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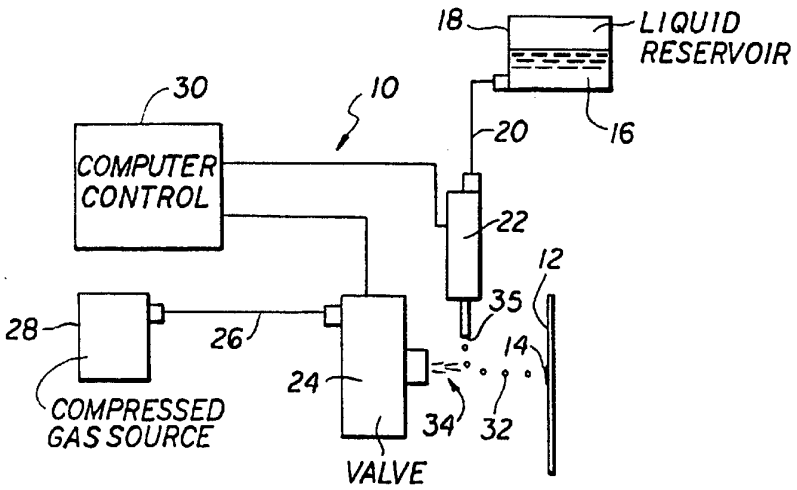
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(54) Title: HYBRID PULSED VALVE FOR THIN FILM COATING AND METHOD



(57) Abstract

An apparatus for coating a substrate with a relatively thin, uniform film of a liquid (14) on a substrate (12) with a minimum waste. The apparatus includes a droplet generator (22) capable of generating droplets of the liquid (32) at a predetermined rate and of a predetermined size, a pulsed gas jet (34) and a computer control (30) which sequentially triggers the droplet generator (22) and gas jet (34) such that droplets (32) are generated, then contacted by the gas jet (34) which accelerates the droplets (32) and propels the droplets (32) to impact and coat the substrate (12). In a preferred embodiment of the invention, the droplet size and velocity are selected such that the droplets break up upon impact with the substrate without splashing or rippling. The apparatus and method are ideal for coating semiconductor wafers with a photoresist solution. Droplets with uniform size and controlled trajectories are generated in one embodiment, with a piezoelectric droplet generator, and then accelerated to precisely defined velocities by the pulsed gas jet toward the surface to be coated. The kinetic energy of the droplets is adjusted to overcome the free energy associated with the surface tension on impact. The collision of the droplet thus results in a uniform, thin coating of photoresist or other coating solution which may then be further processed by conventional techniques.

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HYBRID PULSED VALVE FOR THIN FILM COATING AND METHOD

Background

The present invention relates to systems and processes for coating solid surfaces with thin layers of a liquid, solution, or suspension and, more particularly, the fabrication of uniform layers of photoresist for lithography of semiconductor and other electronic materials.

Lithography of semiconductor materials such as silicon or gallium arsenide wafers requires the application of a very uniform, thin (typically less than 10^{-5} meter) layer of photoresist which is subsequently exposed to light through a mask followed by selective etching of either the exposed or unexposed material in a liquid bath or plasma. In order to obtain high resolution patterns, the photoresist must be less than 10 microns thick with minimal variation of thickness over the entire wafer.

A typical process employs spin-coating, in which a puddle or mist of liquid polymer solution is deposited onto a substrate, after which the substrate is spun at high speed (typically 1000-3000 rpm) so that shear forces lead to a uniform and thin film. An example of such a process is shown in Daraktchiev U.S. Patent No. 4,996,080, which discloses a coating process in which a liquid photoresist composition is atomized, and the atomized spray droplets are permitted to settle by gravity onto a substrate surface, which is spun at between 500 and 6000 rpm. The spinning step may occur either simultaneously with the deposition of the atomized droplets, or subsequent to the deposition.

