Engineered Surfaces Through Surface Preparation and Cleaning

Gary E. McGuire
International Technology Center, Raleigh, NC

Abstract
Substrate preparation is an integral part of any film deposition process. This includes removal of unwanted impurities and residues as well as conditioning of the surface to generate the desired microstructure and composition. The substrate plays a critical role in condensation and nucleation during the initial stages of film growth which in turn influence both the microscopic and macroscopic properties of a growing film. In spite of the wide range of film deposition techniques and associated pressures, temperatures and energies of the deposited species there are many common aspects of surface preparation and cleaning. The nature of the surface and coating plays a role in the choice of surface cleaning and preparation technique and influences the choice of a wet or dry process for this purpose. Selected aspects of surface cleaning will be reviewed as an introduction to this topic.

Diverse Requirements for Surface Cleanliness
Following the early pioneering work of Don Mattox while he was at Sandia National Laboratory regarding the importance of surface preparation and conditioning relative to thin film deposition, the awareness of the interplay between the surface and growing films has grown to the point where it is a fundamental aspect of nearly every coatings technology today. The surface cleanliness, nanostructure and material phase are associated pressures, temperatures and energies of the deposited species. Thus the rational for utilizing ultrahigh vacuums for certain growth techniques is the desire to minimize inadvertent contamination associated pressures, temperatures and energies of the deposited species. Thus the rational for utilizing ultrahigh vacuums for certain growth techniques is the desire to minimize inadvertent contamination as a result of residual gases in the deposition chamber. One can see how quickly a surface can become contaminated in the following illustrative example. Figure 1 presents Auger electron spectroscopy (AES) data for a crystalline InP sample (Figure 1a) which was cleaved in the analysis chamber and analyzed [1]. Analysis of the freshly exposed surface of the cleaved sample reveals it is virtually free of contamination. After a period of time in the vacuum chamber residual gases will interact with the surface and be absorbed; the rate would depend upon the partial pressures of the gases. The characteristic Auger transitions for indium and phosphorus are the only ones detected. In light of the surface sensitivity of AES (first few atomic layers of the sample) adsorbed gases are readily detectable. The absence of any peaks associated with elements other than indium and phosphorus indicates the surface is clean within the detection limit of AES. When the sample is exposed to air (Figure 1b) for even a brief period of time, new peaks associated with carbon and oxygen appear. These are attributed to the adsorption of volatile oxygen- and carbon-bearing gases from air. Even if air exposure was for an even shorter period of time, the carbon and oxygen AES peaks associated with the adsorption of gases on the surface would appear.

Data of this nature quickly dispels the notion that a sample can ever be transferred fast enough into a deposition chamber to avoid air borne contaminant when it has been cleaned ex-situ. Being adsorbed gases, the contamination layer is likely to be a monolayer or less. One gains a sense of this by noticing that the phosphorus and indium peaks are still quiet strong indicating that the signal from the underlying substrate is only partially obscured.

![Figure 1. AES spectra of freshly cleaved InP surface before and after air exposure.](image)

If the cleaved InP surface is first oxidized, for example by exposure to ultraviolet (UV) light in the presence of ozone, before air exposure the extent of adsorption is changed; see Figure 1b. The small carbon AES peak indicates that the adsorption of volatile carbon-containing gases is reduced significantly. It is more difficult to determine if the adsorption of oxygen-containing gases is reduced due to the oxygen AES signal associated with the surface oxide. The shape and peak position of the phosphorus AES transition indicates that compound formation has occurred as a result of the oxidation. As a comparison, if the cleaved InP surface is exposed to a carbon containing ambient, such as xylene, prior to air exposure the extent of contamination by adsorption is not changed as much. The AES signal for oxygen indicates that oxygen-containing gases are still adsorbed on the surface although to a smaller extent than on the freshly cleaved surface. Based upon the AES peak shapes, there is no indication the phosphorus or indium have
reacted with the xylene. Based upon this example, there is evidence that the presence of a surface oxide reduces the extent of adsorption of volatile gases upon air exposure more than the presence of a hydrocarbon such as xylene. This is consistent with the understanding that adsorption is facilitated by dangling bonds at the terminated surface and that compound formation ties up these bonds.

Sources of Contamination
Contamination by volatile molecules and compounds as a result of air exposure is just one of many potential sources of contamination. Air exposure, as well as contact with liquids, poses the risk of particulate contamination. Additional sources of surface contamination include cleaning and etching solutions, rinse baths, and photoresist. The surface may become contaminated as a result of out-diffusion or surface segregation. Depending upon the nature of the contaminant and degree of contamination as well as the nature of the surface, different cleaning procedures may be required. The chemistry of a cleaning solution selected for removal of oxides is very different from that required for the removal of organics. A cleaning solution intended for use with a metallic substrate typically is very different from one planned for use with a polymeric substrate. In all cases, the amount of contaminant to be removed must be taken into consideration.

