Plasma Cleaner: Physics of Plasma

Nature of Plasma

- A plasma is a partially ionized gas consisting of electrons, ions and neutral atoms or molecules
- The plasma electrons are at a much higher temperatures than the neutral gas species, typically around 10^4°K, although the plasma gas as a whole is at near ambient temperature
- The plasma electron density is typically around 10^{11} cm^{-3}
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Plasma Formation

- An RF oscillating electric field is generated in the gas region, either through the use of capacitive plates or through magnetic induction
- At sufficiently low pressures the combined effect of the electric field acceleration of electrons and elastic scattering of the electrons with neutral atoms or field lines leads to heating of the electrons
- When electrons gain kinetic energy in excess of the first ionization threshold in the neutral gas species, electron-neutral collisions lead to further ionization, yielding additional free electrons that are heated in turn

Plasma-Surface Interaction

- The energy of plasma electrons and ions is sufficient to ionize neutral atoms, break molecules apart to form reactive radical species, generate excited states in atoms or molecules, and locally heat the surface
- Depending on the process gases and parameters, plasmas are capable of both mechanical work, through the ablative effect of kinetic transfer of electrons and ions with the surface, and chemical work, through the interaction of reactive radical species with the surface
- In general, plasmas can interact with and modify a surface through several mechanisms: ablation, activation, deposition, cross-linking and grafting - see Plasma-Surface Interaction

Plasma Cleaner: Overall Plasma Advantages

Surface Interaction

- Plasma treatment only affects the near surface of a material; it does not change bulk material properties

- Plasma cleaning leaves no organic residue, unlike many wet cleaning processes; under proper conditions, it can achieve complete contamination removal, resulting in an "atomically clean" surface
- Plasma has no surface tension constraints, unlike aqueous cleaning solutions; it can clean rough, porous or uneven surfaces
- Plasma treatment occurs at near-ambient temperature, minimizing the risk of damage to heat-sensitive materials

Process Flexibility & Consistency

- Depending on process gases and usage configuration, plasma treatment can be used for cleaning, activation, sterilization and general alteration of surface characteristics
- Plasma will react with a wide variety of materials; as such, plasma can also treat assemblies made of different materials
- Plasma cleaning can treat odd-shaped parts with difficult surface geometries
- Plasma treatment is highly reproducible; it is typically characterized by a greater consistency than chemical or mechanical processes

Low Cost / Ease of Use

- Plasma processing is highly efficient, with short processing times, no drying stage and little energy consumed
- Plasma treatment helps to avoid process yield loss due to heat or solvent damage
- Plasma processing is easier to use and maintain than chemical or mechanical processes; in addition, it requires no complicated chemical analysis or maintenance
- Plasma treatment frequently eliminates the need for solvents, along with their ongoing purchase and disposal costs

User & Environmental Safety

- Plasma treatment eliminates safety risks associated with worker exposure to dangerous chemicals
- Plasma processing is contained within a vacuum chamber, with little or no direct worker exposure
- Plasma processing operates at near-ambient temperatures with no risk of heat exposure
- Plasma treatment uses no harmful chlorinated fluorocarbons, solvents, or acid cleaning chemicals
- The EPA has classified most plasma processes as "green" environmentally friendly processes

Plasma Cleaner: Plasma-Surface Interaction

Ablation

- Plasma ablation involves the mechanical removal of surface contaminants by energetic electron and ion bombardment
- Surface contamination layers (e.g. cutting oils, skin oils, mold releases) are typically comprised of weak C-H bonds
- Ablation breaks down weak covalent bonds in polymeric contaminants through mechanical bombardment
- Surface contaminants undergo repetitive chain scission until their molecular weight is sufficiently low for them to boil away in the vacuum
- Ablation affects only the contaminant layers and the outermost molecular layers of the substrate material
- Argon is often used for ablation; high ablation efficiency, no chemical reactivity with the surface material

Activation

- Plasma surface activation involves the creation of surface chemical functional groups through the use of plasma gases - such as oxygen, hydrogen, nitrogen and ammonia - which dissociate and react with the surface
- In the case of polymers, surface activation involves the replacement of surface polymer groups with chemical groups from the plasma gas
- The plasma breaks down weak surface bonds in the polymer and replaces them with highly reactive carbonyl, carboxyl, and hydroxyl groups
- Such activation alters the chemical activity and characteristics of the surface, such as wetting and adhesion, yielding greatly enhanced adhesive strength and permanency

Crosslinking

- Cross-linking is the setting up of chemical links between the molecular chains of polymers
- Plasma processing with inert gases can be used to cross-link polymers and produce a stronger and harder substrate microsurface
- Under certain circumstances, crosslinking through plasma treatment can also lend additional wear or chemical resistance to a material

Deposition

- Plasma deposition involves the formation of a thin polymer coating at the substrate surface through polymerization of the process gas

