IARPA MORGOTH'S CROWN: Preparation Materials for Airbrushed Samples

Contents

Description of Sample Coupons

Sample coupon sets were prepared using multiple target chemicals, four different substrates, and three different mass loadings. These variables are discussed below.

- Target chemical: The different target chemicals were subject to the same deposition variables (in order to provide redundancy in the matrix for the compilation of training, testing, and blind testing samples.) All targets were deposited from solution via a robotic airbrush system (Fisnar).
- Substrates: JHU/APL deposited the target chemicals on four different substrates: sandblasted aluminum, polished aluminum, anodized aluminum (black), and soda lime glass. These substrates provided a variety in surface roughness, spectral signature, transparency, and surface chemistry.
  - Sandblasted aluminum: This substrate was identical to that used in SILMARILS Phase I. Aluminum 6061 alloy was sand blasted with SiC, 150 grit size. The resulting surface was rough, resulting in diffuse reflection.
  - Polished aluminum: Aluminum 6061 was polished to have a "mirror-surface." This substrate was chosen in order to vary roughness, while keeping chemical composition the same.
  - Anodized aluminum: This additional variation on aluminum was chosen in order to vary surface chemistry and spectral signature. The roughness was between that of sandblasted aluminum and polished aluminum.
  - Soda lime glass: This substrate was identical to that used in SILMARILS Phase I. We chose to include this substrate because it provided variation in material transparency, surface chemistry, and spectral signature.
- Mass loading: JHU/APL varied the mass loading of deposited target chemicals. Each target was be deposited at a "low," "medium," and "high" mass loading. Exact mass loadings varied from sample to sample.

Description of Sample Coupon Analysis

Optical profilometry was used to determine the average film thickness and surface roughness of the targets deposited onto the sample substrate. Optical profilers are interference microscopes and are used to measure height variations, such as surface roughness, on surfaces with great precision using the

wavelength of light as the ruler. Optical interference profiling is a well-established method for obtaining accurate surface measurements. This analysis method uses the wave properties of light to compare the optical path difference between a test surface and a reference surface. Inside an optical interference profiler a light beam is split into two paths with a beam splitter, reflecting half the beam from a test material and the other half reflected from the instrument's reference mirror. When the distance from the beam splitter to the reference mirror is the same distance as the beam splitter is from the test surface, the split beams are recombined resulting in constructive and destructive interference. This creates the light and dark bands known as interference fringes. Since the reference mirror is of a known flatness (as close to perfect flatness as possible) the optical path differences are due to height variances in the test surface.

