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Technical White Paper

# Durable Neutral Color Anti-Reflective Coating for Mobile Displays

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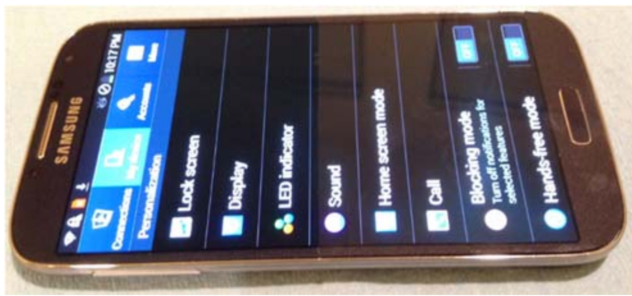


*Figure 1: Samsung S4 with top half of cover glass coated with AR+DLC*

**Abstract**

An in-line PECVD (plasma enhanced chemical vapor deposition) process is used to deposit a high performance AR+DLC coating for cell phone and tablet displays. The coating is a 7 layer stack consisting of a 6 layer AR of alternating SiN and SiO2 thin films and a DLC top coat. The use of SiN as the high index layer benefits not only overall durability, but the low dispersion of SiN widens the process window needed to maintain neutral color. The optical performance inclusive of the DLC is less than 0.70% reflectance from 450-650nm with the a*, b* color range within +/-1.5 absolute value. Key characteristics of the PECVD process are long term stability and uniformity, both critical to AR coating production. The high deposition rate allows a tool with one PECVD source per layer (more for the DLC) to produce 800km$^2$ /year making large quantity production of small displays practical. The experimental data and results for optical measurements and durability and environmental tests are presented.

**Introduction**

Every display - cell phones, tablets, laptops, TV's - needs an anti-reflection (AR) coating. Uncoated glass reflects 8% of incoming light, 4% per side. This is what makes viewing so difficult in high ambient light conditions and degrades display color contrast. The use of sapphire for cover screens makes this worse. Sapphire has twice the light reflection of glass. In spite of the need - and the large market opportunity - AR coatings are not common on displays. The reason for this are the application's challenging environmental and durability specifications and the limitations of existing deposition technology.

Currently, AR coatings are made by either ion beam assisted deposition (IBAD), reactive sputtering or wet coating processes. IBAD can make quality AR films but mass production is not practical due to limits on batch size and cycle time. The IBAD process requires a large box coater and deposits successive layers using electron beam evaporation. The way the substrates are suspended and rotated over the evaporation sources limits the maximum substrate size to 0.1 $m^2$. A typical batch cycle exceeds 1 hour.

Reactive magnetron sputtering is scalable and capable of large volume production. However, as suggested by current sputtered AR products, maintaining absolute thickness uniformity is difficult. This is witnessed by the typical purple or green shading of these AR's. This color bias is intentionally done to hide color variation caused by layer non-uniformity. Another challenge for reactive sputter is deposition rates are low so multiple cathodes are required for each layer. This exacerbates uniformity/stability issues and makes sputter systems large and expensive.

Wet coating is an attractive method to make AR's due to the inherent low cost and high production volume of the process. While limited success has been achieved, the performance of these films remains below thin film vacuum deposited films. This reduced performance includes both the optical AR properties and durability.

**UltraDep™ Technology**

General Plasma has developed a stable, high rate PECVD process for large area coating termed UltraDep™ [i]. In the General Plasma process, the magnetically confined electrodes are hidden in a cavity and are not coated during a production run. The result is General Plasma's PECVD process operates for days and weeks without process variation or loss of uniformity. General Plasma has been granted several patents and has additional patents filed on both the process apparatus and method.

*Figure 2: an UltraDep™ in-line PECVD module*
*A magnetically confined plasma and delivers a dense, linear plasma beam across the substrate. Similar to in-line sputtering, the substrate is moved relative to the source to achieve uniformity. This source is for 1 meter wide substrates.*

In addition to stable operation, UltraDep$^{TM}$ has other important features and benefits:

- Uniform deposition over large substrates to +/-1%
- Generation of an energetic ion flux to the substrate enables dense films on insulating substrates such as glass
- High deposition rate, 5-10x faster than reactive sputtering

**<u>AR Coating with DLC Top Coat</u>**

**Optical Performance**

The novel PECVD process is used to deposit a 7 layer stack consisting of a 6 layer AR film and a DLC coating (patents pending). The 6 layer AR coating is composed of alternating SiN and SiO2 thin films. The optical performance of the complete stack is less than 0.70% reflectance over the visible spectrum (450-650nm) with the a* b* color within +/-1.5 absolute value (neutral color). Figure 3 shows the reflection & color performance for the coating.

