interaction (Sub-wavelength focusing)
Nanodeposition
455
Increased depth of focus
Substrate
V
460
Hollow laser intensity
Gaussian laser Intensity

FIG. 4

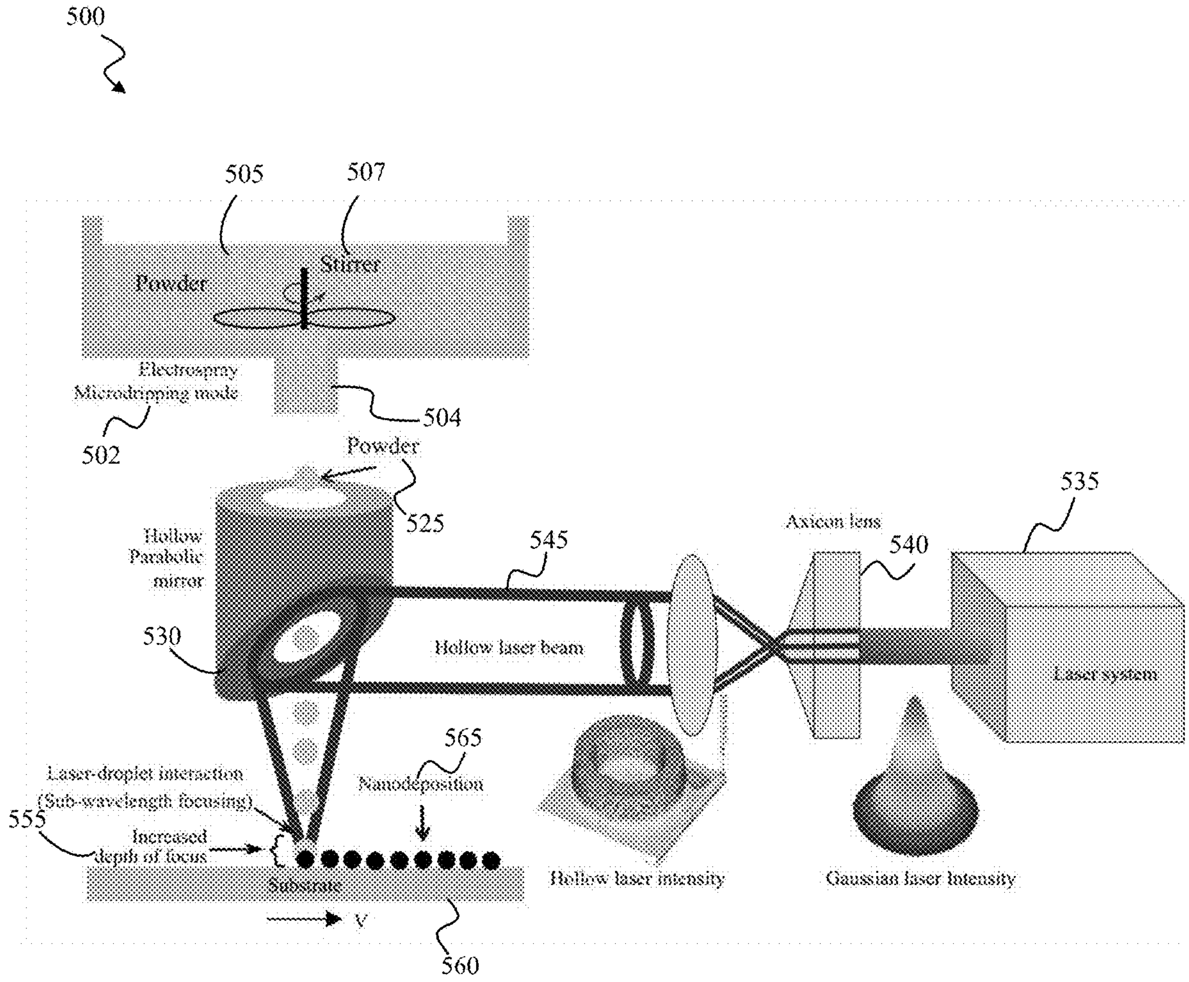
500
505
507
Powder
Stirrer
Electrospray
Microdripping mode
502
504
Powder
525
535
Hollow
Parabolic
mirror
545
Axicon lens
540
530
Hollow laser beam
Laser system
565
Laser-droplet interaction
(Sub-wavelength focusing)
Nanodeposition
555
Increased
depth of focus
Substrate
Hollow laser intensity
Gaussian laser Intensity
V
560

