Carbon Dioxide Snow Cleaning - The Next Generation of Clean

by

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Abstract

Carbon dioxide snow cleaning is capable of satisfying the stringent demands for surface cleaning. By passing either gaseous or liquid carbon dioxide through an orifice, microscopic dry ice or "snow" particles are formed. The resulting mixture of solid and gaseous carbon dioxide removes submicron particles and organic residues from a surface. The thermodynamics that provide for snow formation and the mechanisms that permit the cleaning are reviewed. Examples of particle and organic residue removal from various metals, wafers, polymers, ceramics, glasses, process equipment, vacuum equipment, hard disk drives, and optics, with supporting data, are discussed. The parameters for process automation and effective carbon dioxide snow cleaning are reviewed.

Introduction

Cleanliness in the industrial context is the absence of contamination to a level satisfactory to the manufacturer and the end user. Cleaning beyond these requirements expands energy, efforts and costs; failure to clean to these levels risks product or process failure or (worse yet) business and customer loss. For a cleaning process to provide benefits to industry, it must be capable of meeting the cleanliness standard in a cost effective, efficient and environmentally acceptable manner. Cleaning process choices depend on many factors such as (i) effectiveness in meeting the product and customer needs; (ii) effect on the cost of manufacture or product price; (iii) safety to operate; (iv) environmental acceptability under present and proposed guidelines; and (v) effect on the speed of the production process.

Carbon dioxide cleaning systems satisfy the increasing industrial, customer and environmental demands. Carbon dioxide cleaning is fast, gentle to the component being cleaned, and does not damage the environment. The use of carbon dioxide eliminates the environmental problems associated with currently available CFC and aqueous-based cleaning systems. The cleaning process carries away contaminants and leaves no harmful residue. Unless the contaminants being removed are hazardous, both the contaminants and carbon dioxide can be vented to the atmosphere.

Carbon dioxide snow cleaning refers to the cleaning process in which liquid or gaseous carbon dioxide is passed through an orifice (or two orifices) to produce a high velocity dry ice stream and a flowing gas. The pressure and temperature drop that occurs when passing the CO_2 through a nozzle produces the solid CO_2, referred to as "snow. " Cleaning is accomplished through interactions of this snow stream with contaminated surfaces. In order to discuss this cleaning process and its applications, the basic thermodynamic and phase diagram properties of carbon dioxide need to be addressed.

A typical carbon dioxide snow cleaning system is shown in Figure 1. The system shown consists of a nozzle, an on/off device such as a hand-held gun, and the proper hosing or tubing to connect the cleaning equipment to a carbon dioxide source, i.e., a cylinder. The system shown has addressed many cleaning situations discussed in this paper.
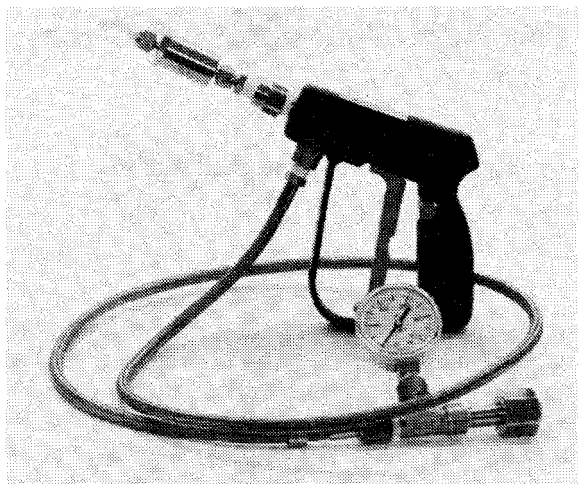
Figure 1 - A basic kit for carbon dioxide snow cleaning - hose, on/off gun and nozzle.

Carbon Dioxide Properties

Carbon dioxide is a non toxic, non flammable gas, and exposure to humans poses no risk except for oxygen replacement or frostbite if liquid CO_2 or snow is applied directly to the skin. Carbon dioxide is non-toxic, non-corrosive and non-ozone depleting. An MSDS (Materials Safety Data Sheet) sheet on carbon dioxide is available from any industrial gas supplier. Although it has been identified as a "greenhouse gas," it is unlikely that the industrial use of carbon dioxide will be restricted. The cleaning process does not create carbon dioxide; instead, it re-uses CO_2 that was created in some other manufacturing process, such as power generation, chemical processing or breweries. Carbon dioxide that would otherwise be immediately released into the atmosphere is captured, purified, and put to an industrial use.

Phase diagram and properties - The carbon dioxide phase diagram with pressure and temperature axes is shown in Figure 2. Four phases -- gaseous, liquid, solid and superfluid, are shown along with the triple and critical points. The triple point (pressure 5.1 atm., temperature -56.7C) is defined as the temperature and pressure where three phases (gas, liquid and solid) can exist simultaneously in thermodynamic equilibrium. Above the critical point (pressure 72.8 atm., temperature 31.1C) the liquid and gas phase cannot exist as separate phases. Above this point the phase, called the superfluid phase, has the properties indistinguishable from the liquid and gas phases.

Another feature is the existence of a solid-gas phase boundary. Physically, this boundary implies that the gas and solid can co-exist and transform back and forth without the presence of the liquid phase as an intermediate phase. The process of a solid evaporating directly into the gaseous phase is called sublimation. At normal atmospheric pressure and temperature, the stable carbon dioxide phase is the gas phase. This means that the final product will be gaseous carbon dioxide and this final state is independent of the initial phase. Any solid or liquid CO_2 will just evaporate or sublime. With the CO_2 present as a gas, the contamination removed is separated from the stream and the CO_2 is available for direct venting outside or can be recovered for re-use.

Carbon dioxide is an excellent solvent for many nonpolar organic compounds as discussed in many references. Like most solvents, the solvent properties of CO_2 improve as the pressure and temperature increase.
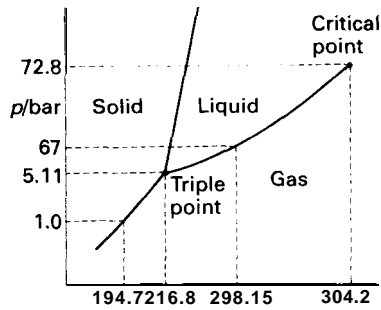
Figure 2 - The carbon dioxide phase diagram - axes not to scale
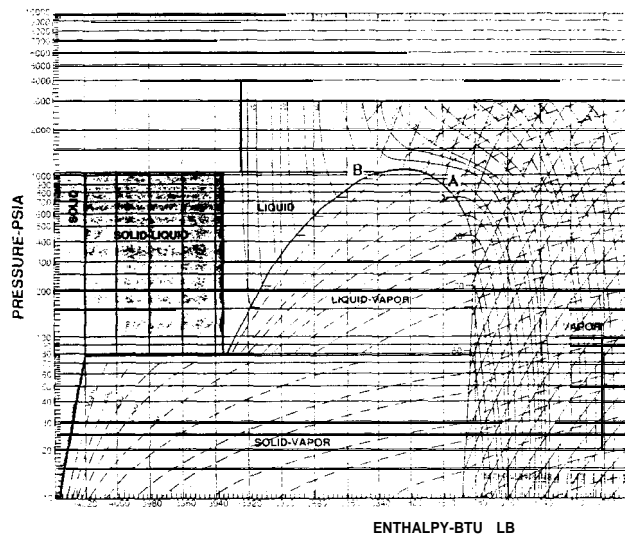
Carbon Dioxide Pressure-Enthalpy Diagram

ENTHALPY-BTU LB

Figure 3 - The pressure enthalpy phase diagram for carbon dioxide
Figure courtesy of Airco Gases

Thermodynamics Figure 3 shows the carbon dioxide pressure - enthalpy diagram. This figure shows the phase changes that occur during the carbon dioxide snow formation. The features in the diagram include the solid, liquid, gaseous and supercritical phases along with the region of pressure and enthalpy where these phases co-exist. What was shown on the phase diagram in the previous figure as a boundary between two phases is now a distinct two phase region. In using this diagram, it is imperative to under-stand that the expansion of carbon dioxide through an orifice is a constant enthalpy process. Therefore, as the pressure drops in an orifice, the thermodynamic state just moves down the enthalpy lines vertically.

A CO_2 cylinder at room temperature has a pressure of 830 psi, and the gas and liquid within the cylinder are in thermodynamic equilibrium. The equilibrium position for the contents of the entire cylinder is along the 830 psi line within the liquid-vapor two phase region. The enthalpy available to the liquid and gaseous phases are those values along the liquid-gas two phase region boundary, in the spots labeled "A" for the gaseous case and "B" for the liquid case.

With a gas fed source, the initial state is at point A and as the pressure drops, liquid droplets nucleate and becomes an increasing larger percentage of the mixture. At the interface between the liquid-gas and

gas-solid regions, all the liquid is converted to solid and the percentage of the solid is determined by the lever rule(c). A rough percentage gives about 5 % dry ice, the remainder gas. With a liquid fed source, the initial state is at "B" and as the pressure drops, gas is formed and the percentage of gas increases until the gas-solid boundary is met. Here, the remaining liquid is transformed into solid and the relative percentage of snow is 45 to SO%. Continuing pressure drops leads to no major changes in the relative percentages in the two phases. The percentage of snow is dependent only on the initial phase, either liquid or gas and also the pressure and temperature

This thermodynamic data does not give any information on the resulting carbon dioxide snow particle size nor its velocity. These are kinetic factors and can not be determined from this diagram; instead, nozzle designs affect kinetic factors.

Cleaning Mechanisms

Thermodynamically, we shown that the passage of CO_2 through an orifice can lead to the formation of dry ice or snow. By choosing a nosecone shaped exit on the nozzle, the snow stream travels at high velocities. With this set up, CO_2 snow cleaning can remove both particulates and organics.

The removal of organic and particulate residue from surfaces during CO_2 snow cleaning can be explained by two different mechanisms - one for particulate removal, the other for organic contamination removal{ 1). The mechanism for particle removal involves a combination of forces related to a moving high velocity gas and momentum transfer between the snow particles and surface contamination. The mechanism for organic contamination removal requires the presence of a liquid carbon dioxide phase during impact.

Generally, a high velocity flowing gas can remove larger particulates from a surface. The moving gas (considered a fluid) exerts an aerodynamic drag force on the surface particle population and the magnitude of this force is proportional to the particle's area (diameter squared). If the drag force exceeds the surface adhesion force, particle removal occurs and the particle is carried away with the moving gas flow. The surface adhesion forces - van der Walls, capillary condensation, dipole attraction - vary with the diameter of the particle. Aerodynamic drag forces can remove larger particles, but as the contaminant diameter decreases, the aerodynamic drag force decreases much faster than the surface adhesive forces. Therefore, as the diameter of the contaminant reduces, the surface adhesion forces tend to dominate and the flowing gas can not overcome these adhesive forces. This cross over is typically in the micron and larger range.

With the addition of dry ice particles to the flowing gas stream, a new process is available for particle removal. This process is schematically shown in Figure 4 where the particle on the surface is impacted by an impinging dry ice snow particle. The impact implies a transfer of momentum between the snow and surface contaminant and this transfer of momentum can overcome the surface adhesive forces. Once liberated from the surface, the contaminants are easily carried away with the high velocity gas stream. Particle removal efficiencies do not decrease for smaller surface particulate sizes as in the case for the aerodynamic drag force. Further, the ability to remove surface contamination by momentum transfer appears to be independent of surface contaminant size as long as the CO_2 snow size is not much smaller than the surface contaminant.
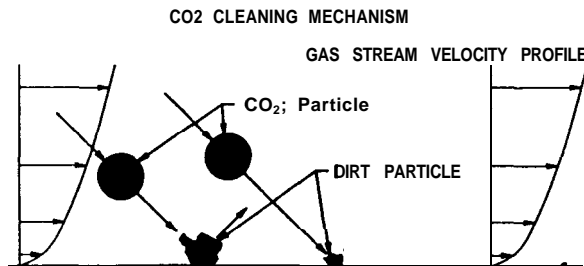

Figure 4 - Schematic of the proposed mechanism for particle removal by CO_2 snow cleaning. The impinging snow particles and flowing gas are shown acting on a surface contaminant.

