

On-Site Generation of Ultra-High-Purity Buffered HF for Semiconductor Processing



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ACTION

BACKGROUND AND SUMMARY OF THE INVENTION

The present invention relates to semiconductor manufacture, and particularly to systems and methods for supplying ultra-high-purity hydrogen peroxide for semiconductor manufacture.

5 Contamination Control in IC Manufacturing

Contamination is generally an overwhelmingly important concern in integrated circuit manufacturing. A large fraction of the steps in modern integrated circuit manufacturing are cleanup steps of one kind or another; such cleanup steps may need to remove organic contaminants, metallic contaminants, photoresist (or inorganic residues thereof), byproducts of
10 etching, native oxides, etc.

As of 1995 the cost of a new front end (integrated circuit wafer fabrication facility) is typically more than a billion dollars (\$1,000,000,000), and a large fraction of this cost is directed to measures for particulate control, cleanup, and contamination control.

One important source of contamination is impurities in the process chemicals. Since
15 the cleanups are so frequent and so critical, contamination due to cleanup chemistry is very undesirable.

Since many corrosive and/or toxic chemicals are commonly used in semiconductor processing, the reagent supply locations are commonly separated from the locations where

front-end workers are present. Construction and maintenance of piping for ultra-high-purity gasses and liquids are well-understood in the semiconductor industry, so most gasses and liquids can be transported to wafer fabrication stations from anywhere in the same building (or even in the same site).

- 5 The present application discloses systems and methods for preparation of ultrapure chemicals on-site at a semiconductor manufacturing facility, so that they can be piped directly to the points of use. The disclosed systems are very compact units which can be located in the same building as a front end (or in an adjacent building), so that handling is avoided.

Wet versus Dry Processing

- 10 One of the long-running technological shifts in semiconductor processing has been the changes (and attempted changes) between dry and wet processing. In dry processing, only gaseous or plasma-phase reactants come in contact with the wafer. In wet processing, a variety of liquid reagents are used for purposes such as etching silicon dioxide or removing native oxide layers, removing organic materials or trace organic contaminants, removing
15 metals or trace organic contaminants, etching silicon nitride, etching silicon.

Plasma etching has many attractive capabilities, but it is not adequate for cleanup. There is simply no available chemistry to remove some of the most undesirable impurities, such as gold. Thus wet cleanup processes are essential to modern semiconductor processing, and are likely to remain so for the foreseeable future.

- 20 Plasma etching is performed with photoresist in place, and is not directly followed by high-temperature steps. Instead the resist is stripped, and a cleanup is then necessary.

- The materials which the cleanup must remove may include: photoresist residues (organic polymers); sodium; Alkaline earths (e.g. calcium or magnesium); and heavy metals (e.g. gold). Many of these do not form volatile halides, so plasma etching can't carry them
25 away. Cleanups using wet chemistries are required.

- The result of this is that purity of process chemicals at plasma etching is not as critical, since these steps are always followed by cleanup steps before high-temperature steps occur, the cleanup steps can remove dangerous contaminants from the surface before high-temperature steps drive in these contaminants. However, purity of the liquid chemicals is
30 much more critical, because the impingement rate at the semiconductor surface is typically a million times higher than in plasma etching, and because the liquid cleanup steps are directly followed by high-temperature steps.

- However, wet processing has one major drawback, namely ionic contamination. Integrated circuit structures use only a few dopant species (boron, arsenic, phosphorus, and
35 sometimes antimony) to form the required p-type and n-type doped regions. However, many

other species are electrically active dopants, and are highly undesirable contaminants. Many of these contaminants can have deleterious effects, such as increased junction leakage, at concentrations well below 10^{13}cm^{-3} . Moreover, some of the less desirable contaminants segregate into silicon, *i.e.* where silicon is in contact with an aqueous solution the equilibrium concentration of the contaminants will be higher in the silicon than in the solution. Moreover, some of the less desirable contaminants have very high diffusion coefficients, so that introduction of such dopants into any part of the silicon wafer will tend to allow these contaminants to diffuse throughout, including junction locations where these contaminants will cause leakage.

