US 20070029189A1

(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2007/0029189 A1

Zach (43) Pub. Date: Feb. 8, 2007

(54) **COMBINATORIAL ELECTROCHEMICAL DEPOSITION SYSTEM**

(75) Inventor: **Michael P. Zach**, Darien, IL (US)

Correspondence Address:
JOAN PENNINGTON
535 NORTH MICHIGAN AVENUE, UNIT 1804
CHICAGO, IL 60611 (US)

(73) Assignee: **THE UNIVERSITY OF CHICAGO**

(21) Appl. No.: **11/444,242**

(22) Filed: **May 31, 2006**

Related U.S. Application Data

(60) Provisional application No. 60/704,558, filed on Aug. 2, 2005.

Publication Classification

(51) **Int. Cl.**
C25B 15/08 (2007.01)

(52) **U.S. Cl.** **204/228.3**

(57) **ABSTRACT**

A combinatorial electrochemical deposition system enables computer control over multiple parameters and allows for systematic exploration of the parameter space. The combinatorial electrochemical deposition system includes a computer providing system control and data acquisition functions. The computer controls a plurality of pumps; each pump is connected to a respective material supply source. The plurality of pumps is coupled via a mixer and a plurality of distribution valves of a cell and fluidics distribution network to deposit a particular composition of materials or solution concentration to individual electrochemical cells of an electrochemical cell array. The computer controls the mixer and the plurality of distribution valves. The electrochemical cell array includes a plurality of singly addressable flow-through isolatable electrochemical cells with a common working electrode.

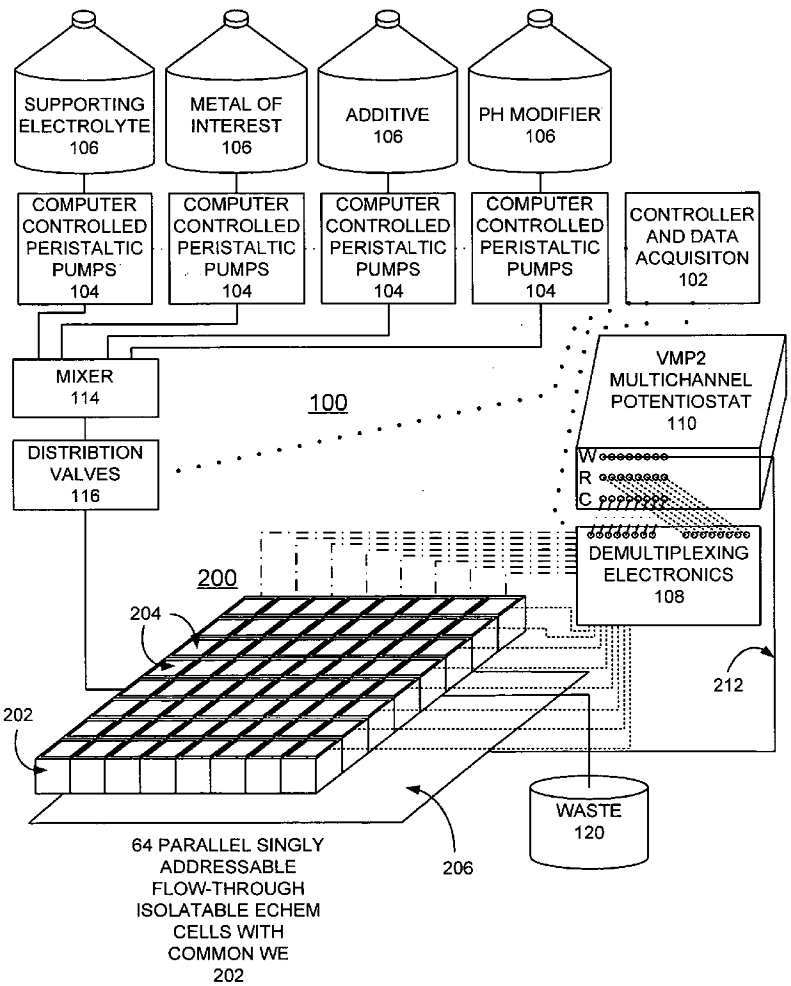
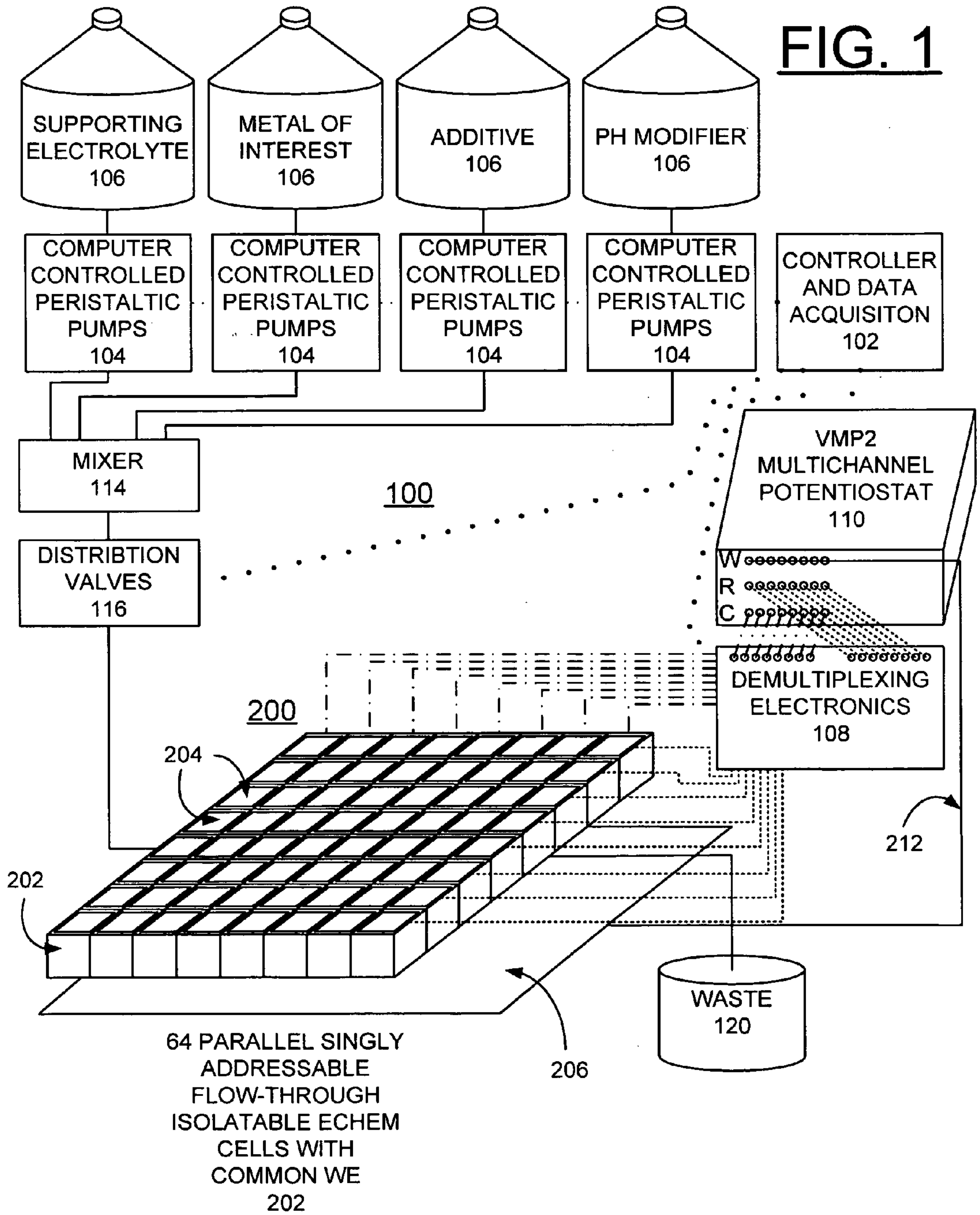


FIG. 1



SUPPORTING ELECTROLYTE 106
METAL OF INTEREST 106
ADDITIVE 106
PH MODIFIER 106
COMPUTER CONTROLLED PERISTALTIC PUMPS 104
COMPUTER CONTROLLED PERISTALTIC PUMPS 104
COMPUTER CONTROLLED PERISTALTIC PUMPS 104
COMPUTER CONTROLLED PERISTALTIC PUMPS 104
CONTROLLER AND DATA ACQUISITON 102
MIXER 114
100
VMP2 MULTICHANNEL POTENTIOSTAT 110
DISTRIBTION VALVES 116
W
R
C
DEMULTIPLEXING ELECTRONICS 108
200
204
212
202
WASTE 120
206
64 PARALLEL SINGLY ADDRESSABLE FLOW-THROUGH ISOLATABLE ECHEM CELLS WITH COMMON WE 202