LIQUID CO2 PHASE GENERATED ON IMPACT

CO2 PARTICLE
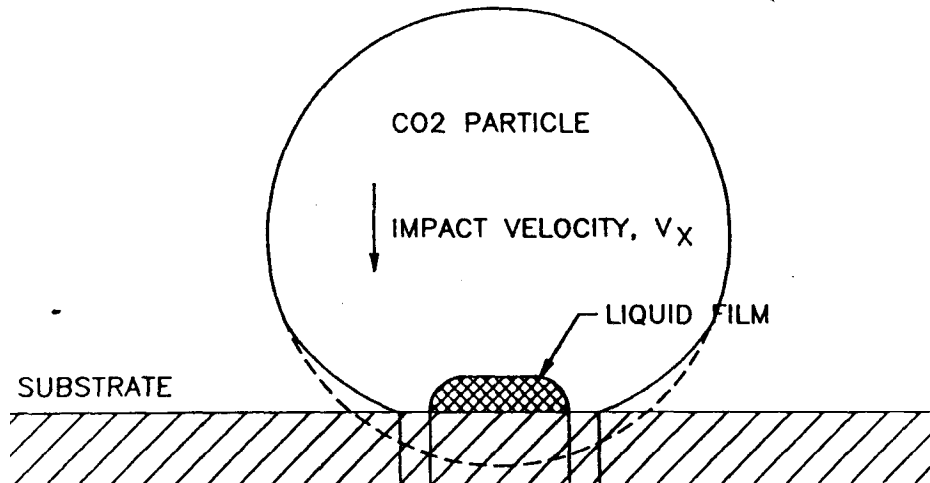
IMPACT VELOCITY, V_X

LIQUID FILM

SUBSTRATE

Figure 5 - Proposed mechanism for removal of organic residues from surfaces during CO_2 snow cleaning. A liquid film is shown between the snow particle and substrate.

The removal of organic residues relies upon a different mechanism, one that involves the presence of a liquid phase. Liquid carbon dioxide is an excellent solvent for hydrocarbons and other non polar substances. An impacting snow particle on a surface is shown schematically in Fig 5. During the short time of impact, high stresses exist at the snow - surface interface and this pressure can easily exceed the yield stress and triple point pressure of the dry ice particle. In this case, the dry ice particle can liquefy and act as a solvent while in contact with the surface. Contamination would be dissolved by the liquid phase and stay within the "liquid - dry ice particle". When the particle starts to rebound off the surface, the interfacial pressures decrease and the dry ice particle re-solidifies, carrying the contamination away.

As pointed out by Whitlock, this surface liquid phase may explain why carbon dioxide snow cleaning is a gentle cleaning process. The presence of a liquid phase would limit the pressure that can be imparted to the surface being cleaned to the liquid phase pressure. When the snow starts to liquefy at the surface/dry ice interface, continued yielding and plastic flow only tend to increase the size of the contact area. Although the solvent action is highly effective, the cleaning process has not achieved removal efficiencies similar to $SFCO_2$. These differences are not clear but may be related to the ability of the solvent CO_2 to only attack and absorb materials that are physically attached to the surface and not able to remove material that is chemically bonded to the surface. Another possibility is the pressure at contact does not exceed the critical point-pressure.

Hill{2} proposed another mechanism for surface cleaning with the large snow flake, low velocity streams. Here, a thermophoretic process - forces caused by thermal gradients, can remove the particles off the surface. A fundamental aspect of this proposed process was that the snow flake does not contact the surface; instead, as the snowflake approaches the surface, the large thermal gradient causes sublimation on the bottom of the flake. This large release of gas separates the flake from the surface and also creates large shear forces on the surface particle population and can lead to liberation of the surface particles. Next, Hill postulates that thermophoretic forces attract the liberated particle to the cold side of the flake and are taken away for removal.

One topic that needs separate clarification is the removal of deposited films or coatings by carbon dioxide snow cleaning. Films that are deposited properly will remain on the substrate while those films that were deposited poorly onto contaminated substrates may easily be removed. The reason for the inability to remove deposited films may be related to the combination of the low abrasive action of CO_2 and the inability of the cleaning process to overcome any chemisorbed, covalent, metallic or ionic bond.

Cleaning Methods - Pellets, SFC and Snow

Cleaning with carbon dioxide can be done by three different methods -- (i) macroscopic dry ice pellets; (ii) snow streams based upon single or double expansion of carbon dioxide and spraying the sample with either microscopic or macroscopic "snow" particles; and (iii) supercritical fluid carbon dioxide (SFC).

Whichever cleaning process is in use, the cleaning process depends on either the liquid carbon dioxide solvent properties, momentum transfer by snow or a combination of these processes. Pellet systems rely upon the abrasive nature of high velocity macroscopic pellets for contamination removal - a momentum and energy transfer process. Snow sprays, depending upon the configuration of nozzles and expansion chambers, rely upon a combination of the solvent action of liquid CO_2 and the momentum transfer of either high velocity microscopic snow particles or low velocity macroscopic snow flakes. The SFC systems rely exclusively upon carbon dioxide's unique supercritical fluid properties.

Pellet systems accelerate dry ice pellets for contamination removal. Cleaning is accomplished by abrasive action and momentum transfer. The key components and steps in a pellet system are first the formation of the pellets of desired size, maintaining the pellets at the proper pressure and temperature, pellet feed, acceleration by either mechanical methods or compressed gas and then the distribution of pellets on the item being cleaned. Thermodynamically, pellet system requires that the initial liquid is fully transformed to solid and maintained in the solid phase. Overall, pellet systems are made for material removal and can only address cleaning situations when the object for cleaning can withstand the expected damage.

Supercritical ($SFC0_2$) systems rely upon the solvent properties of CO_2 and other unique properties of a superfluid. This involves maintaining the pressure and temperature of the system in the supercritical regime, above 31 C and 72.8 atm. Generally, the $SFC0_2$ units are operated at much higher pressures and temperature than the critical point, in the superfluid region shown in Figures 2 and 3. The superfluid has low viscosity (low surface tension) and superior solvent properties than the liquid phase. In a $SFCO_2$ system, the items for cleaning are sealed in a vessel, the vessel is filled, and the temperature and pressure are adjusted. This method is well suited for batch cleaning of small or delicate parts or complex assemblies where the major concern is organic contamination removal. The shortcomings of $SFCO_2$ systems are the batch nature of the process and its inability to remove any inorganic or particulate contamination.

Snow systems rely on the expansion of carbon dioxide in either the gaseous or liquid states for generation of the cleaning media. Cleaning is accomplished by a combination of momentum transfer and solvent action. The key component in the implementation of a stream spray system is the nozzle design. The output is a snow stream, either high or low velocity, carried along with CO_2 gas phase. The presence of dry ice or snow flakes leads to the spray cleaning systems to be referred to as "snow cleaning".

It must be noted that there are two different commercial approaches to the snow spray system technology. The first involves the generation of a high velocity stream of microscopic snow while the second snow spray technology involves the use of a low velocity stream of large snowflakes. The high-velocity, small snow spray systems can remove both particulates and organic residues while the low velocity, large snowflake streams are capable of only removing particulates - no organic contamination removal. The formation of large snow flakes requires a liquid CO_2 source while the microscopic snow stream can be formed with either a liquid or gas CO_2 source. There are other fundamental differences in cleaning capabilities and cleaning mechanism between the two approaches.

Development

Although carbon dioxide cleaning is referenced in material from the 1930's, the work of Rite(3) initiated the development of the current carbon dioxide based cleaning systems. Rice and Franklin described the process of providing "ice" particles in a gas flow with necessary kinetic energy to remove the unwanted portions of materials. This was followed by a patent by Fong(4) in 1977 who developed the

cleaning concept as "sandblasting but without the sand." The design was to provide rough shaped dry ice particles and accelerate these particles with a sonic nozzle. The patent involved equipment for the continuous feed of ice pellets to a nozzle and having an external gas feed accelerate the ice particles to the surface.

Hoening{5} described an instrument for making carbon dioxide snow and directing the snow and gas mixture to a surface being cleaned. The expansion of the liquid carbon dioxide led to formation of soft, low velocity snow flakes. Micron and sub micron particle removal from surfaces was demonstrated. This work led to what is referred to as "snow cleaning"

Whitlock, Weltmer and Clark{6} patented an apparatus that uses either a liquid or gaseous carbon dioxide feed that could remove organics and particulates from various surfaces. This process was based upon a double expansion nozzle with a coalescing chamber between the two orifices. Carbon dioxide liquid droplets nucleate and grow within this chamber. After the feed passes through the second orifice the liquid droplets form dry ice particles that are projected forward by a high velocity CO_2 carrier gas. Further work by Whitlock and others have demonstrated effective micron and submicron particle removal and also organic contamination removal.

Since these developments, other equipment introduced have only been variations on the concepts discussed above. Layden{7} developed a flat double expansion nozzle capable of wide area cleaning. Sherman{8} has used a single expansion nozzle in similar fashion as Whitlock's. The single expansion nozzle design performs similarly. Sherman has also shown that the single and double expansion nozzles can be easily modified to produce the slow velocity, large snow flakes similar to that introduced by Hoeing. Adams{9} has redesigned the double expansion nozzles introduced by Whitlock and offers combination that allows for variations in velocity and snow size. Hughes{10} used a single expansion design but with a variable orifice sizes. These configurations all offer similar performance.

Equipment

Carbon dioxide snow cleaning systems are for the most part straightforward, they consist of a CO_2 source, a nozzle and the means to transport the CO_2 from the source to the nozzle. Laboratory based systems, such as shown in Fig. 1, are made with a CGA320 fitting, tubing, an on/off gun or valve and a nozzle. Most units are made with PTFE lined flexible hosing but one manufacturer(S) has designed an SS316L manifold with orbital welded tubing from the cylinder to the nozzle fitting (or the filter fitting). The available on/off controls include solenoid or pneumatic valves and hand guns. The hand guns provide excellent manual control while valves make for easy automated or repetitive operation.

It should be noted that all CO_2 cylinders are shipped with liquid inside at 830 psi. Liquid fed cylinders have a dip tube allowing for liquid withdrawal. For gas fed cylinders, CO_2 is withdrawn from the top and evaporating liquid replenishes the gas. Therefore, a 60 lb cylinder that is configured for gas withdrawal has 525 cubic feet of usable CO_2. A liquid fed cylinder yields only 40 lbs of usable product, 350 cubic feet. This difference is that liquid can form gas, but gas cannot form liquid within the cylinder at room temperature.

The nozzle design is by far the most important factor in performing carbon dioxide snow cleaning. Nozzles for carbon dioxide cleaning involve either a single or double expansion arrangement. The simplest nozzles are the single expansion nozzles with one orifice. Effective single expansion nozzles are variations on the Venturi orifice design with the exit size usually being elongated with respect to the input side. An example is shown in Figure 6. The exit size is more typically a nosecone and this chamber is where the dry ice nucleates, Its angle and length play an important role in determining the velocity of the stream and the snow size. Another design of single expansion nozzles involves the use of a variable orifice with different choice for nosecone geometry. Increasing the angle of the nose cone yields increases in snow flake size at the expense of stream velocity. Eventually, this trade off results in poor organic removal.
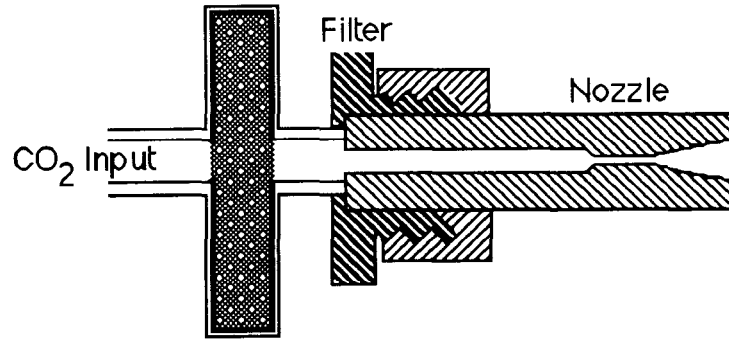
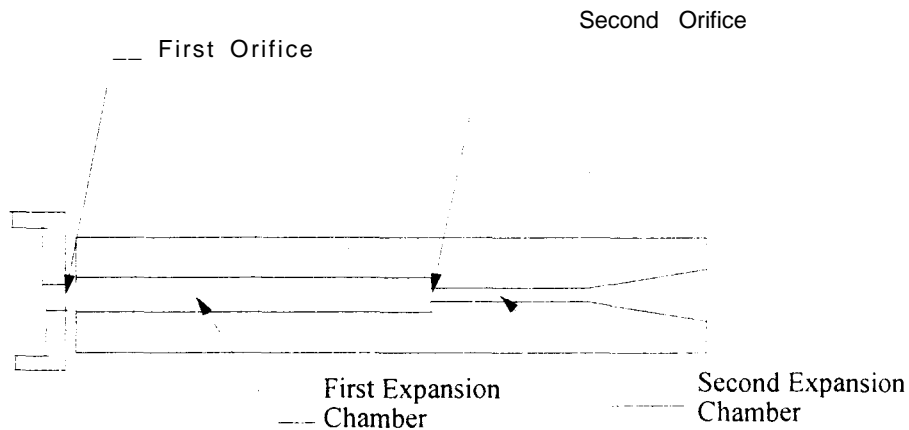Figure 6 - A schematic of a single expansion nozzle with a filter

Figure 7 - A schematic of a double expansion nozzle

Double expansion nozzles, shown schematically in Figure 7, offer another way to control dry ice size and velocity. The first orifice gives an initial pressure drop and takes the CO_2 feed from the phase boundary, either point A or B in Figure 3, into the two phase liquid - gas region. Here, for a gas fed unit and in the coalescing chamber, small liquid droplets nucleate and the size of these particles is related to the choice of first orifice. The liquid droplets travel down the chamber and enter the second orifice, a diameter larger than the first. Upon exiting, the final pressure drop converts all the liquid droplets into dry ice particles. Velocity and snow size are influenced by the design of the second expansion nozzle.

