US 20250072165A1

(19) United States
(12) Patent Application Publication
Andrews et al.
(10) Pub. No.: US 2025/0072165 A1
(43) Pub. Date: Feb. 27, 2025

(54) **AEROSOL JET PRINTED QUANTUM DOT MATRIX**

(71) Applicant: **Wisconsin Alumni Research Foundation**, Madison, WI (US)

(72) Inventors: **Joseph Andrews**, Madison, WI (US); **Anna Meredith**, Long Beach, CA (US)

(21) Appl. No.: **18/236,640**

(22) Filed: **Aug. 22, 2023**

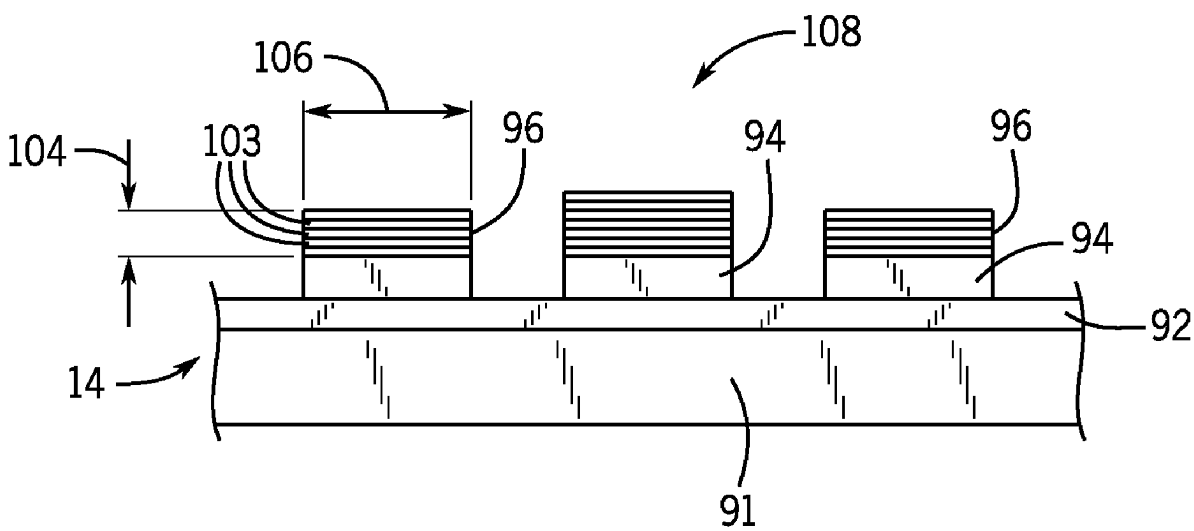
Publication Classification

(51) **Int. Cl.**
H01L 33/04 (2006.01)

(52) **U.S. Cl.**
CPC ***H01L 33/04*** (2013.01)

(57) **ABSTRACT**

An aerosol jet printer is used to deposit freestanding quantum dot matrices over optical elements such as LEDs or photodetectors. The printing process avoids the need for photolithographic masks while allowing variation in matrix height to be obtained. The matrices may be assembled with no or little binder material.



