(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 July 2010 (29.07.2010)

PCT

(10) International Publication Number
WO 2010/085764 A2

(51) International Patent Classification:
G02B 1/11 (2006.01) *C03C 17/32* (2006.01)
B32B 27/08 (2006.01) *C09J 7/02* (2006.01)
C09D 5/32 (2006.01)

(21) International Application Number:
PCT/US2010/022010

(22) International Filing Date:
25 January 2010 (25.01.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/205,766 23 January 2009 (23.01.2009) US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2010/085764 A2

(54) **Title**: METHOD, APPARATUS, AND COMPOSITIONS MAKING ANTI-REFLECTIVE COATINGS FOR SUBSTRATES

(57) **Abstract**: Embodiments of the present system and method are useful for chemical deposition, particularly continuous deposition of anti-reflective films. Disclosed systems typically comprise a micromixer and a microchannel applicator. A deposition material or materials is applied to a substrate, such as aluminum, glass, silicon, or polycarbonate, to form a nanostructured, anti-reflective coating. Uniform and highly oriented surface morphologies of films deposited using disclosed embodiments are clearly improved compared to films deposited by a conventional batch process. In some embodiments, an anti-reflective coating is applied to a surface of a solar catalytic microreactor suitable for performing endothermic reactions, where energy is provided to the reactor by absorption of solar radiation. The process can be used to tailor the composition and morphology of the material deposited on a substrate. The present process can be used at low temperatures as a post-deposition, high-temperature annealing step is obviated.

METHOD, APPARATUS, AND COMPOSITIONS FOR MAKING ANTI-REFLECTIVE COATINGS FOR SUBSTRATES

CROSS REFERENCE TO RELATED APPLICATION

5 The present application claims the benefit of the earlier filing date of United States provisional application No. 61/205,766, filed on January 23, 2009, which is incorporated herein by reference.

FIELD

10 The present disclosure concerns a process for depositing materials, generally as thin films, on substrates, particularly a chemical bath deposition process that uses a microchemical system comprising a micromixer, a microchannel fluid applicator, or both, and articles made according to the process, including nanostructured, anti-reflective coatings for transparent and absorbing surfaces.

15

ACKNOWLEDGMENT OF GOVERNMENT SUPPORT

The present invention was developed, at least in part, using funds from the National Science Foundation's Process and Reaction Engineering program under CAREER grant No. CTS-0348723, and funds from the National Science
20 Foundation's Process and Reaction Engineering program under grant No. CBET-0654434. The government has certain rights in the invention.

BACKGROUND

Chemical bath deposition (CBD), the aqueous analog of chemical vapor
25 deposition with the constituent ions dissolved in a water solution, can be used to deposit epitaxial layers at low temperatures. For example, CBD has been successfully used as a batch process to deposit many semiconductor compounds, including Ag_2S, CdS, CdSe, CoS, Cu_2S, PbS, SnS, SnO, MoS_2, SbS, TiO_2, ZnO, SnSe, CdSnS, $CuInSe_2$, and PbHgS. Batch CBD processes also have been used to
30 make thin film transistors. Gan *et al.,* U.S. Patent No. 6,225,149, for example,

entitled "Method to Fabricate Thin Film Transistors and Circuits," describes forming thin film transistors by preparing a chemical deposition bath and depositing a semiconductor layer using the chemical bath. Other methods for depositing thin films are disclosed in U.S. Publication No. 2007/0184576, which is incorporated herein by reference.

In recent years, metal chalcogenide semiconductors have received much attention for electronic and optoelectronic applications. Typically, metal chalcogenides are deposited as binary or ternary compounds including sulfide, selenide and telluride compounds using a variety of techniques, including electrodeposition, vacuum evaporation, Successive Ionic-Layer Adsorption and Reaction, spray pyrolysis, sputtering, chemical vapor deposition (CVD) and chemical bath deposition CBD. Batch CBD processes already have proved useful for fabricating large area devices, such as high efficiency $CuInSe_2$ and CdTe solar cells. P. K. Nair, M. T. S. Nair, V. M. Garcia, O. L. Arenas, Y. Pena, A. Castillo, I. T. Ayala, O. Gomez-daza, A. Sanchez, J. Campos, H. Hu, R. Suarez, M. E. Rincon. *Sol. Energy Mater. Sol. Cells*. **1998**, *52*, 313. O. Savadogo. *Sol. Energy Mater. Sol. Cells*. **1998**, *52*, 361.

Though CBD has many advantages, it also has drawbacks. One major drawback is the formation of particles, as well as the unwanted deposition that occurs with such processes, which generates waste and causes device defects. For batch CBD processes, the heat needed for chemical reaction may be supplied from the solution bath to the sample surface. With reference to CdS as an example, this results in both heterogeneous CdS nucleation at the surface as well as homogeneous CdS formation in the bath. Hence, with thermal jacket baths (glass beaker etc.) or water baths, significant CdS deposition also occurs on the walls of the vessels. The bath must be stirred continuously to ensure uniform thermal and chemical mixing and to minimize adhesion of homogeneously nucleated CdS particles to the growing film surface. Moreover, the unequal bath volumes used to form desired CdS films generates substantial waste and also creates device defects. Efforts have been made to reduce the bath-to-surface volume using cover plates. P. K. Nair, V. M. Garcia,

O. Gomez-Daza, M. T. S. Nair, *Semicond. Sci. Technol.* **2001**,*16*, 855. Batch CBD processes also typically require that the deposited material be subjected to relatively high-temperature annealing processes. These high temperatures generally are not compatible with substrates, such as polymeric materials, that are used to make
5 flexible electronic devices, such as flexible transistors.

Batch CBD processes are quite useful. However, a low-temperature process that combines large area deposition with high utilization and growth rate for high conversion efficiencies and precise control over particle formation and deposition has not yet been demonstrated.

10

SUMMARY

Embodiments of the present system for chemical deposition, particularly continuous deposition of anti-reflective films, typically comprise: a micromixer, such as an interdigital micromixer or other type of micromixer [such as disclosed in
15 V. Hessel *et al.*, *Chem. Eng. Sci.* 60, 2479 (2005), which is incorporated herein by reference]; a microchannel applicator; or both. Additional examples of micromixers and microchannel devices are disclosed in U.S. Publication No. 2005/0220681, which is incorporated herein by reference. The present system and process provide a substantially constant flux of reactant solution that allows control over the
20 homogeneous reaction of the chemical bath solution before the solution impinges on the substrate.

Working embodiments of the system typically include at least a first fluid source, more typically at least a first and second fluid source, operably coupled to a micromixer. The mixer effectively mixes fluids to initiate formation of the
25 deposition material. A microchannel applicator may then be used to apply the deposition fluid to a substrate, such as an aluminum, glass, polymer, or silicon substrate. Some embodiments may use flexible substrates, such as polymeric materials.

A person of ordinary skill in the art will appreciate that the system can
30 include other components, such as components that facilitate chemical deposition.

For example, the deposition system may comprise one or more heat exchangers to heat the deposition fluid(s) and a heater operably coupled to the substrate for heating the substrate. Furthermore, the system may comprise at least one pump for pumping the first and/or second fluids, or at least two pumps for pumping the first and second fluids through the system, such as to the micromixer.

Uniform and highly oriented materials, such as nanocrystalline, anti-reflective metal oxide thin films, exemplified by zinc oxide films and silicon dioxide films, were successfully deposited on substrates using the system. The surface morphologies of the deposited materials were characterized by scanning electron microscopy (SEM). Reflectance and transmittance were measured with UV-Visible spectroscopy. The analyses demonstrated a marked decrease in surface reflectivity.

A process for chemical deposition, particularly of thin films, also is described. One embodiment of the process comprises providing a first reactant, providing a second reactant, and flowing the first and second reactants to a micromixer to mix the first and second reactants, thereby initiating formation of a deposition material. A person of ordinary skill in the art will appreciate that formation of some deposition materials may require more than two reactant streams. The deposition material is then applied to a substrate, such as by using a microchannel applicator.

Particular embodiments exemplify the invention by reference to the production and/or application to a substrate of a ZnO or SiO_2 anti-reflective film. For ZnO deposition, the first reactant typically was zinc acetate, and the second reactant comprised sodium hydroxide. For SiO_2 deposition, the first reactant typically was tetraethylorthosilicate and the second reactant was ammonium hydroxide/water. Other compounds suitable for producing anti-reflective coatings include, but are not limited to, CeO_2, MgF_2, and ZnS. Additional examples are disclosed in U.S. Publication Nos. 2007/0020400 and 2008/0108122, which are incorporated herein by reference.

A person of ordinary skill in the art also will appreciate that the first reactant, the second reactant, or both may comprise additional materials suitable for various

functions, such as to facilitate the deposition process. For example, such compositions may include a complexing agent or agents, such as a nitrogen-bearing compound, with ammonia being one example of a suitable nitrogen-bearing complexing agent.

5 The process can be used to tailor the composition and morphology of the material as deposited on a substrate. For example, where a thin film is deposited on a substrate, the film may be an epitaxial nanostructured thin film, a nanoparticle film, a nanocrystalline thin film, an epitaxial thin film comprising embedded nanocrystals, a superlattice thin film, a composition gradient thin film, a composite 10 thin film comprising core-shell nanoparticles, and combinations thereof. Desired particles can be produced by a chemical bath deposition process by controlling the residence time of the mixed reacting solution, by using a combined chemical bath deposition and solution-based nanoparticle synthesis process, or by using a nanoparticle solution directly.

15 One advantage of the present process is that it can be used at low temperatures as a post-deposition, high-temperature annealing step is obviated. Because a micromixer is used, reagent volumes are decreased compared to conventional processes with resulting decreases in waste material generated. The present process also can be used to synthesize nanomaterials in the required volumes 20 at the point of application, reducing human exposure to potentially hazardous materials as well as reducing the need to transport and store such potentially hazardous materials. These advantages allow process flexibility and reduce costs relative to known processes. For example, because high-temperature annealing processes are avoided, candidate substrate materials are significantly increased, and 25 include flexible substrate materials, such as polymeric materials, that cannot be used for known, high-temperature chemical bath deposition processes.

The process can be used to produce particular products including, without limitation, anti-reflective coated lenses, fuel cell electrode membranes, photovoltaic films, solar cells, flexible solar cells, solar catalytic microreactors, wearable 30 electronics, biomedical films, etc. The process for making devices comprises at

least one step comprising flowing at least a first, and typically plural, reactants to a micromixer to mix the first and second reactant and initiate formation of a deposition material. The deposition material may then be applied to a substrate using a microchannel applicator. In particular embodiments, the deposition material
5 comprises nanoparticles. Working embodiments of the process were used to make nanostructured, anti-reflective coatings.

The foregoing and other objects, features, and advantages of the invention will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

10

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram illustrating CBD-CdS growth mechanisms.

FIG. 2 is a schematic diagram of one embodiment of a continuous flow microreactor system.

15 FIG. 3 is a schematic diagram of one embodiment of an impinging flow bath deposition reactor, with the inset illustrating one embodiment of an interdigital micromixer.

FIG. 4 is a schematic diagram illustrating one embodiment of a process using a roll-to-roll substrate susceptor or a substrate roll.

20 FIG. 5 is a schematic diagram of one embodiment of a rotating disk substrate susceptor.

FIG. 6 is a schematic diagram of one embodiment of chip-based chemical mixing and deposition system.

FIG. 7 is a schematic diagram of one embodiment of a system for depositing
25 nanostructured thin films onto a substrate in a continuous manner.

FIG. 8 is a schematic diagram of one embodiment of a table-top system for depositing nanostructured thin films onto a substrate.

FIG. 9 is a photograph of one embodiment of a table-top system for depositing nanostructured thin films onto a substrate.

30 FIG. 10 is a schematic diagram of one embodiment of a micromixer array.

FIG. 11 is a schematic cross sectional drawing illustrating thin film morphologies that can be formed using embodiments of the present invention.

FIG. 12 is a schematic drawing illustrating an array of tapered, subwavelength protuberances.

5 FIG. 13 is a schematic drawing illustrating three configurations of nanostructured anti-reflective surfaces.

FIG. 14 is an SEM micrograph of a ZnO structure generated with 0.005 M NaOH.

FIG. 15 is an SEM micrograph of a ZnO structure generated with 0.01 M

10 NaOH.

FIG. 16 is an SEM micrograph of a ZnO structure generated with 0.1 M NaOH.

FIG. 17 is an SEM micrograph of a ZnO structure generated with 0.15 M NaOH.

15 FIG. 18 is a schematic diagram of one embodiment of a solar catalytic microreactor.

FIG. 19 is a schematic diagram of one embodiment of a continuous flow microreactor system.

FIGS. 20A and 20B are SEM micrographs of a ZnO film with "white"

20 morphology.

FIGS. 21A and 21B are SEM micrographs of a ZnO film with "black" morphology.

FIGS. 22A and 22B are SEM micrographs of a mixture of white and black ZnO morphologies.

25 FIG. 23 is a graph of percent reflectance versus wavelength for ZnO films on aluminum.

FIG. 24 is a logarithmic-scale graph of percent reflectance versus wavelength for ZnO films on aluminum.

FIG. 25 is a graph of percent reflectance versus wavelength for ZnO films on

30 glass.

FIG. 26 is a logarithmic-scale graph of percent reflectance versus wavelength for ZnO films on glass.

FIG. 27 is a graph of percent transmittance versus wavelength for a ZnO film on glass.

5 FIG. 28 is a photograph of a ZnO film on a glass substrate laid on top of an image.

FIG. 29 is an SEM image of a ZnO film on a textured silicon substrate.

FIG. 30 is a graph of percent reflectance versus wavelength for a ZnO film on textured silicon.

10 FIG. 31 is a graph of percent transmittance and percent reflectance versus wavelength for a SiO_2 film on a glass substrate.

FIG. 32 is an atomic force microscopy (AFM) image of a SiO_2 film on a glass substrate.

FIG. 33 is an SEM image of a SiO_2 film on a glass substrate.

15 FIG. 34 is a schematic diagram of a SiO_2 film on a polycarbonate eyeglass lens.

FIG. 35 is a graph of percent reflectance versus wavelength for a SiO_2 film on a polycarbonate lens.

FIG. 36 is an AFM image of a SiO_2 film on a polycarbonate lens.

20 FIG. 37 is a series of photographs illustrating reflectance of visible light on coated and uncoated polycarbonate lenses.

DETAILED DESCRIPTION

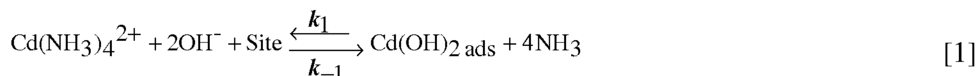
25 **I. CBD**

A. CBD Generally

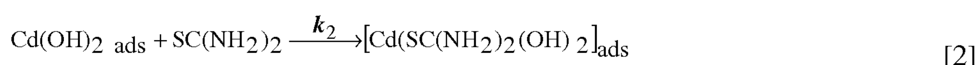
The fundamental aspects of CBD are similar to that of a CVD process. Without being limited to a theory of operation, CBD generally involves mass transport of reactants, adsorption, surface diffusion, reaction, desorption, nucleation,

30 and growth. Earlier studies suggested a colloidal-by-colloidal growth model. I.

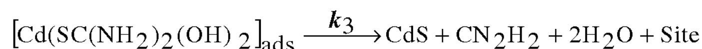
Kaur, D. K. Pandya, K. L. Chopra, *J. Electrochem. Soc.*, **1980**, *140*, 943. However, more recent investigations by Ortega-Borges & Lincot, based on initial rate studies using a Quartz Crystal Microbalance (QCM), suggested that different growth kinetics are involved. R.Ortega-Borges, D. Loncot, *J. Electrochem. Soc.*, **1993**, *140*, 3464. Ortega-Borges *et al.* identified three growth regimes: an induction period with no growth observed; a linear growth period; and finally a colloidal growth period, followed by the depletion of reactants. Ortega-Borges *et al.* proposed a molecular level heterogeneous reaction mechanism for CdS deposition according to the equations provided below.



$$Cd(NH_3)_4^{2+} + 2OH^- + Site \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cd(OH)_{2\,ads} + 4NH_3 \quad [1]$$



$$Cd(OH)_{2\,ads} + SC(NH_2)_2 \xrightarrow{k_2} [Cd(SC(NH_2)_2(OH)_2]_{ads} \quad [2]$$



$$[Cd(SC(NH_2)_2(OH)_2]_{ads} \xrightarrow{k_3} CdS + CN_2H_2 + 2H_2O + Site$$

This model has provided a good understanding of CBD processes at the molecular level. Particle formation plays an important role in CBD processes. Kostoglou *et al.* reported a detailed and comprehensive model for a CBD process for depositing CdS. M. Kostoglou, N. Andritsos, A. J. Karabelas, *Ind. Eng. Chem. Res.*, **2000**, *39*, 3272. This model includes particle nucleation, growth, and deposition in addition to molecule-by-molecule film growth.

Disclosed embodiments of the present invention provide many benefits relative to batch CBD processes. For example, thin films deposited using embodiments of the present method and system are substantially more continuous, and generally have a higher crystallinity, than do thin films deposited by batch processes. Post annealing steps required with batch processes, which are obviated with the present invention, may reduce the porosity of the deposited materials and increase the crystallinity. However, films deposited using the present invention typically are less porous, and often have higher crystallinity, relative to batch processes even without a post deposition annealing step.

Moreover, the present invention provides a more reliable and reproducible deposition result. For batch processes, it is not unusual to make plural deposition attempts to obtain a suitable deposited layer. The occurrence of unsuitable deposition layers is significantly reduced using disclosed embodiments of the
5 present method and system.

The present invention also provides a higher deposition rate than batch processes at the same deposition material concentration. To obtain a deposited layer having a suitable thickness, batch CBD processes often will use plural deposition baths to deposit a single layer. The longer a substrate is immersed in a deposition
10 bath, the more likely it is that deleterious particle formation and deposition will occur on the substrate. This unwanted particle formation and deposition can be minimized in batch processes by moving the substrate from deposition bath to deposition bath, and immersing the substrate in a particular deposition bath for a time selected to minimize particle formation. However, the longer the substrate
15 remains in the deposition bath, the slower the deposition rate is since the reactant concentrations are decreasing. All of these process deficiencies are addressed by using disclosed embodiments of the present invention.

FIG. 1 is a schematic diagram of CBD-CdS growth mechanisms that illustrates the results associated with both homogeneous and heterogeneous
20 reactions. Small particles form and grow even at the beginning of the process as observed by dynamic light scattering and TEM measurements. C. Voss, Y. J. Chang, S. Subramanian, S. O. Ryu, T.-J. Lee, C.-H. Chang, *J. Electrochem. Soc.*, **2004**, *151*(10), C655, incorporated herein by reference. These experimental results indicated the importance of particle formation even in the linear growth regime. It is
25 desirable to develop a process that de-couples homogeneous particle formation and deposition from the molecular level heterogeneous surface reaction for a better understanding and optimization of CBD processes.

B. Deposition Materials

A person of ordinary skill in the art will appreciate that the present CBD process can be used to deposit a variety of different materials. Disclosed embodiments are exemplified with reference to particular materials, such as metal
5 oxides, one example of which is zinc oxide (ZnO), and using such materials to form anti-reflective coatings. Many different materials can be deposited using the present system, and many devices can be produced using the system and process. The appropriate selection of a deposition material, and hence reactants potentially useful for forming the desired deposition material, will depend on several factors, including
10 the end use of the device constructed. For example, the composition of the material to be deposited can be selected to provide a desired result in a product made using the material. Once the deposition material is identified, the reactants used to form the deposition material can be varied to maximize reaction efficiency, reduce production costs, decrease or minimize toxicity, waste, etc., and combinations
15 thereof. Other variables also can be manipulated, such as: varying the concentration of the material to be deposited; using complexing agents, such as nitrogen-bearing compounds, including ammonia, to facilitate the process; varying the temperature of the reactant solutions and/or the substrate; potentially varying the solvent or suspending liquid to be other than water; and combinations of such variables.