The nozzles described above are point sources and can clean about a 1/4 inch diameter. A challenge in CO_2 snow cleaning nozzle design was to devise a nozzle that can generate snow over a large linear distance. Layden(7) introduced large area double expansion nozzles and made units ranging from 1/2 inch to over 28 inches in length. Further, these nozzles can operate with either liquid or gaseous carbon dioxide feeds. Two examples of this large area nozzle are shown in Fig 8. One nozzle is 2 inches, the other is 12 inches. To seal these two plates, a complex seal of 1 mil thickness was designed. The seal has a set of channels per linear inch and the channel width is dependent on the feed source. These large area, or flat nozzles, were used in generating the cleaning application related to cleanroom and process equipment. Adams redesigned the flat nozzle to remove the thin seal material and instead used a seal variation of the UHV conflat knife edges. Flat nozzles from 1/2 inch to over 8 inches have been made for various applications.
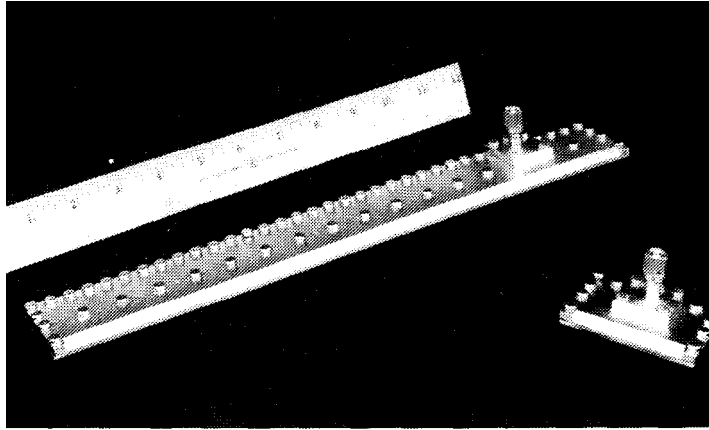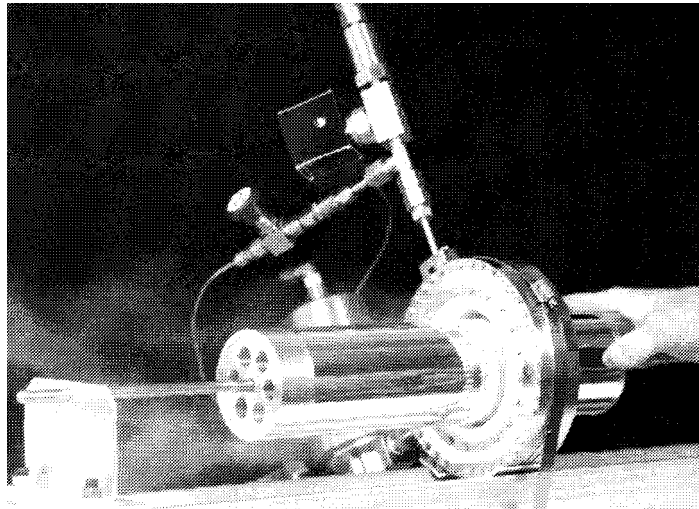
Figure 8 - Two large area nozzles

Figure 9 - Photograph of outer tube CO_2 snow cleaning nozzle

Other special nozzles have been designed to address the cleaning of complex geometry's. Layden designed an inner diameter tube cleaner and this nozzle can clean the inner diameter surfaces for tubes as small as 3/4" ID up to and over 3 to 4 inches. The unique feature of this nozzle is that provides for continuous snow stream over a full 360 degrees. Similar units have been designed by Layden to clean the outer diameter of tubes and even larger diameter drums, as shown in Fig. 9. Here, a continous CO_2 snow stream is shown cleaning the surface over 360 degrees.

Cleaning Examples - Proof of Process

Analytical Methods Before discussing cleaning examples, the various analytical methods for testing effectiveness are mentioned. These methods included light microscopy, particle counting, scanning electron microscopy, microprobe, X-ray photoelectron spectroscopy, and mass spectroscopy.

Light microscopy is the optical inspection of surfaces with high powered microscopes. Scanning electron microscopy (SEM) offers a straightforward method to identify micron and submicron size particles at high magnifications. Energy Dispersive Spectroscopy (EDS) within an SEM allows for elemental identification of individual particles. In one paper, an automated microprobe (an SEM with EDS) was used to automatically find, count and identify the composition of particles. Particle counters use

light scattering methods to count and size particles from flat surfaces. X-ray Photoelectron Spectroscopy (XPS) and Auger electron Spectroscopy are surface analysis methods capable of measuring all elements (except H and He) present on and within the first few atomic layers of a surface. This technique offers a simple method to monitor small changes in atomic layer chemistry(11). Mass spectroscopy within a vacuum environment has been referred to as residual gas analysis and yields the elemental and compounds present within the vacuum system.

Initial Laboratory Studies - Particle Removal - The first set of laboratory measurements that quantified the effectiveness of removing micron and submicron particles from a surface was performed by Whitlock {1}. The approach was to disperse an aerosol of micron and submicron particles on a wafer, count and size them, clean the wafer with CO_2 snow and finally count the remaining particles.

Zinc orthosilicate powder was suspended in ethyl alcohol and sprayed on to a 2 inch silicon wafer with an air brush. Spraying continued until a noticeable deposit was observed. An automated 7331 JEOL automated microprobe was used for particle counting and sizing{ 12). The EDS was set to detect only zinc rich particles. When the EDS identified a particle as Zn rich, the microprobe software then would proceed to size the particle (assumed spherical) and add this particle to the count. A total of 295 particles were identified after counting 100 frame, each frame being a 27.4 by 20.0 micron area. Next, the wafer was cleaned using the carbon dioxide snow stream and standard operating conditions. The nozzle was about l/2 to 1 inch from the surface, about 45 degrees and was moved over the surface manually.

After cleaning, the wafer was analyzed again in the automated microprobe and only 3 zinc rich particles were found after scanning 1600 frames. Normalizing the initial measurements to 1600 frames gives an initial particle population of 4720 particles. This gives a removal ratio of over 99.9% under laboratory cleanroom conditions. Another comparison would be to normalize the particle populations to a square centimeter. In this situation, an initial particle population of 538,00 particles per square centimeter was reduced to 342 particle per square centimeter for particles larger than 0.1 micron.

Further comparisons can be obtained by studying the size distribution of these particles. Fig 10 shows the population versus size distribution with the initial particle distribution normalized to 1600 frames. The particle size distribution before cleaning for the zinc-rich particles ranged from 0.1 micron to larger than 2.0 microns. After cleaning, the three particles found in the 1600 frames were sized between 0.5 and 0.6 microns, 0.8 and 0.9 microns and 1.5 to 1.6 microns. Table 1 lists the particle removal efficiency as a function of particle size. The table lists the efficiency for removal of particle greater than a certain size. In all cases, efficiencies were above 99.9%. In summary, Whitlock demonstrated that CO_2 snow cleaning has excellent efficiencies for removing micron and sub-micron sized particles from contaminated wafers.
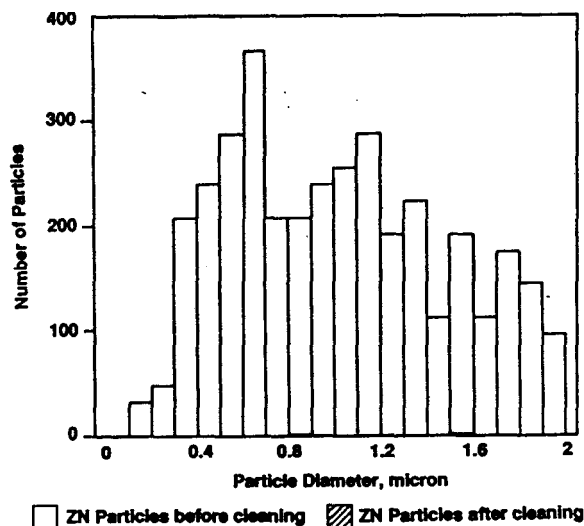

Figure 10 - Bar graph showing the relative particle populations before and after CO2 snow cleaning

Sherman{ 13) has qualitatively demonstrated particle removal using optical microscopy. Fig 11 shows a pair of micrographs at 1000x magnifications that demonstrates particle removal effectiveness by comparing the exact same areas before and after cleaning. A silicon wafer was scribed with a carbide tip, and many micron and submicron particles were generated near the scratch (as seen in Fig. 1 la). After CO_2 snow cleaning, the micrograph in Figure 1 lb shows no particles. This example demonstrates the cleaning of silicon dust from scribed wafers and this data would be typical of particle removal from many different substrates including other wafers, glass, ceramics, etc.
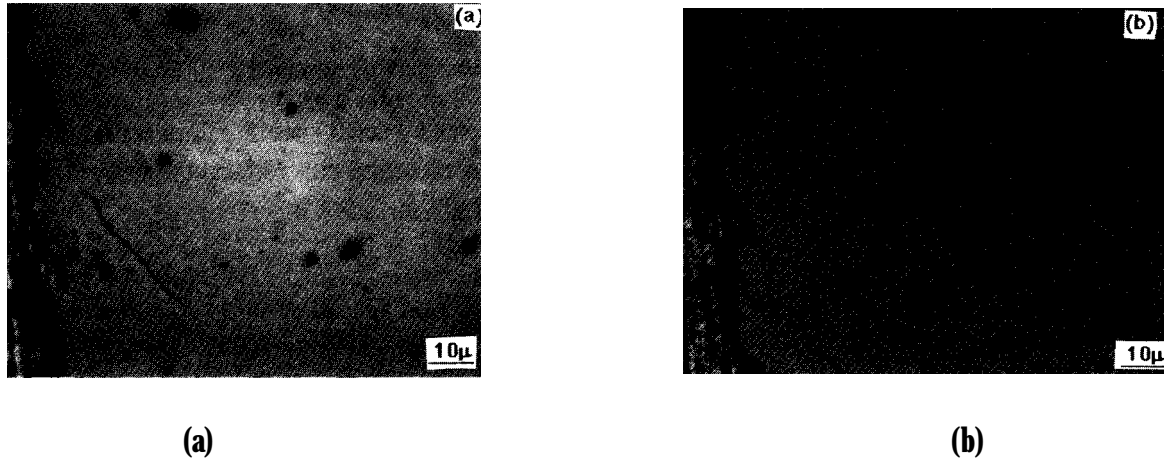

(a) **(b)**

Figure 11 - Micrographs at 1000x magnification showing a scribed region of a wafer(a) before and (b) after CO_2 snow cleaning.