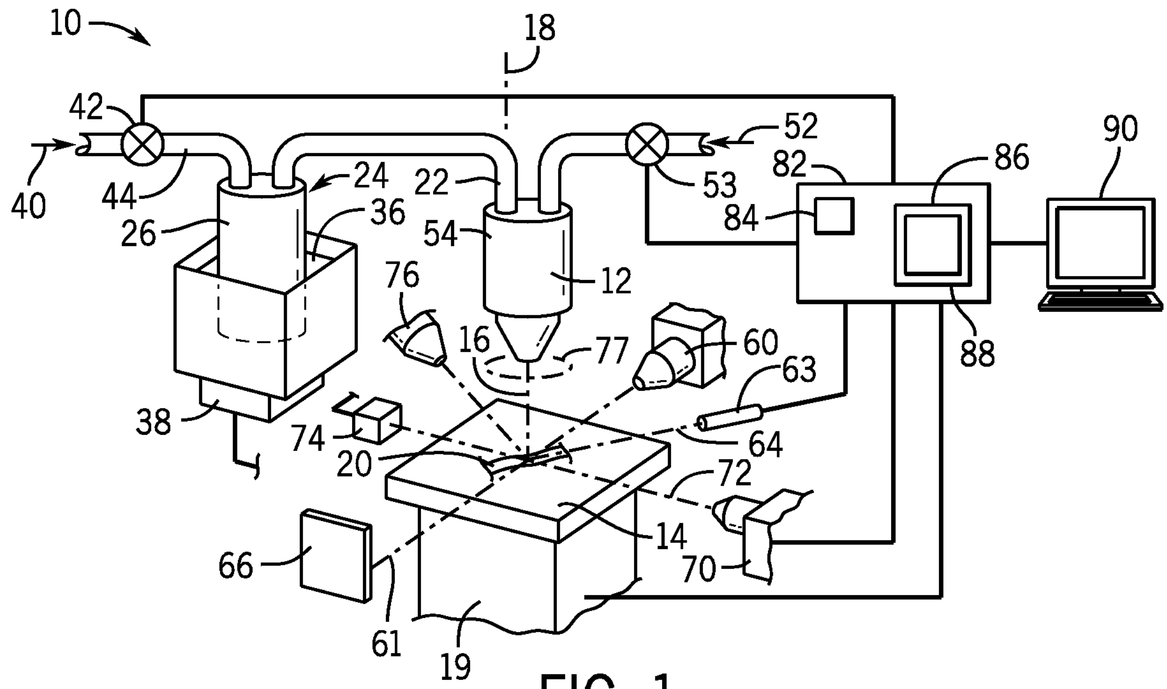

10
18
42
52
40
44
24
22
82
86
90
53
26
36
54
84
12
76
16
77
60
63
88
38
74
64
20
72
14
66
70
61
19