However, an inherent disadvantage with such coating processes is that it can waste as much as 95% or more of the photoresist solution, which cannot be recycled. Further, such spin-coating processes typically do not work well on substrates which are not circular, not flat, or are larger

than a few tens of centimeters in diameter. Accordingly, there is a need for an apparatus and process for coating solid surfaces with thin layers of a liquid, solution or suspension which minimizes the amount of coating material wasted, and which can be employed satisfactorily on surfaces which are not circular, flat or smaller than a few tens of centimeters in diameter.

Summary of the Invention

The present invention is a method and apparatus for depositing a thin, uniform film of material, in particular photoresist material, on a substrate in which a larger fraction of the deposited material is utilized than in prior art processes, and which can apply uniform coatings of film on relatively large, irregular and eccentric substrates. The apparatus of the present invention includes a hybrid atomizer having two components: a pulsed liquid droplet generator and a pulsed gas valve. The droplet generator produces droplets of uniform size and at a predetermined rate, and the gas valve is oriented to release bursts of pressurized gas which contact and propel the droplets to the target substrate.

The advantages of the method and apparatus of the invention are that the rate of droplet formation and velocity of the droplets can be controlled with high precision. Consequently, kinetic energy is imparted to the droplets which is sufficient to overcome the cohesive surface tension forces holding the droplets together so that the droplets spread and "wet" the surface of the substrate at impact, but is below the level of energy which would cause splashing or ripples in the layer of deposited film.

In a preferred embodiment of the invention, the droplet generator and the gas valve are actuated by a computer control, which synchronizes the production of particles and bursts of gas from the valve. In another embodiment of the

invention, the droplet generator and gas valve each include a plurality of orifices, paired so that an array is formed. Such a device is capable of coating large areas quickly and efficiently. Consequently, the invention may be considered a digitally programmable paintbrush.

Accordingly, it is an object of the present invention to provide a method and apparatus for depositing a thin film on a substrate; a method and apparatus for depositing a thin film on a substrate in which the amount of material wasted in the coating process is minimized; a method and apparatus for coating a substrate in which the quality of the film coating remains high even when the coating is applied to uneven, eccentric or relatively large substrates; a method and apparatus for coating a substrate in which droplets of coating material and droplet velocity can be controlled with high precision; and a method and apparatus for coating a substrate in which the coating mechanism may comprise an array which can coat large areas evenly and rapidly.

Other objects and advantages of the present invention will be apparent from the following description, the accompanying drawings and the appended claims.

Brief Description of the Drawings

Fig. 1 is a schematic diagram of a preferred embodiment of the coating apparatus of the present invention;

Fig. 2 is a schematic diagram of an alternate embodiment of the invention in which the coating component is in the form of an array; and

Fig. 3 is a detail in perspective of the coating head of the embodiment of Fig. 2.

Detailed Description

The physics of a single bristle will be described first, after which the use of a one or two dimensional array of bristles for coating large areas efficiently will be described.

As shown in Fig. 1, the apparatus of the present invention, generally designated 10, is used to coat a plate substrate 12 with a film 14 of a solution 16. The solution 16 may be a liquid, solution or suspension and is contained in a reservoir 18. The reservoir is connected by liquid supply line 20 to a droplet generator 22. A preferred droplet generator is shown and described in G. Switzer, "A versatile system for stable generation of uniform droplets," Reviews of Scientific Instruments, pp. 2765-71 (1991), the disclosure of which is incorporated herein by reference. Alternately, a thermal ink jet or electrospray droplet source may also be employed without departing from the scope of the invention, so long as the distributions of droplet sizes and velocities are narrow.

A pulsed gas valve 24 is connected by gas supply line 26 to a source 28 of gas under pressure, and is oriented to direct blast of gas at the substrate 12. The valve 24 preferably is a Lasertechnics model LPV pulsed supersonic molecular beam valve, manufactured by Lasertechnics, Inc., Albuquerque, New Mexico. Alternately, the valve 24 may be one of the magnetic solenoid gas valves, such as the Series 9 high-speed solenoid valve manufactured by General Valve Corporation, Fairfield, New Jersey.

The droplet generator 22 and gas valve 24 are actuated by a computer control 30. Control 30 coordinates the generation of droplets 32 of solution 16 with the production of a gas puff 34 by valve 24.

