In the market for eye-catching finishes, there is a persistent desire for a dark, high gloss look on both metal and plastic parts. The automotive fashion trend emphasizes subdued metallic palettes that provide a sense of depth and refinement. Consumers are willing to pay a premium for styles that are visually and/or technologically unique, but many colors are marketed to match current fashionable or decorator color trends. In addition, blacks/smokes tend to be associated with performance brands and/or luxury that transcend the need for flashy, bright colors.

In many applications, the mechanical properties of plastic are sufficient, as the plastic is lighter and less costly to produce. However, applications such as automotive wheels require metals to withstand significant mechanical loads. Where possible, finishers prefer coating processes with the option to coat both plastic and metal substrates in the same system. In addition to color, durability is important to all applications. Decorative coatings that require high durability include automobile components, sanitary fixtures such as faucets, and durable goods such as home appliances. While multi-layer painted coatings are used for some of these applications, there can be issues with cost, durability, and the handling and recycling of volatile chemicals. Also, aggressive cleaning methods such as scrubbing with steel wool and strong cleaning chemicals used commonly for plumbing fixtures and car wheels are too aggressive for painted surfaces.

When paints are insufficient for the look, performance, or durability, electroplating has been another common approach. Vendors of electroplating chemicals have developed proprietary systems to produce a range of dark coatings of different gloss levels. Many metals can be plated, but good plating of plastics is possible only on certain types of plastics. Plastic plating requires what are referred to as plating grade plastics, either acrylonitrile butadiene styrene (ABS) or polycarbonate/ABS blends. The electroplated substrate requires a butadiene etch to provide an anchoring texture. Several suppliers have invested significant capital for plating processes, but a deterrent to growth of electroplating, at least in the US and Europe, is the cost and risk of safely handling the required chemicals, often including hexavalent chromium. Hexavalent chromium is a known human carcinogen. This is not only required in some plating baths, but also to etch the ABS substrates.

Physical vapor deposited (PVD) coatings offer a pathway to produce colorful, hard, durable decorative coatings on many different substrates. Furthermore, PVD offers an acceptable capital outlay while completely avoiding the use of hazardous materials. However, PVD can be a hot process, and every substrate has temperature limits. Most metals have higher tolerance to heat compared to plastics. Since so many parts have been already qualified for electroplating, PVD needs to be capable of coating the...
common plating grade substrates. Plating grade plastics have a temperature limit in the range of 50°C to 130°C. Mixed substrates are not uncommon for plastic plating fixtures to begin with an electroplated surface to which a PVD decorative layer is applied. Conversely, metal automotive wheels often have an organic powder coat that receives the PVD coating. This article shows the approach to developing a coating on electroplated plastic used in plumbing fixtures, which could also apply without an electroplated coating or be used on metal substrates.

**Product Definition and the Science of Characterization**

Defining the exact appearance of a coating quantitatively can be a challenge. Color is scientifically defined by the CIE color space, CIELAB D65 is commonly used. An example of this color space is shown in Fig. 1. CIELAB uses the U* lightness index to define pure black to pure white (0-100). The color opponents are defined as a* and b*. The component a* represents red as positive and green as negative numbers. The component b* represents yellow as positive and blue as negative numbers. By “dark,” a common negative number. The component b* represents yellow as positive and green as negative numbers. The component a* represents red as positive and green as negative numbers. The component b* represents yellow as positive and green as negative numbers. The component a* represents red as positive and green as negative numbers. The component b* represents yellow as positive and green as negative numbers. The component a* represents red as positive and green as negative numbers. The component b* represents yellow as positive and green as negative numbers.

