

Surface Preparation for Plastics

Surface preparation or treatment is defined as one or a series of operations including cleaning, removal of loose material, and physical and/ or chemical modification of a surface to which an adhesive is applied for the purpose of bonding. In plastics bonding, surface preparation is aimed at increasing the surface polarity, improving surface wettability, and creating sites for adhesive bonding. Metal surfaces are typically covered with oxide layers, rendering the surface highly polar and fit for good adhesive bonding.

The following techniques are typically used as practices for good surface preparation:

Degreasing

Degreasing is carried out in order to remove any loosely held dirt or other contaminants from the surface. Surfaces can be degreased using volatile solvents such as toluene, acetone, methyl ethyl ketone, methyl alcohol, isopropyl alcohol and trichloroethylene. However, kindly make sure that all the environmental, health and safety regulations are met prior to selecting a solvent. The most common methods used, typically include the three main steps:

1. Vapor degrease/ clean/rinse the parts with the appropriate solvents.
2. Immerse the substrates in a fresh bath of solvent for the wash and follow by an immersion in the second tank for a rinse.
3. Cleaning and drying the substrate post the degreasing.

Abrasion

The surfaces need to be degreased and cleaned before as well as after abrasion to remove any pre-existing contaminants on the surface. Once the surfaces have been abraded, they need to be degreased to remove the debris from abrasion.

Depending on the exact plastic being used, the abrasion technique that is eventually employed might vary.

Physical Methods

These techniques make use of the surface reactivity of the plastics and modify the surface chemistry to achieve better adhesion, rather than making use of hazardous chemicals. Some the most common physical methods include:

Corona Discharge: The ionized air generated by a corona discharge, reacts with the surface of the substrate to form free radicals. They react with oxygen in the atmosphere and increase the surface energy of the substrate to be bonded.

Flame Treatment: Flame treatment involves exposing the surface to be bonded to a gas flame for a few seconds. The flame oxidizes the surface to be bonded and increases the surface energy by forming higher surface energy functional groups. Warping might be a potential hindrance during processing with this method.

Plasma Treatment: Plasma treatment differs from corona discharge and flame treatments in a sense that plasma treatment is typically carried out under partial vacuum. In plasma treatment, gas plasma is activated by the appropriate techniques to produce excited species that react with the plastic substrate. Often plasma treatment tends to provide substrates with better stability as compared to corona discharge, chemical treatment or flame treatment.

Since the shelf life of such surface treatment procedures can be short lived based on the substrate being treated, it might be a good processing procedure to treat the parts in line.

Chemical Treatments

Specific chemical techniques have been developed for treating different substrates. These treatments change the physical as well as the chemical properties of the surface in order to improve the adhesion. A wide range of acids and alkalis are used for this purpose. Typically, the specific chemical or a mixture of chemicals is placed in a chemically resistant container. The chemical bath is then heated to the appropriate temperature and the plastic is immersed in the chemical bath for the required amount of time. After chemically treating the surfaces, it is important to rinse the surface with DI water and thoroughly dry the surface before it is subjected to further use. Extreme care should be taken while handling chemicals. Good laboratory skills should be used while handling these chemicals. The personnel should be wearing the appropriate personal protective equipment and should be well trained in handling of these chemicals.

The table below lists the chemical treatments typically used for some most commonly used plastic substrates:

Substrate	Etching Solution	Composition (Wt%)	Pretreatment Conditions
Polyphenylene Sulfide (PPS)	Conc. Chromic Acid	100	Immersion: 2 min. @ 71°C Rinse: Tap water followed by DI water Dry by evaporation
Acetal (Delrin)	Conc. Chromic Acid (69%) Sodium dichromate Distilled Water	84.2 0.6 15.2	Immersion: 5 min. @ 20°C Rinse: Tap water followed by DI water Dry in warm air
Nylon	Aq. Phenol (80%)	100	Immersion: 15 - 20 min. @ 70°C - 90°C Rinse: Tap water followed by DI water Air Dry @ 60°C - 70°C
Acrylonitrile Butadiene Styrene (ABS)	Conc. Sulfuric Acid (69%) Sodium dichromate Distilled Water	84.2 0.6 15.2	Immersion: 20 min. @ 60°C Rinse: Tap water followed by DI water Dry in warm air
Polytetrafluoroethylene (PTFE)	Tetrahydrofuran Naphthalene Sodium	85.5 12.3 2.2	Immersion: 1 - 2 min. @ 70°C - 90°C Rinse: Ketone followed by DI water Dry in warm air @ 65°C
Polyethylene (PE) or Polypropylene (PP)	Plasma or Corona treatment Alternatively, use X17 primer	-	-

Table 1

A combination of degreasing, abrasion, and chemical treatment techniques can be employed for preparing plastic surfaces.