The apparatus 10 of Fig. 1 operates as follows. Control 30 generates a trigger to actuate droplet generator 22

to produce a liquid droplet 32 of precisely defined size and velocity from orifice 35. After a programmed delay, control 30 sends a trigger to pulsed gas valve 24, which results in a precisely defined puff of gas 34 that flows around the droplet 32. The droplet 32 is accelerated by viscous drag to a velocity which makes its kinetic energy, when it strikes the substrate 12, large enough to overcome the droplet's surface tension. The result is a broken droplet which wets the substrate and spreads to an extent determined by energy balance in the droplet surface collision.

The resulting puff of gas 34 efficiently accelerates the droplet 32 toward the substrate in part because the drag coefficient for small particles is inversely proportional to the Reynolds number of the flow. The flow velocity of the gas puff 34, and thus the velocity of droplet 32, are varied by adjusting the pressure generated by gas source 28 behind the gas valve 24, as well as the distance and orientation of the valve with respect to the substrate 12. The radius of the droplet 32 may be controlled by varying the size of the orifice 35.

The energy which holds the droplet 32 in a spherical shape depends on the radius r of the droplet and the surface tension σ of the liquid: $E_s = 4\pi\sigma r^2$. By altering the velocity of the droplet, the kinetic energy is varied: $E_k = 4\pi\rho v^2 r^3/3$; where v is the velocity of the droplet 32 and ρ is the liquid mass density. Thus, when the ratio $\rho v^2 r/3\sigma < 1$, the droplet 32 bounces off of the substrate 12. In contrast, when the ratio is very much greater than one, the excess kinetic energy must be dissipated by splashing of the solution 16 or creating surface waves on the film 14.

The apparatus 10 allows one to vary v over a wide range while controlling r so that conditions where the ratio is just enough greater than one to give uniform films may be identified. How much greater than one this ratio must be for

successful film deposition depends on precisely how well the solution 16 wets the substrate 12, a factor which depends intimately on many variables, such as surface roughness and chemical pretreatment. The essential point is that the invention permits detailed control of **r** and **v** of the droplets 32 so that optimal conditions may be reproducibly identified for specific coating solutions and substrates.

The single bristle shown in Fig. 1 and described in the preceding paragraphs is easily generalized to a one dimensional housing array 36 of hybrid nozzles as shown, for example, in Fig. 2. An acceptable multi-orifice array is also shown and described in Lyon et al. U. S. Patent No. 3,739, 393, the disclosure of which is incorporated herein by reference. One might employ individual piezoelectric drivers for each gas orifice 38 and liquid orifice 40 to achieve fine control for deposition of layers of solution with programmed film thickness variations. However, the preferred mode for photoresist application with this embodiment permits multiple orifices to be driven by a single pulsed driver.

Liquid solution 16 is fed into the liquid chamber 42 of the housing array 36 through cylindrical channel 44 (see Fig. 3) and forms meniscuses at the ends of the pinholes 40 (shown enlarged for clarity) which are connected to the channel. Alternately, the channel 44 may be rectangular in cross section. The liquid chamber 42 preferably includes a recirculation line 45 from the end of the channel 44 back to the reservoir 18; however, it is possible to provide a liquid chamber 42 without a recirculation line 45.

An acoustic wave generated by a piezoelectric driver 46 is launched down the channel 44, breaks the meniscuses and liberates a droplet (not shown) from each pinhole 40. Alternately, a shock wave could be produced by driver 46. A suitable driver 46 is shown and described in Dressler U. S. Patent No. 3,868,698, the disclosure of which is incorporated

herein by reference. After a programmed delay, a pulse of gas is admitted by valve 24 through cylindrical channel 48 in a gas chamber 50 and a second array of pinholes 38 or nozzles, which are connected to channel 48. A shaped slot might also be employed, and not depart from the scope of the invention. The resulting gas flow accelerates the droplets toward a substrate (not shown) as in the single bristle example of Fig. 1.