For some technologies, choosing to remove the contamination with or without changing the surface is an important decision. Among the best illustrations where removing a portion of the sample surface is undesirable is for the most advanced semiconductor devices. With the ongoing shrinkage of device dimensions in all directions, dopant elements introduced to form an electrical junction have an increasingly shallow profile. Different schemes are utilized to achieve and preserve a shallow dopant profile. Since the dopant is concentrated near the surface, any cleaning step that removes a portion of the surface will also remove a significant fraction of the dopant changing the electrical properties of the device. For comparison, removal of the surface of a tool bit that is being prepared for the deposition of a hard coating may have beneficial effects. Removal of hundreds of nanometers of material during cleaning does not change the character of the tool steel. However, the etching that occurs during cleaning may cause surface roughness on a microscopic scale which contributes to stronger bonding between the hard coating and the tool steel.

Cleaning procedures fall into a small number of categories that are put into practice in hundreds of different ways. These include through the application of force, chemical processes and lift-off techniques. Force may be applied by mechanical (brushing, scrubbing and polishing), hydrodynamic (pressurized liquid or gas) or vibrational (ultra- or megasonic transducer) means. Chemical cleaning may be carried out in solution (solvation or dissolution) or in the gas phase (volatilization or reaction products). Lift-off is carried out by depositing a sacrificial layer which protects the surface from contamination until later removed. Combinations of the different cleaning techniques often work best such as the use of a solvent in a megasonic bath so that both the chemical and mechanical mechanisms are utilized.

In Table 1 a few examples of common aqueous cleaning chemistries for removing oxide and organics are presented for illustration. Aqueous-based cleaning formulations for removing oxides are based upon the presence of fluorine ions. A simple HF bath may be used or one with NH₄F which serves as a buffer where the fluorine is replenished by dissociation of the NH₄F as the fluorine is consumed in the reaction with the oxide. When combined with an oxidizing medium such as H₂O₂ or HNO₃, the surface is consumed as a result of the on-going combination of oxidation and oxide removal. The resultant surface may be covered with a slight residual oxide if the sample is continued on page 40.
not rinsed quickly following removal from the etch bath. An oxidizing medium is utilized to remove organics by reaction with the hydrocarbon chains. For low levels of contamination a very modest oxidizing medium is required. With more extensive contamination a more reactive or aggressive oxidizing medium is preferred. The oxidizing medium not only removes the organic residue but also oxidizes the surface. Due to costs associated with treating the waste stream, the use of \( \text{O}_3/\text{H}_2\text{O} \) has become increasingly popular due to the inherent instability and natural degradation of the \( \text{O}_3 \).

The examples in Table 1 bring us to the point where one begins to recognize that we often trade one contaminant for another as a result of cleaning procedures. In these examples, the organic contaminant is removed while the surface becomes oxidized. There are many wet and gas phase cleaning procedures where the initial surface layer is replaced by another as a result of the chemistry of the cleaning procedures. Often one must make a conscious decision regarding which surface termination is preferred. Generally organics provide a weak boundary layer and the boundary layer is even removed from polymeric substrates. The presence of an oxide is often not acceptable, for example in the case of a substrate to be electroplated.

Until the emergence of the surface characterization tools scanning tunneling microscopy (STM) and atomic force microscopy (AFM) along with the many related techniques that emerged later, probes that provided insight into the surface topography on an atomic scale were not available. It was only then that it became apparent that cleaning often lead to surface roughness. Since the presence of surface defects, atomic steps and clusters of atoms influence the nucleation process, the insights provided by these new surface probes allowed more thorough investigation of the cleaning procedures. In one of the earliest studies with a focus on the relationship between cleaning and surface morphology on an atomic scale, Ohmi et al. [2] showed that the roughness of a Si (100) surface following oxidation in ozonated water and removal of the formed oxide led to a surface roughness of less than 0.2 nm after repeated cycles of cleaning. The oxide thickness is only approximately 1 nm when the ozone-injected ultra-high purity water is used as the cleaning agent. The ozone concentration was between 1 to 2 ppm. Recently Clark et al. [3] showed that a nearly atomically flat Si (100) surface can be achieved when the surface is etched in \( \text{NH}_4\text{F} \). That nearly atomically flat surfaces can be achieved over large areas is a major advancement relative to the early studies by Ohmi et al. [2]