20 Solely by way of example and without limitation, useful materials that may be formed and deposited by the present CBD process include Au, Ag, Cu, Co, Cr, Ge, Ni, Pt, Pd, Rh, Se, Si, Ru, Ag_2S, Ag_2Se, AgO, Ag_2O, Al_2O_3, As_2S_3, BaO, Bi_2S_3, Bi_2Se_3, CdO, CdS, CdSe, CdSnO, CdTe, CdZnS, CeO_2, CoS, CoSe, CoO, CrO_2, $CuBiS_2$, $CuGaSe_2$, $Cu(In,Ga)Se_2$, $CuInSe_2$, $CuInS_2$, $Cu_{2-x}S$, $Cu_{2-x}Se$, Cu_2O,
25 FeO(OH), Fe_2O_3, Fe_3O_4, GaAs, GaN, Ga_2O_3, GaP, Ge, GeO_2, HfO_2, HgS, HgSe, InGaAs, InAs, In_2O_3, InP, In_2S_3, In_2Se_3, La_2O_3, MgO, MnS, MnO_2, MoO_2, MoS_2, $MoSe_2$, NbO_2, NiS, NiSe, NiO, PbHgS, PbS, PbSe, PbTe, PbO_2, ReO_3, RhO_2, RuO_2, Sb_2S_3, Sb_2Se_3, SiGe, SiO_2, SnS, SnS_2, SnSe, SnO_2, Sb_2S_3, TiO_2, TlS, TlSe, Tl_2O_3, VO_2, WO_2, Y_2O_3, ZnO, ZnS, ZnSe, ZrO_2, etc., and combinations thereof.

Zinc oxide films have been produced in working embodiments of the present apparatus and system. For ZnO, the continuous deposition reactor included a microprocessor-controlled dispensing pump (ISMATEC® pumps), a T-mixer, and a substrate heater. The ZnO thin films were prepared from source solutions I,
5 comprising aqueous zinc acetate and ammonium acetate, and II, comprising aqueous sodium hydroxide. The source solutions were mixed through a T-mixer by a peristaltic pump and entered a micro-tube, which kept at about 70-80°C with a water circulation system. Over a period of four minutes, the mixed solution was impinged on a substrate that was maintained at about 70-80°C by a heater. The substrate was
10 spun at about 1500 rpm during deposition. Coatings were prepared on aluminum having a smooth, mirror-like surface, micro glass slide substrates, and textured silicon substrates.

Silicon dioxide films also have been produced in working embodiments of the present apparatus and system. The SiO_2 thin films were produced from source
15 solutions I, comprising tetraethylorthosilicate in ethanol, and II, comprising ammonium hydroxide and deionized water in ethanol. The source solutions were mixed through a T-mixer by a peristaltic pump and entered a micro-tube at ambient temperature. The mixed solution was impinged on a substrate that was spun at 2000 rpm at ambient temperature. Coatings were prepared on glass and polycarbonate
20 substrates.

As will be apparent to a person of ordinary skill in the art, many of the metals, alloys, semiconductors, etc., that are desirably deposited using the present invention are produced by mixing precursor materials that react to form the desired deposition material. Any effective metal precursor material can be used with the
25 present invention. Solely by way of example, and without limitation, particular examples of metal precursors include halides, acetates, nitrates, sulfates and carbonates. Mixtures of such precursors also can be used.

The reactant sources can be formulated with other materials that facilitate the process. For example, the metal source, such as the zinc (II) source, can be
30 formulated with other materials, such as complexing agents. Many of the useful

complexing agents are nitrogen-bearing compounds, including by way of example, and without limitation, ammonia, aliphatic amines, and aliphatic amides, with particular examples including ammonia, triethanolamine, ethanolamine, diethylenetriamine, ethylenediaminetetracetate, hydrazine, nitrilotriacetate and
5 triethylenetriamine. Plural different complexing agents also can be used in combination. The reactant sources also can be formulated in different solvents, such as water and/or organic solvent(s), to form a first fluid mixture and a second fluid mixture. The deposition material, such as zinc oxide, is then formed by combining the first mixture with the second mixture.

10 The reactants also can include chalcogens, and hence chalcogenide precursors are compounds potentially useful for practicing the present invention. Examples of chalcogenide precursors include, by way of example and without limitation, thiourea, thioacetamide, thiocarbazide, thiosemicarbazide, ethylthiourea, allylthiourea, selenourea, N,N dimethyl selenourea, thiosulfate, selenosulfate, water,
15 peroxide, persulfate, sodium hydroxide, urea, dimethylamineborane, trimethylamineborane, acetamide, hexamethyleneteramine, and combinations of such materials.

II. Continuous Flow CBD Systems

20
A. Working Embodiments

Embodiments of a continuous flow microreactor system have been developed for performing CBD. FIG. 2 is a schematic diagram of one embodiment of a continuous flow microreactor CBD system 10. System 10 includes a mixer 12, particularly a micromixer, such as an interdigital micromixer. A detailed schematic
25 diagram of one embodiment of a micromixer is shown in the FIG. 2 inset. Micromixers offer features that cannot be easily achieved using macroscopic devices, such as ultrafast mixing on the microscale. D. Bökenkamp, A. Desai, X. Yang, Y.-C. Tai, E. M. Marzluff, S. L. Mayo., *Anal. Chem.*, **1998**, *70*, 232. As illustrated in FIG. 2, two fluids A and B to be mixed are introduced into the mixer
30 12, often as two counter-flowing fluid streams. For an interdigital micromixer 12,

the two fluids A and B enter interdigital channels (30 μm in a working embodiment) and form plural interpenetrated substreams. The substreams exit the interdigital channels perpendicular to the direction of the feed flows, initially with a multilayered structure. Fast mixing through diffusion soon follows due to the small
5 thickness of individual layers.

The continuous flow microreactor system 10 includes a reactant source, typically plural reactant sources, such as reactant sources 14, 16, that are combined to form the deposition material or materials. Again, as discussed above, the composition of the reactant sources 14 and 16 may vary, such as to provide desired
10 deposition materials, reduce cost, reduce toxicity, provide flexibility in the selection of appropriate reactants, etc. The illustrated embodiment of system 10 includes two syringe pumps 18, 20 that pump desired quantities of reactants A and B at desired flow rates to the mixer 12. In working embodiments, two syringe pumps (V6 module from Kloehn Ltd.) of 25 milliliters each were used for reactant streams A
15 and B. Each pump 18, 20 had three ports (A, B, C). One port of each pump aspirated the reactant streams and one port was used for dispensing the same. Syringe pumps 18, 20 were fluidly coupled to mixer 12 using polyetheretherketone (PEEK) conduits 22, 24 (1/16" OD, 0.03" ID from Upchurch Scientific).

For the illustrated embodiment, a commercial interdigital micromixer
20 (SSIMM from Institut für Mikrotechnik Mainz, Germany) was used. This interdigital micromixer included a stainless steel (SS 316Ti) housing with inlaid, thermally oxidized silicon to form 30 μm x 100 μm microchannels. Reactant streams A and B were pumped through PEEK conduits 22 and 24, respectively, for mixing in mixer 12.
25 The fluid mixture flowing from mixer 12 comprises the chemical species useful for deposition. In the embodiment 10 illustrated in FIG. 2, conduit 26 was a 5-foot-long coil of PEEK. PEEK conduit 26 was immersed in a water bath 28 to provide temperature control. Water bath 28 generally was maintained at an effective temperature for processing, such as a temperature of from about 60 °C to about 80
30 °C (using a VWR hot plate stirrer) when forming ZnO films. A person of ordinary

skill in the art will appreciate that the effective temperature may vary depending on, for example, the composition of the deposition material. In some embodiments, the temperature may be ambient temperature, *e.g.*, 15-30 °C. In other embodiments, the temperature may be 15-100 °C, 15-30 °C, 20-25 °C, 50-90 °C, 60-80 °C, or 65-75 °C.

5 Moreover, the homogeneous chemistry of the impinging flux can be controlled by selecting various factors, such as the length of the channel 26, the flow rate through channel 26, residence time in channel 26, etc., and combinations thereof. In some embodiments, the residence time ranges from one second to several minutes. For example, the residence time may be one second to 10 minutes,

10 30 seconds to 8 minutes, 10 seconds to 2 minutes, 5-30 seconds, or 2-10 seconds.

The fluid mixture formed by mixing fluids A and B was applied to substrate 32. In the illustrated embodiment, the substrate 32 was coupled to a metal plate 34. Certain embodiments of CBD are facilitated by heating. In the embodiment illustrated in FIG. 2, system 10 includes a hotplate 36 (2" dia. x 0.75" thick SS disk

15 from Watlow). For certain working embodiments employing ZnO as a deposition material, the hot plate was maintained at a temperature of from about 70 °C to about 80 °C. The temperature controller 40 was effectively coupled to the hot plate 36 to control the temperature thereof. Once the process was completed, the substrate 32 was removed from the plate 34, washed with Millipore DI water and dried under a

20 stream of nitrogen gas. In certain working embodiments employing SiO2 as a deposition material, the substrate is maintained at ambient temperature, *e.g.*, 15-30 °C. The substrate temperature during deposition depends on the particular substrate and deposition material and, in some instances, the desired morphology of the anti-reflective film. Thus, the substrate may be maintained at a temperature from about

25 15-200 °C, 15-30 °C, 20-25 °C, 50-90 °C, 60-80 °C, or 65-75 °C.

FIG. 3 is a schematic cross sectional drawing illustrating an impinging flow chemical bath deposition reactor 50. The inset to FIG. 3 is an enlarged view of the micromixer 52 illustrated schematically in FIG. 3. FIG. 3 shows that a first reactant stream 54 and a second reactant stream 56 flow into micromixer 52, thereby forming

30 a third stream 58 comprising the desired chemical species for substrate deposition.

Third stream 58 flows through a channel 60, particularly a microchannel, for direct impingement on to the substrate 62.

B. Commercial Implementation

5 System 10 may be modified to provide various CBD systems. A commercial system 10 might include, for example, a continuous susceptor. FIG. 4 illustrates one embodiment of a continuous roll-to-roll susceptor 100. The illustrated embodiment includes a first roller 102 comprising a feed roll of a substrate or susceptor material 104. Material 104 is fed to a second roller 106. Rollers 102 and 106 move material 10 104 into a position effective to receive an impinging solution flow of a deposition material 108 from channel 110.

Alternatively, system 10 may include a rotating disk substrate susceptor system 120, such as illustrated in FIG. 5. System 120 includes a rotating disk 122. While the illustrated disk is substantially circular, a person of ordinary skill in the art 15 will realize that the disk 122 need not be circular, and can have any geometric shape reasonably suited for use as a rotating disk susceptor. Substrate 124 is coupled to the disk 122 to allow rotation of the substrate 124. Disk 122 is effectively coupled to a rotator, such as a motor, via shaft 126.

An impinging solution flow of deposition material 128 is directed to 20 substrate 124 via channel 130. As with other disclosed embodiments, heat may facilitate the deposition process. As a result, a heater 132 also optionally may be included in a manner effective to transfer heat to the substrate 124.

System 10 also can be provided as a chip-based system. A schematic drawing of a chip-based system 150 is illustrated in FIG. 6. System 150 includes a 25 first micromixer section 152. For embodiments comprising plural fluid reactants, at least a first fluid 154 and a second fluid 156 are flowed into the mixer 152. A third port, such as port 158, can be provided to aspirate fluids in mixer 152. Alternatively, at least a third fluid stream 159 can be flowed into micromixer system 152. The number and composition of the fluid streams will vary as determined by 30 the chemical system in use. Impinging fluid streams 154, 156 and/or 159 are

thoroughly mixed in mixer 152 to form a deposition material 160 that is flowed to the substrate via a fluid channel 162.

Many devices, such as electrical devices including transistors, may require deposition of a more than one material onto a substrate. Furthermore, such
5 material(s) typically must be applied in a particular order to produce a working device. The possibility of depositing more than one material is contemplated by the chip-based system 150. In this embodiment, at least a second micromixer 164 optionally is provided. As with micromixer 152, at least a first fluid 166 and a second fluid 168 are flowed into the mixer 164. A third port 170 can be provided to
10 aspirate fluids in mixer 164. Alternatively, at least a third fluid stream 172 can be flowed into micromixer 164. The fluid streams 166, 168 and/or 172 are mixed in mixer 164 to form a deposition material 174. Deposition material 174 may be the same as deposition material 160, or can be a different deposition material. Thus, by using plural different deposition materials, a deposited layer may have a
15 composition gradient throughout its cross section.

System 150 can include a heat transfer section. One example of a device useful for heat transfer is a heater, such as a thin film heater 180.

Once formed, the deposition materials 160, 174, etc. are flowed through channel 162 to impinge on a substrate 190. Again, in the illustrated embodiment,
20 the device formed includes plural layers 192, 194, 196 and 198, all of which layers may be different in composition or morphology, all of which layers may be the same in composition and morphology, and all possible combinations thereof.

FIG. 7 illustrates a deposition system 200 suitable for depositing nanostructured thin films on a substrate 202 in a substantially continuous manner.
25 The deposition system 200 includes a continuous flow reactor system 204, a surface activation unit 206, a flow distributor 208, and substrate support means 210 for supporting and moving the substrate 202. In some embodiments, system 200 also includes a waste solution collector and waste vapor filter (not shown).

The continuous flow reactor system 204 includes two or more pumps 212,
30 214, one or more heat exchangers 216, one or more mixers 218, and one or more

activation and residence time channels 220. First and second fluid streams are pumped through pumps 212 and 214, respectively. The fluid streams pass through one or more heat exchangers 216, which add or remove heat from the fluid streams to achieve a desired temperature. The fluid streams pass through a mixer 218 and
5 are combined to form a deposition material, which flows into an activation and residence time channel 220. The activation and residence time channel 220 may include one or more activation sources (not shown). Suitable activation sources may include thermal, chemical, photochemical, electrochemical, microwave, and/or ultrasonic activation means. The activation sources provide energy to the deposition
10 material and generate reactive species (*e.g.*, molecules, clusters, particles, and/or macromolecules) within the deposition material. The deposition material flows from the activation and residence time channel 220 onto the substrate 202.

The substrate 202 is supported by suitable substrate support means 210. In the illustrated embodiment, means 210 includes a support surface 222 and a plurality
15 of rollers 224. Rotation of the rollers 224 moves the substrate 202 in a substantially continuous fashion as the deposition material flows onto the substrate 202. In another embodiment (not shown), the support surface 222 is absent and the substrate 202 is placed directly on the plurality of rollers 224. Other suitable substrate support means 210 may include, for example, a conveyor. A surface activation unit 206 is
20 positioned proximate the substrate 202 and upstream from the activation and residence time channel 220. The surface activation unit 206 typically extends across a width of the substrate 202 and is operable to provide energy (*e.g.*, thermal, chemical, photochemical, microwave, and/or ultrasonic energy) to the substrate 202. For example, the surface activation unit 206 may provide thermal energy to heat the
25 substrate 202 to a desired temperature. As the heated substrate 202 passes beneath the activation and residence time channel 220, deposition material flows from the activation and residence time channel 220 onto the substrate 202. A flow distributor 208 is positioned proximate the substrate 202 and downstream from the activation and residence time channel 220. The flow distributor 208 typically extends across

the width of the substrate 202 and functions to distribute the deposition material uniformly across the substrate 202.

The inset to FIG. 7 is an enlarged view of the deposition material flowing onto the substrate 202 between the surface activation unit 206 and the flow
5 distributor 208. The deposition material is spread on the substrate 202 by the flow distributor 208. Molecules or particles within the deposition material adsorb to the substrate surface, diffuse across the surface and react, promoting nucleation and growth of a nanostructured thin film.

One embodiment of a table-top deposition system 230 is illustrated in FIG. 8.
10 The table-top deposition system 230 includes a continuous flow reactor system 232, a rotating disk 234 for supporting and moving a substrate 236, a waste solution collector 238, and a waste vapor filter 240.

The continuous flow reactor system 232 includes two or more pumps 242, 244, one or more heat exchangers 246, a mixer 248, and an activation and residence
15 time channel 250. First and second fluid streams are pumped through pumps 242 and 244, respectively. The fluid streams pass through one or more heat exchangers 246, which add or remove heat from the fluid streams to achieve a desired temperature. The fluid streams pass through a mixer 248 and are combined to form a deposition material, which flows into an activation and residence time channel
20 250. In some embodiments, the activation and residence time channel 250 may be a coil of microchannel tubing 252. In particular embodiments, the microchannel tubing coil 252 is flexible, as illustrated by the flexed coils on either side of coil 252. The activation and residence time channel 250 may include one or more activation sources (not shown). Suitable activation sources may include thermal, chemical,
25 photochemical, electrochemical, microwave, and/or ultrasonic activation means. The activation sources provide energy to the deposition material and generate reactive species (*e.g.*, molecules, clusters, particles, and/or macromolecules) within the deposition material. The deposition material flows from the activation and residence time channel 250 onto the substrate 236.

The substrate 236 is supported by a rotating disk 234. A surface activation unit (not shown) is positioned proximate the rotating disk 234. In some embodiments, the surface activation unit is positioned beneath the rotating disk 234. The surface activation unit is operable to provide energy (*e.g.*, thermal, chemical,
5 photochemical, microwave, and/or ultrasonic energy) to the substrate 236 and/or the deposition material. For example, the surface activation unit may provide thermal energy to heat the rotating disk 234 and the substrate 236 atop the rotating disk to a desired temperature. Deposition material flows from the activation and residence time channel 250 onto the substrate 236 atop the rotating disk 234. The deposition
10 material flows across the substrate 236. Excess deposition material flows from the substrate 236 into a waste solution collector 238. In some embodiments, as the deposition material is heated by contact with the substrate 236, gas vapors 252 are produced and are removed via a waste vapor filter 240.

The inset to FIG. 8 is an enlarged view of the deposition material flowing
15 onto the substrate 236. Molecules or particles within the deposition material adsorb to the substrate surface, diffuse across the surface and react, promoting nucleation and growth of a nanostructured thin film on a surface of the substrate 236.

FIG. 9 is an exterior photograph of a working embodiment of a table-top deposition system as described in FIG. 8.

20 Micromixers are used effectively with certain embodiments of the present invention. Micromixers can be provided as unitary devices that can be used singularly, or plural such micromixers can be used. With chip-based systems, micromixer arrays, such as the array 260 shown in FIG. 10 comprising plural micromixers 262, can be used. One arrangement of plural micromixers to form an
25 array is illustrated in FIG. 10. A person of ordinary skill in the art will appreciate that other micromixer arrangements can be used, such as a linear array of micromixers.

30

C. Thin Film Structures

The present invention provides embodiments of a process and apparatus useful for depositing thin films on substrates. The process and apparatus can be used to deposit various films with tailored micro- and nanostructures. FIG. 11 is a
5 schematic cross sectional representation providing examples of thin films that can be formed according to embodiments of the present invention. FIG. 11A is a schematic representation of an epitaxial nanostructured thin film; FIG. 11B is a schematic representation of a nanocrystalline thin film; FIG. 11C is a schematic representation of nanocrystals embedded in an epitaxial thin film; FIG. 11D is a schematic
10 representation of a superlattice thin film; FIG. 11E is a schematic representation of a composition gradient thin film; and FIG. 11F is a composite film comprising core-shell nanoparticles.

III. Applications

15 The present system can be used to fabricate high-performance, anti-reflective films, such as "moth-eye" anti-reflective films, that are useful for a variety of applications, including anti-reflective coated lenses, fuel cell membranes, chemical/biological sensor sorbents, wearable electronics, and photonic, thermoelectric, photovoltaic and biomedical films, among others. For example, the
20 films may be used to coat flat panel displays and solar cells.

Reflection occurs when there is a sudden change in the index of refraction of the material that light is traveling through. In the case of air the index is 1.0, while most glass is about 1.47. When light traveling through the air contacts the glass, the sudden change in refractive index causes reflection to occur. This happens again
25 when the light leaves the glass and returns to the air. The surfaces of the materials the light travels through are known as interfaces, so that reflection occurs at each interface light passes through. The amount of light reflected from untreated glass is roughly 4% at each interface. Thus, when light passes through a pane of glass, about 8% of the light is reflected and 92% passes through the glass pane.