- The deposited thin coatings can possess various properties or physical characteristics, depending on the specific gas and process parameters selected
- Such coatings exhibit a higher degree of crosslinking and much stronger adherence to the substrate in comparison to films derived from conventional polymerization

Plasma Cleaner: Plasma Process Gases

Gas Sources for Plasma Surface Cleaning and Modification

Air

- Contamination Removal (chemical)
- Oxidation Process
- Surface Activation

O_2

- Contamination Removal (chemical)
- Oxidation Process
- Surface Activation (wetting & adhesion)
- Etch (organics)
- Deposition (glass (w/ Si))

Note: a special 'oxygen service' vacuum pump must be used in conjunction with O2 process gas in order to avoid risk of possible injury; inquire with Harrick Scientific for details

N_2

- Surface Activation
- Deposition (silicon nitride (w/ Si), metal nitride (w/ M))

Ar

- Contamination Removal (ablation)
- Crosslinking

H_2

- Contamination Removal (chemical)

- Surface Modification (curing)
- Reduction Process (metal oxide)
- Deposition (metals (w/ M))
- Note: Extreme caution must be exercised when working with H_2 process gas in order to minimize the risk of possible injury.

Plasma Cleaner: Product Features

Features

- Compact, tabletop unit
- Adjustable RF power
- Low, Medium, and High power settings
- Two Plasma Cleaner models available:
  - *PDC-32G (110V); PDC-32G-2 (220V)*
    - Basic model with a 3" diameter by 7" long chamber and a removable cover
    - Applies a maximum of 18W to the RF coil, with no RF emission
    - Size: 8"H x 10"W x 8"D
  - *PDC-001(110V); PDC-002 (220V)*
    - Expanded model with a 6" diameter by 6" long chamber and an integral switch for a vacuum pump
    - Its hinged cover features a magnetic closure and a viewing window
    - Applies a maximum of 30W to the RF coil, with no RF emission
    - Size: 11"H x 18"W x 9"D
- Optional quartz Plasma Cleaner chamber
- Optional flow mixer allows individually metered intakes for up to two different gases and monitors the pressure in the chamber
- Compatible vacuum pump available

Requires

- A vacuum pump with a minimum pumping speed of 1.4 m^3/hr and a maximum ultimate total pressure of 200 mtorr

Includes

- 1/8" NPT needle valve to admit gases and control the pressure
- Pyrex Plasma Cleaner chamber

Power Settings

Description	*PDC-32G or PDC-32G-2*			*PDC-001 or PDC-002*		
Input Power	**100W**			**200W**		
	Applied to the RF Coil					
Low Setting	680V DC	10 mA DC	6.8W	716V DC	10 mA DC	7.16W
Medium Setting	700V DC	15 mA DC	10.5W	720V DC	15 mA DC	10.15W
High Setting	720V DC	25 mA DC	18W	740V DC	40 mA DC	29.6W

Plasma Cleaner: Details of Operation

Note: A detailed User's Manual is provided with all Harrick Scientific Plasma Cleaner models.

Principles of Operation

- The sample is placed in the plasma vacuum chamber
- Process gas(es) are admitted to the chamber at low flow rates (1-2 SCFH) using either a needle valve or the PlasmaFlo accessory and are kept at low pressure (~200-600 mTorr) through vacuum pumping
- The gases are subject to induced RF magnetic and electric fields generated by a solenoidal coil current
- Plasma is generated through the subsequent RF/collisional heating of the electrons in the gas

Details of Operation

- The plasma vacuum chamber door has an o-ring quick disconnect seal for easy access to the chamber
- The vacuum pump is connected to an outlet at the back of the reaction chamber
- The needle valve can be used to break the vacuum gently, to control the pressure or to admit a special gas for plasma processing
- The RF power level can be adjusted by means of a three-way selector switch
- The plasma will emit a characteristic glow, which visibly indicates the successful generation of the plasma state
- The temperature change of a substrate during plasma treatment is minimal

Surface Cleaning / Modification

- The interaction between the plasma and the surface is determined by:
    - The nature of the substrate and surface contaminant layers
    - The process gases used
    - The pressure and flow rate of the gases
    - The RF power level & length of sample exposure
- For surface cleaning, a few seconds exposure, following pump down of the chamber and formation of plasma, is often adequate
- Surface cleanliness can be tested most easily by observing the wettability of the sample: on a clean surface, water drops will not bead, but will spread out in a uniform film

Plasma Cleaner Applications: Plasma Cleaning

Plasma Cleaning

- Conventional cleaning methods often fail to completely remove surface films, leaving a thin contamination layer; additionally, solvent cleaning typically leaves a surface residue
- Plasma cleaner use exposes the surface to a gas plasma discharge, gently and thoroughly scrubbing the surface
- Plasma cleaning will remove non-visible oil films, microscopic rust or other contaminants that typically form on surfaces as a result of handling, exposure or previous manufacturing or cleaning processes; additionally, plasma cleaning does not leave a surface residue

- A plasma cleaner can treat both a wide variety of materials - including plastics, metals and ceramics - as well as complex surface geometries
- A plasma cleaner is most commonly used prior to adhesive bonding both to clean away loosely held contaminant residues and to activate the surface for increased bonding strength

Figures 1 and 2 below show the ATR spectra, respectively, of Ge and Si substrates prior to and following surface contaminant removal via plasma cleaning.