FIG. 5

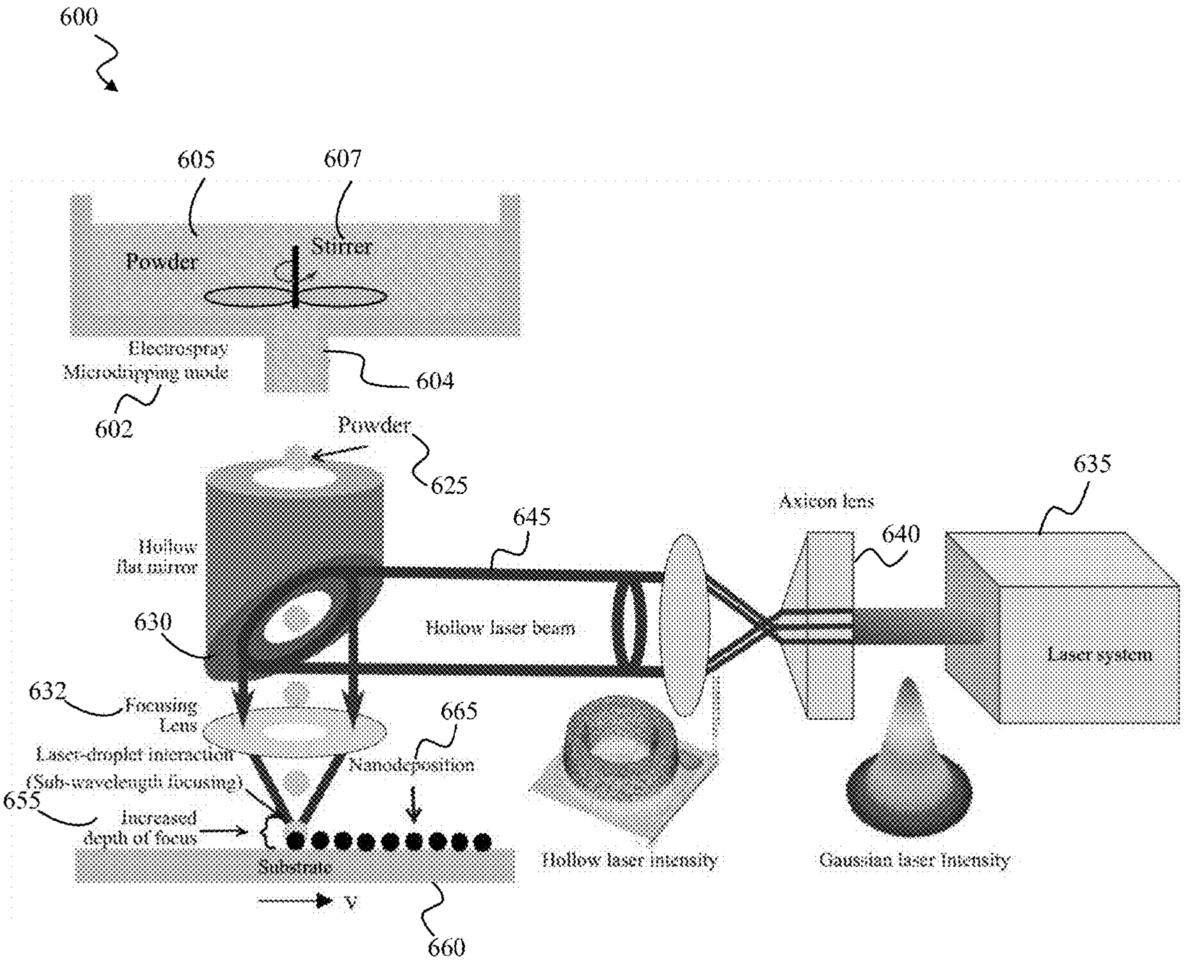
600
605
607
Powder
Stirrer
Electrospray
Microdripping mode
604
602
Powder
625
645
Axicon lens
640
635
Hollow
flat mirror
630
Hollow laser beam
Laser system
632
Focusing
Lens
665
Laser-droplet interaction
(Sub-wavelength focusing)
Nanodeposition
655
Increased
depth of focus
Substrate
V
660
Hollow laser intensity
Gaussian laser Intensity

FIG. 6

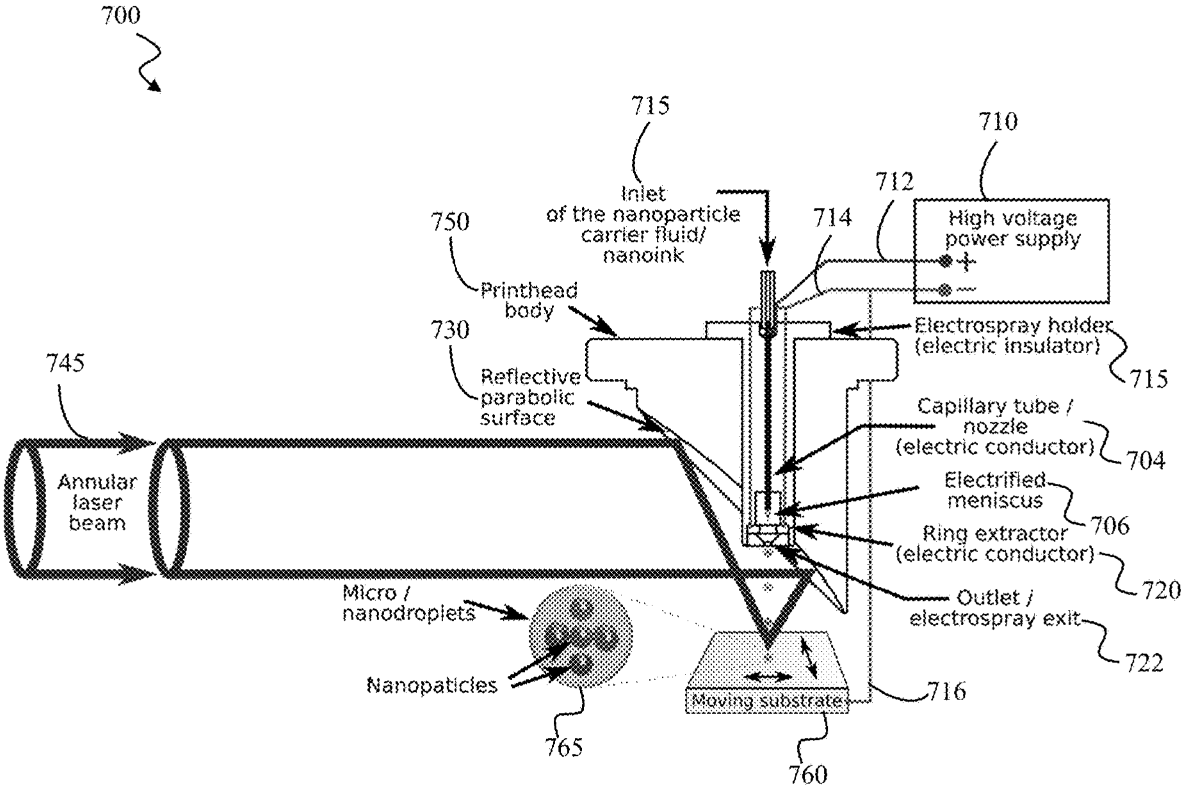
700
715
Inlet of the nanoparticle carrier fluid/ nanoink
710
High voltage power supply
+
−
712
714
750
Printhead body
Electrospray holder (electric insulator)
715
730
Reflective parabolic surface
745
Annular laser beam
Capillary tube / nozzle (electric conductor)
704
Electrified meniscus
706
Ring extractor (electric conductor)
720
Micro / nanodroplets
Outlet / electrospray exit
722
Nanopaticles
Moving substrate
716
765
760

