



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

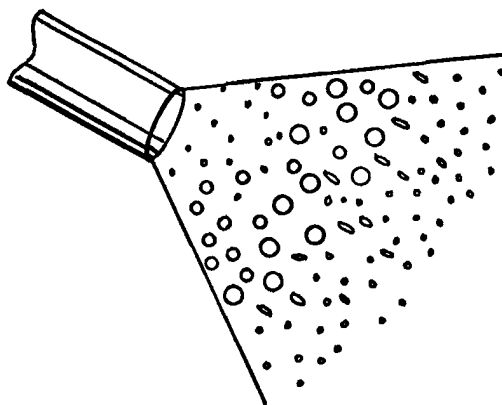
<b>(51) International Patent Classification <sup>6</sup> :</b> <b>H01L 21/306, F25J 1/00, B08B 5/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/57365</b> <b>(43) International Publication Date:</b> 17 December 1998 (17.12.98)
<b>(21) International Application Number:</b> PCT/US98/12256 <b>(22) International Filing Date:</b> 11 June 1998 (11.06.98)  <b>(30) Priority Data:</b> 08/872,958 11 June 1997 (11.06.97) US  <b>(71) Applicant:</b> FSI INTERNATIONAL, INC. [US/US]; 322 Lake Hazeltine Road, Chaska, MN 55318-1096 (US).  <b>(72) Inventors:</b> PATRIN, John, C.; 8572 Drake Court, Chanhassen, MN 55317 (US). HEITZINGER, John, M.; 3828 Joppa Avenue South, St. Louis Park, MN 55416 (US).  <b>(74) Agents:</b> STEINKRAUS, Walter, J. et al.; Suite 2000, 6109 Blue Circle Drive, Minnetonka, MN 55343-9131 (US).		<b>(81) Designated States:</b> JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** TREATING SUBSTRATES BY PRODUCING AND CONTROLLING A CRYOGENIC AEROSOL

**(57) Abstract**

A method is disclosed for treating a substrate by impinging the substrate with a cryogenic aerosol spray wherein the cryogenic aerosol spray is formed by expanding a pressurized liquid or liquid/gaseous stream of one or more cryogens through a nozzle at a given distance from the substrate into a process chamber with a pressure of about  $1.6 \times 10^{-4}$  Pascal or less so as to form at least substantially solid aerosol particles of said one or more cryogens downstream from the nozzle by the cooling resulting from the expansion and/or evaporation to form an at least substantially solid particle containing aerosol.

LOW PRESSURE CHAMBER



"EFFERVESCENT FLASHING"

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## TREATING SUBSTRATES BY PRODUCING AND CONTROLLING A CRYOGENIC AEROSOL

### Background of the Invention

5 The present invention relates to a process for producing a cryogenic aerosol and controlling the physical properties of a cryogenic aerosol.

10 The present invention has been developed for its applicability to the semi-conductor and micro-electronics industries and in particular to the cleaning of contaminated substrates, including, for example, semiconductor wafers of silicon and of gallium arsenide, multiple chip carriers, flat panel displays, magnetic hard disks, MEMs (microelectromechanical systems) and other electronic devices. Many methods have been developed to clean such surfaces. Techniques include the use of solvents or chemical cleaning for removing contaminant films from surfaces, the use of high energy sonic waves, and combinations thereof. Solvents for chemicals may be applied as gas jets or liquid spray. Aerosol sprays using frozen water vapor have been disclosed by  
15 Tada et al. (US 5,035,750, US 5,025,597 and US 4,974,375).

20 More recently, cryogenic aerosols have been developed for jet spraying against surfaces, particularly within the semi-conductor industry to facilitate particulate decontamination as described in McDermott et al. (U.S. 5,294,261) and Tamai et al. (U.S. 5,512,106), both of whose contents are incorporated herein by reference, and for the elimination of stiction as described in copending application assigned to the same assignee hereof filed concurrently herewith, entitled "Eliminating Stiction with the Use of Cryogenic Aerosol", attorney docket number F32.2-6379 incorporated herein by reference.

25 Cryogenic aerosols are formed by delivering a gaseous and/or liquid cryogen to a nozzle. Upon expelling the mixture from the nozzle, the cryogenic aerosol is formed as described in copending US application serial number 08/773,489, filed December 23, 1996 and incorporated herein by reference. The cryogenic aerosol contains at least substantially solid aerosol particles of the cryogen. The term "aerosol particles" as used herein refers to droplets comprised of liquid and/or solid generally of  
30 about 0.01 to about 100 microns in diameter or larger. The aerosol particles may further be partially solid or partially liquid.

Typically, cryogenic aerosols are formed from chemicals such as argon, nitrogen, carbon dioxide and mixtures thereof. Argon and nitrogen, both of which are

inert, are the preferred components of cryogenic aerosols. Other inert chemicals may be used as well.