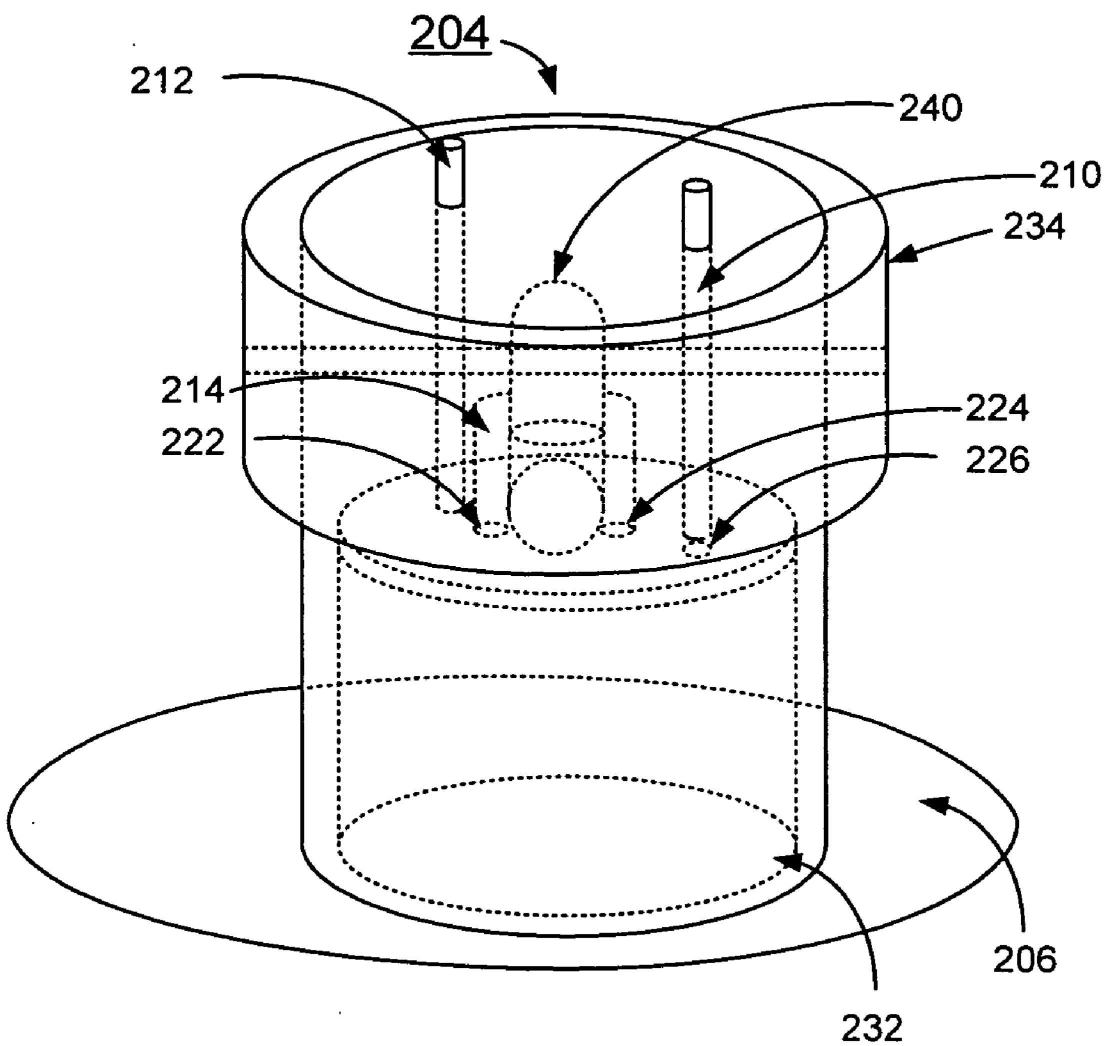


FIG. 2A

204

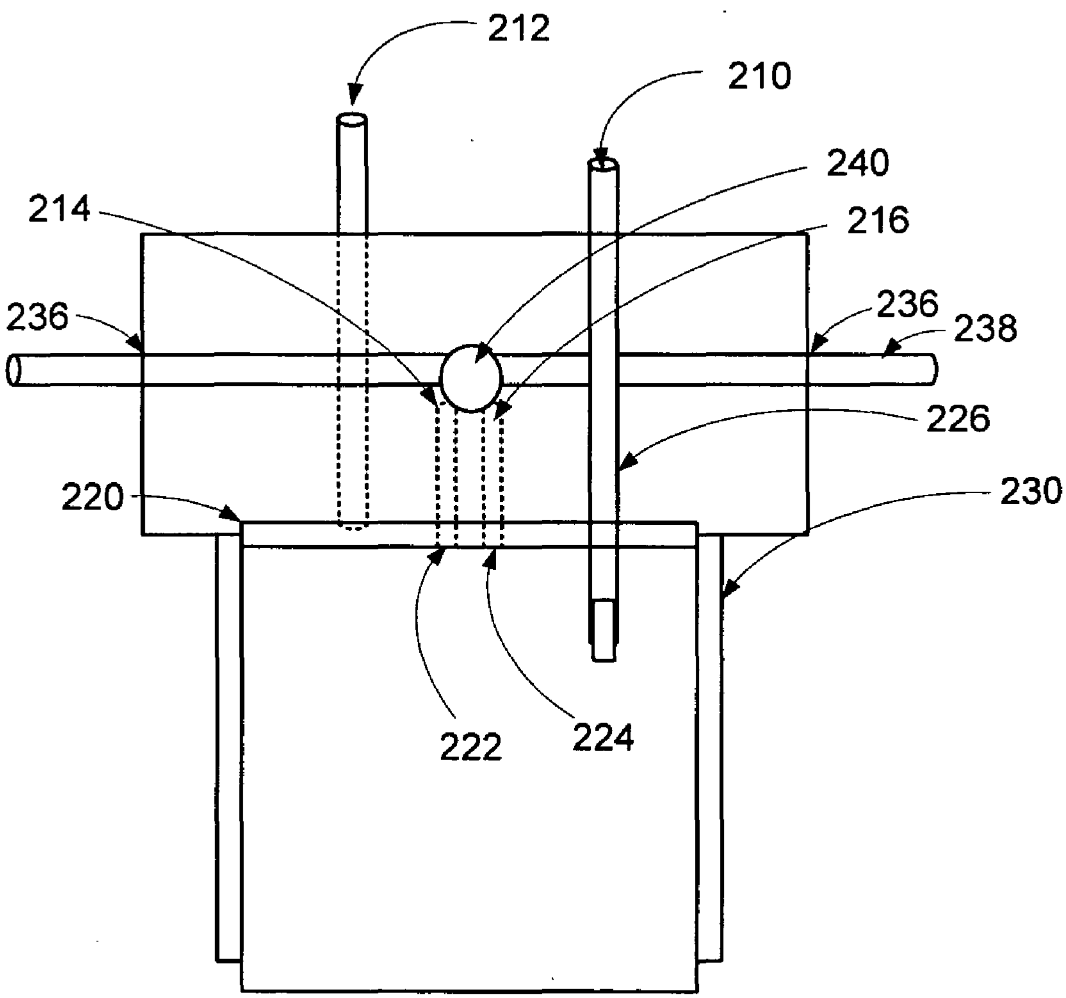


FIG. 2B

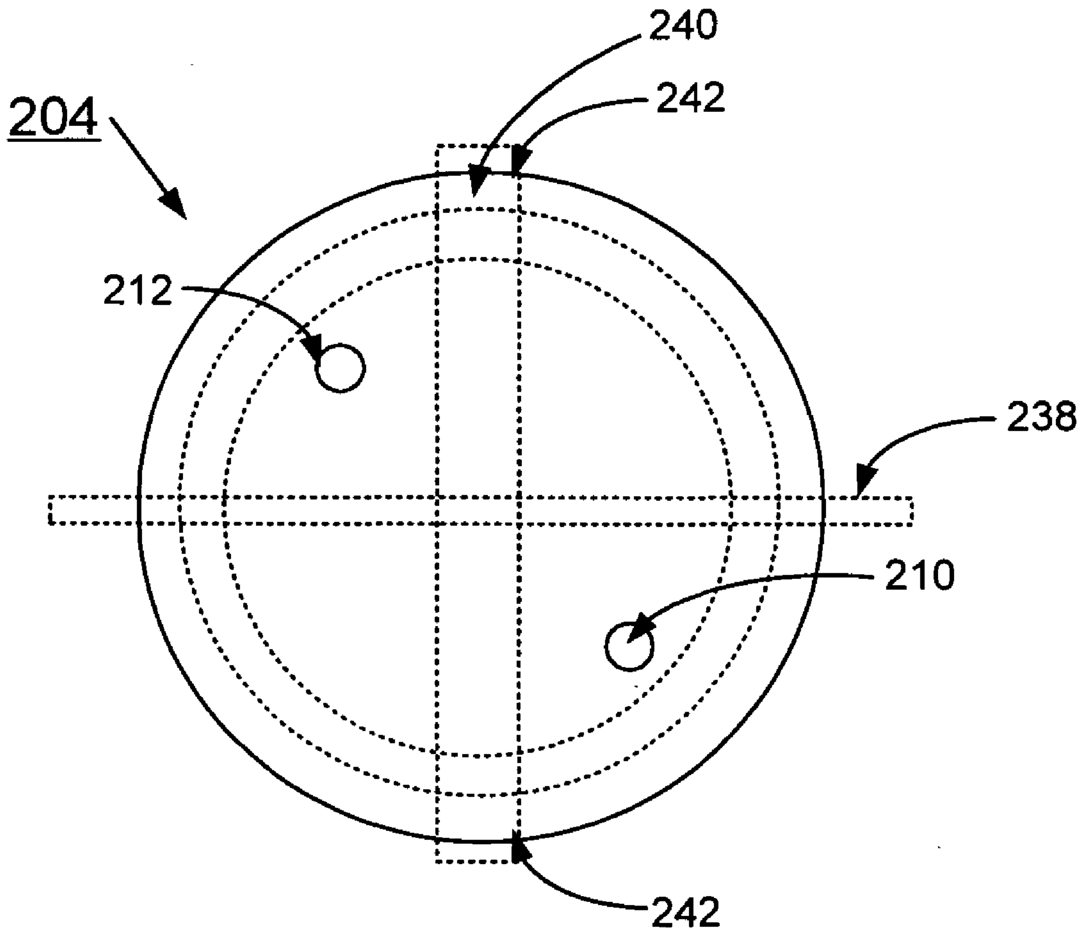


FIG. 2C

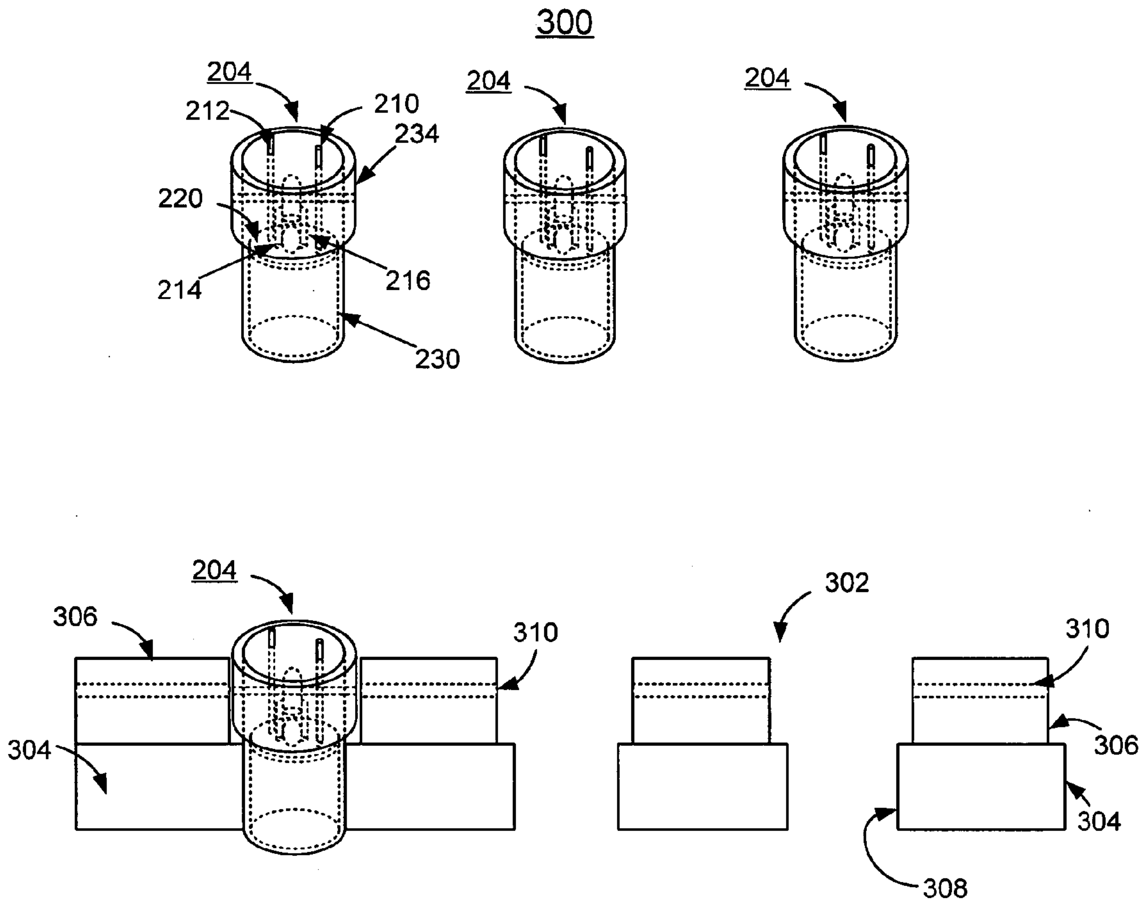

300
204
212
210
234
220
214
216
230
204
204
204
306
310
304
302
310
306
304
308

FIG. 3

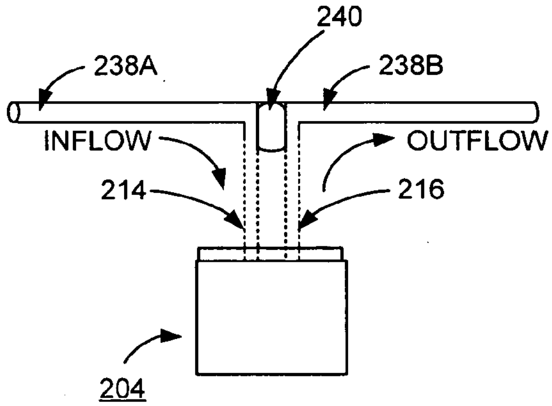


FIG. 4A

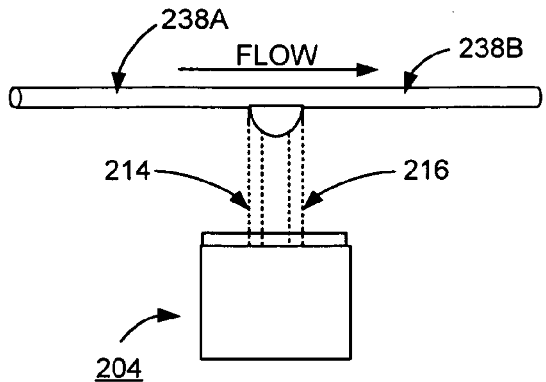


FIG. 4C

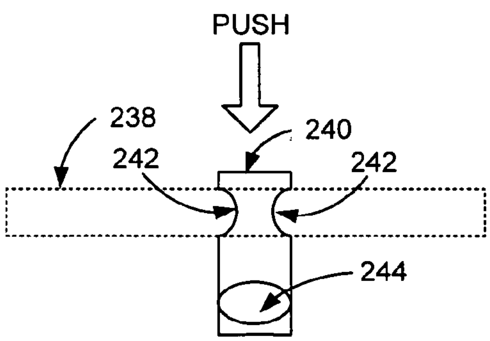


FIG. 4B

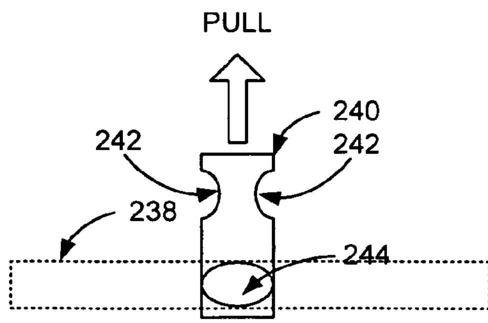


FIG. 4D

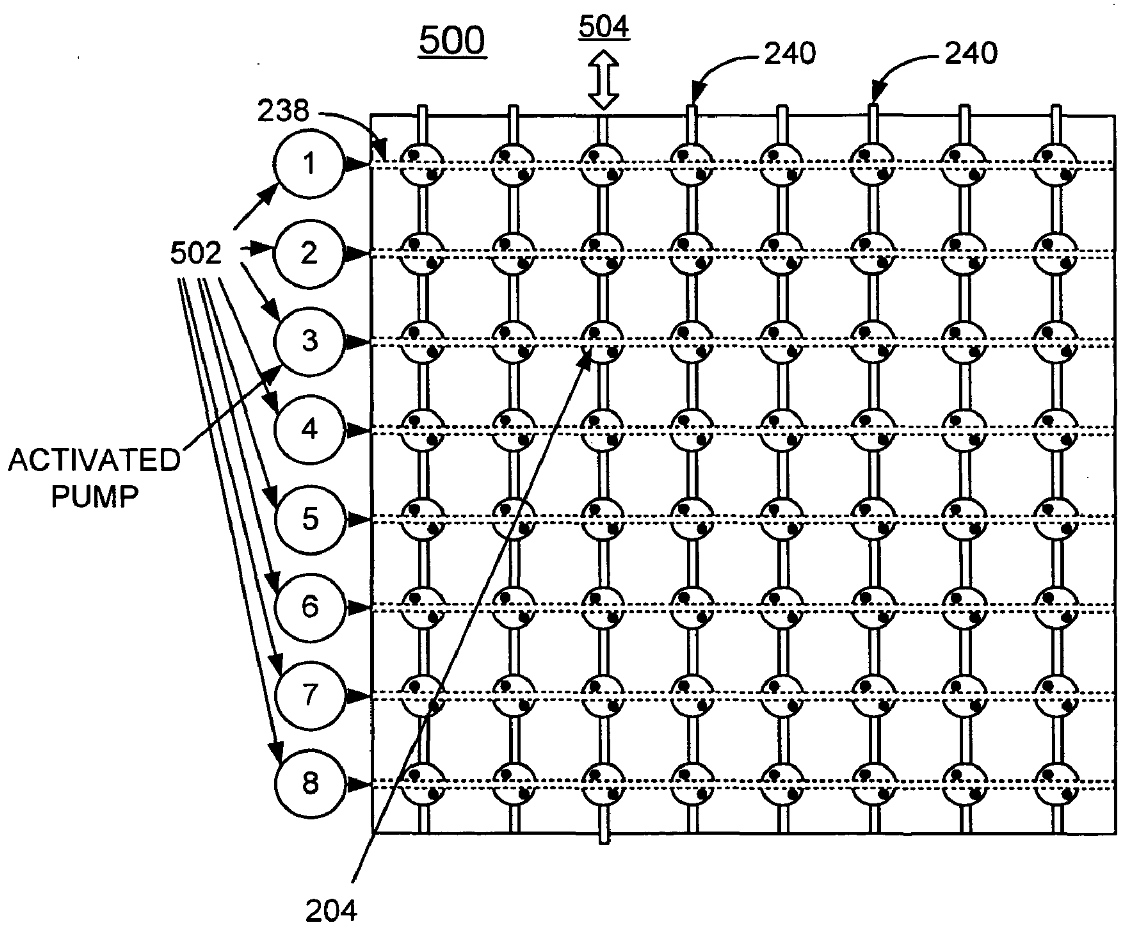


FIG. 5A

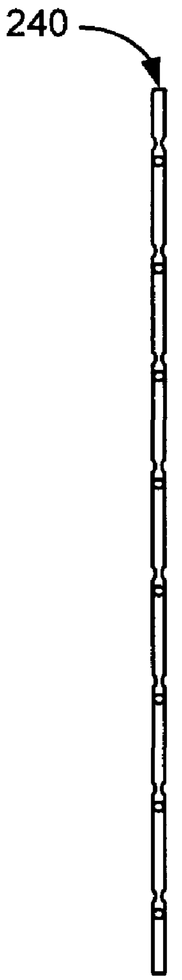


FIG. 5C

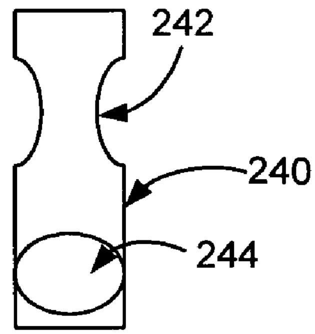


FIG. 5D

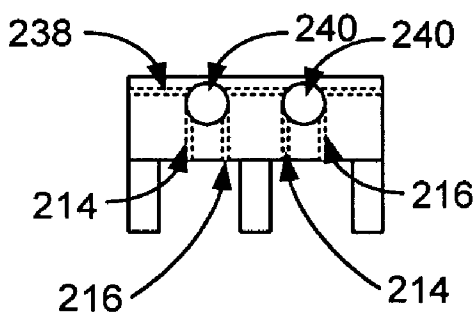


FIG. 5B

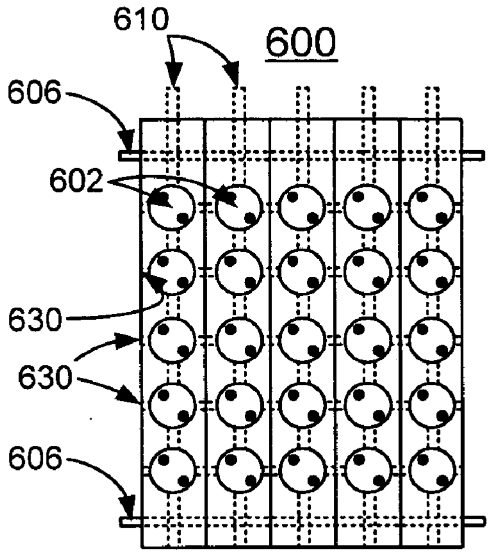


FIG. 6A

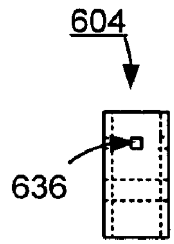


FIG. 6C

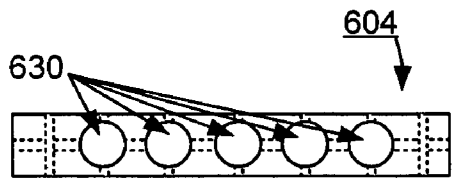


FIG. 6D

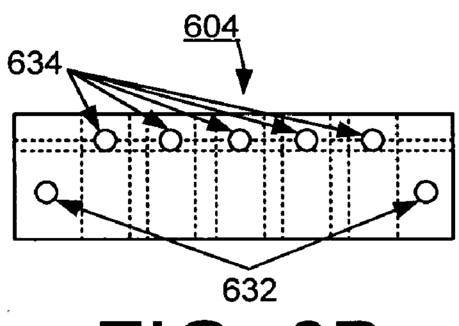


FIG. 6B

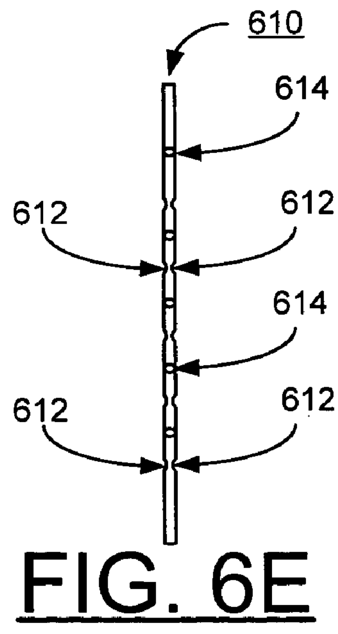


