Materials characterization capabilities of SilcoTek

Overview

Materials characterization capabilities serve an essential role at SilcoTek to develop new products, and an equally essential role in assisting customers with scale up as well as process troubleshooting. Various characterization techniques enable SilcoTek's scientists to study coatings, analyze surface bonding mechanisms, and develop a deep understanding of the coatings' protection properties. Meanwhile, SilcoTek's technicians use characterization tools in their daily QA/QC process to make sure all coatings meet SilcoTek's quality standards and satisfy our customers' needs. Last but not least, it is not uncommon for SilcoTek to receive customer requests to provide characterization help with their specific substrates or coated parts.

In addition to the in-house characterization capabilities, SilcoTek also enjoys convenient access to a wide variety of characterization techniques at the Pennsylvania State University (PSU), thanks to our physical proximity to the University's main campus, and an established academic/industry relationship between PSU and SilcoTek. As a result, SilcoTek's R&D scientists are all trained users of many of the instruments at the Materials Characterization Lab (MCL) at Penn State University.

This white paper aims to provide a brief introduction of different materials characterization techniques available to SilcoTek, both in-house and through Penn State University, to give our customers a glimpse of the possibilities.

SilcoTek's in-house characterization capability

1) X-ray Fluorescence (XRF) Analyzer

SilcoTek receives in hundreds of customer parts for coating every day. The majority of these parts are made of stainless steel, which is a standard substrate for SilcoTek to treat. There are, however, a few materials that are not compatible with our deposition process, either due to the low melting point, inhomogeneous film growth and/or poor adhesion of the substrate material. These include lead, zinc, pure nickel plating, copper, copper alloys such as brass and Monel, and gold and silver. A complete list of material compatibility with SilcoTek CVD coating process can be found by following this link.

In order to avoid process disruptions caused by incompatible substrates, SilcoTek uses a Thermo Scientific X-ray fluorescence (XRF) analyzer, a non-destructive elemental analysis tool, to identify any unfamiliar incoming metal substrates.

In XRF, an X-ray photon with enough energy strikes an atom in the sample and knocks out an inner shell electron. The atom regains stability by filling the inner shell vacancy with an outer shell electron, and in the process releases fluorescent X-ray whose energy equals the binding energy difference between the inner and outer shells. Since each element in the sample emits its own unique fluorescent X-ray spectrum, by collecting and analyzing these fluorescent X-rays, XRF can determine the elements present in a sample and their relative concentrations.

Standard detection range for our XRF analyzer covers from sulfur (S) to uranium (U). For samples with specifically defined chemical composition, such as common grades of metal alloys, the instrument also identifies most sample types by name in a matter of a few seconds. Figure 1 below shows an example output from the XRF analyzer of stainless steel 316.

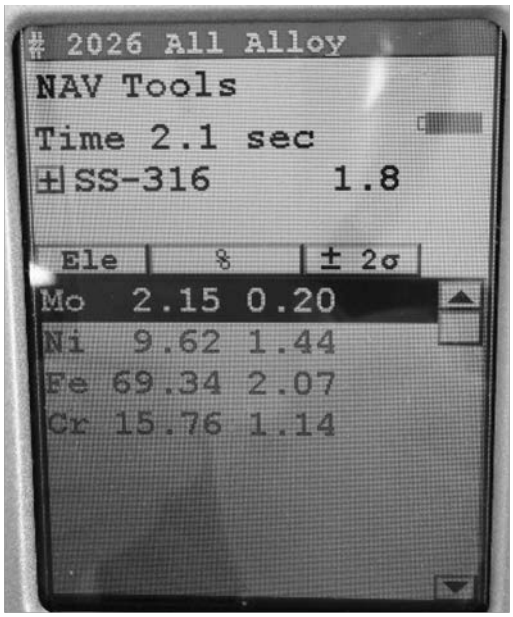

Figure 1. An example XRF output of 316 stainless steel.

XRF benefit to SilcoTek's customers: help identify metal type of substrate material; avoid issues caused by substrate incompatibility.

2) FTIR

Fourier Transform Infrared Spectroscopy (FTIR) uses a broad band infrared radiation as the excitation source to probe molecular structures of various chemical species in gas, liquid or solid state. The wavelengths at which absorption occurs are identified by detecting the change in the intensity of light after reflection or transmission as a function of wavelength. These absorption wavelengths correspond to specific chemical bond excitations and can serve as signature indications for the type of bonds and the group of atoms involved in the vibration. Thus, information can be deduced about what functional groups are present and how atoms are connected to each other in a molecule. Unlike diffraction methods which are limited to crystalline substances, FTIR can be used to characterize both crystalline and amorphous materials.

SilcoTek's Thermal Scientific Nicolet FTIR instrument is equipped with the standard, the Smart iTR™ (Attenuated Total Reflectance), and Smart SAGA (Specular Apertured Grazing Angle) sampling accessories, enabling both transmission and reflection measurements in a versatile form of samples, including thin films, liquid, powders, and pellets etc. The FTIR technique is used by SilcoTek's technicians on a regular basis to perform the QA/QC duties, as well as by SilcoTek's scientists to assist in their R&D projects.