Ideally surface cleaning can be carried out in the chamber in which the subsequent deposition will occur. This helps to minimize the presence of oxides which result from wet cleaning processes as well as adsorbed gases which occur during the transfer of the substrate to the deposition chamber. Various plasma and reactive ion etching processes have been utilized for the in-situ cleaning. One of them, in-site hydrogen cleaning, presents an opportunity to remove oxide and organic residues as well as sulfur and other elements that form a volatile compound. Due to the volatility of these compounds, hydrogen as a cleaning agent is more broadly applicable than others which may only remove one species. Figure 3 presents x-ray photoelectron spectroscopy (XPS) data of an oxidized GaAs surface that has been cleaned with hydrogen. Shown here are the XPS spectra of the Ga 3d core shell which shows a chemical shift in the peaks between Ga in GaAs and Ga in the oxide of Ga. Initially a thin oxide is present; the overlying oxide is thin enough so that the Ga 3d spectrum from the bulk GaAs is still detectable. When the surface is bombarded with hydrogen ions the surface oxide is gradually removed eventually leaving a clean GaAs surface with the presence

<table>
<thead>
<tr>
<th>Solution</th>
<th>Purpose</th>
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<tbody>
<tr>
<td>HF/H(_2)O</td>
<td>Oxide removal</td>
</tr>
<tr>
<td>HF/\text{NH}_4\text{F}/H(_2)O</td>
<td>Oxide removal/slight Si etch</td>
</tr>
<tr>
<td>HF/H(_2)O(_2)</td>
<td>Oxide removal/slight Si etch</td>
</tr>
<tr>
<td>HF/HNO(_3)</td>
<td>Organics/light oxidation</td>
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<tr>
<td>O(_3)/H(_2)O</td>
<td>Organics/light oxidation/metals</td>
</tr>
<tr>
<td>H(_2)SO(_4)/H(_2)O</td>
<td>Heavy organics/oxidation</td>
</tr>
<tr>
<td>H(_2)SO(_4)/O(_3)/H(_2)O</td>
<td>Organics</td>
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</tbody>
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Table 1. Aqueous Cleaning Chemistries

Figure 2. STM images of Si(100) etched in aqueous \( \text{NH}_4\text{F} \) at room temperature show a near atomically flat morphology. The calculated root-mean-square surface roughness is 0.57 A [3]
of oxygen below the detection limit. While the surface is free of oxygen and carbon contamination, it is commonly not noted that the surface is likely hydrogen terminated after this cleaning process. While hydrogen may be present, there is no significant evidence that hydrogen interferes with bonding at this interface. Hydrogen termination is also present following HF-based etching of Si surfaces and again there is no evidence that it plays a significant role regarding nucleation and growth on this surface. So hydrogen cleaning is attractive both from the standpoint that it is capable of removing many of the common contaminants as well as leaving a surface that is likely hydrogen terminated that does not interfere with the subsequent deposition process.

Cleaning in situ is attractive for many reasons, but ex-situ dry cleaning methods are attractive for cases where the subsequent processing does not occur in a vacuum chamber. Recently there has been a rapid increase in the use of atmospheric pressure plasma systems for film growth, surface modification and cleaning. There are several different means of generating atmospheric pressure discharges including RF and pulsed dielectric barrier discharges as well as microplasmas. One disadvantage of most high pressure plasmas is the non-uniform filamentary discharge that occurs unless an easily ionized gas such as helium or argon is added to the ambient. The requirement for helium or argon adds to the operating cost of such a plasma technology. Shown in Figure 4 is a photograph of a dielectric barrier plasma discharge operating uniformly in air without filaments over 1 meter long electrodes and area of over 500 cm². For the plasma system, charge transfer scales linearly with electrode area with no impedance matching network required. Energetic electrons generated as a result of the overvoltage potential initiate chemical processes in the treatment gas making the system an attractive new technique for surface cleaning.

From this brief review of surface cleaning, one can see that it is an integral aspect of coatings technology and that on-going scientific advances have been made which allow greater insight into the process and subsequent control which lead to better film quality.

References

Gary E. McGuire is the President of the International Technology Center, a non-profit research corporation. Dr. McGuire received his Ph.D. in Inorganic Chemistry from the University of Tennessee before joining Texas Instruments where he conducted research on surfaces of semiconductor materials. Later after joining Tektronix he held several management positions directing research in electronic, display and color copier materials. He joined the Microelectronics Center of North Carolina in 1987 and was the Director of Electronic Materials and Devices. Dr. McGuire has 12 patents, over 130 publications plus 35 books and book chapters. He is editor of the Journal of Vacuum Science and Technology B and Past-President of the AVS.

For further information, contact Gary E. McGuire, International Technology Center, at gmguire@itc-inc.org

Figure 3: Ga 3d XPS data for GaAs before and after hydrogen cleaning. [4]