Until now, cryogenic aerosols have been formed by expanding the gaseous and/or liquid cryogen into a process chamber at a pressure upwards of  $2 \times 10^4$  Pascal. At such pressures, cryogenic aerosols are characterized by high mass and low velocity aerosol particles. Also, the aerosol density (number of aerosol particles per unit volume) is low. Treatment of surfaces with these high mass aerosol particles can result in insufficient cleaning, especially for contaminant particles five microns in diameter or smaller. As the semiconductor industry moves to ever smaller geometries, the need for 'cleaner' substrates becomes more pronounced. While present standards allow for up to 1700 contaminant particles of size 0.12 microns and greater per square meter, it is projected that by 2010, industry standards will allow for no more than 150 contaminant particles of size 0.02 microns and greater per square meter. With these increasingly stringent industry demands, there is a need for more efficient treatment methods, in particular, treatment methods that are capable of successfully treating surfaces with small contaminant particles.

#### Summary of the Invention

It is an object of the present invention to provide a method for treating substrates, the method characterized by an improved contaminant particle removal efficiency, the method being well suited for removing small contaminant particles.

The present invention provides a method for forming a cryogenic aerosol by expanding a pressurized liquid or liquid/gaseous stream of one or more cryogens through a nozzle into a process chamber with a pressure of about  $1.6 \times 10^4$  Pascal or below. At least substantially solid aerosol particles of the one or more cryogens are formed by the cooling resulting from the expansion and/or evaporation thus resulting in an aerosol containing at least substantially solid aerosol particles.

In another aspect, the present invention provides a method for treating a substrate by impinging the substrate with a cryogenic aerosol spray formed as described above.

In another aspect, the invention provides a method for forming a cryogenic aerosol by expanding a pressurized liquid or liquid/gaseous stream of one or more cryogens through a nozzle into a process chamber of lower pressure such that the

pressurized liquid or liquid/gaseous stream is subjected to effervescent flashing downstream of the nozzle thereby forming a cryogenic aerosol of at least substantially solid aerosol particles. The term 'effervescent flashing' as used herein shall refer to a mechanism for aerosol formation in which rapid bubble growth occurs and is responsible for the breakup of the cryogen stream. Said bubbles may exist in the cryogen stream prior to the expulsion of the cryogen from the nozzle and/or the bubbles may be nucleated following expulsion of the cryogen from the nozzle.

In another embodiment, the invention provides a cryogenic aerosol spray formed by effervescent flashing a liquid or liquid/gaseous stream as described above.

The present invention, in its various embodiments, marks a departure from the prior art in that the aerosol particles of the cryogenic aerosol are formed by expanding the liquid or liquid/gaseous stream in a low pressure regime where a new mechanism for aerosol particle formation is operative and predominates. The resulting cryogenic aerosols, formed downstream of the nozzle, are characterized by higher velocity and lower mass aerosol particles than cryogenic aerosols formed by other methods. Additionally, the aerosol density (number of particles per unit volume) is higher. The present invention results in greater contaminant removal efficiency in general, and in dramatic improvement in particle removal efficiency for contaminant particles smaller than about 0.3 micron.

#### Brief Description of the Figures

Figure 1 depicts aerosol atomization occurring at high process chamber pressure as a result of breakup of a liquid cylindrical core by surface oscillations creating large drops.

Figure 2 depicts aerosol atomization occurring at high process chamber pressure by liquid breakup from a high velocity gas jet.

Figure 3 depicts aerosol atomization occurring at low process chamber pressure by the rapid nucleation and growth of bubbles within a liquid cryogen.

Figure 4 is a schematic representation of the apparatus used in the present invention.

Figures 5a and 5b depict the velocity distribution for an inventive aerosol at a chamber pressure of  $1.6 \times 10^3$  Pa and a prior art aerosol at a chamber pressure of  $4.0 \times 10^4$  Pa respectively.

Detailed Description of the Invention

Cryogenic aerosol cleaning of substrates is carried out by impinging a stream of aerosol particles at a high velocity against a substrate to be cleaned. Without being bound by a particular theory, the impinging aerosol particles are believed to impart sufficient energy so as to dislodge contaminants from the surface of the substrate. The dislodged contaminants may then be carried away in a gas flow. In producing aerosol particles, care must be taken to avoid the production of aerosol particles that are massive and result in a low density aerosol (low number of particles per unit volume) and inefficient cleaning of the substrate. Decreasing the mass of the aerosol particles, however, results in a linear decrease in the energy of the aerosol particles. Since energy is related to the square of the velocity, this decrease in energy can be offset by increasing the velocity of the aerosol particle. Most desirable are aerosols with a high aerosol density (large number of aerosol particles per unit volume) comprising high velocity, low mass aerosol particles that are capable of efficiently cleaning a substrate and removing both large contaminant particles ( $\geq$  about 0.3 micron) and small contaminant particles ( $\leq$  about 0.3 micron).

A method for forming a cryogenic aerosol has been discovered comprising high velocity, low mass aerosol particles. The cryogenic aerosol of the present invention is particularly useful in removing small contaminant particles from the surface of a substrate and fills a developing need in the semiconductor industry.

Cryogenic aerosols are formed by delivering a liquid or liquid/gaseous cryogen to a nozzle. Upon expelling the mixture from the nozzle, a cryogenic aerosol is formed. The so-formed cryogenic aerosol may contain substantially solid and/or liquid aerosol particles of the cryogen. The aerosol particles may further be partially solid or partially liquid.

