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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 November 2001 (15.11.2001)

PCT

(10) International Publication Number
WO 01/85364 A1

(51) International Patent Classification[7]: B05D 5/12, C23C 16/00

(21) International Application Number: PCT/US01/14979

(22) International Filing Date: 8 May 2001 (08.05.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/566,866 8 May 2000 (08.05.2000) US

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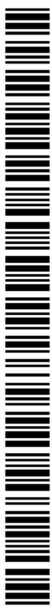
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

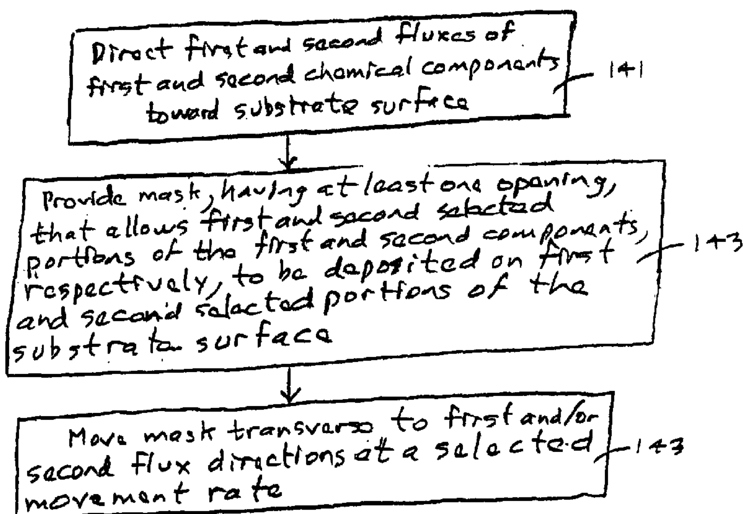
(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



(54) Title: COMBINATORIAL SYNTHESIS OF MATERIAL CHIPS



(57) Abstract: Systems and methods for providing in situ, controllably variable concentrations of one, two or more chemical components on a substrate to produce an integrated materials chip. The component concentrations can vary linearly, quadratically or according to any other reasonable power law with one or two location coordinates. In one embodiment, a source and a mask with fixed or varying aperture widths and fixed or varying aperture spacings are used to produce the desired concentration envelope. In another embodiment, a mask with one or more movable apertures or openings provides a chemical component flux that varies with location on the substrate, in one or two dimensions. In another embodiment, flow of the chemical components through nuzzle slits provides the desired concentrations. An ion beam source, a sputtering source, a laser ablation source, a molecular beam source, a chemical vapor deposition source and/or an evaporative source can provide the chemical component(s) to be deposited on the substrate. Carbides, nitrides, oxides, halides and other elements and compounds can be added to and reacted with the deposits on the substrate.

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COMBINATORIAL SYNTHESIS OF MATERIAL CHIPS

Field of the Invention

This invention relates to methods and systems for deposition of chemicals in controllably variable amounts on a substrate.

5 ## Background of the Invention

In the past decade, several workers have applied a combinatorial synthesis approach to development of new materials, or to construction of known materials in new ways. Material chip samples, with varying chemical compositions involving two or three components and with discrete or
10 continuous composition change, can, in principle, be synthesized, using multilayers and masks. However, a true multi-composition compound probably cannot be formed unless each multilayer is formed and uniformly diffused at relatively low temperatures. This appears to require an in situ approach, which is not well understood and is not developed in the
15 background art.

What is needed is an in situ approach and/or a multilayer approach for formation of chemical compounds having two, three or more components and having controllably variable composition on a substrate. Preferably, the approach should be flexible and should easily allow change of one or more
20 geometric, physical and chemical parameters describing the formation process and the variation of composition with location on the substrate. Preferably, the approach should allow a choice of the geometric variation (linear, nonlinear, etc.) of one or more composition parameters according to the intended use and environment of the material chip.

25 ## Summary of the Invention

These needs are met by the invention, which provides several systems and associated methods for controllably variable in situ or multilayer deposition of two or more chemical components on a substrate. In one embodiment, an ultra-high vacuum (UHV) ion beam sputtering system or
30 evaporation system includes a multi-target carousel, a precision mask that is movable in one or two coordinate directions, x and y, and a stepper motor to move the mask by controllable amounts in the x- and/or y-directions in a timed sequence. Pure metal sputtering or evaporation targets are used to

deposit precursors in selected layers. Use of a UHV environment ensures that the precursor layers are not oxidized during or after deposition. A heating element, built into or associated with a sample holder, provides thermally-driven precursor diffusion after the deposition, without exposing the sample to
5 air during sample transfer. Ion beam sputtering has several advantages: target exchange is relatively simple; most metal targets are available; and precursor interdiffusion occurs at much lower temperatures and over shorter time intervals than are required for distribution of metal-inorganic compounds. As a further benefit, where a second ion gun is added to the assembly, oxides,
10 nitrides, carbides, halogens and similar substances can be formed in situ from the metal precursor films.

A second embodiment involves a chemical vapor deposition (CVD) approach and provides large area uniformity for the deposition, the possibility of co-deposition of multi-component thin films with individually controllable
15 growth rates, and control of growth of the profile.

Another embodiment uses a deposition system equipped with two or more profile-controllable, precursor sources for in situ generation of continuous phase diagrams. This embodiment uses co-deposition with a nuzzle design to generate a linear or other geometric deposition profile for each
20 component deposited on the substrate.

In another embodiment, a mask with variable center-to-center aperture spacings and variable aperture sizes is used to deposit each of two or more chemical components onto a substrate, with the concentration of each chemical being variable independently with a location coordinate x. The concentration
25 may vary linearly with x (preferable), as a power or combination of powers of x, or in some other nonlinear manner with the coordinate x, and two or more component concentrations may have qualitatively or quantitatively different geometric variations with x. The concentration may also vary independently in each of two location coordinate directions, for example, with
30 the Cartesian coordinates x and y or the polar coordinates r and θ.

Brief Description of the Drawings

Figure 1 is a schematic view illustrating ion beam sputtering deposition for combinatorial synthesis of a material.

Figure 2 is a schematic view illustrating use of controlled movement of a mask to generate a linear thickness profile for two chemical components.

Figures 3A, 3B and 3C illustrate use of deposition and interdiffusion to promote formation of metal-inorganic compounds.

5 Figure 4 is a schematic view illustrating use of CVD for combinatorial synthesis of a material.

Figures 5A and 5B are graphical views of possible deposition patterns generated using the apparatus of Figure 4 or Figure 6A.

Figures 6A and 6B are schematic views illustrating use of a movable 10 slot window or slit to control growth rate in a linear ramp for in situ formation of a compound $A_u B_{1-u}$.

Figures 7A, 7B, 8 and 9 are schematic views illustrating use of two or three nuzzles to generate a linear deposition profile for in situ formation of a compound A_uB_{1-u}. or $A_uB_vC_{1-u-v}$.

15 Figures 10A/10B and 11A/11B are pairs including a schematic view and a graphical view illustrating two embodiment of the invention, using one and two sources, respectively.

Figures 12, 13 and 14 are schematic views of other embodiments.

Figure 15 is a flow chart illustrating practice of the invention.

20 Description of Best Modes of the Invention

Figure 1 schematically illustrates an embodiment of the invention that uses ion beam sputtering as part of a combinatorial synthesis of a desired material. A substrate 11 is positioned inside an ultra-high vacuum chamber 13, preferably having a pressure level of 10^{-9} Torr or lower, using a cryogenic 25 pump, ion pump or other pump means (not shown) suitable for metal alloy deposition. Preferably, a load-and-lock chamber 15 is provided to facilitate sample exchange without breaking the vacuum of the main chamber 13. A sputtering target 17 receives an ion beam 19, provided by an ion source 21, and produces deposition or precursor particles DP having a desired chemical 30 composition. A portion of the precursor particles DP is received at, and deposited on, an exposed surface of the substrate 11. Growth rate of the deposited layer on the substrate 11 can be controlled, within a high precision range, by the power applied to the ion beam sputtering source 21 and by the

angular orientation of the target 17 to the ion source and to the substrate 11. Real time control can be implemented using real time monitoring of, and a negative feedback loop to control, ion beam current.

Some advantages of an ion beam sputter approach are: (1) inter-diffusion between metals occurs at lower temperatures and at higher diffusion rates, in comparison with inter-diffusion of metal-inorganic compounds, where temperatures above 1000 ^{o}C are often required; (2) most metal targets are already available as precursor sources; and (3) more than one ion beam, each with a different precursor source material, can be provided in order to form compounds including lithium, sodium, potassium, rubidium, cesium, berkelium, magnesium, calcium, strontium, barium, boron, aluminum, carbon, silicon, nitrogen, phosphorous, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine, bromine, iodines and similar compounds following inter-diffusion of the deposited constituents.

A carousel 25 holds and presents any one of a number N of metal or similar targets 17 for an ion beam, to produce a stream 19 of precursor particles DP that are received by the substrate 11, where N can be 1-50, or any other reasonable number. A second reactive chemical source 27 is optionally located near the substrate 11 and is oriented to provide a beam 29 of chemical particles to act as a reactive agent for in situ formation of a compound containing at least one different chemical element. After precursor deposition and interdiffusion processes are carried out, the precursors are reacted with each other and/or with any other compounds containing elements from the lithium, berkelium, boron, carbon, nitrogen, oxygen and/or fluoride columns of the Periodic Table, or other similar compounds, to form the desired final products.

