ABLATION AND SORPTIVE REMOVAL OF FILMS AND PARTICLES FROM SURFACES USING CARBON DIOXIDE

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ABSTRACT

The use of carbon dioxide in its various states: supercritical (SC-CO_2), liquid (L-CO_2) or pellet form (snow-CO_2) for cleaning the surfaces of precision metallic/optical components and semiconductor electronic devices is well documented in the literature, but an understanding of the fundamental mechanisms responsible for carbon dioxide-based cleaning processes is lacking. Although carbon dioxide is an excellent solvent for removing non-polar contaminants from a variety of surfaces, other CO_2-based cleaning processes are based on mechanical or morphological-induced changes in the interfacial region. The extremely low surface tension of CO_2 is a favorable property in terms of its rapid and complete removal from the substrate after cleaning has been affected, while this characteristic of CO_2 also accounts for its negligible effect on the morphology of the substrate, as utilized in critical point drying. However, this is counter intuitive to what is achieved when using SC-CO_2 or L-CO_2 for surface cleaning or alteration.

Mechanical ablation of particulates and other contaminants on surfaces with CO_2 is governed by a complex array of factors including van der Waals and electrostatic interactions, drag and lift forces, and phase changes that occur when the CO_2 molecule impacts on the surface. Ultimately particle removal from surfaces is dependent on the viscosity and density of SC-CO_2, two factors which impact on the hydrodynamics of the boundary layer at the fluid-surface interface. Theoretical calculations show that the boundary layer is a parabolic function of the CO_2 velocity, exhibiting only a weak dependence on temperature; and it is these factors which determine the size of the particle that can be removed with SC-CO_2.

By contrast, CO_2-based cleaning of surface films exhibiting low or negligible solubility in SC-CO_2 requires a different mechanistic or theoretical treatment as well as experimental confirmation. Application of adhesion science principles using such parameters as Hamaker constants or two-dimensional solubility parameters (d) can be used to qualitatively explain the ability of SC-CO_2 or snow-CO_2 to remove some surface films. For polymeric films, such as those that occur on semiconductor devices, there is a complex array of factors which can account for the observed effect of SC-CO_2 “cleaning”. Interaction between the supercritical fluid and polymeric film can result in sorption of the fluid by the polymer, resulting in swelling or crystallization. SC-CO_2 can also alter the molecular weight distribution of the polymeric film via extraction of specific oligomers, induce depolymerization, or increase the molecular weight of the polymer by a pressure-induced polymerization reaction.

Studies on Si/Al wafers with respect to photoresist stripping illustrate the effectiveness of a SC-CO_2 –cleaning process. Results from surface characterization studies such as FTIR, SEM, Auger and nuclear reaction analysis (NRA) confirm the efficacy of CO_2 as a cleaning and stripping agent, even in the “trench” profiles. Using the patented LANL-SCOOR process as an example, the effects of CO_2 and incorporation of a co-solvent on removal of the masking polymeric film will be illustrated. The above process is enhanced by ablative-based pulsing and rastering of the CO_2 –cleaning agent across the substrate surface at a specified delivery angle. Elastic deformation of the polymeric film under the above conditions occurs most readily at temperatures below the glass transition, T_g, of the polymer. NRA analysis suggests that SC-CO_2 cleaning removes contamination at a level equivalent to 1-10 monolayers, certainly below the level of $10 \mu g/cm^2$, which is considered a criterion for precision cleaning of surfaces.

INTRODUCTION

Carbon dioxide (CO_2)-based cleaning processes can utilize several states or forms of CO_2, such as SC-CO_2, L-CO_2, or the pelletized form of CO_2, frequently referred to as CO_2 snow cleaning. Such processes are often employed in the cleaning of metal parts, electronic components, and component raw materials [1,2], and are attractive because of their ecological compatibility and relative low cost. These processes are of increasing importance in the semiconductor microchip industry where production of a 2-g microchip can consume 32 kg of water, 700 g of ultra-pure gases, 1.6 kg of fossil fuels, and 72 g of chemicals in the production of each 2-g chip. In addition, current techniques used in the production of baked-photoresists require the use of highly acidic or alkaline aqueous solutions and/or organic solvents. The magnitude of this problem becomes even more apparent when one considers that a typical semiconductor plant might use up to 6 million gallons of water/day along with thousand gallons of organic solvents.