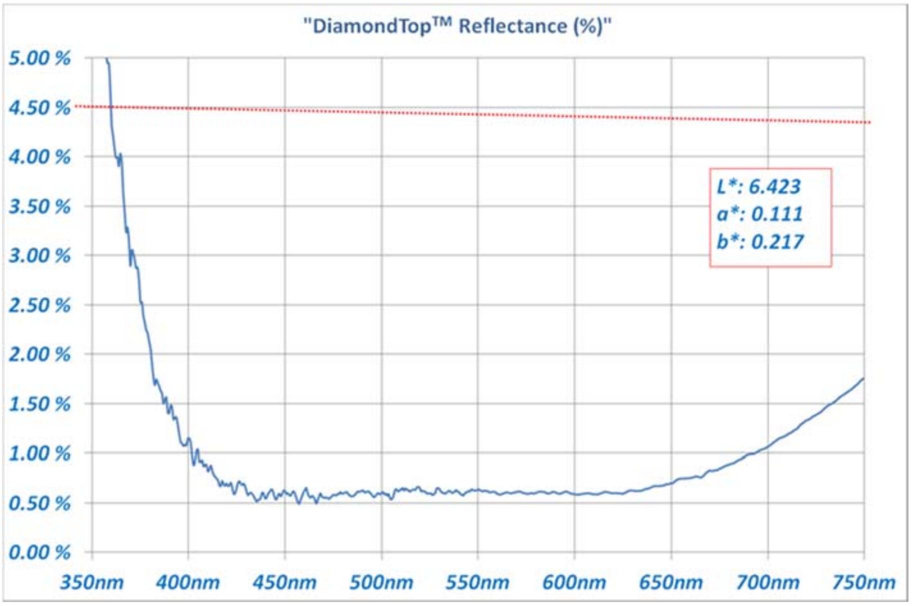


*Figure 3: Anti-reflective optical reflection spectrum*

Figure 4 overlays reflectance curves from different runs over 5 days of production. As can be seen, coating reflectance variations are less than 0.1% at all visible wavelengths.