In optical devices involving multi-component optical trains or high wattage applications, anti-reflective coatings significantly enhance performance. Consider an optical device with four optical components each having two air-quartz interfaces. Optical interfaces reflect light according to Maxwellian physics:

5

$$R = [(n_1 - n_2)/(n_1 + n_2)]^2$$

where R is the Fresnel reflection coefficient and n_1 and n_2 are the indices of refraction of the respective media. Accordingly, each air-quartz interface would be expected to have approximately 4% reflection. Over four components, almost 30% of the source light is lost due to internal reflection, which can have adverse effects

10 on device performance, *e.g.*, poor contrast.

One way to reduce reflection is to insert a material between the two original materials, where the inserted material has an index between the two starting media. As an example, the reflection between ZnO (n=2.04 at 550 nm) and air (n=1.0 at 550nm) alone is about 11.7%. This reflection can be reduced by inserting a material

15 film between the two original materials that has an index between the two starting media. For instance, placing silica (SiO_2; n = 1.46) between the air and ZnO reduces the overall reflection to about 7.5%. Reflection can further be reduced by taking advantage of destructive interference if the thickness of the film is made to be quarter wavelength (QW) and the index is optimized to be: $n_i = \sqrt{n_1 \cdot n_2}$. Based on

20 this formula, glass/air interfaces ($R \approx 4\%$) would need indices as low as 1.2 which are difficult to find. Typically MgF_2 films are used with an index of about 1.35, yielding QW air/glass reflectivities around 2% at normal incidence. The quarter-wavelength (QW) effect can be amplified by depositing multiple QW films. Reflectivities as low as 0.5% for air/glass are routinely reported by multi-layer anti-

25 reflective coating (ARC) vendors. However, QW films should be precise to produce the desired advantages, and typically are fabricated using physical vapor deposition under high vacuum conditions.

For high wattage applications such as photovoltaics, problems with conventional ARCs include thermal expansion mismatch, thin film processing costs

30 and the inability to coat large, highly contoured or textured surfaces. Processing

costs have begun to be addressed by wet deposition methods, which are not as precise and therefore do not perform as well (> 1.0%), but are significantly less expensive. Other issues include the using harsh chemical solvents that pose environmental hazards and damage to sensitive optical components. More recently, polymer coatings have been demonstrated with optimized refractive indices using either subwavelength bubbles or nanoparticles. Reflectivities below 0.5% have been reported for these films at certain wavelengths. However, these films provide variable performance across a wide spectrum of wavelengths and are sensitive to incidence angles making them not ideally suited to a "broadband" application such as photovoltaics requiring anti-reflection across a broad spectrum at oblique incidence. Also, these polymer films are not mechanically tenacious particularly for glass surfaces.

Alternatively, if an interface between two media (*e.g.*, air/glass) is made *gradual*, such as a continuous gradient index of refraction over some finite thickness, such as on the order of a few hundred nanometers, the interface can be made to reflect even less light than QW films. These gradient surfaces can be thought to have a low net reflectance based on the destructive interference of an infinite series of reflections at each incremental change in refractive index. One means for producing this gradient is an array of tapered, subwavelength protuberances as shown in FIG. 12. This structure was first reported based on the electron microscopy of the corneas of nocturnal moths by Bernhard (*Endeavour*, 26:79, 1967) who hypothesized that the resultant index gradients were responsible for the reduced eye reflection at night which the moths needed for camouflage. The gradient surfaces are thought to have a low net reflectance based on the destructive interference of an infinite series of reflections at each incremental change in refractive index. Subsequently, the term "moth-eye" anti-reflective surface (ARS) has been adopted as describing a tapered array of subwavelength proturbances.

More recently, researchers have found that the structures do not need to be periodic, only that the features on the whole are smaller than the wavelengths of visible light. (Bökenkamp *et al.*, *Anal. Chem.*, 70:232-236, 1998.) Visible light

typically is considered to encompass wavelengths from about 400 nm to about 700 nm. Thus, if the surface structures are smaller than 400 nm, reflection of all visible light is reduced.

A number of configurations can produce a subwavelength, nanostructured,
5 anti-reflective surface with a gradient index of refraction. FIG. 13 illustrates three types of nanostructured anti-reflective surfaces: a) a porous coating, b) a period tapered coating, and c) a stochastic tapered coating. Effective refractive indices (n_{eff}) are formed based on the volume fraction of the subwavelength nanostructured materials and air.

10 Moth-eye structures have some advantages. The behavior of the surface is tied both to the surface geometry and the material properties of the surface. As long as a method can be found to produce the desired geometry on a surface, the technique can be applied to all materials. Moth-eye structures are suitable across a wide spectrum of wavelengths and incidence angles with a greater tolerance to the
15 angle of incidence than quarter-wavelength structures.

Microreactor-assisted nanoparticle deposition (MAND) is capable of producing high-performance anti-reflective films with moth-eye type structures. MAND involves mixing very small amounts of reactant solutions under controlled temperature conditions and then depositing the mixed solution onto a substrate. As
20 the solutions are mixed and deposited, nanoparticles form and produce a film on the substrate.

In some embodiments, a microreactor-assisted, continuous-flow system is used to produce the anti-reflective film. The system allows precise control of chemical and physical reactions. As reagents pass through the continuous-flow
25 reactor, reactive species are generated using activation schemes. For example, reactive species may be generated by addition of energy to the system, including thermal, chemical, microwave, photochemical, electrochemical and plasma activation. Reactive species are mixed in the reactor and deposited onto a substrate surface, where they adsorb to the surface, diffuse across the surface, and react with
30 one another, promoting nucleation and growth of a nanostructured thin film.

The concentration and temperature of the reagents within the reactor and the residence time of the mixed reagents within the reactor are controlled to either allow or minimize formation of nanoparticles within the continuous-flow reactor. For example, SiO_2 nanoparticles were synthesized by controlling reactive species and
5 residence time. Two stock solutions (tetraethylorthosilicate (TEOS) in ethanol and deionized water/ammonium hydroxide in ethanol) were prepared. The solutions were mixed in the microreactor-assisted, continuous-flow system and deposited onto chemically activated substrates (*e.g.*, glass, polycarbonate eyeglass lenses) on a rotating substrate holder (see, *e.g.*, FIG. 8). Nanoparticles ranging in size from tens
10 to several hundred nanometers were produced by varying the reagent concentrations and residence times.

In some embodiments, substrate surface activation also is performed by addition of energy to the substrate. For example, a substrate may be heated to a particular temperature to promote desired heterogeneous growth and/or morphology
15 of nanoparticles. In some working embodiments, the morphology and optical characteristics of ZnO films were varied by changing the substrate surface temperature.

In contrast to commercial multilayered anti-reflective films formed from layers having different chemical compositions, embodiments of the disclosed anti-
20 reflective films have a substantially homogeneous chemical composition (*e.g.*, ZnO, SiO_2) throughout a cross-section of the film. However, while the chemical composition is substantially homogeneous, the film typically has heterogeneous physical attributes. For example, the disclosed anti-reflective films typically include nanoparticles or nanoparticle clusters of different sizes or different morphologies.
25 Additionally, the particle density (*i.e.*, the number of particles per unit volume of the film) of the nanoparticles or nanoparticle clusters may vary within the film.

In particular embodiments, the nanoparticle structures are, on average, smaller than 400 nm and are capable of reducing reflectivity of visible light and longer wavelengths such as infrared light. In some embodiments, the structures
30 form a size gradient throughout the thickness of the anti-reflective film, with larger

nanoparticles deposited in the lower portion of the film and smaller particles deposited in the upper portion of the film. Without being bound to any particular theory of operation, such a size gradient may form as a result of increased time for particle growth in portions of the film deposited earlier in the deposition process as compared to portions of the film deposited later in the process.

Desirable properties for such anti-reflective films include low reflectivity (0.1%), anti-abrasion, thermal compatibility, and good adhesion. Other advantages of MAND include uniform heating and mixing, production of substantially agglomerate-free films, reduced use and cost of reactants, and the possibility of synthesizing nanomaterials in the required volumes at the point of application, which minimizes the need to store and transport potentially hazardous materials while providing opportunities for tailoring novel, functionally-gradient structures.

A. ZnO Anti-reflective Coatings

The film's morphology can be varied by varying the conditions under which the film is formed and deposited. For example, the morphology of ZnO films depends, at least in part, upon the pH of the reactants and the temperature. ZnO films are prepared by mixing a zinc acetate solution with a sodium hydroxide solution, and depositing the mixture onto a heated substrate. The substrate typically is heated to about 70-80 °C. By varying the concentration of NaOH, two different flower-like structures can be formed. A series of ZnO films were produced using the continuous flow microreactor. In each case, 0.05 M zinc acetate dihydrate and 0.25 M ammonium acetate were mixed with different concentrations of NaOH. The solutions were deposited on a silicon substrate.

FIGS. 14-17 illustrate the different morphologies of ZnO films that have resulted by varying concentrations of NaOH in working embodiments. The films were formed in the presence of 0.005 M NaOH, 0.01 M NaOH, 0.1 M NaOH, and 0.15 M NaOH, respectively. A flower-like ZnO morphology with broad "petals" was formed preferentially at higher concentrations of NaOH, *i.e.*, greater than 0.05 M. This morphology is also termed "white" ZnO because the films appear white

when deposited on an opaque substrate. As the NaOH concentration decreases, the petals become narrower in width, smaller in size, sharper at the tip, and simpler in shape. At lower concentrations of NaOH, a chrysanthemum-like structure formed with many narrow, small petals that had sharp tips and were simpler in shape than
5 the structures formed at high concentrations of NaOH. This morphology is termed "black" ZnO because the films appear black when deposited on an opaque substrate. At 0.005 M NaOH, the petals are narrow and nano-sized, as shown in FIG. 14. At intermediate concentrations of NaOH (*e.g.* at about 0.05 M), a mixture of the two structures forms. Both black and white ZnO films are substantially transparent when
10 coated onto transparent substrates such as clear glass.

Temperature also affects whether the white or black morphology is produced. At temperatures below 70 °C, only white ZnO forms irrespective of the NaOH concentration. At temperatures above 70 °C, black ZnO begins to form and predominates at higher temperatures. A mixed state including both white ZnO and
15 black ZnO may occur when the temperature is about 70 °C or if the temperature fluctuates during film deposition.

Suitable substrates for ZnO film deposition include metals and alloys, including aluminum and copper, silica-based materials, such as glass, silicon wafers, and polymeric materials, including polycarbonate, among others. Many other
20 materials are suitable for use as anti-reflective coatings, including but not limited to TiO_2, CeO_2, MgX_2 where X is a halogen such as fluoride, SiO_2, and ZnS. For example, SiO_2 can be deposited as an anti-reflective coating on polycarbonate eyeglass lenses.

25 **B. Anti-reflective Coatings for Eyeglass Lenses**

The amount of light reflected from untreated glass is roughly 4% at each interface. Thus, a typical glass lens reflects about 8% of the total light. There are several ways that this reflection can be reduced, including quarter-wavelength films, multi-layer films, and sub-wavelength gradients.

Quarter-wavelength films are uniform films with a thickness that is one-quarter of an incident wavelength. For example, to reduce reflection of light having a wavelength of 600 nm, a 150-nm coating will be applied. Typically, quarter-wavelength films are made of magnesium fluoride, a material with an index of reflection between those of glass and air to attempt to reduce reflection further by easing the transition from air to glass. This technique has some disadvantages, however, including using very stringent environmental controls during film application. It is also a narrow band anti-reflective treatment due to the single layer. Anti-reflective films of the present disclosure employ sub-wavelength gradients and can reduce the amount of total reflected light from 8% to well under 0.5%.

Multi-layer films are similar to quarter-wavelength films in that sub-wavelength films are applied. In this case, however, the goal is to create a gradient in the index of refraction by applying multiple film layers of varying composition. For example, with three layers, materials with index values of 1.10, 1.20 and 1.30 may be used. The resulting gradient makes the transition from air to glass less abrupt than a single layer and reduces reflection. However, with the addition of multiple new interfaces, reflection will occur at each interface. While the overall reflection is reduced over a moderate breadth of wavelengths, there are diminishing returns as each additional layer creates its own reflections.

The gradients that can be partially created through varying materials used in multi-layer film are achieved more fully using sub-wavelength gradients. This method is accomplished in different ways depending on the substrate. For example, with a polymeric substrate, it is possible to press a sub-wavelength pattern into the material while it is malleable, imprinting the pattern into the surface. When treating glass, plasma etching is commonly used. This is a very slow, precise, and expensive process. The goal is to create cone or pyramid shaped structures, having a diameter less than the wavelength of the incident light, on the surface of the glass. When done correctly this creates a near perfect gradient in the index of refraction between the air and glass or polymer.

Certain embodiments of the present disclosure are suitable for creating sub-wavelength gradients through nanoparticle deposition, thus producing an anti-reflective coating suitable for eyeglass lenses. Creating and preparing nanoparticles of varying sizes and shapes allows for precise control of the coating composition and/or morphology. In some embodiments, the particles are applied more densely at the beginning. In other embodiments, the particles formed at the beginning of the deposition process are larger than particles formed later in the process. By varying the size, shape, and density of the particles as they are applied, it is possible to create structures similar to those with plasma etching.

To provide a uniform coating, the glass being treated typically is spun as particles are applied. In the case of smaller pieces of glass, such as eyeglass lenses, the glass is spun at about 1000-2000 rotations per minute (rpm). The glass is heated to between 100 °C and 300 °C to adhere the nanoparticle film to the glass substrate by creating a chemical bond between the nanoparticles and glass surface.

All incident light with a longer wavelength than the size of the structures will pass through the applied film. If the structures are 400 nm or smaller, reflection of all visible light and longer wavelength light will be reduced.

Some materials, *e.g.*, cerium oxide, present some UV absorption properties as well and will reduce the amount of UV light passing through the glass lens. CeO_2 films can be prepared, for example, by reacting $Ce(NO_3)_2$ and NH_4OH solutions, as described in U.S. Publication No. 2008/0108122, which is incorporated herein by reference. An additional advantage to CeO_2 films is that they can be deposited at ambient temperature onto the desired substrate.

Suitable anti-reflective coatings for polycarbonate lenses include SiO_2, ZnO, CeO_2, MgF_2, and ZnS, among others, and combinations thereof. For example, SiO_2 films can be deposited onto polycarbonate lenses from an aqueous solution of dispersed SiO_2 nanoparticles or via hydrolysis of $Si(OC_2H_5)_4$ (tetraethyl orthosilicate, TEOS) or $SiCl_4$. The disclosed anti-reflective coatings also are suitable for coating lenses made of glass(including borosilicate crown glasses and

fluorite crown glasses), CR-39 (allyl diglycol carbonate), TRIVEX® plastic, and polyurethane.

Currently when a consumer purchases eyeglasses with an anti-reflective coating, the optical retailer must order AR-coated lenses from the manufacturer's
5 labs and/or independent labs , or send the uncoated lenses to a central lab, which requires anywhere from a few days to a week to get the lenses back to the retailers. The eyeglass retailers order uncut coated lenses from manufacturers and use an edging machine to cut the lenses into the shape that fits the selected eyeglass frames. The disclosed technology, however, offers significant advantages. The coating
10 machines utilizing the disclosed microreactors are small and can be placed in the retailer's lab next to the edging machine without interrupting work flow since the size of the coating machine is about the size of the edging machines. Thus, the retailer can apply an anti-reflective coating to lens in-house before the edging process, eliminating any need to send the lens out for coating, and thereby
15 eliminating the associated delay and costs involved. Additionally, the consumer receives the eyeglasses sooner because they are prepared on site.

C. High-Temperature Solar Catalytic Microreactor

Among various renewable energy sources, the conversion of sunlight directly
20 into electricity and fuels is a very promising alternative energy source. A catalytic microreactor can be utilized for solar thermal fuels production where solar energy is used to provide heat for catalytic reactions that produce fuels. In certain embodiments, an anti-reflective film is applied to a solar catalytic microreactor to minimize reflectance of solar radiation.
25 FIG. 18 is a schematic diagram of one embodiment of a solar microchannel reactor 1800. The reactor 1800 includes a substrate 1810 having a first major planar surface 1812 and a second major planar surface 1814. The first major planar surface 1812 is coated with a nanostructured absorber layer 1820. The absorber layer 1820 is an anti-reflective film applied to the substrate 1810 to minimize reflectance of
30 solar radiation 1830. The absorber layer 1820 contains nanoparticles that are sub-

wavelength in size. In some embodiments, the nanoparticles are smaller than about 400 nm. Solar radiation 1830 is captured to provide energy for endothermic catalytic reactions. A microchannel reactor coated with nanostructured catalysts (not shown) is disposed on the second major planar surface 1814.

5 A feedstock 1840 is provided to the microchannel reactor. Absorbed solar radiation 1830 provides energy to convert the feedstock 1840 to fuel 1850. For example, propane may be converted to hydrogen through a steam-reforming reaction: $C_3H_8 + 3\ H_2O + \text{heat} \rightarrow 3\ CO + 7\ H_2$. In particular embodiments, a renewable biological feedstock may be used to produce clean fuels. The design of 10 microreactor 1800 allows scalable fabrication of different size reactors as desired based upon the intended use.

Efficient conversion of solar energy to heat requires that a solar absorbing surface is in thermal contact with the fluids, and that thermal losses to the surrounding environment are minimized. In exemplary embodiments, the solar 15 microreactor maximizes absorption of solar energy, A_{sol}, while minimizing radiation heat losses, E_{therm}. A nanostructured anti-reflective coating as shown in FIG. 9 produces a reflectivity of less than 0.5%. In some embodiments, a compositional gradient film is utilized to obtain a desired thermal expansion coefficient and extend the reactor lifetime.

20

IV. EXAMPLES

Working examples are provided to illustrate particular features of the disclosed embodiments. The scope of the present invention should not be limited to the features exemplified by these working embodiments.

25

Example 1 – Anti-reflective ZnO Films on Aluminum and Glass Substrates

Aluminum and glass substrates were cleaned according to a standard AMD (acetone, methanol, deionized water) procedure. ZnO thin films were prepared from source solutions of A, comprising 200 milliliters of 0.005 M zinc acetate, and 10 30 milliliters of 0.25 M ammonium acetate; and B, comprising 200 milliliters of 0.1 M

sodium hydroxide. As shown in FIG. 19, the continuous deposition reactor 1900 included a microprocessor-controlled dispensing pump 1910 (ISMATEC® pumps), a T-mixer 1920, and a substrate heater 1930. The source solutions 1940, 1942 were mixed through the T-mixer 1920 by the peristaltic pump 1910 and entered a micro-
5 tube 1950, which was kept at about 70 °C with a water circulation system 1960. Over a period of four minutes, the solution was applied to a substrate 1970 that was maintained at about 70 °C by the heater 1930. The substrate was spun at 1500 rpm during deposition. Coatings were prepared on aluminum having a smooth, mirror-like surface and micro glass slide substrates. Following deposition, the coated
10 substrates were rinsed with deionized water and dried at room temperature under a stream of nitrogen gas. In one embodiment, a ZnO film deposited on an aluminum substrate was annealed at 600 °C for 30 minutes. Reflectance was measured with an Ocean Optics (Dunedin, FL) HR2000+ high-resolution spectrometer having a DH-2000 UV-VIS-NIR light source with a halogen bulb and reflection probes with
15 SpectraSuite software.

FIGS. 20A-22B illustrate the effect of temperature on the film morphology. The formation of flower-like structures with broad "petals" (FIGS. 16A-B) occurred in areas where the temperature was lower, *i.e.*, below 70 °C. This morphology is termed "white" ZnO because the film appears white on the opaque aluminum
20 substrate. A chrysanthemum-like morphology with many smaller, narrower, sharper-tipped petals (FIGS. 21A-B) formed in areas where the temperature of the solution and/or substrate was higher, *i.e.*, greater than 70 °C. This morphology is termed "black" ZnO because the films appears black on the opaque aluminum substrate. FIGS. 22A-B show a mixture of white and black ZnO morphologies.
25 Such a mixture can occur if the temperature is very near 70 °C or if the temperature varies as the film is produced.