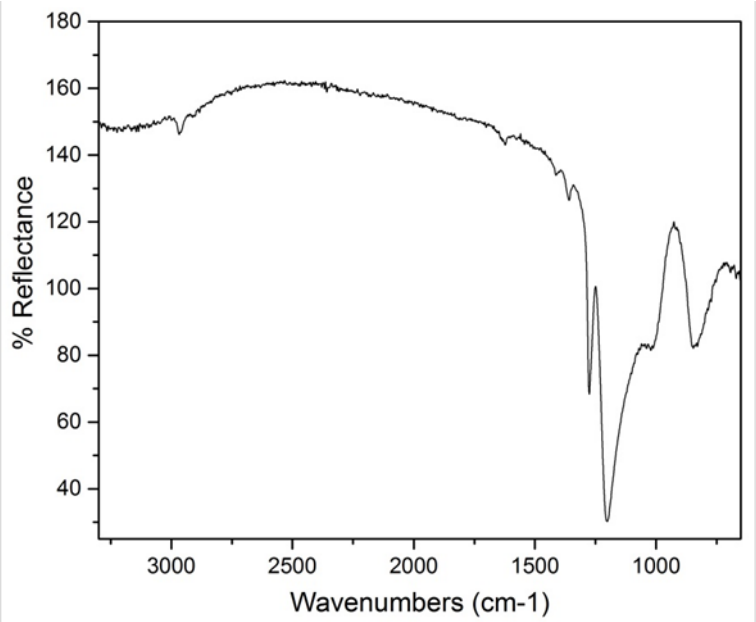

Figure 2. FTIR spectrum of SilcoTek's Dursan® coating, consisting of C-H (2966 cm-1), Si-CH3 (1272, 835 cm-1) and Si-O-Si bonds (1197 and 1017 cm-1).

Figure 2 illustrates a typical FTIR spectrum of SilcoTek's Dursan® coating, taken in the reflection mode. It shows Dursan's characteristic absorption peaks that correspond to its constituent functional groups. The FTIR serves as one of the several essential quality control methods for SilcoTek's production crew.

FTIR benefit to SilcoTek's customers: help identify any organic contaminants; ensure integrity of the coating layer.

3) F20 Thin-film Analyzer

SilcoTek's F20 thin-film analyzer (manufactured by Filmetrics Inc.) is a bench top tool that can be configured to measure thin film thicknesses (30Å to 350 μm), optical constants (n and k: refractive index and extinction coefficient) and transmittance. It is primarily used by SilcoTek as a quick, accurate and non-destructive way to measure coating thicknesses.

The F20 measures thin film thickness by either reflecting or transmitting light through the sample over a range of wavelengths (SilcoTek typically uses the reflection mode). When light interacts with a coated sample, it goes through reflection twice, at the upper and lower boundaries of the coating. These two reflections will either add (called in-phase and shows up as a peak) or subtract with each other (called out-of-phase and shows up as a valley), depending on the wavelength of the light as well as the thickness and optical properties (n and k) of the coating. If the wavelength and the optical properties of the coating are known, the thickness of the coating can then be extracted from the measurement. The resulting reflectance spectrum is characterized by intensity oscillations, and generally the thicker a coating is (i.e. the longer the optical path difference between the two reflection waves), the more oscillations there are in a given wavelength range.

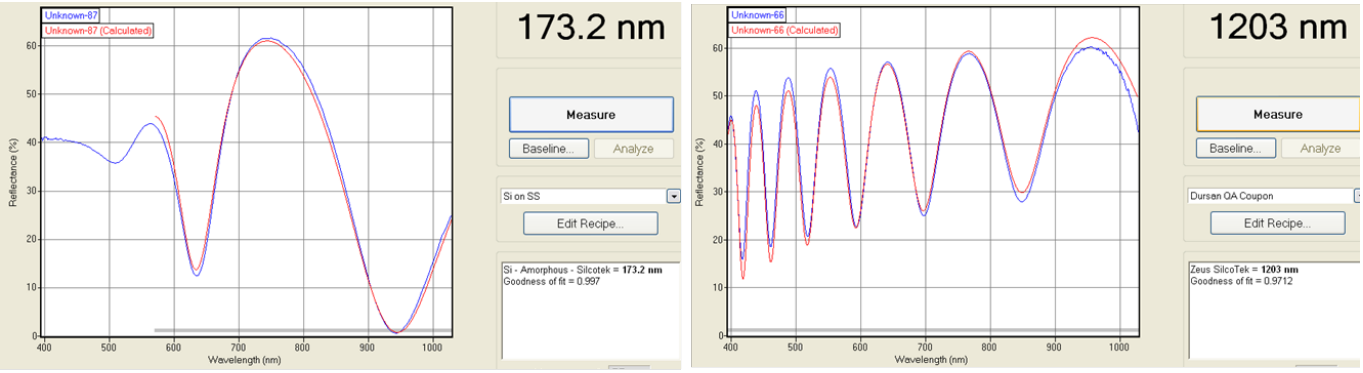

Figure 3. Two F20 thickness measurement examples showing the thicker coating with more oscillations in the output spectrum.

Figure 3 above shows two sample outputs from the F20 coating thickness measurement, illustrating how the number of oscillations relates to film thickness. The F20 measurement is calibrated to a NIST-traceable sample, and has shown excellent agreement with a direct cross-sectional measurement using the FIB/FESEM technique.

F20 benefit to SilcoTek's customers: provide thickness verification of the coating.