FIG. 7

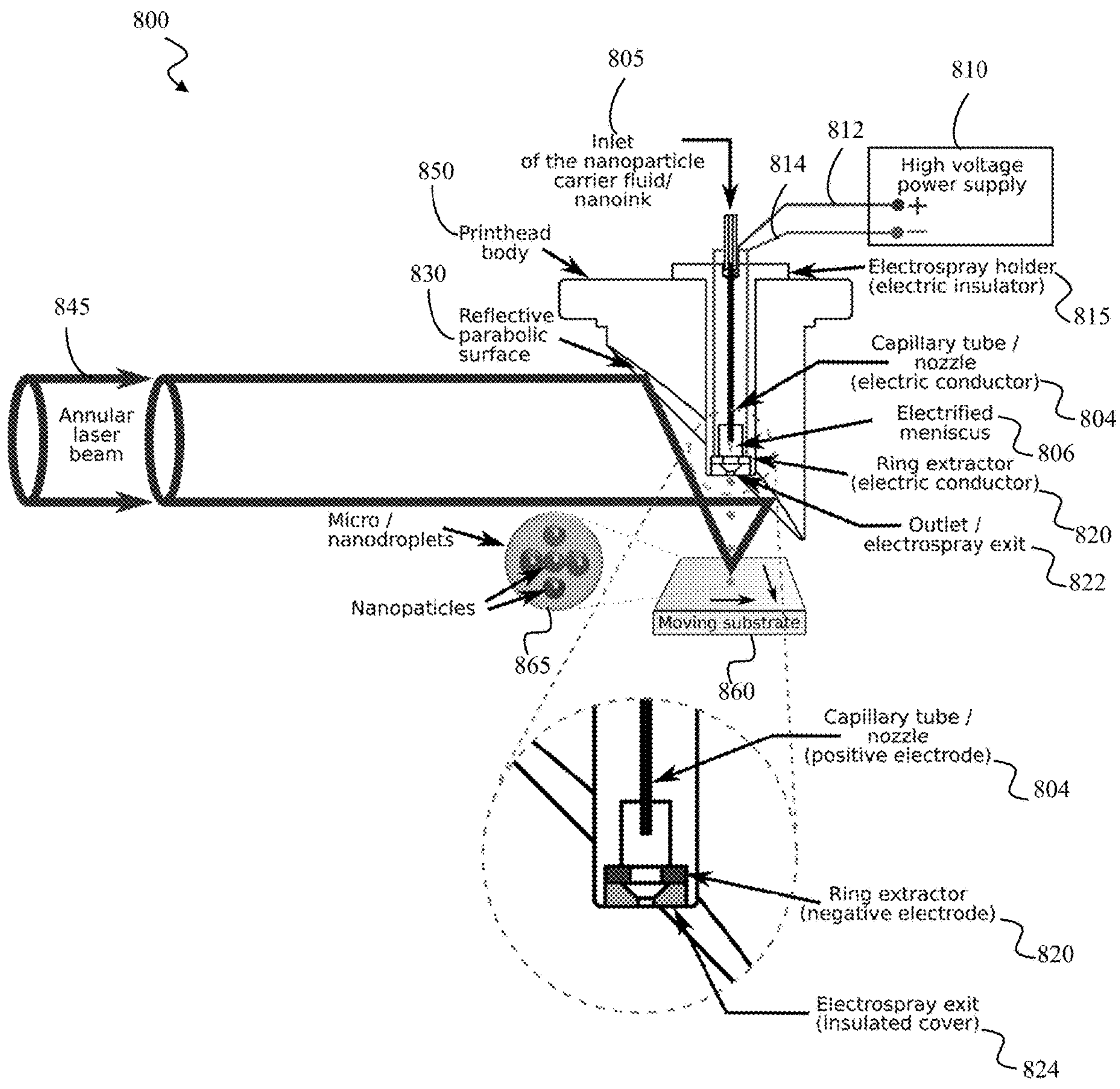
800
805
Inlet of the nanoparticle carrier fluid/ nanoink
810
High voltage power supply
+
−
812
814
850
Printhead body
830
Reflective parabolic surface
845
Annular laser beam
Electrospray holder (electric insulator)
815
Capillary tube / nozzle (electric conductor)
804
Electrified meniscus
806
Ring extractor (electric conductor)
820
Outlet / electrospray exit
822
Micro / nanodroplets
Nanopaticles
865
Moving substrate
860
Capillary tube / nozzle (positive electrode)
804
Ring extractor (negative electrode)
820
Electrospray exit (insulated cover)
824

FIG. 8

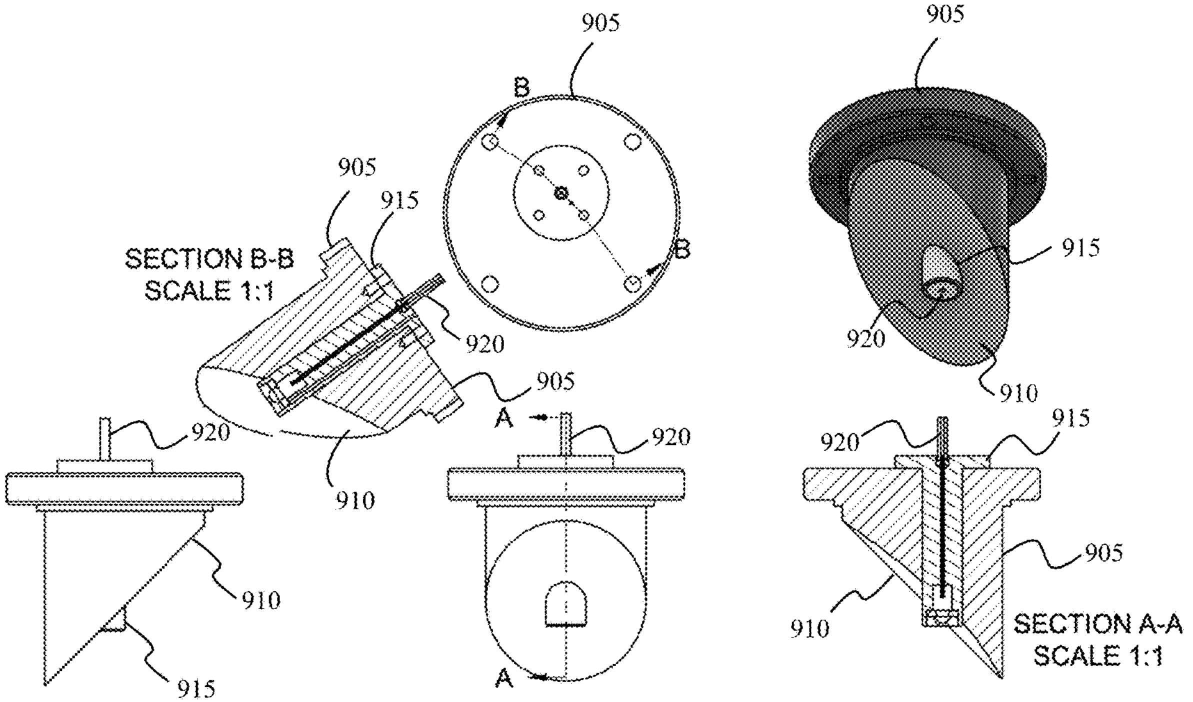
905
B
B
905
915
SECTION B-B
SCALE 1:1
920
905
910
905
915
920
910
920
A
920
A
910
915
920
915
905
910
SECTION A-A
SCALE 1:1

