PLASMAtech, inc

Ultra-pure Cleaning with Low Pressure Gas Plasma

In some cleaning applications, removal of contaminants such as dust, oil, or other gross contaminants is sufficient. Other applications demand that surfaces be clean at an atomic level. This is particularly important when bonding or coating is required since an absolutely clean surfaces facilitates covalent bonds. Gas plasma is a dry, environmentally green and worker-friendly method to achieve ultra-pure surfaces on metal, ceramic, polymer and glass substrates. In addition to cleaning, plasma treatment can also serve to functionalize a surface via attachment of polar groups.

How Plasma Cleaning Works

Plasma is a partially ionized gas generated by introducing gas into a vacuum chamber and exposing it to an electromagnetic field. Free electrons are accelerated and obtain high energies; while neutrals and ions gain relatively low energy. Under these non-equilibrium conditions, collisions of electrons with other gas molecules result in a cascade of chemical reactions that react with a surface. This results in the same type of reactive intermediates that are created thermally or chemically – but at low temperatures between ambient and 50C.

Plasma cleaning removes organic contamination from surfaces primarily via chemical reactions with physical ablation being secondary. During cleaning the plasma species react with the surface, resulting in contaminant being "lifted off." In the case of oxygen plasma, excited oxygen species decompose low molecular weight organic molecules by breaking the C-H and C-C bonds to form water vapor and CO_2 which are then evacuated from the chamber via the vacuum pump. Continual replenishment and elimination of the gas eliminates cross contamination.

An important characteristic of low-pressure plasma is its extraordinary penetration capability. Narrow spaces where liquids can not penetrate present no problem for gas plasma permitting parts with complex shapes and even micrometric cracks to be treated.

Polyimide Cleaning/Functionalization.

Polyimide films used in flex circuit board applications must be cleaned to remove carbon residuals from laser drilling. In addition, it has been shown that an oxygen plasma treatment increases the adhesive bond strength between the polyimide film and the metal layer.

As shown in Table 1, plasma cleaning resulted in a significant decrease in surface carbon content. A higher degree of cleanliness was further indicated by increased nitrogen exposure from the base polymer surface. The increase was due at least partly to oxidation of the polymer, while the increase in nitrogen was due primarily to exposure of the nitrogen in the base polymer due to removal of contaminants. The associated contact angle was reduced from 65^{o} on the untreated film to <5^{o} after plasma treatment.

XPS spectra (Figures 1 and 2) indicate that the plasma process provides both surface cleaning and surface modification by incorporation of additional functional groups (C-O, C-OH) into the upper atomic layer of the polymer.

Polyimide Film	Cleaning Process:	
Element:	Uncleaned	Plasma Cleaned
Carbon	75.3%	63.5%
Oxygen	19.0%	29.6%
Nitrogen	5.7%	6.9%

Table 1. Atomic composition of untreated and plasma-treated polyimide film

Figure 1 shows a representative spectrum obtained prior to plasma treatment, and is typical of a polyimide surface. Figure 2 shows the corresponding spectrum obtained after treatment. In this spectrum, the increase in peak area of the component shifted approximately 1.5 eV from the main C(1s) peak indicating that the excess oxygen has been incorporated into the polymer surface as oxidized hydrocarbon species.

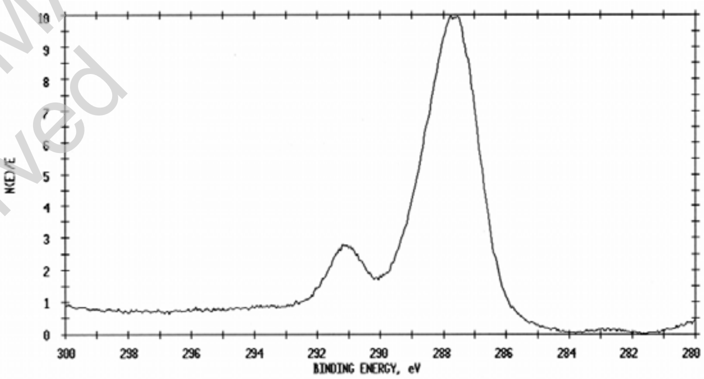

Figure 1. XPS survey spectrum of untreated polyimide film

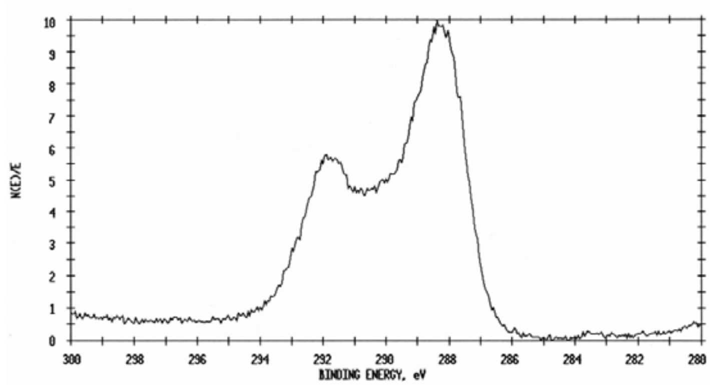

Figure 2. XPS survey spectrum of polyimide film after oxygen plasma treatment

Ceramics. Ceramics are inorganic materials that usually contain metal ions. Some examples of ceramic materials include aluminates, carbides, nitrides, oxides, and silicates. Table 2 illustrates XPS results of plasma cleaning on a ceramic sample composed of carbon, oxygen and aluminum. The application required a surface free of hydrocarbon contamination to ensure maximum bonding to another component. After solvent cleaning adhesion was still unacceptable and use of harsher solvents, acidic or caustic cleaners were environmentally undesirable alternatives.