4) Surface contact angle measurement

Contact angle is the angle that a drop of liquid makes to its (usually solid phase) contacting surface. It is measured through the droplet, with the angle formed between the solid surface and the liquid meniscus near the line of contact. The contact angle gives an indication of the wettability of a surface to a liquid (usually water), and the value of the contact angle can vary with the volume of the liquid drop. Conventionally, a surface is referred to as "hydrophobic" if its water contact angle is larger than 90°, and "hydrophilic" if its water contact angle is smaller than 90°.

The contact angle produced with an increasing liquid drop volume is called the advancing contact angle, and it senses the hydrophobic portion of the surface properties and represents the maximum angle

value on that surface. Similarly, the contact angle produced with a decreasing liquid drop volume is called the receding contact angle, and it senses the hydrophilic portion of the surface properties and represents the minimum angle value on that surface. The difference between the advancing and receding values is termed contact angle hysteresis, and it is a measurement of the surface "stickiness". Low hysteresis is desired in an application where liquid droplets are expected to "roll off" a surface readily. Contact angle hysteresis is generally believed to be caused by surface roughness and/or heterogeneity.[1]

The effect of surface roughness on wetting state is typically described by two models, known as Wenzel and Cassie-Baxter. In the Wenzel model, the liquid-solid contact follows the contours of a rough surface, and surfaces in the total wetting Wenzel state are "sticky" in that water drops tend to adhere more to them than to a corresponding flat surface. The Cassie-Baxter model describes situations where it is more energetically favorable for a liquid drop to rest upon a composite surface of flat solid tops and flat air gaps between them, effectively bridging across the tops of surface features. Surfaces following the Cassie-Baxter regime are "slippery" and allow liquid drops to roll off more easily than on an equivalent flat surface. These two states can convert from one to another, with the Cassie-Baxter state being the more preferred state in a superhydrophobic application. Experiments show that surfaces with multiple scale roughnesses favor the transition into Cassie-Baxter state, thus allowing easy roll-off of water drops.[2] Figure 4 below illustrates the wetting states discussed herein.

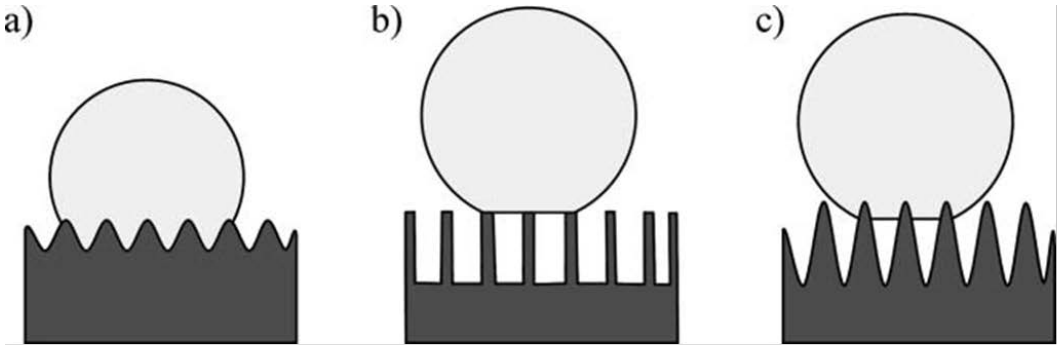

Figure 4. Wetting states of (a) Wenzel, (b) Cassie-Baxter and (c) combined models.[2]

SilcoTek has two contact angle analysis instruments: a ramé-Hart Model 200 goniometer that measures static equilibrium contact angles, and a Krüss K100 tensiometer that provides bulk analysis of a larger surface area with both advancing and receding values. Figure 5 below illustrates contact angle photos taken with the Ramé-Hart goniometer on a range of SilcoTek coatings, showing how surface roughness increases the contact angle values. SilcoTek's scientists rely heavily on the contact angle measurement in their research of hydrophobic and superhydrophobic surface development, where properly designed surface topography can bring out the extreme water-repellent property in a surface. To learn more on

SilcoTek coatings' contact angle properties, please refer to our white paper "Contact Angle Evaluation of SilcoTek Depositions".

Contact angle measurement benefit to SilcoTek's customers: ensure anticipated surface hydrophobicity/hydrophilicity as required by application; confirm successful surface bonding.