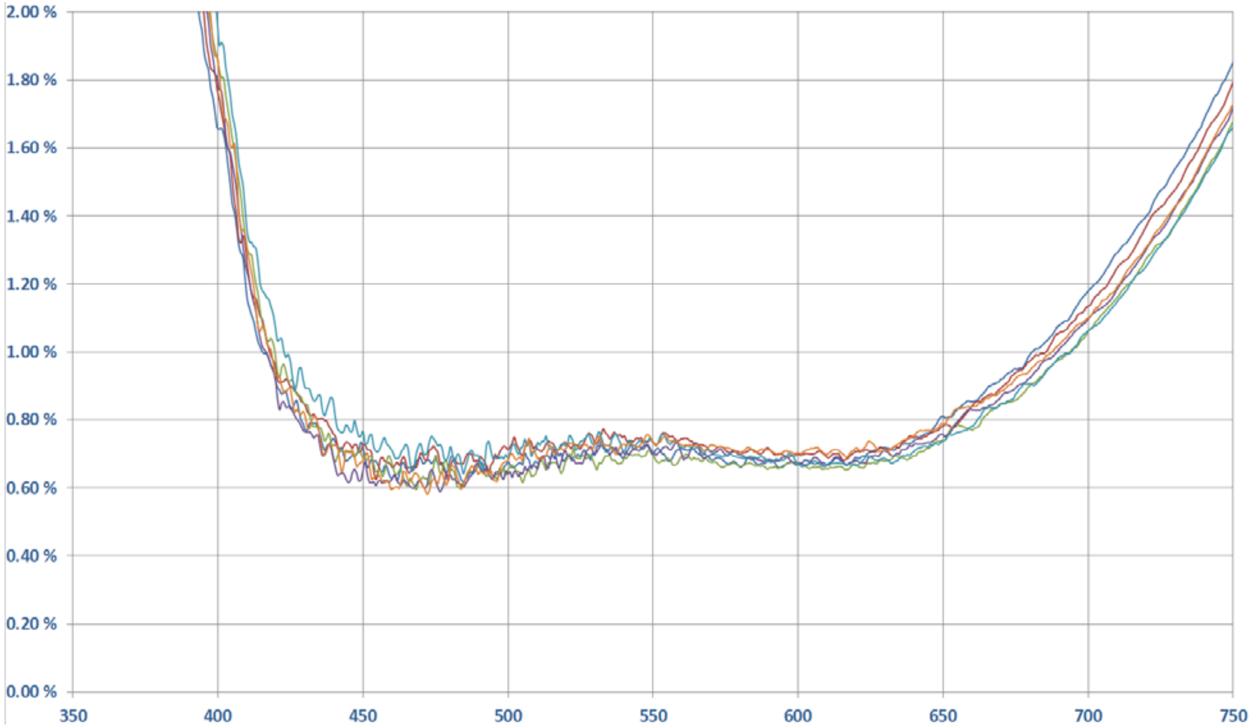


*Figure 4: Anti-reflective optical reflection spectrums from run to run over 5 days of production*

The color of the AR coating is equally, if not more important than reflection performance. The ideal AR has a neutral color without a purple or green color bias. GP's AR+DLC coating achieves this ideal performance with a*, b* color within +/-1.5 absolute value. Two aspects of General Plasma UltraDep™ technology make a neutral color AR possible: 1) Dense, amorphous SiN can be deposited with a sufficiently high index (>1.9) film for the AR design. SiN has lower dispersion than TiO2 and this importantly widens the color process window. And 2), the PECVD process is uniform and stable. Uniformity is +/-1% and this uniformity is maintained as shown in Figure 2.

**Scratch Resistance and Environmental Durability**

The DLC top coating applied to the AR stack provides resistance to scratching and environmental durability. DLC has been applied to glass before for these reasons.[ii] Using UltraDep™ however enables conditions that make DLC coating practical for glass and other non-conductive substrates:

- With an RI of ~2.0, a DLC coating alone on glass can make reflection worse (depending upon DLC thickness). Because of the before mentioned sputtering uniformity challenges, a multi-layer AR coating in combination with a DLC was not possible. With the UltraDep™ process, a DLC can be coated on top of a high performance 6 layer AR with little difficulty.
- DLC deposition, like other PECVD processes, presents source electrode coating challenges. As with the optical layers, the self-cleaning operation of UltraDep™ electrodes allows for long term DLC deposition.
- The dense ion beam produced by UltraDep™ technology provides the ideal energy per particle flux to create a non-absorbing, high performance DLC film.

The result is an extremely tough film that is harder and more scratch resistant than the native cover glass. Figure 5 compares the scratch resistance of chemically strengthened glass to GPI's AR+DLC coated glass.

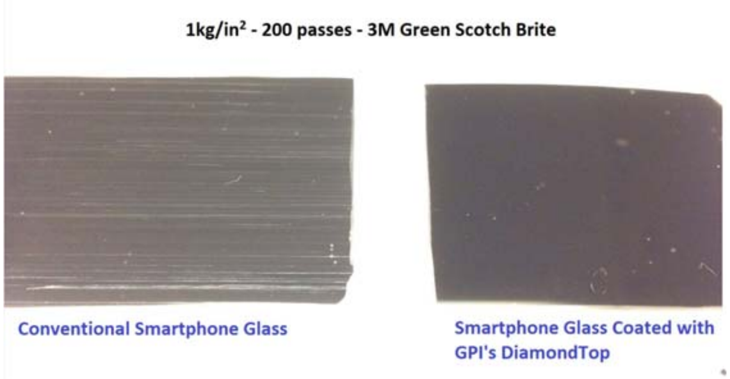


*Figure 5: Scratch comparison between glass and AR+DLC coated glass*

Additionally, the hydrophobicity of the film is equally durable. Using an automated scratch tester with 0000 steel wool covering a 1cm2 'finger' and a 1kg weight, after more than 10,000 cycles the DLC coated AR stack shows no change in water contact

angle (Figure 6).

*Figure 6: Water contact angle before and after 10,500 pass scratch test*

Using the Erichson pencil test, the DLC +AR hardness was 4.0N vs. the 0.5N of other high quality AR coatings.