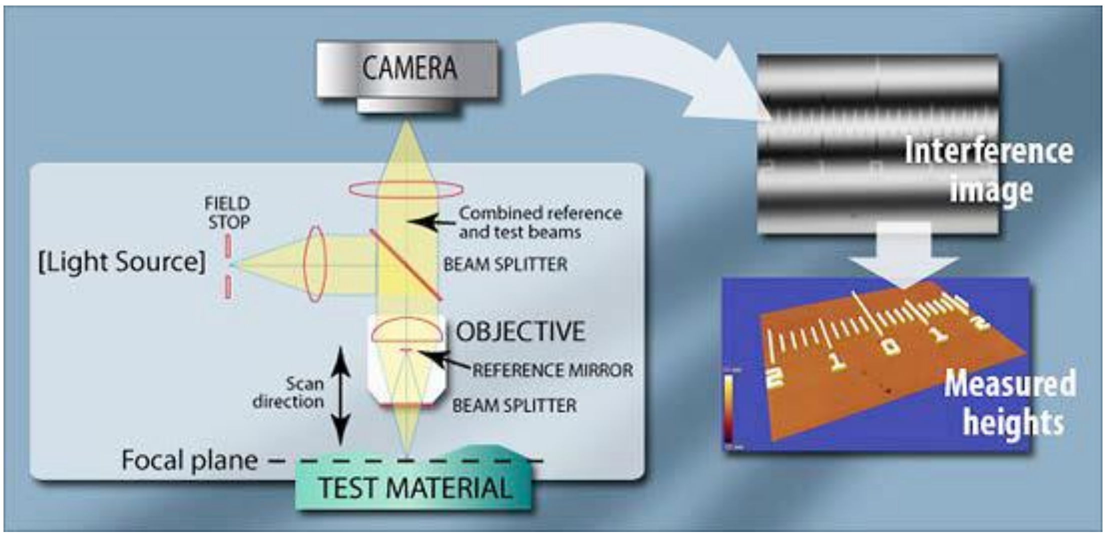

Figure 1. Diagram of a generic optical profilometer.

Differential interference contrast (DIC) microscopy was used to obtain images of the deposited films for fill factor analysis. Since many of the sample coupons consisted of target chemicals existing as transparent films, regular brightfield microscopy was inadequate for further analysis. The DIC optical technique can generate images of transparent films by converting gradients in a specimen optical path length into amplitude differences that can be visualized as improved contrast in the resulting image. The specimen optical path difference is determined by the product of the refractive index difference (between the specimen and its surrounding medium) and the geometrical distance (thickness) traversed by a light beam between two points on the optical path. Images produced in differential interference contrast microscopy have a distinctive shadow-cast appearance, as if they were illuminated from a highly oblique light source originating from a single azimuth. It is important to keep in mind that since this effect renders the image into a pseudo three-dimensional relief, the image cannot be used to directly infer information about film thickness, rather this technique can just be used to better visualize a transparent film.

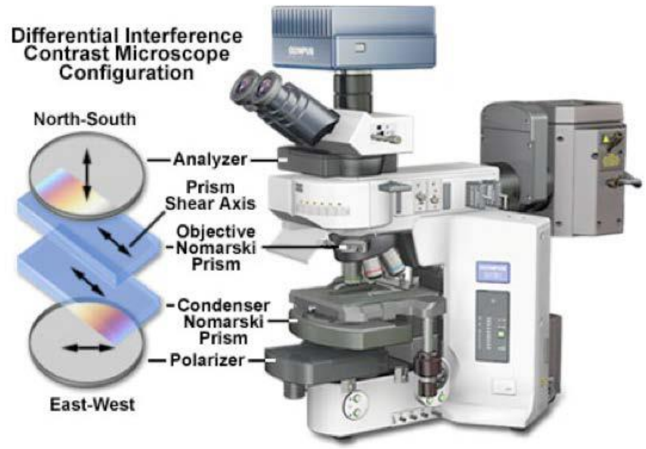

Figure 2. Diagram of a typical differential interference contrast (DIC) microscope.

For the fill factor analysis, images obtained from DIC microscopy were analyzed using tools available in the ImageJ software package. The analysis process involved properly thresholding the deposited film, and then using the software's particle counting feature to determine total amount of surface area covered by the film. Thresholding works by separating pixels into a user defined intensity range. With non-ideal images (images with indiscrete contrast) the intensity values of the features of interest can get lost in the background image, and appropriate thresholding can be very difficult. The thresholding protocols varied based on the details of the sample and choices made by the user. Due to the limits of the analysis technique and contrast of the films, only samples deposited onto smooth surfaces can be analyzed with this process. Fill factor is not given for sample coupons with roughened aluminum as a substrate: the contrast related to surface roughness is greater than the contrast related to the deposited film and proper thresholding is not possible. All fill factor data reported in this document are considered semi-quantitative values.

In images shown throughout this report, black corresponds to coated regions, and white corresponds to uncoated regions.