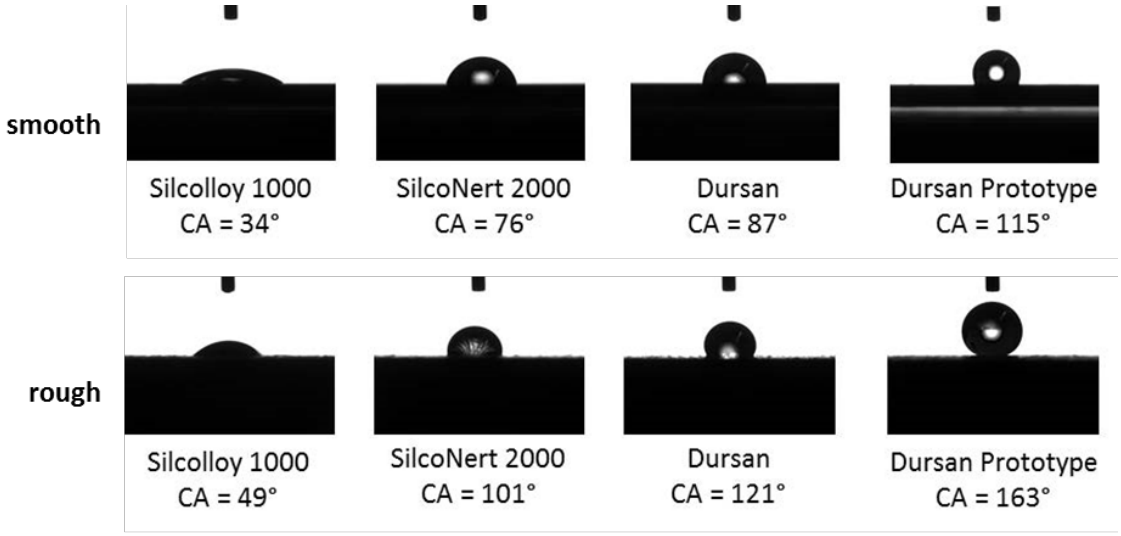

Figure 5. Contact angle photos of DI water on various SilcoTek coatings on smooth vs. rough surfaces.

5) Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a mostly non-destructive and very useful tool to study and evaluate the performance of protective coatings on metal substrates. The measurement gives information such as coating resistance, coating capacitance, double layer capacitance and Faradaic impedance which are related to the performance and failure process of coatings.[3]

Electrical impedance is a measure of the ability of a circuit element to oppose the flow of electrical current when a voltage is applied. It can be considered as an extension of the simple "resistance" concept to an AC circuit. Unlike resistance which has only magnitude, impedance possesses both magnitude and phase, and is therefore a complex quantity.

EIS measures the current response of an electrochemical cell by applying an AC potential to it. Data obtained from the measurement is commonly analyzed by fitting it to an equivalent electrical circuit model. A good coating that exhibits excellent protection to the base metal shows pure capacitive behavior, and usually displays very high impedance at low frequencies.

Figure 6 below is what the Bode plot of an ideal protective coating would look like.[4] A Bode plot is a presentation method of the EIS measurement results, with one x-axis value (the log frequency), and two y-axis values (Figure 6 left: the y axis is the magnitude of the impedance in ohm; Figure 6 right: the y-axis is the phase shift of the impedance in degree).

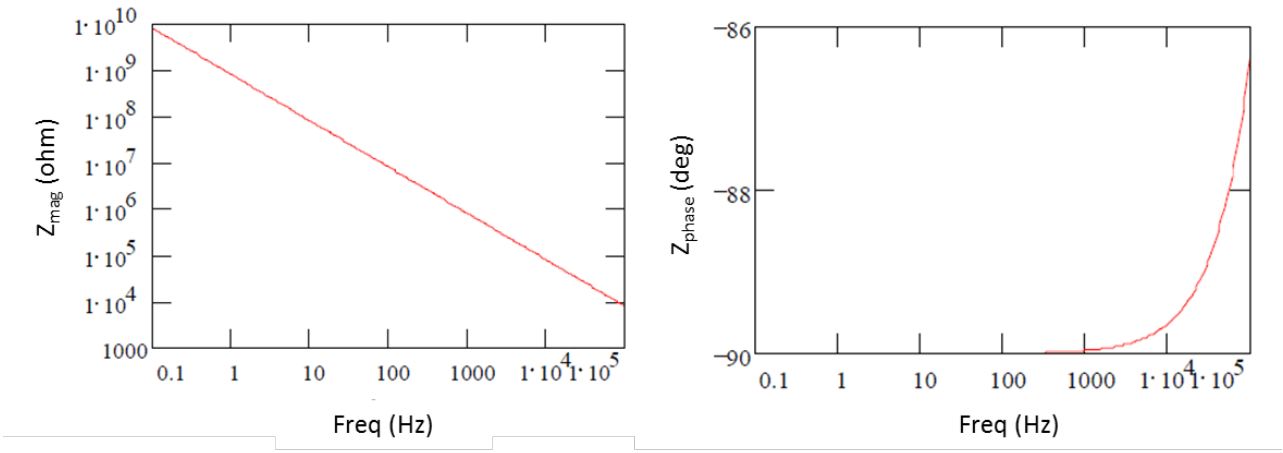

Figure 6. Typical Bode plot for a good protective coating.[4]

Figures 7 below shows the EIS behavior of a protective SilcoTek Dursan coating in 5% NaCl solution. Note that as the frequency decreases, the impedance magnitude increases steadily in a straight line (left), and the phase angle stays flat and low near -90 degrees (right). This is in excellent agreement with the behavior of an ideal protective coating as illustrated in Figure 6.