In this presentation, the basic mechanisms which contribute to the efficacy of CO_2 – based cleaning methods are described and optimized. Carbon dioxide cleaning may be utilized for the removal of solid particulates, deformable surface films (i.e., organic contaminants) or polymeric substrates, such as occur in the photoresist development process. In the latter process, the various forms CO_2 – based cleaning have the potential to remove the photoresist, post-ash products, etchants, and chemical polishing residues (CMPs). However CO_2 – based cleaning can be employed in other applications, ranging from the precision cleaning of metal parts to decontamination of radioactive residues found in the nuclear industry. Examples of such applications are discussed in the latter sections.

BASIC CONCEPTS

Ablative-Based Processing

Cleaning with CO_2 involves several discrete mechanisms often acting in concert to achieve the final end effect. Removal of particulate matter by the process of abrasion or ablation involves dynamics of the cryogenically developed particle and its interaction with the surface boundary layer. Upon ejection from a specially designed nozzle orifice, CO_2 exists in both solid and fluid forms. Subsequent cleaning of the surface involves; (1) impact momentum of the CO_2 particles to overcome the force of adhesion binding the particle to the surface, (2) the

drag force of CO_2 to remove the particle from the surface, and (3) and possible dissolution of the particle into fluid CO_2. The velocity of the cryogenic CO_2 particle decreases by 36% of its initial velocity over one relaxation time to cross the boundary layer. This relaxation time increases for larger particles of CO_2 indicating that they cross the boundary layer with an increasing velocity. The relaxation time also decreases with an increase in the viscosity of the CO_2 flowing over the surface, hence increasing the drag force that the cryogenic particles of CO_2 exhibit in the boundary layer.

From a practical point of view, the adhesion forces governing effective particle removal have been discussed by Busnaina [3]. Space does not permit a thorough discussion of the contribution of the 7 basic adhesion forces governing particle removal, but an elegant discussion is available in a LANL report [4] available at www.scrub.lanl.gov. Analysis of these forces governing adhesion for SiO_2 particle being removed by either LCO_2 or SC-CO_2 from a silica surface versus those governing the dynamics of an identical particle-surface with water indicate that additional force must be generated for the case of dense phase CO_2 – cleaning processes versus those available during aqueous-based cleaning. These supplemental forces for the CO_2 cleaning can be generated increasing the shear flow via higher CO_2 flow rates, mechanical agitation of the substrate, or other force fields.

Further edification on the dynamics of particle removal have been described by Chitanvis et al. [5] and more recently Toscano and Ahmadi [6]. The seminal concept in these studies is the mathematical description of discrete regions of the attendant boundary layer undergoing impact of a cryogenic CO_2 particle. Coupled with the mathematical formalism of the contributing forces of adhesion or de-adhesion, along with CO_2 density and viscosity data as a function of temperature, it is possible to describe the thickness of the boundary layer as an inverse function of the velocity of CO_2 impinging on the substrate surface. From this dependence, the radius of the smallest particle that can be detached from a surface as a function of impingement velocity and temperature can be estimated. In general, operation at a lower temperature is more efficient, e.g., using SC-CO_2 at 300 bar and between 325 – 375 K and a turbulent flow of 100 – 200 cm/s will permit removal of particles down to 0.1 micron.. This translates into delivering SC-CO_2 flow rates in the range of 30 – 60 L/min.

Carbon dioxide "snow gun" cleaning can also be applied to deformable film contamination on surfaces, such as organic contaminants, as indicated in Fig. 1. Here the impact of cryogenically-generated CO_2 particle deforms the contaminant film distributing the surface pressure forces and aiding in film removal. Results generated at LANL's Supercritical Fluid Facility and elsewhere have shown that SC- and L- CO_2 cleaning of films of oils, greases, and model sorbates can be highly effective, and meet the 10:g/cm2 contaminant removal level that defines "precision" cleaning. However a bias in cleaning effectiveness exists which is dependent on the contaminant (sorbate) – substrate (sorbent) interaction, and each individual case requires experimental verification.

Sorptive-Based Processing

The removal of polymeric films such as those utilized in photoresist development processes can be somewhat more difficult than some of the previously cited examples. L- and SC- CO_2 interaction with polymeric substrates can produce several effects which facilitate cleaning, or could perhaps better described as "debonding" of the polymer from the base substrate.