ZrCN coatings have been prepared by different techniques including plasma assisted CVD [10], arc evaporation [11,12], magnetron sputtering [13] and ion beam sputtering [14]. Literature concerning ZrCN films deals with the process details of plasma-aided chemical vapor deposition, mainly discussing how to grow ZrCN films at relatively low temperature [10,13]. Holstein et al. [11] deposited a group of ZrCN films by means of cathodic arc and investigated their use for tools used in minimally invasive surgery. The result indicated that ZrCN is a candidate for coatings on surgical tools where short-term biocompatibility is required. Re et al. [14] deposited a group of Zr-based films and found good corrosion resistance with ZrCN films. Yao et al. [15] showed that over an acetylene-nitrogen (C\textsubscript{2}H\textsubscript{2}:N\textsubscript{2}) reactive gas flow rates. Using a flow of methane (CH\textsubscript{4}) ion beam sputtering revealed a maximum in hardness of ZrCN at x = 0.6, corresponding well to a theoretical model [16].

Direct current reactive magnetron sputtering offers a few potential advantages over a cathodic arc approach to ZrCN on plastic parts. Many molded parts have complex, high aspect ratio geometries. To achieve uniform coating on the visible areas, it is necessary to move parts through many angles and positions. This is usually done with either a single axis or planetary rotation arrangement. The plastic is also electrically insulating, unless electroplated. Cathodic arc coatings typically rely on an electrical bias for density and hardness. The motion and insulating nature of substrates can make applying a bias challenging in a production environment. A sputtered coating may not need bias. The defined coating appearance has to be durable. The need for sputtering mechanisms for sputtered films have been well documented [17,18]. The need for sputtering mechanisms for sputtered films have been well documented [17,18].

**Determination of Film Optical Properties**

Although many approaches to determining the absorption coefficients of thin films have been addressed over the decades [21] using spectrophotometers or ellipsometers, a rapid and inexpensive method was sufficient to guide process refinements. Films with thickness, d, thin enough to allow low transmission across the visible spectrum were deposited onto glass slides. Transmission and film-side reflection were measured with an Ocean Optics USB2000 fiber optic spectrometer. Since these films were so specular (non-scattering) all the measured light is accounted for. The sum of transmittance, T, reflectance, R, and absorbance, A, \((T + R + A = 1)\) under the ideal conditions of absorption coefficient, \(a_{\lambda}\), and thickness, d, and where (\(A_{\lambda}\)) and (\(A\)) are the initial and final light levels measured, is expressed by:

\[
A_{\lambda}(\lambda) = 1 - T(\lambda) - R(\lambda)
\]

\[
A_{\lambda}(\lambda) \approx A_{\lambda}(\lambda) a_{\lambda}(\lambda) = e^{-nm}
\]

We found we could ignore errors in derivation of a from sources such as back side reflection and mis-registration between T and R measurement locations for the purpose of selecting process parameters. For the lower power transistors, since the films were so specular (non-scattering) all the measured light is accounted for. The sum of transmittance, T, reflectance, R, and absorbance, A, \((T + R + A = 1)\) under the ideal conditions of absorption coefficient, \(a_{\lambda}\), and thickness, d, and where (\(A_{\lambda}\)) and (\(A\)) are the initial and final light levels measured, is expressed by:

\[
A_{\lambda}(\lambda) = 1 - T(\lambda) - R(\lambda)
\]

\[
A_{\lambda}(\lambda) \approx A_{\lambda}(\lambda) a_{\lambda}(\lambda) = e^{-nm}
\]