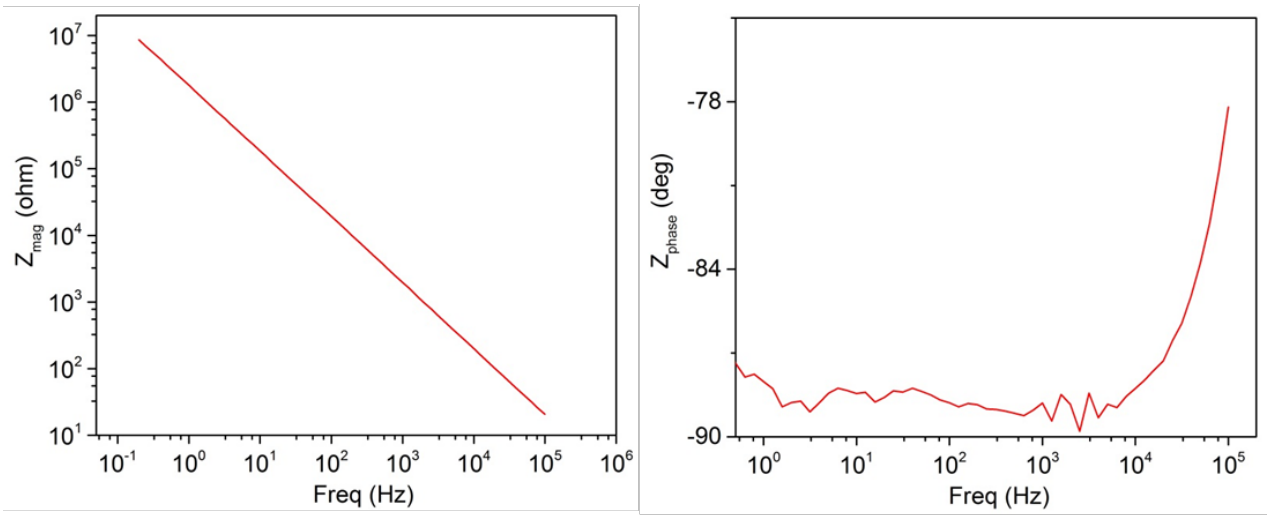

Figure 7. Example Bode plot of a protective SilcoTek Dursan coating.

Figure 8 shows the degradation of a purely capacitive coating through uptake of the solution into the coating. Solution penetration of the coating adds a resistor component (solution resistance) to the electrochemical system, and as a result the impedance magnitude loses its linear characteristics when the slope starts to change at approximately 100 Hz. The phase angle deviates from the ideal -90 degrees continuously, indicating the permeation of the coating by the solution and initiation of electrochemical reactions under the coating.

EIS benefit to SilcoTek's customers: provide corrosion performance evaluation of coating; help analyze failure mechanisms.

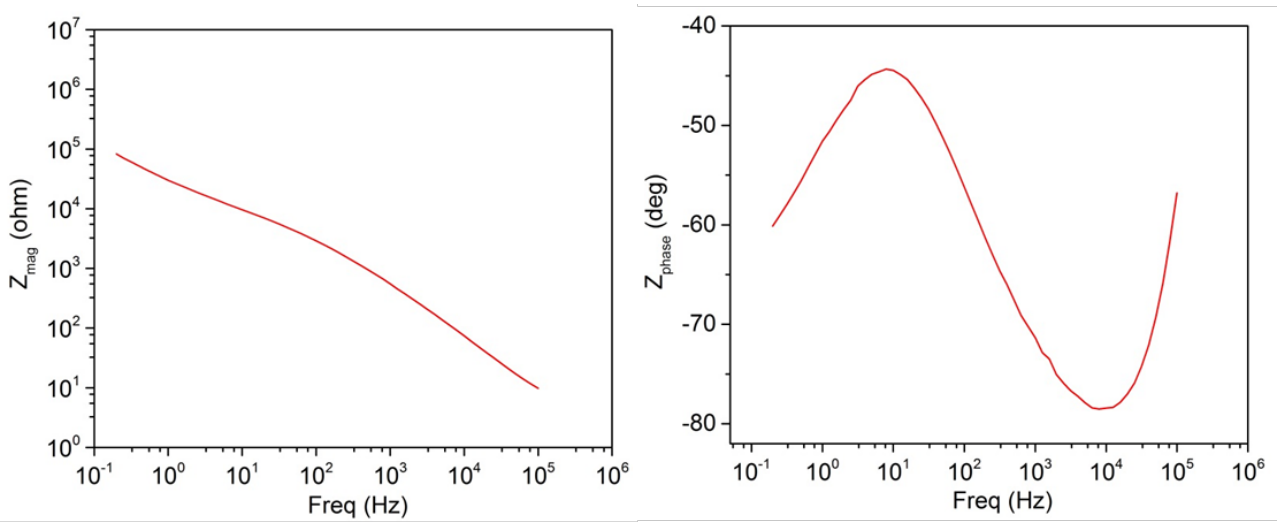

Figure 8. Example Bode plot of a failed coating.

Characterization capability through Penn State University

Located in Bellefonte Pennsylvania, SilcoTek is only a few miles away from the main campus (University Park) of Penn State University, and has thus transformed this geographic proximity into a strong collaborative relationship with a world-class research institute.

SilcoTek's R&D scientists are all trained users of the University's Materials Characterization Lab (MCL), where not only a wide variety of characterization techniques and equipment, but also a group of experienced staff scientists are available to answer any questions related to materials science (click to see MCL's website). The following sections will focus on a few techniques that are frequently used by SilcoTek's scientists through Penn State University. Other than the ones to be discussed below, SilcoTek also has access to all the other techniques listed on PSU MCL's website, should a particular need arise.

1) Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope (SEM) is developed to enable a "closer" look at a material when the optical microscope fails to provides adequate resolution at the detail levels needed. The SEM has overcome two intrinsic limitations that hinder the traditional optical microscope: low resolution and poor depth of field.[5]

The theoretical highest resolution of an imaging technique is the size of half of the wavelength of the imaging energy. Since SEM uses electrons instead of visible light (as in optical microscope) as the imaging source, and wavelengths of electrons are orders of magnitude lower than that of visible light, SEM can achieve a significantly higher resolution than the optical microscope. The second limitation of the optical microscope, the poor depth of field, is due to its large aperture angle at high power objective

lenses (short focal lengths increase the aperture angles). An SEM on the other hand, has a long working distance and a very small aperture angle, and thus provides a much better depth of field.

