Cleaning/Activation of Polymer Surfaces
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INTRODUCTION
Ion beams are used for cleaning surfaces prior to the deposition of thin films on those surfaces.\(^1\) The cleaning of metal and refractory-compound surfaces is well understood and, when properly done, removes physisorbed contaminants with few adverse effects on the surfaces being cleaned.\(^1,2\) Similar cleaning of a polymer surface, however, can include effects such as increased electrical surface conductivity, improved biocompatibility for medical implants, or making possible the chemical bonding of a thin film applied to that surface.\(^3,4\)

METALS AND REFRACTORY COMPOUNDS
It is helpful to review the ion cleaning of metals or refractory compounds (such as SiO\(_2\) or Al\(_2\)O\(_3\)), because of the similarities with that process for polymers. This cleaning is best carried out in the low-energy \(-25-100\) eV range, where the ions have sufficient energy to remove physisorbed contaminants, but there is negligible penetration of the substrate lattice.\(^1,2\) The accepted cleaning dose of \(10^{15}\) ions/cm\(^2\) \((1.6 \times 10^4\) C/cm\(^2\)) results in about one incident ion for each surface atom. The greater than unity "sputter yields" of physisorbed contaminants assures adequate cleaning with this dose. As long as the ions are in the low-energy range, there are few adverse effects of cleaning doses larger than \(10^{15}\) ions/cm\(^2\).

CLEANING/ACTIVATION OF POLYMERS
The atomic bonds in polymers are more varied than in either metals or common refractory compounds. As indicated by the limited temperature capabilities of most polymers, many of these bonds are quite weak. The multiple elements and relatively weak bonds result in a process that is much more complicated than for metals and refractory compounds. The exposure of different elements with different bonding capabilities has been called functionalizing, activating, or creating free radicals or dangling bonds. The single term "activating" will be used in this brief review. The effects of different working gases are described below. Keep in mind that physisorbed contamination is removed, in addition to the activation. Also, the activation can be subject to ageing.\(^4\)

ARGON
The effects of argon ions on polymer substrates have been studied over a range of ion energies.\(^1,5^e\) The effects are generally similar at different energies, but the thickness of the affected layer and the rate of damage both increase with energy.\(^3,8\) This observation is shown by the similarity of the sputtered products over a range of energy,\(^8\) with many of the products being small clusters of atoms (e.g., C\(_x\)H\(_y\)). Further, the formation of an amorphous graphite layer is favored at high energy. For good adhesion, the primary objective is to activate a thin surface layer with minimal damage to the bulk material below that layer, which implies ion energies of \(<100\) eV. The general similarity of effects at higher energies, however, suggests that higher-energy investigations can extend the understanding in the \(<100\) eV range of interest.

X-ray photoelectron spectroscopy (XPS) has a maximum detection depth of about 50 Å and may be limited to roughly 20 Å.\(^3,9\) The most common XPS observation with increasing Ar\(^+\) dose is the decrease of C\(_x\)O bonds and increase of amorphous graphitic carbon near the surface.\(^7,8\) There is also an increase of surface electrical conductivity.\(^7\) The sputter yields tend to be high - as high as 30 for nitrocellulose at 100 eV.\(^10\) The importance of the activated carbon sites in adhesion is indicated by the detection of TiC near the interface of a Ti film deposited on the activated polymer surface.\(^8\)

The optimum dose for surface activation is the dose sufficient to obtain most or all of the desired property or structure. (This is consistent with the definition of optimum cleaning dose, except that the desired property can be other than cleanliness.) Experimental data on optimization are not available at \(<100\) eV, but studies at both 500 eV and 2 keV give several optimums that are within a factor of two of the standard cleaning dose of \(10^{15}\) ions/cm\(^2\).\(^2,3,6\) These optimums are based on the availability of surface carbon bonds or the experimental adhesion of a film deposited on that surface.

The cleaning of polymers can be attempted without any knowledge of the required ion dose. In such cases, later calculations have sometimes shown the cleaning doses to be 100 times or more greater than \(10^{15}\) ions/cm\(^2\). Such massive cleaning doses can result in the accumulation of low-sputter-yield carbon, while removing normally gaseous products such as H, O, and N. The activation of carbon bonding sites is often desirable, but covering the surface with a graphitic layer is seldom useful.

OXYGEN
The effects of using oxygen with polymer substrates have also been studied over a range of ion energies.\(^2,8\) The sputtered
products were generally similar to those with argon, with acetylene (C₂H₂) again being important. Sputter yields were not available for <100 eV, but the oxygen values at 500 eV and 1 keV were roughly a factor of 10 greater than for argon. This large increase in sputter yield with oxygen indicates a substantial reactive component to the sputtering process, with this reactive component probably still present at <100 eV. A high sputter yield for oxygen at <100 eV would in turn indicate a dose of 10^{15} ions/cm² should be more than adequate.

Compared to argon, higher ion energies were required to form a carbonaceous layer with oxygen. However, another study found a general absence of a graphitic surface layer, as well as an oxygen etch rate that depended on the total oxygen arrival rate, from both the ion beam and the background. The formation of a carbonaceous layer may therefore depend on the background pressure of oxygen in addition to the ion-beam characteristics. Modeling of the oxygen etch process indicated near unity coverage of the etched surface with oxygen, if enough oxygen was available. This coverage was not evident in XPS, but the averaging over the top several layers by XPS could have masked this effect.

NITROGEN

A study in which 60-100 eV nitrogen ions were used to treat a polypropylene surface showed an optimum dose near 10^{15} ions/cm². This treatment gave a surface N/C ratio of about 0.11. There were also effects of varying energy within the 60-100 eV range, but some of this variation could be due to lack of polymer homogeneity.

CONCLUDING REMARKS

Available information indicates the need to keep cleaning/activation doses for polymers near 10^{15} ions/cm² (1.6×10^{4} C/cm²), probably not exceeding twice that value. Limited data and the reasonable objective of minimizing damage beneath the polymer surface both indicate that the ion energy should be <100 eV. Because of the wide range of activation effects, the best gas for a new application may have to be determined experimentally.

REFERENCES