As shown in Figs 2 and 3, the orifices 38, 40 of the liquid and gas chambers of the array housing are formed in angled faces 52, 54 which form an acute angle with respect to each other, which facilitates the projection of droplets into the paths of the gas jets from orifices 38. Further, the orifices 38, 40 are paired in one-to-one correspondence such that each droplet is projected into the path of a corresponding gas jet from orifice 38. A two dimensional array may be formed, for example, by stacking a series of one-dimensional arrays 36 with independent or coupled drivers 24, 46.

Very small droplet radii and high velocities may be achieved by causing a supersonic expansion from the gas valve 24. At high Reynolds numbers, a shock may be generated which can cause distortion or breakup of the liquid droplets. Use of the shock or gas flow to force distortion or breakup of the droplets is a second mode of operating the hybrid valve 10.

While the forms of apparatus and methods herein described constitute preferred embodiments of the invention, it is to be understood that the invention is not limited to these precise forms of apparatus, and that changes may be made therein without departing from the scope of the invention.

What is claimed is:

1. A hybrid pulsed valve for thin film coating comprising:

means for generating liquid droplets; and

means for generating a pulsed gas jet to contact said droplets, whereby said droplets are accelerated and propelled toward a target substrate in response thereto.

2. The valve of claim 1 further comprising control means for triggering said droplet generating means and said gas jet generating means at predetermined sequences, whereby said droplet generating means generates a droplet of liquid which is positioned to be contacted by said pulsed gas jet and accelerated and propelled toward said target substrate when said gas jet generating means is actuated.

3. The valve of claim 2 further comprising reservoir means, connected to said droplet generating means, for supplying liquid thereto.

4. The valve of claim 3 further comprising means, connected to said gas jet generating means, for supplying gas under pressure thereto.

5. The valve of claim 4 wherein said droplet generating means includes an array of droplet orifices, each in fluid communication with said reservoir means.

6. The valve of claim 5 wherein said array of droplet orifices includes a liquid chamber having first channel means communicating with said reservoir means; and said droplet orifices each communicate with said first channel means.

7. The valve of claim 6 wherein each of said droplet orifices is shaped to retain a meniscus of said liquid from said first channel means.

8. The valve of claim 7 further comprising wave generating means for generating an acoustic wave along said first channel means such that said meniscuses of said liquid are broken and said droplets ejected from said droplet orifices.

9. The valve of claim 7 further comprising wave generating means for generating a shock wave along said first channel means such that said meniscuses of said liquid are broken and said droplets ejected from said droplet orifices.

10. The valve of claim 8 further comprising an array of gas orifices, each in fluid communication with said gas supplying means.

11. The valve of claim 10 wherein said array of gas orifices includes a gas chamber having second channel means communicating with said gas supplying means; and said gas orifices each communicate with said second channel means.

12. The valve of claim 11 wherein said droplet orifice and gas orifice arrays include a housing shaped such that said gas and droplet orifices are spaced and arranged in one-to-one correspondence, whereby each of said droplet orifices ejects a droplet to be contacted by a gas stream from a paired one of said gas orifices.

13. The valve of claim 1 wherein said gas jet generating means generates a gas jet at supersonic speeds, whereby said droplets from said droplet generating means contacted by said supersonic gas jet are further broken up into smaller particles.

14. The valve of claim 1 wherein said gas jet generating means generates a gas jet having a predetermined pressure; and said droplet generating means generates a droplet having a predetermined size such that, upon impacting said substrate,

said droplet breaks up and coats said substrate without splashing or rippling.

15. A hybrid pulsed valve for thin film coating comprising:

a source of gas under pressure;

a gas valve connected to said source of pressurized gas and shaped to direct a stream of gas at a substrate;

a reservoir of liquid photoresist material;

a droplet generator in fluid communication with said reservoir; and

a digitally programmable computer control, connected to said gas valve and said droplet generator, for triggering said gas valve and said droplet generator in predetermined sequences, whereby a droplet is produced by said droplet generator and said gas valve generates a stream of gas which contacts, accelerates and propels said droplet toward a target substrate, thereby producing a thin, even film of said photoresist thereon with a minimum of waste.