In an SEM, a focused beam of electrons impinges upon a specific area of the sample specimen in a raster pattern. The incident electrons can take one of three pathways: 1) they can pass through the space within the sample without any collision events; or 2) they can have an inelastic collision with an electron in the sample atom and create secondary electrons (energy < 50 eV); or 3) they can experience elastic collisions (i.e. no loss of kinetic energy) with the nucleus of the sample atoms and create backscattered electrons (energy > 50 eV). Appropriate detectors can be used to collect secondary or backscattered electrons emitted from the sample surface, and consequently process them into images which are projected onto a cathode ray tube (CRT) that our eyes can see.

Typically the secondary electron (SE) imaging mode provides excellent surface topographical contrast, whereas the backscattered electron (BSE) imaging mode highlights density differences in the sample.

Penn State's MCL maintains a number of SEM instruments that offer either beam deceleration or low vacuum operation mode (click to see PSU MCL's SEM capability), boasting resolutions down to sub-nanometer scale with the latest tool addition.

Figure 9 below shows SEM images of the surfaces of two SilcoTek coatings (taken in SE mode), where our R&D scientists experiment with ways to control the coating's surface topography (smooth vs. rough).

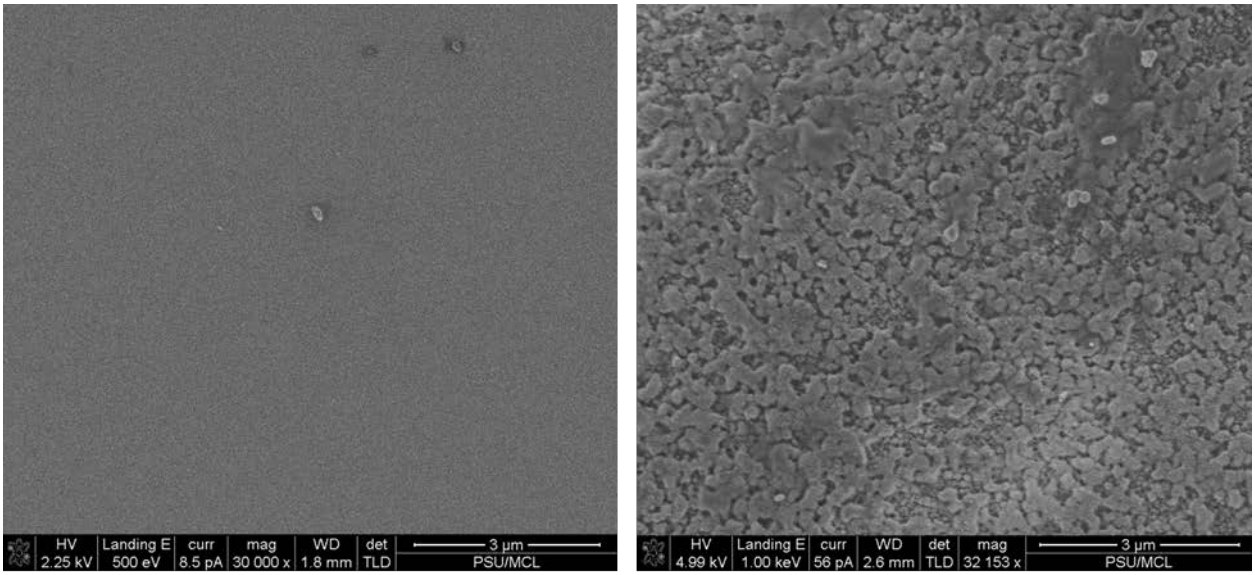

Figure 9. SEM images of two SilcoTek coatings taken at Penn State MCL.

SEM benefit to SilcoTek's customers: provide coating's visual characteristics at very high magnifications; highlight surface imperfections; assist in troubleshooting.

2) Energy-dispersive X-ray Spectroscopy (EDS)

As an elemental analysis technique, EDS application is usually installed in electron column instruments such as the SEM, therefore it is often used in conjunction with SEM and referred to as SEM-EDS.

When the incident electron beam in an SEM bounces through the sample to create secondary electrons, these secondary electrons get knocked out of their shells (to be collected by a detector to form an SEM image), and leave behind thousands of vacant shells in the sample atoms. A vacant inner shell is an unstable state for an atom, and an electron from a higher energy outer shell will drop into the vacant inner shell to fill the "hole", and in the process release the energy difference between the two shells in the form of an X-ray emission. The wavelength and energy of the X-ray is unique to each element as well as the shells involved (for example, a Kα line refers to the X-ray emitted as the result of an L-shell electron filing a vacant K-shell). Therefore, collecting and analyzing these characteristic X-ray lines allow the sample's elemental composition to be resolved.

As the X-ray emission comes from the same sample area where the electron beam strikes, the area that is being imaged (in an SEM) is also the same area that is getting elemental analysis by EDS. Depending on the sample density and the incoming electron beam energy, the EDS depth of information is usually from 0.5 to 3 μm.[5] Thus EDS is considered as a bulk elemental analysis technique, and does not provide adequate resolution to the top tens of nanometers of a surface. A variety of analysis modes can be employed in an EDS measurement, including spectrum acquisition, mapping of the elements, and elemental line scans.