FIG. 1

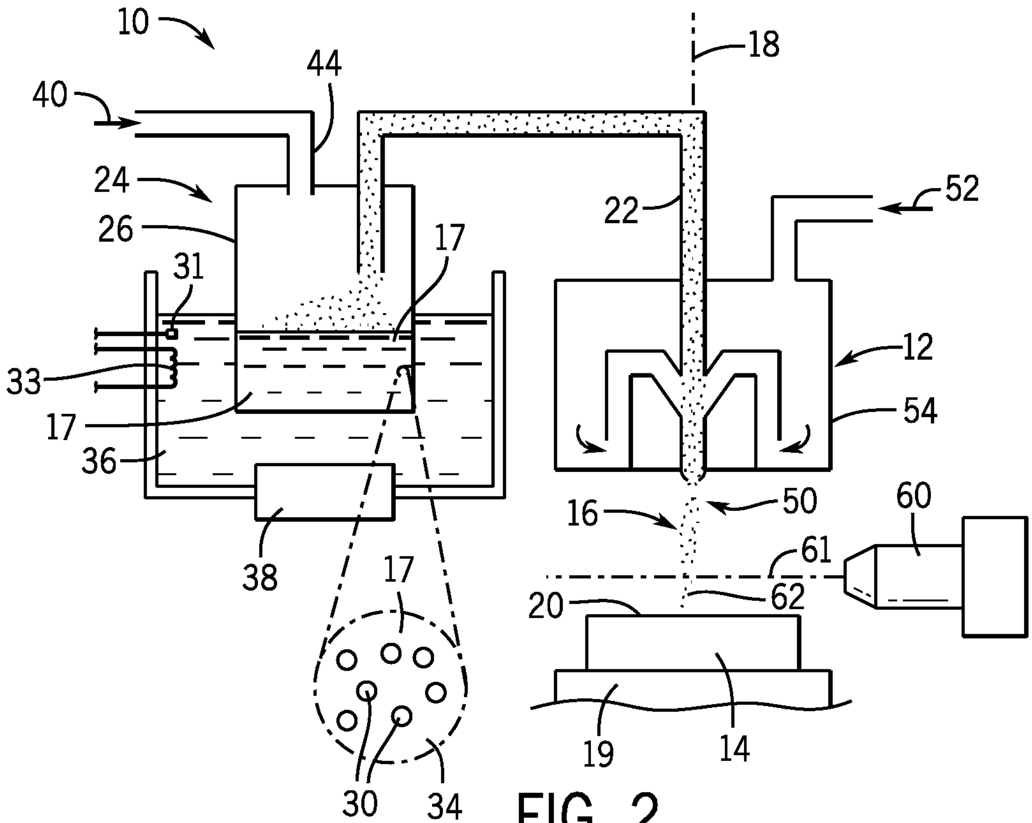

10
44
18
40
24
52
26
22
31
17
12
33
54
17
36
16
50
60
38
61
17
62
20
19
14
30
34

FIG. 2

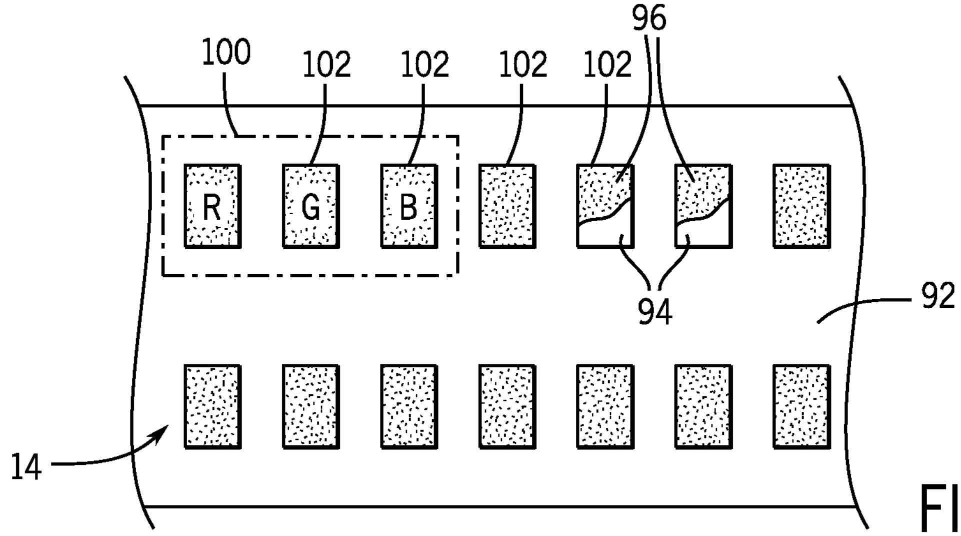


FIG. 3

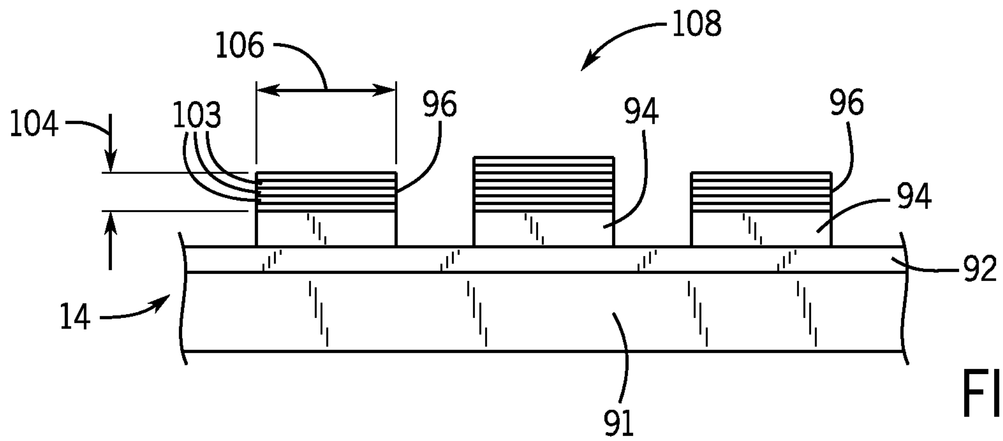


FIG. 4

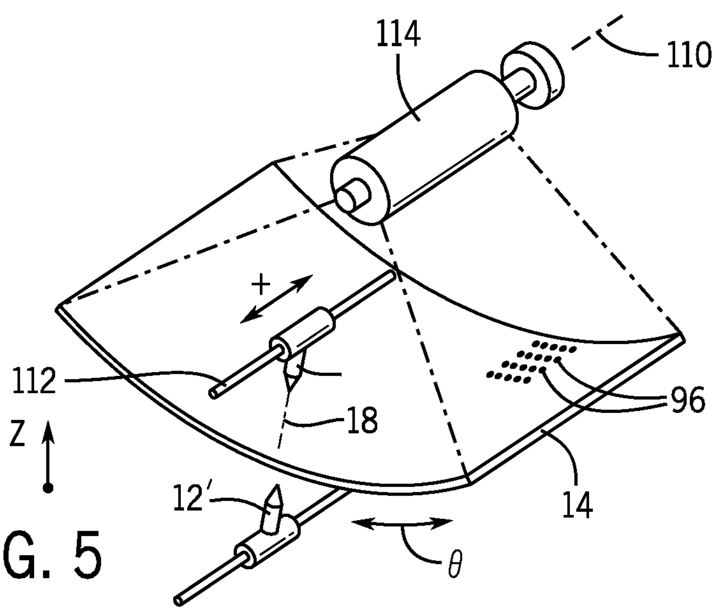


FIG. 5

AEROSOL JET PRINTED QUANTUM DOT MATRIX

BACKGROUND OF THE INVENTION

[0001] The present invention relates to aerosol jet printing and in particular to an aerosol jet printing system for producing high aspect ratio quantum dot matrices.

[0002] Quantum dots are nanometer-sized semiconductors with optical properties that result from a combination of their small size and quantum mechanical effects. In one important application, quantum dots may operate as down-converters, excited by a first higher frequency of light into photoluminescence to emit a second lower frequency narrowband light.