Unlike the case of the deformable or soluble organic films noted previously, solubility of the polymeric films in the various forms of CO_2 is limited except at very high pressures [6]. However imbibition of SC- or L-CO_2 into polymeric films is well known [7-10] and will be documented in the Results section. Dissolution of CO_2 can result in plastization, crystallization, extraction/fractionation, and possible further polymerization of the polymeric film, all which may all aid in removal of the film.

Table 1 tabulates experimental measurements of CO_2 solubility in various polymers [7-10]. The absorption of CO_2 under the conditions listed is significant and can have several effects:

(1) Sorption of CO_2 generally lowers the glass transition, Tg, of the polymer
(2) Dissolution of CO_2 in polymeric matrix will swell the polymer, particularly if the polymer is held above its Tg.
(3) Swelling of the polymer reduces polymer-polymer interactions, lowering the overall solubility parameter, $*$, of the polymeric film.

Photoresist stripping with CO_2-based agents can be further facilitated by adjusting operational parameters. As will be illustrated in the results section, the addition of a small amount of co-solvent can further induce swelling and debonding. Pneumatic pulsing of the CO_2 accompanied by defined rastering of CO_2 jet accentuates the above effects, resulting in a shattering of the polymeric coating and its physical removal, even in high aspect ratio configurations. It is also best to operate above the Tg (if known) for the polymeric film to imbibe more CO_2 which facilitates swelling.

RESULTS

Typical "snow gun" results obtained on a LANL-modified VAN-TRAN apparatus (Fig. 2) are shown in Table 2 for the removal of an Apiezon N grease. Typical experimental parameters were nozzle angle variance of 60 – 80°, nozzle distance from substrate (4mm – 2.5 cm), 10 min. total processing time, with a delivery pressure of 800 psi. These results were optimized using a low pressure nozzle as opposed to the higher pressure option. As can be seen in Table 2, the most promising results corresponded to those in shaded portion of the Table 2. Snow gun cleaning effectiveness is somewhat dependent on the identity of the contaminant, e.g, a Mobil brand of lubricating oil and the Apiezon N appear to be more easily removed, while silicone oil films are more resistance to snow gun cleaning. Similarly, snow gun cleaning has been employed at LANL in the cleaning of Pu metal surfaces. Shown in Fig. 3 are the scanning Auger spectroscopy results for Pu coupons cleaned with CO_2 for only 15 secs. The Auger spectrum indicates substantial removal of surface hydrocarbon-based contamination, yielding surface impurity levels to those found on sputter-etched Pu metal.

An example of utilizing SC-CO_2 for the surface cleaning of photoresists is provided by using the LANL-patented SCOOR process [11]. In this case, samples of GaAs and GaP wafers covered with positive (AZ-4330) photoresist, as well as Si wafer samples with Al, Ti-Pt, Ti-W and In-Sn oxide metallizations covered with the same positive photoresist were treated via the SCOOR process using SC-CO_2. These ½ inch square samples utilized a smaller SCOOR system consisting of a compressed gas cylinder which feeds a high pressure syringe pump that supplies high-pressure, ambient-temperature SC-CO_2 into a ballast tank and eventually the treatment vessel. The ½-inch square sample is centrally mounted inside the treatment

vessel. The initial conditions for the ballast tank and treatment vessel are 1600 psi and 50°C and 1100 psi and 50°C, respectively. Once the ballast tank and treatment vessel are brought to their initial conditions, a valve leading from the ballast tank to the treatment vessel is opened, allowing the solvent mixture to flow into the vessel and on to the sample surface. This flow, directed by a nozzle, and continues for several seconds, until the pressures in the tank and cleaning vessel equilibrate (the final pressure of the treatment vessel rising to about 1400 psi). Subsequently, a needle valve leading from the treatment vessel to a surge tank is then opened until the treatment vessel pressure drops back to 1100 psi. The surge tank is maintained at atmospheric pressure and empties into an effluent tank to recycle the solvent. When the treatment vessel de-pressurizes to 1100 psi, the ballast tank is re-pressurized to 1600 psi. This pressurization/de-pressurization cycle is repeated three times, applying SC-CO_2 with 5 vol.% propylene carbonate (PCO_3) in three separate pulses. Following completion of the third treatment cycle, the PCO3 source is shut-off, and a pure CO_2 "rinse and dry" step is applied to the treated sample, to remove all residual solvent and particulates. The sample is then removed from the treatment vessel and analyzed for the presence of residual photoresist using surface nuclear reaction analysis (NRA).