The distribution of aerosol particle sizes and energies in a cryogenic aerosol depends on the thermodynamic conditions including pressures and temperatures of the cryogen and process chamber, on the initial phase of the cryogen, on the flow rate of the cryogen and the technique that is used to form the cryogenic aerosol. In the present application, the pressure of the process chamber as well as the pressure of the cryogen prior to expansion is of interest. Using one of the standard techniques for formation of cryogenic aerosols, wherein a liquid and gaseous mixture is expanded from a higher pressure to a process chamber at a pressure of at least  $2 \times 10^4$  Pascal, a

disturbance of the liquid stream occurs by some method (non-symmetric flow, air flow etc.) leading to droplet formation. If the wavelength of the disturbance is less than some minimum wavelength, the disturbance is damped out by the surface forces of the liquid. If the wavelength of the disturbance is longer than this minimum wavelength, the liquid stream will breakup into droplets. One mechanism for disturbing the liquid stream is illustrated in Figure 1 which depicts aerosol atomization by liquid breakup from surface oscillations. Another mechanism for disturbing the liquid stream is illustrated in Figure 2 which depicts aerosol atomization by liquid breakup from a high velocity gas jet at high process chamber pressure.

It has been discovered, however, that when the same mixture is expanded into a process chamber with a pressure below  $1.6 \times 10^4$  Pascal, a third mechanism for breaking up the liquid stream, described herein as effervescent flashing, becomes a major factor. At such low pressures, rapid bubble formation and/or growth occurs in the liquid stream. Without being bound by a particular theory, breakup of the liquid stream into droplets by this mechanism is thought to occur in the following way in the case of expansion into a low pressure chamber. Upon exiting the nozzle orifice, the liquid experiences a large pressure drop. Because the pressure in the process chamber is very low (e.g., about  $1.6 \times 10^4$  Pascal or less) the liquid is well above its boiling temperature (superheated) at the process chamber pressure. Rapid growth of bubbles pre-existing in the cryogen stream and/or formation of bubbles followed by rapid growth ensues leading to shattering of the liquid into small droplets as depicted in Figure 3. Because the bubble growth rate decreases with increasing process chamber pressure, the newly discovered mechanism appears to be of significant importance only in determining the characteristics of the cryogenic aerosol at low process chamber pressures.

These different mechanisms affect both the droplet size as well as the phase (liquid or solid) of the droplet. At higher (e.g. about  $2.0 \times 10^4$  Pascal) process chamber pressures the standard break up mechanisms dominate leading to larger droplets. In contrast, at process chamber pressures lower than that taught by the prior art, i.e. about  $1.6 \times 10^4$  Pascal or less, the effervescent flashing mechanism appears to be dominant. This leads to smaller droplets. A given mass flow through the nozzle will, therefore, produce more aerosol particles under the conditions where effervescent flashing is operative leading to a higher density aerosol. In addition, evaporation of material from the aerosol particles removes heat from the aerosol particles and may

assist in solidification of some or all of the remaining particle mass. When the aerosol particles are small, less heat needs to be removed to cause solidification. Thus, small aerosol particles freeze rapidly leading to many small solid or partially solid aerosol particles.

5                   The process implications are important. Control of the process chamber pressure dramatically affects the characteristics of the cryogenic aerosol. For contaminant particle and residue removal, in particular for the removal of small contaminant particles ( $\leq$  about 0.3 micron), as well as for elimination of stiction in MEMS devices, a cryogenic aerosol that is composed of mostly solid aerosol particles is  
10 considered desirable for improved performance. Operating at process chamber pressures below that of the prior art is thus highly and unexpectedly beneficial.

Additional benefits of operating at a low pressure are less dependence on aerosol impingement angle, nozzle to substrate distance and gas/liquid pressure upstream of the nozzle.

15                   Other parameters that affect the fraction of solid aerosol particles in the aerosol include the gas:liquid ratio of the cryogen delivered to the nozzle, gas/liquid pressure, dewar back pressure, chemical composition of the cryogen, the total gas flow, and the distance between the substrate and the nozzle. The gas:liquid ratio influences the droplet size formed upon expulsion of the aerosol from the nozzle. A higher  
20 gas:liquid ratio generally leads to smaller droplets in the aerosol that are more likely to freeze prior to impacting the substrate. The gas/liquid pressure in the nozzle can impact the aerosol particle size distribution and velocity. In general, a higher gas/liquid pressure in the nozzle can produce smaller aerosol particles with higher velocity compared to a lower gas/liquid pressure in the nozzle. The dewar back pressure  
25 controls the amount of heat exchange between the process gas(es) and the heat exchanger. The amount of heat exchanged, in turn, impacts the gas:liquid ratio discussed above. The chemical composition of the cryogen will also affect the aerosol properties because the condensation temperature will change for different chemicals and chemical mixtures. The chemical composition also affects the gas:liquid ratio discussed  
30 above. The total gas flow will impact the gas/liquid pressure and the gas:liquid ratio. Another parameter that will affect the amount of solid aerosol particles impinging on the substrate surface is the distance between the substrate and the nozzle. A larger distance will allow more time for aerosol particles to freeze and lead to more solid aerosol



particles striking the surface. Of course, increasing the distance to the substrate may result in reducing aerosol particle velocity due to turbulent mixing in the jet and may reduce the number of aerosol particles due to evaporation. The optimal balance of these parameters is well within the skill in the art.