[0003] This feature of quantum dots may be used, for example, in producing a color television-type display in which individual blue LEDs associated with display sub-pixels (red, green, or blue) are overlaid with quantum dots down converting the blue light into red, green, or blue light respectively. This feature of quantum dots may also be useful in producing color image sensors in which the quantum dots provide a narrowband filtering of light received by broadband photo detecting elements such as photodiodes, CMOS detectors, or CCD detectors.

[0004] In one manufacturing technique, a substrate containing an array of optical elements such as LEDs or photos sensors may be coated with an ink including quantum dots applied using an aerosol jet printer. The bell-shaped profile of the printed ink on the substrate limits the ability to obtain the high light-conversion efficiency over the entire area of the optical element.

[0005] For this reason, a photo lithographic mask may be applied before printing, the mask including openings over each optical element. The printing process is then used to fill selected openings with an ink of quantum dots of the appropriate color. The mask contains and supports a desired thickness of the liquid ink over the optical element prior to drying.

SUMMARY OF THE INVENTION

[0006] The present inventors have determined that by extracting the solvent necessary to provide an aerosolizable quantum dot ink, during the time that the droplets are in-flight, assemblies of quantum dots may be printed having a substantially uniform height without a constraining photolithographic mask. Eliminating this mask greatly simplifies manufacture, reduces material waste, and allows of the thickness and profile of the quantum dot matrix to be varied on a matrix by matrix basis to maximize the light output of different quantum dots associated with different colors. The process eliminates or greatly reduces the need for a binder, improving the printing density, conversion efficiency, and further lowering material costs.

[0007] More specifically, in one embodiment, the invention provides an optical array having a set of electro-optical semiconductors arranged along a substrate and having an optically active area. A set of freestanding quantum dot matrices are positioned over the optically active area of the electro-optical semiconductors, the matrices comprised of subsets of different quantum dots associated with different electro-optical semiconductors and having different emission characteristics. The quantum dot matrices have a height of at least 5 μm and a cross-sectional area along a narrowest dimension of the active area that is at least 60% of the cross-sectional width times the cross-sectional height.

[0008] It is thus a feature of at least one embodiment of the invention to provide an optical array with substantially uniform thicknesses that can be produced using aerosol jet printing. Controlled evaporation of the solvent (the solvent being necessary for aerosolizing the ink) is performed during transit of the ink to the substrate to provide sufficient adhesion with greatly reduced post-printing spread.

[0009] The freestanding quantum dot matrices may include less than 0.1% by weight of a binder material.

[0010] It is thus a feature of at least one embodiment of the invention to eliminate or reduce the solvent necessarily associated with binder material.

[0011] The matrices maybe separated from each other by open gaps.

[0012] It is thus a feature of at least one embodiment of the invention to provide an optical array eliminating the need for a lithographic mask for corralling the quantum dots, thus reducing manufacturing costs and allowing assembly on curved surfaces that are not amenable to photolithographic techniques.

[0013] The average heights of the freestanding quantum dot matrices between different subsets may differ by greater than 10%.

[0014] It is thus a feature of at least one embodiment of the invention to permit tailoring of the height of the quantum dot matrices to the conversion efficiencies of the quantum dots used for different sub-pixels.

[0015] The substrate may have a curved surface so that different quantum dot matrices extend along nonparallel axes according to the curved surface.

[0016] It is thus a feature of at least one embodiment of the invention to provide curved displays using quantum dot matrices.

[0017] These particular objects and advantages may apply to only some embodiments falling within the claims and thus do not define the scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. **1** is a perspective block diagram of an aerosol jet printer suitable for use with the present invention showing the location and orientation of three different cameras positioned with respect to an aerosol nozzle for monitoring the print jet and printed line and a central controller controlling multiple elements of the printer including ink temperature and carrier gas and sheath gas flow;

[0019] FIG. **2** is a simplified cross-sectional view of the atomizer and print nozzle of FIG. **1** showing the path of carrier gas and sheath gas;

[0020] FIG. **3** is a top plan view of an optical array, being either a display or sensor, showing an array of pixels divided into sub-pixels of different colors;

[0021] FIG. **4** is an elevational side view of a pixel of FIG. **3** showing placement of quantum dot matrices on top of optimal elements; and

[0022] FIG. **5** is a schematic representation of a printer system for curved televisions rendered practical by the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0023] Referring now to FIG. **1**, an aerosol jet printer **10** may include a print head **12** positioned above a substrate **14** on which material will be printed using a jet **16** of aerosolized quantum dot ink **17**. The aerosolized quantum dot ink **17** is directed from the print head **12**, generally along an axis **18** perpendicular to the broad extent of the substrate **14**, while motion between the substrate **14** and the print head **12** is provided, for example, by an x-y-z table **19**. A print head **12** suitable for the present invention is commercially available under the trade name Aerosol Jet **200** commercially available from Optomec of New Mexico, USA.