Beyond scratch testing, the complete AR+DLC stack demonstrates excellent hardness and durability. A selection of results are:

- Nano-indentation test measurement of 9.4 GPa. (Note that this is a measurement of the underlying SiN/SiO AR only as the DLC is too thin to be detected by this test.) For reference, nano-indentation test measurement of Corning's Gorilla glass 3 is 8.6 GPa.[iii]
- Adhesion to the base glass and between film layers is excellent. Using standard grid/tape test methods, a 1mm square grid was cut into the stack to the substrate and a pull tape test done. The adhesion result met a 5B (no visible delamination) on the test scale. After this the sample, with the cut grid, was immersed in boiling water for 10 minutes and then repeat tape tested. Again, no adhesion failure was seen. Finally, sample is immersed in salt bath (150mg pure NaCl in 600ml of DI water) at 80°C for 24 hours and repeat tape tested. This series of tests, boiling a grid cut sample, is extremely aggressive. Any columnar film structure, excessive hydrogen or interlayer defects in the layers will cause delamination when the exposed stack is boiled in water.
- After repeated and extended contact with cleaning agents such as IPA and acetone, no loss of adhesion or damage to coating occurs.

**Anti-Fingerprint Functionality**

DLC is hydrophobic and therefore a natural anti-fingerprint coating. In testing, the water drop contact angle exceeds 90 degrees and the roll off angle is 15 degrees. Figure 6 shows an S4 phone half coated with the AR+DLC coating. Both halves of the screen were equally smudged before this photo was taken.

While the water contact angle is not as high as that of evaporated fluorocarbon layers, DLC AFP properties are durable and relatively insensitive to chemicals and solvents.

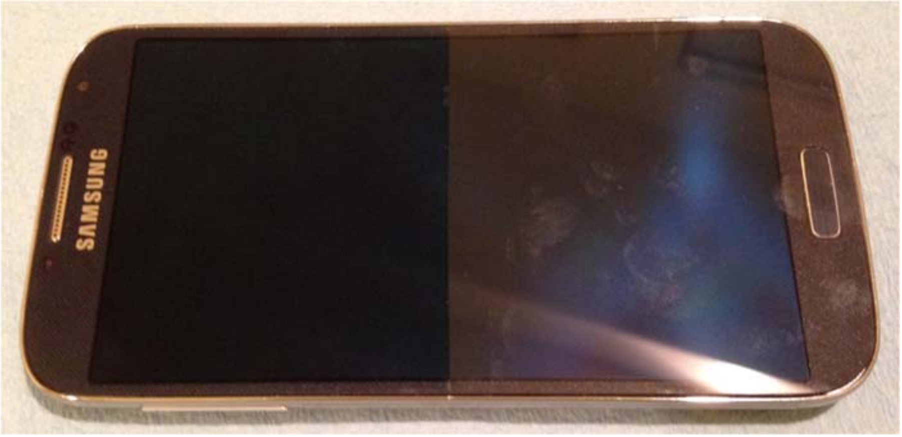


*Figure 6: Anti-Fingerprint demonstration shows top side AR+DLC resists fingerprinting (top half coated with AR+DLC)*

**Conclusion**

For the first time a durable AR+DLC coating is available for cell phones, tablets and other displays. The AR performance, neutral color appearance and exceptional durability meet and exceed the tough requirements for mobile displays. A new in-line PECVD process invented by General Plasma, makes this coating possible and meets industry requirements for high volume/low cost manufacturing.

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[i] Plasma Enhanced Chemical Vapor Deposition (PECVD) for Large Area Applications, John Madocks, W. Seaman, M.A. George, Q. Shangguan, General Plasma, Tucson, Arizona, USA, 2010 Society of Vacuum Coaters 53rd Annual Technical Conference Proceedings

[ii] Large Area Ion-Beam Deposition of Hydrogenated Tetrahedral Amorphous Carbon on Soda-Lime Glass, V.S. Veerasamy, R.H. Petrmichl, H.A. Luten, and S.V. Thomsen, Guardian Industries Corporation, Carleton, MI, 2002 Society of Vacuum Coaters 45th Annual Technical Conference Proceedings

[iii] Corning Gorilla Glass 3 with NDR / Product Information Sheet / E_050613, Corning Corporation, www.corninggorillaglass.com, 2013