Etching Process

Etching is a pitting process and surface modification for a specific material by removing areas from the material surface by the effect of another material or another effective.

Etching is a surface preparation process that takes advantage of the specific plastic material to be plated. Etchants are strong oxidizing solutions that micro-roughen and chemically alter the surface of moulded plastic parts.

In general, there are two types of etching processes:

1. Wet etching where the material is dissolved when immersed in a chemical solution.
2. Dry etching where the material is sputtered or dissolved using reactive ions or a vapor phase etchant.

	Wet	Dry
Method	Chemical solutions	Ion bombardment or chemical reactive
Environment and equipment	Atmosphere , bath	Vacuum chamber
Advantage	1- low cost , easy to implement 2- high etching rate 3- good selectivity for most materials	1- capable of defining small feature size (< 100 nm)
Disadvantage	1- inadequate for defining feature size < 1 nm 2- potential of chemical handling hazards 3- wafer contamination issues	1- high cost , hard to implement 2- low throughput 3- poor selectivity 4- potential radiation damage

Table 2

Isotropy and anisotropy:

When a material is attacked by a liquid or vapor etchant, it is removed isotropically (uniformly in all directions) or anisotropic etching (uniformity in vertical direction). The difference between isotropic etching and anisotropic etching is shown in Figure 1. Material removal rate for wet etching is usually faster than the rates for many dry etching processes and can easily be changed by varying temperature or the concentration of active species.

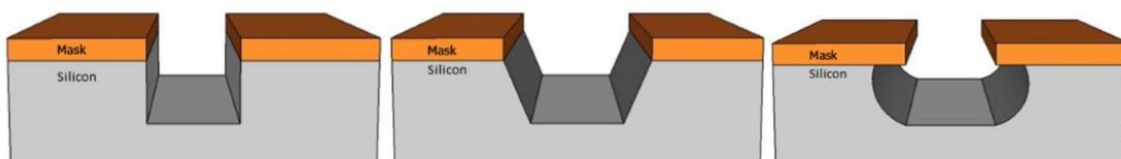


Figure 1 (a) completely anisotropic (b) Partially anisotropic and (c) Isotropic etching of silicon.

Wet Etch

Definition: Wet etching is a material removal process that uses liquid chemicals or etchants to remove materials from a wafer. The specific patterns are defined by masks on the wafer. Materials that are not protected by the masks are etched away by liquid chemicals. These masks are deposited and patterned on the wafers in a prior fabrication step using lithography.

A wet etching process involves multiple chemical reactions that consume the original reactants and produce new reactants. The wet etch process can be described by three basic steps.

- (1) Diffusion of the liquid etchant to the structure that is to be removed.
- (2) The reaction between the liquid etchant and the material being etched away. A reduction-oxidation (redox) reaction usually occurs. This reaction entails the oxidation of the material then dissolving the oxidized material.
- (3) Diffusion of the byproducts in the reaction from the reacted surface.

Anisotropic wet etching:

Liquid etchants etch crystalline materials at different rates depending upon which crystal face is exposed to the etchant. There is a large difference in the etch rate depending on the silicon

crystalline plane. In materials such as silicon, this effect can allow for very high anisotropy. Some of the anisotropic wet etching agents for silicon are potassium hydroxide (KOH), ethylenediamine pyrocatechol (EDP), or tetramethylammonium hydroxide (TMAH). Etching a (100) silicon wafer would result in a pyramid shaped etch pit as shown in Figure 2a.