[0024] The x-y-z table may be of conventional design incrementally moving the substrate **14** controllably in three Cartesian axes having a z-axis aligned with axis **18**, for example, using stepper or servo motors. This relative motion allows the jet **16** of aerosolized quantum dot ink **17** to paint lines **20** on the substrate **14** describing arbitrary shapes and areas in two dimensions and, by building up material in multiple layers, arbitrary volumes in three dimensions.

[0025] Referring also to FIG. **2**, the print head **12** provides a central lumen **22** generally aligned along axis **18** that may receive aerosolized quantum dot ink **17** from an atomizer **24**, for example, the latter being a pneumatic atomizer or an ultrasonic atomizer as shown.

[0026] The ultrasonic atomizer provides a reservoir **26** holding a quantum dot ink **17** generally comprised of quantum dots **30** in a suspending solvent **34**. Non-limiting examples of quantum dot ink **17** include CdSe/CdZnS (core-shell) quantum dots **30** in toluene solvent **34** with an emission wavelength of 620 nm and CdSe/ZnS (core-shell) quantum dots **30** in toluene solvent **34** with an emission wavelength of 620 nm, both commercially available from Sigma-Aldrich of Darmstadt, Germany. These quantum dot inks **17**, for example, at a concentration of 100 mg/mL may be mixed with terpineol (at 5 v/v %) to adjust viscosity as needed. Both toluene and terpineol are sufficiently volatile to fully evaporate from the quantum dot matrices to be produced, and thus may be distinguished from a binding material not used in the present invention such as would be expected to persistently bind the quantum dots together to form a matrix thereabout.

[0027] Generally different quantum dots (e.g., having different dimensions) are used to provide emissions in narrowband visible red, green, and blue frequencies. Narrowband emissions may have a bandwidth with a full width half maximum (FWHM) of less than 100 nm and typically less than 50 nm.

[0028] The reservoir **26** may be immersed, for example, in a water bath **36** coupling the quantum dot ink **17** acoustically with the ultrasonic transducer **38** serving, when the transducer is active, to generate a mist of aerosolized quantum dot ink **17** above the surface of the non-aerosolized quantum dot ink **17**. A carrier gas **40**, such as nitrogen, controlled by a valve **42** is introduced into the reservoir **26** through an inlet **44** that suspends and scavenges the aerosolized quantum dot ink **17** and carries it down the central lumen **22** toward an exit orifice of print nozzle **50** of the print head **12**.

[0029] The water bath **36** may communicate with a thermocouple or other temperature sensor **31** and a temperature control element **33** allowing control of the water temperature bath and hence the temperature of the quantum dot ink **17**. The temperature control element **33** may be a resistive heater or a Peltier device providing heating or cooling.

[0030] A sheath gas **52**, such as nitrogen, controlled by a valve **53**, may be introduced into a deposition head **54** around the central lumen **22** of the print head **12** to create a coaxial sheath of gas passing out of the exit orifice of the print nozzle **50** of the print head **12** in a ring around the aerosolized quantum dot ink **17** to focus the jet **16**. Generally, the ratio of the volume of the sheath gas **52** to the carrier gas **40** defines a focus ratio which may be adjusted by adjusting the volume flow of each of the carrier gas **40** and the sheath gas **52**. As will be discussed below, the focus ratio may be adjusted substantially to remove the solvents **34** from the quantum dots **30** prior to striking the substrate **14**.

[0031] A high-speed, high-resolution droplet imaging camera **60** having an optical axis **61** parallel to and positioned above the printed surface of the substrate **14** allows imaging of the jet **16** sufficient to freeze and resolve the individual droplets of the aerosolized quantum dot ink **17** in rapidly acquired sequential images. The optical axis **61** is generally perpendicular to axis **18**, and a focal plane **62** of the camera **60** provides sufficient depth of field to fully encompass the jet **16**.

[0032] A laser **63** is positioned to direct a beam of light **64** in a frequency range of the camera **60** at an angle to the optical axis **61** of the imaging camera **60** to illuminate the jet **16** and its individual particles through backscatter. The laser **63** may be pulsed to "freeze" the droplets in the image in the manner of a stroboscope, allowing a wide variety of CCD type cameras to obtain successive images spaced apart by a few microseconds so that two images of a set of droplets at different times can be obtained within the field of view of the camera **60**. The laser **63** and the camera **60** together provide a camera system producing the necessary images, although the invention contemplates other camera systems, for example, having continuous illumination and high-speed shutters or the like. For improved contrast, a light-absorbing background **66** may be placed opposite the camera **60** along the optical axis **61** and across the substrate **14**.