Another example, similar to the experiment performed by Whitlock, was to photograph the differences in cleaning the wafer as described above. Micron and larger sized fluorescent zinc sulfide powder was sprayed on a 4" Si wafer. The central third of the wafer was cleaned and photographed under ultraviolet light (Fig 12). No particles are seen in the central region indicating a high efficiency for particle removal.
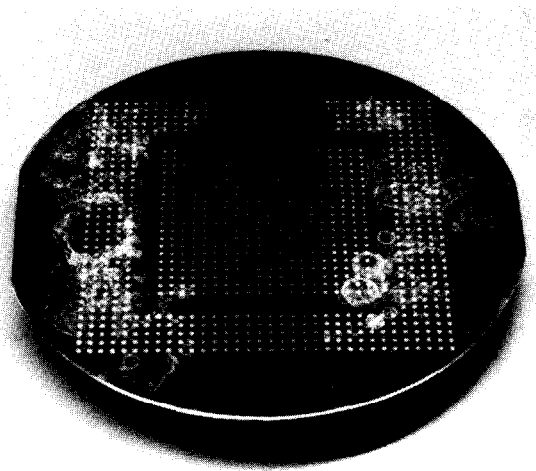

Figure 12 - A contaminated silicon wafer with the central region cleaned with CO_2 snow.

Organic Removal One of the first published studies on the effectiveness of carbon dioxide snow cleaning in removing organic residues from surfaces was by Sherman and Whitlock{ 14). Here, XPS was used to investigate the surface chemistry of new silicon wafers, contaminated wafers, and then carbon

dioxide snow cleaned wafers. First, a section of the wafer was analyzed, and this region served as a measure of the background hydrocarbon level. Next, fingerprint, facial grease (nose print) or vacuum grease was applied to the wafers and the extent of the contamination was measured by XPS.   Finally, each of the stains was removed using CO_2 snow cleaning and the cleaned regions were analyzed by XPS. Analyses were performed in the exact same spots on each sample. The changes in the surface hydrocarbon concentrations for the various tests are listed in Table 2. The typical background level for the surface hydrocarbons was from 27 to 29 atomic percentage. The fingerprint and nose print increased the contamination levels by a factor of 2 to 3. Cleaning with CO_2 snow, removed all visible sign of the contamination and the surface analysis results in Table 2 showed hydrocarbon levels that are actually lower than the initial "new" wafer values (between 19 - 23 atomic percent). These results not only demonstrated that CO_2 snow cleaning can remove contamination but it can also reduce the native hydrocarbon contamination found on many surfaces.

The possibility of reducing this hydrocarbon background was further tested by Sherman and Whitlock. Here, another control wafer was analyzed and 28 atomic percent carbon was present on the surface. This region was CO_2 snow cleaned and only 16 at. % carbon was found - see Table 2. This reduction in the hydrocarbon surface concentration demonstrates that CO_2 snow cleaning can reduce the adventitious carbon, or native hydrocarbon contamination, found on almost all surfaces.

Another part of the tests involved removing silicone grease from a wafer. This time, we focused on the shape of the silicon peak and it peaks position. The initial silicon spectrum was typical of a thin oxide on top of an elemental silicon peak. The XPS peak locations are found at 99.3 eV for elemental silicon and 103.4 eV for the oxide.   The silicone stain had its XPS Si 2s peak at 101.8 eV. Cleaning removed the silicone and left a peak structure identical to the initial condition. The peak positions after cleaning were identical to those found on the initial wafer surface. These peaks shape changes are shown in Fig 13.
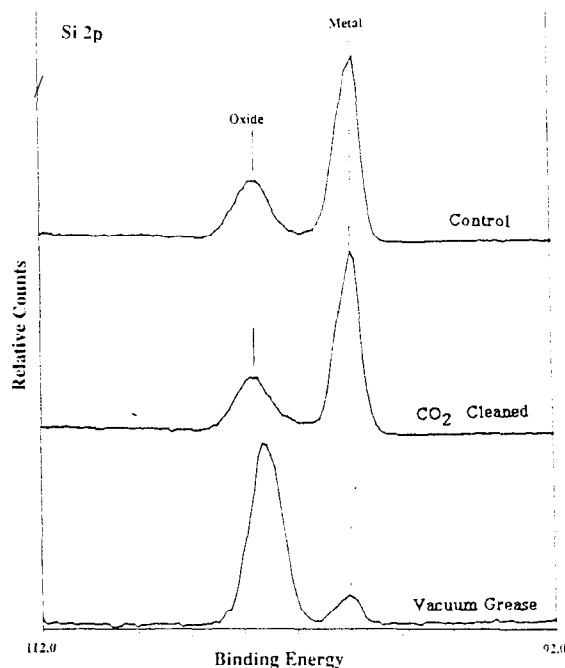
Figure 13 - The silicon 2p XPS spectra from the new, CO_2 cleaned, and silicone grease contaminated Si wafers

Sherman{ 13) provided further microscopic evidence of organic removal by comparing the exact same areas before and after cleaning a facial grease residue. A pair of micrographs is shown at 1000x magnification of a scribed silicon wafer before and after cleaning. The scratches at the bottom of the micrographs indicate the same areas. The initial wafer condition is shown in Fig. 14a with extensive

contamination and after CO_2 snow cleaning, no contamination is observed as shown in Fig 14b. This visual evidence of removing organic contamination is typical for many surfaces and materials.
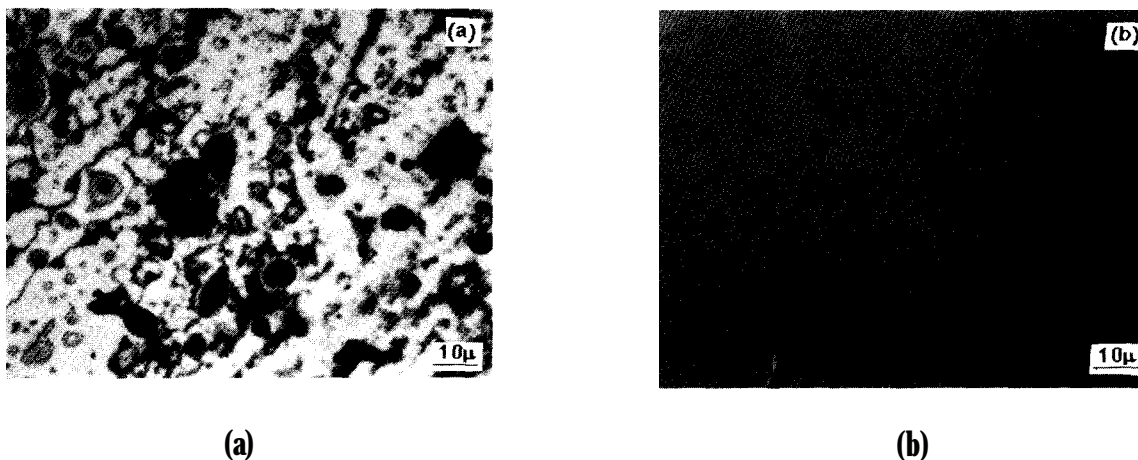

(a)   **(b)**

Figure 14 - Optical micrographs at 1000x magnification of a scratched Si
wafer that was (a) contaminated with facial grease and then (b) CO_2 snow cleaned.

Applications - Materials

Further work has been performed by Sherman{ 13,l5) to test organic and particulate removal of CO_2 snow cleaning on a wide variety of materials including wafers, metals, ceramics, glass, optics, and polymers.   For the most part, these samples were obtained from other engineers, scientists and prospective users.

Metals - Various metals were cleaned including an aluminum sheet, a used OFHC copper gasket and electropolished stainless steel (SS3 16L) tube surface. The results for these cleaning tests are shown in Table 3 in which the surface chemistries were measured before (labeled as "control") and after cleaning by XPS. The resulting data indicate that carbon dioxide snow cleaning can reduce the organic contamination found on these surfaces. This contamination reflected background levels typically found on air exposed or processed samples. The amount of organic reduction found was 45% on Al, 15% on Cu, and 27% on the 316L SS surface. An example of the reduction in organic contamination is highlighted in the carbon 1s spectra shown in Fig 15. The overlaid spectra show the intensity changes in the carbon 1s peak. The carbon spectra showed decreases in the'C-C and C-H bonding levels after cleaning while the other functional groups (C-O, C=O) did not exhibit any intensity changes. This finding lends support that the cleaning process only removes the organics, not the other functional groups. This finding of selective removal held for all tests except for the stainless steel sample and an amide wax (discussed later).
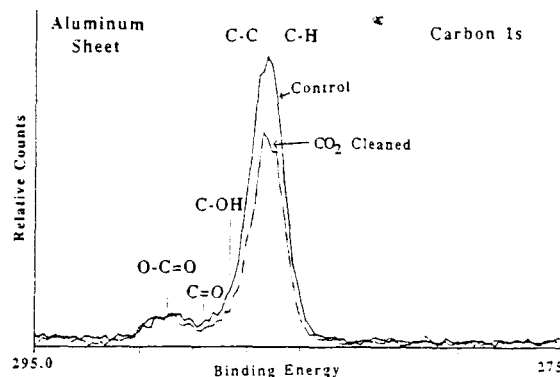

Figure 15 - The carbon 1s XPS spectra from the aluminum sample before and
after CO_2 snow cleaning - not the reduction in the C-C and C-H peak after cleaning.

(a)

Stainless Steel   **C-C**   **C-H**   **Carbon 1s**

Relative Counts

←Control

O-C=O

←CO₂ Cleaned

295.0   **Binding Energy**   275.0

(b)

Stainless Steel

Relative Counts

←Control   **Oxygen 1s**

←CO₂ Cleaned

O-M
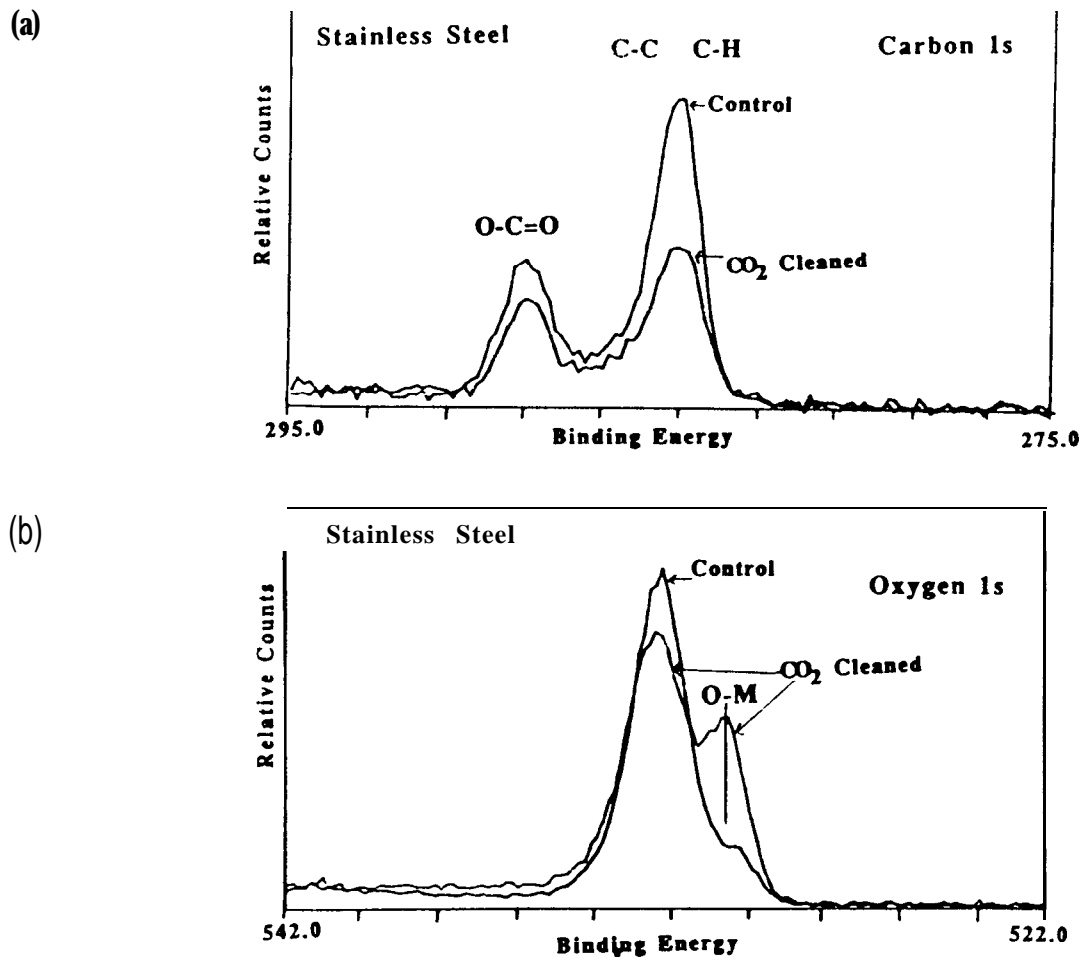
542.0   **Binding Energy**   522.0

Figure 16 - A comparison of the carbon and oxygen 1s XPS
spectra before (a) and after (b) CO_2 snow cleaning

The changes in the carbon and oxygen 1s XPS spectra as a result of cleaning stainless steel are shown in Fig. 16. The carbon 1s spectra exhibit reductions in the hydrocarbon and carbonate (0-C=O) peaks. The reduction in the carbonate peak may be related to the removal of microscopic corrosion and electropolishing residues. The major changes in the oxygen 1s spectra were also tied to the removal of contamination. The major portion of the oxygen peak before cleaning probably reflected OH bonding along with other carbon-oxygen structures. Initially, the metal-oxygen bonds were weak; and after cleaning, the relative intensity of this peak increased. These results agree with the concept of removal of contamination over an oxide layer.