FIG. 9

METHOD FOR LASER-ASSISTED MANUFACTURING

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional of, and claims priority to, U.S. patent application Ser. No. 16/110,668, which is now a U.S. Pat. No. 11,084,100, entitled "LASER-ASSISTED MANUFACTURING SYSTEM AND ASSOCIATED METHOD OF USE", filed Aug. 23, 2018, which claims priority to U.S. Provisional Patent Application No. 62/549,176, entitled "LASER-ASSISTED MICROFLUIDICS MANUFACTURING PROCESS", filed Aug. 23, 2017 and U.S. Provisional Patent Application No. 62/581,434 entitled "LASER-ASSISTED MANUFACTURING PROCESS USING MICROFLUIDIC SUSPENSIONS AND DRY POWDERS," filed Nov. 3, 2017, the entirety of which are incorporated herein by reference.

GOVERNMENT SUPPORT CLAUSE

This invention was made with government support under Grant Number 1563448 awarded by National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

The ability to create thin films, in addition to 2-D and 3-D structural arrays of functional materials, addresses a technological need for many applications, including: flexible electronics, bio-sensing, optical coatings, energy conversion/harvesting, and data storage. Accordingly, high-resolution, scalable techniques that can achieve mass production of printed patterns using a variety of functional inks are currently needed in the art.

Microfluidic manufacturing process are known in the art for the fabrication of additively manufactured structures, such as Intermediate-Band Solar Cells (IBSCs). IBSCs incorporate an intermediate energy band that is partially filled with electrons within the forbidden bandgap of a semiconductor and are designed to provide a large photogenerated current, while maintaining a high output voltage. Photons having insufficient energy to advance electrons from the valence band to the conduction band use the intermediate energy band to generate an electron-hole pair. Nanostructured materials and microfluidic manufacturing processes have been employed in the practical implementation of intermediate-band devices, although manufacturing challenges remain.

Accordingly, what is needed in the art is an improved system and method for additive manufacturing that overcomes the challenges of the fabrication of new architecture

SUMMARY OF INVENTION

The present invention provides a laser-assisted microfluidics manufacturing system and method for the fabrication of additively manufactured structures, e.g., optoelectronic devices, intermediate band solar cells (IBSC), etc.

The inventive concept can be used for scalable large structures using roll-to-roll manufacturing. In the inventive system, the cylinders (feed spool and take-up spool) move or roll the flexible substrate through an electrospray module, which is placed above the flexible substrate. The electrospray module sprays microdroplets containing nanoparticles onto the substrate through both hydrodynamic and electrodynamic shear. As the substrate moves, the nanoparticles are sintered using a laser beam, and fused onto the substrate one layer at a time. The same concept can also be used for depositing regular arrays of microdots and nanodots.

In one embodiment, the present invention provides a method for laser-assisted manufacturing. The method includes, forming one or more sintered thin film layers on a substrate using an electrospray printhead operating in a cone-jet spray mode and forming one or more sintered structural layers adjacent to the one or more sintered thin film nanoparticle layers using the electrospray printhead operating in a micro-dripping mode. In particular, the method includes, providing a laser-assisted electrospray printhead comprising, a printhead body comprising a reflective surface, a laser beam and an electrospray holder positioned within the printhead body and extending from the reflective surface forming an electrospray exit. The method further includes, positioning the reflective surface of the printhead body to focus the laser beam onto a focal region above a deposition surface of a substrate, forming one or more sintered thin film layers on the substrate using the laser-assisted electrospray printhead operating in a cone-jet spray mode and forming one or more sintered structural layers adjacent to the one or more sintered thin film layers using the laser-assisted electrospray printhead operating in a micro-dripping mode.

The sintered thin film layers and the sintered structural layers are formed from a suspension selected from a microparticle suspension, a nanoparticle suspension, a biological tissues suspension, a microparticle powder, a nanoparticle powder and a biological tissue powder. Additionally, the sintered structural layers may be 2-dimensional or 3-dimensional layers.

Forming one or more sintered thin film layers on a substrate using an electrospray printhead operating in a cone-jet spray mode may further include, spraying a suspension from the electrospray printhead while simultaneously moving the substrate in a longitudinal direction relative to the electrospray printhead, thereby forming a thin layer of the material on the substrate and then laser sintering the material sprayed onto the substrate using a sintering laser beam.

Forming one or more sintered structural layers adjacent to the one or more sintered thin film layers using the electrospray printhead operating in a micro-dripping mode may further include, ejecting droplets of material from the electrospray printhead, heating the droplets with the laser beam in the focal region to form a paste of the material and depositing the paste of the material onto the deposition surface.

In an additional embodiment, a laser-assisted electrospray printhead is provided which includes, a printhead body comprising a reflective surface that is positioned to focus the laser beam onto a focal region above a deposition surface of a substrate, an electrospray holder positioned within the printhead body and extending from the reflective surface forming an electrospray exit and a capillary tube comprising a cone-shaped meniscus at a first end, the capillary tube positioned within the electrospray holder.

In one embodiment, the capillary tube may be coupled to an electrically positive terminal of a power supply and a ring electrode positioned within the electrospray holder may be coupled to an electrically negative or ground terminal of the power supply.

In one embodiment, the reflective surface of the printhead is a parabolic mirror and in another embodiment, the reflective surface is a flat mirror

In another embodiment, the present invention provides a laser-assisted electrospray system which includes, a movable substrate, a laser system, a source of material and a printhead coupled to the source of material, wherein the printhead includes a printhead body comprising a reflective surface, an electrospray holder positioned within the printhead body and extending from the reflective surface forming an electrospray exit and a capillary tube comprising a cone-shaped meniscus at a first end, the capillary tube positioned within the electrospray holder.

In the laser-assisted electrospray system of the present invention, the electrospray printhead is operated in a cone-jet spray mode to form one or more sintered thin film layers of the material and the electrospray printhead is operated in a micro-dripping mode to form one or more sintered structural layers adjacent to the one or more sintered thin film nanoparticle layers of the material.