FIGS. 23 and 24 illustrate the reflectivity of several ZnO films deposited on aluminum. Aluminum without an anti-reflective coating had a reflectivity of about 60-70% over a range of wavelengths from about 400 nm to about 900 nm. A ZnO
30 film (A) deposited on aluminum had a reduced reflectivity of about 40-50% over the

same wavelength range. In one embodiment, the ZnO film (B) was annealed at 600 °C for 30 minutes. The annealed ZnO film had a reflectivity of about 10-20%. A ZnO film (C) with a "white" morphology had a markedly reduced reflectivity of about 3-5% over a range of wavelengths from about 400 nm to about 900 nm. Two ZnO films (D-E) with a "black" morphology had extremely low reflectivity, *i.e.*, less than about 1%, over the same wavelength range. The improved reduction in reflectivity is attributed to the smaller particle size of black ZnO. Compared to white ZnO, black ZnO has a larger percentage of particles that are sub-wavelength in size, *i.e.* smaller than about 400 nm.

FIGS. 25 and 26 illustrate the reflectivity of a ZnO film deposited on glass. Glass without an anti-reflective coating had a reflectivity of about 6-8% over a range of wavelengths from about 400 nm to about 900 nm. A ZnO film deposited on the glass had a reduced reflectivity of less than about 4% over the same wavelength range, such as a reflectivity of about 3-4%.

Despite its reduced reflectivity, the ZnO film on glass was substantially transparent with a percent transmittance of greater than about 80%, such as about 80-95%, over a broad spectrum from 400-800 nm, as shown in FIG. 27. FIG. 28 also illustrates the transparency of a ZnO film deposited onto a glass substrate. A ZnO film (indicated by the dotted line) deposited onto a glass substrate allows a clear view of an Oregon State University logo below the glass substrate.

Example 2 – Anti-reflective ZnO Films on Textured Silicon Substrates

ZnO films were also formed on textured silicon. Polished silicon wafers were etched in 2 vol. % of isopropyl alcohol (IPA) in 0.5 M sodium hydroxide (NaOH) at 80 °C for 30 minutes. During the etching process, the solution was stirred at 400 rpm to facilitate consistent etching quality over the large surface area. The textured silicon was rinsed with DI water, followed by diluted HCl, and then DI water. Finally, it was dried by a stream of dry nitrogen gas.

Two stock solutions were prepared: 200ml aqueous solution of 5mM zinc acetate and 10 ml aqueous solution of 0.25 M ammonium acetate were well mixed

and prepared as solution I; solution II was composed of 200 ml aqueous solution of 0.1 M sodium hydroxide (NaOH). The two stock solutions containing the reactive species were pumped up by a compact REGLO peristaltic tubing pump (ISMATEC®) and mixed through a T-mixer. The mixed solution flowed through a 1-meter length of 1.22 mm ID Tygon tubing, which was maintained at a temperature of 70 °C by water circulation. The residence time of this flow was 6.2 sec. The textured silicon substrate was placed on rotating holder and was maintained at a constant temperature of 70 °C controlled by a heating coil and thermal couple. First, a seed layer of prepared Ag nanoparticles with an average diameter of approximately 20 nm was deposited onto the textured silicon surface and spun at 2400 rpm for a few seconds. Subsequently, the mixture of reactive species was impinged on the Ag seed layer on the textured silicon substrate. The rotating speed for the deposition of nanostructured ZnO on textured silicon was reduced and maintained at 300 rpm. The deposition time for highly dense and crystalline nanostructured ZnO was 5 min. The deposited ZnO film was dried on a hot plate at 100 °C for a few minutes.

FIG. 29 is an SEM image of a ZnO film on textured silicon at 893x magnification, with inset images at 4,633x and 53,555x. FIG. 30 illustrates the reflectivity of a ZnO film on textured silicon. Polished silicon has a reflectance of about 30% over the visible region. Texturing silicon, *e.g.*, by etching, reduces reflectance to about 10%. A ZnO film deposited on the textured silicon reduces reflectance about 3-fold (*i.e.*, to about 3%) compared to the reflectance of the textured silicon surface.

Example 3 – Anti-Reflective SiO_2 Films on Glass and Polycarbonate Substrates

Nanostructured SiO_2 films were prepared and deposited onto glass substrates and polycarbonate eyeglass lenses. Before depositing the synthesized SiO_2 nanoparticles (NPs) onto the glass slide and polycarbonate (PC) eye glass lens substrates, each substrate was cleaned to produce the desired hydrophilic surface properties. The glass slide was treated with 1M NaOH aqueous solution for ~ 5min

in an ultra-sonicator and rinsed with deionized (DI) water. The glass slide then was dried by a stream of dry nitrogen gas. The PC eye glass lens was treated with 5 vol. % of 3-(aminopropyl) triethoxysilane (APTS) in isopropanol for 2 hours. It then was rinsed with isopropanol, followed by DI water. Finally, it was dried by a stream of dry nitrogen gas.

Solution I was prepared by dissolving 2.23 ml of tetraethylorthosilicate (TEOS) in 25 ml of ethanol. Solution II was prepared by mixing 1 ml of NH_4OH (28.0-30.0%) and 1-10 ml of DI water into 25 ml of ethanol. Each solution was well mixed prior to use. A compact REGLO peristaltic tubing pump (ISMATEC®) was used to pump each stock solution. A 10 ft. length of PEEK tubing with I.D. 0.010" as a flexible microchannel and a T-mixer were used for this unit. Residence times in range of 0.5 minute to 8 minutes were used to control nanoparticle formation and size within the microchannel. The synthesis of SiO_2 NPs was carried out at atmospheric temperature and pressure.

An anti-reflective coating of SiO_2 NPs was deposited onto the surface-treated substrates (the glass slide and PC eyeglass lens). During the deposition process, the substrates were spun at 2000 rpm at room temperature. The deposited films were dried at a temperature in the range of 100-135 °C.

FIG. 31 is a graph of percent transmittance versus wavelength for a glass substrate with a nanostructured SiO_2 film deposited on both upper and lower surfaces of the substrate (A) and a bare glass substrate (B). The glass substrate with the nanostructured SiO_2 film demonstrated up to 98.5% transmittance. FIG. 31 also shows percent reflectance versus wavelength for the glass substrate with the nanostructured SiO_2 film (D) and the bare glass substrate (C). The presence of the nanostructured film reduced percent reflectance to a minimum of about 1% at 400-500 nm, and reflectance remained reduced by more than 50% compared to bare glass from 500 nm to about 700 nm. FIG. 32 is an AFM image of a nanostructured SiO_2 film on a glass substrate. FIG. 33 is an SEM photograph of a nanostructured SiO_2 film on a glass substrate at two magnifications (scale bars = 1 μm and 300 nm). The SiO_2 nanoparticles had an average size of 26-30 nm.

FIG. 34 is a schematic diagram of a coated polycarbonate eyeglass lens 2000. Commercially available polycarbonate eyeglass lenses 2010 include a hard coat 2020. The hard coat increases the durability of the polycarbonate lens. Typically, hard coats are based on acrylic or polysiloxane chemistries. Synthesized
5 SiO_2 nanoparticles are deposited onto the hard coat 2020 to form an anti-reflective coating 2030.

FIG. 35 is a graph of percent reflectance versus wavelength for a polycarbonate lens (A), an Avancé™ lens (B, a commercially available lens with an anti-reflective coating, Essilor of America Inc., Dallas, TX), an Alizé™ lens (C, a
10 commercially available lens with an anti-reflective coating, Essilor of America Inc.), and a nanostructured SiO_2 film on both upper and lower surfaces of a polycarbonate lens (D). The reflectance of the nanostructured SiO_2 film on a polycarbonate lens was much lower than the bare polycarbonate lens or the commercially available Avancé™ and Alizé™ lenses, with reduced reflectance over a broad range of
15 wavelengths and a mean reflectance of about 1% in the range of 400 nm to 900 nm.
FIG. 36 is an AFM image of a nanostructured SiO_2 film on a polycarbonate lens.
FIG. 37 is a series of photographs illustrating the reflectance of visible light from a polycarbonate lens (A), a commercially available polycarbonate lens (Avancé™) with an anti-reflective coating (B), a nanostructured SiO_2 film on one side of a
20 polycarbonate lens (C), and a nanostructured SiO_2 film on both sides of a polycarbonate lens (D).

The following patents and applications are considered to be part of the disclosure of this application and are incorporated herein by reference: U.S. Patent No. 7,507,380, issued May 24, 2009, U.S. Patent Application No. 11/490,966 (U.S.
25 Publ. No. 2007/0020400), filed July 21, 2006, U.S. Patent Application No. 11/564,759 (U.S. Publ. No. 2007/0184576), filed November 29, 2006, and U.S. Patent Application No. 11/897,998 (U.S. Publ. No. 2008/0108122), filed August 31, 2007.

The present invention has been described with reference to exemplary
30 embodiments. The scope of the present invention is not limited to these exemplary

features. For example, certain features of the invention have been exemplified by reference to the formation of ZnO and SiO_2 films. A person of ordinary skill in the art will appreciate that other materials can be formed using disclosed embodiments of the present method and system.

5 In view of the many possible embodiments to which the principles of the disclosed invention may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention. Rather, the scope of the invention is defined by the following claims. We therefore claim as our invention all that comes within

10 the scope and spirit of these claims.

We claim:

1. An anti-reflective product, comprising:

a substrate; and

5 an anti-reflective film adhered to at least one surface of the substrate, wherein the anti-reflective film comprises nanoparticles having an average diameter smaller than at least some wavelengths of incident light, and wherein the anti-reflective product has a reflectivity of less than about 4% across a 400-nm to 900-nm spectrum.

10

2. The anti-reflective product of claim 1, where an average size of the nanoparticles is smaller than about 400 nm.

3. The anti-reflective product of claim 1, where the reflectivity is less 15 than about 1% across a 400-nm to 900-nm spectrum.

4. The anti-reflective product of claim 1, where the anti-reflective film is substantially transparent.

20 5. The anti-reflective product of claim 1, where the anti-reflective film comprises heterogeneous physical attributes selected from particle size, particle morphology, particle density, and combinations thereof.

6. The anti-reflective product of claim 1, where the anti-reflective film 25 has a substantially homogeneous chemical composition throughout a cross-section of the film.

7. The anti-reflective product of claim 6, where the anti-reflective film comprises heterogeneous physical attributes selected from particle size, particle 30 morphology, particle density, and combinations thereof.

8. The anti-reflective product of claim 1, where the substrate is a lens.

9. The anti-reflective product of claim 1, where the substrate is
5 polycarbonate and the anti-reflective film comprises SiO_2 nanoparticles.

10. The anti-reflective product of claim 9, where the substrate is a
polycarbonate eyeglass lens.

10 11. The anti-reflective product of claim 10, where the anti-reflective film
is adhered to two surfaces of the polycarbonate eyeglass lens.

12. The anti-reflective product of claim 1, where the substrate is
aluminum and the anti-reflective film comprises ZnO nanoparticles.
15

13. The anti-reflective product of claim 1, where the substrate is textured
silicon and the anti-reflective film comprises ZnO nanoparticles.

14. The anti-reflective product of claim 1, where the substrate is glass
20 and the anti-reflective product has a percent transmittance greater than about 80%
across a 400-nm to 800-nm spectrum.

15. An apparatus, comprising:
a substrate having a first major planar surface and a second major planar
25 surface;
an anti-reflective film disposed on the first major planar surface, wherein the
film comprises nanoparticles having an average diameter smaller than at least some
wavelengths of incident light; and
a microchannel reactor disposed on the second major planar surface, wherein
30 the microchannel reactor is coated with nanostructured catalysts.

16. The apparatus of claim 15, where the nanoparticles have an average size less than about 400 nm.

5 17. The apparatus of claim 16, where the anti-reflective film on the first major planar surface is capable of absorbing solar radiation.

18. The apparatus of claim 17, where less than about 0.5% of the solar radiation is reflected.

10

19. The apparatus of claim 15, where the microchannel reactor coated with nanostructured catalysts is configured to perform an endothermic reaction.

20. The apparatus of claim 19, where the anti-reflective film on the first
15 major planar surface is capable of absorbing solar radiation and the solar radiation provides energy for the endothermic reaction.

21. A method for preparing an anti-reflective coating, comprising:

providing a substrate;

20 providing a first reactant solution;

providing a second reactant solution;

combining the first reactant solution with the second reactant solution to form a deposition material; and

applying the deposition material to the substrate to provide an anti-reflective
25 coating comprising nanoparticles smaller than at least some wavelengths of incident light on the substrate.

22. The method of claim 21, where an average size of the nanoparticles is smaller than about 400 nm.

30

23. The method of claim 21, further comprising providing energy to the deposition material to produce reactive species, where the energy is thermal, chemical, microwave, photochemical, electrochemical, plasma, ultrasonic, or a combination thereof.

5

24. The method of claim 21, further comprising providing energy to the substrate to produce an activated substrate surface, where the energy is thermal, chemical, microwave, photochemical, electrochemical, plasma, ultrasonic, or a combination thereof.

10

25. The method of claim 21, further comprising allowing an effective period of time to elapse before applying the deposition material to the substrate, where nanoparticles form in the deposition material during the effective period of time.