16. A hybrid pulsed valve for thin film coating comprising:

a source of gas under pressure;

a gas valve connected to said source of pressurized gas and shaped to direct a stream of gas at a substrate;

a reservoir of liquid photoresist material;

a first array including a first channel connected to said reservoir and a plurality of droplet orifices communicating with said first channel, said orifices being shaped such that meniscuses of said liquid photoresist material are formed therein;

a piezoelectric driver connected to said first channel to generate a shock wave therethrough such that said meniscuses are broken and droplets of said material are ejected from said droplet orifices;

a second array including a second cylindrical channel connected to said gas valve and a plurality of gas

orifices, said gas orifices being shaped and positioned such that said gas orifices are paired in one-to-one correspondence to said droplet orifices, whereby a plurality of droplets is generated and accelerated to a target substrate simultaneously; and

a digitally programmable computer control connected to actuate and trigger said gas valve and said driver in predetermined sequences, whereby droplets generated by said first array are accelerated and contacted by pulses of gas from said second array when said droplets are between said second array and a target substrate, and said droplets form an even film on said substrate with a minimum of waste.

17. A method of coating a thin film on a substrate comprising the steps of:

generating a droplet of a liquid to coat said substrate; and

generating a pulse of gas to contact and envelop said droplet, whereby said droplet is accelerated and propelled toward a substrate.

18. The method of claim 17 wherein said gas pulse generating step includes the step of propelling said droplet toward said target substrate at a velocity at impact sufficient to break up said droplet without splashing or rippling.

19. The method of claim 18 wherein said droplet generating step includes the step of generating a droplet of a predetermined diameter such that, at impact with said substrate, said droplet breaks up without splashing or rippling.

20. The method of claim 17 wherein said droplet generating step includes the step of actuating a piezoelectric driver to generate a shock wave in a channel to eject meniscuses of said

liquid to be contacted and propelled by said gas pulse.

21. A method of coating a thin film on a substrate comprising the steps of:

simultaneously generating a plurality of droplets of a liquid to coat said substrate; and

subsequent to said droplet generating step, generating a plurality of pulses of gas to contact and envelop said droplets, whereby said droplets are accelerated and propelled toward a substrate.

22. A method of coating a thin film on a substrate comprising the steps of:

simultaneously generating a plurality of droplets of a liquid to coat said substrate; and

subsequent to said droplet generating step, generating a plurality of pulses of gas to contact and envelop said droplets, whereby said droplets are accelerated and propelled toward a substrate at a ratio $\rho v^2 r/3\sigma$ which is slightly greater than 1, where ρ is the mass density of said liquid, v is the velocity of said droplets, r is the radii of said droplets and σ is the surface tension of said liquid.

23. A method of coating a thin film on a substrate comprising the steps of:

generating a droplet of a liquid to coat said substrate; and

accelerating said droplet relative to said substrate at a ratio of $\rho v^2 r/3\sigma$ which is slightly greater than 1, where ρ is the mass density of said liquid, v is the velocity of said droplets, r is the radii of said droplets and σ is the surface tension of said liquid, whereby said droplet impacts said substrate such that surface tension of said droplet is broken to form a uniformly thin film on said substrate without ripples or splashing.

24. A method of coating a thin film on a substrate comprising the steps of:

generating a droplet of a liquid to coat said substrate; and

accelerating said droplet relative to said substrate sufficiently such that said droplet impacts said substrate at a predetermined velocity so that surface tension of said droplet is broken to form a uniformly thin film substantially without forming ripples or splashing.

25. A method of coating a thin film on a substrate comprising the steps of:

generating a droplet of a liquid to coat said substrate; and

accelerating said droplet relative to said substrate, by means other than gravity at impact, to a relative velocity such that said droplet impacts said substrate and is broken up as a result of said impact to form a film of uniform thickness thereon.

26. A method of coating a thin film on a substrate comprising the steps of:

simultaneously generating a plurality of droplets of a liquid from a plurality of forming means to coat said substrate; and

subsequent to said droplet generating step, generating a plurality of pulses of gas to contact and envelop said droplets in a one-to-one correspondence, whereby said droplets are accelerated and propelled toward a substrate.