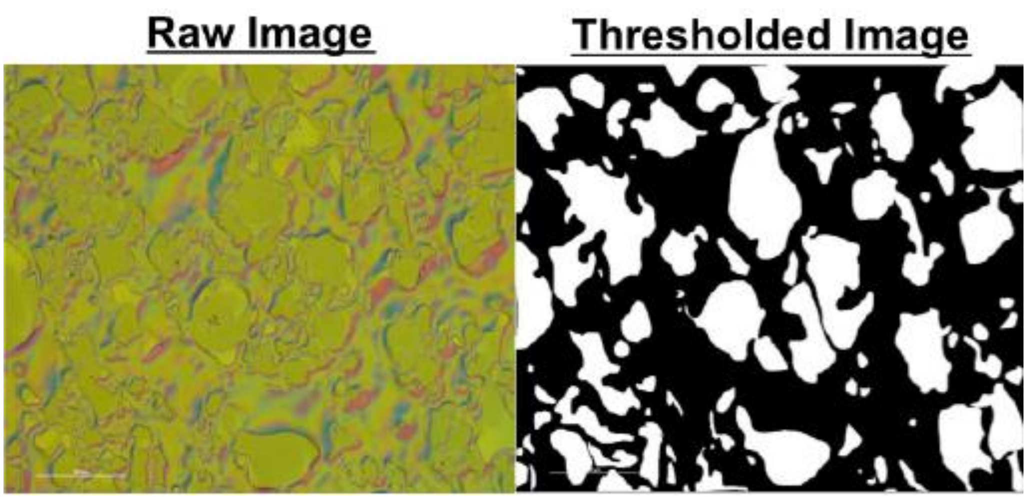

Figure 3. Example image depicting a sample that was difficult to determine fill factor (MORGOTH'S CROWN sample PCC-00052). Notice how there is a lack of contrast between the deposited film (slightly hazy, multi-colored shape) and substrate (flat looking, single colored shape) in the raw image. This lack of contrast between the film and substrate made it difficult to use the auto-threshold feature in ImageJ, and manual thresholding was required to determine the fill factor. Black corresponds to coated area, and white corresponds to uncoated substrate. The fill factor was calculated as approximately 62%.

Prize Challenge Sample Data Characterization Details

Instrumentation

All DIC images were taken using a Nikon LV100ND upright DIC microscope equipped with a Nikon DS-Ri2 camera. All optical profilometer images were taken using a Zeta instruments model Zeta-20 optical profilometer.

Film Thickness Measurement

The film thickness measurements were made by removing a small portion of the deposited film from the substrate using a cotton swab dipped into a solvent appropriate for the target molecule. Film removal was done at each of the coupon corners as depicted in Figure 4. Step height measurements of the bare substrate and deposited films were made using the Zeta-20 software. The measurements were averaged together to obtain an average film thickness. Target material was removed at the corners so as not to disturb the portion of the sample coupon that would be probed in subsequent FTIR measurements by PNNL. It is important to keep in mind that the films deposited in these samples were heterogeneous, and it is natural that film height variations occurred from one location on the sample to another.

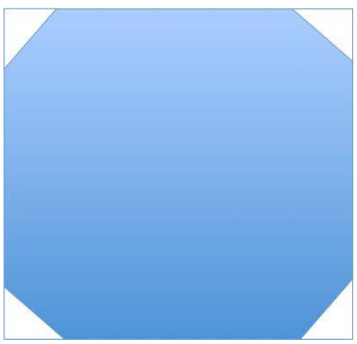

Figure 4. Diagram depicting where the film was removed from the sample coupons for thickness measurements. The white area is where the target chemical was removed and blue area is where the target chemical remained undisturbed.

Analysis of Blank Substrates

Prior to target chemical deposition, blank substrates were characterized. DIC and optical profilometry images were collected. These images were all taken with a 10x objective; scale bars for optical profilometry and DIC images are 149 µm and 100 µm respectively. Since there was no target chemical deposited onto these substrates, fill factor was not calculated. All of the surface roughness measurements have units of microns and are root mean square values.

Analysis of Deposited Films

DIC and optical profilometery images were also collected from all samples following chemical deposition. For some samples, the fill factor analysis proved to be difficult using ImageJ's automatic thresholding features due to the films having low contrast. Images were therefore manually thresholded to calculate fill factor. The fill factor number should be regarded as a semi-quantitative value. All DIC images were taken with a 10x objective; scale bars for optical profilometry and DIC images were 149 µm and 100 µm respectively.