As such, the present invention allows for the fabrication of new architecture devices and lowers the manufacturing cost by utilizing a roll-to-roll process and a novel laser electrospray printhead.

BRIEF DESCRIPTION OF THE DRAWINGS

For a fuller understanding of the invention, reference should be made to the following detailed description, taken in connection with the accompanying drawings, in which:

FIG. **1** illustrates an exemplary intermediate band solar cell (IBSC) device that can be manufactured with the laser-assisted microfluidics manufacturing process of the present invention.

FIG. **2** illustrates an integrated manufacturing process of thin films, wherein a wet layer of nanoink is deposited on the substrate by electrospray operated in steady cone-jet spray mode and sintered by a laser sheet, in accordance with an embodiment of the present invention.

FIG. **3** illustrates an integrated manufacturing process for discrete deposition of microdots and nanodots using the electrospray module operating in a micro-dripping mode in addition to using the thin jet produced in the steady cone-jet spray mode when a hollow parabolic mirror is used to focus an annular laser beam.

FIG. **4** illustrates an integrated manufacturing process for discrete deposition of microdots and nanodots using the electrospray module operating in a micro-dripping mode in addition to using the thin jet produced in the steady cone-jet spray mode when a hollow flat mirror and an annular lens are used to focus an annular laser beam.

FIG. **5** illustrates an integrated manufacturing process for deposition of dry powders. A hollow parabolic mirror is used to focus the annular laser beam.

FIG. **6** illustrates an integrated manufacturing process for deposition of dry powders. A hollow flat mirror and an annular lens are used to focus the annular laser beam.

FIG. **7** illustrates a schematic of the manufacturing process of structural arrays, including the operation and functionality of the laser electrospray printhead with a 3-electrode configuration for the deposition of microdots and/or nanodots, in accordance with an embodiment of the present invention.

FIG. **8** illustrates a schematic of the manufacturing process of structural arrays, including the operation and functionality of the laser electrospray printhead with a 2-electrode configuration for the deposition of microdots and/or nanodots, in accordance with an embodiment of the present invention.

FIG. **9** illustrates the laser electrospray printhead (LEP), including isometric, plane, and section views of the LEP, in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In various embodiments, the present invention provides a novel additive manufacturing technique that overcomes the challenges of the fabrication of various devices. In one embodiment, a new generation photovoltaic (PV) cell that may be fabricated using the laser-assisted manufacturing process of the present invention is an intermediate band solar cell (IBSC).

FIG. **1** illustrates an exemplary embodiment of a new architecture of an IBSC **100**, wherein each layer of the cell is fabricated one at a time by the deposition of nanoparticles through electrospray technology followed by sintering using a laser beam. As shown in FIG. **1**, the IBSC **100** includes various thin film layers fabricated on a substrate **105** having a metal back contact **110**. The thin film layers include an n^+-SiC (silicon carbide) contact layer **110**, an n-SiC base layer **117** and a barrier layer **120**. As described in detail below, the thin film layers are fabricated by operating a laser-assisted printhead in a steady cone-jet spray mode. An intermediate band region **125** is then formed on top of the plurality of thin film layers. The intermediate band region **125** includes and n-type Si nanodot superlattice **130** comprising layers of nanodots arrays separated by a thin film. As described in detail below, the nanodots are fabricated by operating a laser-assisted printhead in a micro-dripping mode. Following the deposition of the intermediate band region **125**, a thin film p-SiC emitter **135**, a p^+-SiC contact **140** and an electrode **150** are subsequently deposited to complete the IBSC.

In various embodiment, the nanoparticles (e.g. 3C—SiC) can be deposited as thin films at low temperatures on glass as well as flexible substrates, such as polyimide (Kapton) plastics, because of the large diffusion coefficient and low melting temperature of the nanoparticles in comparison to that of the corresponding bulk material. The same concept can also be used for deposition of structural arrays, thereby allowing for the fabrication of the intermediate band region of the IBSC. The superlattice can be formed by placing Si nanodots **130** and each layer of nanodots can be covered with a 3C-SiC barrier layer **120**, as shown in the solar cell of FIG. **1**.

The fabrication procedure of the new architecture devices, such as IBSCs, can be described in two major steps. The first step involves the fabrication of thin films. In this step, solid layers are obtained through the thin-film deposition of nanoparticles, wherein a steady cone-jet spray mode of the electrospray module is utilized to accomplish electrospraying of liquid carrying nanoparticles, followed by the subsequent laser sintering of the nanoparticles. In various embodiments, the liquid carrying nanoparticles include nanoparticle suspensions as precursors.

In general, during the fabrication of the thin films, thin wet layers of colloidal precursor (nanoink), comprising an aqueous suspension of nanoparticles, are formed on the substrate by the above-mentioned electrospray technique and each of the thin wet layers are subsequently heated with a laser beam to achieve nanoscale sintering.

FIG. **2** illustrates an exemplary schematic of the manufacturing process **200** for the production of thin films (e.g., layer deposition of each of the thin layers of the IBSC solar cell **100**, such as the n-type **110**, **115** and p-type **135**, **140**

3C-SiC nanoparticles, as shown in FIG. **1**). As shown, to produce a wet thin film, the electrospray printhead **205** is placed above the moving substrate **245**. More specifically, a nanoparticle suspension **220** is provided as a nanoparticle carrier fluid **215** to the electrospray module **205**. The electrospray module **205** is coupled to a power supply **210** to establish an electrospray utilizing electricity to disperse a liquid or a fine aerosol. Using a plurality of nozzles **225** of the electrospray module **205**, a wet layer **230** is first deposited on the substrate **245** by the electrospray module **205** operated in steady cone-jet spray mode as the substrate **245** moves in the longitudinal direction, using a feed spool **246** and take-up spool **248**, at a constant speed, thereby allowing the process to be adapted to roll-to-roll manufacturing. The wet layer **230** is then dried by laser heating to form the sintered layer **235**. Rapid heating and rapid cooling inherent in laser processing enable heating only a thin layer of materials at the substrate surface without melting the substrate. This heat transfer mechanism makes the proposed laser technology advantageous over other deposition techniques, especially for manufacturing solar cells on plastic substrates. The dry nanoparticles are then sintered and recrystallized through a laser heat treatment.