Thus all liquid solutions which will be used on a semiconductor wafer should preferably have extremely low levels of all metal ions. Preferably the concentration of all metals combined should be less than 300 ppt (parts per trillion), and less than 10 ppt for any one metal, and less would be better. Moreover, contamination by both anions and cations must also be controlled. (Some anions may have adverse effects, *e.g.* complexed metal ions may reduce to mobile metal atoms or ions in the silicon lattice.)

Front end facilities normally include on-site purification systems for preparation of high-purity water (referred to as "DI" water, *i.e.* deionized water). However, it is more difficult to obtain process chemicals in the purities needed.

On-Site Purification

The present inventors have developed a method for preparing ultra-high-purity ammonia, in an on-site system located at the semiconductor wafer production site, by: drawing ammonia vapor from a liquid ammonia reservoir, passing the ammonia vapor through a microfiltration filter, and scrubbing the filtered vapor with high-pH purified water (preferably deionized water which has been allowed to equilibrate with the ammonia stream). This discovery permitted conversion of commercial grade ammonia to ammonia of sufficiently high purity for high-precision manufacturing without the need for conventional column distillation. The drawing of the ammonia vapor from the supply reservoir serves by itself as a single-stage distillation, eliminating nonvolatile and high-boiling impurities, such as alkali and alkaline earth metal oxides, carbonates and hydrides, transition metal halides and hydrides, and high-boiling hydrocarbons and halocarbons. The reactive volatile impurities that could be found in commercial grade ammonia, such as certain transition metal halides, Group III metal hydrides and halides, certain Group IV hydrides and halides, and halogens, previously thought to require distillation for removal, were discovered to be capable of removal by scrubbing to a degree which is adequate for high-precision operations. This is

a very surprising discovery, since scrubber technology is traditionally used for the removal of macro-scale, rather than micro-scale, impurities.

Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is an important process chemical in semiconductor manufacturing. It is very commonly used for cleanup solutions. For example, the widely used "piranha" cleanup solution typically uses $H_2O_2 + H_2SO_4$ in proportions of 30:70; the
5 widely used "RCA" cleanup is a three-stage cleanup which uses hydrogen peroxide in two of the stages.

Thus ultra-high-purity aqueous hydrogen peroxide is a staple of integrated circuit processing. Hydrogen peroxide is not an easy chemical to purify, since its decomposition is exothermic and temperature sensitive, and is catalyzed by various possible metals and
10 contaminants. Moreover, H_2O_2 is a powerful oxidant. However, substantial work has been done in this area; for example, it has been reported in the literature that an anionic exchange resin for purifying hydrogen peroxide should preferably be loaded with bicarbonate (HCO_3^-) ions, since other commonly used anions (such as OH^- or Cl^-) will catalyze the decomposition of H_2O_2 under some circumstances.

15 Elimination of organic acidic components contained in H_2O_2 is described in, for example: French patent/application 1,539,843 (1968) (using non-functionalized resins and neutralized base acid); US patent 3,294,488 (1966) (Basic resin [HCO_3^-] + CO_2); Japanese patent 6,725,845 (1967) (non-functionalized resins); US patent 297,404 (1967) (Basic resin [HC_3] and CO); US patent 3,305,314 (1967) (Basic resin [HCO_3^-] and ($CO_2/3^-$); US patent
20 4,792,403 (1988) (Halogenated resin).

H_2O_2 purification on cationic and anionic resins (tertiary, quaternary) is described in, for example: French patent application 10,431 (1953) (use of Sulfonic resins); Polish patent 50,982 (1961) (cationic + anionic resins); Polish patent 55,378 (1968); Spanish patent 328,719 (1961) (sulfonic resins, acrylic, strong base and acid [gel type]); U.S. patent
25 3,297,404 (1967) (use of mixed resins cationic and anionic [HCO_3^-] described in line 53 col. 2); U.S. patent 4,999,179 (1991) (sulfonic resin + anionic resin [HCO_3^-], $CO_2/3^-$ + brominated). Different configurations are described; French patent 2,677,010 (1992) (strong cationic resin + medium strength anionic resin of the gel type + non-functionalized resin); French patent 2,677,011 (1992) (medium strength anionic resin); world PCT application
30 92/06918 (1992) (cationic, anionic resins, description of the fluidized bed technology).