Column 2 in Table 3 gives the experimental proton yield from the NRA analysis of residual C on the surface on the listed samples. As indicated in Table 3, each sample analyzed by NRA analysis must have an experimental background and adjusted proton count applied to eventually yield the C-atoms/cm^2 on the surface of the CO_2- treated specimens (Column 5 – Table 3). These surface concentrations of C-atoms divided by the approximate value for a monolayer of C-atoms on a surface (1×10^{15} C-atoms/cm^2) yields the approximate number of monolayers of carbon atoms on the surfaces (Column 6 – Table 3), and hence the relative cleanliness of the surfaces after treatment with SC-CO_2. These monolayer values indicate that a high degree of photoresist removal has been achieved, particularly for these test specimens that were cleaned in an open laboratory environment and not a clean room. In addition, the presence of residual adsorbed CO_2 left over from the cleaning process cannot be discounted.

Some additional examples of the effectiveness of SC-CO_2 surface cleaning on semiconductor photoresist surfaces are shown in the scanning electron microscopy (SEM) photomicrographs in Figs. 4 and 5. Fig. 4a shows an intermediate, partial strip of the polymeric photoresist by the SCOOR process, while Fig. 4b shows that the photoresist and concomitant polymeric residue products are removed from the surface. Figs. 4c and 4d show before/after SEM scans of a similar fluorinated residue stripped from the top of a photoresist via SC-CO_2 using the SCOOR process. This is further confirmation of the overall effectiveness of CO_2-based stripping and cleaning as applied in the semiconductor industry. These results were achieved employing SC-CO_2 at 2900 psi, 85°C, and propylene or butylene carbonate as a cosolvent at 1.0-3.8 vol.% concentrations. Such conditions have also proven effective for delaminating poly(methylmethacrylate) and Novalac resin from Si and Al/C surfaces.

In summary, photoresist stripping via SC-CO_2 is optimized by using a co-solvent, rastering of the nozzle assembly over the target area, and a pulsed-flow system to dislodge and remove the surface film and contaminants. The mechanism by which the above process occurs is still not totally understood, but appears to be a combination of a number of physicochemical effects such as swelling of the polymer film, lowering of the polymer's Tg, and possible degradation of the polymeric matrix by the combined effects of pressure and presence of a

reactive co-solvent. Evidence of these effects is shown in the SEM view (Fig. 5) of a photoresist film that has undergone delamination after swelling in the trench of an etched silicon wafer. This situation is best achieved using temperatures between the Tg and melting point of the polymer composing the photoresist film. It should be noted that cleaning of semiconductor surfaces with CO_2 does not effect most metallic substrates studied to date, including low-k, dual Damascene laminations that are used extensively in the semiconductor industry. Such successes bode well for the further adoption of CO_2 – based cleaning processes in precision cleaning applications as well as the semiconductor industry.

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Table 1. Experimental CO_2 Solubilities in Various Polymers

Polymer	Approximate Density g/cm^3	CO_2 conditions of Press and Temp	Sorption of $[CO_2]$ (moles CO_2/cm^3 polymer) x 10^{-3}	Ref
PMMA	1.19-1.26	3000 psi, 40 °C	3.53	7
ABS	1.04-1.06	3000 psi, 40 °C	1.75	7
HIPS	1.04-1.09	3000 psi, 40 °C	1.07	7
PPO	1.0-1.07	3000 psi, 40 °C	0.32	7
PET	1.38-1.41	3000 psi, 40 °C	0.55	8
PVC	1.38-1.41	3000 psi, 40 °C	0.48	7
PET	1.38-1.41	915 psi, 35 °C	2.19	9
PVC	1.38-1.41	915 psi, 35 °C	2.49	10
LDPE	0.89-0.93	3000 psi, 70 °C	0.17	8
PP	0.85-0.92	3000 psi, 70 °C	0.04	8

Table 2. Contamination Levels Before/After Automated Snow Gun Cleaning of Apiezon N as a Contaminate