The reactive chemical source 27 can be replaced or supplemented by a source 28 of a low reactivity beam, such as Ne or Ar particles, to etch the substrate or to enhance the energy locally on the substrate, useful in creating high quality thin films. Metal films have been prepared using a first ion gun for target sputtering and a second ion gun for assisting controlled growth of a thin film on a substrate. A movable mask 31 or sequence of movable masks, controlled by a mask movement device 33, covers different portions of the

substrate surface at different times to perform layer-by-layer precursor deposition. A heating element 35 (optional) located adjacent to the substrate 11, helps to perform and control precursor interdiffusion after the initial deposition.

5 As an alternative, to use of an ion beam to deposit precursor particles DP on a substrate, the ion beam 21 may be replaced by an irradiation unit 23 or by a high temperature (T = 600-1500 ^{0}C) heating unit 24 that acts upon the target 17 to cause evaporation of precursor particles from the target surface. A selected fraction of the evaporated particles DP are then caused to travel
10 toward and to deposit on the substrate 11 by a particle direction control mechanism (not shown explicitly in Figure 1).

Figure 2 schematically illustrates a deposition procedure for combinatorially synthesizing an alloy, A_uB_{1-u} , on a substrate 41 with the index u varying continuously or in small increments between 0 and 1. A mask
15 43, which is movable from left to right and/or from right to left by a mask stepper motor or other suitable movement device 44, is located between the substrate 41 and one or more chemical component sources 45. The source 45 provides a flux of the chemical constituent A, or a flux of the chemical constituent B. Each source 45 of a chemical constituent, A or B, can be located
20 at the same location, or two or more sources, 45 and 46, may be located at different locations relative to the substrate 41. In a preferred approach, each source 45 is sequentially moved into a beam focus position, and the ion beam or other beam is activated to provide a stream of source particles that preferably move in the general direction of the substrate 41.

25 In one approach, the mask 43 is moved from left to right and only the first beam-activated source provides a (first) stream of deposition particles in a first time interval. In a second time interval, the second beam-activated source provides a (second) stream of precursor particles. Because the first and second particle streams are provided within different time intervals, this
30 approach produces a multilayer deposition on the substrate.

As the mask 43 moves from the left toward the right, the portion LES of the substrate to the left of the left end LEM of the mask 43 is exposed, for varying amounts of time, with portions of the substrate 41 near the left end

LES being exposed for longer times than portions of the substrate near the right end RES of the substrate. This produces a heavier deposit of precursor particles at the left end LES of the substrate 41. The number of precursor particles from the source 45 deposited per unit area decreases monotonically as one moves from the left end LES toward the right end RES of the substrate; and the number of precursor particles deposited per unit area increases monotonically as one moves from the left end LES to the right end RES of the substrate. If, instead, the mask 43 moves from the right toward the left, the number of precursor particles deposited on the substrate 41 decreases monotonically as one moves from the right end RES toward the left end LES.

As a first alternative, the mask 43 can be held fixed and the substrate 41 can be moved from left to right and/or from right to left by a substrate stepper motor or similar movement device 44 to provide a multilayer deposition. As a second alternative, the substrate 41 and the mask 43 can each be moved, independently and at different rates, from left to right and/or from right to left to provide a multilayer deposition.

Preferably, the mask length ML is at least equal to the substrate length SL and the right end REM of the mask 43 begins at a point above the left end LES of the substrate and moves rightward monotonically until the left end LEM of the mask is above the right end RES of the substrate. The amounts of time, $\Delta t(x;A)$ and $\Delta t(x;B)$, that a particular location (x) on the substrate is exposed to particle flux from a source 45 must be coordinated in order to deposit appropriate relative amounts of the A and B particles. If the mask length ML and the substrate length SL are equal, the total amount of time

$$\Delta t(tot) = \Delta t(x;A) + \Delta t(x;B) \quad (1)$$

any location (x) on the substrate is exposed will be the same, no matter how the mask is moved from left (where REM and LES correspond) to right (where LEM and RES correspond).

The mask may be moved at a linear rate, thus producing a linearly varying alloy composition $A_{u(x)}B_{1-u(x)}$, with $u(x) = a \cdot x + b$ where x is a location coordinate, measured from the left end LES of the substrate 41, and a and b are real numbers related to the speed of movement of the mask from left to right. Alternatively, the mask 43 may be moved at a non-constant rate

from left to right, and the chemical composition, u(x) versus 1-u(x), of the alloy $A_{u(x)}B_{1-u(x)}$ will vary nonlinearly as a function of the location coordinate x. The composition u(x) versus 1-u(x) for the relative amounts of A and B components is determined by a prescription such as

5 $$w(x) = \int \chi[x - s(t)]dt / \Delta t(tot), \quad (2)$$

where s(t) ($0 \leq s(t) \leq SL$; $0 \leq t \leq \Delta t(tot)$) is the x coordinate of the right end REM of the mask 43 at any time t, measured from the left end of the substrate LES, $\chi(u)$ is a characteristic function satisfying

$$\chi(u) = 0 \ (u < 0)$$

10 $$= 1 \ (u > 0), \quad (3)$$

and the integral extends over the time interval $0 \leq t \leq \Delta t(tot)$.

Figures 3A, 3B and 3C illustrate deposition, interdiffusion and chemical conversion processes. In Figure 3A, the precursors DP are incident on and received at the substrate 11, forming one or more layers, optionally with a
15 concentration gradient. In Figure 3B, the substrate 11 is subjected to interdiffusion and/or annealing of the precursors DP deposited in Figure 3A. This produces a further redistribution of the precursors DP. In Figure 3C, the interdiffused precursors of Figure 3B are combined with ion beam sputter-assisted carbon, oxygen, nitrogen, carbon, halogen or other selected
20 compounds to provide carbidized, nitridized, oxidized, halogenated or other desired compounds on the substrate 11, using the reactive chemical source 27 of Figure 1 or another source.

Figure 4 schematically illustrates combinatorial synthesis of a compound on a thermally controlled substrate 51 using chemical vapor deposition (CVD)
25 to provide in situ or multilayer deposition for combinatorial synthesis. A carrier gas source 52 provides a carrier gas (preferably inert) that is passed through a selected number of one or more precursor evaporators or "bubblers", 53A, 53B and 53C, that provide the active vapor substance(s), 54A, 54B and 54C, for CVD, either simultaneously or sequentially.
30 Optionally, the active vapors, 54A, 54B and 54C, pass through corresponding flow controllers, 55A, 55B and 55C, that determine the active vapor flow rates of the respective vapors at any given time. The active vapors enter a pre-deposition chamber 56 and are moved axially along the chamber by a push gas

provided by a push gas source 57. Flux f_{54S} of the active vapor mix (S = A, B and/or C) is stopped by, or is allowed to pass beyond, a movable mask or shutter or aperture 58 whose transverse location, given by s = s(t), is controlled by a mask stepper motor or other mask movement device 59 that
5 moves the mask transversely (not necessarily perpendicularly), relative to a line of sight extending from the source (predeposition chamber 56) toward the substrate 51, across an exposed surface of the substrate 51. As a first alternative, the mask 58 is fixed in location and a substrate stepper motor or other substrate movement device 59 moves the substrate 51 transversely. As a
10 second alternative, the mask movement device 59 and substrate movement device 60 independently move the substrate 51 and the mask 58 transversely at the same time.

By separately controlling the precursor evaporators, 53A, 53B and 53C, and the corresponding flow controllers, 55A, 55B and 55C, the mix of active
15 vapors 54S that issues from the pre-deposition chamber 56 can be closely controlled as a function of time. By controlling the mask location, x = s(t), the relative amounts of the vapors 54S deposited on different regions of the substrate 51 can be varied independently from point to point. For example, the relative fraction f(x;54S) ($0 \le x \le L$) of the active vapor 54S (S = A, B, C)
20 deposited on the substrate 51 can be caused to vary linearly with lateral distance coordinate x from the left end of the substrate as

$$f(x;54A) = a1 + b1 \cdot x, \quad (4A)$$

$$f(x;54B) = a2 + b2 \cdot x, \quad (4B)$$

$$f(x;54C) = a3 + b3 \cdot x, \quad (4C)$$

25 where the magnitudes and signums of the coefficients a1, a2, a3, b1, b2 and b3 are independently chosen, subject to the constraint

$$0 \le f(x;54A) + f(x;54B) + f(x;54C) \le 1 \ (0 \le x \le L). \quad (5)$$

For example, the coefficients b1 and b2 may be positive and negative, respectively, so that the relative or absolute concentrations of the vapors 54A
30 and 54B are increasing and decreasing, respectively, as the coordinate x increases, as illustrated in Figure 5A. The linear changes in concentration with the coordinate x in Eqs. (4A)-(4C) may be replaced by nonlinear changes in one or more of the quantities f(x;54S) by appropriate control of the flow

controllers 55A-55C and of the location of the movable mask 58. One possible result of such nonlinear deposition is shown in Figure 5B. If a uniform concentration of an active vapor 54S is desired, the substrate 51 can be rotated during the time(s) this vapor is deposited. One or both of the concentrations of
5 the deposited vapors 54A and 54B may be linear or may be nonlinear. Combinatorial deposition of two or more vapors 54S occurs by CVD, either one layer at a time or simultaneously, producing a multilayer or an in situ deposition, in the apparatus shown in Figure 4.

The source of each active vapor 54S (S = A, B, C) can be (1) a solid or
10 liquid substance packed into the corresponding evaporator 53S, (2) a solid powder or liquid dissolved into an organic solvent or (3) any other source that will provide a vapor substance of the desired precursor when heated to a temperature in a selected temperature range. Where source (1) is present, vaporizer temperature and flow rate of the carrier gas can be used to control
15 the rate of delivery of a precursor. Where source (2) is present, the rate of delivery of a precursor is controlled by vaporizer temperature, carrier gas flow rate and pumping rate of the precursor solution into the corresponding vaporizer unit, such as 53A.