5                   An apparatus as depicted in Figure 4 may be used to treat the substrate. Referring to Figure 4, the substrate 12 is mounted on a movable chuck 14, which is at ambient or heated temperature. The term chuck is used to mean a device which functionally supports the object to be treated. The chuck includes an appropriate slide or glide mechanism or a turntable. A rotatable nozzle 18, from which the cryogenic  
10 aerosol emanates, is supported within the process chamber 16. Nozzle 18 is connected with a supply line 26, which itself may be connected further with discreet supply lines 28 and 30 connected with the actual gas or liquid supplies of argon, nitrogen or the like, depending on the specific process. Further processing steps, such as gas cooling, may take place within the supply line 26, again, depending on the specific process, so that the  
15 nozzle 18 expels the desired cryogenic aerosol. The inside of the process chamber 16 may be connected further with either a vacuum device or a pressurizing device or both for selectively controlling the desired pressure within the process chamber 16 based on the specific process. A vacuum device (not shown) may be connected through the exhaust duct 20.

20                   To control the fluid dynamics within the process chamber 16, a flow separator comprising a baffle plate 34 is connected to an end of the moveable chuck 14 and to extend into the exhaust duct 20. Additionally, a shroud 36 is provided within the process chamber 16 and comprises a plate connected to the process chamber 16, such as its upper wall, for controlling flow around the nozzle. The controlling of the fluid  
25 dynamics within the process chamber 16 by the baffle plate 34 and the shroud 36 are more fully described in copending U.S. application serial number 08/712,342, filed September 11, 1996 and incorporated herein by reference.

                  Also shown in Figure 4, a curtain gas, preferably an inert gas such as nitrogen, can be introduced into the process chamber 16 via one or more supply conduits  
30 38. Although not necessary, such curtain gas is preferably introduced at a location opposite the exhaust in the process chamber 16. The curtain gas may be used to compensate or make-up for slight pressure deviations within the process chamber caused by instabilities in the nozzle and pressure controls allowing for the overall

positive flow across the process chamber. Conventional supply techniques may be used. The nozzle angle is optimized for particle removal and flow dynamics.

In one embodiment, an argon/nitrogen mixture is filtered free of any contaminating particles and cooled to a temperature at or near its liquification point in a heat exchanger. Following the cooling operation, the argon/nitrogen mixture is a combination of gas and liquid.

In another embodiment, an argon/nitrogen mixture is filtered free of any contaminant particles and pre-cooled to a temperature slightly above its liquification point. Following the pre-cooling operation, the argon/nitrogen mixture is gas. The pre-cooling operation permits additional purification by allowing for condensation and removal of any remaining trace impurities onto the heat exchanger walls. Pre-cooling may be combined with simultaneous removal of trace impurities using a molecular sieve or catalytic impurities removal device or any other suitable impurities filter upstream of the heat exchanger. The argon/nitrogen mixture may then be fed into a second heat exchanger for the purpose of further cooling the mixture near to the temperature of liquification. Such methods for removing trace molecular impurities from inert gases are well known in the field. The pressure of the argon/nitrogen mixture is typically held in the range of  $2.4 \times 10^5$  Pascal to  $4.8 \times 10^6$  Pascal, preferably  $2.4 \times 10^5$  Pascal to  $7.8 \times 10^5$  Pascal. The temperature of the mixture is typically in the range of from about  $-200^\circ\text{C}$  to about  $-120^\circ\text{C}$  and preferably from about  $-200^\circ\text{C}$  to about  $-150^\circ\text{C}$ . The nitrogen flow rate is between 0 and 600 standard liters per minute (slpm), preferably 100-200 slpm, and the argon flow rate is between 0 and 600 slpm, preferably 300-600 slpm.

The cooled mixture, whether liquid or liquid/gaseous, is then expanded from a nozzle or expansion valve from a pressure of approximately  $2.4 \times 10^5$  Pascal to  $4.8 \times 10^6$  Pascal, preferably  $2.4 \times 10^5$  Pascal to  $7.8 \times 10^5$  Pascal, to a lower pressure, and a temperature at or near the liquification temperature of the argon/nitrogen mixture to form at least substantially solid aerosol particles of the mixture in a mixture with gaseous argon and/or nitrogen, the aerosol particles being formed downstream of the nozzle as a result of the effervescent flashing that occurs on expansion of the liquid and gas. To accomplish this result, the process chamber is maintained at a pressure of about  $1.6 \times 10^4$  Pascal or less where the aerosol breakup is dominated by the rapid nucleation and growth of bubbles within the liquid. More preferably, the process chamber is

maintained at a pressure of about  $1.2 \times 10^4$  Pascal or less and most preferably, at a pressure of about  $8.0 \times 10^3$  Pascal or less. The nozzle preferably is rotatable and translatable toward or away from the substrate to be treated as described in copending application 08/773,489 filed December 23, 1996. The nozzle may be a nozzle within  
5 nozzle design as disclosed in copending application 08/773,489. Single tube and other nozzles may also be used as well.

The nozzle and the cryogenic aerosol emanating from the nozzle, are directed at the substrate at an angle between substantially parallel and perpendicular, suitably at an inclined angle between  $0^\circ$  and  $90^\circ$ , more preferably at an angle between  
10  $30^\circ$  and  $60^\circ$  toward the surface of the substrate 12 containing the contaminant. One skilled in the art will recognize that the cryogenic aerosol will likely diverge from the nozzle such that a steady single stream of particles will not necessarily be directed at a contaminant. Rather, the aerosol itself may diverge from the nozzle in a range from a  $1^\circ$  to  $180^\circ$  angle. The jet is typically at a vertical distance of approximately several  
15 millimeters to several centimeters above the contaminant. Depending on the choice of nozzle and/or chamber design, multiple substrates may be treated simultaneously.