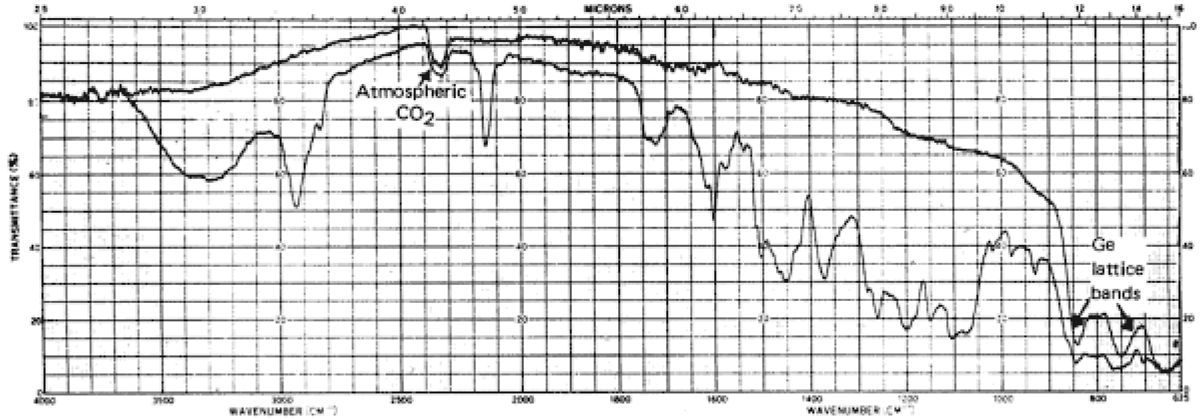

Figure 1. ATR spectra (qave=45°, N=20) of a Ge surface before and after plasma cleaning with a Harrick plasma cleaner. The lower trace shows Ge coated with a thick (about I micron) film of photoresist (AZ111). The upper trace shows same surface after fifteen minutes of plasma cleaning with 0_2, indicating Ge is restored to its original organic free condition with the photoresist stripped off the surface.