**Developing the ZrN Deposition Process**

Development began with locating a suitable ZrN coating process. The first step was to supply and having the deposition chamber ready as an anode. Gases were introduced through stainless steel tubing with occasional small holes. Maintaining a 50/50 mix of Ar and H\textsubscript{2} flow was found where the target was fully poisoned. The produced well-known gold color. From there, acetylene (C\textsubscript{2}H\textsubscript{2}) was added. It was found that resulting film was not only very hard, but also very electrically insulating, creating a strong peeling and adhesion effect. The only part of the system that remained electrically conductive was a few mm around the gas feed holes of the manifold. Since all the current was focused there, the manifold was water-cooled in a water-cooled discrete anode and an Advanced Energy AMS/DMS operated in what has been referred to as “Pellemoine [20], although with only a single cathode.” We also discovered a significant impact of gas flow within the system for the incorporation of carbon into the sputtered films. The magnetron is positioned approximately 2 feet (61 cm) from the gas feed holes of the manifold. Since all the current was focused there, the manifold was water-cooled in a water-cooled discrete anode and an Advanced Energy AMS/DMS operated in what has been referred to as “Pellemoine [20], although with only a single cathode.” We also discovered a significant impact of gas flow within the system for the incorporation of carbon into the sputtered films. The magnetron is positioned approximately 2 feet (61 cm) from the gas feed holes of the manifold. Since all the current was focused there, the manifold was water-cooled in a water-cooled discrete anode and an Advanced Energy AMS/DMS operated in what has been referred to as “Pellemoine [20], although with only a single cathode.”

\[
A_{\lambda}(\lambda) = 1 - T(\lambda) - R(\lambda)
\]

\[
A_{\lambda}(\lambda) \approx A_{\lambda}(\lambda) a_{\lambda}(\lambda) = e^{-nm}
\]

**Table 1. Reactive sputtering process parameter settings for ZrCN films. The total gas flow rates ranged from 400 sccm to 600 sccm. Relative flow rates of the three process gases are shown in Table 1.**
Determination of Film Stress

A subsequent series of coatings that were thick enough to be opaque were produced on both plastic and silicon wafer substrates. Many of these films displayed high compressive stress; some films spontaneously delaminated. Stress was measured using pre-characterized silicon (100) wafers, a profilometer to measure curvature, and Stoney’s equation (22) for a single film on a substrate, where \( s \) is the film stress, \( E \) is Young’s modulus of the substrate, \( R \) is the radius of curvature of the wafer, and \( t \) and \( \nu \) are substrate and film thickness, respectively. Fig. 5 shows stresses measured on silicon wafers as compressive as -800 MPa. However, on the plastic substrates, the film stress is likely to be much more compressive.

The stress due to thermal contraction can be estimated as follows. The coating is deposited hot, and the entire system contracts as it cools to room temperature. The film is much thinner than either of the substrates, so the substrates contract, apply a stress to the film. The total stress on the film is comprised of the thermal stress, the intrinsic film stress, and any externally applied forces. The total stress on the wafer is what is measured with the profilometer. When these are subtracted we get,

\[
\sigma_{\text{total}} = \sigma_{\text{thermal}} + \sigma_{\text{intrinsic}} + \sigma_{\text{external}}
\]

The film coefficient, \( \alpha \), disappears from the relationship. Using values gleaned from literature, compiled in Table 2 the film on plastic, \( \alpha_{\text{Covestro T65XF® (plastic)}} = 80 \times 10^{-6}/\degree \text{K} \), and on silicon, \( \alpha_{\text{Si (100)}} = 2.6 \times 10^{-6}/\degree \text{K} \), can be used.

The film coefficient, \( \alpha \), varies over the temperature range,

\[
\sigma_{\text{thermal}} = \frac{E_f}{1 - \nu_f} \left( \alpha_f - \alpha_v \right) \left( T_{\text{dep}} - T_{\text{ambient}} \right)
\]

If external forces are negligible or identical for both the wafer and plastic,

\[
\sigma_{\text{wafer}} = \sigma_{\text{plastic}} = \sigma_{\text{total}} = \sigma_{\text{thermal}} + \sigma_{\text{intrinsic}} + \sigma_{\text{external}}
\]

The determination of the thermal effect cannot be ignored. Since it assumes the system was at thermal equilibrium before any coating was applied, and that the different substrates absorb heat equally. However, it shows that the thermal effect cannot be ignored.

Determination of Film Abrasion Resistance

Abrasion was assessed as the percentage of area where coating was removed. Films made with very high C/H flows were easily damaged. Films that required microscopic observation to assess steel wool abrasion were assessed between 0% and 2% removal. Among these, Fig. 6 shows that flows near 10% C2H2/N2 were tolerated. Films made with very high C/H flows (0.08 to 1.0) showed low chromaticity was achieved at higher values of both reactive gases.