[0033] An optional particle-loading camera **70** may be positioned to have an optical axis **72** orthogonal to the axis **61** to receive light from, for example, an infrared backlight **74**. The particle loading camera **70** has a resolution in time and space comparable to camera **60** and is used for measuring light absorption by the droplets of the jets **16** to deduce particle loading, that is, the amount of quantum dots **30** in the droplets **32**.

[0034] A third optional print imaging camera **76** may be directed generally downwardly to the substrate **14** to provide imaging of the print line **20** for assessing that line quality as will be described below. Illumination for the third imaging camera **76** may be provided by a ring light **77** or the like centered about axis **18** to provide even illumination to the printed surface of the substrate **14**.

[0035] A controller **82** having at least one processor **84** communicates with an electronic memory **86** holding a stored program **88**, as will be discussed in more detail below, and operating to control the various components of the printer **10**. The controller **82** may communicate with a control terminal **90**, for example, including a graphic control screen, keyboard, mouse and the like, allowing for user input and output as is generally understood in the art.

[0036] The controller **82** may receive signals from process sensors including the cameras **60**, **70**, and **76** (in the form of sequential image frames) as well as from the temperature sensor **31**. In addition, the controller **82** may provide signals to control process variables, for example, the flow rate of the carrier gas **40** and sheath gas **52** (via valves **42** and **53**) as well as the temperature control element **33**. In addition, the controller **82** may provide control signals to the laser **63** and infrared backlight **74** for turning them on and off and signals to the x-y-z table **19** to maneuver it during the printing process to provide the desired print.

[0037] Generally, the controller **82** will execute the program **88** to conduct two separate tasks. The first task is that of reading a data print file describing a volume or area to be printed and providing control signals to the x-y-z table **19** to sequentially align different portions of the substrate with the jet **16**. At each location, the computer controls the jet **16**, for example, by modulating the carrier gas **40** and sheath gas **52**, to print quantum dots **30** after removing most of the solvent **34** from the quantum dot ink **17** during flight and to selectively deposit quantum dots **30** on the substrate **14** in the desired pattern for the desired number of layers.

[0038] A second task may be conducted simultaneously with the first task or periodically and serves to adjust the operation of the printer to control the print line **20** with respect to desired line width, desired line density and consistency, line edge smoothness, and reduced overspray and post printing flow.

[0039] Further operating details and description are provided in U.S. patent application Ser. No. 17/404,345 filed Aug. 17, 2021, naming the assignee of the present application and hereby incorporated in its entirety by reference.

[0040] Referring now to FIGS. **3** and **4**, the substrate **14** may provide a support layer **91** having on its upper surface a connection layer **92** comprised of an integrated array of thin film transistors and interconnections between attached optical elements **94** such as light emitting diodes, or light sensor such as CCD sensors, CMOS sensors, photodiodes or the like whose fabrication and interconnection into arrays is generally understood in the art. In the case of a display, the optical elements **94** may all be identical blue-green LEDs having substantially identical turn on voltages for convenient control.

[0041] Positioned on top of each optical element **94** is a quantum dot matrix **96** printed in self-supporting form by the above-described printer. Aerosol jet printing of a self-supporting quantum dot matrix **96** is possible by proper reduction of the solvent **34** in the ink **17** during flight and further assisted by eliminating binding material (e.g., to zero or less than 0.1% by weight) and the additional solvent necessary to lower the viscosity of such binding materials. A binding material can be understood to be a material other than the quantum dots **30**, that is, effectively nonvolatile and thus retained indefinitely within the quantum dot matrix **96**.

[0042] The optical elements **94** may be arranged in rows and columns and grouped in groups of three to form pixels **100**, each pixel **100** thus having three sub-pixels **102** associated with individual optical element **94**. Sequential sub-pixels **102** will use different colors of quantum dots **30** (i.e. having different photoluminescent frequencies) in the overlying matrix **96**. For example, different sets of quantum dots **30** may have, respectively, frequencies centered within red, green, and blue portions of the visible spectrum.

[0043] Prior to printing, the optical elements **94** may be briefly treated with ultraviolet ozone to increase surface energy and material adhesion.

[0044] During printing, the carrier gas **40** and sheath gas **52** are adjusted in a closed loop with monitoring of the in-flight particles of quantum dots **30** so that the quantum dot matrices **96** may be built up in multiple layers **103** to a height **104** above their supporting optical element **94**, with this height typically being eight to −12 μm.