Combinatorial deposition on a substrate 61 can also be performed by in
20 situ co-deposition, using the apparatus shown in Figures 6A and 6B. A precursor vapor flux f_{64S} (S = A, B, C), which may include a mixture of vapors at any given time, is incident upon two or more spaced apart movable masks, 68-1 and 68-2, in Figure 6A that together form one or more movable slots or apertures 67, as shown in Figure 6B. The relative mix of vapors 64S
25 may vary from one time to another time, and the slot(s) 67 need not move at a uniform rate across the exposed surface of the substrate 61. Further, the width $w_{slot}(t)$ of a slot or aperture may vary according to a selected function with time t so that the slot aperture is wider at some times than at other times and may close altogether at one or more times. If the slot width $w_{slot}(t)$ is fixed
30 and the rate v(t) at which the slot moves across the exposed surface of the substrate 61 is uniform, in situ co-deposition of two vapors with constant concentration gradients can be obtained, as illustrated in Figure 5A, by varying the relative concentrations of the vapors 64A and 64B with time. This

approach will produce a chemical mixture of $(64A)_{u(x)}(64B)_{(1-u(x))}$ as x varies from 0 to L across the exposed surface of the substrate 61, with the index u(x) increasing or decreasing, linearly or nonlinearly, with increasing x. The concentration fractions of the two or more components, 64A and 64B,
5 may also be arranged to vary nonlinearly, as illustrated in Figure 5B.

As a first alternative, the masks 68-1 and 68-2 are fixed in location and a substrate stepper motor or other substrate movement device 70 moves the substrate 51 transversely. As a second alternative, the mask movement devices 69-1 and 69-2 and the substrate movement device 70 independently move the
10 substrate 51 and the masks, 58-1 and 58-2, transversely relative to the direction of the flux $\mathbf{f}_{64S}$.

One advantage of the in situ co-deposition process illustrated in Figures 6A and 6B, over the multilayer process, illustrated in Figure 3, is that the post-anneal procedure may be eliminated or minimized in the co-deposition
15 process. Another advantage is that the temperature at which a post-anneal process, if any, is performed can be reduced. The in situ co-deposition process, illustrated in Figures 6A and 6B, can also be applied to co-sputtering, to co-evaporation, to co-ablation (e.g., using a laser ablating source), and to molecular beam epitaxy (MBE). Among these approaches, ion beam sputtering
20 and MBE are especially attractive, because the deposition rates for these approaches can be more closely controlled through monitoring with a negative feedback loop.

Figure 7A illustrates another co-deposition approach, using two or more nuzzle slits, 75A and 75B, located at the exits of two vapor source
25 chambers, 73A and 73B, respectively. Vapors, 74A and 74B, that exit through the nuzzle slits, 75A and 75B, may be arranged to vary independently in a linear or nonlinear manner with respective angles, θA and θB, measured relative to a reference line RR such as shown in Figure 7A. Figure 7B schematically illustrates a nuzzle slit, in which a throat associated with the slit
30 is shaped to produce a desired relative flow rate $\psi(\theta)$ that varies in a controllable manner with an angle θ, measured relative to a reference line. An example of a nuzzle slit is a garden hose nozzle, in which movement of a small flow obstruction changes the spread of water that issues from the hose.

With reference to Figure 8, assume that the nuzzle slits, 75S (S = A, B), are located at a distance D from the exposed planar surface of the substrate and are designed to provide flow rates, $\psi(\theta A)$ and $\psi(\theta B)$, given by

$$(d/dx)\ \psi(\theta A)\cdot\sin(\theta A) = -\{\sin^2\theta A/D\}\ (d/d\theta A)\ \psi(\theta A)\cdot\sin(\theta A)$$

5 $$= b1 = \text{constant}, \qquad (6A)$$

$$(d/dx)\ \psi(\theta B)\cdot\sin(\theta B) = -\{\sin^2\theta B/D\}\ (d/d\theta B)\ \psi(\theta B)\cdot\sin(\theta B)$$

$$= b2 = \text{constant}, \qquad (6B)$$

where b1 and b2 are selected constant coefficients. The deposition rates, g(x;74A) and g(x;74B), of the respective vapors, 74A and 74B, on the

10 substrate 71 will then vary linearly according to

$$g(x;74A) = a1 + b1\cdot x \qquad (7A)$$

$$g(x;74B) = a2 + b2\cdot x \qquad (7B)$$

where a1 and a2 are appropriate constant coefficients. This will provide a linearly varying co-deposition mix on the exposed surface of the substrate 71

15 of $(74A)_{(x/L)}(74B)_{(1-x/L)}$ as the coordinate x varies from 0 to x/L. An ultrasonic nuzzle can be used for the apparatus shown in Figures 7A and 7B.

A CVD approach is suitable where the precursor vapors can be pressurized and deposited according to the linear patterns in Eqs. (7A) and (7B). However, the nuzzle approach may be difficult to apply using ion beam

20 sputtering, co-sputtering, co-evaporation, co-ablation and MBE, because the precursor particles used in these processes are generated by point sources and the normal deposition profile on a substrate is Gaussian, rather than varying linearly with the coordinate x. A magnetron sputtering gun can be constructed to provide a nuzzle configuration. Ion beam deposition, for example, as

25 developed by SKION Corporation in Hoboken, New Jersey, can also be used with this approach to deposit C, Si, Ni, Cu and other metals and alloys, using an electrical field to control the initial velocity of the ion that issues from the ion beam sputtering source.

Two or more nuzzle slits and corresponding vapor sources can also be

30 arranged in a non-parallel array, as illustrated in Figure 9, to provide a two-dimensional relative concentration fraction f(x,y) of the three vapors, 84A, 84B and 84C, given by

$$f(x,y;A;B;C) = (84A)_{h(x,y;A)}(84B)_{h(x,y;B)}(84C)_{h(x,y;C)}\,, \qquad (8)$$

where h(x,y;A), h(x,y;B) and h(x,y;C) are two-dimensional distributions that are determined by the designs of the nuzzle slits 85A, 85B and 85C, respectively. Three nuzzle slits may be arranged at the vertices of, or along three sides of, a general triangle, not necessarily isosceles or equilateral.

5 Figures 10A and 10B illustrate, schematically and graphically, an embodiment of the invention. A chemical component source 91 provides a chemical component, denoted A, that is to be deposited on a substrate 99. In a preferred embodiment, the source 91 provides a flux $\mathbf{f}_A$ of the chemical component A that is approximately uniform in a selected coordinate direction
10 z. If the flux $\mathbf{f}_A$ is not approximately uniform in a plane Π perpendicular to the z-direction, but is known as a function of the Cartesian coordinates, x and y, measured in the plane Π, the details of this embodiment can be varied to achieve substantially the same result. Alternatively, a portion of the flux $\mathbf{f}_A$ from the source can be masked to provide an approximately uniform flux
15 through the mask aperture(s).

In this embodiment, a mask 93 having a sequence of spaced apart apertures 95-i (i = 1, 2, 3, 4, ...) with aperture widths di is positioned in an xy-plane, transverse to the z-direction of the flux $\mathbf{f}_A$ from the source 91 and spaced apart from the source by a selected distance s1. The mask 93, in turn,
20 is spaced apart from the substrate 99 by a distance s2. The space 97 between the mask 93 and the substrate 99 is either evacuated to a high vacuum or is filled with a selected gas at a selected low density ρ97.

The aperture 95-i has an aperture width di in a selected x-direction, and two adjacent apertures, such as 95-2 and 95-3, have a selected aperture spacing
25 distance D(2,3). In one version of this embodiment, the aperture spacings D(i,i+1) are uniform. In another version of this embodiment, the aperture spacings D(i,i+1) are variable according to the substrate deposition pattern desired. If a single aperture 95-i receives the flux $\mathbf{f}_A$ from the source 91, the precursor particles A passed through the mask 93 at the aperture 95-i will
30 arrive at and deposit on the substrate 99 in an approximately Gaussian or normally distributed concentration pattern C(x;i), as a function of the transverse coordinate x, as illustrated in Figure 10B. However, if a collection of three or more apertures 95-i is provided with suitable aperture widths di

and suitably chosen aperture spacings D(i,i+1), the sum of these apertures will produce a concentration envelope C(x) (or C(x,y)) of selected shape at the substrate shown in Figure 10B. The aperture widths and aperture spacings shown in Figure 10A are relatively large for display purposes. In practice,
5 these dimensions would be relatively small, probably in the range 0.01-1 mm, or larger or smaller where suitable.

The concentration envelope C(x) may be chosen to be linear,

$$C(x) = a + b \cdot x, \quad (9A)$$

or to be linear-symmetric,

10 $$C(x) = a + b|x|, \quad (9B)$$

or to obey a more general power law

$$C(x) = a' + b' \cdot |x|^q \quad (q \neq 0), \quad (9C)$$

where a, b, a', b' and q are selected real numbers. The particular concentration envelope C(x) (or C(x,y)) produced will depend upon the
15 parameters di (aperture widths), D(i,i+1) (aperture spacings), s1 (source-to-mask spacing), s2 (mask to substrate spacing), the gas, if any, and its density ρ97 in the space 101, the range of flux $\mathbf{f}_A$ of the chemical component A produced in the z-direction by the source 91, and other parameters describing the source.