As shown in FIG. **2**, each wet film **230** is vaporized and the particles are subsequently sintered by laser heating to form the functional film, prior to depositing the next layer. A laser beam **265** from a laser source **270** is directed through a cylindrical lens **255** using a mirror to establish a divergent laser sheet **250** incident upon the substrate **245**. The sintering laser beam is shaped into a divergent laser sheet **250**, to achieve a rectangular heat source on the substrate surface **245** so that the entire width of the substrate **245** can be sintered to obtain a continuous film. In this exemplary embodiment, the electrosprays **205** are fed with nanoink comprising a nanoparticle suspension in deionized water.

The second step in the manufacturing of the new architecture devices involves the fabrication of structural arrays. In this step, the structural arrays are obtained through the discrete deposition of microdroplets and nanodroplets using the electrospray module operating in a micro-dripping mode, in addition to using the thin jet produced in the steady cone-jet spray mode. The resulting structural array is then sintered by the laser beam, thereby allowing the fabrication of microdot and nanodot superlattice structures.

FIG. **3** illustrates an integrated manufacturing process **300** for discrete deposition of microdots and nanodots using the electrospray module operating in a micro-dripping mode **302**. In the micro-dripping mode, only fragments of liquid (microdroplets) **325** from the nanoparticle suspension **305** are ejected from the capillary tube **304** by deformation and detaching of the liquid meniscus and the steady cone-jet spray mode contains a thin jet portion which is used for discrete deposition. A high voltage power supply **310** coupled to the capillary tube **304** and an electrode ring **320** of the electrospray printhead is used to form the microdroplets **325** from the nanoparticle suspension **305**. The nanodot array **365** is subsequently heated with a laser beam to adhere the nanodots to the solid layers on the substrate **360**. In this manner, several structural array layers can be deposited to complete the fabrication process.

The system shown in FIG. **3** employs an axicon lens **340** to convert the incoming Gaussian beam from the laser system **335** into an annular laser beam **345**. In this embodiment, a hollow parabolic mirror **330** of the electrospray printhead is used to focus the annular laser beam into a focal region having a long depth of focus **355** just above the surface of a substrate **360**. At this long focal region **355**, the liquid droplets, which are suspensions of micro-particles and nanoparticles, remain for a longer period of time under the laser heating conditions. The suspensions can also contain various elements such as Fe, Cr and Ni, alloys such as steel, brass and superalloy, amorphous materials such as glass and metallic glass, and crystalline materials such as Si, Ge, SiC and GaN crystals. The laser heating in the long focal region **355** evaporates the liquid component of the droplet and causes the nanoparticles or other solid components in the droplet suspension to reach temperatures close to their melting (approximately 95% of the melting temperature) or softening temperature. A paste-like soft matter emerges from the long focal region **355** like tooth paste and deposits on the substrate **360** to form two-dimensional or three-dimensional structures, as in additive manufacturing. The paste-like soft matter can also be deposited on the substrate as isolated dots to form an array of dots.

In a specific application for bio-printing, the nanoparticle suspension can be replaced with a suspension of biological tissues to produce two-dimensional and three-dimensional structures including biosensor, bioactuator, regenerative medicine, and the seeding and impregnation of cells for homogeneous or heterogeneous tissue engineering.

With reference to FIG. **4**, in another configuration of the manufacturing process for micro-dot and nano-dot arrays, the above-mentioned hollow parabolic mirror is replaced with an annular flat mirror **430** and an annular lens **432**. The annular flat mirror **430** turns the horizontal hollow beam into a vertical hollow beam **445**, and the annular lens **432** focuses the vertical hollow beam into a focal region having long depth of focus **455** just above the surface of a substrate **460**. The converging laser beam interferes in the focal region **455** and forms a diffraction-free beam known as the Bessel beam. This Bessel beam can have a smaller diameter than the original Gaussian beam that is produced by the laser system **435** and converted into the annular laser beam **445**. In this embodiment, the manufacturing process **400** for discrete deposition of microdots and nanodots utilizes the electrospray module operating in a micro-dripping mode **402**. In the micro-dripping mode, only fragments of liquid (microdroplets) **425** from the nanoparticle suspension **405** are ejected from the capillary tube **404** by deformation and detaching of the liquid meniscus and the steady cone-jet spray mode contains a thin jet portion which is used for discrete deposition. A high voltage power supply **410** coupled to the capillary tube **404** and an electrode ring **420** of the electrospray printhead is used to form the microdroplets **425** from the nanoparticle suspension **405**. The nanodot array **465** is subsequently heated with a laser beam to adhere the nanodots to the solid layers on the substrate **460**. In this manner, several structural array layers can be deposited to complete the fabrication process. The suspensions can also contain various elements such as Fe, Cr and Ni, alloys such as steel, brass and superalloy, amorphous materials such as glass and metallic glass, and crystalline materials such as Si, Ge, SiC and GaN crystals. The laser heating in the long focal region **455** evaporates the liquid component of the droplet **425** and causes the nanoparticles or other solid components in the droplet suspension to reach temperatures close to their melting (approximately 95% of the melting temperature) or softening temperature. A paste-like soft matter emerges from the long focal region **455** like tooth paste and deposits on the substrate **460** to form two-dimensional or three-dimensional structures as in additive manufacturing. The paste-like soft matter can also be deposited on the substrate **460** as isolated dots to form an array of dots.

Additionally, in this embodiment for bio-printing applications, the nano-particle suspension can be replaced with a suspension of biological tissues to produce two-dimensional and three-dimensional structures including biosensor, bioactuator, regenerative medicine, and the seeding and impregnation of cells for homogeneous or heterogeneous tissue engineering.

During the basic steps of the fabrication of the structural arrays of the present invention utilizing a nanoparticle suspension, fragments of the liquid nanoink are ejected from the tip of the capillary tube by deformation and detaching of the electrified liquid meniscus. A wet point is then deposited on top of the substrate by the impingement of the liquid nanoink (microdroplets and nanodroplets) and the wet point is dried using laser heating. The dry nanoparticles are then sintered and recrystallized by a laser heat treatment. The substrate then moves in the longitudinal direction to permit deposition at another point on the substrate. Multilayer deposition of the structural array can be achieved by heating the droplets with the laser beam to adhere them to the previous layer. In this manner, several layers can be deposited to complete the fabrication process.