15

26. An anti-reflective product prepared by the method of claim 21.

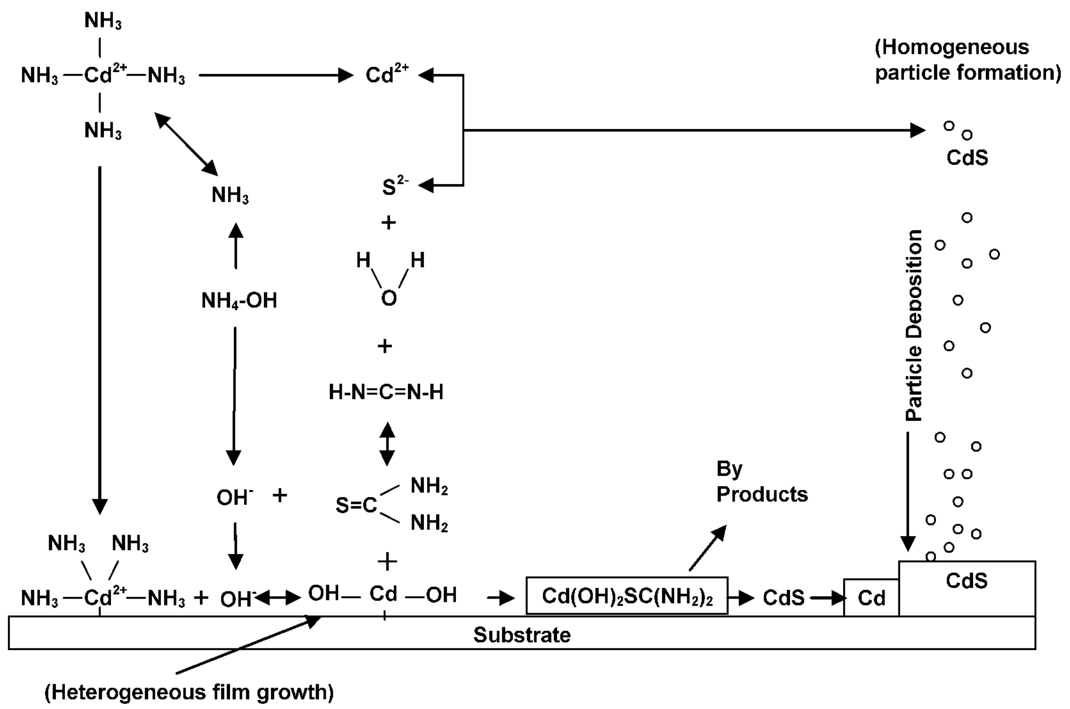


FIG. 1

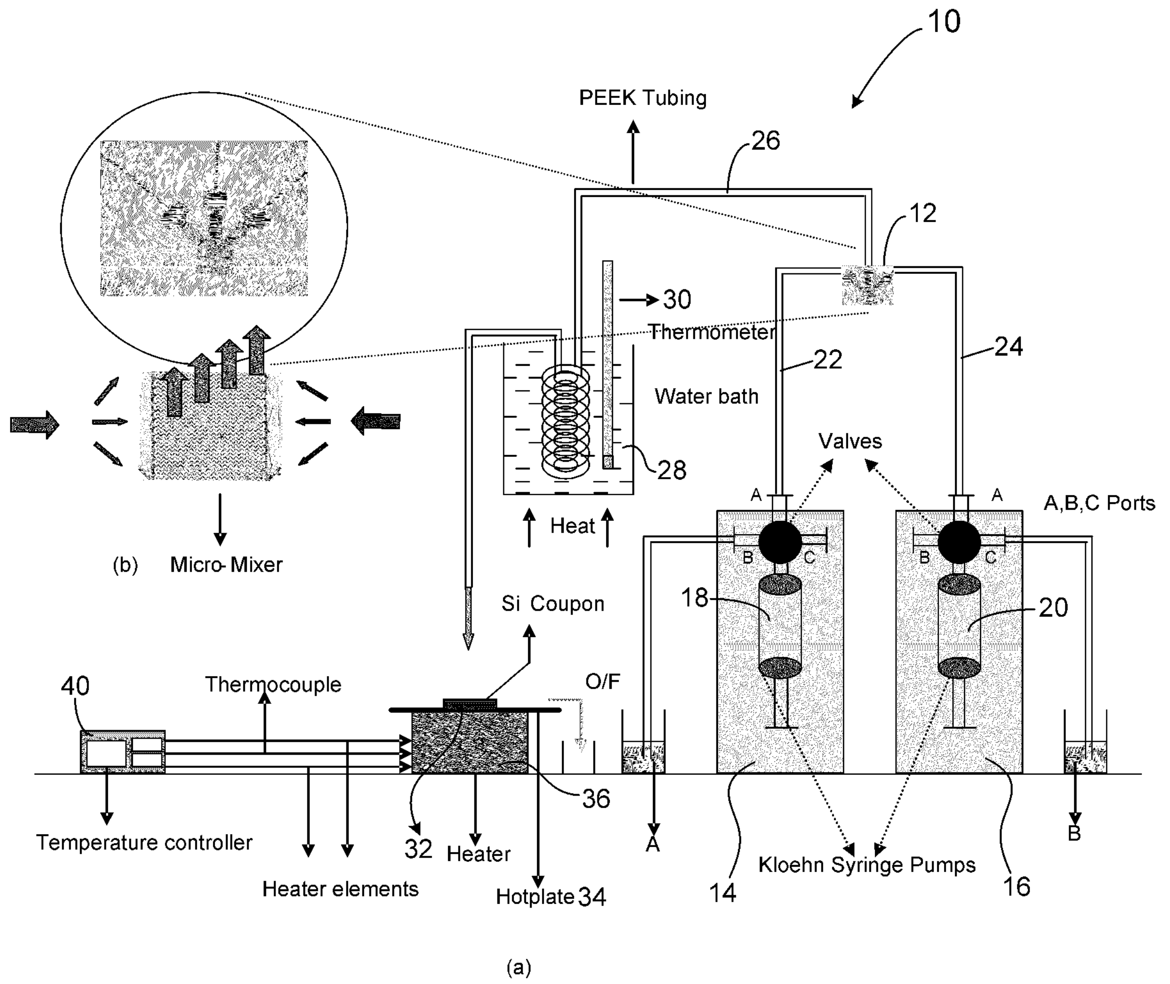


FIG. 2

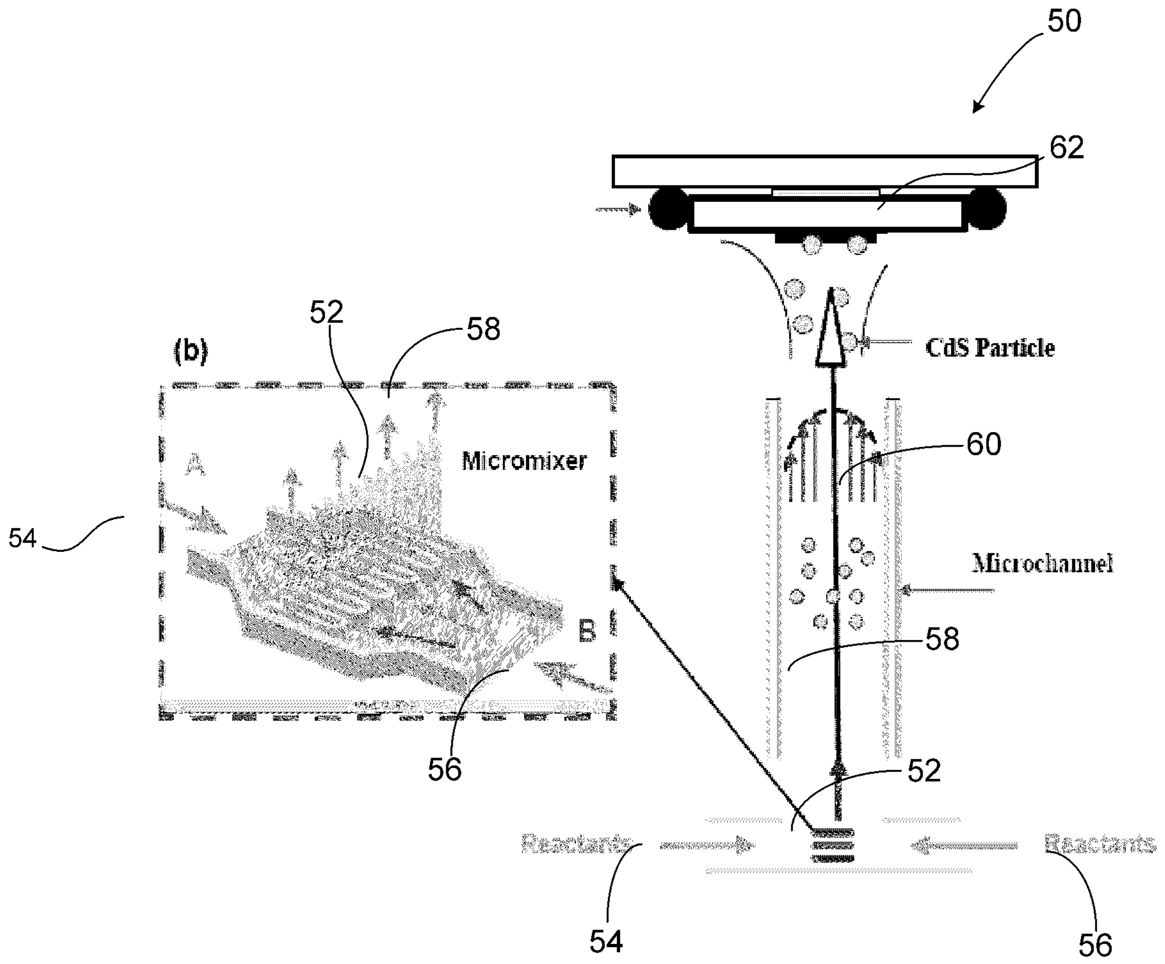


FIG. 3

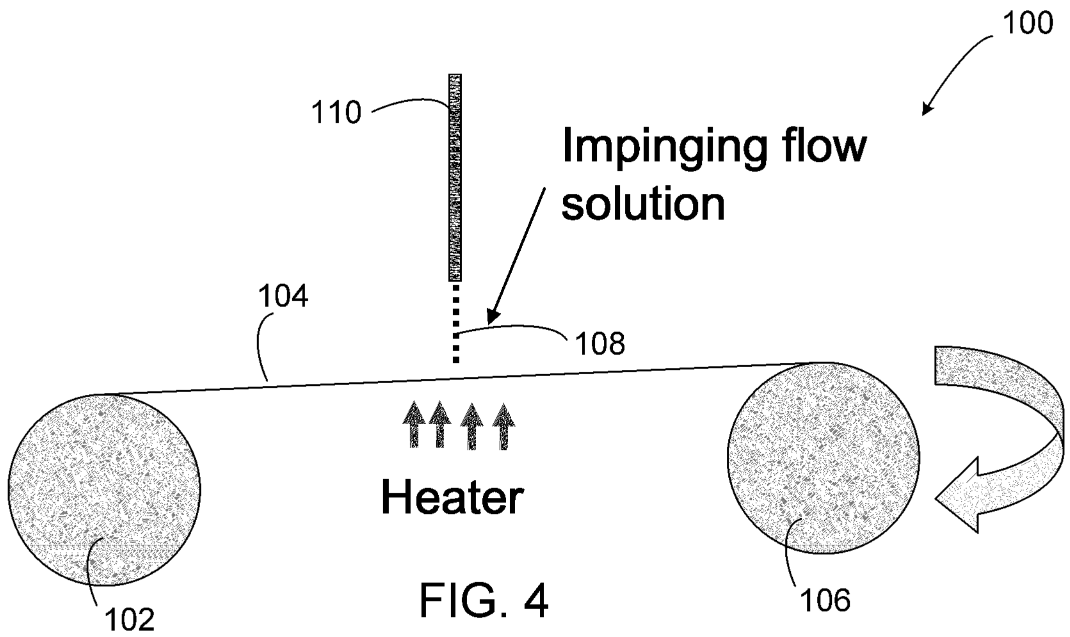


FIG. 4

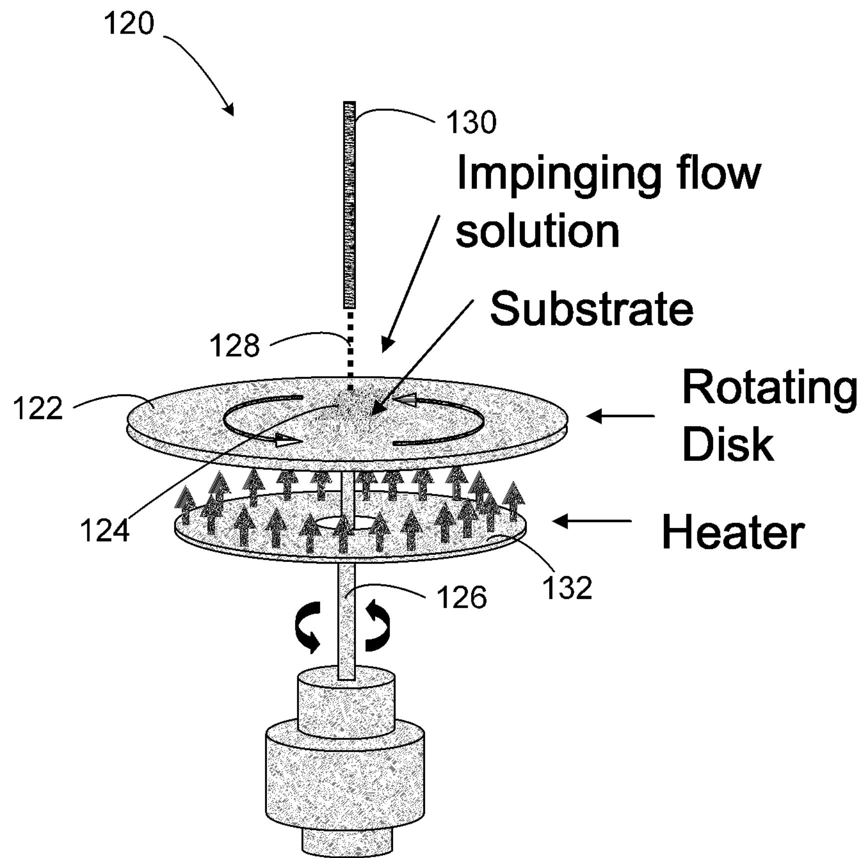


FIG. 5

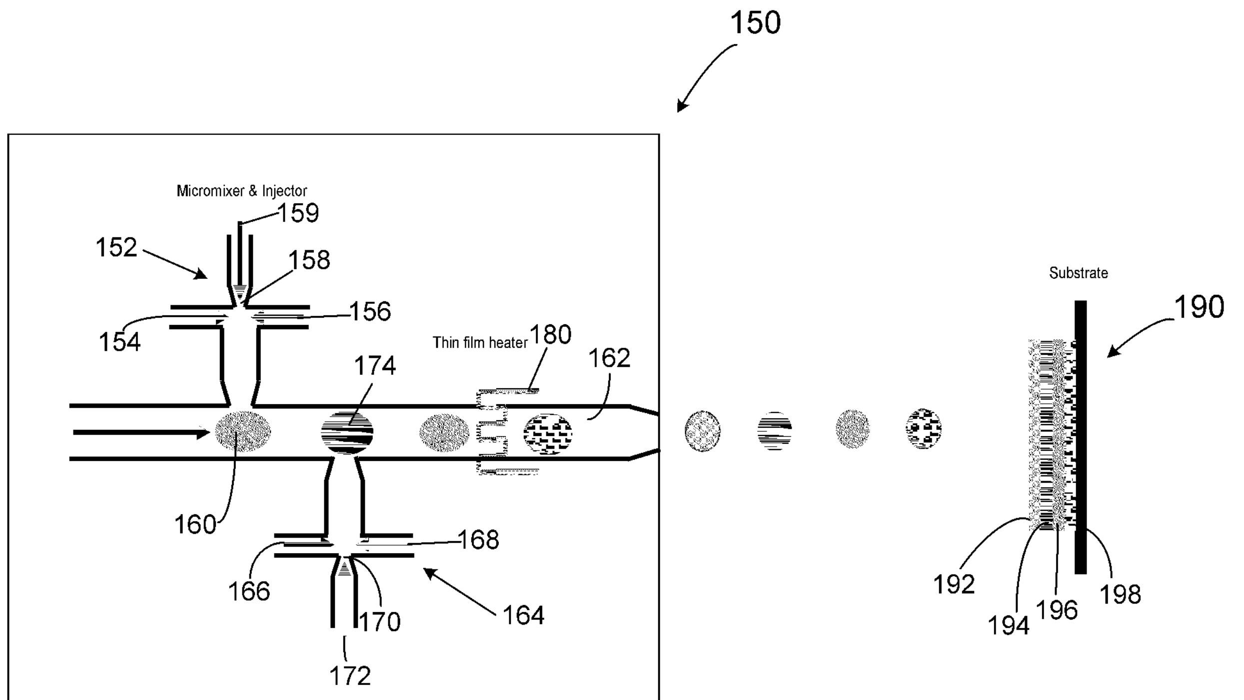


FIG. 6

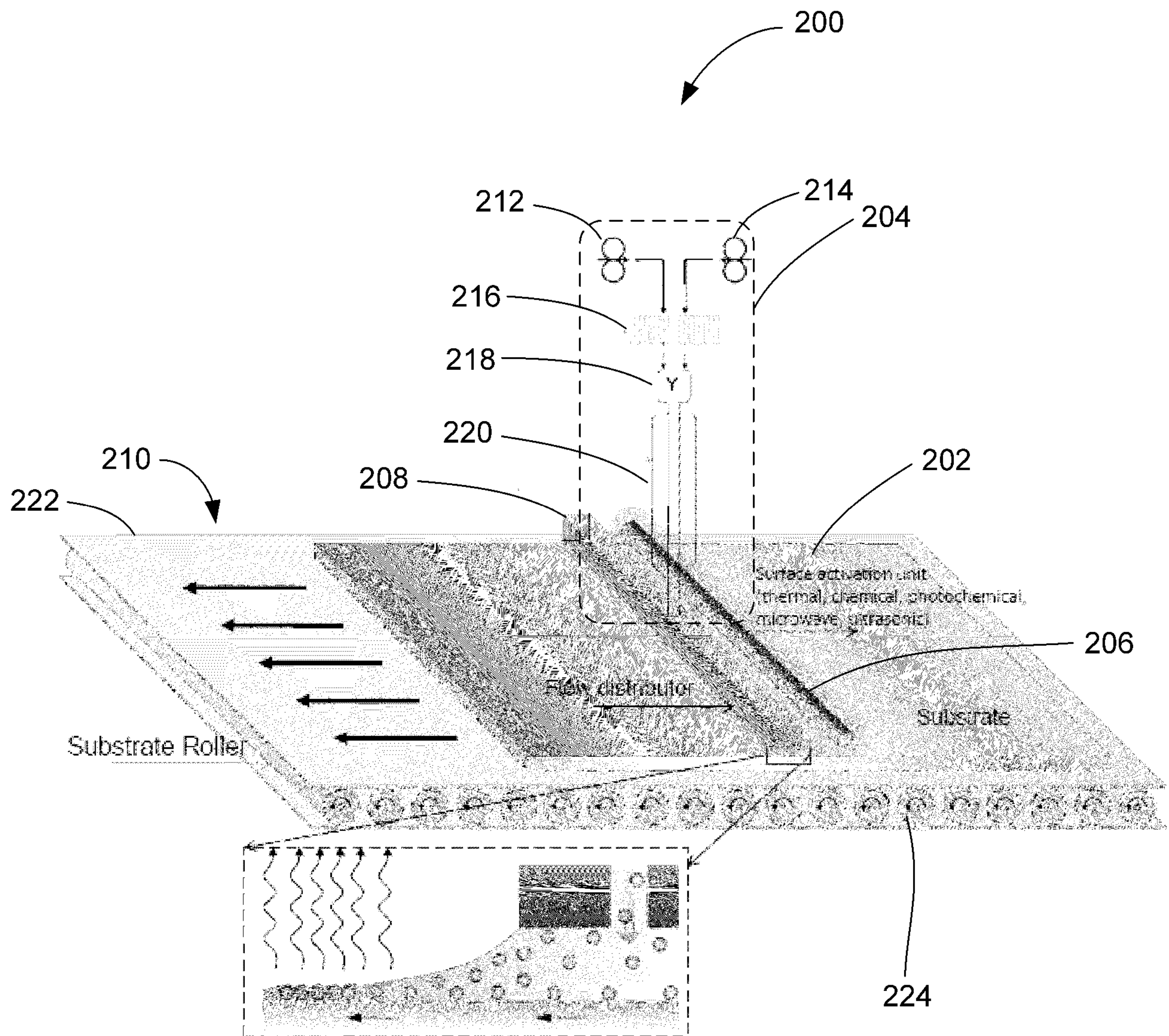


FIG. 7

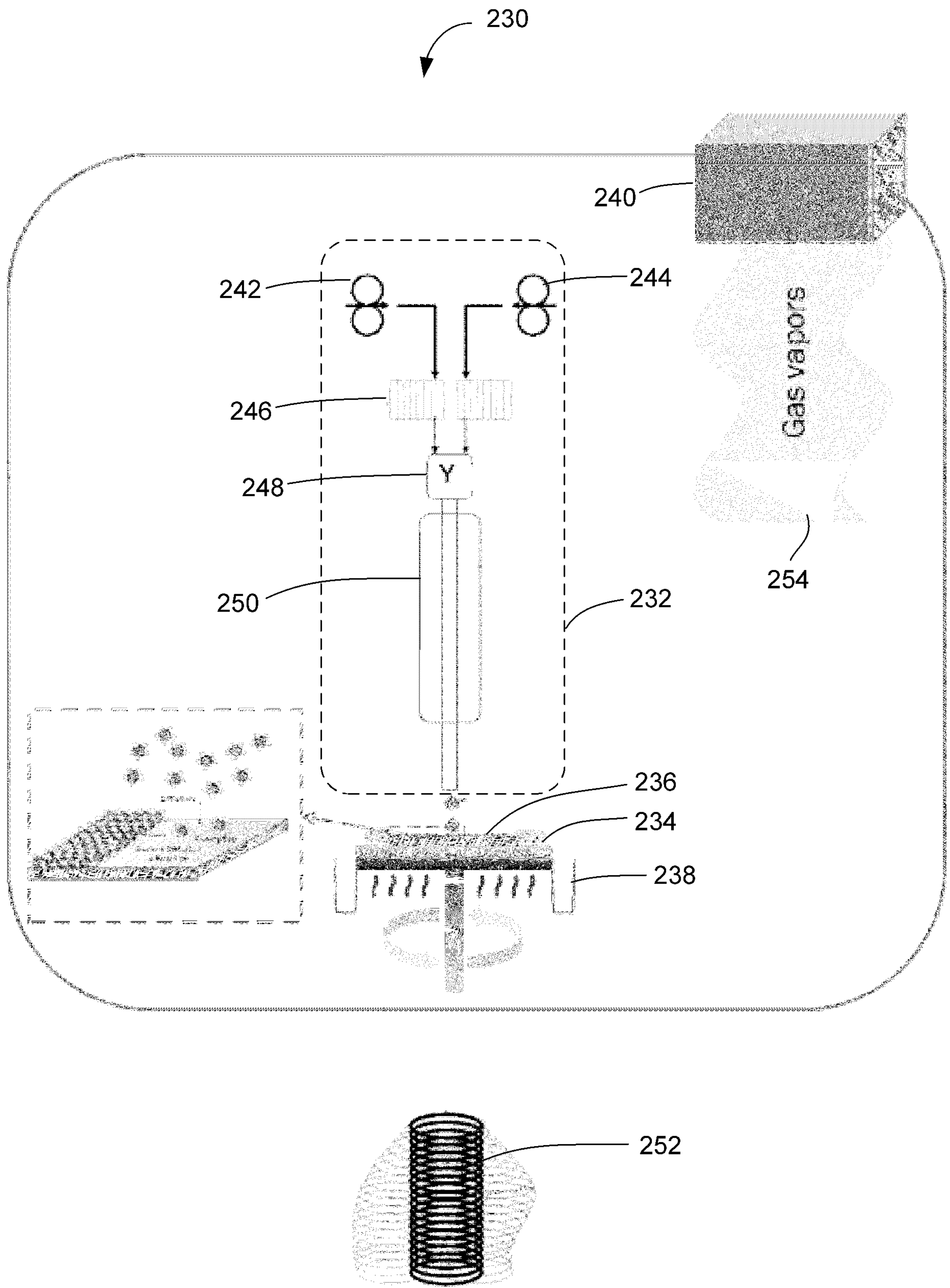


FIG. 8

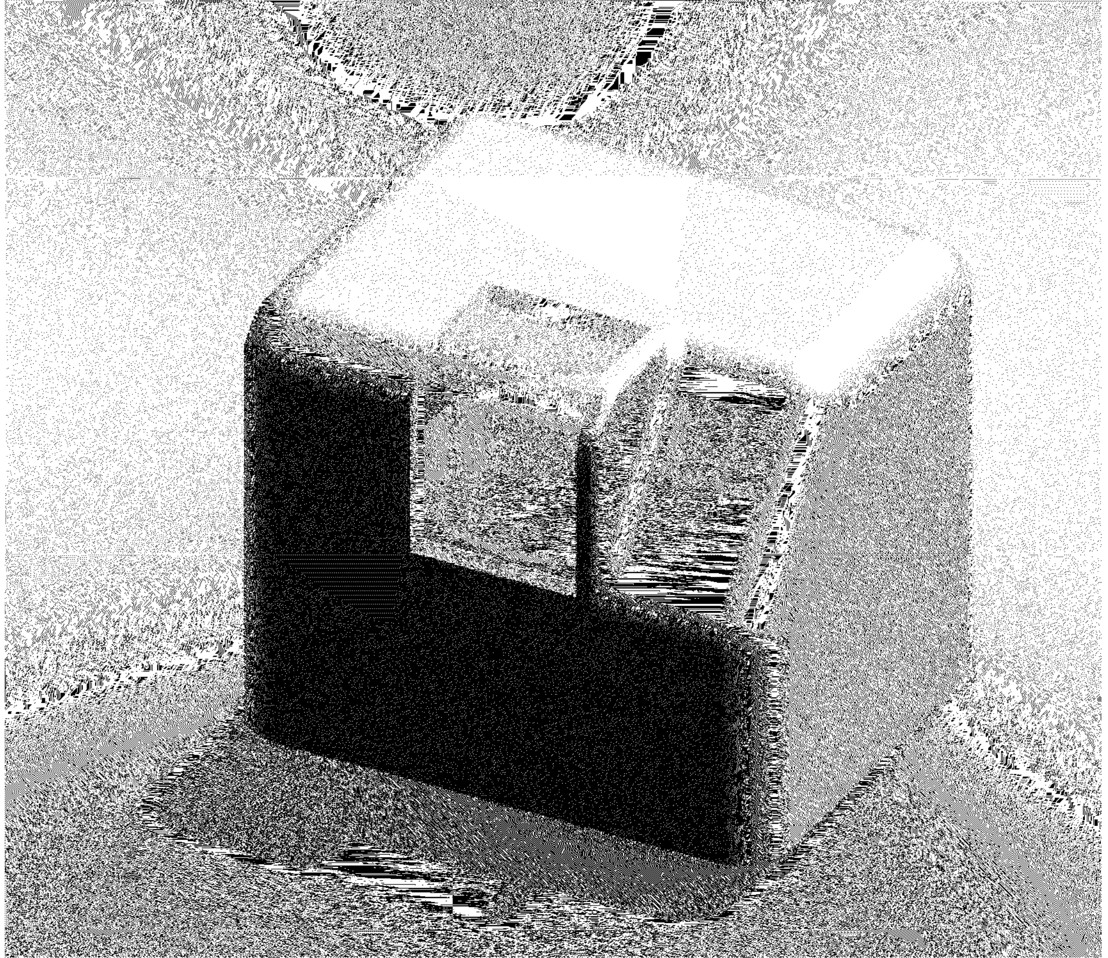