Another example of gross organic based contamination removal involved a case where a gold contact material was nonconducting. XPS spectra of the contaminated and cleaned gold contact is shown in Fig. 17, and surface compositions are listed in Table 4. The initial surface concentration listed less than 1 atomic percent gold and over 80 at. percent carbon. Silicon was also identified suggesting a silicone contaminant. After CO_2 snow cleaning, the gold surface concentration increased to over 24 atomic % and the carbon concentration decreased to below 64 atomic %. The silicon and other contaminant peaks were removed. Another way of viewing this data is to compare the carbon to gold surface compositions. Before cleaning, this ratio was 281; after cleaning, this ratio was 2.6. This represents a decrease of over 100 in the relative extent of surface contamination. Furthermore, the gold contact was conductive after cleaning.
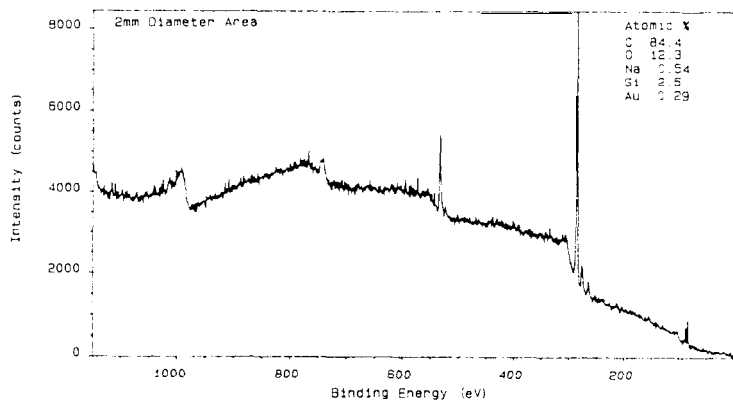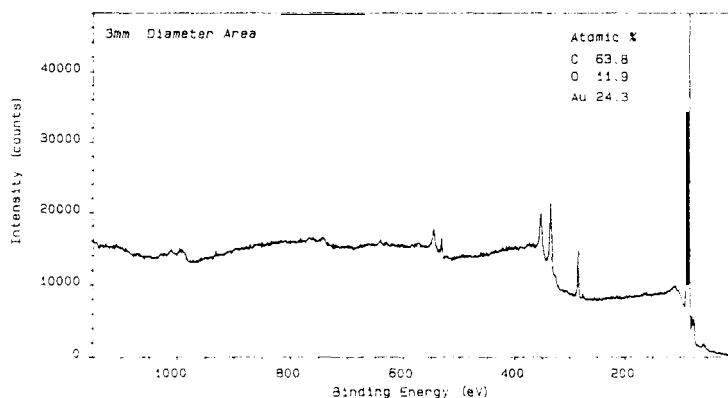
Figure 17 - The wide scan XPS spectra of the gold contact before and after cleaning.
Not the large change in the C and Au peaks.

Ceramics - Alumina and sapphire substrates were cleaned in order to establish the extent of hydrocarbon removal from these surfaces. These substrates had no visible contamination and XPS analysis indicated hydrocarbon levels at 38 % on the sapphire and 49 % on the alumina before cleaning. After CO_2 snow cleaning, the hydrocarbon levels were reduced to 17 at. % on the sapphire surface and 24 at. % on the alumina surface. These reductions in surface carbon based contamination were 55% and 51%, respectively.

Glass and Optics - Similar reductions in surface hydrocarbon contamination were also noted for plate glass and other glass substrates. Surface hydrocarbon contamination found on clean plate glass surface were typically in the 40 to 50% range. Glass samples cleaned included soda lime glass, other glasses and quartz. Tin oxide and indium tin oxide coated glass surfaces were also cleaned. In these cases, the cleaning process did not alter, remove, or abrade the metal oxide coating. Carbon dioxide snow cleaning has been used to clean plate glass and optical filters. A comparison of surface compositions before and after CO_2 snow cleaning for a plate glass and a contaminated bandpass filter is shown in Table 5. Here, the cleaning process led to large reductions in the hydrocarbons present on the glass surfaces, by about 44% for the plate glass sample and 61% for the dirty bandpass filter.

Carbon dioxide snow cleaning has also been used to clean optical components including mirrors, gratings, filters, and many other items. One test involved cleaning contaminated mirrors and comparing the surface to an optical flat standard using a differential surface roughness measuring device. The results suggest that cleaning contaminated mirrors can restore the quality similar to that of clean and unused mirrors.

Wafers - Many different wafer substrates were cleaned and in all cases, the cleaning removed any visible contamination, reduced particle populations and also reduced the hydrocarbon background found on clean wafers. Wafers cleaned include Si, InP, GaAs, patterned Si chips, hybrids, X-ray mirrors, photoresist, and diamond. The wafer cleaning process is nondestructive. This finding is based upon independent measurements of carrier densities and dislocations; no changes were notes as a result of cleaning. Further, we have cleaned a 2 mil thick Si wafer without damage. The key is to provide proper backing with a vacuum chuck.

Data on cleaning Si wafers were presented in Tables 1 and 2 for particle and organic contamination removal. Data related to cleaning "clean" Si wafers will be discussed later in Tables 8 and 9. Overall, new Si wafers with thick thermal oxides or thin native oxides can be cleaned.

An InP wafer coated with a paraffin wax was cleaned. The wax was normally removed by a chlorinated solvent. Typically, the wax was "thick" and the initial surface analysis indicated over 96% carbon and remainder oxygen, silicon and chlorine. After cleaning, the carbon content was reduced to between 35 to 40 atomic percent with the remainder being In, P and 0. These elements are related to the wafer and its thin oxide. In another test, a solvent cleaned InP wafer was cleaned and the hydrocarbon levels were reduced from an initial 45% to 34%. This finding suggests that CO_2 snow cleaning can clean beyond the solvents that are used during wax removal.

Integrated circuits were examined to investigate the potential of cleaning. One example involved a hybrid chip that had an organic residue as shown in Fig 18. In the first micrograph, an organic residue is seen and after CO_2 snow cleaning, there are no signs of the organic residue. Another example of cleaning a chip was shown by Sherman et al.{ 15).

a) Stain

b) After CO_2 Cleaning
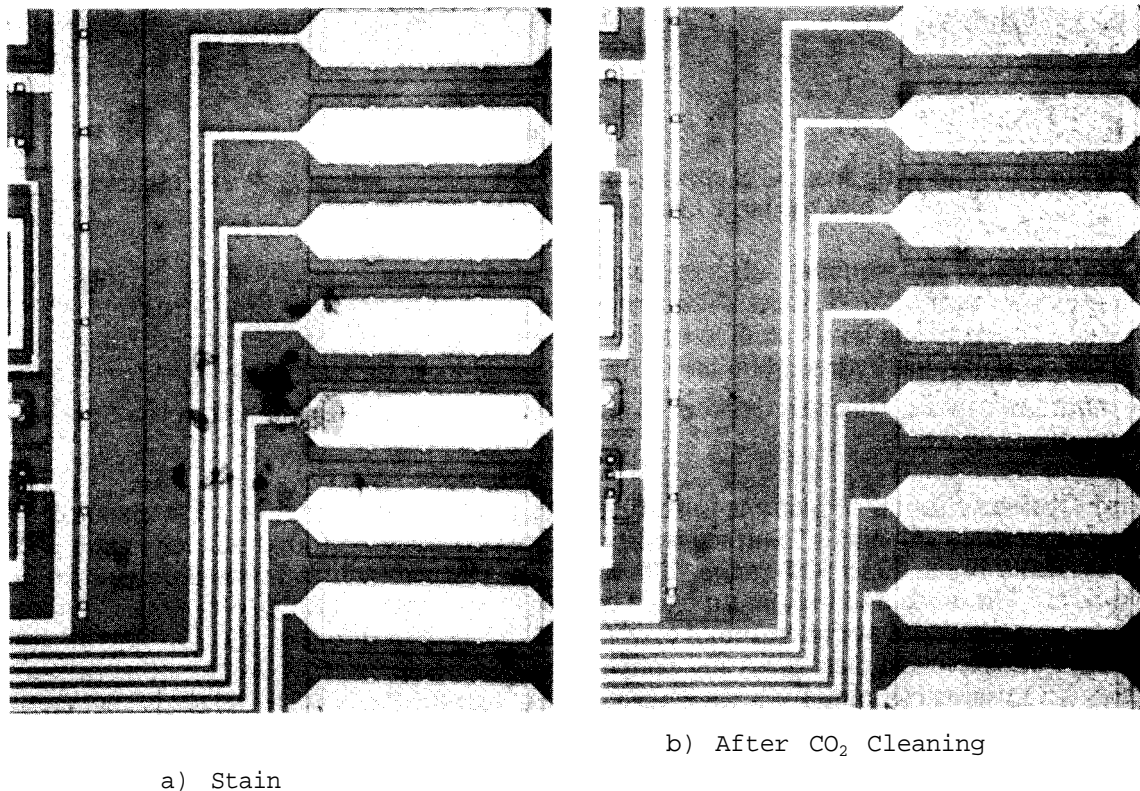
Figure 18 - Optical micrographs at 200x of a contaminated and CO_2 snow cleaned hybrid chip

Polymers Carbon dioxide snow cleaning of a PTFE sheet and two PEU (polyetherureathane) catheters was performed. The results indicate that cleaning can reduce contamination on these materials without adversely affecting the base material. For PTFE, the initial scan of the carbon region indicated a

strong fluorocarbon peak and a smaller hydrocarbon peak as shown in Fig 19. The hydrocarbon peak comprised 6 % of the carbon intensity before cleaning; and after cleaning, the hydrocarbon peak comprised only 2 % of the carbon peak intensity.
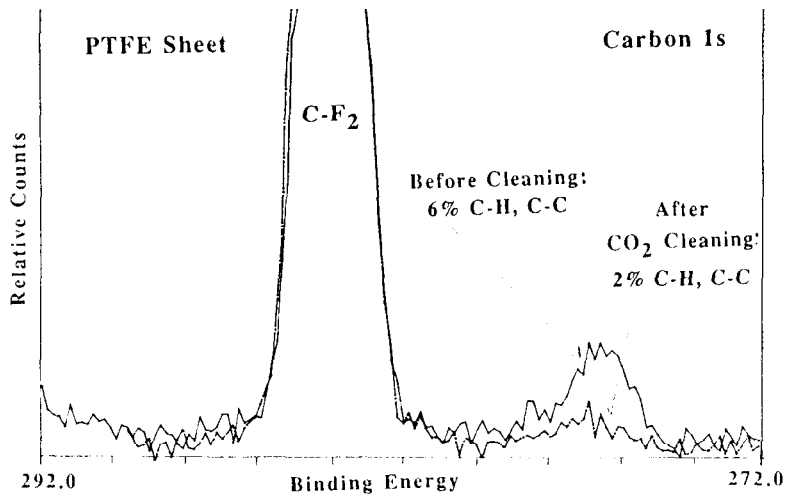
Figure 19 - The carbon 1s spectra from a PTFE sheet before and after CO_2 snow cleaning - note the reduction in the hydrocarbon peak.
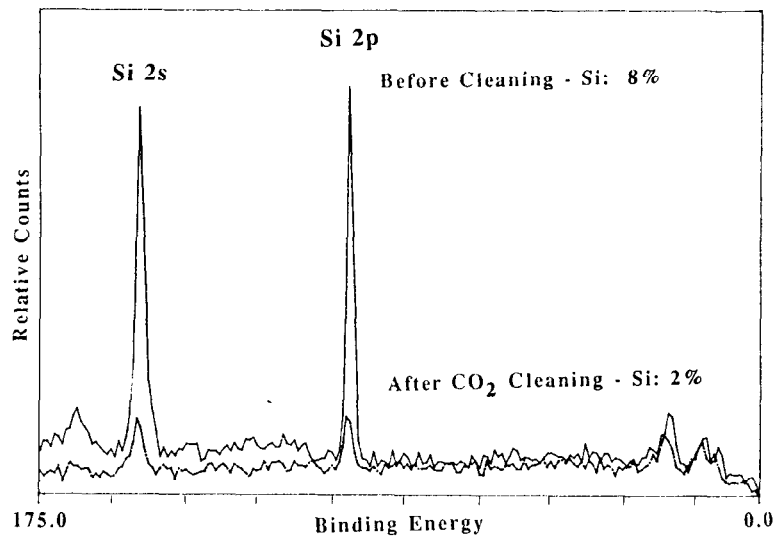
Figure 20 - A comparison of the low binding energy region of XPS spectra acquired from a silicone contaminated catheter before and after CO_2 snow cleaning. Note the reduction in the surface silicon peak - from 8 to 2 atomic percent.