FIG. 6E

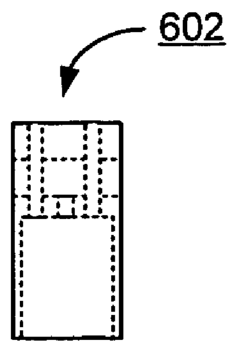


FIG. 7A

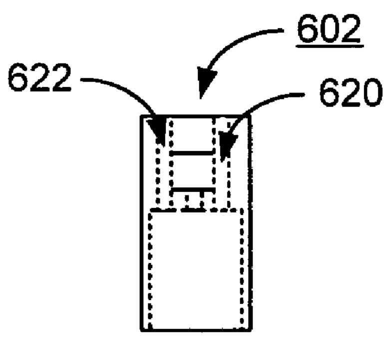


FIG. 7B

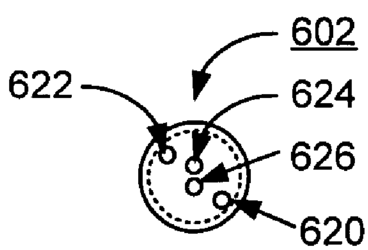


FIG. 7C

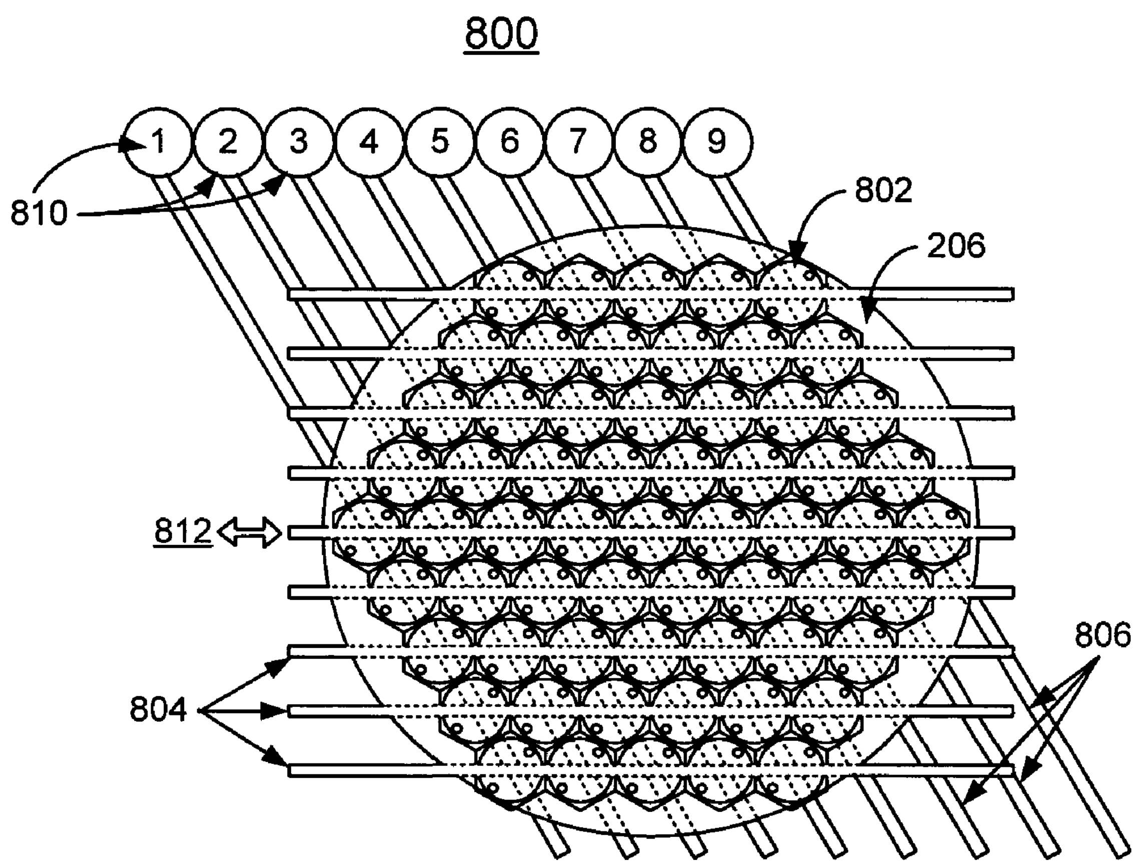


FIG. 8A

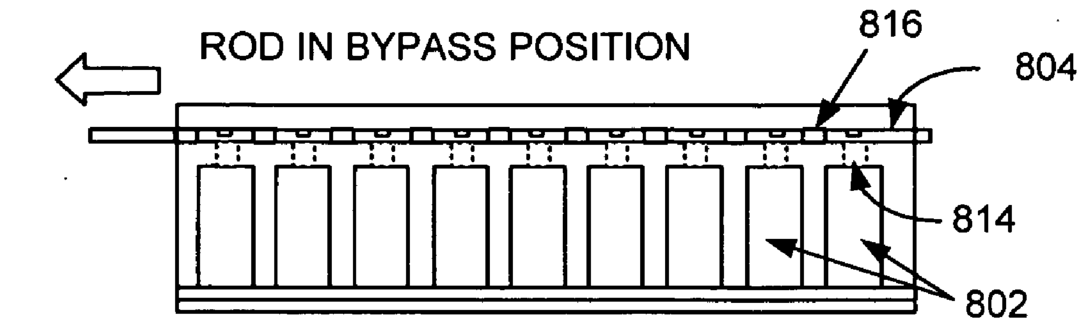


FIG. 8B

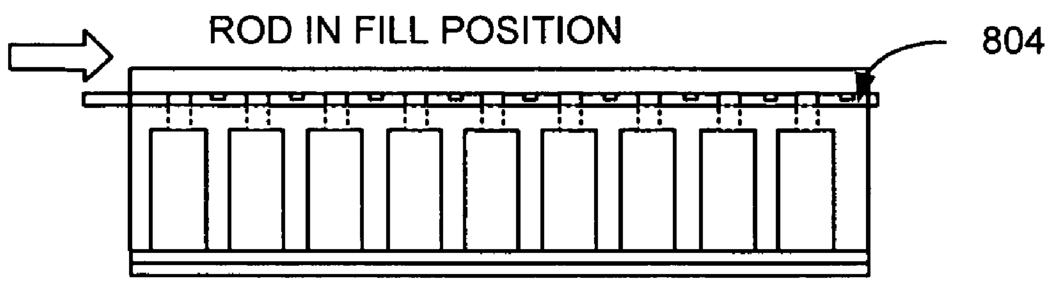


FIG. 8C

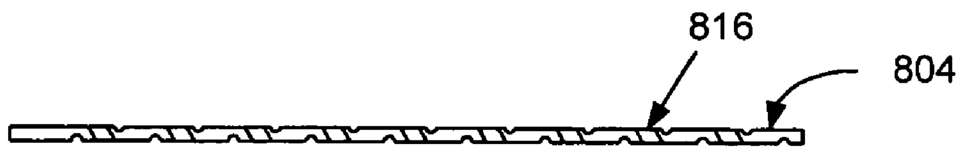


FIG. 8D

FIG. 8E

COMBINATORIAL ELECTROCHEMICAL DEPOSITION SYSTEM

[0001] This application claims the benefit of U.S. Provisional Application No. 60/704,558, filed on Aug. 2, 2005.

CONTRACTUAL ORIGIN OF THE INVENTION

[0002] The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the United States Government and Argonne National Laboratory.

FIELD OF THE INVENTION

[0003] The present invention relates to a combinatorial electrochemical deposition system enabling computer control over parameters and allowing for systematic exploration of the parameter space.

DESCRIPTION OF THE RELATED ART