[0045] The self-supporting nature of the matrices **96** allows a natural gap **108** (for example, less than 20 μm) between matrices **96** during printing and eliminates the need for a lithographic mask to separate the matrices **96** during printing.

[0046] By using the self-supporting printing approach, the height **104** of the optical matrices **96** above the optical element **94** may be varied for different sub-pixels **102** to reflect the conversion efficiencies of the respective quantum dots **30** optimizing light conversion. More generally, the quantum dot matrices **96** may provide for a fill factor, being an elevational cross-sectional area along a narrowest dimension **106** of the optical element **94** divided by the width times the height of this cross-section, and thus a measure of how rectangular the cross-sectional area is, of greater than 50% and typically greater than 80% when assembled from multiple printed layers **103** to at least 5 μm in height **104**. Typically, the number of printed layers **103** will vary from 20 to 30 and will be greater than 2. More generally, the fill factor may be greater than 60% or greater than 70%.

[0047] Each layer **103** may, for example, be greater than 4 μm in thickness and may have a width of less than 35 μm and in some cases less than 20 μm or less than 15 μm.

[0048] The in-flight imaging system described above may be used to determine droplet density per unit length in the vertical direction and the corresponding velocity of the droplets and thus the total number of droplets that flow out of the nozzle **50** per unit time. This calculated flow rate can be compared to the number of droplets impinging on the substrate per unit time as verification and both factors can be used to control the operation of the printer through empirically derived relationships to permit the self-supporting printing of the quantum dot matrices **96**.

[0049] In this regard, focus ratios of the carrier gas **40** and sheath gas **52** help remove solvent **34** from the quantum dots **30** in the droplets **32** and can reduce the column width of the printed droplets **32** promoting high-resolution printing, up to a point where the removal of solvent **34** creates greater line widths because a reduction in droplet mass reduces the ability of the droplets to follow the flow field of the carrier gas **40** and sheath gas **52**. Dryer droplets **32** can also undesirably reduce the likelihood of droplets adhering to the substrate upon initial impact. Nevertheless, the dryer droplets permit steeper profiles of matrices **96** to be created.

[0050] In one nonlimiting example, a sheath gas flow rate of 60 and a carrier gas flow rate of 15 maybe used respectively with a nozzle diameter 100 μm. The standoff distance between the nozzle **50** and the substrate **14** may be approximately 3 mm. Ideally, the print speed is adjusted to allow a constant stream of material to be deposited while permitting an adequate dwell time during which evaporation of the remaining solvent can take place while minimizing the time during which there is sufficient solvent for the material to begin to spread.

[0051] Referring now to FIG. **5**, the present invention provides the ability to readily assemble quantum dot matrices **96** on a curved substrate **14**, for example, being a portion of a cylindrical wall about a central axis **110** for making curved television displays or the like. The XYZ table of FIG. **1** may be changed to an XZθ table where a conventional mechanical carriage **112** moves the print head **12** along an extra action parallel to the axis **110** and toward and away from the axis **110** along a Z direction.

[0052] The substrate **14** may be rotated about a pivot **114** coaxial with the axis **110** by a stepping motor or the like to provide printing over the entire curved surface, a process that would be difficult with photolithographic techniques. This relative motion allows the jet **16** of aerosolized quantum dot ink **17** to paint lines **20** on the substrate **14** describing arbitrary shapes and areas in two dimensions and, by building up material in multiple layers, arbitrary volumes in three dimensions. Printing on the external side of the curved surface may also be performed simply by inverting the location and orientation of the print head **12** to **12'** as indicated. It will be appreciated that this process can be used on any irregular surface including one curved in two dimensions or having irregular curvature limited only by the ability to place the optical elements **94**. In cases where the substrate is manufactured in a flat state and then curved, the gaps **108** shown in FIG. **4** may relieve stresses caused by the curvature on the quantum dot matrices **96**.

[0053] Certain terminology is used herein for purposes of reference only, and thus is not intended to be limiting. For example, terms such as “upper”, “lower”, “above”, and “below” refer to directions in the drawings to which reference is made. Terms such as “front”, “back”, “rear”, “bottom” and “side”, describe the orientation of portions of the component within a consistent but arbitrary frame of reference which is made clear by reference to the text and the associated drawings describing the component under discussion. Such terminology may include the words specifically mentioned above, derivatives thereof, and words of similar import. Similarly, the terms “first”, “second” and other such numerical terms referring to structures do not imply a sequence or order unless clearly indicated by the context.

[0054] When introducing elements or features of the present disclosure and the exemplary embodiments, the articles “a”, “an”, “the” and “said” are intended to mean that there are one or more of such elements or features. The terms “comprising”, “including” and “having” are intended to be inclusive and mean that there may be additional elements or features other than those specifically noted. It is further to be understood that the method steps, processes, and operations described herein are not to be construed as necessarily requiring their performance in the particular order discussed or illustrated, unless specifically identified as an order of performance. It is also to be understood that additional or alternative steps may be employed.