A PEU catheter was analyzed before and after CO_2 snow cleaning. The surface composition before cleaning is listed in Table 6 and a silicon-based contamination (silicone) layer at about 8 at. % was found. After cleaning, the silicon concentration is reduced to 2 at. %, a value associated with about 1 monolayer coverage. Figure 20 highlights the change in the silicon peaks heights before and after cleaning.

Another PEU catheter with an amide (N-C=O) wax coating was examined. The wax is from processing and must be removed for acceptable biocompatible properties. Figure 21 shows typical SEM of different sections of the catheter before and after cleaning. The first micrograph shows extensive surface contamination while the second micrograph shows little or no surface contamination after CO_2 snow cleaning. Both micrographs were taken at 10,000x. The cleaning also modified the surface chemistry of the catheter as shown in Figure 22 and Table 7 . The overall surface compositions before and after cleaning indicated the removal a carbon based compound. Support for this finding is seen in the high resolution carbon 1s XPS peak for the catheter before and after cleaning shown in Figure 22. The initial spectrum of the catheter before cleaning showed a strong peak related to C-C and C-H structures and weaker peaks related an amide and possible ether structures. No urethane linkages were found. After cleaning, the shape of the carbon 1s XPS peak structure was typical of a PEU - strong C-C and C-H peak, a strong ether peak, and a small urethane peak. No amide structure was noted.
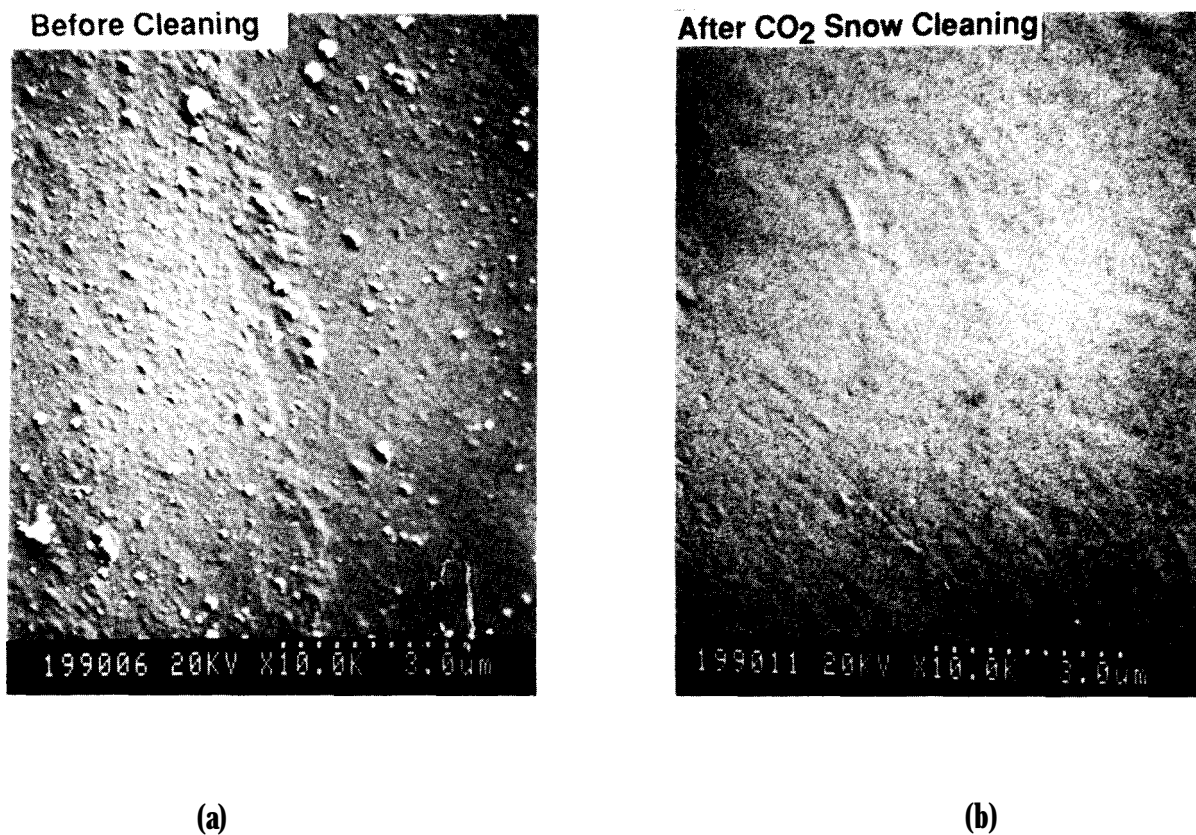

(a)

(b)

Figure 21 - Scanning electron micrograph at 10,000x acquired from different
regions of an amide contaminated PEU catheter surface before and after CO_2 snow cleaning.
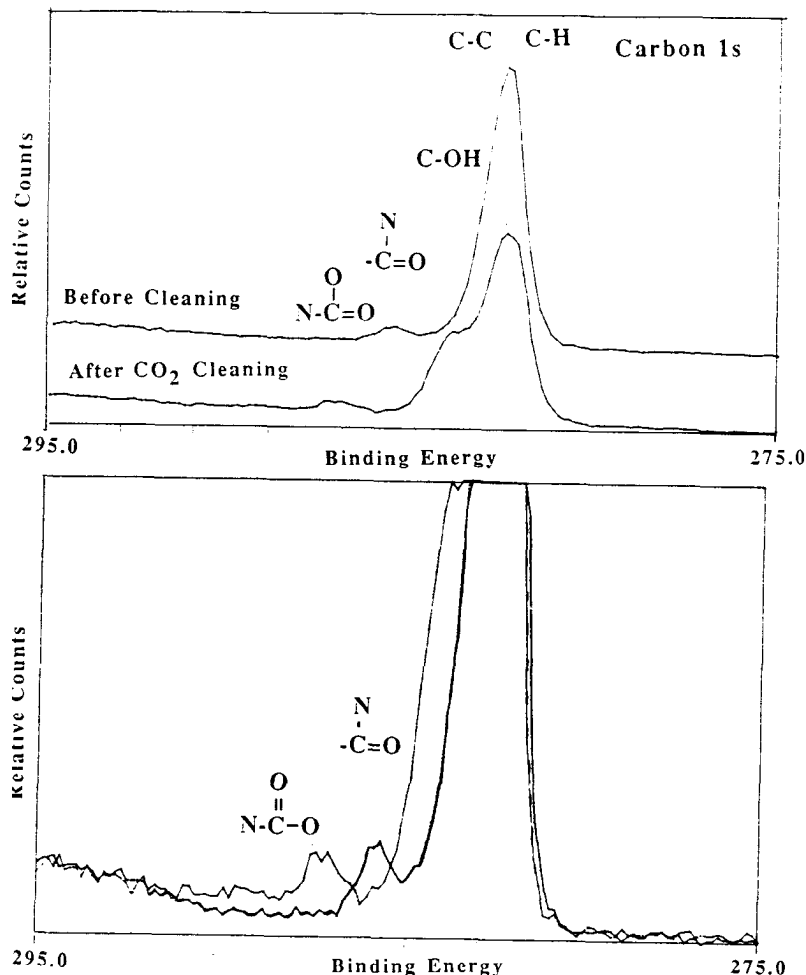
gure 22 - The carbon 1s XPS spectra from a PEU catheter with the amic contamination and after the contamination was removed.

Applications - Equipment and Process Related

The versatility of CO_2 snow cleaning is in that its cleaning applications can span from simple laboratory applications to production and real world contamination control problems. The applications discussed above were performed by an-equipment manufacturer; the applications discussed below come from users located in R&D laboratories and manufacturing environments.

- **Vacuum Technologies** Many applications in vacuum sciences were developed including the cleaning of electron, ion and x-ray optics, samples for surface analysis, cleaning of vacuum components and assemblies.

Layden and Wadlow{ 16) investigated the cleaning of a residual gas analyzer (RGA) and compared the CO_2 snow cleaning to solvent cleaning. The RGA was designed to operate below 1 micron pressure range and initial pumpdown times proved too slow even after the first solvent cleaning. Solvent cleaning was done by total disassembly of the unit and ultrasonically cleaning in isopropanol. This pumpdown time is shown in Figure 23 and after over 50 hours, the pressure was still over 2 microns. Repeated solvent cleaning led to an improved pumpdown time but still not as fast as needed. For CO_2 cleaning, just the filament and beam aperture were removed. All parts were cleaned including ceramics and plastic parts. Pumpdown times now were on the order of 1 hour or less. RGA analysis of scans after solvent cleaning showed hydrocarbons and alkaline based contamination; and after CO_2 snow cleaning, these peaks were reduced or eliminated. This simple test by Layden demonstrates the ability to clean complex vacuum equipment with carbon dioxide snow cleaning.
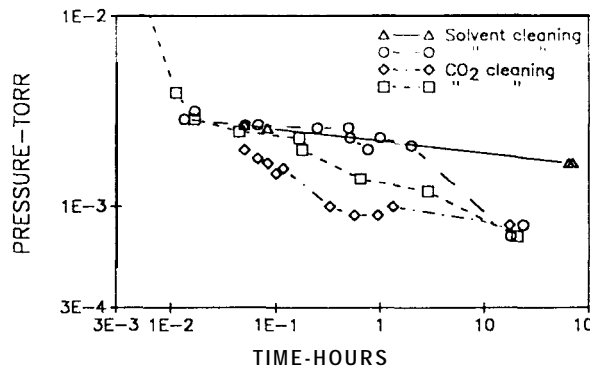
Figure 23 - The pumpdown times measured for the solvent cleaned and
CO_2 snow cleaned residual gas analyzer.

A major component in SIMS (Secondary Ionization Mass Spectroscopy) equipment is the ion source and the cleaning these sources is difficult. D. Salamida{ 17) has used CO_2 snow cleaning to assist in the maintenance and repair of a cesium source. The source was cleaned to remove the Cs residue by standard methods and then final cleaning was done with CO_2 snow. It was noted that this cleaning led to removal of residual Cs debris and other particulates. This conclusion was drawn from the ease of ramping up the high voltage after cleaning. In the past, many high voltage arcing events were noted.

- **Surface Science** In this area, applications involved using carbon dioxide snow cleaning as an assistance in surface analysis, STM/AFM, substrate preparation, and other laboratory applications. Many users are involved in surface analysis (Auger, XPS, SIMS) and their applications include cleaning inadvertently contaminated samples, cleaning standards, and cleaning the surface analysis equipment.

Morris{ 18) has cleaned many different uncoated and metal coated polymer samples before performing AFM (Atomic Force Microscopy). Surface particle populations and organic deposits were reduced. This reduction in organic contamination led to reduced "tip artifacts" and tip to sample binding events during AFM investigation. Morris attributed this to reduction of the "nanoscum" or adventitious hydrocarbons on the surface. Morris also found that cleaning did not damage any of the polymer surface except for uncoated polycarbonate. Small signs of abrasion were noted; polycarbonates have low yield stress and are easily scratched (macroscopically). Aluminum coated polycarbonates were not abraded.

A large number of users of carbon dioxide snow cleaning are in the surface analysis laboratory. Applications include cleaning standards, cleaning inadvertently contaminated samples, cleaning organic residues and particles left after testing, andcleaning the equipment. One example involved a metal sample that was testing in an engine oil. Initial surface analysis after solvent cleaning still showed over 95% hydrocarbons on the surface and made analysis of the underlying surface oxide improbable. Carbon dioxide snow cleaning reduced the surface hydrocarbon level to about 80% and the analysis of the underlying metal oxide layer was now possible.