FIG. 9

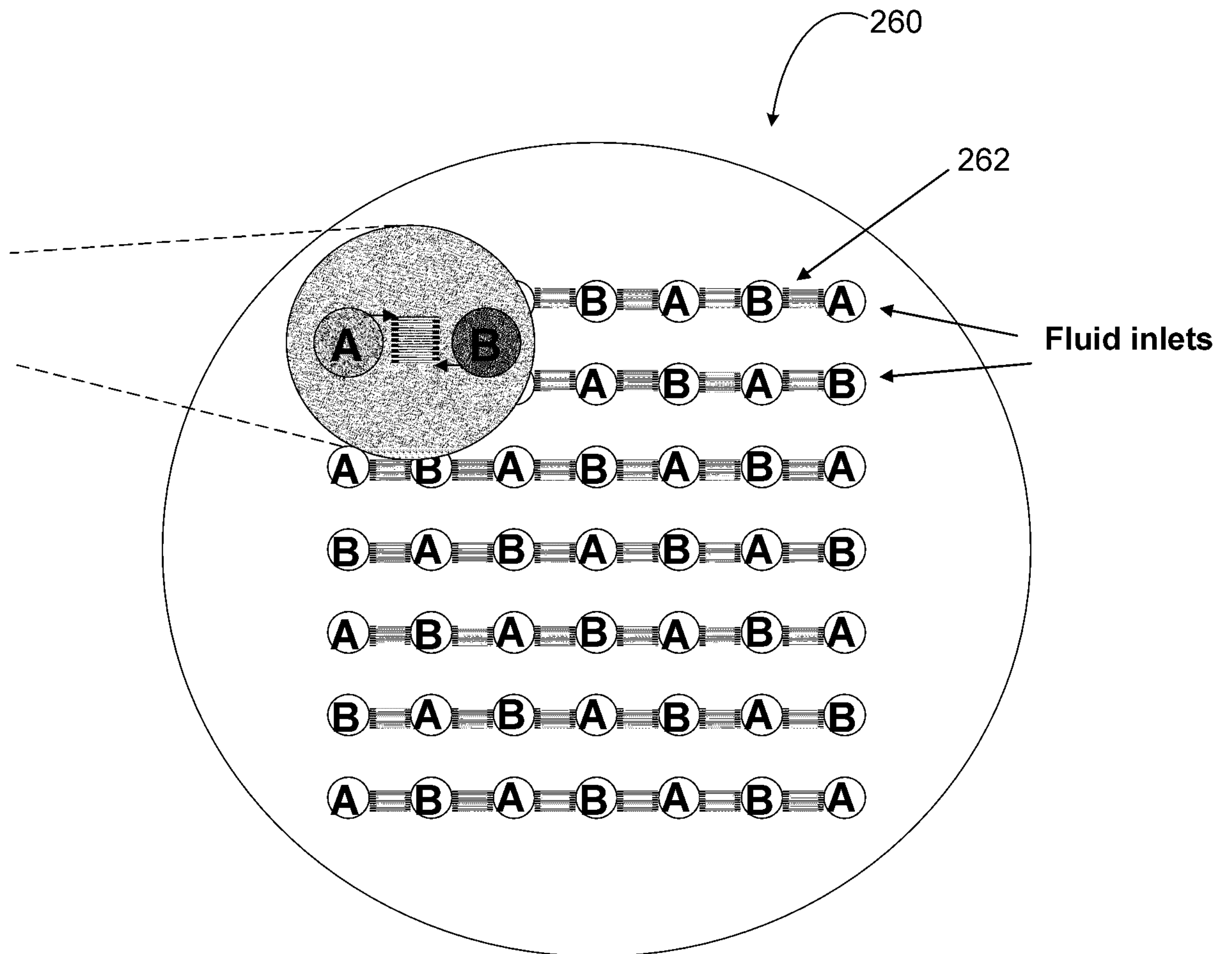


FIG. 10

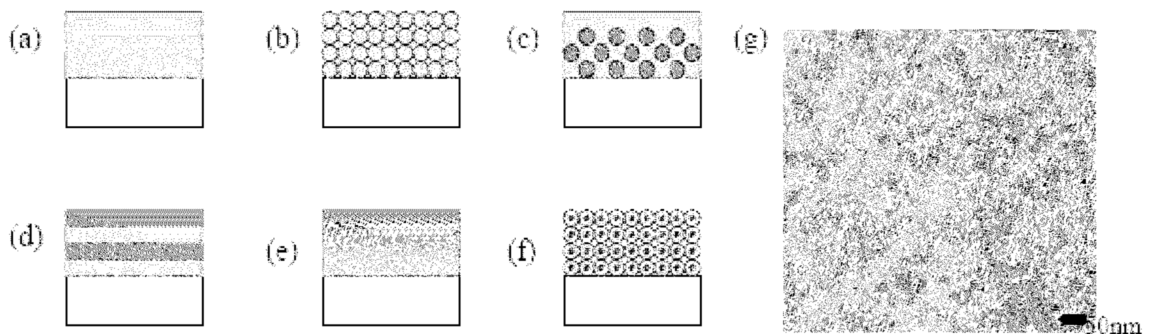


FIG. 11

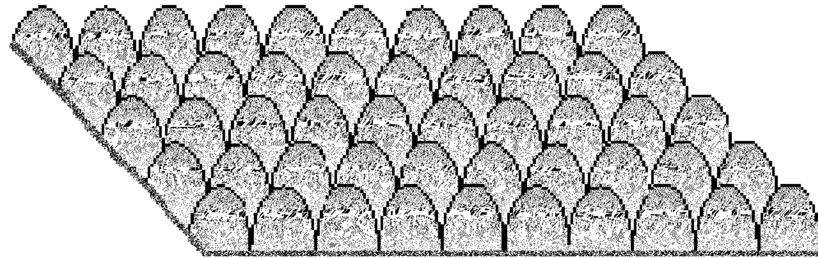


FIG. 12

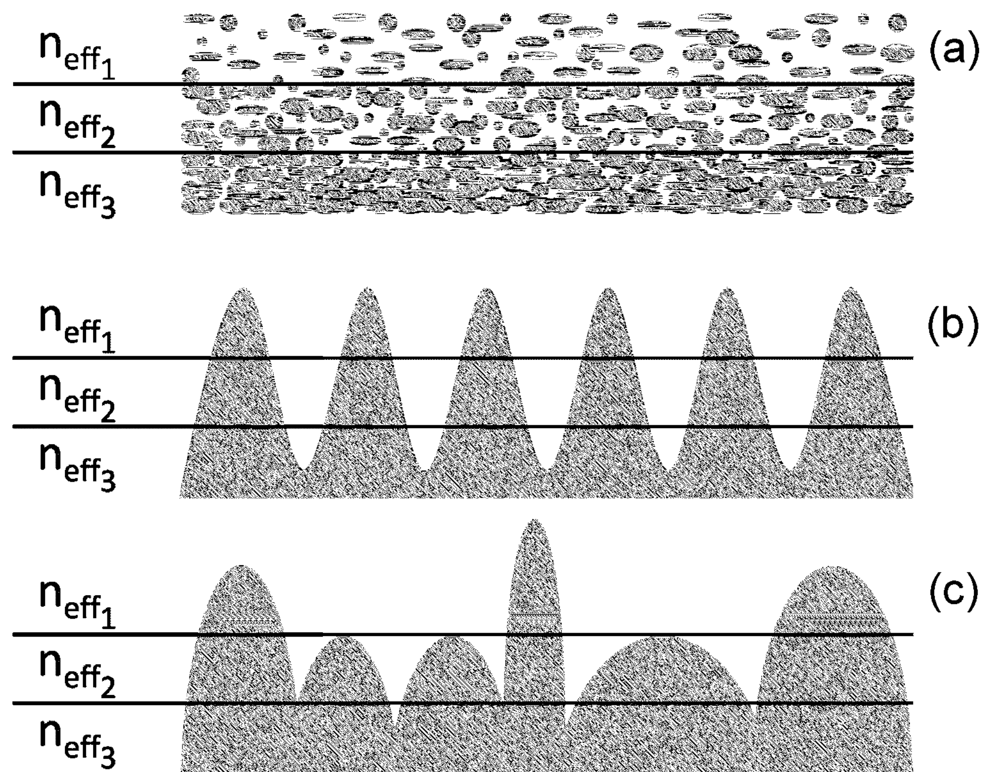


FIG. 13

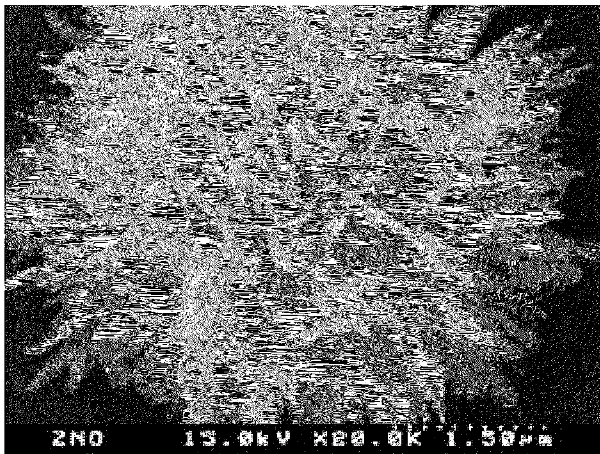


FIG. 14

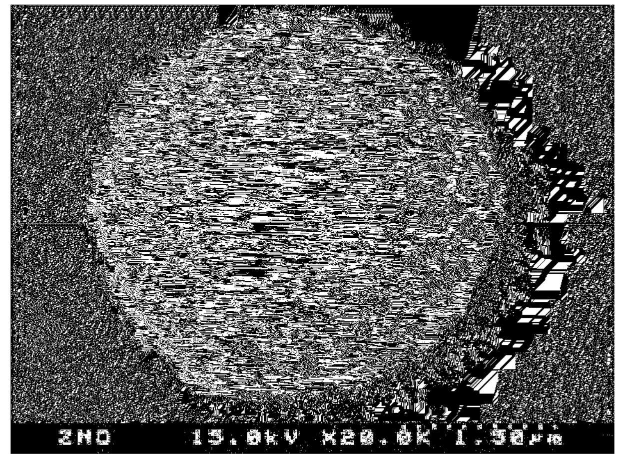


FIG. 15

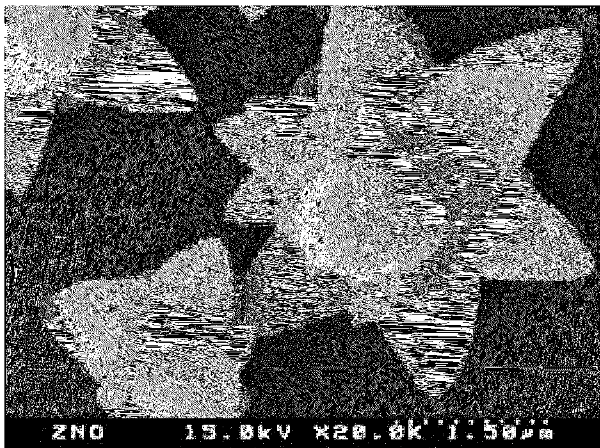


FIG. 16

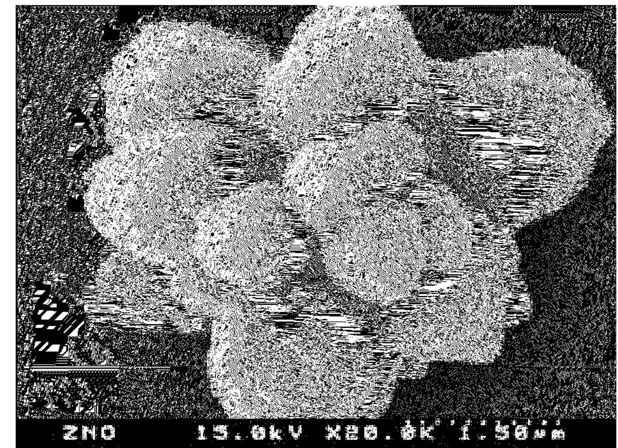


FIG. 17

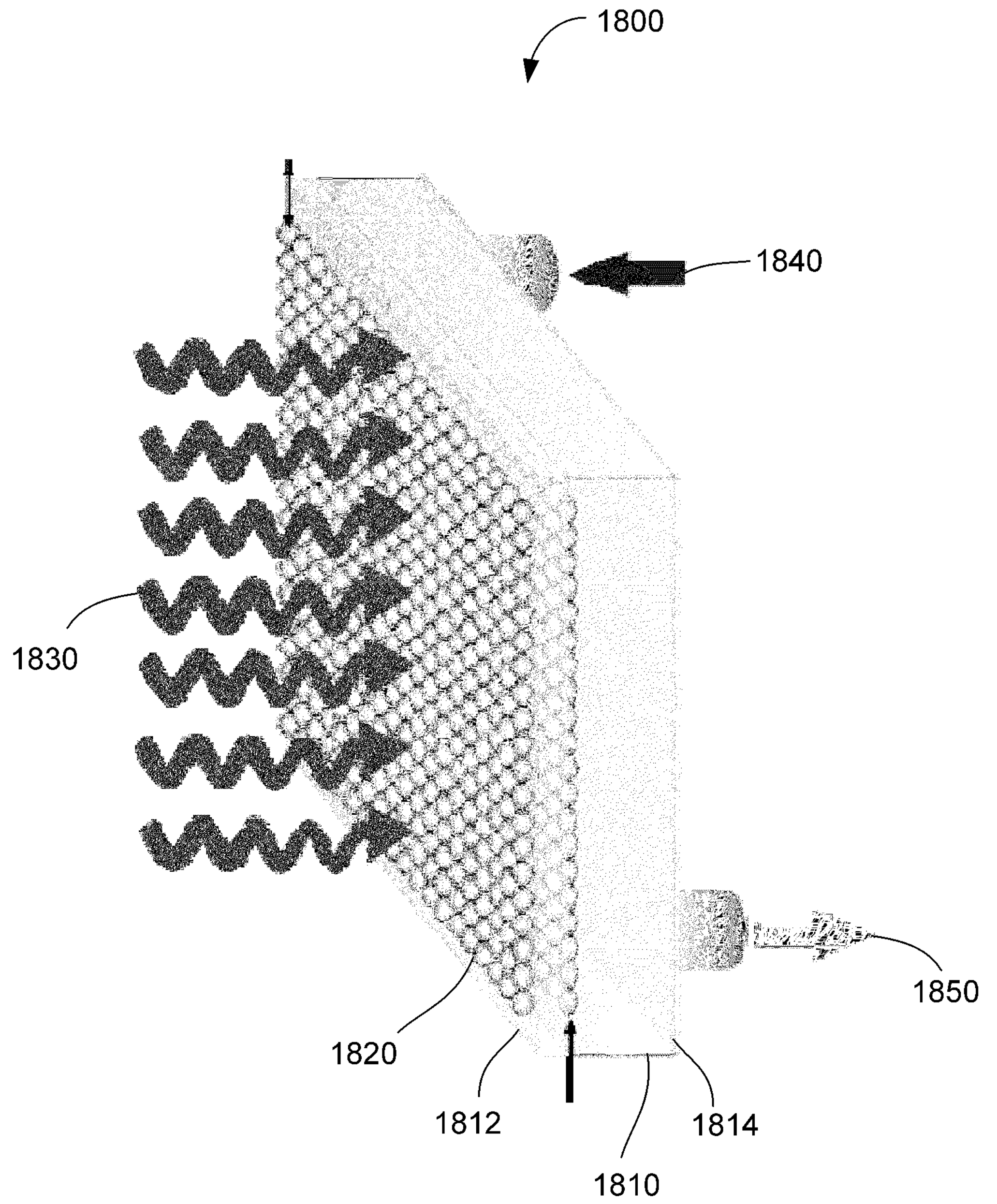


FIG. 18

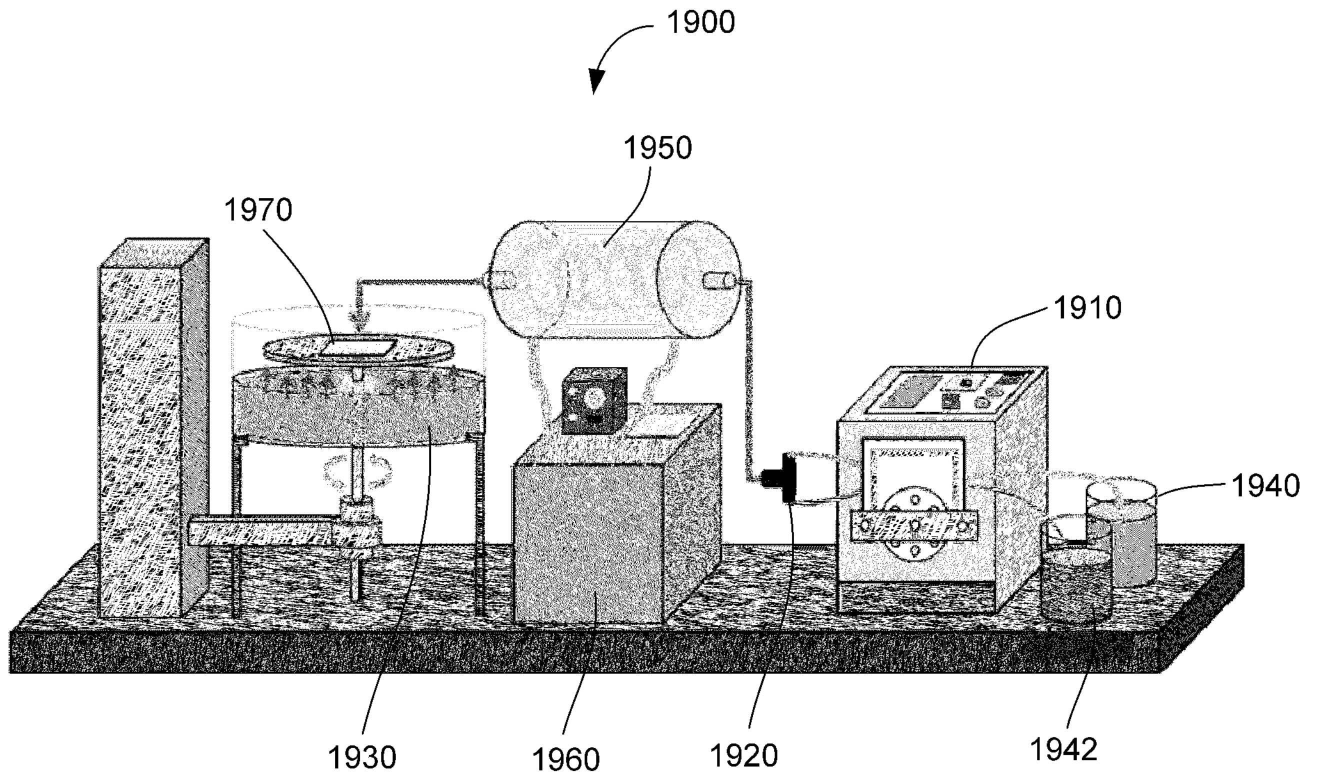


FIG. 19