One device capable of forming such a cryogenic aerosol and so treating substrates is an ARIES™ cryogenic aerosol tool, supplied by FSI International, Inc. Chaska, Minnesota, and configured with the above described process chamber and  
20 nozzle.

In the preferred embodiment, a nitrogen/argon mixture is used as the cryogen. Other chemicals, however, such as helium, nitrogen, neon, argon, krypton, xenon, carbon dioxide, inert hydrocarbons and mixtures thereof may be used as well. In another embodiment a nitrogen-only aerosol is used. Gas and/or liquid nitrogen are  
25 used as the cryogen. A Dewar filled with liquid nitrogen and pressurized with nitrogen gas supplies a stream of liquid and gaseous nitrogen directly to the nozzle. Nitrogen flow rates of up to 1000 slpm may be used. In yet another embodiment, an argon-only aerosol is used. Gas and/or liquid argon are used as the cryogen. A Dewar filled with liquid argon and pressurized with gas argon or nitrogen supplies a stream of liquid and  
30 gaseous argon directly to the nozzle. In yet other embodiments, the cryogenic aerosol comprises one or more chlorofluorohydrocarbons.

The invention is illustrated by the following non-limiting examples.

Example 1a, Comparative Example 1b

A cryogenic aerosol was formed by expanding a stream of nitrogen into a modified ARIES™ SYSTEM process chamber at 5 different process chamber pressures. The ARIES™ SYSTEM process chamber was modified to allow for optical access to areas in close proximity to the nozzle. The nitrogen was cooled in a heat exchanger to produce a liquid/gaseous stream. The heat exchanger was a Dewar containing liquid nitrogen. The Dewar back pressure was 0 psig. The nitrogen gas flow was 50 slpm and the nitrogen pressure was 36-40 psig.

An Aerometrics, Inc. Phased Doppler particle analyzer (PDPA) was used to perform the particle velocity analysis. The PDPA system splits the single light beam generated by an argon laser operating at a wavelength of 488 nm into two beams then sends both beams through collimating and transmitting lenses (100 mm). The light beams passed through a 3/8 inch thick optical grade Pyrex® window and entered the vacuum chamber. The light beams intersected the aerosol, and each other, at a distance .04 meters (1.75 inches) from the aerosol nozzle. The distance between the laser light transmitting lens and the beam crossing was 0.1 m. The measurement volume was approximately 1 mm long with a  $100 \mu\text{m}^2$  cross section. The laser light (scattered and not scattered) exited the vacuum chamber through a second 3/8 inch thick optical grade Pyrex® window. The detector was located approximately 0.5m from where the laser beams intersected the aerosol at an angle of approximately  $30^\circ$  with respect to the initial light direction (but in the same horizontal plane as the laser). The raw data was deconvoluted and fit to a gaussian curve using proprietary software supplied with the PDPA.

Figures 5a and 5b depict the distribution of aerosol particle velocities for an aerosol spray of the present invention at chamber pressures of  $1.6 \times 10^3$  Pa and for a prior art aerosol spray at  $4.0 \times 10^4$  Pa. The figures demonstrate that at the reduced chamber pressure of the present invention, the mean velocity of the aerosol particles increases significantly from 24 m/s at  $4.0 \times 10^4$  Pa to 61 m/s at  $1.6 \times 10^3$  Pa.

Example 2

A cryogenic aerosol was formed as in Example 1 except that the nitrogen gas flow was 95 slpm. A Malvern Instruments Fraunhofer diffraction apparatus (model #2600) was used to perform the aerosol size measurements. This instrument has two main parts; a transmitter box and a receiver box. The front of the transmitter box was

located approximately 0.3 m from the front of the receiver box. The transmitter box contains a He-Ne laser with a wavelength of 633 nm. The laser beam was collimated by a lens on the Malvern Instrument and the resulting beam diameter was between 7 and 10 mm. The laser light was then passed into a vacuum chamber through a 3/8 inch thick optical grade Pyrex® window. The laser light then intersected the aerosol normal to the aerosol flow direction at a distance of 0.1 m (4.5 inches) from the aerosol nozzle. The measurement area was between 7 and 10 mm. The laser light (scattered and not scattered) exited the vacuum chamber through a second 3/8 inch thick optical grade Pyrex® window. The receiving lens of the Malvern Instrument receiver box focused the scattered light as well as the transmitted light onto a detector. The transmitted light is focused to a point on the optical axis while the scattered light forms a series of concentric rings (Fraunhofer diffraction pattern). Because the receiving lens performs a Fourier transform on the scattered light, light scattered at a given angle by a particle located anywhere in the illuminated sample volume will be focused at the same radial position in the transform plane. Thus, the resulting pattern is unaffected by particle location or motion. The raw data was deconvoluted and then fit to a log normal distribution using proprietary software supplied with the Fraunhofer diffraction apparatus.