[0004] Electrodeposition can be used for making many different materials ranging from bulk materials, films, nanowires, and nanoparticles. The material can be metals, semiconductors, insulators, superconductors or have multiple components. Very importantly the materials can be amorphous, nanocrystalline, or single crystalline which can have very dramatic affect on the properties of the deposit. The deposits and the properties depend upon how the conditions of deposition are controlled.

[0005] Literature often cites the conditions used to make a sample with a few of the key parameters, which usually include applied potential, concentration of the ion to be reduced, identity of the supporting electrolyte and temperature. If the system is robust enough, the results can be reproduced from this information.

[0006] Often times another lab will have difficulty in reproducing this because not all the parameters are identified. Seldom disclosed information such as exact geometry of the electrochemical cell, the type of isolation from the reference electrode, contamination of the starting reagents water, cleaning method of the equipment, pH, dissolved oxygen content and many other parameters may have a huge impact on the morphology and ultimately on the reproducibility of the system. In addition most publications do not tell the full story because experiments were done one at a time, in a serial manner within a small variation of the parameter space.

[0007] Principal aspects of the present invention are to provide a combinatorial electrochemical deposition system enabling computer control over parameters and allowing for systematic exploration of the parameter space.

[0008] Other important aspects of the present invention are to provide such combinatorial electrochemical deposition system substantially without negative effect and that overcome some of the disadvantages of prior art arrangements.