20 The concentration envelope C(x) may be modeled as a faltung integral that takes into account the aperture widths and aperture spacings chosen for the mask 93, namely

$$C(x) = \int F(x')\, Ap(x')\, H(x-x')\, dx', \quad (10)$$

where F(x') represents the A particle flux $\mathbf{f}_A$ and Ap(x') is a mask
25 characteristic function (= 1 where a mask aperture is present; = 0 where no mask aperture is present). The presence of the faltung function H(x-x') in the integrand in Eq. (10) accounts for the fact that an A component particle that passes through the mask at a transverse location coordinate x' may become deposited on the substrate at another transverse location coordinate x, due to
30 scattering, initial velocity vector of the particle and other interference phenomena. A suitable approximation for a faltung function for a single aperture is

$$H(w) = (2\pi\sigma^2)^{-1/2} \exp\{-w^2/2\sigma^2\}, \quad (11)$$

where the parameter σ (having the units of length) characterizes the transverse spread of flux through a single aperture. Invoking the superposition principle, this faltung function, with possibly a different σ parameter, may be used for each aperture in the mask.

5 The concentration envelope C(x) shown in Figure 10B may be reproduced in one direction only, if each aperture 95-i in the mask is uniform in a second transverse coordinate direction y to produce a concentration envelope C(x,y) that depends non-trivially on each of the coordinates x and y.

Each chemical component A, B, ... to be deposited on the substrate may 10 have a different mask with a different aperture pattern and may have different separation distances, s1 and s2. For example, two chemical components, A and B, may (but need not) use the same mask and/or the same separation distances, s1 and s2. Figure 11A illustrates use of two sources, 101A and 101B, each with its own component mask, 103A and 103B, which are optionally part of 15 an overall mask 103, positioned between the two sources and a substrate 109. The net effect of deposit of components A and B on the substrate 109, either simultaneously or sequentially, is the concentration envelope C(x;A;B), which is a sum of the concentration envelopes C(x;A) and C(x;B) shown in Figure 11B.

20 As a first alternative for multi-component deposition, two or more chemical components, A, B, ..., each with its own source 111A, 111B, etc. can be simultaneously deposited on a single substrate 119, as illustrated in Figure 12. A single mask 113, having suitable aperture widths and aperture spacings (not shown explicitly in Figure 12), is positioned transverse to a direct path or 25 line of sight from at least one source 111A, 111B, etc. to the common substrate 119. The first source 111A and mask 113 produce a first concentration envelope C(x;A) on the substrate 119; and the second source 111B and mask 113 produce a second concentration envelope C(x;B) on the substrate 119. The sum of these concentration envelopes,

30 $$f(x;A;B) = [A]\cdot C(x;A) + [B]\cdot C(x;B), \qquad (12)$$

defines the total concentration of the chemical components, A and B, deposited on the substrate. Subsequent processing of the coated substrate, for example,

by thermally driven diffusion, may produce a concentration pattern that differs from the initial total concentration envelope f(x;A;B).

As a second alternative, illustrated in Figure 13, each of two or more sources, 121A, 121B and 121C, arranged adjacent to and above two or more sides of a polygon (a triangle in Figure 13) may have its own mask, 123A, 123B and 123C, respectively, and each source mask combination will produce a different two-dimensional concentration envelope, C1(x,y;A) and C(x,y;B) and C(x,y;C), on a common substrate 129 that is positioned adjacent to the sources, with the masks being located between the sources and the substrate. In this embodiment, each of the masks can be separately designed, and thus optimized, for the particular concentration envelope desired for that chemical component.

Figure 14 illustrates an alternative arrangement of the system in Figure 13, in which sources, 131A, 131B and 131C, are located adjacent to and above two or more vertices of a polygon, and masks, 133A, 133B and 133C, are located between a common substrate 139 and the respective sources.

Figure 15 is a flow chart generally illustrating the processes used to practice the invention. In a process 141, first and second fluxes of respective first and second chemical components are directed toward a substrate. In a process 143, a mask, having at least one opening (e.g., an aperture or an edge) is provided across the flux field that allows first and second selected portions of the respective first and second chemical components to be deposited on selected first and second portions of the substrate surface. In a process 145 (optional), the mask is moved transversely to at least one of the first and second flux directions at a selected movement rate, to provide a desired concentration of the first and second components on the substrate surface.

What is claimed is:

1. A system for depositing on a substrate a mixture of selected first and second chemical components having concentrations of the first and second components that vary controllably with a location coordinate measured along a surface of the substrate, the system comprising:

first and second sources of respective first and second chemical components, spaced apart from the substrate, with the first source and the second source providing first and second fluxes, respectively, of the first and second components;

a mask, having a first end and a second end, having a mask opening and being positioned between the substrate and the first and second sources, that is movable in a direction transverse to at least one of a first line of sight extending from the first source to the substrate and a second line of sight extending from the second source to the substrate; and

a motor that moves the mask, from a first location, in which at least a portion of the substrate is visible through the opening from the first source, to a second location in which the substrate is not visible from the first source and that moves the mask, from a third location, in which the substrate is not visible from the second source, to a fourth location in which at least a portion of the substrate is visible through the opening from the second source.

2. The system of claim 1, wherein said first and second sources are positioned relative to said substrate so that, when said mask is located at a selected fifth location, no portion of said substrate is visible from said first source and no portion of said substrate is visible from said second source.

3. The system of claim 1, wherein at least one of said first source, said second source, said mask and said motor is configured to provide a mixture of said chemical components on said substrate surface in which said concentration of at least one of said first chemical component and said second chemical component varies linearly with a location coordinate measured along said substrate surface.

4. The system of claim 1, wherein at least one of said first source, said second source, said mask and said motor is configured to provide a mixture of said chemical components on said substrate surface in which said concentration of at least one of said first chemical component and said second chemical component varies nonlinearly with a location coordinate measured along said substrate surface.

5. The system of claim 1, wherein at least one of said first source and said second source is configured to provide a corresponding chemical component flux that varies with time according to a selected function of time.

6. The system of claim 1, wherein said motor moves said mask at a uniform rate with respect to time in said direction transverse to at least one of said first line of sight and said second line of sight.

7. The system of claim 1, wherein said motor moves said mask at a non-uniform rate with respect to time in said direction transverse to at least one of said first line of sight and said second line of sight.

8. The system of claim 1, wherein at least one of said first source and said second source is drawn from a group of chemical component sources consisting of an ion beam sputtering source, a sputtering source, a laser ablating source, a molecular beam source, a chemical vapor deposition source and an evaporative source.

9. The system of claim 1, wherein at least one of said first and second chemical components includes at least one chemical element drawn from a group of chemical elements consisting of lithium, sodium, potassium, rubidium, cesium, berkelium, magnesium, calcium, strontium, barium, boron, aluminum, gallium, carbon, silicon, germanium, nitrogen, phosphorous, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine, bromine and iodine.

10. The system of claim 1, wherein said opening is an aperture having an aperture width that is fixed at a selected value.

11. The system of claim 1, wherein said opening is an aperture having an aperture width that varies with time in a selected manner.

12. The system of claim 1, wherein said opening is a region adjacent to one of said first end and said second end of said mask.

13. A system for depositing on a substrate a mixture of selected first and second chemical components having concentrations of the first and second components that vary controllably with a location coordinate measured along a surface of the substrate, the system comprising:

first and second sources of the respective first and second chemical components, spaced apart from the substrate, with the first source and the second source providing first and second fluxes, respectively, of the first and second components;

first and second nuzzle slits, associated with the first and second sources, respectively, that direct the first and second fluxes of the first and second components toward the substrate in selected first and second flux patterns, respectively, in a selected coordinate direction.

14. The system of claim 13, wherein said first nuzzle slit directs said first flux in said first pattern in said first coordinate direction and in a selected third pattern in a selected second coordinate direction.

15. The system of claim 13, wherein said first and second nuzzle slits direct said first flux and second fluxes in said first and second flux patterns, respectively, and in selected third and fourth patterns, respectively, in a selected second coordinate direction.

16. The system of claim 13, wherein at least one of said first source and said second source is drawn from a group of sources consisting of an ion beam sputtering source and a chemical vapor deposition source.

17. The system of claim 13, wherein at least one of said first and second chemical components includes at least one chemical element drawn from a group of chemical elements consisting of lithium, sodium, potassium, rubidium, cesium, berkelium, magnesium, calcium, strontium, barium, boron, aluminum, gallium, carbon, silicon, germanium, nitrogen, phosphorous, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine, bromine and iodine.

18. A system for depositing on a substrate a selected chemical component having a concentration that varies controllably with a location coordinate measured along a surface of the substrate, the system comprising:

a source of a selected chemical component, spaced apart from the substrate by a selected distance, s1 + s2, where the source provides a chemical component flux in a flux direction extending from the source toward the substrate;

a mask, positioned between the source and the substrate at a selected distance s1 from the source, having two or more apertures with selected aperture widths and selected aperture spacings in a coordinate direction x that is transverse to the flux direction,

where the aperture widths and the aperture spacings are selected so that a concentration envelope C(x), representing the concentration of the chemical component deposited on the substrate as a function of the coordinate x, is substantially equal to a selected function f(x).

19. The system of claim 18, wherein said function f(x) is drawn from the group of functions consisting of: $f(x) = a + b\cdot x$, $f(x) = a + b|x|$ and $f(x) = a' + b'\cdot(x)^q$, where a, b, a', b' and q are selected real numbers.

20. The system of claim 18, wherein said source is drawn from a group of chemical component sources consisting of an ion beam sputtering source, a sputtering source, a laser ablating source, a molecular beam source, a chemical vapor deposition source and an evaporative source.