27. The method of claim 17 wherein said step of generating a droplet further comprises the step of generating a stream of said droplets, each having a substantially uniform drop size; and said step of accelerating said droplets propels said droplets to said substrate at a substantially uniform velocity.

28. The method of claim 21 wherein said step of generating a plurality of droplets generates droplets having a substantially uniform drop size and said step of accelerating said droplets propels said dropleets to said substrate at a substantially uniform velocity.

29. The method of claim 26 wherein said step of generating a plurality of droplets generates droplets having a substantially uniform drop size and said step of accelerating said droplets propels said droplets to said substrate at a substantially uniform velocity.

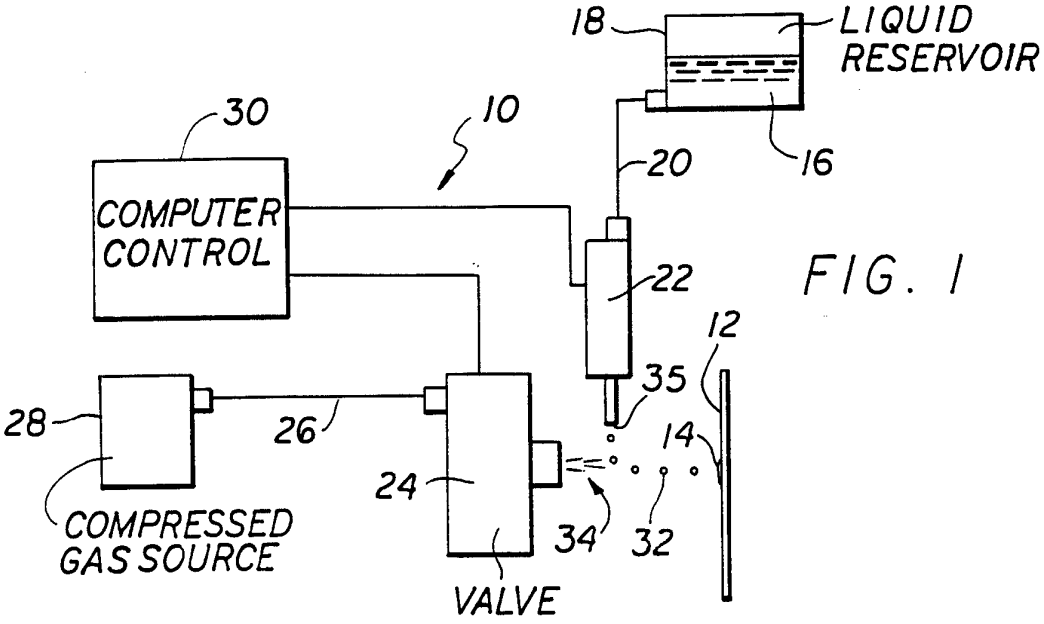


FIG. 1

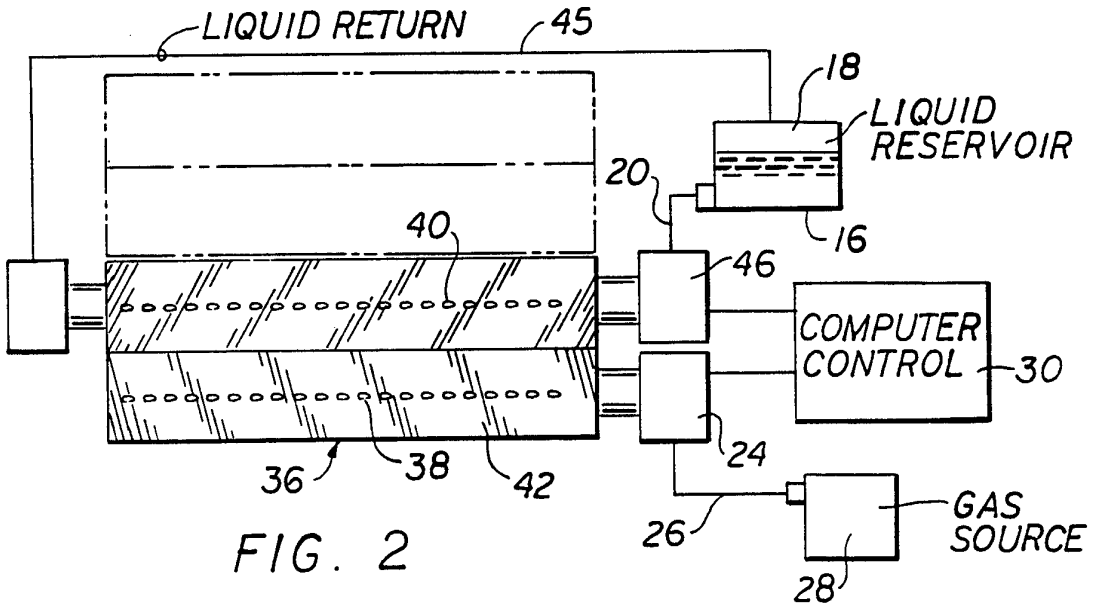


FIG. 2

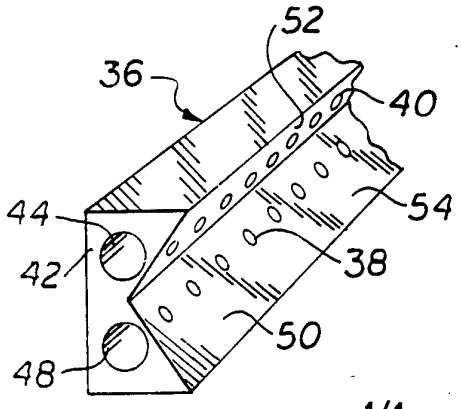


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B05D 1/02
US CL :427/180,421; 239/8,11,99,101,102.2; 118/300,323
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. : 427/180,421; 239/8,11,99,101,102.2; 118/300,323