Table 1 demonstrates that at the decreased chamber pressure of the present invention, the Sauter mean diameter of aerosol particles is decreased from the Sauter mean diameter of aerosol particles of the prior art at higher chamber pressure.

TABLE I

Particle size for various chamber pressures

Pressure (Pa)	Sauter mean diameter (microns)
$5.3 \times 10^3$	8
$4.0 \times 10^4$	48

Example 3

Silicon substrates contaminated with particulate matter ( $\text{Si}_3\text{N}_4$ ) were subjected to cryogenic aerosol treatment in an ARIES™ cryogenic aerosol tool at two different process chamber pressures. The cryogenic aerosol was formed by expanding a 3:1 mixture of argon and nitrogen into a process chamber. Argon gas flow was 360 slpm, nitrogen gas flow was 120 slpm. Argon and nitrogen were combined in a process

gas line prior to cooling in a heat exchanger. The heat exchanger was a Dewar containing liquid nitrogen. The Dewar back pressure was 36 psia. The cooled liquid/gaseous mixture was then expanded through a nozzle into the process chamber. Removal efficiency was calculated based on the number of contaminant particles prior to treatment and the number of contaminant particles post treatment. Table II demonstrates that contaminant removal efficiency increases with a decreased process chamber pressure. In particular, for small contaminant particle sizes of 0.15-0.3 microns, a dramatic improvement in contaminant removal efficiency results from operating at lower process chamber pressures.

TABLE II

Removal efficiency for various particle sizes (percent)

Pressure (Pa)	0.15-0.2 $\mu$ m	0.2-0.3 $\mu$ m	0.3-1.0 $\mu$ m	1.0-5.0 $\mu$ m	>5.0 $\mu$ m
$8 \times 10^3$	93.7%	98.6%	99.2%	98.9%	98.4%
$4 \times 10^4$	60.9%	86.0%	96.2%	95.8%	96.8%

The inventive process can also be usefully employed to eliminating stiction as disclosed in the application of David S. Becker, Ronald J. Hanestad, Gregory P. Thomes, James F. Weygand, Larry D. Zimmerman entitled, "Eliminating Stiction With The Use Of Cryogenic Aerosol" filed concurrently herewith and incorporated herein by reference.

Those skilled in the art will recognize that the process of the invention will also be useful in applications other than those specifically identified herein and such other applications should be considered to be within the scope of the patent granted hereon.

What is claimed is as follows:

5           1.           A method for treating a substrate by impinging the substrate with a cryogenic aerosol spray wherein said cryogenic aerosol spray is formed by expanding a pressurized liquid or liquid/gaseous stream of at least one cryogen through a nozzle into a process chamber at a pressure of about  $1.6 \times 10^4$  Pascal or less so as to form at least substantially solid aerosol particles of said at least one cryogen downstream from the  
10           nozzle.

          2.           The method of claim 1 wherein the cryogenic aerosol spray comprises at least one gas and substantially solid aerosol particles, both the gas and the particles comprising at least one chemical selected from the group consisting of helium, nitrogen,  
15           neon, argon, krypton, xenon, carbon dioxide, chlorofluorohydrocarbons, inert hydrocarbons and mixtures thereof.

          3.           The method of claim 1 wherein the at least one cryogen is selected from the group consisting of argon, nitrogen and mixtures thereof.

20           4.           The method of claim 1 wherein the pressure of the process chamber is about  $1.2 \times 10^4$  Pascal or less.

          5.           The method of claim 1 wherein the pressure of the process chamber is  
25           about  $8.0 \times 10^3$  Pascal or less.

          6.           A method for treating a substrate by impinging the substrate with a cryogenic aerosol spray wherein said cryogenic aerosol spray is formed by  
                    forming a first aerosol spray by expanding a pressurized liquid or liquid/gaseous  
30           stream of one or more cryogens through a nozzle into a process chamber of lower pressure; and  
                    effervescent flashing said first aerosol spray so as to form a cryogenic aerosol spray of at least substantially solid aerosol particles downstream from the nozzle.

7. The method of claim 6 wherein the cryogenic aerosol spray comprises at least one gas and substantially solid aerosol particles, both the gas and the particles comprising at least one chemical selected from the group consisting of helium, nitrogen, neon, argon, krypton, xenon, carbon dioxide, chlorofluorohydrocarbons, inert hydrocarbons and mixtures thereof.

8. The method of claim 7 wherein the cryogenic aerosol spray is formed from liquid and gaseous nitrogen.

9. The method of claim 7 wherein the cryogenic aerosol spray is formed from liquid and gaseous argon.

10. The method of claim 7 wherein the pressure of the process chamber is about  $1.2 \times 10^4$  Pascal or less.

11. The method of claim 7 wherein the pressure of the process chamber is about  $8.0 \times 10^3$  Pascal or less.

12. The method of claim 1, the pressurized liquid or liquid/gaseous mixture comprising a liquid, wherein the aerosol particles of the cryogenic aerosol are formed predominantly through rapid nucleation and growth of bubbles within the liquid, said bubbles being nucleated upstream and/or downstream of the nozzle.

13. A method for forming a cryogenic aerosol spray by expanding a pressurized liquid or liquid/gaseous stream of at least one cryogen through a nozzle into a process chamber with a pressure of about  $1.6 \times 10^4$  Pascal or less so as to form at least substantially solid aerosol particles of said at least one cryogen.