Figure 10 below shows the SEM-EDS analysis results of an aluminum substrate with silicon dioxide (SiO2) contamination (study performed at Penn State University's MCL). The elemental mapping mode was used to highlight different elements in different colors. SilcoTek's scientists used this technique to quickly identify the contamination species on an aluminum substrate during a trouble-shooting process.

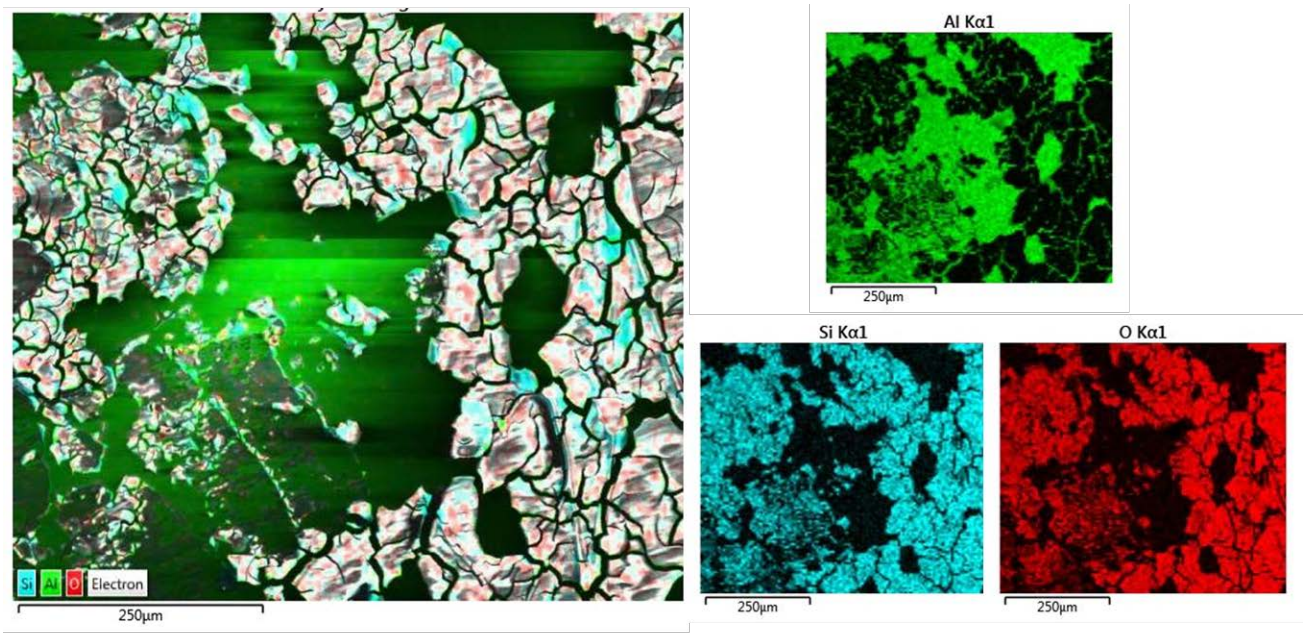

Figure 10. SEM-EDS analysis of an aluminum substrate contaminated with silicon dioxide particles.

EDS benefit to SilcoTek's customers: provide elemental analysis information; assist in troubleshooting.

3) X-ray Photoelectron Spectroscopy (XPS)

XPS is one of the most useful surface sensitive analytical techniques available today. It can detect all elements except hydrogen and helium, and offers a depth of information from the top 1 to 10 nm of the surface region of a sample.[5]

In XPS, an incoming X-ray beam bombards a sample surface, and its energy gets absorbed by the sample atoms in the surface. If the energy of an X-ray photon is sufficient to free an electron from its nucleus, the escaped electron, known as a photoelectron, will emit out of the sample surface. According to Einstein's photoelectric law, the energy of the incoming photon is split into two portions: one portion is used to overcome the electron's binding energy (BE) to free the electron from its core, and the remaining portion is transferred to the photoelectron as its kinetic energy.

As the energy of the incoming X-ray photon is known, a measurement of the photoelectron's kinetic energy helps to determine the value of BE. The BE is characteristic of the specific element as well as its chemical state, therefore XPS can not only identify the elements present in a sample surface, but also extract information about the chemical state and binding environment of those elements. The intensity of the photoelectrons can be used to determine the relative concentrations of each element.

Figure 11 below gives an example of using XPS in the PSU MCL to study oxidation process in a coating. SilcoTek's scientists use this technique to study the oxidation of the silicon atoms in a coating, which is demonstrated by the binding energy shift from Si-C to Si-O.