Residue Analysis		CO2 Snow Gun Parameters		
Amount of contaminate ug/cm2	Amount of Residue ug/cm2**	Number of Passes*	Nozzle Distance to target	Nozzle Angle by degrees
250	**88.2**	4	2.5 cm	**80**
250	**102.9**	4	1 cm	**56**
250	**127.9**	4	1 cm	**68**
250	**80.7**	2	2.5 cm	**80**
125	**20.8**	2	1.0 cm	**80**
250	**30.6**	3	1.0 cm	**80**
250	**25.0**	3	2.5 cm	**80**
125	**22.2**	2	2.5 cm	**80**
250	**30.2**	2	4 mm	**70**
250	**34.2**	5	4 mm	**70**
250	**10.5**	4	2.5 cm	**70**
125	**-1.4**	4	2.5 cm	**60**
125	**12.5**	4	2.5 cm	**60**
250	**12.5**	4	2.5 cm	**60**
250	**11.1**	6	2.5 cm	**60**
250	**22.2**	6	2.5 cm	**60**
250	**23.6**	6	2.5 cm	**60**
250	**<5**	TCE Cleaned		
125	**<5**	TCE Cleaned		

Table 3. NRA surface analysis results for Si-metallization systems treated by a SC-CO_2 - based cleaning process (SCOOR).

Sample description	Experimental gross yield, Y (counts)	Experiential background (counts)	Adjusted Yield, $Y^{1,2}$ (counts)	(nt) $\left(\frac{\text{carbon atoms}}{cm^2}\right)$	Equivalent conc. of surface carbon atoms
Al film on Si	189	8	116 ± 14	$(1.0 \pm 0.1) \times 10^{16}$	10 monolayers
Al film on Si	194	24	105 ± 15	$(9.3 \pm 1.3) \times 10^{15}$	"
In-Sn oxide film on Si	138	7	66 ±12	$(5.9 \pm 1.1) \times 10^{15}$	6 monolayers
Ti/W film on Si	97	5	27 ± 4	$(2.4 \pm 0.4) \times 10^{15}$	2 monolayers
Ti/W film on Si	159	4	-		-
Pt/Ti film on Si	74	6	3 ± 4	$(2.7 \pm 3.6) \times 10^{14}$	1/3 monolayers