21. The system of claim 18, wherein at least one of said first and second chemical components includes at least one chemical element drawn from a group of chemical elements consisting of lithium, sodium, potassium, rubidium, cesium, berkelium, magnesium, calcium, strontium, barium, boron, aluminum, gallium, carbon, silicon, germanium, nitrogen, phosphorous, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine, bromine and iodine.

22. A system for depositing on a substrate a selected chemical component having a concentration that varies controllably with a location coordinate measured along a surface of the substrate, the system comprising:

a target surface that includes selected precursor particles;

an ion beam source, directed at the target surface, to provide a flux of precursor particles in response to collision of the ion beam with the target surface;

direction control means for directing at least a portion of the precursor particles flux toward a surface of a substrate;

a mask, positioned between the target surface and the substrate surface and having at least one aperture of selected aperture shape and diameter that permits at least a portion of the precursor particle flux to reach at least a portion of the substrate surface, where the aperture shape and diameter are selected to provide a selected non-uniform distribution of precursor particles that are received by the substrate surface.

23. The system of claim 22, wherein said source is configured to provide a corresponding chemical component flux that varies with time according to a selected function of time.

24. The system of claim 22, further comprising:

a motor that moves the mask, from a first location, in which at least a portion of the substrate is visible from said source, to a second location in which no portion of the substrate is visible from said source.

25. The system of claim 24, wherein at least one of said source, said mask and said motor is configured to provide a mixture of said chemical components on said substrate surface in which said concentration of at least one of said first chemical component and said second chemical component varies linearly with a location coordinate measured along said substrate surface.

26. The system of claim 24, wherein at least one of said source, said mask and said motor is configured to provide a mixture of said chemical components on said substrate surface in which said concentration of at least one of said first chemical component and said second chemical component varies nonlinearly with a location coordinate measured along said substrate surface.

27. The system of claim 24, wherein said motor moves said mask at a uniform rate with respect to time in said direction transverse to at least one of said first line of sight and said second line of sight.

28. The system of claim 24, wherein said motor moves said mask at a non-uniform rate with respect to time in said direction transverse to at least one of said first line of sight and said second line of sight.

29. The system of claim 22, further comprising:

a source of a selected compound, containing an element drawn from a group of elements consisting of lithium, sodium, potassium, rubidium, cesium, berkelium, magnesium, calcium, strontium, barium, boron, aluminum, gallium, carbon, silicon, germanium, nitrogen, phosphorous, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine, bromine and iodine, located

adjacent to said substrate, and particle means for producing particles of the selected compound; and

second direction control means for directing at least a portion of the selected compound particles toward said substrate surface.

30. A method for depositing on a substrate surface a mixture of selected first and second chemical components having a relative concentration of the first and second components that varies controllably with a location coordinate, the method comprising:

directing first and second fluxes of first and second chemical components, respectively, toward at least one surface of a substrate; and

providing a mask, having a mask opening, that allows a first selected portion of the first chemical component flux to be deposited on the substrate, that prevents a second selected portion of the first chemical component flux from being deposited on the substrate, that allows a first selected portion of the second chemical component flux to be deposited on the substrate, and that prevents a second selected portion of the second chemical component flux from being deposited on the substrate, where the mask has at least one opening that is chosen to allow deposit of at least one of the first and second chemical components on the substrate according to a selected variable concentration.

31. The method of claim 30, further comprising the step of moving said mask at a selected movement rate in a direction that is transverse to a selected line of sight that is approximately parallel to at least one of said first chemical component flux and said second chemical component flux.

32. The method of claim 31, further comprising configuring at least one of said first source, said second source, said mask and said mask movement rate to provide a mixture of said chemical components on said substrate surface in which said concentration of at least one of said first chemical component and said second chemical component varies linearly with a location coordinate measured along said substrate surface.

33. The method of claim 31, further comprising configuring at least one of said first source, said second source, said mask and said mask movement rate to provide a mixture of said chemical components on said substrate surface in which said concentration of at least one of said first chemical component and said second chemical component varies nonlinearly with a location coordinate measured along said substrate surface.

34. The method of claim 30, further comprising configuring at least one of said first source and said second source to provide a corresponding chemical component flux that varies with time according to a selected function of time.

35. The method of claim 30, further comprising providing at least one of said first chemical component and said second chemical component from a group of chemical component sources consisting of an ion beam sputtering source, a sputtering source, a laser ablating source, a molecular beam source, a chemical vapor deposition source and an evaporative source.

36. The method of claim 30, further comprising choosing at least one of said first and second chemical components to include at least one chemical element drawn from a group of chemical elements consisting of lithium, sodium, potassium, rubidium, cesium, berkelium, magnesium, calcium, strontium, barium, boron, aluminum, gallium, carbon, silicon, germanium, nitrogen, phosphorous, arsenic, oxygen, sulfur, selenium, tellurium, fluorine, chlorine, bromine and iodine.

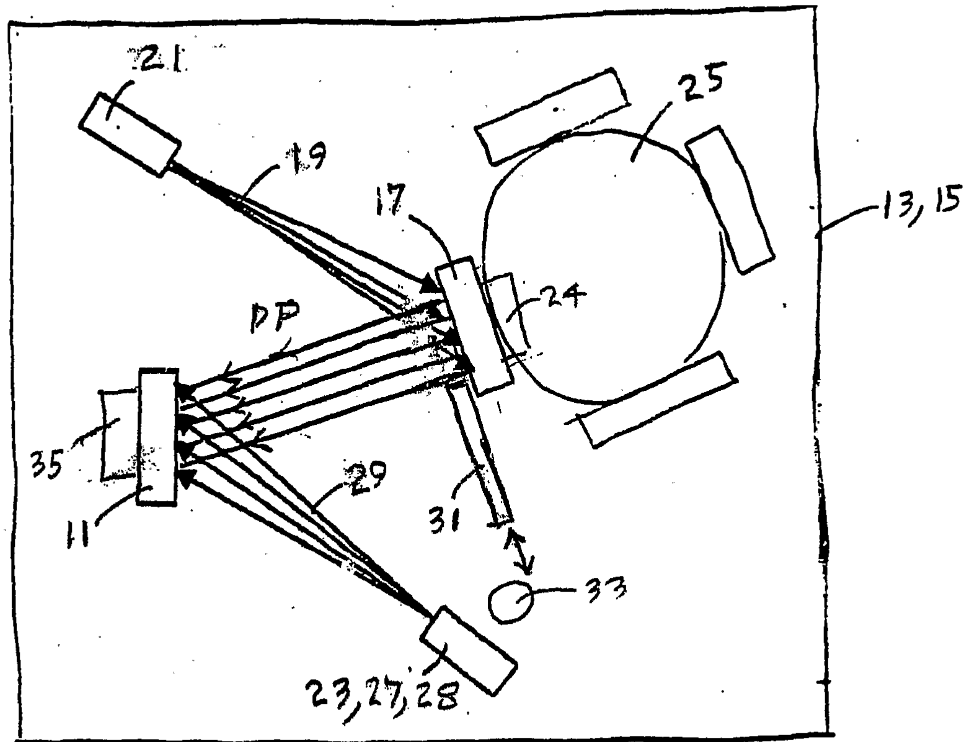


FIG. 1

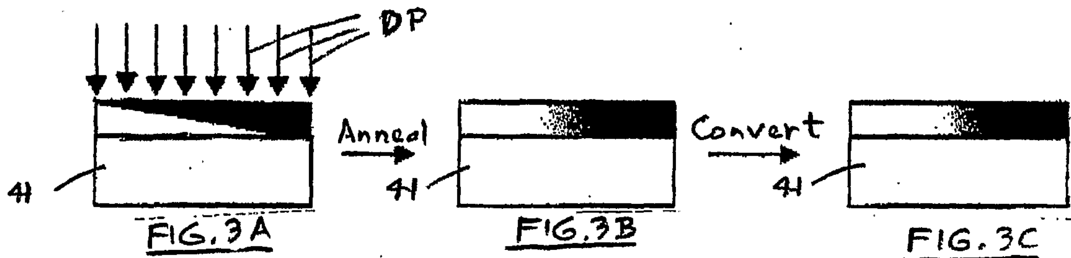
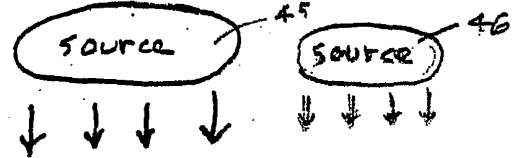