H_2O_2 purification on sulfonic and pyridinic resins is described in, for example: Swedish patent 1,643,452 (1991) (cationic resin + 2,5 methyl base resins -pyridinic vinyl [HCO_3^-]); Japanese patent 62,187,103 (1966) (cationic resins + pyridilic anionic structure).

H_2O_2 purification on resins and chelatants is described in, for example: French patent
35 2,624,500 (1988) (adding carboxylic or phosphonic chelatant to the basic resin); German patent 3,822,248 (1990) (EDTA added to basic resin); European patent 502,466 (1992)

(Chelatant added to H_2O_2 and passing into non-functionalized resin); US patent 5,200,166 (1993) (addition of a stabilizing acid into H_2O_2 and reacting with basic resin [HCO_3^- , CO_3^{2-}]); European patent 626,342 (1994) (chelant resin with phosphates <0.1 ppm A^- or A^-/C^+ + chelant Al and Fe).

- 5 Several patents have reported success in achieving purity below 1 ppb: TOKKAI's French patent 624,500 (using resins and complexing agents); INTEROX's WO90/11967 (using SnO_2 + ultrafiltration); and NEC's French patent application 3,045,504 (using Silica treatment). All of these are hereby incorporated by reference.

On-Site Preparation of Ultrapure Hydrogen Peroxide

- 10 The present application describes systems and methods for preparing ultra-high-purity hydrogen peroxide on-site at an integrated circuit fabrication front-end facility. The starting point is high-purity aqueous H_2O_2 (e.g. 30% H_2O_2). The incoming aqueous H_2O_2 is further purified in on-site purification units before it is made available for combination with other reagents. (In the presently preferred embodiment, the on-site purification units consist of
- 15 anionic and cationic exchange beds, together with one or more particulate filters.)

 The present application also describes systems and methods for preparing ultra-high-purity mixed cleanup solutions on-site at an integrated circuit fabrication front-end facility, by combining hydrogen peroxide which has been ultrapurified on-site with an acid or base which has been ultrapurified on-site.

On-Site Preparation of Ultrapure Mixed Cleanup Solutions

20 The present application discloses preparation of mixed cleanup solutions, such as the RCA acidic cleanup and the RCA basic cleanup, at the site of a wafer fabrication facility, from ingredients which themselves have been ultrapurified at the same site.

- The RCA cleanup includes: 1) solvent wash to remove gross organics - in
- 25 tetrachloroethylene or comparable solvent; 2) basic cleanup - $NH_4OH + H_2O_2 + H_2O$; and 3) acid cleanup - $HCl + H_2O_2 + H_2O$.) See W.Runyan and K.Bean, SEMICONDUCTOR INTEGRATED CIRCUIT PROCESSING TECHNOLOGY (1990), which is hereby incorporated by reference. For semiconductor manufacturing, such cleanup reagents are normally bought as packaged containers. However, this implies that some handling of the solutions in those
- 30 containers will be necessary, both at the manufacturer's plant and at the use location. As noted above, such handling of ultra-high purity chemicals is always undesirable.

 Various other cleanup chemistries have been proposed. For example, the Shiraki cleanup is an aggressive, pre-epitaxy cleanup, which adds a nitric acid step to the cleanup sequence, and uses somewhat higher temperatures and concentrations. See Ishizaki and

Shiraki, "Low Temperature Surface Cleaning of Silicon and its application to Silicon MBE," 133 J. ELECTROCHEM. SOC. 666 (1986), which is hereby incorporated by reference.

5 The RCA basic cleanup solution is typically $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ in proportions of 1:1:5 or 1:2:7. According to one of the innovative teachings disclosed herein, RCA basic cleanup (or analogous cleanup solutions) is generated at the site of a wafer manufacturing plant, by combination of ultra-pure ammonia which has been purified on-site with ultra-pure hydrogen peroxide which has been purified on-site. Thus purity is increased, and the risk of undetected accidental contamination is reduced.

10 The RCA acid cleanup solution is typically $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ in proportions of 1:1:6 or 1:2:8. According to one of the innovative teachings disclosed herein, RCA acid cleanup (or analogous cleanup solutions) is generated at the site of a wafer manufacturing plant, by combination of ultra-pure HCl which has been purified on-site with ultra-pure hydrogen peroxide which has been purified on-site. Thus purity is increased, and the risk of undetected accidental contamination is reduced.