14. A cryogenic aerosol spray formed by expanding a pressurized liquid or liquid/gaseous stream of at least one cryogen through a nozzle into a process chamber with a pressure of about  $1.6 \times 10^4$  Pascal or less so as to form at least substantially solid aerosol particles of said at least one cryogen.

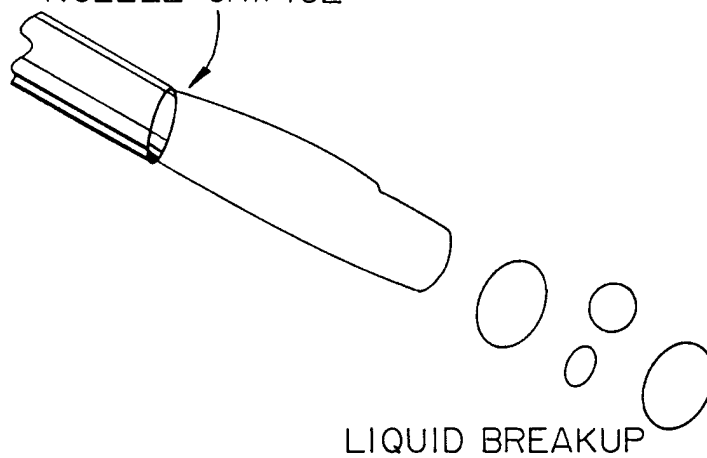


15. The method of claim 1 wherein the substrate is contaminated with particles smaller than about 0.3 micron.

*Fig. 1*

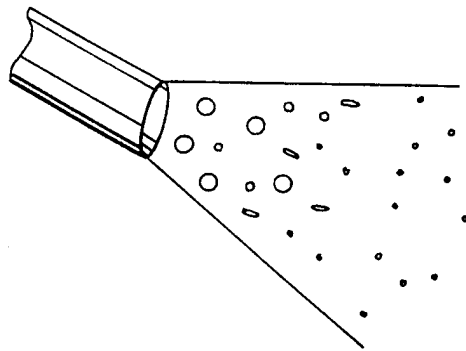
HIGH CHAMBER PRESSURE

NOZZLE ORIFICE



*Fig. 2*

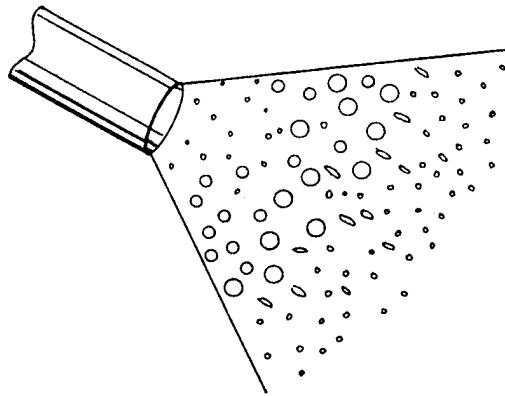
HIGH CHAMBER PRESSURE



LIQUID BREAKUP FROM A  
HIGH VELOCITY GAS

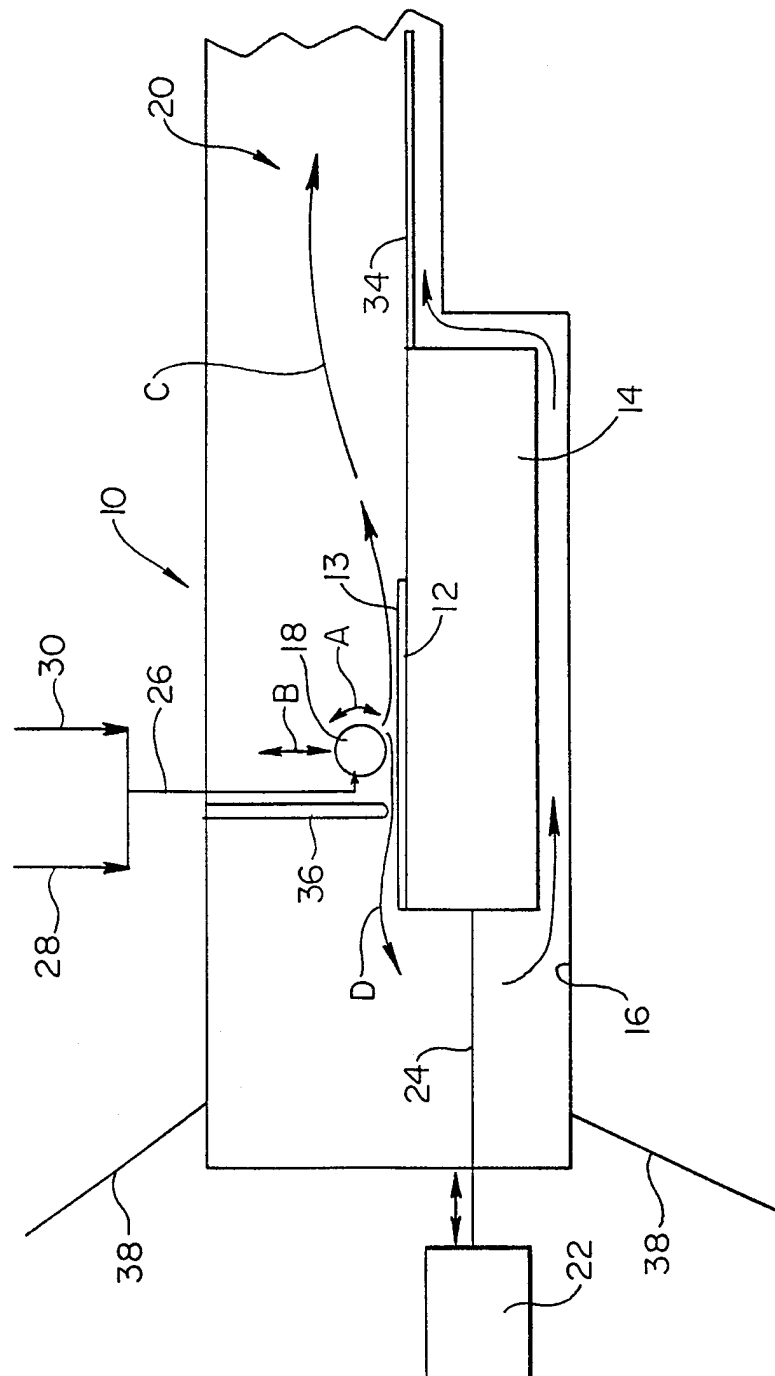
*Fig. 3*

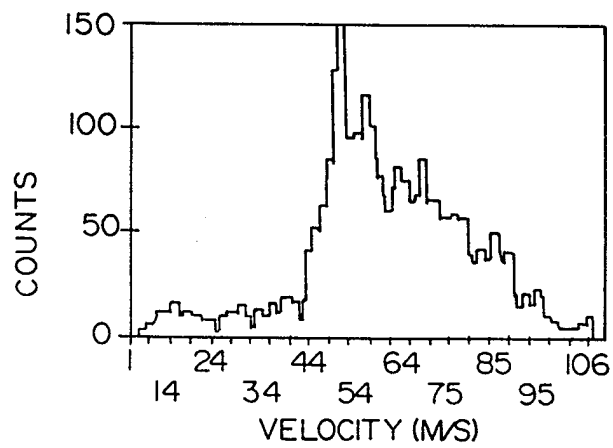
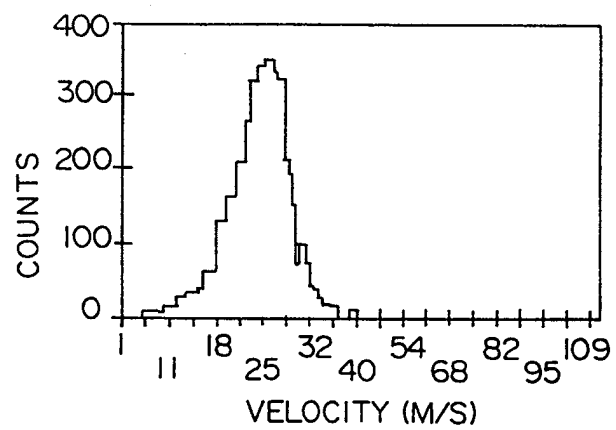
LOW PRESSURE CHAMBER



"EFFERVESCENT FLASHING"

**Fig. 4**



*Fig. 5a**Fig. 5b*

# INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 98/12256

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01L21/306 F25J1/00 B08B5/02

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)

IPC 6 H01L F25J B08B B24C

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 practical, 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.
X	PATENT ABSTRACTS OF JAPAN vol. 4, no. 166 (C-031), 18 November 1980 -& JP 55 106538 A (HIROSHI), 15 August 1980 see abstract ---	1-14
X	US 5 512 106 A (TAMAI ET AL) 30 April 1996 cited in the application see column 5, line 11 - line 51 ---	1-3,6-9, 12-14