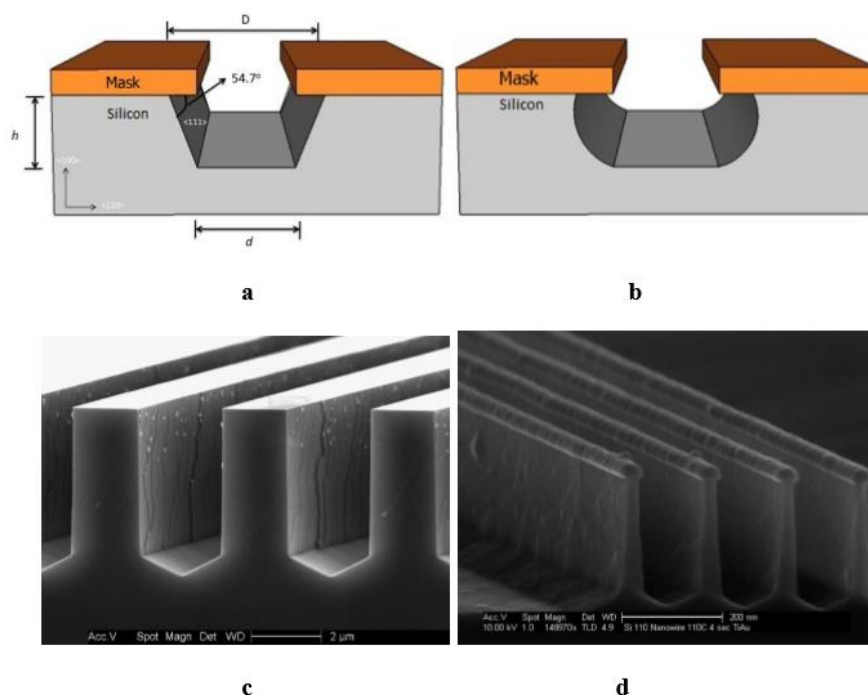


Figure 2 Schematics of an etch profile in (a) an anisotropic and (b) an isotropic etch of a (100) oriented silicon surface. (c-d) KOH based wet etching of (110)oriented Si surfaces with micro and nanoscale two-dimensional walls.

The etched wall will be flat and angled. The angle to the surface of the wafer is 54.7°. Figure 2c-d depicts scanning electron micrographs of (110)-oriented two-dimensional silicon walls with micro and nanoscale dimensions generated based on KOH based wet etching.

The relationship between mask dimensions, etch depth and the floor width is given in equation 1.

$$d = D - \left(\frac{2h}{\tan(54.7^\circ)} \right) \text{ [equation 1]}$$

Isotropic wet etching: For isotropic wet etching, a mixture of hydrofluoric acid, nitric acid, and acetic acid (HNA) is the most common etchant solvent for silicon. The concentrations of each etchant determines the etch rate. Silicon dioxide or silicon nitride is usually used as a masking material against HNA. As the reaction takes place, the material is removed laterally at a rate similar to the speed of etching downward. This lateral and downward etching process takes places even with isotropic dry etching which is described in the dry etch section.

Wet chemical etching is generally isotropic even though a mask is present since the liquid etchant can penetrate underneath the mask (Figure 2b). If directionality is very important for high-resolution pattern transfer, wet chemical etching is normally not used.

Dry Etch

Definition: In dry etching, plasmas or etchant gasses remove the substrate material. The reaction that takes place can be done utilizing high kinetic energy of particle beams, chemical reaction or a combination of both.

Physical dry etching: Physical dry etching requires high energy kinetic energy (ion, electron, or photon) beams to etch off the substrate atoms. When the high energy particles knock out the atoms from the substrate surface, the material evaporates after leaving the substrate. There is no chemical reaction taking place and therefore only the material that is unmasked will be removed. The physical reaction taking place is illustrated in Figure 3.

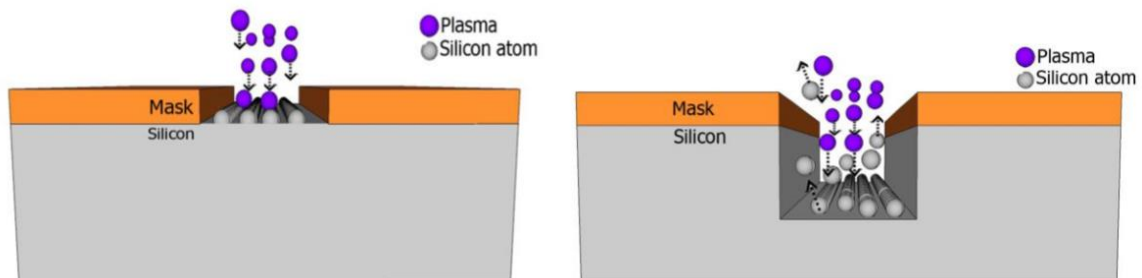


Figure 3 The plasma hits the silicon wafer with high energy to knock-off the Si atoms on the surface. (a) The plasma atoms hitting the surface. (b) The silicon atoms being evaporated off from the surface.

Chemical dry etching

Chemical dry etching (also called vapor phase etching) does not use liquid chemicals or etchants. This process involves a chemical reaction between etchant gases to attack the silicon surface. The chemical dry etching process is usually isotropic and exhibits high selectivity. Anisotropic dry etching has the ability to etch with finer resolution and higher aspect ratio than isotropic etching. Due to the directional nature of dry etching, undercutting can be avoided. Figure 4 shows a rendition of the reaction that takes place in chemical dry etching. Some of the ions that are used in chemical dry etching is tetrafluoromethane (CF_4), sulfur hexafluoride (SF_6), nitrogen trifluoride (NF_3), chlorine gas (Cl_2), or fluorine (F_2).