- **Optics** The cleaning of glass substrates before coating has become a major application area for CO_2 snow cleaning. This cleaning can serve as either an initial or final cleaning of uncoated and coated glass substrates. One common application is to clean individual optical components during final assembly.

One cleaning example involved a gyroscope subassembly. This part is made from a low thermal expansion glass and its geometry includes a total of over 24 faces and over 40 holes. Cleaning this part for particles and residual organic contamination is critical for the end application and carbon dioxide snow cleaning has been shown to fulfill the requirement.

One application that made it into space had a user clean a sunshield on a satellite. The engineer modified one of the above nozzles into a large area, lower velocity stream by placing a Tygon tube over a

metal nozzle. Their interest was to remove the contamination that fell on the shield while the unit was in storage awaiting launch (over a year). The Tygon tube was bent to provide proper access to the aluminum coated beryllium shield. The fragile nature of the part and its coating eliminated any type of contact cleaning and CO_2 appeared as the right choice.

- **Hard Disks Assemblies and Components** - Cleaning of subassemblies and parts within hard disk drives have always presented challenges to contamination control engineers. The elimination of CFC's from the cleaning process and the continued reduction in the flying heights within the drives continues to drive the precision cleaning requirements. CO_2 snow cleaning has met the needs of this industry. Microscopic inspection of many individual components and subassemblies reveal the presence of contamination that cannot be quickly and reliably removed with current generation of cleaning methods.

Sliders become contaminated with a variety of materials during their manufacturing and processing. Individual sliders have been cleaned on a repetative basis without damage to the sliders. Successful cleaning on an individual basis with a point nozzle required that the slider he sprayed from all four sides, for a cleaning cycle of 8 seconds. Multiple sliders were fixtured and cleaned with a flat nozzle with a total cleaning cycle of three seconds.

Head gimbal assemblies, containing a slider bonded to an aluminum flexure were cleaned of particulate contamination without damage to either the fine wires into the slider or the aluminum suspension. Voice coil motors collect particles and are often cleaned with cotton swabs, a process that can leave fine cotton contamination. A short burst of CO_2 removed the contamination without any residue. Although head stack assemblies are very delicate and difficult to clean, they have been successfully cleaned with a gentle stream of CO_2 snow. Additionally, CO_2 has cleaned disk media without damage to the surface.

Cleaning of the head stack assemblies and components mentioned above are well suited for automation and the system discussed later has addressed these contamination control applications.

- **Cleanrooms** - One of the unique cleaning features of CO_2 snow cleaning is the ability to clean cleanrooms. This may be opposite expectations because the CO_2 stream would make the particles airborne, but that is the required step. The key is to clean counters and exterior of process equipment during maintenance, when the critical surfaces and equipment are closed or covered. Any particle that becomes airborne during cleaning will more than likely be captured by the HEPA filters. Tests have been done and this concept has been verified. Over the course of routine cleaning of several countertops about a process chamber, reduced particle populations were noted during the following weeks and months compared to historical averages.

- **Process Equipment** - The same concepts as in the preceding paragraph also apply to cleaning process equipment. The chamber is opened during routine maintenance and snow cleaning is used in addition to the normal cleaning process. Again, as in cleanroom environments, the HEPA filters remove the liberated particles. In non-cleanroom environments, redeposition of liberated particles can occur but the particles will probably be about the room and outside the chamber. A series of tests was performed on a silicide deposition system in a cleanroom. Both the nearby counters and also the interior of the chamber were cleaned with the goal of reducing particle contamination that would be found on test wafers. After the cleaning process was instituted and followed for several months, it was noticed that the particle populations on test wafers were reduced by a factor of five even after a longer period of time between measurements. This particle population reduction led to increased yields.

Miscellaneous - Tooling of various types are often used to hold components during precise manufacturing operations. This tooling can become contaminated and thereby contaminate the ultimate assembly. In one application, CO_2 is used to remove alumina contaminants from critical tooling used in the manufacturing of disk drive components. The tooling was examined by SEM and EDS before and after CO_2 cleaning. There were no measurable traces of alumina after cleaning. After the initial testing, CO_2 was used for cleaning of the tooling for a six month period. This tooling is used in a cleanroom and

is periodically passed out of the cleanroom to a cleaning station where it is cleaned. Total cleaning time is 5 seconds. At the end of the six month evaluation, it was determined that CO_2 cleaning contributed to an increase in manufacturing yield[19].

Many manufacturers use carriers of various types and configurations to transport assemblies during operations. CO_2 has effectively cleaned carriers for disk drive sliders, disk substrate and media and wafers. In an operation that resulted in a deposit of silicon dioxide inside of a 2" exhaust pipe, CO_2 effectively removed contaminants to a level cleaner than required for unit operation. Additionally, CO_2 has proven effective in removing a thin glue residue, as well as certain cutting oils used during machining.

Cleaning Issues

Successful snow cleaning, as for any cleaning process, requires attention to several parameters related to economics, moisture condensation, carbon dioxide purity, static charge, etc. By addressing these issues in a test program, it becomes relatively simple to scale a bench top cleaning system shown earlier in Fig 1 to systems involving automation and process control environments.

- **Economics** - CO_2 costs depend upon three choices, nozzle design (orifice size or flat nozzles), liquid or gaseous feed and the CO_2 purity. With respect to nozzle design and choice, typical round nozzles that can clean a 1/4 inch spot consume from 1/2 to 2 cubic foot of CO_2 per minute while a 1 inch flat nozzle consumes about 1 cubic foot of CO_2 per minute. With respect to choosing either liquid or gaseous CO_2 feed, present costs for 60 lbs of CO_2 in a cylinder range from $50 to $250 for welding grades to "SFC" (supercritical fluid chromatography) grades. Recalling the difference in choosing a gas or liquid fed cylinder, a gas fed cylinder has 60 lbs (525 cubic feet) of usable product while a liquid fed cylinder has 40 lbs (350 cubic feet) of usable product. Taking a CO_2 consumption rate of 1 cubic foot per minute, a liquid fed cylinder costs range of $0.17 to $0.71 per cubic foot per minute while a gas fed cylinder cost range is $0.11 to $0.48 per cubic foot per minute. Therefore, if a part requires one minute to clean and assume a usage of 1 cubic foot per minute, then costs related to the carbon dioxide range from $0.11 to $0.71. In most situations, the cleaning time is 5 seconds per part, permitting the cleaning of 12 parts per minute, resulting in a cost per part of $0.01 to $0.06. Bulk carbon dioxide is available at significantly reduced costs for high volume operations.

As an example, consider a 200 mm wafer being cleaned with a 205 mm flat nozzle and consumption would be 8 cubic feet per minute. With a high purity gas feed the cost per minute of operation would be $3.84 ($5.68 if liquid fed) per minute. Using an estimated cleaning time of 5 seconds, a total of 12 wafers would be cleaned for each minute of operation, at a cost of $0.32 per wafer. For another example, consider the non-critical cleaning of a 2" square plate using a 2" flat nozzle and a liquid feed. With CO_2 consumption of 2 cubic feet a minute and a cleaning time of 2 seconds, the cost of cleaning each part is less than $0.01. Similar numbers and costs can be generated for different applications, with significant cost reductions being achieved through the use of bulk purchased CO_2.

Equipment Costs - The cost of the cleaning equipment ranges from less than $1500.00 for the basic kit (shown in Fig 1) to approximately $50,000 for the automated unit shown in Fig 24. Assuming the wafer example above, operation of the unit for 200 days for 8 hours per day gives an equipment cost of less than $.05 per wafer. This number represents the costs associated with a continuous operation of an automated system. For less than fully automated systems, the costs decrease and the cost of any cleaning operation still stays low as long as usage remains adequate. The kits used for initial laboratory testing and development are usually priced as non capital items.

Recontamination Issues - **Gas Purity.** The risk of recontamination by a cleaning process must be investigated before any process can be implemented. Two separate studies on recontamination were performed, the first by Whitlock and the latter by Sherman.

Whitlock[1] performed a series of tests in a class 1 cleanroom on new 4 inch wafers. Wafers were

analyzed by an Estek WIS-600 particle counter for the initial particle population. The CO_2 snow cleaning nozzle was held over the center of the wafer and the stream was turned on for 10 seconds. Carbon dioxide source was the Spectra Clean grade from Airco - a grade with low heavy hydrocarbon level. Then the particle population was counted after this exposure. The test was repeated for 9 different wafers. An initial particle population was raised from an average total of slightly less than 16 particles before cleaning to over 80 particles after cleaning the entire wafer. This corresponds to an increase of about 1 particle per square centimeter that was added to the wafer surface.

Attempts were made to identify the elemental composition of these particles. EDS failed to identify any element heavier than sodium suggesting that these added particles are hydrocarbon-based. Further support for this identification came about in that particle population could be reduced by extended high temperature baking in air. The sources of these hydrocarbon particles have never been conclusively identified but the suspected source is twofold, the hydrocarbon impurity that is typically found in carbon dioxide and also from the cleanroom ambient air.

Sherman{ 13) studied the effects of different CO_2 sources on the cleaning of clean Si wafers. The focus was to compare changes in surface chemistry by using different grades of carbon dioxide and also to compare the difference between liquid and gaseous CO_2 feeds. CO_2 sources tested included welding grade, food grade, instrument grade and supercritical fluid chromatography grade (SFC). The SFC grade is widely available and is directed towards the supercritical extraction field.

The method was to initially analyze the surface chemistry of clean Si wafers (control - CTL), CO_2 snow clean this region and then analyze the surface chemistry after cleaning. All the samples except for SFC-2 were silicon wafers with thin native oxides; sample SFC-2 had a thicker thermal oxide. At least 7 runs were made, and the surface chemistry results (as determined by XPS) are listed in Tables 8 and 9. The cylinders were all gas fed except for one listed as "liquid" in the table. The CO_2 source was same cylinder as "gas" fed welding cylinder - the cylinder was laid on its side.

The changes in surface chemistry for the three SFC grades indicated a decrease in surface carbon concentration while the carbon concentration increased for the other carbon dioxide grades. These results imply that the SFC grades are acceptable for cleaning "clean" samples while the other grades may not be acceptable for cleaning "clean" samples. Still, the four grades that led to an increase in the surface hydrocarbon concentration would still remove visible carbon contamination and particles from surfaces. It should be noted that the samples shown in micrographs 11, 12 and 14 were cleaned with welding gas. Note that these "lesser quality" CO_2 grades still remove gross contamination and the samples appear cleaned up to and above 1000X magnifications.

Further comparison of the data can be obtained by defining a ratio of the initial carbon concentration to the carbon concentration after cleaning. Values of this ratio less than 1 would imply hydrocarbon removal while values of this ratio greater than 1 would imply contamination of the clean surface. We see that the values of ratio, cleaning effectiveness, are less than one for the SFC grades and greater than for the other grades. Therefore, for critical cleaning applications, an SFC grade is recommended.

The liquid fed welding source led to a greater contamination than the gas fed welding source. This suggest that cleaning with a liquid fed cylinder can lead to a greater recontamination on a surface than a gas fed cylinder. Since liquid CO_2 is such an excellent solvent, it is expected that the hydrocarbon contamination in a cylinder is concentrated in the liquid. Then the amount of contamination in a given quantity of liquid will be greater than in the same quantity of gas. Therefore, at similar cleaning rates, a liquid fed cleaning stream would contain greater contamination and can potentially deposit a greater number of hydrocarbon contaminants.

The SFC grades and newer SFE (supercritical fluid extraction) grades of carbon dioxide are specially purified to minimize the heavy hydrocarbon. The purification systems have no lubricants, residual oils or vacuum pump oils. Additionally, the cylinders for these grades are usually set aside for special handling and cleaning. Simply stated, use of the wrong grade of CO_2 will put oils on your samples. The extent of

this contamination may or may not harm the surface cleanliness.

Filtration - For critical cleaning applications, it is necessary to filter the carbon dioxide. The cylinders, hoses and all the equipment have particles and the flowing gas or liquid will transport these particles out of the nozzle and on to the sample. Generally, the cleaning process will remove these particles, but there are risks that some will stay. Further, these particles coming through can be abrasive. In choosing carbon dioxide for critical cleaning applications, it is imperative to have in-line filters at the proper location. The best choice, as established by methods in the semiconductor industry, is to use point-of-use filtration. This means placing the filter right before the nozzle. With this, all particulate contamination introduced will be eliminated. Filtering of gaseous CO_2 sources is much easier than with liquid sources because it is easier to filter a gas than a liquid. Therefore, for critical cleaning applications, filtration of a gaseous CO_2 source is recommended.