FIG. 3A FIG. 3B FIG. 3C



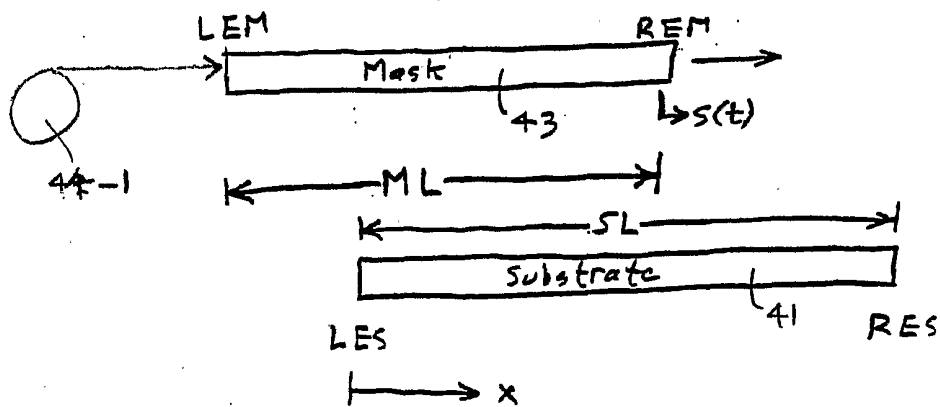


FIG. 2

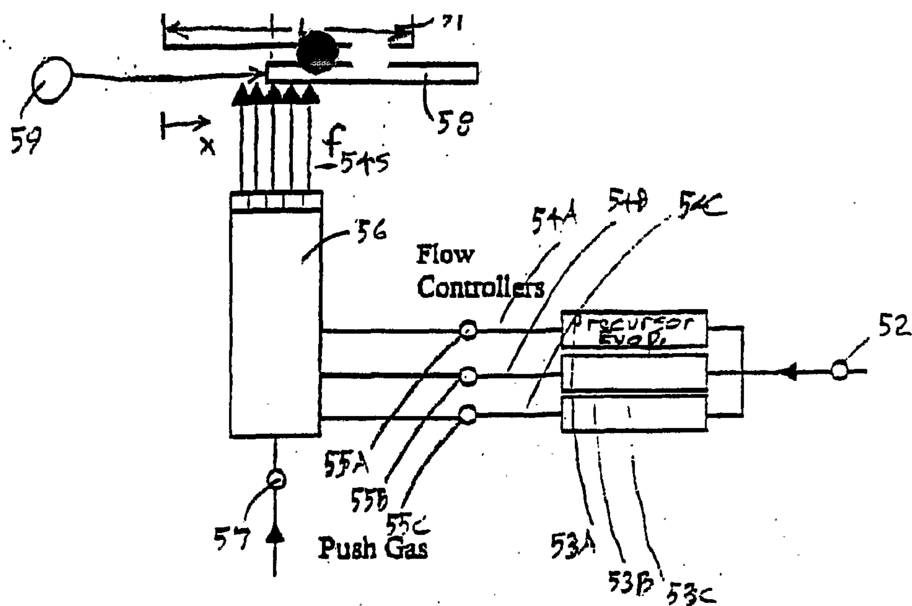


FIG.4

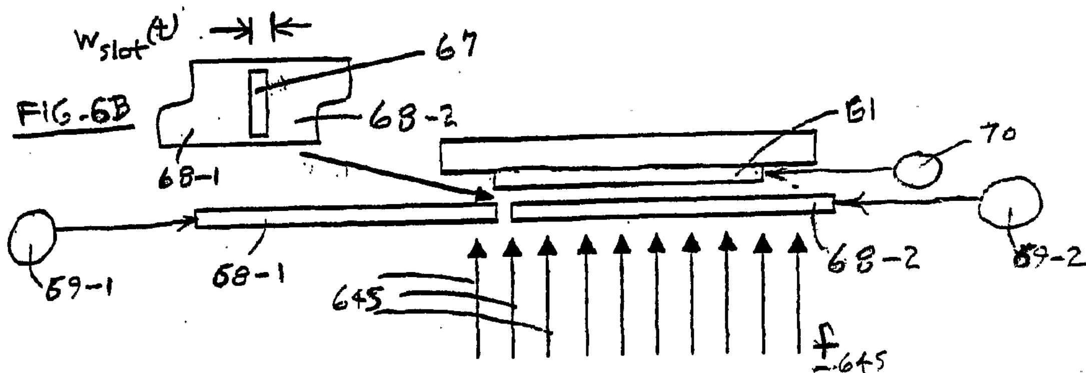


FIG.6A

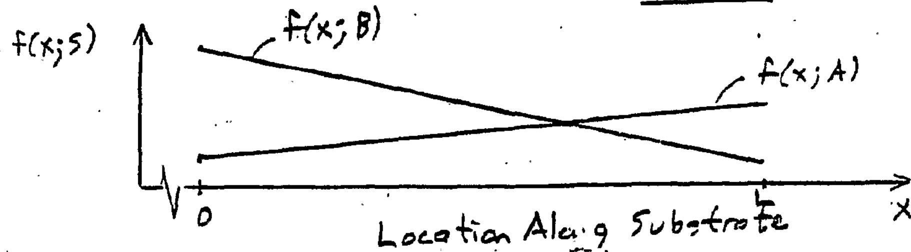


FIG.5A

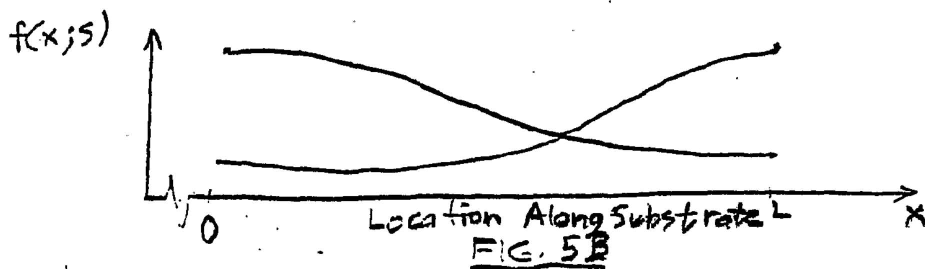


FIG.5B

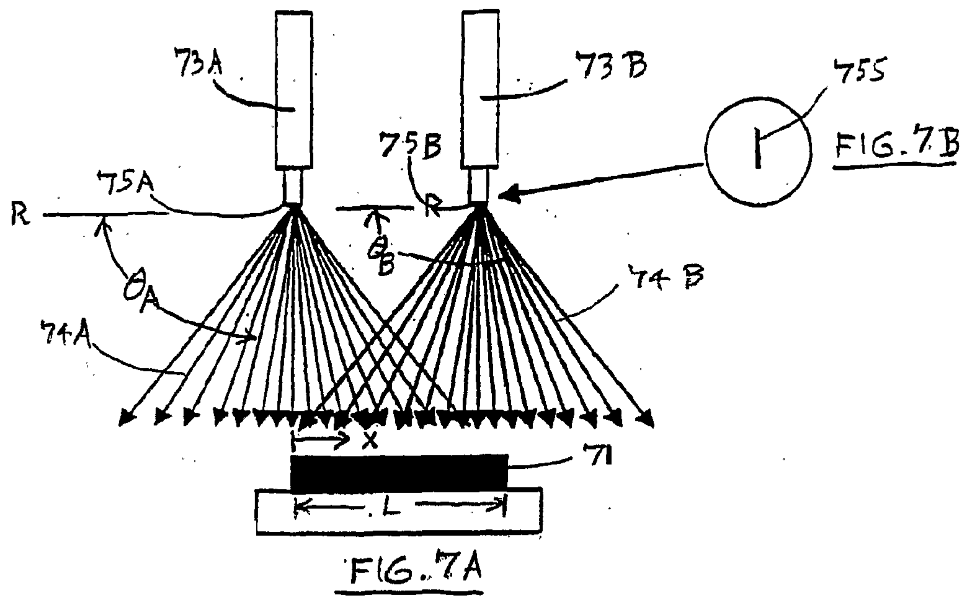


FIG. 7A

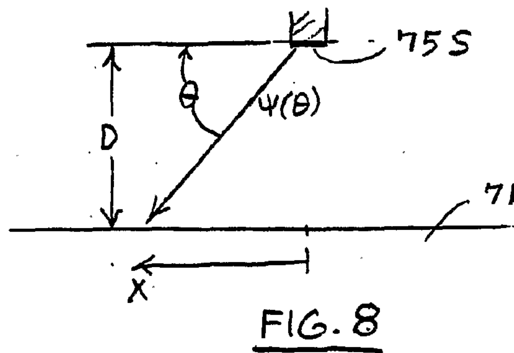


FIG. 8

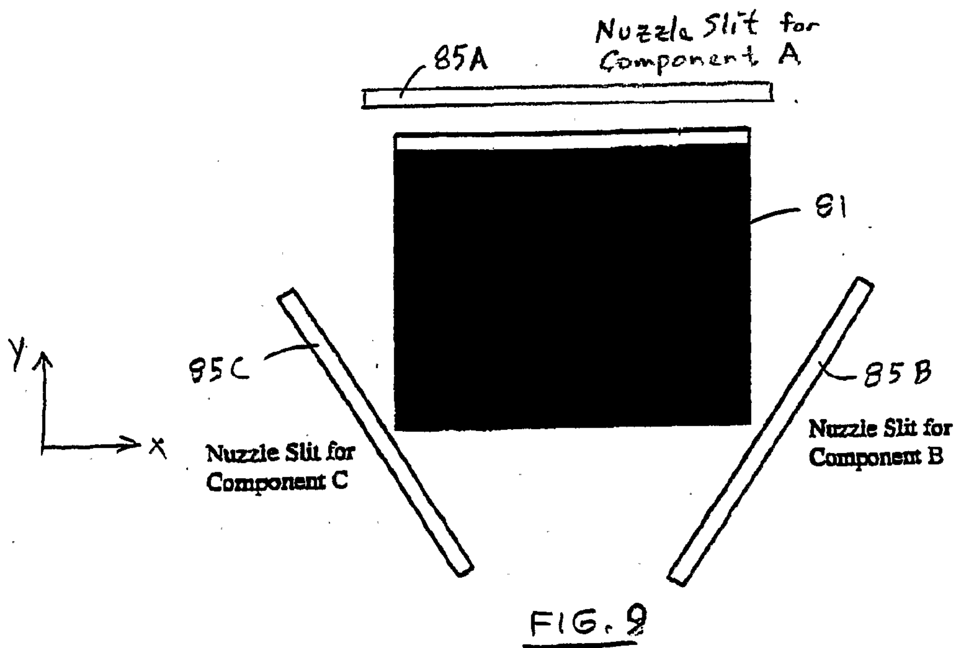


FIG. 9

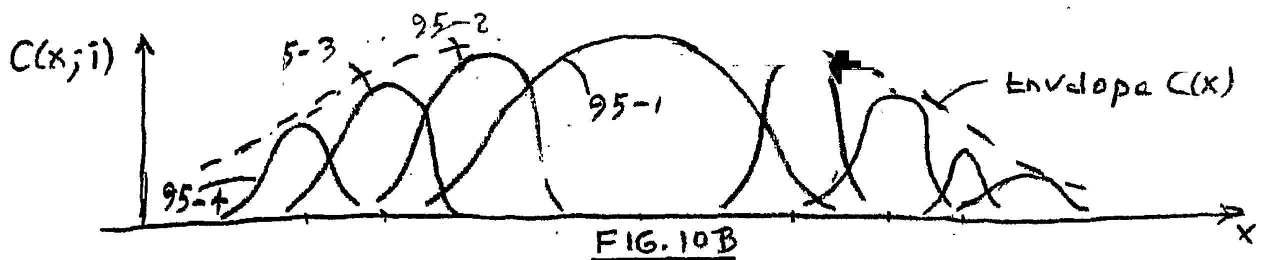


FIG. 10B

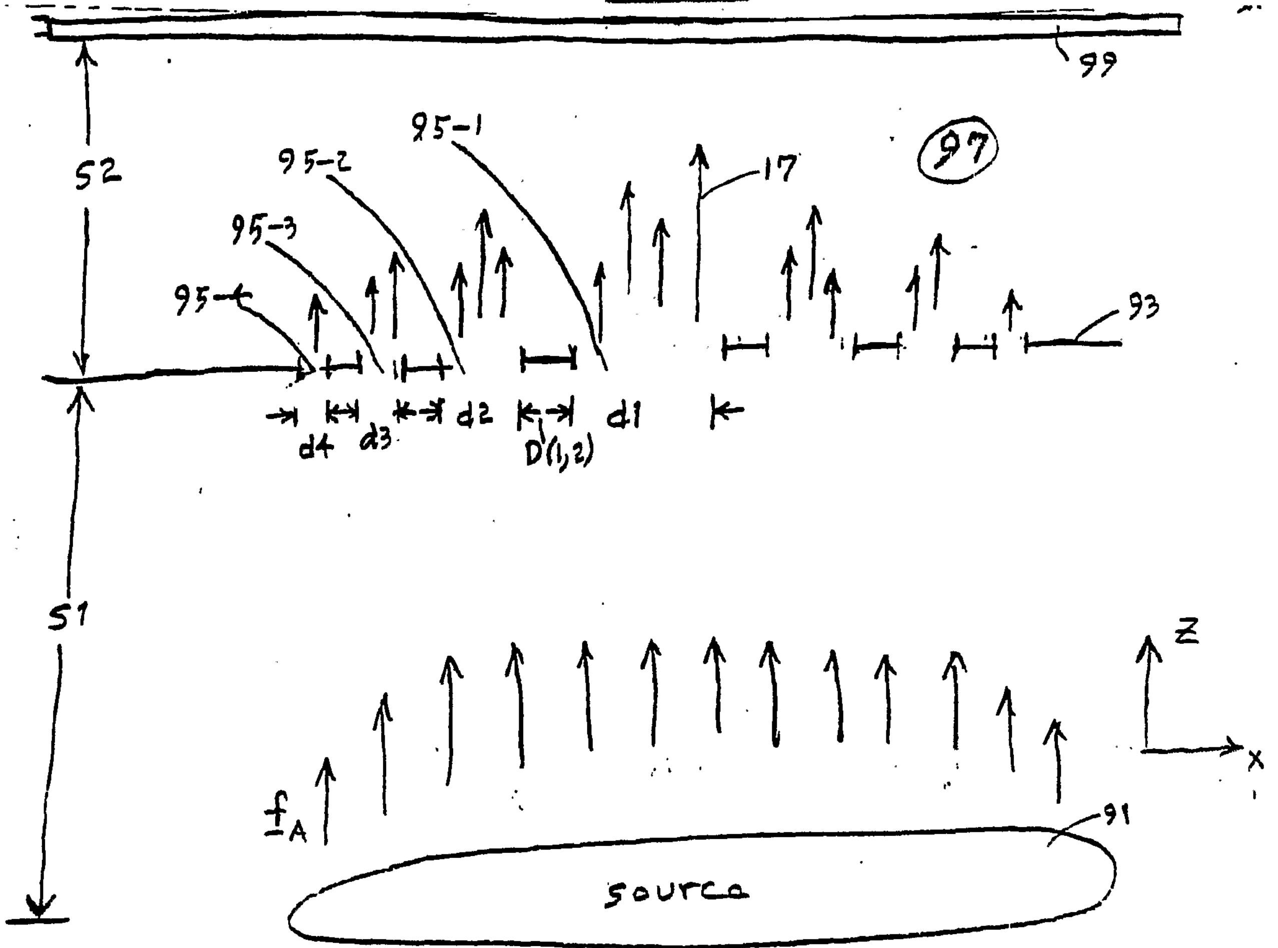