X	PATENT ABSTRACTS OF JAPAN vol. 14, no. 200 (E-920), 24 April 1990 -& JP 02 043730 A (TOSHIKI ET AL), 14 February 1990 see abstract ---	1,13,14
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in 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 but 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

8 September 1998

Date of mailing of the international search report

22/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Gori, P

# INTERNATIONAL SEARCH REPORT

Interr. .nal Application No

PCT/US 98/12256

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 300 (M-848), 11 July 1989 -& JP 01 092071 A (TAKESHI ET AL), 11 April 1989 see abstract ----	1,13,14
X	EP 0 535 680 A (PETERSON ET AL) 7 April 1993 see column 8, line 29 - column 32 ----	1,13,14
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 67 (M-566), 28 February 1987 -& JP 61 223311 A (KENJI ET AL), 3 October 1986 see abstract -----	1



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/12256

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5512106 A	30-04-1996	JP 6252114 A	09-09-1994
		JP 6283489 A	07-10-1994
		JP 6295894 A	21-10-1994
		JP 7045571 A	14-02-1995
		DE 4402247 A	28-07-1994
		GB 2274742 A, B	03-08-1994
		JP 6295895 A	21-10-1994
EP 535680 A	07-04-1993	US 5315793 A	31-05-1994
		CA 2077463 A	02-04-1993
		DE 69209957 D	23-05-1996
		DE 69209957 T	19-09-1996
		JP 2765787 B	18-06-1998
		JP 5253551 A	05-10-1993