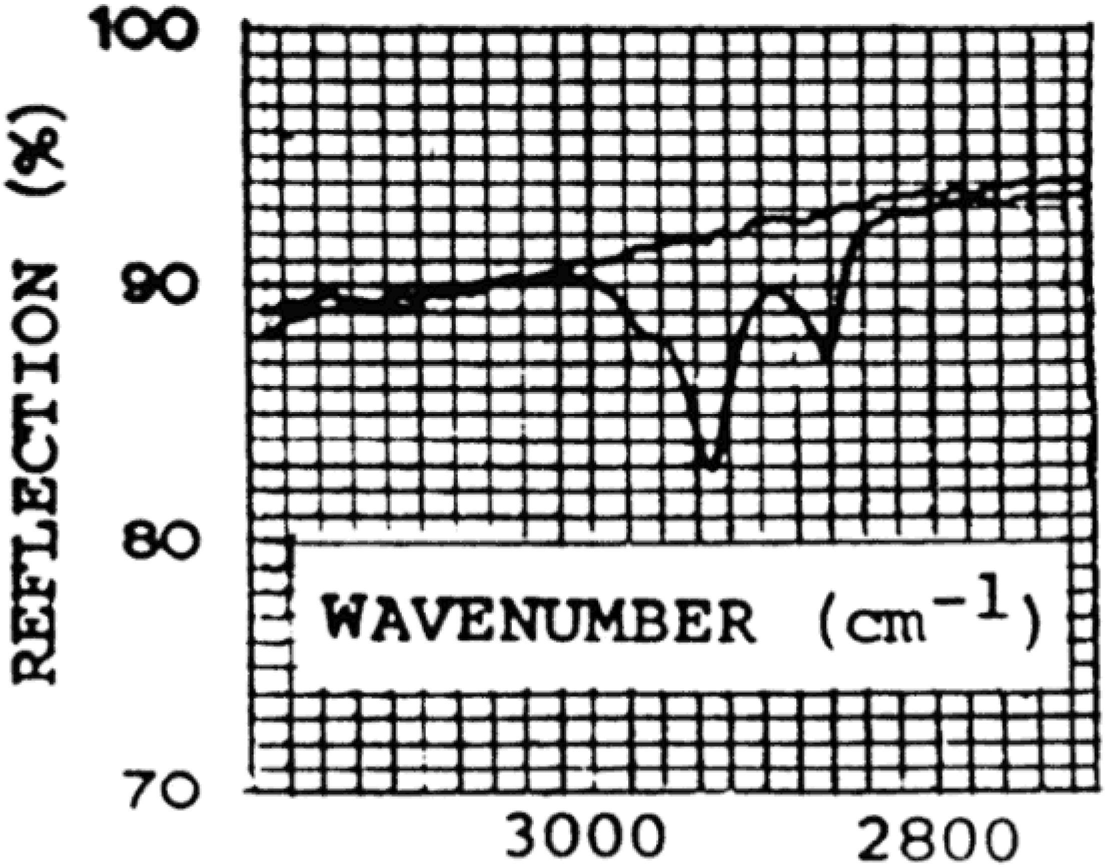

Figure 2. Harrick plasma cleaner hydrocarbon removal from the surface of a silicon ATR plate (60 reflections, q = 45°). The C-H band (bottom trace), representing 10% absorption, is completely eliminated (top trace) after one minute exposure to an air plasma.

Plasma Cleaner Applications: Polymers

Surface Cleaning of Polymers

- Plasma ablation mechanically removes contaminant layers through energetic electron and ion bombardment of the surface - see **Ablation**
- Plasma surface cleaning removes surface contaminants, unwanted surface finish from polymers and weak boundary layers which may be present in certain processed polymers

Surface Restructuring of Polymers

- The breaking of polymer surface bonds by plasma ablation using an inert gas leads to the creation of polymeric surface free radicals
- A surface free radical can rebond in its original polymeric structure, it can bond with an adjoining free radical on the same polymeric chain, or it can bond with a nearby free radical on a different polymeric chain - see **Crosslinking**

- Such polymer surface restructuring can improve surface hardness, as well as tribological and chemical resistance

Surface Alteration of Polymers

- The breaking of polymer surface bonds by plasma ablation leads to the creation of polymeric surface free radicals
- The bonding of these surface free radicals with atoms or chemical groups from the plasma leads to the replacement of surface polymer functional groups with new functional groups, based upon the chemistry of the plasma process gas - see **Activation**
- Typical polymer functional groups formed through plasma surface activation and grafting include: amine amino-carboxyl, carboxyl hydroxyl and fluorination carbonyl
- Such polymer surface alteration can modify the chemical properties of the surface while leaving the bulk properties unchanged

Surface Deposition of Polymers

- Plasma deposition involves the formation of a thin polymer coating on the substrate surface through polymerization of the process gas
- If a process gas comprised of more complex molecules, such as methane or carbon tetrafluoride, is employed, these may undergo fragmentation in the plasma, forming free radical monomers; these in turn bind to the surface and recombine into deposited polymeric layers
- These polymer thin-film coatings can dramatically alter the permeation and tribological properties of the surface - see **Deposition**

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Plasma Cleaner Applications: Biomaterials

Sterilization

- Plasma sterilization treatment is gaining growing acceptance for disinfecting and sterilizing medical devices
- Plasma treatment offers the potential for simultaneous cleaning and sterilization of medical instruments
- Plasma sterilization is particularly appropriate for medical or dental implants and devices that are sensitive to the high temperature, chemical or irradiative

environments associated with autoclaving, EtO or gamma sterilization, respectively

Adhesion Promotion

- Many biomaterials have a low to medium surface energy, making it difficult to effectively apply adhesives or coatings
- Plasma surface activation leads to the formation of surface functional groups that increase surface energy and improve interfacial adhesion for biomaterial bonding

Wetting Properties

- Most untreated biomaterials have poor wettability (hydrophilicity)
- Plasma surface treatment has been used to enhance or decrease the wetting characteristics on a wide variety of biomaterials
- Surfaces may be rendered hydrophilic through plasma activation, and may be rendered hydrophobic through plasma deposition of thin films

Low-Friction & Barrier Coatings

- Some silicones and polymers such as polyurethanes have a typically high coefficient of friction against other surfaces
- Plasma coating deposition of a lower coefficient of friction polymer coating yields a more lubricious surface for biomaterials applications
- Plasma coating deposition can also be used to form thin, dense barrier coatings that decrease permeability to liquids or vapors for biomaterials applications

Biocompatibility

- Biomaterials that come in contact with blood or protein require special surface treatments to enhance biocompatibility
- Plasma activation of biomaterial surfaces prepares them for cell growth or protein bonding; additionally, biomaterial surfaces may also be modified to decrease the bonding of proteins
- Biomaterials with modified surfaces exhibit improved "biocompatibility", including enhanced cell adhesion, improved cell culture surfaces, non-fouling surfaces and promotion of selective protein adsorption

http://www.harricksci.com/plasma.cfm