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,019,188 (HOCHBERG ET AL.) 19 APRIL 1977, ABSTRACT AND COL. 7, LINES 27-53.	17-29
Y	US, A, 4,659,013 (LEDEBUHR ET AL.) 21 APRIL 1987, COL. 6, LINES 3-50.	1-29
X --- Y	US, A, 4,290,384 (AUSSCHNITT ET AL.) 22 SEPTEMBER 1981, ABSTRACT AND COL. 1 LINE 66 - COL. 2 LINE 25.	17-29 -------- 17-29
X --- Y	US, A, 5,166,000 (SINGH ET AL.) 24 NOVEMBER 1992, ABSTRACT AND COL. 1 LINE 59 - COL. 2, LINE 60.	17-29 -------- 17-29
Y	US, A, 4,407,450 (CHEGOLYA ET AL.) 04 OCTOBER 1983, COL. 2, LINE 65 - COL. 3, LINE15.	1-29

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,150,836 (McKAY ET AL.) 29 SEPTEMBER 1992, ABSTRACT AND COL. 1, LINE 19 - COL 5 LINE 10.	1-29
Y	US, A, 3,868,698 (DRESSLER) 25 FEBRUARY 1975, ABSTRACT AND COL. 4 LINES 9-23.	1-29
Y	US, A, 4,996,080 (DARAKTCHIEV) 26 FEBRUARY 1991, ABSTRACT AND COL. 2, LINE 33 - COL. 3 LINE 30.	1-29
Y	US, A, 3,840,391 (SPITZ ET AL.) 08 OCTOBER 1974, ABSTRACT AND COL. 1, LINE 13 - COL. 2, LINE 9.	17-29
Y	"A VERSATILE SYSTEM FOR STABLE GENERATION OF UNIFORM DROPLETS", (SWITZER), REVIEW OF SCIENTIFIC INSTRUMENTS, 62 (11) NOVEMBER 1991, ENTIRE REFERENCE	1-29
Y	US, A, 3,739,393 (LYON ET AL.) 12 JUNE 1973, COL. 4, LINE 7 - COL. 6, LINE 48.	1-29