SUMMARY OF THE INVENTION

[0009] In brief, a combinatorial electrochemical deposition system is provided for enabling computer control over multiple parameters and allowing for systematic exploration of the parameter space. The combinatorial electrochemical deposition system includes a computer providing system control and data acquisition functions. The computer controls a plurality of pumps, each pump is connected to a respective material supply sources. The plurality of pumps is coupled via a mixer and a plurality of distribution valves of a cell and fluidics distribution network to deposit a particular composition of materials or solution concentration to individual electrochemical cells of an electrochemical cell array. The computer controls the mixer and the plurality of distribution valves. The electrochemical cell array includes a plurality of singly addressable flow-through isolatable electrochemical cells with a common working electrode. Each of the electrochemical cells includes a counter electrode and a reference electrode.

[0010] In accordance with features of the invention, the combinatorial electrochemical deposition system includes a multi-channel potentiostat coupled to the computer for applying a selected voltage potential to the common working electrode, and to the counter electrode and the reference electrode of each of the electrochemical cells. Demultiplexing electronics are coupled to the computer and the multi-channel potentiostat for applying the selected voltage potential to the counter electrode and the reference electrode of each of the electrochemical cells. The material supply sources include a supporting electrolyte, a selected metal of interest, and predetermined additives. The predetermined additives include, for example, pH modifiers, complexing agents, and surface-active adsorbents.

[0011] In accordance with features of the invention, the reference electrode includes a capillary saturated calomel electrode (SCE) reference electrode. The counter electrode includes a platinum counter electrode. The working electrode includes a unitary sheet member supporting a container of each of the electrochemical cells. The working electrode can be implemented by a single crystal silicon wafer or a substantially uniform thin film deposited across a single wafer.

[0012] In accordance with features of the invention, the container of each of the electrochemical cells includes a cylindrical container, such as a glass tube, or a glass plate with a plurality of holes. A glass rod is coupled to a set of the electrochemical cells and is selectively moved between a fill position and a bypass position for opening and closing the set of electrochemical cells.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The present invention together with the above and other objects and advantages may best be understood from the following detailed description of the preferred embodiments of the invention illustrated in the drawings, wherein:

[0014] FIG. **1** is a schematic and perspective view illustrating an exemplary Combinatoral Electrochemical Deposition system in accordance with the preferred embodiment;

[0015] FIG. **2**A is a schematic and perspective view illustrating an exemplary single electrochemical cell of the cell and fluidics distribution network of the Combinatoral Electrochemical Deposition system of FIG. **1** in accordance with the preferred embodiment;

[0016] FIG. **2**B is a side view of the exemplary single electrochemical cell of FIG. **2**A;

[0017] FIG. 2C is a top view of the exemplary single electrochemical cell of FIG. 2A;

[0018] FIG. 3 is a schematic and exploded perspective view illustrating an exemplary fragmentary portion of an electrochemical cell array of the cell and fluidics distribution network of the Combinatoral Electrochemical Deposition system of FIG. 1 in accordance with the preferred embodiment;

[0019] FIGS. 4A, 4B, and FIGS. 4C, 4C are respective schematic, side and top views illustrating opening and closing of an electrochemical cell of the cell and fluidics distribution network of the Combinatoral Electrochemical Deposition system of FIG. 1 in accordance with the preferred embodiment;

[0020] FIG. 5A is a schematic and plan view illustrating an exemplary electrochemical cell array of the cell and fluidics distribution network of the Combinatoral Electrochemical Deposition system of FIG. 1 in accordance with the preferred embodiment;

[0021] FIG. 5B is a schematic and side view illustrating a fragmentary portion of the electrochemical cell array of FIG. 5A;

[0022] FIG. 5C is a schematic and plan view illustrating a glass rod of the electrochemical cell array of FIG. 5A;

[0023] FIG. 5D is a schematic and plan view illustrating an enlarged fragmentary detail of the glass rod of the electrochemical cell array of FIG. 5C;

[0024] FIGS. 6A is a schematic and plan view illustrating another exemplary electrochemical cell array of the cell and fluidics distribution network of the Combinatoral Electrochemical Deposition system of FIG. 1, which can be manufactured in strips for further assembly into the complete array in accordance with the preferred embodiment;

[0025] FIG. 6B is a partially schematic side view illustrating a block of the electrochemical cell array of FIG. 6A;

[0026] FIG. 6C is a partially schematic end view illustrating the block of the electrochemical cell array of FIG. 6A;

[0027] FIG. 6D is a partially schematic top view illustrating the block of the electrochemical cell array of FIG. 6A;

[0028] FIG. 6E is a partially schematic top view illustrating a glass rod of the electrochemical cell array of FIG. 6A;

[0029] FIGS. 7A, 7B, and 7C are respective partially schematic opposing side views and a top view illustrating an electrochemical cell of the electrochemical cell array of FIGS. 6A, 6B, 6C, and 6D in accordance with the preferred embodiment;

[0030] FIGS. 8A is a schematic and plan view illustrating yet another exemplary electrochemical cell array of the cell and fluidics distribution network of the Combinatoral Electrochemical Deposition system of FIG. 1 in accordance with the preferred embodiment;

[0031] FIG. 8B is a partially schematic side view illustrating a bypass position of an electrochemical cell row of the electrochemical cell array of FIG. 8A;

[0032] FIG. 8C is a partially schematic end view illustrating a fill or open position of an electrochemical cell row of the electrochemical cell array of FIG. 8A; and

[0033] FIGS. 8D, and 8E are respective partially schematic top and side views illustrating an exemplary glass rod of the electrochemical cell array of FIG. 8A.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0034] Having reference now to the drawings, in FIG. 1 there is shown an exemplary Combinatoral Electrochemical Deposition System generally designated by the reference character 100 in accordance with the preferred embodiment. Combinatoral Electrochemical Deposition System 100 includes a computer 102 for providing system control and data acquisition functions.

[0035] In accordance with features of the invention, a Combinatoral Electrochemical Deposition System 100 is provided for implementing total computer control over generally all parameters and that allows for systematic exploration of the parameter space. Computer automation is provided for all tasks from mixing of the solutions to rates of filling and controlling the potential and treatment of the sample post deposition.

[0036] In accordance with features of the invention, Combinatoral Electrochemical Deposition System 100 enables rapid high throughput for materials synthesis and rapid testing. Combinatoral Electrochemical Deposition System 100 enables systematic exploration of complex multi-dimensional parameter space and automation of multiple tedious tasks. Combinatoral Electrochemical Deposition System 100 typically is an aqueous system that can be implemented with generally inexpensive instrumentation, while Combinatoral Electrochemical Deposition System 100 does not necessarily have to be aqueous. Combinatoral Electrochemical Deposition System 100 implements a programmed self-assembly process.

[0037] Computer 102 is coupled to a plurality of pumps 104. Each of the multiple pumps 104 is connected to a respective supply source 106 containing, for example, a supporting electrolyte, a selected metal of interest, a predetermined additive, and a pH modifier. Computer 102 controls an electrochemical deposition of materials of a selected composition.

[0038] Combinatoral Electrochemical Deposition System 100 includes an exemplary cell and fluidics distribution network generally designated by the reference character 200 including an array 202 of electrochemical cells 204. A common working electrode (WE) 206 of the preferred embodiment is provided for the multiple cells 204 of the electrochemical cell array 202. The common working electrode (WE) 206 of the preferred embodiment advantageously can be implemented with a single crystal silicon wafer or a substantially uniform thin film deposited across a single wafer.

[0039] Cell and fluidics distribution network 200 implements a much different approach to the problem than has been used in conventional arrangements. Most conventional arrangements for combinatorial electrochemistry have utilized a common bath, with a common reference electrode for an array of working electrodes. While this conventional method of manufacture can be much simpler, there are many problems with diffusion from one electrode's environment to another and having separate working electrodes that may differ in composition, unlike a single crystal silicon wafer or a uniform thin film deposited across a single wafer. There are also many problems with systems that are open to the atmosphere allowing contamination. Likewise, systems that perform experiments without being able to control all the parameters like solution mixing and fluidics distribution may suffer from irreproducibility.

[0040] Cell and fluidics distribution network **200** is the heart of the Combinatoral Electrochemical Deposition system **100**. As shown in FIG. **1**, the electrochemical cell array **202** is a **64** electrochemical cell array including **64** parallel singly addressable flow-through isolatable electrochemical (echem) cells **204** with the common working electrode (WE) **206**. An exemplary electrochemical cell **204** of the preferred embodiment is illustrated and described with respect to FIGS. **2**A, **2**B, and **2**C.