[0055] References to “a microprocessor” and “a processor” or “the microprocessor” and “the processor,” can be understood to include one or more microprocessors that can communicate in a stand-alone and/or a distributed environment(s), and can thus be configured to communicate via wired or wireless communications with other processors, where such one or more processor can be configured to operate on one or more processor-controlled devices that can be similar or different devices. Furthermore, references to memory, unless otherwise specified, can include one or more processor-readable and accessible memory elements and/or components that can be internal to the processor-controlled device, external to the processor-controlled device, and can be accessed via a wired or wireless network.

[0056] It is specifically intended that the present invention not be limited to the embodiments and illustrations contained herein and the claims should be understood to include modified forms of those embodiments including portions of the embodiments and combinations of elements of different embodiments as come within the scope of the following claims. All of the publications described herein, including patents and non-patent publications, are hereby incorporated herein by reference in their entireties.

[0057] To aid the Patent Office and any readers of any patent issued on this application in interpreting the claims appended hereto, applicants wish to note that they do not intend any of the appended claims or claim elements to invoke 35 U.S.C. 112(f) unless the words “means for” or “step for” are explicitly used in the particular claim.

What we claim is:

1. An optical array comprising:

a set of electro-optical semiconductors arranged along a substrate and having an optically active area; and

a set of freestanding quantum dot matrices positioned over the optically active area of the electro-optical semiconductors, the matrices comprised of subsets of different quantum dots associated with different electro-optical semiconductors and having different emission characteristics, wherein the quantum dot matrices have a height of at least 5 μm and a cross-sectional area along a narrowest dimension of the active area that is at least 60% of the cross-sectional width times the cross-sectional height.

2. The optical array of claim **1** wherein the freestanding quantum dot matrices include less than 0.1% by weight of a binder material.

3. The optical array of claim **1** wherein the average height of the freestanding quantum dot matrices between different subsets differs by greater than 10%.

4. The optical array of claim **1** wherein the substrate has a curved surface so that different quantum dot matrices extend along nonparallel axes according to the curved surface.

5. The optical array of claim **1** wherein the different emission characteristics of the subset include narrowband red emissions, narrowband blue emissions, and narrowband green emissions.

6. The optical array of claim **1** wherein the electro-optical semiconductors are selected from the group consisting of:

(1) light emitting diodes and wherein the optical array provides a display, and

(2) light detectors wherein the optical array provides an image sensor.

7. The optical array of claim **6** wherein the light emitting diodes are identical blue-green LEDs.

8. The optical array of claim **1** wherein the quantum dot matrices have a height of at least 4 μm and a cross-sectional area along a narrowest dimension of the active area that is at least 75% of the cross-sectional width times the cross-sectional height.

9. A method of producing an optical array having a set of electro-optical semiconductors arranged along a substrate and a set of quantum dot matrices positioned over the electro-optical semiconductors, the method comprising the steps of:

positioning a set of electro-optical semiconductors on a substrate;

aerosolizing an ink of quantum dots and solvent material to form an aerosolized jet of ink directed toward the substrate to form a set of layers spaced in time by a drying interval; and

controlling the aerosolized jet to remove solvent prior to impact with the electro-optical semiconductors to deposit a matrix of quantum dots having different emission characteristics over the electro-optical semiconductors to a height of at least 5 μm and with cross-sectional area along a narrowest dimension of the active area that is at least 60% of the cross-sectional width times the cross-sectional height.

10. The method of claim **9** wherein the aerosol jet printing uses an ink having less than 0.1% by weight of a binder material.

11. The method of claim **9** including the step of monitoring droplet velocity in flight to control a relative sheath gas and carrier gas flow rate.

12. The method of claim **9** wherein the substrate is free from masking around the optical elements having openings defining the matrices.

13. The method of claim **9** wherein aerosol jet printing is controlled to provide matrices of different emission characteristics with different corresponding different heights.

14. The method of claim **9** wherein the aerosol jet printing uses a printer head and controls the printer head to follow a curved surface of a substrate so that different quantum dot matrices extend along nonparallel axes according to the curved surface.

15. The method of claim **9** wherein the aerosolized jet is controlled to remove solvent prior to impact with the electro-optical semiconductors to deposit a matrix of quantum dots having different emission characteristics over the electro-optical semiconductors to a height of at least 5 μm and with cross-sectional area along a narrowest dimension of the active area that is at least 70% of the cross-sectional width times the cross-sectional height.

* * * * *