FIG. 10A

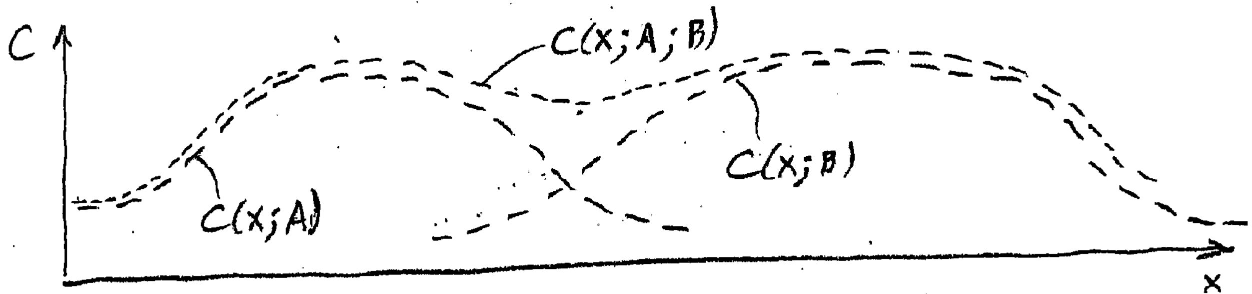


FIG. 11B

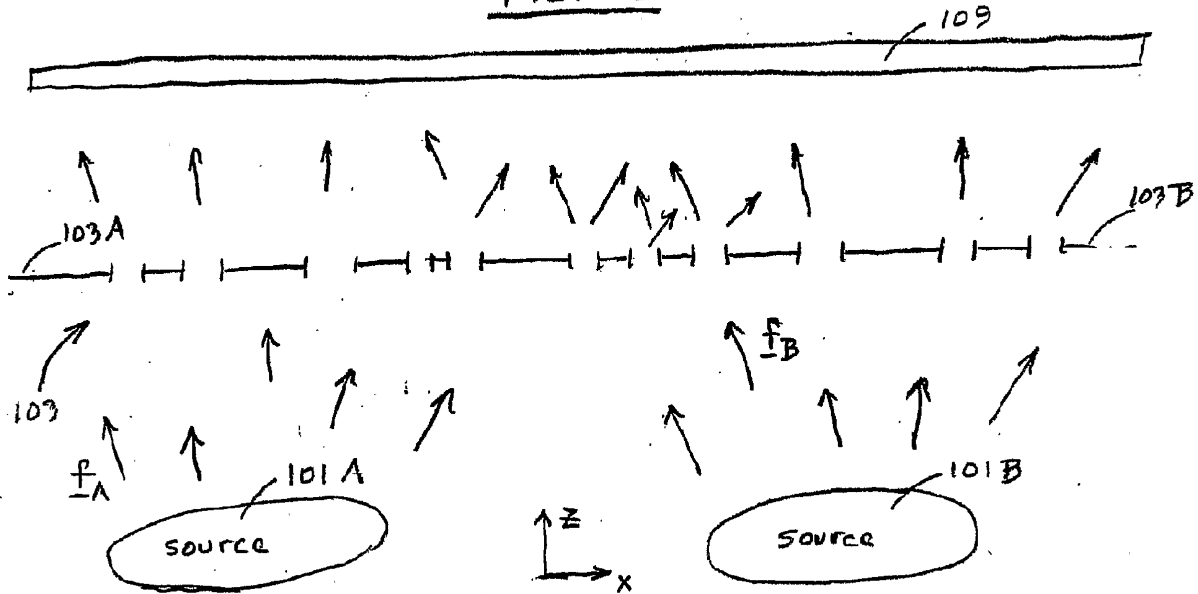


FIG. 11A

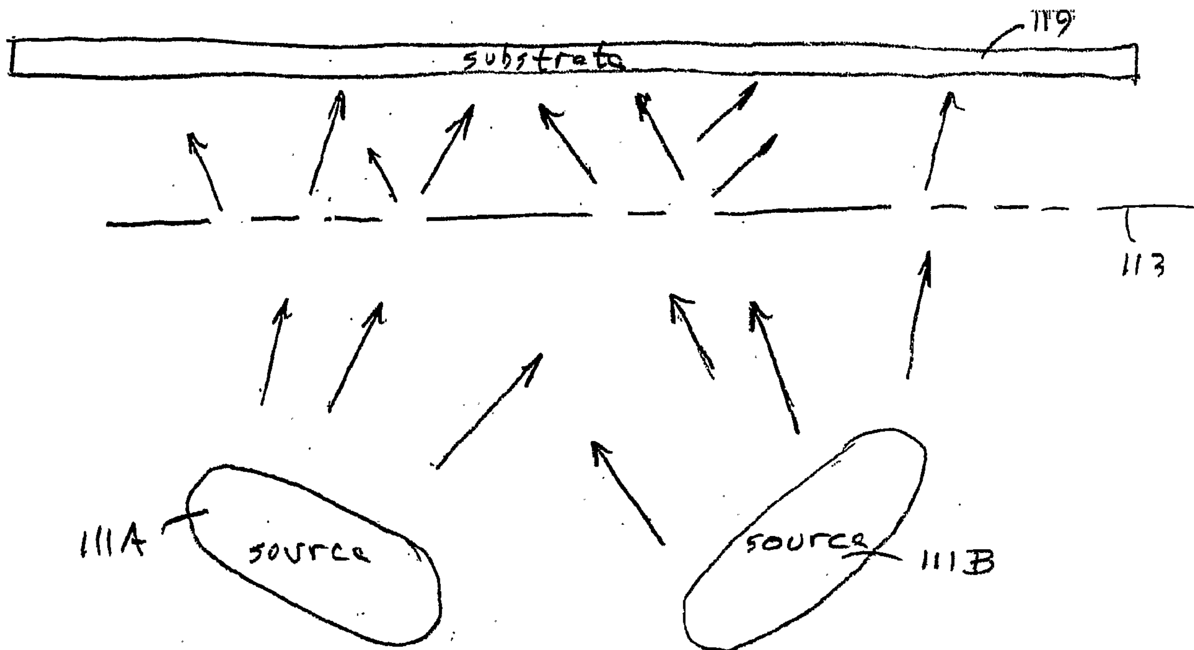


FIG. 12

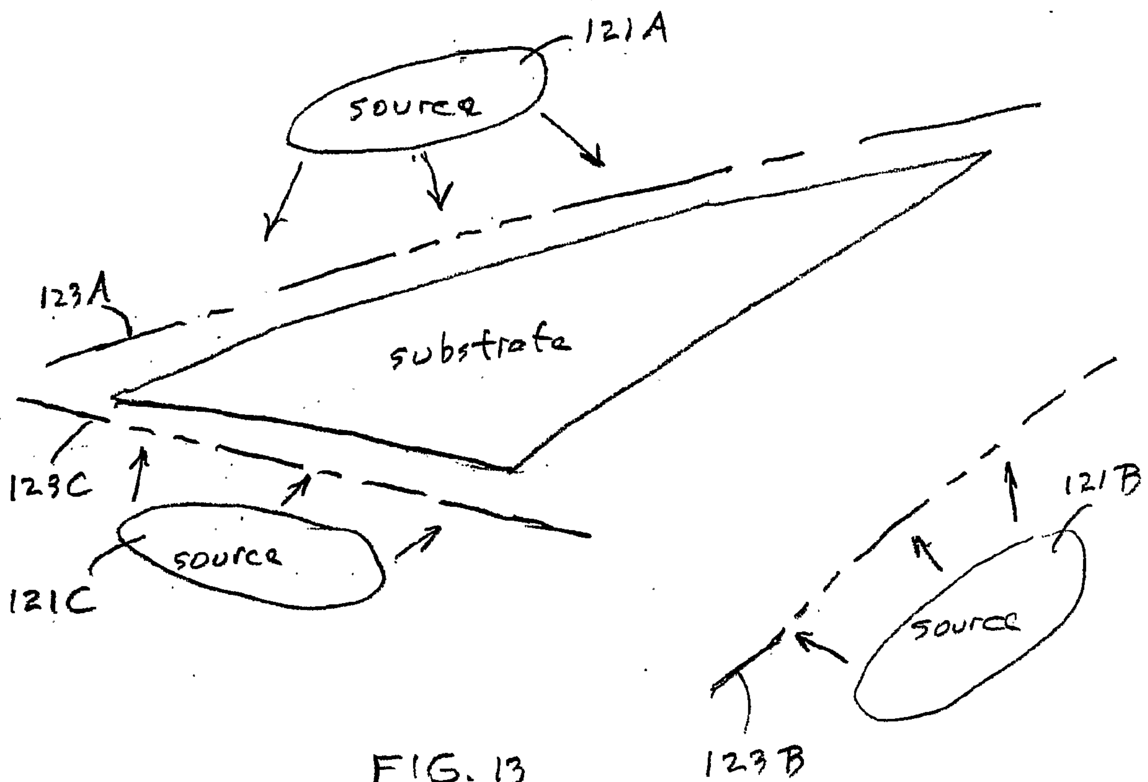


FIG. 13

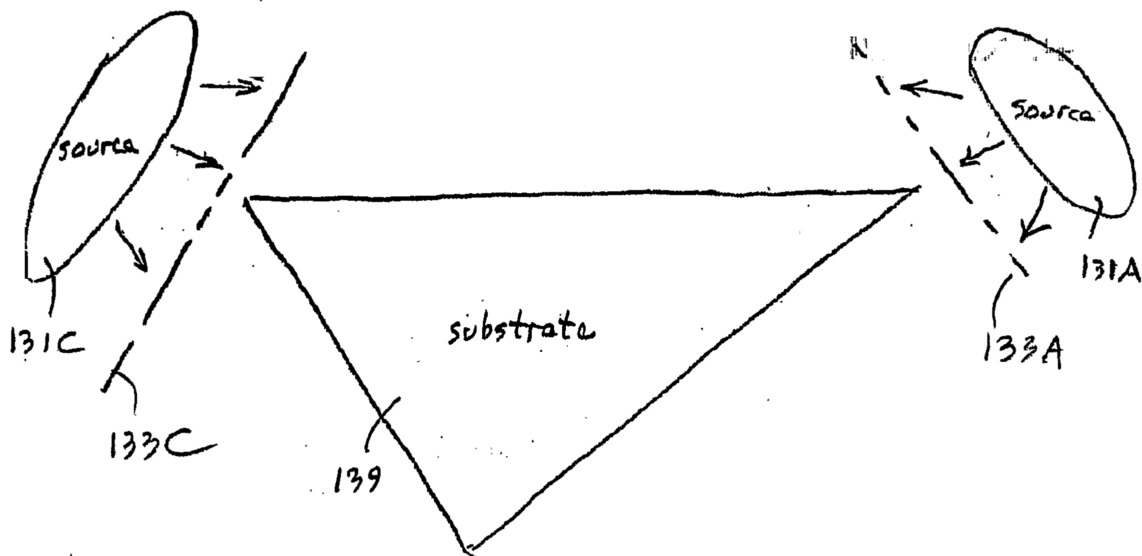


FIG. 14

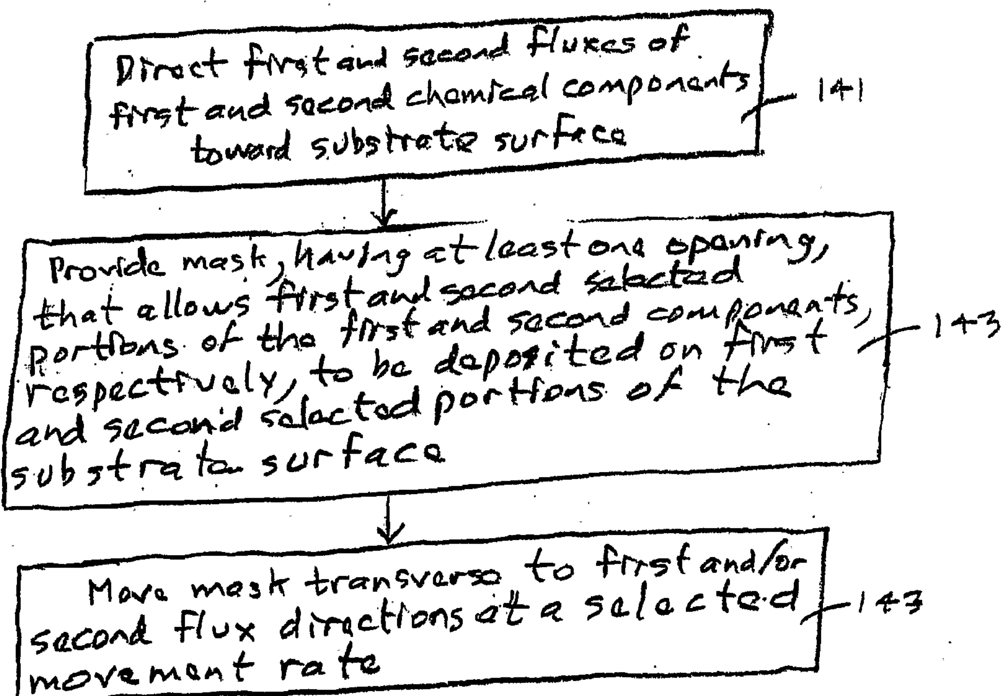


FIG. 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/14979

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B05D 5/12; C23C 16/00
US CL : 427/282, 561, 566, 585; 118/723VE, 723CB, 723 EB, 726
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/282, 561, 566, 585; 118/723VE, 723CB, 723 EB, 726

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,097,800 A (SHAW ET AL.) 24 March 1992, abstract, col. 4, Line 20 - col. 6, Line 60.	1-36
Y	US 6,045,671 A (WU ET AL.) 04 April 2000. Abstract and col. 7, Line15 - col. 28, Line 45	1-36

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
22 JUNE 2001

Date of mailing of the international search report
22 AUG 2001

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