[0041] Combinatoral Electrochemical Deposition System **100** includes demultiplexing electronics **108** and a multichannel potentiostat **110**, both coupled to and controlled by computer **102**. Computer **102** controls the potentiostat **110** which controls the potential applied to a particular cell **204** and period of time the selected potential is applied to each cell **204** within the electrochemical cell array **206** and records the data generated which is relayed back to the computer **102** for storage and further analysis. Multi-channel potentiostat **110** is operatively controlled by computer **102** to provide a"virtual ground" to the working electrode **206** by connection to the ports labeled W via a connection **112**.

[0042] Multi-channel potentiostat **110** and demultiplexing electronics **108** are operatively controlled by computer **102** to provide a plurality of selected reference electrode potentials indicated by ports labeled R via the demultiplexing electronics **108** to the electrochemical cell array **206**. Multichannel potentiostat **110** and demultiplexing electronics **108** are operatively controlled by computer **102** to provide one or a plurality of controlled counter electrode potentials indicated by multiple ports labeled C via the demultiplexing electronics **108** to the electrochemical cell array **206**.

[0043] Combinatoral Electrochemical Deposition System **100** includes a mixer **114** and a plurality of distribution valves **116** coupled between the pumps **104** and the electrochemical cell array **202**, and coupled to computer **102**. Computer **102** controls the mixing of solutions and rates of filling of the electrochemical cell array **202**. An output waste flow from the electrochemical cell array **202** is collected in a waste vessel **120**. After an electrochemical deposition process is completed, a gas, such as argon, is blown through the electrochemical cell array **202** to empty all the multiple cells **204**

[0044] Various computers can be used to implement computer **102**, such as personal computer using the commercial program Labview® functioning as a data acquisition computer system by executing two way communication with the system **100** via serial port, parallel port, GPIB, TCP/IP or a data acquisition (DAQ) interface. A commercially available multi-channel potentiostat manufactured and sold by Princeton Applied Research, Ametek® can be used for the multi-channel potentiostat **110**. Masterflex® computer controlled peristaltic pumps can be used for the plurality of pumps **104**.

[0045] Referring also to FIG. **2**A, **2**B, and **2**C, each electrochemical cell **204** includes a reference electrode **210**, a counter electrode **212**, the common working electrode **206**, an inlet port **214** and an outlet port **216**.

[0046] A capillary SCE (saturated calomel electrode) reference electrode can be used to implement reference electrode **210**, while other reference electrode types such as MSE (mercurous sulfate electrode), Ag/AgCI electrode, quasi-reference electrode also can be used. The counter electrode **212** includes a generally circular disk **220** having a pair of generally centrally disposed, spaced apart openings **222**, **224** respectively for receiving the cell input **214** and cell outlet **216**. A third opening **226** in the circular disk **220** of the counter electrode **212** is provided for receiving the reference electrode **210**. The wire attached **212** to the circular disk **220** provides electrical contact to the counter electrode.

[0047] For example, a platinum counter electrode can implement the counter electrode **212**, while the counter electrode **212** may also be implemented by a platinized titanium, gold or any other metal inert to modification or dissolution under the conditions being studied.

[0048] In accordance with features of the invention, the independent electrochemical cells **204** of Combinatoral Electrochemical Deposition System **100** avoid cross contamination and mass transport from adjacent electrodes. The electrochemical cells **204** being constructed of inert materials enables consistent results to be obtained after aggressive cleaning with reagents known to clean contaminants to the highest degree possible such as concentrated sulfuric acid and concentrated nitric acid. Avoidance of materials such as base metals, polyethylene, silicone, nylon and other non-fluorinated plastics prevents trace contamination of the solutions or electrode surfaces, which can be problematic for obtaining pure, consistent electrochemistry. Combinatoral Electrochemical Deposition System **100** combines both synthesis and characterization in the single system. The separate electrochemical cells **204** of Combinatoral Electrochemical Deposition System **100** allow systematic exploration of solution concentration, which is a very important parameter affecting conditions of growth and are necessary to change for characterization. Combinatoral Electrochemical Deposition System **100** enables ease of connection and allows experimentation with generally any parameter within, for example, more than a 20 dimensional parameter space. Combinatoral Electrochemical Deposition System **100** includes sealed and integrated robotic mixing and fluidic distribution network **200** enabling cleanliness without requiring a clean room environment.

[0049] Each electrochemical cell **204** is singly addressable flow-through isolatable electrochemical cell. For example, different selected potentials are applied via the demultiplexing electronics **108** to the respective counter electrode **212** of the singly addressable electrochemical cells **204** with respect to the respective reference electrode **210** for each cell. The potentiostat connection **112** to the working electrode (WE) **206** hold the WE at virtual ground, while the potential is sensed by the individual reference electrodes **210** of respective electrochemical cells **204** which provides a feedback mechanism and allows the potentiostat **110** to raise or lower the potential of the counter electrode **212** until the desired potential is achieved at the working electrode **206**. Because a single common working electrode **206** is used for the electrochemical cell array **202** allows a homogenous single silicon wafer to be used to define the working electrode **206** for all the singly addressable electrochemical cells **204**. This is an important feature of Combinatoral Electrochemical Deposition System **100**.

[**0050**] The electrochemical cell **204** including a generally cylindrical, stepped container **230** mounted on the common WE **206** within a masked off area **232** of a wafer defining the common WE **206**. It should be understood that the container **230** is not necessarily stepped. For example, the container **230** can be defined by a single diameter container, such as shown in FIG. **7**A. The cylindrical, stepped container **230** includes an enlarged upper portion **234**. For example, a glass, Viton or Teflon, stepped tube can implement the cylindrical container **300**.

[**0051**] As shown in FIG. **2**B, the enlarged upper portion **234** of the cell container **230** including a pair of aligned openings **236** for receiving an inert tube (High Purity PFA tubing) **238**. A second glass rod **240** is received through a second offset pair of openings **242** as indicated in the top view of FIG. **2**C.

[**0052**] Referring to FIG. **3**, there is shown an exploded perspective view of an exemplary fragmentary portion of an electrochemical cell array generally designated by the reference character **300** of the cell and fluidics distribution network **200** of the Combinatoral Electrochemical Deposition system **100** in accordance with the preferred embodiment. The same reference characters used in FIG. **2**A, **2**B, and **2**C, with respect to electrochemical cell **204** are used for similar or identical components in FIG. **3** and following description.

[**0053**] As shown, electrochemical cell array portion **300** includes multiple electrochemical cells **204** with one shown mounted within a support structure **302**. Support structure **302** includes a base member **304** supporting an upper member **306**. The base member **304** is a glass member that is bonded with the upper member **306**, for example, formed of Teflon. Support structure **302** includes a plurality of stepped openings **308**, each for receiving a respective electrochemical cell **204**. An opening extends through the upper Teflon member **306** for receiving the fluid pathway **238** that is received through the multiple electrochemical cells **204**.

[**0054**] Referring to FIGS. **4**A, **4**B, and FIGS. **4**C, **4**C, there are shown respective schematic, side and top views illustrating opening and closing of the electrochemical cell **204** of the cell and fluidics distribution network **200** in accordance with the preferred embodiment. As shown in FIGS. **4**A and **4**B, the electrochemical cell **204** is provided in the filling position with the glass rod **240** having respective flow-through notches **242** aligned to admit inflow to the cell from upstream flow path channel **238**A through the inflow channel **214** and outflow from the cell through outflow channel **216** to the downstream flow channel **238**B. As shown in FIGS. **4**C and **4**D, the electrochemical cell **204** is provided in the bypass position with the glass rod **240** moved to aligned bypass opening **244** relative to the openings of channels and provide a direct pathway between the upstream flow path and outflow channels **238**A and **238**B.

[**0055**] Referring to FIG. **5**A, **5**B, and **5**C, there is shown an exemplary electrochemical cell array generally designated by the reference character **500** used with the Combinatoral Electrochemical Deposition system **100** in accordance with the preferred embodiment. Electrochemical cell array **500** includes an 8 cell by 8-cell array. A plurality of input valves **502**, **1-8** couple a particular composition of materials or solution concentration via channel **238** to a respective fill input **214** to the electrochemical cell **204** of the electrochemical cell array **500**. A respective air cylinder or solenoid **504** (one shown) is coupled to each glass rod **240** to selectively move the glass rod for opening and closing the individually addressable electrochemical cells **204**. Valves **502** and air cylinders **504** are operatively controlled by computer **102**.