	Cleaning Process:	
Element:	**Solvent-based**	**Plasma**
O	42%	44%
Al	22%	24%
Inorganic C	2.5%	25.9%
Organic C	33.5%	6.1%

Table 2. Composition of the upper few nanometers of an alumina-based ceramic after a solvent cleaning process and subsequent oxygen plasma cleaning.

In this example, the total percentage of carbon, which is usually a good indicator of relative cleanliness, decreased only a small amount with plasma cleaning. Closer inspection, however, showed that the carbon signal consisted of organic carbon and inorganic carbides. The inorganic carbon was a component of the base ceramic. Although the total amount of carbon remained unchanged with plasma cleaning, the amount of organic carbon decreased to only 6% of the total surface atomic composition. This represents an extremely clean surface. The remaining carbon is the inorganic carbon of the base ceramic that was exposed by removal of the adventitious layer.

Metal. Aluminum is a very surface active metal that rapidly adsorbs organic contaminants from the atmosphere. Because of this surface activity, critical cleaning of aluminum can be quite difficult, and frequently involves dissolution of the oxide along with contaminants using acidic or basic cleaner/deoxidizers.

The effectiveness of a short plasma process for aluminum cleaning was demonstrated using XPS. The relative amount of organic carbon on the surface of a small aluminum alloy coupon was measured after various cleaning procedures. The coupon was evaluated in the as-received condition, after a solvent wipe, after deoxidation with a commercial acid cleaner, and after plasma cleaning in oxygen.

Figure 3 shows the XPS survey spectrum of the as-received aluminum. The Al electrons produce a peak at a binding energy of 74 eV, and the O electrons produce a peak at about 532 eV. The large C peak near 285 eV is due to the presence of organic carbon-containing contaminants that were not removed by the relatively vigorous cleaning process. The relative atomic concentrations of the various elements are shown in the first column of Table 3. After plasma cleaning, the sample was re-analyzed. The spectrum is shown in Figure 4, and the relative atomic concentrations are also included in Table 3. The remaining carbon contamination on the surface has been reduced to less than 3%

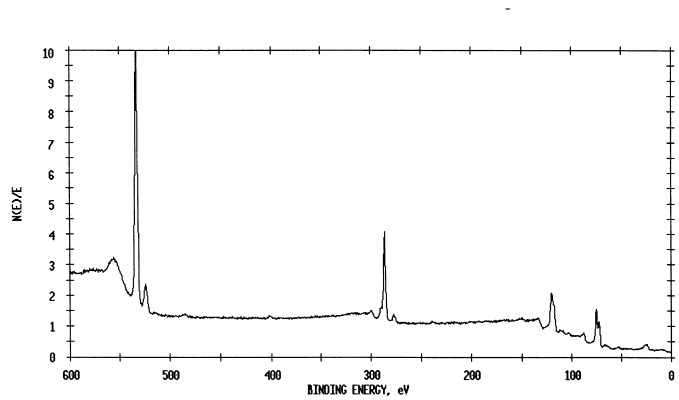

Figure 3. XPS survey spectrum of mechanically polished aluminum, cleaned with detergent and acetone.

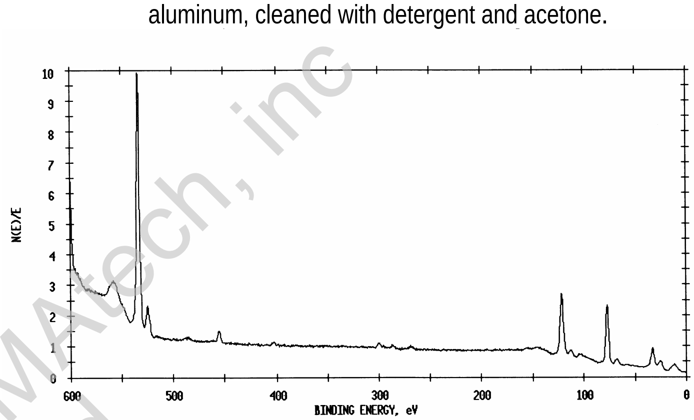

Figure 4. XPS survey spectrum of mechanically polished aluminum after oxygen plasma cleaning.

	Cleaning Process:	
Element:	Detergent/Solvent-based	Plasma
Aluminum	27%	43%
Oxygen	42%	55%
Carbon	31%	2.5%

Table 3. Atomic composition of aluminum surface after detergent/solvent cleaning and after plasma cleaning.

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