15 Brief Description of the Drawing

The disclosed inventions will be described with reference to the accompanying drawings, which show important sample embodiments of the invention and which are incorporated in the specification hereof by reference, wherein:

20 **Figure 1** shows an on-site system for purification of aqueous hydrogen peroxide at a semiconductor facility.

Figure 2 is a block diagram of semiconductor cleanup stations, in a wafer fabrication facility in which the ammonia purification of Figure 1 may be incorporated.

25 **Figure 3** shows generation of an RCA cleanup solution on-site, at a wafer fabrication facility, using two components (in addition to ultrapure water) which have both been ultrapurified on-site at the same facility.

Detailed Description of the Preferred Embodiments

The numerous innovative teachings of the present application will be described with particular reference to the presently preferred embodiment (by way of example, and not of limitation). In this embodiment:

30 The target for purity of the aqueous H_2O_2 is:

- cation concentration < 1.0 ppb;
- anion concentration < 20 ppb;
- total organic contaminants < 20ppm.

Process and System Overview

The containers and piping are preferably chosen to be inert and non-catalytic to H_2O_2 . Inert fluoropolymers are preferred, since most metals catalyzed H_2O_2 decomposition to some extent.

5 **Figure 1** shows an on-site system for purification of aqueous hydrogen peroxide at a semiconductor facility. In this system incoming hydrogen peroxide (preferably already high-purity) is further purified to sub-ppb levels by an on-site ultrapurification system.

In the presently preferred embodiment the on-site ultrapurification system uses an anionic exchange column in combination with a cationic exchange column. However, other
10 conventional techniques for sub-ppb polishing can also be used.

As shown in **Figure 1**, a filtration stage is preferably used downstream of the exchange resin columns, to remove any particulates which may have been introduced by the columns.

Anionic Exchange Column

15 This column is preferably initially loaded with bicarbonate ions. (Use of bicarbonate preconditioning is shown, e.g., by US patents 3294488 or 3305314, which are hereby incorporated by reference.) This is preferably achieved by use of a concentrated NH_4HCO_3 solution. (Possible alternatives include use of an alkali bicarbonate, which requires removal of the alkali metal ions, or use of CO_2 , which is inefficient due to the low solubility of CO_2 .)

20 In the presently preferred embodiment, the anionic resin is IRA 958 from Rohm and Haas. However, other suitable anionic resins can alternatively be used.

Cationic Exchange Column

This column is preferably initially loaded with acid. This can be done, e.g., with a wash in e.g. a 10% solution of H_2SO_4 .

25 In the presently preferred embodiment, the cationic resin is Rohm and Haas A-35. However, other suitable cationic resins can alternatively be used.

Generation of Mixed Cleanup Solutions

Figure 3 shows generation of an RCA cleanup solution on-site, at a wafer fabrication facility, using two components (in addition to ultrapure water) which have both been
30 ultrapurified on-site at the same facility.

Wafer Cleaning

Some cleanup stations in a conventional line for semiconductor fabrication are depicted in **Figure 2**. The first unit in the cleaning line is a resist stripping station 41 where aqueous hydrogen peroxide 42 and sulfuric acid 43 are combined and applied to the semiconductor surface to strip off the resist. This is succeeded by a rinse station 44 where
5 deionized water is applied to rinse off the stripping solution. Immediately downstream of the rinse station 44 is a cleaning station 45 where an aqueous solution of ammonia and hydrogen peroxide are applied. This solution is supplied in one of two ways. In the first, aqueous ammonia 31 from the dissolving unit 29 is combined with aqueous hydrogen peroxide 46, and the resulting mixture 47 is directed to the cleaning station 45. In the
10 second, pure gaseous ammonia 32 is bubbled into an aqueous hydrogen peroxide solution 48 to produce a similar mixture 49, which is likewise directed to the cleaning station 45. Once cleaned with the ammonia/hydrogen peroxide combination, the semiconductor passes to a second rinse station 50 where deionized water is applied to remove the cleaning solution. The next station is a further cleaning station 54 where aqueous solutions of hydrochloric acid
15 55 and hydrogen peroxide 56 are combined and applied to the semiconductor surface for further cleaning. This is followed by a final rinse station 57 where deionized water is applied to remove the HCl and H₂O₂, and finally a drying station 58. The wafer or wafer batch 51 will be held on a wafer support 52, and conveyed from one workstation to the next by a robot 63 or some other conventional means of achieving sequential treatment. The means
20 of conveyance may be totally automated, partially automated or not automated at all. Note that purified HCl for the acid cleaning station 54 may be prepared and supplied on site in a manner similar to that of the ammonia purification system of FIG. 1.