[**0056**] As shown in FIG. **5**A, in the array **500** a third glass rod **240** is moved by the illustrated air cylinder or solenoid **504** and valve **502**, **3** is opened to fill the corresponding electrochemical cell **204** indicated by reference character A. Each of the electrochemical cells **204** can be sequentially filled or by-passed by opening each valve **502**, **1-8** and selectively moving the glass rod **240** between the fill and bypass positions. The air cylinder or solenoid **504** can be implemented with a commercially available air cylinder, such as, manufactured and sold by Clippard and Minimatics.

[**0057**] FIGS. **5**B, **5**C, and **5**D illustrate electrochemical cells **204** and the glass rod **240** of the electrochemical cell array **500**. As described above, the notches **242** are respectively aligned with the cell inlet **214** and cell outlet **216** for filling any electrochemical cells **204** in the array **500**. The bypass **244** of the glass rod **240** is moved relative to the channel **238** so that electrochemical cell **204** is provided in the closed or bypass position.

[**0058**] FIGS. **6**A, **6**B, **6**C, **6**D and **6**E there is shown another exemplary electrochemical cell array generally designated by the reference character **600** used with the Combinatoral Electrochemical Deposition system **100** in accordance with the preferred embodiment. Electrochemical cell array **600** includes a five by five (5 by 5) array of electrochemical cells **602**. Electrochemical cells **602** are illustrated and described with respect to FIGS. **7**A, **7**B, and **7**C.

[**0059**] Electrochemical cell array **600** is defined by a plurality of identical blocks **604** secured together by a pair of tie rods **606**. Each block **604** contains five electrochemical cells **602**, as shown in FIGS. **7**A, **7**B, and **7**C. As shown in FIG. **6**A, a plurality of inert tubes (high purity PFA tubing) **608** extend horizontally through the blocks **604** that together define respective corresponding rows of electrochemical cells **602** within the electrochemical cell array **600**. A glass rod **610** extends through the electrochemical cells **602** within each of the multiple blocks **604** defining the electrochemical cell array **600**. As shown in FIG. **6**A, the respective second glass rods **610** extend vertically through respective corresponding columns of electrochemical cells **602** within the electrochemical cell array **600**.

[**0060**] Referring also to FIGS. **7**A, **7**B, and **7**C, each electrochemical cell **602** of the electrochemical cell array **600** includes a reference electrode **620**, a counter electrode **622**, the common working electrode **206** as shown in FIG. **2**A, an input **624** and an outlet **626**. The container for each electrochemical cell **602** is defined by a respective one of a plurality of openings **630** extending from top to bottom through each block **604** as shown in FIGS. **6**A and **6**D. A pair of openings or holes **632** extending from side to side through each block **604** is defined near opposite ends of the block as shown in FIGS. **6**A and **6**B for receiving the tie rods **606**. A respective one of a plurality of spaced apart openings **634** defined near an upper portion of the block **604** as shown in FIGS. **6**A and **6**B for receiving a respective glass rod **608**. An elongated opening **636** is defined near the upper portion of the block **604** as shown in FIGS. **6**A and **6**C for receiving a respective glass rod **610**.

[0061] The glass rods **610** include notches **612** respectively positioned relative to the channels **608** to admit inflow to the cell **602** from flow path channel **608** and outflow from the cell **602** to the channel **608**. Then the notches **612** of glass rods **610** are selectively moved to position bypass grooves **614** into a bypass position for the cells **602**, operatively controlled by computer **102** via an air cylinder or solenoid (not shown in FIG. **6**A).

[0062] Referring to FIGS. **8**A, **8**B, **8**C, and **8**D, there is shown yet another exemplary electrochemical cell array generally designated by the reference character **800** used with the Combinatoral Electrochemical Deposition system **100** in accordance with the preferred embodiment. Electrochemical cell array **800** includes a hexagonal shaped spacing for group of 61 electrochemical cells **802** to maximize utilization of a wafer defining a common working electrode (WE) **206**.

[0063] Electrochemical cell array **800** includes a plurality (nine) of glass rods **804** extending horizontally and a plurality (nine) of flow path channels **806** extending diagonally, at 60° from the glass rods **804**, as shown in FIG. **8**A. A plurality of input valves **810**, **1-9** couple a particular composition of materials or solution concentration via channel **806** to a respective electrochemical cell **802** of the electrochemical cell array **800**. A respective air cylinder or solenoid **812** (one shown) is coupled to each glass rod **804** to selectively move the glass rod for opening and closing the individually addressable electrochemical cells **802**. Computer **102** operatively controls valves **810** and air cylinders **812**.

[0064] FIG. **8**B illustrates a bypass position of a row electrochemical cells of the electrochemical cell array **800** with the glass rod **804** positioned at a bypass position with notches **816** in the glass rod **804** offset from cell flow paths indicated by **814**.

[0065] FIG. **8**C illustrates a fill or open position of the electrochemical cell row with the glass rod **804** positioned at an aligned position with notches **816** in the glass rod **804** aligned with the cell flow paths **814**. FIGS. **8**D, and **8**E provide top and side views of the glass rod **804** the electrochemical cell array **800**.

[0066] While the present invention has been described with reference to the details of the embodiments of the invention shown in the drawing, these details are not intended to limit the scope of the invention as claimed in the appended claims.

What is claimed is:

1. A combinatorial electrochemical deposition system comprising:

a computer providing system control and data acquisition functions;

a plurality of pumps coupled to said computer, each pump being connected to a respective material supply source;

a fluidics distribution network including a mixer and a plurality of distribution valves coupled to said computer and said plurality of pumps;

an electrochemical cell array coupled to said plurality of distribution valves, said fluidics distribution network being controlled by said computer for depositing a particular composition of materials or solution concentration to individual electrochemical cells of said electrochemical cell array;

said electrochemical cell array includes a plurality of singly addressable flow-through isolatable electrochemical cells with a common working electrode, each of said electrochemical cells including a counter electrode and a reference electrode.

2. A combinatorial electrochemical deposition system as recited in claim 1 includes a multi-channel potentiostat coupled to said computer for applying a selected voltage potential to said common working electrode, and to said counter electrode and said reference electrode of each of said electrochemical cells.

3. A combinatorial electrochemical deposition system as recited in claim 2 includes demultiplexing electronics coupled to said computer and said multi-channel potentiostat for applying said selected voltage potential to said counter electrode and said reference electrode of each of said electrochemical cells.

4. A combinatorial electrochemical deposition system as recited in claim 1 wherein said reference electrode includes a capillary SCE reference electrode.

5. A combinatorial electrochemical deposition system as recited in claim 1 wherein said counter electrode includes a platinum counter electrode.

6. A combinatorial electrochemical deposition system as recited in claim 1 wherein said working electrode includes a unitary sheet member supporting a container of each of said electrochemical cells.

7. A combinatorial electrochemical deposition system as recited in claim 6 wherein said container of each of said electrochemical cells includes a cylindrical container.

8. A combinatorial electrochemical deposition system as recited in claim 7 wherein said containers of said electrochemical cells are defined by a plurality of through holes in a single glass plate.

9. A combinatorial electrochemical deposition system as recited in claim 7 wherein said cylindrical container includes a glass tube.

10. A combinatorial electrochemical deposition system as recited in claim 1 wherein said computer controls each of said pumps connected to said respective material supply source and said mixer for mixing of the solution concentration.

11. A combinatorial electrochemical deposition system as recited in claim 10 wherein said respective supply sources include a supporting electrolyte, a selected metal of interest, and a predetermined additive.

12. A combinatorial electrochemical deposition system as recited in claim 1 wherein said computer controls a rate of filling of said electrochemical cells in said electrochemical cell array.

13. A combinatorial electrochemical deposition system as recited in claim 1 wherein said electrochemical cells of said electrochemical cell array include said common working electrode defined by a single crystal silicon wafer.

14. A combinatorial electrochemical deposition system as recited in claim 1 wherein said electrochemical cells of said electrochemical cell array include said common working electrode defined by a generally uniform thin film supported on a single wafer.

15. A combinatorial electrochemical deposition system as recited in claim 1 wherein said electrochemical cells of said electrochemical cell array include a glass rod coupled to a set of electrochemical cells, said glass rod selectively moved between a fill position and a bypass position for opening and closing said set of electrochemical cells.

16. A combinatorial electrochemical deposition system as recited in claim 15 include an air cylinder coupled to said glass rod for controlling movement of said glass rod between said fill position and said bypass position.

* * * * *