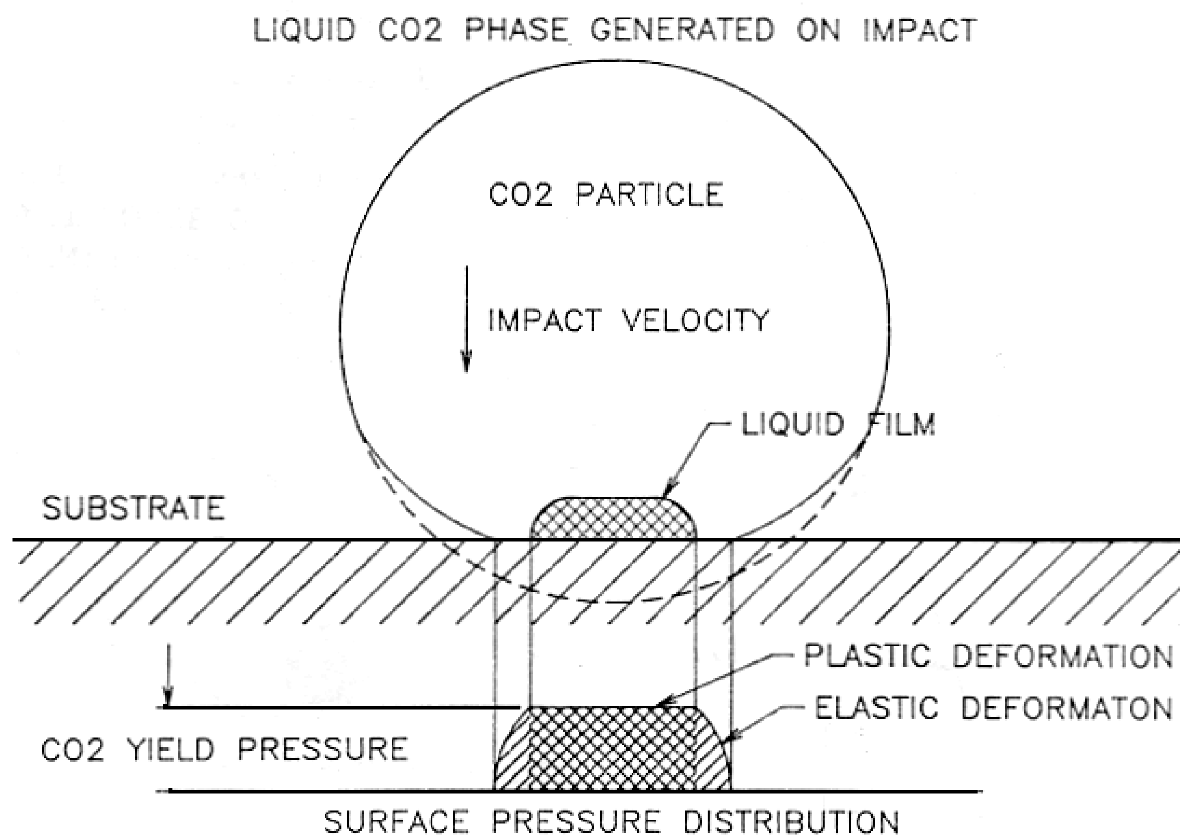

Fig. 1 Suggested CO_2 "snow" cleaning mechanism

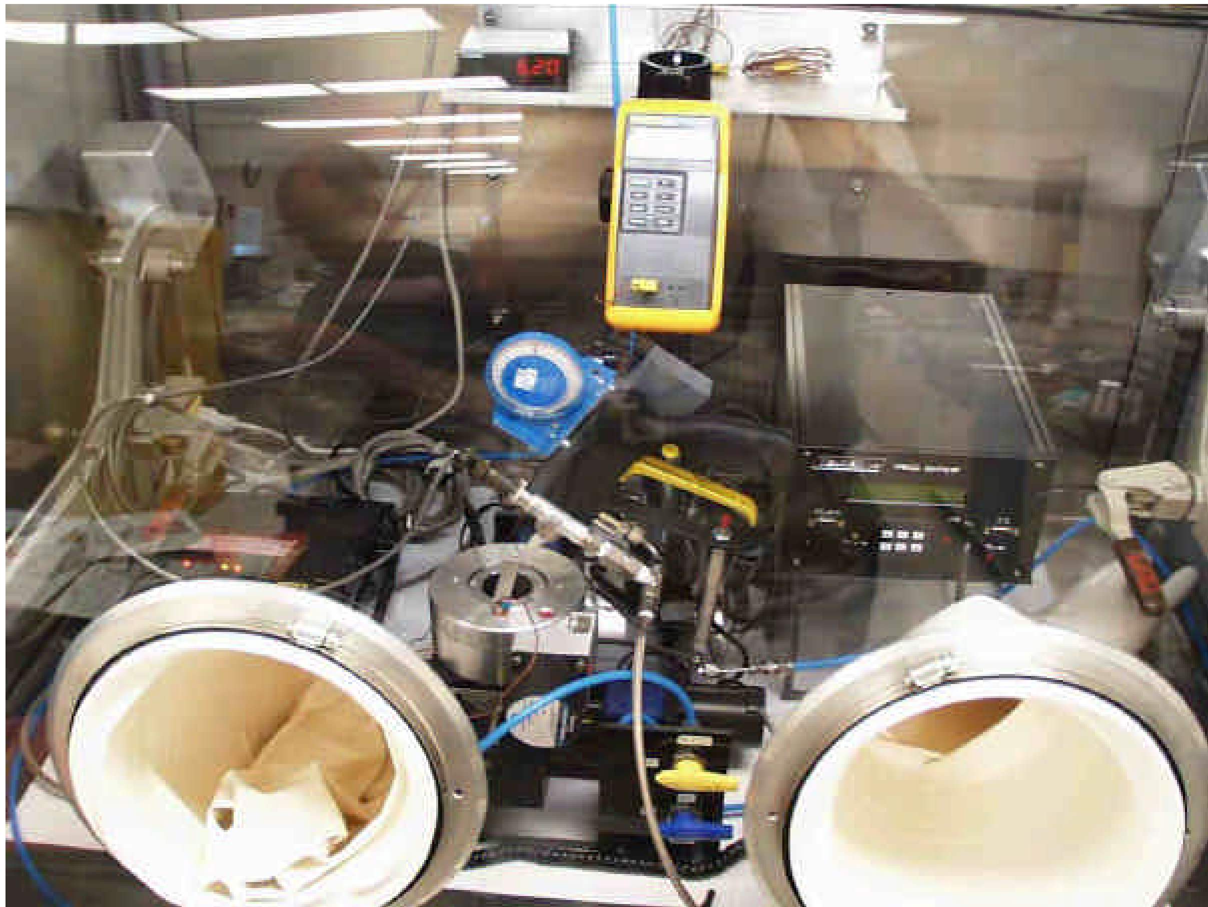

Fig. 2. VA-TRAN Snow Gun Apparatus in a Glove Box

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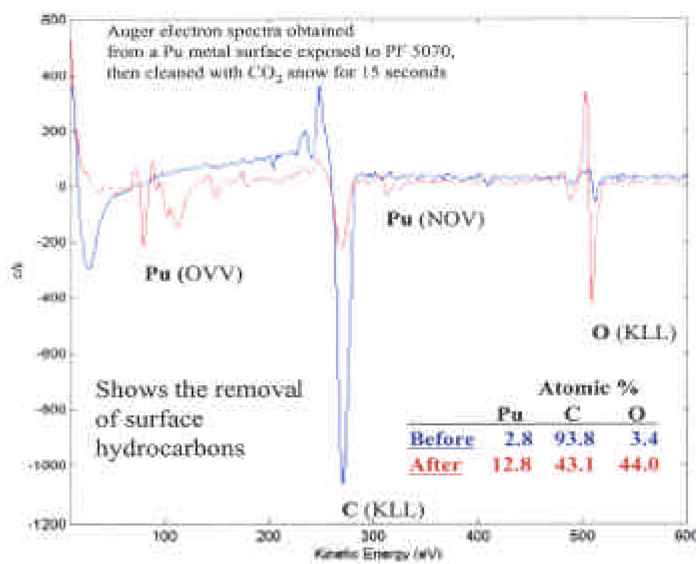
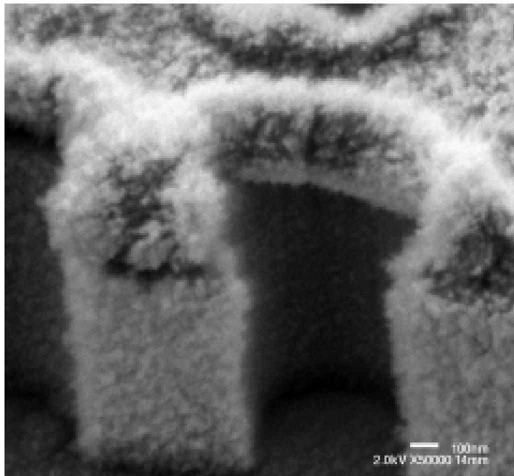
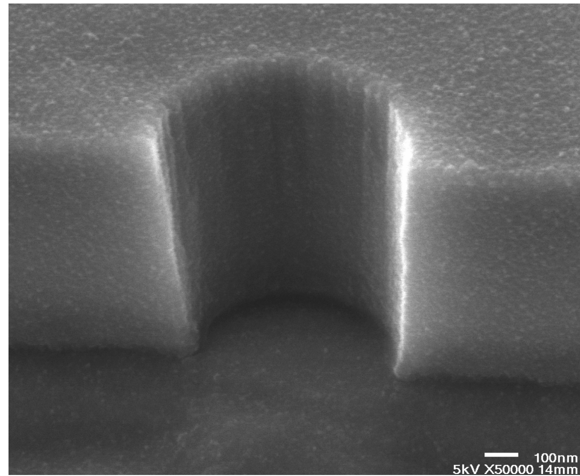


After cleaning with CO_2 snow, surface impurity levels are similar to those seen for sputter-etched Pu metal that is briefly exposed to the atmosphere.

Fig. 3 Auger spectrum of Pu metal before and after cleaning with CO_2 snow.

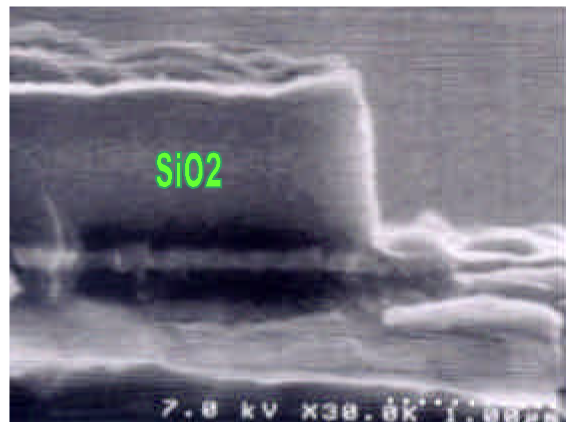


(a) Partial strip



(b) Total removal

(c) SEM before



(d) SEM after

Fig. 4 SEM study of the removal of photoresist film using SC-CO_2 (SCOOR process).

Fig. 5 Swelling and delaminating of polymer film in a trench of a semiconductor wafer induced by SC-CO_2.