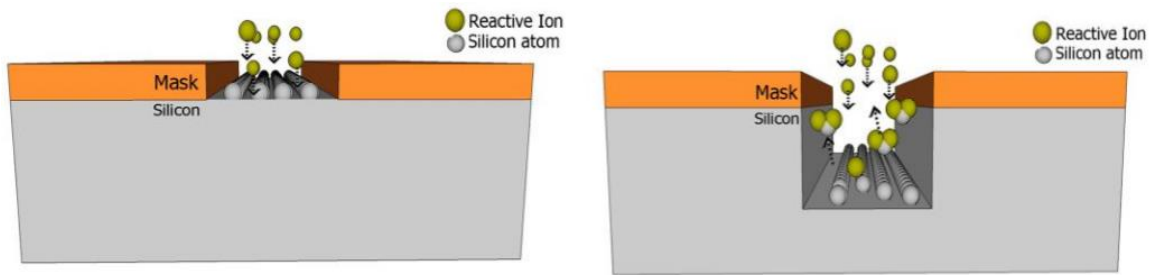


Figure 4 Process of a reactive ion interacting with the silicon surface. (a) The interaction between the reactive ion and the silicon atom. (b) A bond between the reactive ion and the silicon atom then chemically remove the silicon atoms from the surface.

Reactive Ion Etching: Reactive ion etching (RIE) uses both physical and chemical mechanisms to achieve high levels of resolution. The process is one of the most diverse and most widely used processes in industry and research. Since the process combines both physical and chemical interactions, the process is much faster. The high energy collision from the ionization helps to dissociate the etchant molecules into more reactive species.

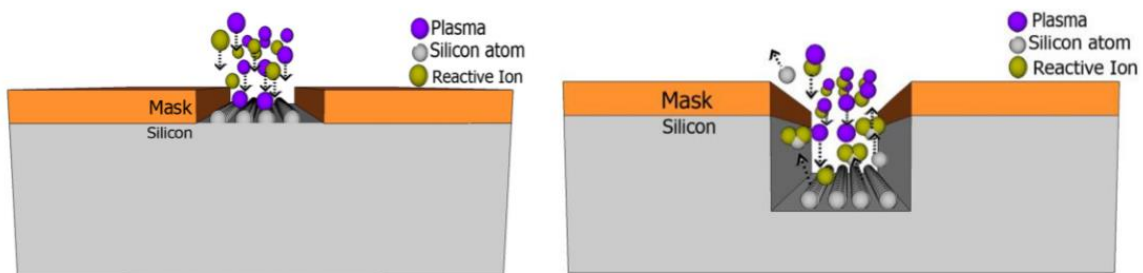


Figure 5 The RIE process. This process involves both physical and chemical reactions to etch off the silicon.

In the RIE-process, cations are produced from reactive gases which are accelerated with high energy to the substrate and chemically react with the silicon. The typical RIE gases for Si are CF_4 , SF_6 and $\text{BCl}_2 + \text{Cl}_2$. As seen in Figure 5, both physical and chemical reaction is taking place. Figure 6 depicts some micro/nano structures with high aspect ratio etched using RIE process

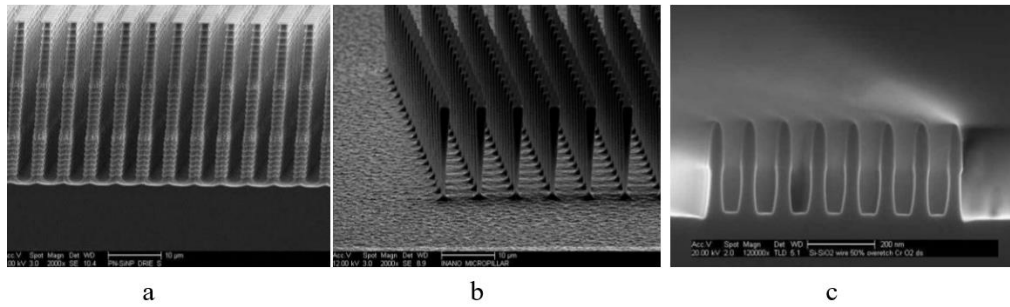


Figure 6 (a-b) Silicon micro-pillars fabricated using deep reactive ion etching (DRIE). These pillars were made using a Bosch process. The Bosch process is a pulsed-multiplexed etching technique which alternates between two modes to achieve extremely long and vertical micron-scaled nanowires.[1] (c) SiO₂ and Si nanowalls etched via RIE process.

An extensive study was done to determine the dependence of the etching performance by Chen et al.[4] Factors such as applied coil or electrode power, reactant gas flow rates, duty cycles, and chamber pressures were considered. These process parameters were modeled and experimentally determined to see the effect on the surface morphology and the mechanical performance of the silicon structures.

References

1. Ebnesajjad, C. F. (n.d.). **Surface Treatment of Materials for Adhesion Bonding** assisted by, Copyright © 2006 by William Andrew, Inc.
2. Avinash P. Nayak*, Logeeswaran VJ¥ and M. Saif Islam‡, **Wet and Dry Etching**, University of California, Davis. California.