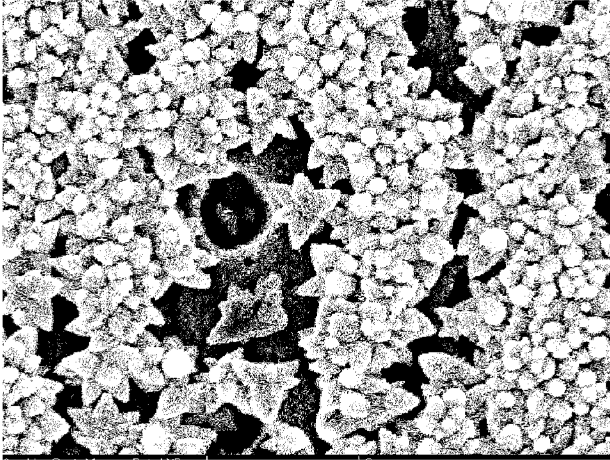


FIG. 20A

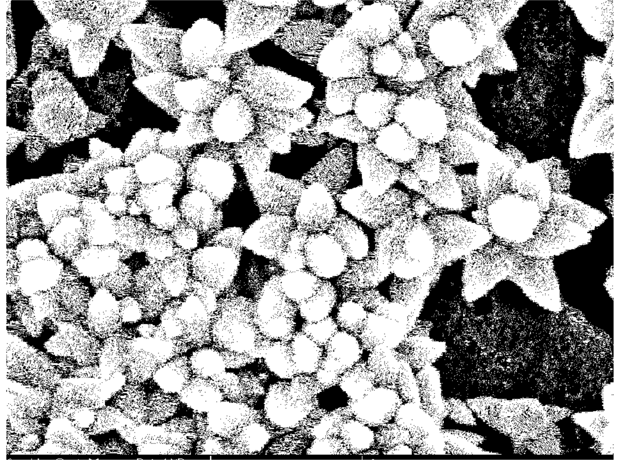


FIG. 20B

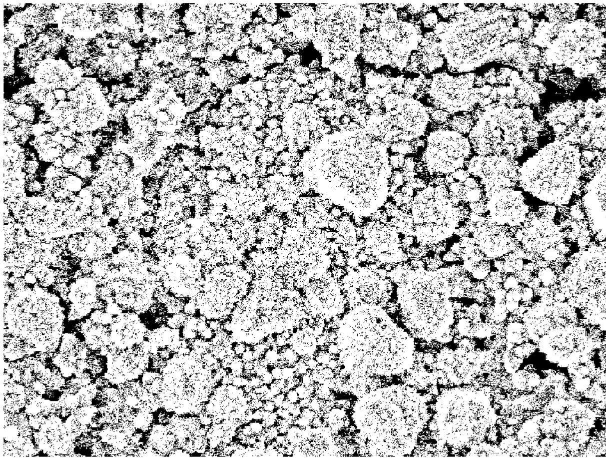


FIG. 21A

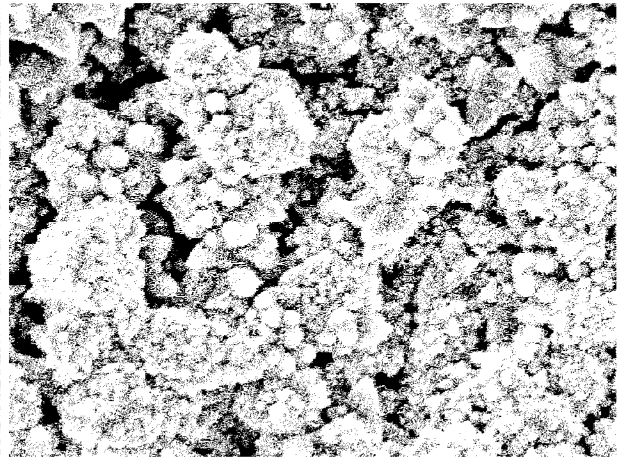


FIG. 21B

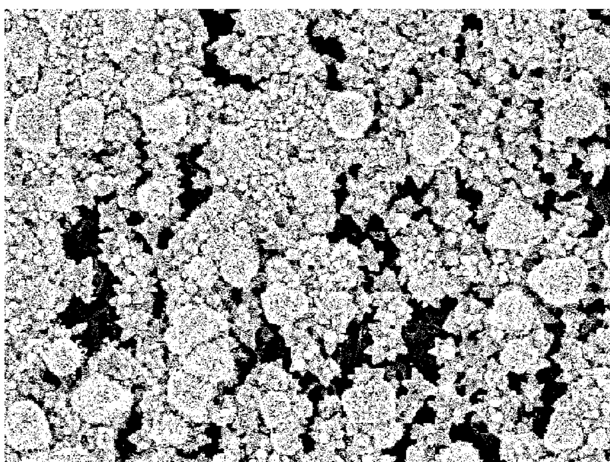


FIG. 22A

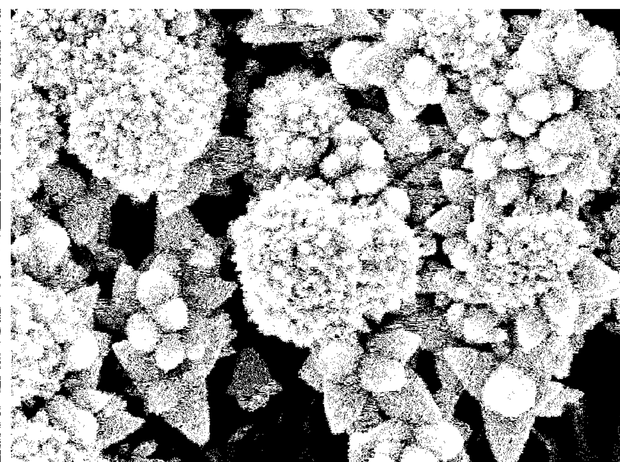


FIG. 22B

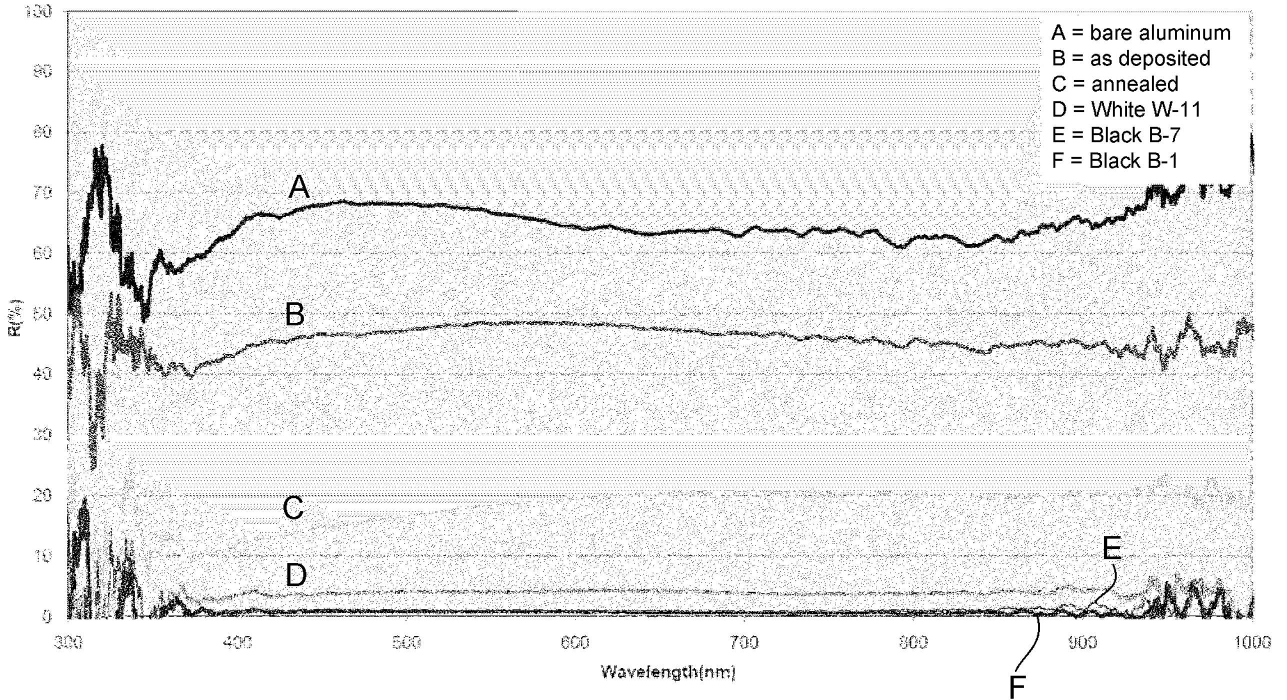


FIG. 23

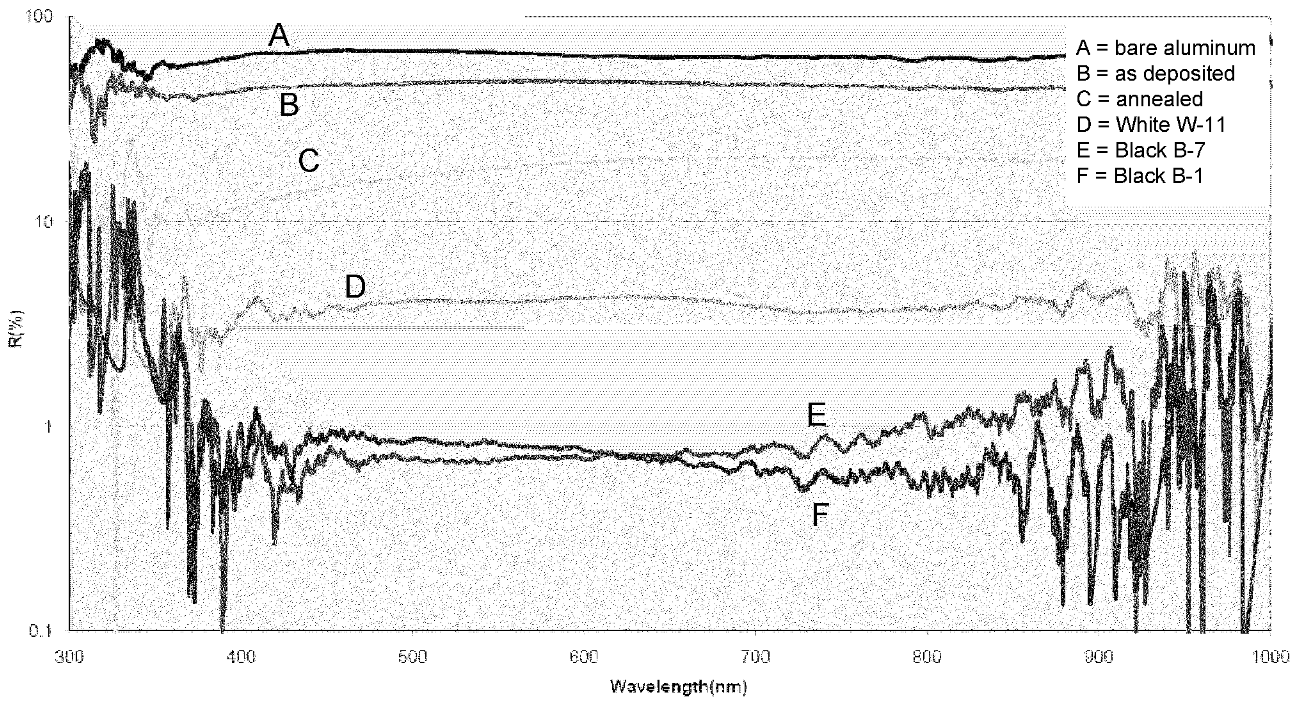


FIG. 24

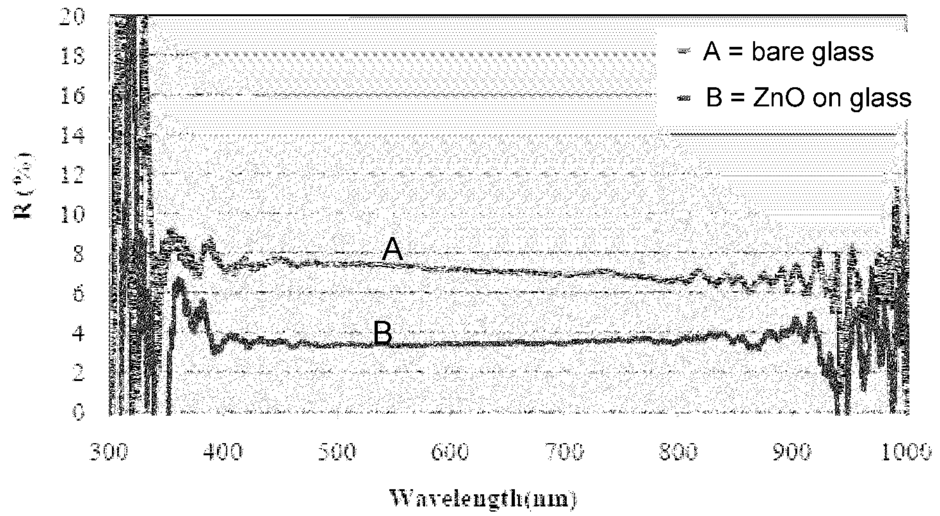


FIG. 25

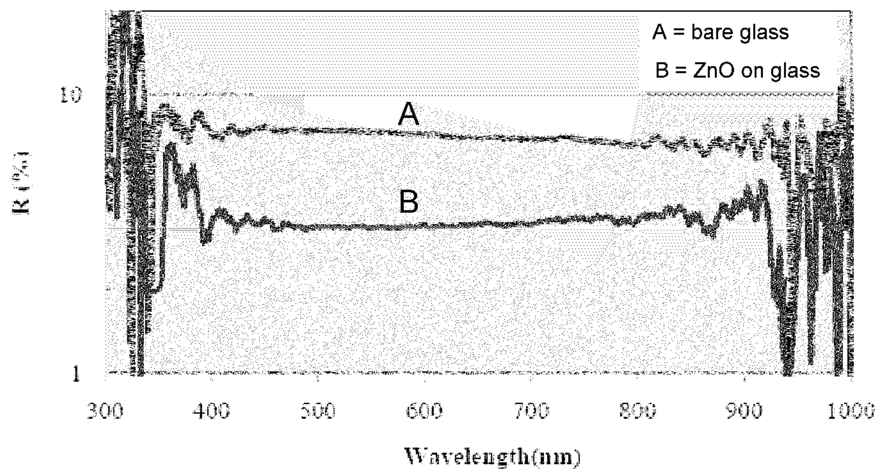


FIG. 26