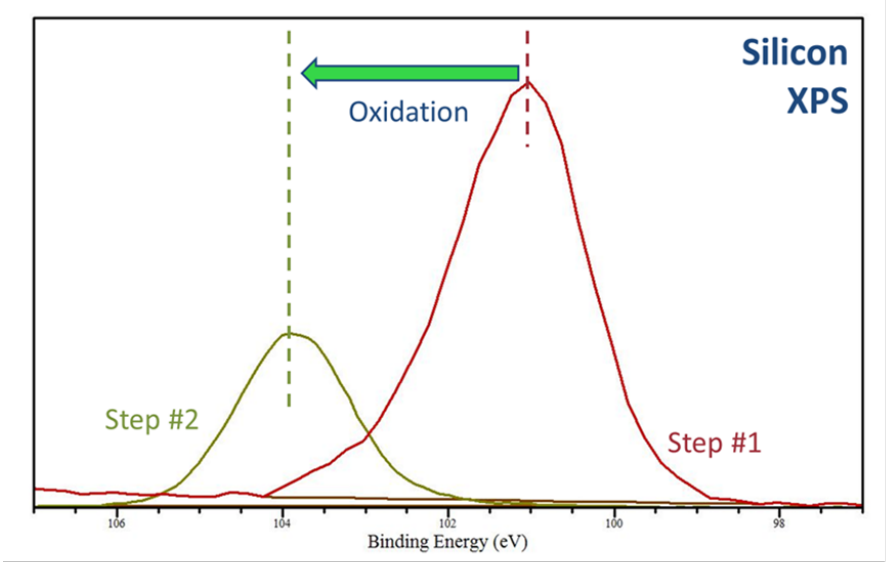

Figure 11. XPS study shows the binding energy shift of Si (from Si-C to Si-O) before and after an oxidation step of a coating.

XPS benefit to SilcoTek's customers: provide true "surface" (top 1~10 nm) information; confirm successful surface bonding; identify surface contamination; detect surface chemical changes.

4) Dielectric P-E Measurement

There has been an increasing amount of inquiries from SilcoTek's customers on the electrical properties of our coatings. In general, SilcoTek's silicon-based coatings (SilcoNert and Silcolloy) exhibit resistor-like behavior (i.e. they allow electric current to flow through them), whereas Dursan is a dielectric coating (i.e. an electrical insulator that gets polarized by an applied electric field and through the polarization stores electrical energy).

SilcoTek performs a P-E (polarization vs. electric field) measurement at the Dielectric Properties Lab at Penn State MCL to characterize our coatings' dielectric properties. As the name suggests, a P-E loop for a device is a plot of the charge or polarization (P) developed against the field (E) applied to that device at a given frequency. The P-E loop for an ideal linear capacitor is a straight line whose gradient is proportional to the capacitance. If, however, there is current leakage through resistive losses (also known as a lossy capacitor), the straight line will open up into a narrow loop, indicating resistive leakage in the device.

Figure 12 below shows the P-E responses of two Dursan coatings. The left graph represents what would be described as a "lossy capacitor", and the right graph shows the linear P-E response of an ideal dielectric coating with low loss. This characterization tool has helped SilcoTek's scientists to develop process improvements to eliminate the "lossy capacitor" response towards a good dielectric coating. For more details on this subject, please refer to our white paper "Electrical Property Characterization of SilcoTek Coatings".

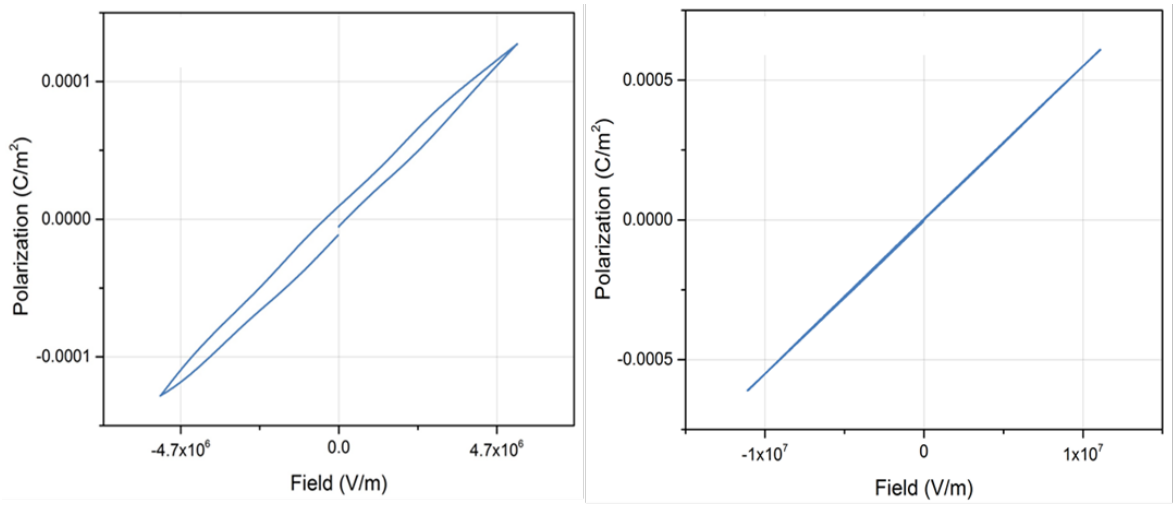

Figure 12. P-E response of a lossy coating (left) vs. a low-loss good dielectric coaing (right).

P-E measurement benefit to SilcoTek's customers: provide dielectric property information; detect current leakages in a coating.

Summary

This white paper gives a brief review of a range of materials characterization techniques available to SilcoTek. It aims to help our customers understand the scope and capability of SilcoTek's R&D activities, as well as to demonstrate how different tools can be used to facilitate SilcoTek in the development of more innovative solutions, to help our customers solve various application challenges. Easy availability of these tools also allows SilcoTek's manufacturing team to keep a tight quality control on our coating products, thereby providing consistent and reliable coating service to all our customers. Additionally, SilcoTek's close ties with Penn State University give us access to some of the most advanced characterization equipment/techniques available. Our goal is to convert that advantage into providing the best coating services and solutions possible for our customers.

References

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5) C. R. Brundle, C. A. Evans Jr. and S. Wilson, "Encyclopedia of materials characterization: surfaces, interfaces, thin films", Butterworth-Heinemann, **1992**.