Not all vendors place filters on their systems nor do they place the filters in the proper location. For many cleaning applications this is not an issue but there are many cases when incorrect filter choice has negatively influenced the cleaning process. Proper filter placement means that the filter must be placed just before the nozzle to remove all particle that can enter from the cylinder, hosing, on/off valves or guns.

Moisture Condensation - The cold carbon dioxide snow stream easily lowers the surface temperature and moisture can condense. This moisture condensation is a function of the dew point of the cleaning environment. Generally, moisture condensation does not interfere with cleaning, unless the moisture "freezes." Cleaning setups usually have a method to minimize moisture condensation - the easiest method is use a hot plate as part of the sample support. Usual set point for the hot plate is at most 100F; generally, lower temperatures are acceptable in less humid environments. The samples can be held on the hot plate by vacuum chucks or other special rigs. Generally, the moisture condensation goes away quickly when using a hot plate and samples have adequate thermal conductivity. For samples with poor thermal conductivity, such as thicker glass plates, an overhead hot air gun or lamp can be used. Other choices for moisture control are to have dry boxes, enclosed hoods or environmental chambers that are purged or heated. All have been successfully demonstrated.

Static Charge - There is a potential for build up of static charge on surfaces during cleaning. This is caused by the ionization of a flowing gas. Obviously, this static charge buildup is not a problem for metal samples. From our experience, if the sample is grounded, static charge is not a problem. Charging is usually worse for glass samples or for electrically isolated parts on complex structures. For these cases, positive ionization sources can be obtained and counter the charge. These units are commercially available from many sources. Installations of static control units in automated units have been done and yield satisfactory results.

Feed Pressure - The feed pressure is important to maintain in these snow spray systems. If the feed pressure decreases, the velocity of the jet stream decreases. As the velocity falls, the ability to remove organic contamination falls until no organic removal occurs. Thermodynamically, referring to Fig 2, as the pressure fall for a gas fed cylinder, the percentage of snow formed decreases until no snow is formed. With liquid fed sources, reductions in pressure will lead to a higher percentage of snow formation but the snow will have a lower velocity. Reduced feed pressures can be achieved using a leak valve in line or by having the expansion chamber diameter much larger than the orifice diameter. The advantage of reduced pressure feeds are the ease in cleaning smaller or delicate parts.

Automation - Once it has been established that carbon dioxide snow cleaning can address the cleaning requirements, the next step is to integrate the cleaning process into the existing manufacturing process. The automated cleaning system must be repeatable, reliable, and must improve the speed, safety and economics of the manufacturing process. Some of the issues in designing and implementing an automated system were discussed above. Issues related to speed, equipment, process chambers and minimization of redeposited particles are discussed below.
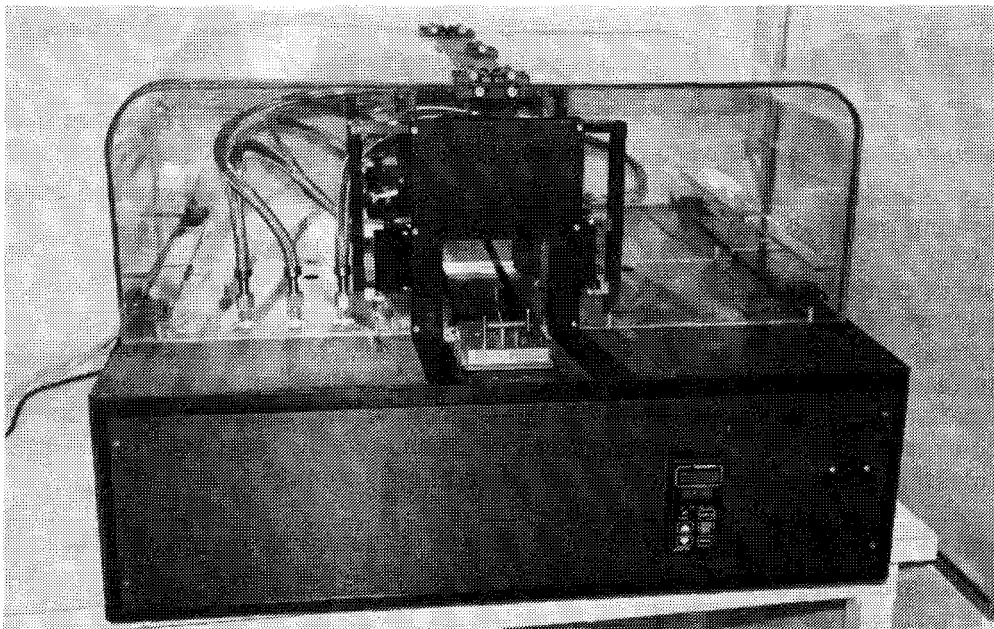
Figure 24 - PCS2000 automated CO_2 cleaning system, footprint of 30" x 30" x 19"H.

The more axis of movement required to perform the cleaning operation, the more expensive the system. In automating the cleaning process, one can choose to hold the part and move the nozzle or fix the nozzle and move the component, or a combination of the two. A simple procedure would be to rotate the sample and clean counter the rotation and move the nozzle out along the radius. Another method would be to design a robotic system to move the nozzle about the sample. A third method, similar to the system shown in Figure 25 would be to fix the nozzle and have the sample transport under the nozzle.. The standard nozzle cleans only about a quarter inch wide stripe on each pass. Therefore, a 4 inch square plate could require 16 passes to cover the entire surface, while a 4" wide large area nozzle would clean this surface in one pass. For components larger than l/2", the flat nozzle would provide a shorter cleaning cycle.

As the amount of movement during the cleaning cycle increases, there is an increased risk of particle generation. Accordingly, it is best to keep these movements from occurring in any position above or upwind of the surface being cleaned. Further, the automated system is a continuous operation, not a batch operation. This means as each part is cleaned, it is removed and available for the next step in production and a new part is loaded for cleaning. Further, by fixing the nozzle, the cleaned part, if large enough, can be moved into a protective environment within the cleaning chamber to minimize recontamination. In some applications, multiple parts can be fixtured onto a carrier and cleaned with a flat nozzle, thereby providing increased cleaning throughput and reduced costs per part.

The environmental chamber chosen for cleaning is also critical. Moisture control as shown above is an important consideration and automated systems must be enclosed in an environmentally control chamber. The chamber or a filtered air flow in the chamber can be heated, or the chamber can be flushed with nitrogen. The goal of any such process is to control the dew point of the chamber so that moisture will not condense during the cleaning process. Automated chambers can also be equipped with static control devices to neutralize any surface charge build up. Further, these chambers are designed to provide a carbon dioxide flow that is only in one direction, from the nozzle, out to the sample and then immediately towards the exhaust. Turbulence within the chamber that is near the side walls can lead to particle deposition within the chamber and future recontamination problems. Interestingly enough, the CO_2 generally cleans the chamber as well as the part being cleaned, minimizing maintenance. Overall, the automated systems available, such as that shown in Fig. 24, address these and other issues.

Summary and Conclusions

Taking advantage of the physical properties of carbon dioxide, an effective cleaning stream containing solid CO_2 can be created using proprietary nozzles. Data has been presented to show that the process can remove particles of all sizes and also organic residues. Many examples were provided covering the cleaning of different materials, wafers, and process equipment.

Applications of carbon dioxide snow cleaning are numerous and include:
- microelectronic - substrate preparation, wire bond pads, ICs, hybrids, tooling
- optics - UV, IR and Visible lenses, laser filters, substrate cleaning, mirrors
- surface analysis - XPS, Auger, SIMS, AFM/STM, cleaning the equipment
- vacuum technologies - cleaning vacuum system and components, deposition systems
- contamination control - cleaning cleanrooms and process tools
- substrate preparation - metals, wafers, ceramics, polymers,

The parameters necessary to perform cleaning with CO_2 snow were reviewed. These issues include the importance of carbon dioxide purity, filtration of source CO_2, static charge, moisture condensation and feed pressure. By paying attention to these details, it is possible to automate the cleaning process and remove particulates and organics from a wide range of materials. Further, the carbon dioxide snow cleaning process can address the contamination control problems facing engineers not only in the cleanroom but also in a wide variety of industrial applications.

Table 1

Particle Populations and Removal Efficiencies

Size(microns)	Zn Before	Zn After	% Zn Remaining	% Zn Removed
>0. 1	4720	3	**0.064**	99.936
>0.2	4688	3	**0.064**	99.936
>0. 3	4640	3	0.065	99.935
>0.4	4432	3	0.068	99.932
>0.5	4192	3	0.072	99.928
>0.6	3904	2	0.051	99.949
>0.7	3536	2	0.057	99.943
>0.8	3328	2	0.060	99.940
>0.9	3120	1	0.032	99.968
>1.0	2880	1	0.035	99.965
>1.1	2624	1	0.038	99.962
>1.2	2336	1	0.043	99.957
>1.3	2144	1	0.047	99.953
>1.4	1920	1	0.052	99.948
>1.5	1808	1	0.055	99.945
>1.6	1616	0	0.00	100.00
>1.7	1504	0	0.00	100.00
>1.8	1328	0	0.00	100.00
>1.9	1184	0	0.00	100.00
>2.0	1088	0	0.00	100.00

Table 2

Surface Hydrocarbon Removal from Silicon Wafers
(atomic percent carbon)

	Control	Contamination	CO_2 Snow Cleaned
Test1	29	54	20
Test2	27	63	19
Test3	28	88	23
Test4	28		12

Test1 - fingerprint
Test2 - noseprint
Test3 - repeat noseprint
Test4 - cleaning a "clean" region

Table 3

Metal Cleaning Tests
(atomic percentages)

	Al Test			Cu Test			SS Test	
	Control	CO2 Cleaned		Control	CO2 Cleaned		Control	CO2 Cleaned
Al	12	28	Cu	4	7	Cr	3	5
0	22	37	0	22	29	Fe	1	2
C	60	33	C	71	60	0	41	48
Si	4	1	Cl	3	3	C	45	33
N	<1	<1				N	4	4
Na	<1	–--				S	1	2
						Si	3	3
						P	2	3

Table 4

Gold Surface Contact
(atomic percentages)

	Contaminated Gold Contact	CO2 Snow Cleaned Gold Contact
C	84.4	63.8
0	12.3	11.9
Na	0.5	
Si	2.5	
AU	0.3	24.3
C/AU	281	2.6

Table 5

Glass and Optic Cleaning
(atomic percent)

	Plate Glass		Bandpass Filter	
	Initial Surface	Cleaned	Initial Surface	Cleaned
Si	19	23	8	21
0	41	48	16	45
C	27	15	72	28
Mg	9	10	---	1
Na	4	3	2	2
S			2	--
K			---	1
N			---	2

Table 6

Silicone Removal
(atomic percent)

	Initial Surface	CO_2 Snow Cleaned
	70	78
O	19	16
N	2	3
Si	8	2
S	1	
Cl		<1*

*less than 1 at. %

Table 7

Wax Removal
(atomic percent)

	Initial Surface	CO_2 Snow Cleaned
C	91	82
0	5	14
N	3	3
Si	<1	
S	<1	

< implies less than 1 at. %

Table 8

Relative Cleaning Effectiveness

	SFC1		SFC2		SFC3	
	CTL	Cleaned	CTL	Cleaned	CTL	Cleaned
Si	42	61	29	31	51	53
O	35	31	54	58	37	40
C	22	8	16	11	12	7
N	1	<1	<1	---	---	---

	Medical		Welding (liquid)		Welding (Gas)		Instrument	
	CTL	Cleaned	CTL	Cleaned	CTL	Cleaned	CTL	Cleaned
Si	49	44	49	43	47	46	29	26
O	36	33	34	40	37	34	54	54
C	15	23	17	28	16	20	17	20

Table 9

Relative Cleaning Effectiveness

CO2 Source	Cleaning Effectiveness
SFC-1	0.36
SFC-2	0.69
SFC-3	0.58
Medical	1.53
Welding - liquid	1.65
Welding - Gas	1.25
Instrument	1.18

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c) The Lever Rule allows for the determination of the relative percentages of each component in a two phase region.

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