The system shown in FIG. 2 is just one example of a cleaning line for semiconductor fabrication. In general, cleaning lines for high-precision manufacture can vary widely from
25 that shown in FIG. 2, either eliminating one or more of the units shown or adding or substituting units not shown. The concept of the on-site preparation of high-purity hydrogen peroxide, however, in accordance with this invention is applicable to all such systems.

The use of ammonia and hydrogen peroxide as a semiconductor cleaning medium at workstations such as the cleaning station 45 shown in FIG. 2 is well known throughout the
30 industry. While the proportions vary, a nominal system would consist of deionized water, 29% ammonium hydroxide (weight basis) and 30% hydrogen peroxide (weight basis), combined in a volume ratio of 6:1:1. This cleaning agent is used to remove organic residues, and, in conjunction with ultrasonic agitation at frequencies of approximately 1 MHz, removes particles down to the submicron size range.

35 The on-site system for ultrapurification of H₂O₂ and generation of ultrapure cleaning solution will be connected to the point of use in the production line by piping which does

not cause any exposure to an uncontrolled ambient. The distance of travel between the unit and the production line may be short (in the case of a dedicated point-of-use mixing facility), or more preferably the ultrapure cleaning solution generator may be connected to multiple points of use through ultraclean piping. In large systems, intermediate holding tanks may be used to average the flow rate to compensate for varying demand, but in any case the cleaning solutions are maintained in an ultrapure environment, and are never exposed to ambient contamination. This avoids the risks of contamination due to packaging, transport, or transfer between containers. Thus the distance between the point at which the cleanup solution leaves the generation system and its point of use on the production line may be from one foot (30 cm) up to 1,000 meters or more (in the case where ultraclean piping is routed between buildings at a single manufacturing site). Transfer can be achieved through an ultra-clean transfer line of a material which does not introduce contamination. In most applications, stainless steel or polymers such as high density polyethylene or fluorinated polymers can be used successfully.

Due to the proximity of the ultrapure purification, generation and/or mixing units to the production line, deionized water (purified in accordance with semiconductor manufacturing standards) is readily available for purposes such as concentration adjustment, flushing, or dissolution of gasses. The standards commonly used in the semiconductor industry are well known among those skilled in the art. Typical standards for the purity of the water resulting from these processes are a resistivity of at least about 15 megohm-cm at 25°C (typically 18 megohm-cm at 25°C), less than about 25ppb of electrolytes, a particulate content of less than about 150/cm³ and a particle size of less than 0.2 micron, a microorganism content of less than about 10/cm³, and total organic carbon of less than 100ppb.

In the process and system of this invention, a high degree of control over the product concentration and hence the flow rates is preferably maintained, by precise monitoring and metering using known equipment and instrumentation. A convenient means of achieving this uses ultrasonic wave propagation to monitor density. Other methods will be readily apparent to those skilled in the art.

Modifications and Variations

As will be recognized by those skilled in the art, the innovative concepts described in the present application can be modified and varied over a tremendous range of applications, and accordingly the scope of patented subject matter is not limited by any of the specific exemplary teachings given.

For example, the disclosed innovative techniques are not strictly limited to manufacture of integrated circuits, but can also be applied to manufacturing discrete semiconductor components, such as optoelectronic and power devices.

5 For another example, the disclosed innovative techniques can also be adapted to manufacture of other technologies where integrated circuit manufacturing methods have been adopted, such as in thin-film magnetic heads and active-matrix liquid-crystal displays; but the primary application is in integrated circuit manufacturing, and applications of the disclosed techniques to other areas are secondary.

10 For another example, it is not strictly necessary to use a scrubber to perform the liquid-vapor contact; a bubbler could be used instead, although this is much less desirable because of the less efficient gas/liquid contact.

Optionally other filtration or filtration stages can be combined with the disclosed purification apparatus.