Conclusions

Excellent fundamental work on designed experiments to optimize process conditions in multivariable response surfaces has been available for years. Also, more mathematically oriented approaches exist in the literature. They essentially rely on devising weighting functions for the various responses. Designed experiment methods are excellent when a rudimentary process is already established. Here, no such process existed. However, 9 shows that low chromaticity was achieved at higher values of both reactive gases.

Fig. 2 - Spectral Absorptivity of four ZrCN films. Results are shown for different process conditions A, E, H, and K, as detailed in Table 1.

Fig. 3 - Absorptivity (a measure of absorption coefficient) at 550 nm as a function of relative gas flows and manifold position.

Determination of Film Abrasion Resistance

Absorption tracks C2H2/N2.

Table 2 - Nominal values of materials used in the thermal stress calculation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nominal value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_f )</td>
<td>400 GPa</td>
</tr>
<tr>
<td>( \nu_f )</td>
<td>0.25</td>
</tr>
<tr>
<td>( \alpha_{\text{Covestro T65XF® (plastic)}} )</td>
<td>80 ( \times 10^{-6}/\degree \text{K} )</td>
</tr>
<tr>
<td>( \alpha_{\text{Si (100)}} )</td>
<td>2.6 ( \times 10^{-6}/\degree \text{K} )</td>
</tr>
<tr>
<td>( T_{\text{dep}} )</td>
<td>100°C</td>
</tr>
<tr>
<td>( T_{\text{ambient}} )</td>
<td>25°C</td>
</tr>
</tbody>
</table>

Fig. 5 - Contour plot showing compressive stress dependence on relative flow of gases. The pink dots indicate values were data was collected. The red triangular outlined field denotes a process region to be avoided.

Fig. 7 - ZrCN film color opponents a* and b* produced with reactive gas ratios of C2H2/N2 of 0.8 to 1.0.

Fig. 9 - Chromaticity as a function of reactive gas flow ratios. The red outlined region denotes a process area to be avoided.
rather than a purely empirical approach, a method of overlaid contour plots is roughly followed [24]. This is good for three variables. The need was to identify the main variables and determine boundaries for a best possible operating space.

The competing demands of good abrasion resistance, moderate stress for good adhesion, and dark, neutral color are almost mutually exclusive. By overlaying plots of chromaticity, absorptivity, film stress and damage with respect to process gas flow rates, acetylene and nitrogen, a composite plot in Fig. 10 was used to show potentially the process conditions to make a film with the best characteristics. Direct current reactive magnetron sputtering with a discrete anode produced moderately dark, neutral ZrCN coatings on plastic parts in a very narrow process space. More generally, a method was shown how to approach a new coating that has multiple, and sometimes conflicting requirements.

In the future, we will develop methods of creating greater incorporation of carbon to make a darker coating without overheating the plastic substrate or losing abrasion resistance. This may include addition of a.c. or r.f. electrodes with the sputtering process. The sputtering process space for both hard and dark films may be widened by operating at less than fully poisoned conditions using emission spectrometry control. This could change the relative arrival rate of metal/non-metal which shows a way to increase film hardness [25].

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References


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Michael Brazil is the senior scientist at Vergason Technology, Inc. A process engineer at heart, Michael has been developing vacuum deposited thin films and the tools to manufacture them since the early 1980s for a wide variety of industries in the US and China, including automotive windshields and trim, architectural glass, recording media, lithographic printing, flexible circuits, EMI shielding, photovoltaics, consumer electronics and telecommunications. He patented the XIR windshield coating, now owned by Eastman and in more than 20 million cars. He has worked for large, well-known companies like Guardian Industries, Seagate and Corning, as well as small companies like Southwest and Prentek. He graduated from Pomona College with a B.A. in physics and from the University of California at Berkeley with a Ph.D. in materials science.