As shown in FIG. **5**, in another embodiment of this invention, the nanoparticle suspension tank of FIG. **3**, in the integrated manufacturing process **500**, can be replaced with a dispenser **505** containing powders (1 to 250 micrometer size) of various elements such as Fe, Cr and Ni, alloys such as steel, brass and superalloy, amorphous materials such as glass and metallic glass, and crystalline materials such as Si, Ge, SiC and GaN crystals. The dispenser **505** can also contain a stirrer **507** that drives the powder **525** downward to a vertical tube **504**. The powder falls through the tube **504** by gravity, passes through the hollow region of the parabolic mirror **530**, and eventually enters into the long focal region **555** of the laser beam. The laser system **535** provides a Guassian laser that is converted to a hollow laser beam **545** by an axicon lens **540**. The parabolic mirror **530** of the electrospray printhead directs the hollow laser beam to form the long focal region **555** of the laser beam. When operating the electrospray printhead in the electrospray micro-dripping mode **502**, the laser beam in the long focal region **555** heats the powder particles very close to their melting (approximately 95% of the melting temperature) or softening temperature. A paste-like soft matter emerges from the long focal region **555** like tooth paste and deposits a nanodeposition **565** on the substrate **560** to form two-dimensional or three-dimensional structures, as in additive manufacturing. The paste-like soft matter can also be deposited on the substrate as isolated dots to form an array of dots.

In an additional embodiment, illustrated in FIG. **6**, the integrated manufacturing process **600** includes a dispenser **605** containing powders (1 to 250 micrometer size) of various elements such as Fe, Cr and Ni, alloys such as steel, brass and superalloy, amorphous materials such as glass and metallic glass, and crystalline materials such as Si, Ge, SiC and GaN crystals. The dispenser **605** can also contain a stirrer **607** that drives the powder **625** downward to a vertical tube **604**. The powder falls through the tube **604** by gravity, passes through the hollow region of the parabolic mirror **630**, and eventually enters into the long focal region **655** of the laser beam. In this embodiment, the laser system **635** provides a Guassian laser that is converted to a hollow laser beam **645** by an axicon lens **640**. A hollow flat mirror **630** of the electrospray printhead directs the hollow laser beam to a focusing lens **632** that forms the long focal region **655** of the laser beam. When operating the electrospray printhead in the electrospray micro-dripping mode **602**, the laser beam in the long focal region **655** heats the powder particles very close to their melting (approximately 95% of the melting temperature) or softening temperature. A paste-like soft matter emerges from the long focal region **655** like tooth paste and deposits a nanodeposition **665** on the substrate **660** to form two-dimensional or three-dimensional structures, as in additive manufacturing. The paste-like soft matter can also be deposited on the substrate as isolated dots to form an array of dots.

In an additional embodiment, the system may include one or more ultrasonic sources coupled to the substrate. The ultrasonic sources transmit ultrasonic beams to the substrate where the nanoparticle droplets, the laser and the substrate interact. The ultrasonic beams, or waves, from the ultrasonic source are effective in vibrating the nanoparticles and dispersing the nanoparticles in a predetermined pattern, depending upon the frequency of the ultrasonic waves, the repetition rates of the ultrasonic beam and the energy of the ultrasonic beam.

In a particular embodiment, the system may include two or more ultrasonic sources that transmit ultrasonic waves to the substrate, wherein the two or more ultrasonic beams. In this embodiment, the ultrasonic beams interfere at the interaction zone to create an interference pattern consisting of spatially alternating regions of high ultrasonic energy followed by low ultrasonic energy. This interference pattern vibrates the nanoparticles and redistributes the nanoparticles in a predetermined pattern, depending on the interference pattern. The total energy in the interference pattern and the spacing between the regions of high and low energies depend on the frequency of the ultrasonic waves, repetition rates of the ultrasonic beams and the energy of each ultrasonic beam.

As described, in the present invention, the electro spray module can be operated in both a steady cone-jet spray mode and in a micro-dripping mode by changing the electric field and the feed rate of the electrospray module. The electric field can be generated by an AC or a DC current source. The present invention additionally provides a new laser electrospray printhead that facilitates the fabrication of structural arrays in the new architecture devices.

In various embodiment, the laser-assisted electrospray printhead of the present invention provides a novel solution for additive manufacturing. FIG. **7** and FIG. **8** illustrate the operating principle of the laser-assisted electrospray printhead, in accordance with the present invention, wherein each layer is fabricated one at a time by the deposition of nanoparticles through electrospray technology and subsequently sintered using a laser beam. The nanoparticles can be deposited at discrete points at low temperatures on glass substrates as well as flexible substrates, such as polyimide (Kapton) plastics, because of the large diffusion coefficient and low melting temperature of nanoparticles compared to the corresponding bulk material. Therefore, the proposed nanoparticle-based printhead will lower the overall manufacturing and material costs.

The laser-assisted electrospray process of the present invention can operate in a 3-electrode or a 2-electrode configuration. With reference to FIG. **7**, in the 3-electrode system **700**, the electric field from the high voltage power supply **710** is applied between the capillary tube **704** and the ring extractor (extractor electrode) **720**, as well as between the capillary tube **704** and the substrate (collector electrode) **760**. As shown, the capillary tube is electrically coupled **712** to a positive terminal of the power supply **710** to establish an electrified meniscus **706**, the ring extractor **720** is electrically coupled **714** to a negative terminal of the power supply **710** and the substrate **760** is electrically coupled **716** to the negative terminal of the power supply **710**. A printhead body **710** holds the capillary tube **704** that is positioned within an electrospray holder **715**. In operation, the capillary tube **704** receives the nanoparticle carrier fluid at an inlet **705** and dispenses micro/nanodroplets **765** from an outlet **722** onto the moving substrate **760**. The reflective parabolic surface **730** of the printhead body **750** then directs the annular laser beam **745** into a long focal region above the surface of the substrate **760** to establish the structural array on the substrate **760**.

With reference to FIG. **8**, in the 2-electrode system **800**, the electric field from the high voltage power supply **810** is applied between the capillary tube **804** and the ring extractor (extractor electrode) **820**, however in this embodiment, the bottom part of the ring extractor **820** is protected with an insulative cover **824** at the electrospray exit **822**. The electrospray exit insulative cover **824** is made of an insulator material to prevent the return of the micro- and nano-droplets **865** to the ring extractor **820**, since the electrically charged droplet can get attached to this electrode due to the action of the electric field. As shown, the capillary tube is electrically coupled **812** to a positive terminal of the power supply **810** to establish an electrified meniscus **806** and the ring extractor **820** is electrically coupled **814** to a negative terminal of the power supply **810**. A printhead body **810** holds the capillary tube **804** that is positioned within an electrospray holder **815**. In operation, the capillary tube **804** receives the nanoparticle carrier fluid at an inlet **805** and dispenses micro/nanodroplets **865** from an outlet **822** onto the moving substrate **860**. The reflective parabolic surface **830** of the printhead body **850** then directs the annular laser beam **845** into a long focal region above the surface of the substrate **860** to establish the structural array on the substrate **860**.