15 It should also be noted that additives can be introduced into the purification water if desired, although this is not done in the presently preferred embodiment.

As noted above, the primary embodiment is an on-site purification system. Alternatively, in a less preferred class of embodiment, the disclosed purification system can also be adapted to operate as a part of a manufacturing unit to produce ultra-high-purity chemicals for shipment; however, this alternative embodiment does not provide the advantages of on-site purification as discussed above. Such applications encounter the inherent risks of handling ultra-high-purity chemicals, as discussed above; but for customers who require packaged chemicals (with the attendant handling), the disclosed innovations at least give a way to achieve an initial purity which is higher than that available by other techniques. Again, in such applications a dryer stage may also be used after the ionic purifier.

25 As noted above, the primary embodiment is directed to providing ultrapure aqueous chemicals, which are most critical for semiconductor manufacturing. However, the disclosed system and method embodiments can also be used for supply of purified gas streams. (In many cases, use of a dryer downstream from the purifier will be useful for this.)

30 It should also be noted that piping for ultrapure chemical routing in semiconductor front ends may include in-line or pressure reservoirs. Thus references to "direct" piping in the claims do not preclude use of such reservoirs, but do preclude exposure to uncontrolled atmospheres.

CLAIMS

What is claimed is:

1. An on-site subsystem, in a semiconductor device fabrication facility, for providing ultra-high-purity reagents comprising H_2O_2 to a semiconductor manufacturing operation, comprising:
 - a tank connected to receive aqueous H_2O_2 and to provide a flow of H_2O_2 therefrom;
 - 5 an anionic exchange bed and a cationic exchange bed connected to receive said flow of H_2O_2 from said tank, and to produce therefrom a purified H_2O_2 flow with a reduced level of ionic contaminants;
 - wherein said cationic exchange bed is preconditioned with acid and said anionic bed is preconditioned with bicarbonate ions;
 - 10 a filter downstream of said anionic exchange bed and said cationic exchange bed; and
 - a piping connection which routes said aqueous H_2O_2 from said filter to points of use in the semiconductor device fabrication facility without exposure to any uncontrolled ambient.
2. An on-site subsystem, in a semiconductor device fabrication facility, for providing ultra-high-purity reagents comprising H_2O_2 to a semiconductor manufacturing operation, comprising:
 - a tank connected to receive aqueous H_2O_2 and to provide a flow of H_2O_2 therefrom;
 - 5 an anionic exchange bed and a cationic exchange bed connected to receive said flow of H_2O_2 from said tank, and to produce therefrom a purified H_2O_2 flow with a reduced level of ionic contaminants;
 - an ionic purifier system, connected to pass a gaseous reagent precursor through an area of gas/liquid contact to produce an ultrapure gaseous reagent;
 - 10 generation and mixing subsystems, connected to combine said ultrapure gaseous reagent with deionized water and with said purified H_2O_2 flow to produce an ultrapure cleanup solution;
 - a piping connection which routes said aqueous H_2O_2 from said filter to points of use in the semiconductor device fabrication facility without exposure to any uncontrolled
 - 15 ambient.
3. The system of Claim 2, wherein said generation and mixing subsystems are separate.

4. The system of Claim 2, wherein said generation and mixing subsystems are combined.
5. The system of Claim 2, wherein said gaseous reagent is HCl.
6. The system of Claim 2, wherein said gaseous reagent is NH_3 .
7. A method for providing ultra-high-purity reagents comprising H_2O_2 to a semiconductor manufacturing operation, comprising the steps of:
 - providing a flow of aqueous H_2O_2 from a tank which is located at the same site as the semiconductor manufacturing operation;
 - 5 passing said flow of H_2O_2 through an anionic exchange bed and a cationic exchange bed, to produce a purified H_2O_2 flow with a reduced level of ionic contaminants; wherein said cationic exchange bed is preconditioned with acid and said anionic bed is preconditioned with bicarbonate ions;
 - filtering said purified flow, to produce a flow of ultra-purity aqueous H_2O_2 solution; and
 - 10 routing said flow of ultra-purity aqueous H_2O_2 solution through a piping connection which routes said aqueous H_2O_2 from said filter to points of use in the semiconductor device fabrication facility without exposure to any uncontrolled ambient.