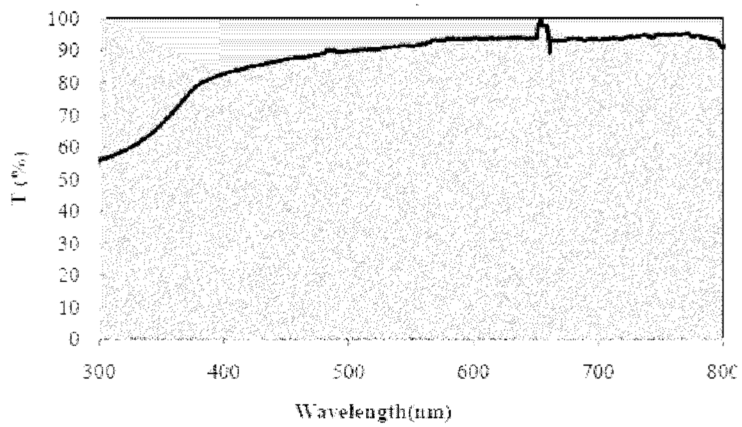


FIG. 27

FIG. 28

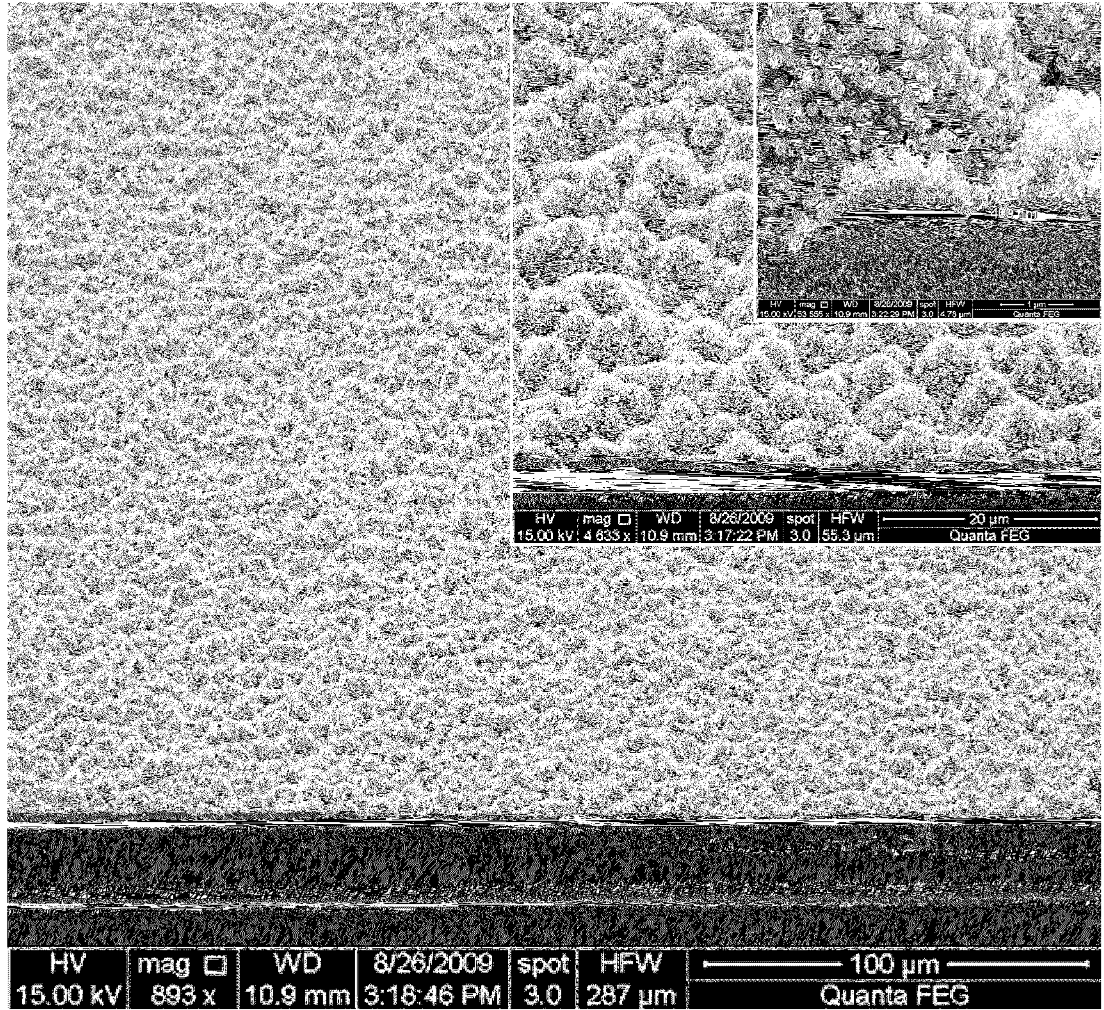


FIG. 29

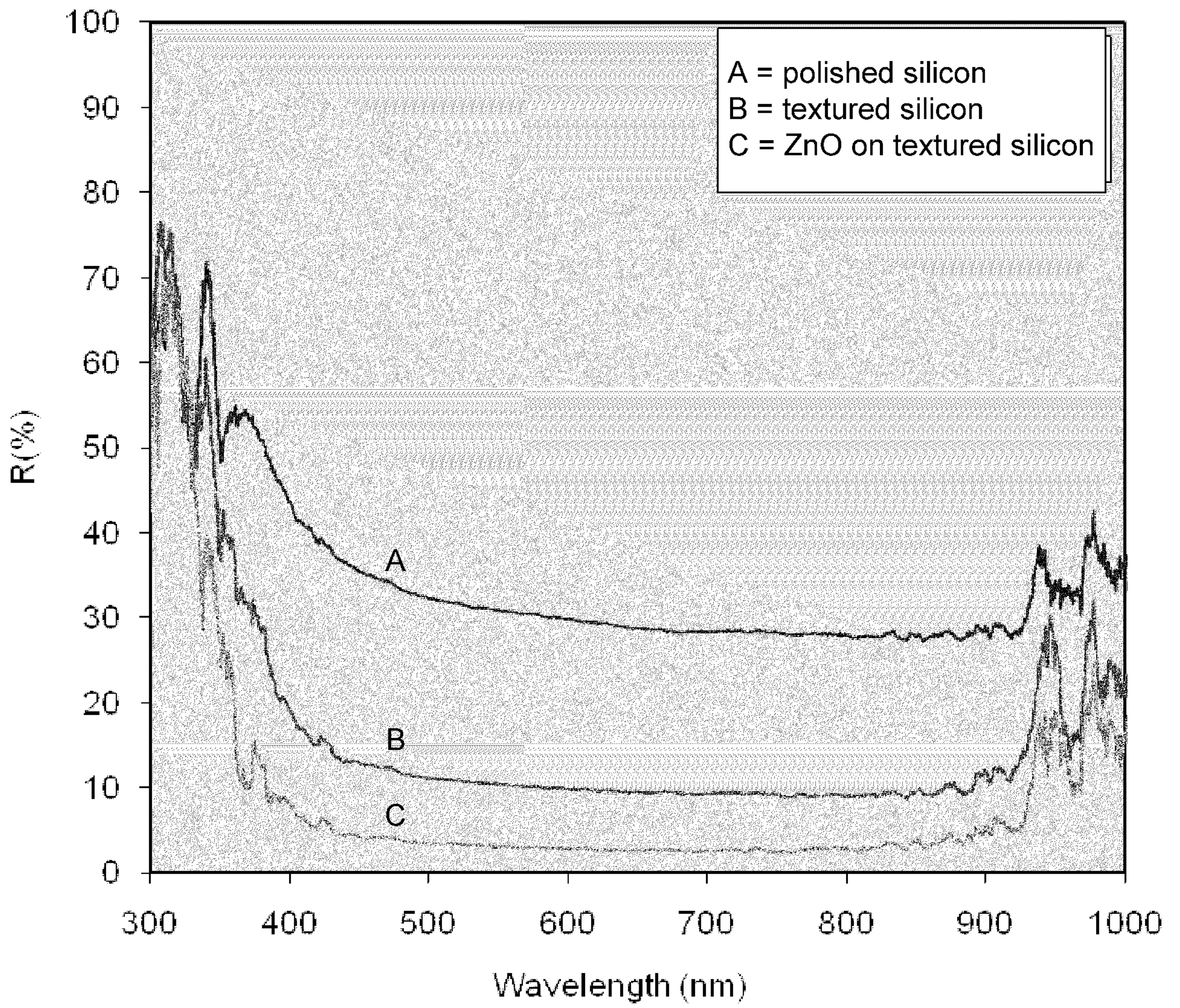


FIG. 30

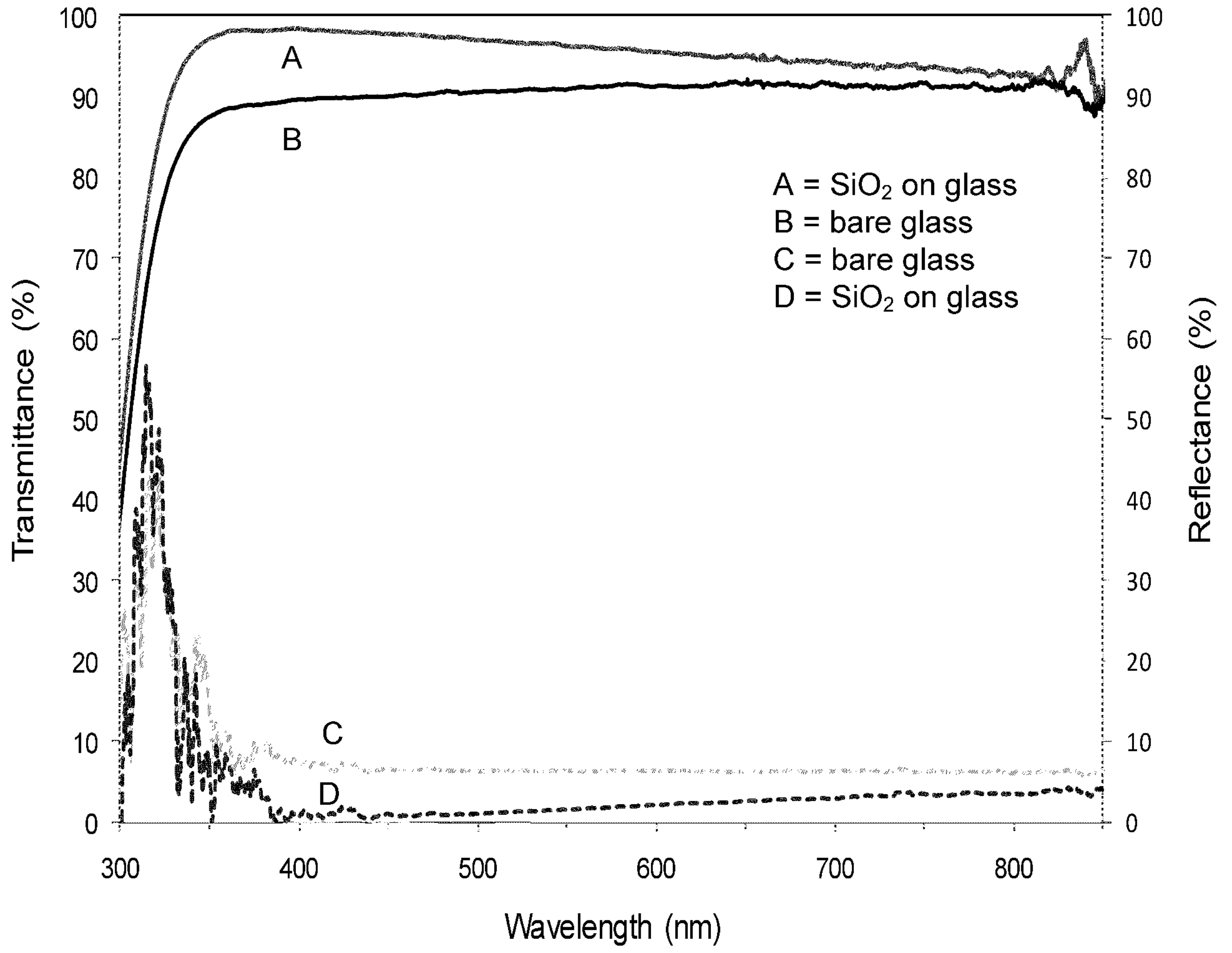


FIG. 31

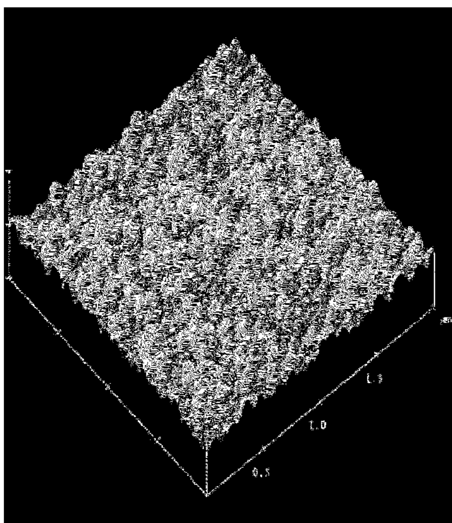


FIG. 32

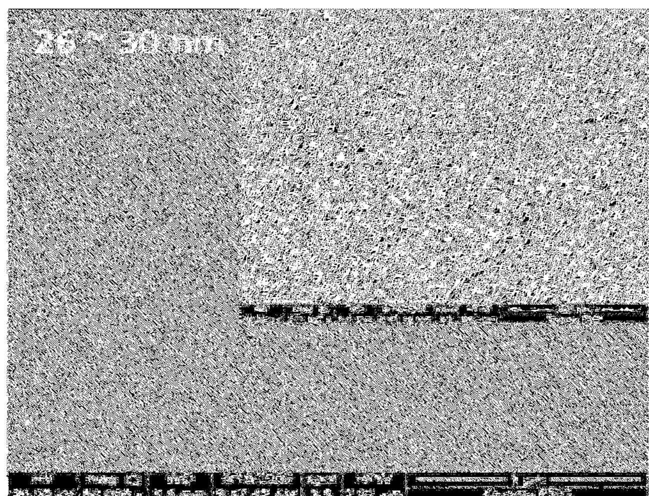


FIG. 33

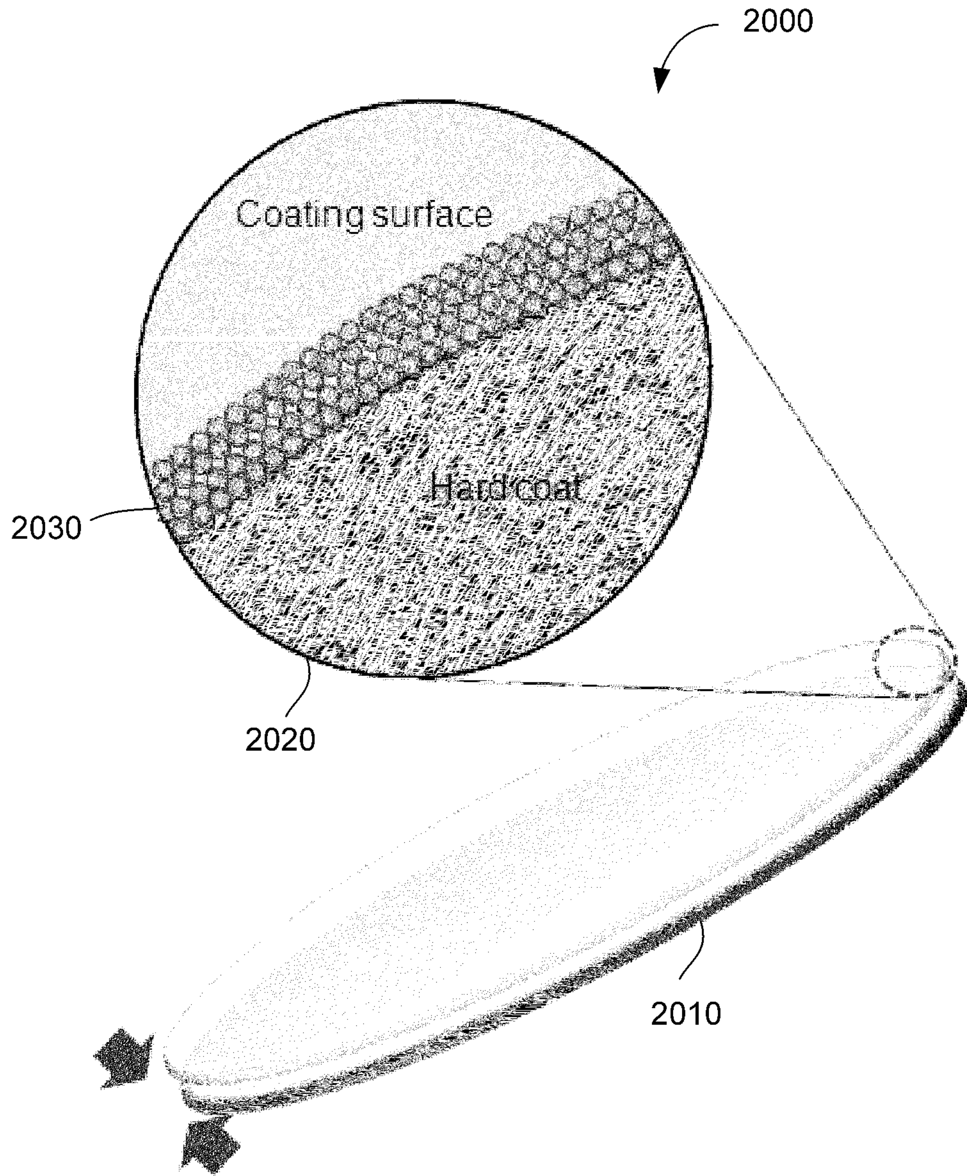


FIG. 34

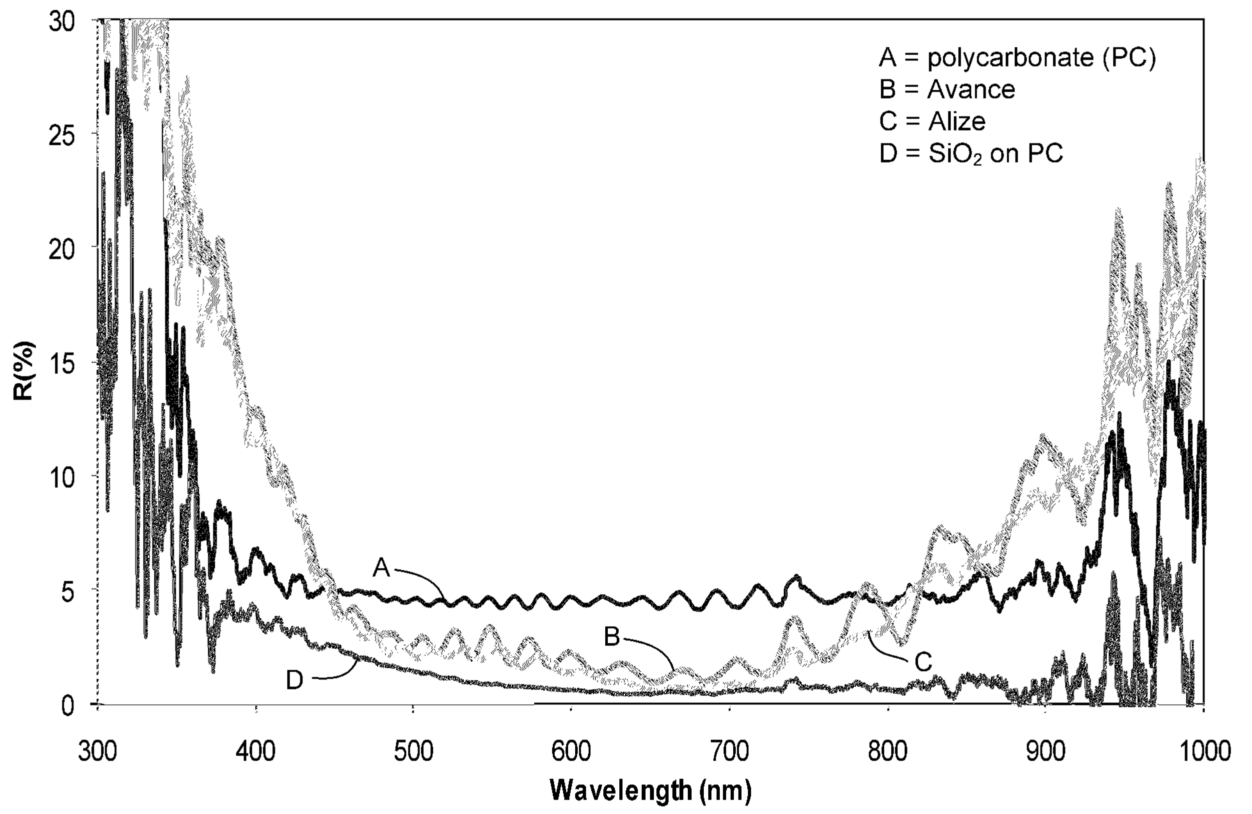


FIG. 35

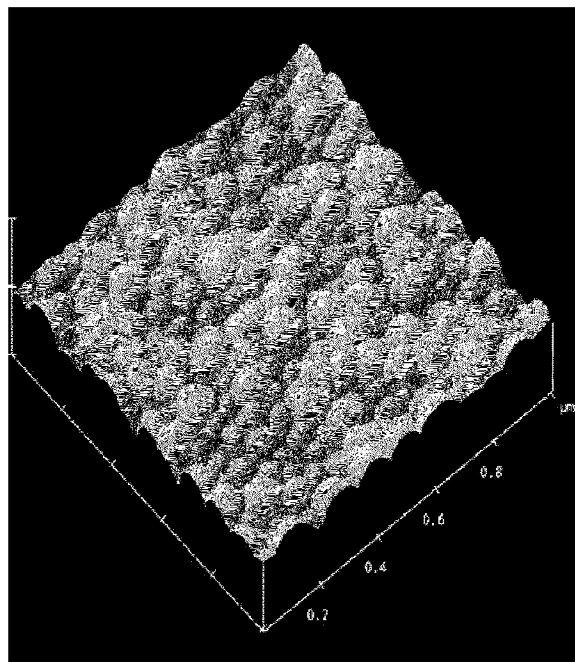


FIG. 36

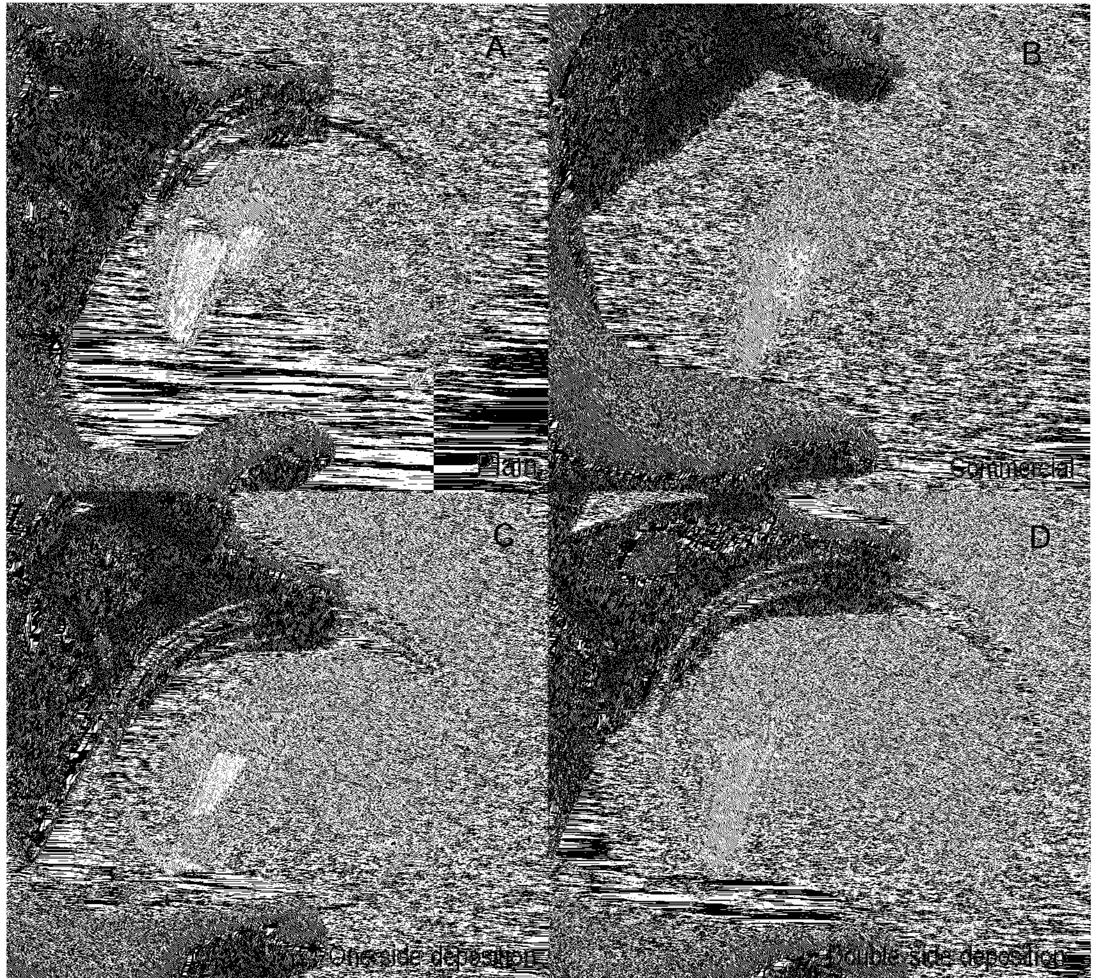


FIG. 37