In the laser-assisted electrospray printhead of the present invention, an electric field is applied between the two internal electrodes (capillary tube and ring extractor) in order to generate microdroplets and/or nanodroplets from the operation of the electrospray in micro-dripping mode and in steady cone-jet spray mode, depending upon the feed rate and the electric field strength through both hydrodynamic and electrodynamic shear. This allows the deposition of the nanoparticle carrier fluid (nanoink) on a moving substrate. Each microdroplet serves dual roles as a nanoparticle carrier to the substrate and as a superlens that focuses the laser beam to a subwavelength diameter. The printhead receives an annular laser beam of nearly uniform radial intensity distribution for the sintering process of the nanoparticles. The invention includes a special parabolic reflective surface (mirror) with a hole, which is used to focus the annular laser beam while microdroplets and/or nanodroplets are injected into the hollow beam. The laser beam is refocused by the microdroplet and nanodroplet superlens and the droplet is heated by the beam, thereby causing the water to evaporate and the nanoparticles to sinter and form microlayers and/or nanolayers on the substrate. Rapid heating and rapid cooling inherent in laser processing enable heating only on a thin layer of material at the substrate surface without melting the substrate. This heat transfer mechanism makes the proposed laser technology advantageous over other deposition techniques, especially for manufacturing solar cells on plastic substrates.

FIG. **9** illustrates the isometric, plane, and section view of the proposed laser electrospray printhead (LEP) As shown in FIG. **9**, the main components of the LEP include, a body **905** for containing all the components of the LEP. The body holds a parabolic reflective surface **910** that focuses the incoming laser annular beam and the body **905** has a hole to accommodate the electrospray holder **915**. The parabolic reflective surface **910** acts as a mirror that reflects almost all the incoming radiation from the hollow laser beam. The capillary tube **920** is used to transport the nanoparticle carrier fluid (nanoink) from the inlet to ejection point. The capillary tube **920** is connected to a positive terminal, so that the nanoparticle carrier fluid, which is forced through it, can be electrically charged. Note that an electric field is created between the capillary tube **920** and the ring extractor **925**, so that a cone-shaped meniscus is present at the end of the capillary tube **920**. The ring electrode **925** is either grounded or connected to a negative terminal using either one or more wires or a concentric cylinder to produce a symmetric electric field in the capillary tube **920** so that the electrified micro- and nano-droplets have a vertically straight trajectory until the deposition on the substrate. Once the microdroplets and/or nano-droplets are ejected from the electrified cone-shaped meniscus, they pass through the center of the ring electrode **925** and continue their path until they hit the substrate, where the deposition is taking place. The electrospray holder **915** holds the capillary tube **920** and the ring extractor **925**. The electrospray holder **915** is made of an electric insulator to insulate the capillary tube **904** and the ring extractor **925** from the rest of the components. Note that the electrospray can be operated in both micro-dripping and steady cone-jet spray mode by changing the electric field between the capillary tube **920** and the ring extractor **925**.

As described, in various embodiments, the present invention provides a novel additive manufacturing technique and novel laser electrospray printhead that overcomes the challenges of the fabrication of new architecture devices, including new generation photovoltaic cells.

It will be seen that the advantages set forth above, and those made apparent from the foregoing description, are efficiently attained and since certain changes may be made in the above construction without departing from the scope of the invention, it is intended that all matters contained in the foregoing description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween. Now that the invention has been described,

What is claimed is:

1. A method for laser-assisted manufacturing, the method comprising:

providing a laser-assisted electrospray printhead comprising a printhead body, wherein the printhead body comprises a reflective surface;

providing a laser beam from a laser source;

positioning the reflective surface of the printhead body to focus the laser beam onto a focal region above a deposition surface of a substrate;

forming one or more sintered thin film layers on the substrate using the laser-assisted electrospray printhead operating in a cone-jet spray mode; and

forming one or more sintered structural layers adjacent to the one or more sintered thin film layers using the laser-assisted electrospray printhead operating in a micro-dripping mode.

2. The method of claim **1**, wherein the sintered thin film layers and the sintered structural layers are formed from a suspension selected from a microparticle suspension, a nanoparticle suspension, a biological tissues suspension, a microparticle powder, a nanoparticle powder and a biological tissue powder.

3. The method of claim **1**, wherein the sintered structural layers are selected from 2-dimensional and 3-dimensional layers.

4. The method of claim **1**, further comprising adjusting an electric field of a power supply coupled to the laser-assisted electrospray printhead and a feed rate of material into the laser-assisted electrospray printhead to change the operation of the laser-assisted electrospray printhead from the cone-jet spray mode to the micro-dripping mode.

5. The method of claim **1**, wherein forming the one or more sintered thin film layers on the substrate using the laser-assisted electrospray printhead operating in the cone-jet spray mode further comprises:

spraying a suspension from the laser-assisted electrospray printhead while simultaneously moving the substrate in a longitudinal direction relative to the laser-assisted electrospray printhead, thereby forming a thin layer of the material on the substrate; and

laser sintering the material sprayed onto the substrate using a sintering laser beam.

6. The method of claim **5**, wherein the sintering laser beam forms a divergent laser sheet.

7. The method of claim **1**, wherein forming the one or more sintered structural layers adjacent to the one or more sintered thin film layers using the laser-assisted electrospray printhead operating in the micro-dripping mode further comprises:

ejecting droplets of material from the laser-assisted electrospray printhead;

heating the droplets with the laser beam in the focal region to form a paste of the material; and

depositing the paste of the material onto the deposition surface of the substrate.

8. The method of claim **7**, wherein heating the droplets with the laser beam in the focal region to form a paste of material further comprises, heating the droplets to about 95% of the melting temperature of the material.

9. The method of claim **7**, further comprising, vibrating the substrate utilizing one or more ultrasonic sources to distribute the material in a predetermined pattern on the deposition surface of the substrate.

10. The method of claim **1**, wherein the printhead body further comprises an electrospray holder positioned within the printhead body and extending from the reflective surface forming an electrospray exit.

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