High Index, UV Stable NIL Formulation for XR Waveguides

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Abstract

High refractive index waveguides are a key requisite to achieving both a large field of view and high efficiency in extended reality (XR) displays. Manufacturing these waveguides requires nanoimprintable formulations that result in highly transparent structures with high refractive index. This paper focuses on Pixelligent's UV-stable, high-index nanoimprint formulation, PixNIL® SCS1, as tested on a EVG®7300 SmartNIL system by the industry-leading EV Group. PixNIL®SCS1 produces high quality binary, blazed, and high aspect ratio gratings with unparalleled nanoparticle distribution in the structures while maintaining <2 nm surface roughness. Additionally, this formulation enables a large process window with > 24h pot life stability and results in nanocomposites that are stable under UV exposure at > 405 nm.

Keywords: nanoparticle, nanocrystal, nanoimprint, high refractive index, nanocomposites, extended reality, field of view, low residual layer thickness, waveguide, surface relief gratings

Introduction

Extended Reality (XR) displays join virtual images with real-world content to create new possibilities for human and machine interactions. Such displays rely on diffractive, or reflective waveguides, combine the virtual content with the ambient images seen through the XR lenses. For next-generation XR displays, diffractive waveguides with Surface Relief Gratings (SRG) on high refractive index substrates are now considered an essential enabling technology.

High refractive index resins processable by using Nanoimprint Lithography (NIL) are vital when manufacturing XR glasses on a wafer level to achieve low production costs and a high field of view (FOV). In addition to low haze, high visible light transparency, and high refractive indices (RI), these resins must deliver nanoimprint lithography (NIL) performance with optimal filling of the waveguide structures, excellent compatibility with industrial stamp materials, and robust mechanical properties. During the manufacturing process, these resins should be easy to process, possess long shelf-life and pot-life, and produce high-quality waveguides with optimal and consistent structures. Common issues associated with high index materials include poor control over nanoparticle surface chemistry and size, resulting in poor dispersion and larger-sized particle aggregates that cause light scattering and haze. Additionally, next generation waveguides will require increasingly smaller feature sizes, i.e., smaller than 100 nm, that will become difficult to fill homogeneously with larger and non-uniform nanoparticles.

Pixelligent has been developing its proprietary method of synthesizing and capping nanocrystal metal oxides for well over a decade. This has resulted in the company's industry-leading PixClear® Zirconia and Titania nanocomposites that have refractive indices ranging from 1.7 – 2.0. Through our proprietary capping chemistry processes, Pixelligent can customize the surface of nanocrystals to be compatible with a vast array of resin systems. The recently launched PixNIL® and PixJet® formulations, for example, are an excellent demonstration of these combined capabilities and were engineered to be compatible with nanoimprint lithography (NIL) and inkjet printing manufacturing processes respectively. These products exemplify Pixelligent's unique abilities to tune RI, viscosity, and mechanical properties while delivering the highest transparency, lowest haze, and best reliability. Superior control of capped particle sizes with a narrow size distribution ranging from 5nm to 20 nm particles, provides unparalleled optics and compatibility with even the smallest required grating structures. Table 1 shows Pixelligent's PixNIL® solvent-based formulations with film refractive index values ranging from 1.7 to 2.0.

With the recent introduction of the PixCor™ technology, and the corresponding PixNIL® SCS1 formulation, Pixelligent has delivered significant improvements in optical film stability under light exposure above 405 nm. This UV-stable material, based on growing a ZrO_2 shell around a PixClear® TiO_2 nanocrystal, provides an RI of 1.86, while maintaining excellent waveguide imprinting that is equivalent to the lower-RI organic-based materials currently available in the market.

This paper focuses on Pixelligent's UV-stable, high-index nanoimprint resin formulation, PixNIL® SCS1, as tested on the industry-leading EV Group's EVG®7300 SmartNIL system. The analysis will highlight the best-in-class optical properties, formulation stability, uniform dispersion of nanocrystals throughout the nanostructures with the NIL process, and the capacity to achieve high structural fidelity with both binary and slanted gratings. Additionally, SCS1 showcases a wide process window, providing greater flexibility during nanoimprint production.

Table 1. Pixelligent's PixNIL® formulation products

Product	Core	RI (589 nm)	FT Range (nm)
PixNIL® SZ1	PixClear® ZrO_2	1.7	200 – 1200
PixNIL® SCS1	PixCor™	1.86	100 – 500
PixNIL® ST2	PixClear® TiO_2	1.9	100 – 1200
PixNIL® ST5	PixClear® TiO_2	2.0	100 – 1200

Methodology

SmartNIL® Replication with EV Group

For the wafer-level NIL replication process, the SmartNIL® technology was used. The process flow consists of two steps: First, manufacturing multiple low-cost polymer working stamps (WS) out of a previously manufactured master and then utilizing them for the actual imprints during the second step. This intermediate approach avoids wearing out the original master template and improves the overall production economics, as the achievable number of imprints is increased tremendously. Defective working stamps can be replaced quickly and at low cost, proving particularly advantageous during high-volume production runs. The NIL process is depicted in detail in Figure 1.

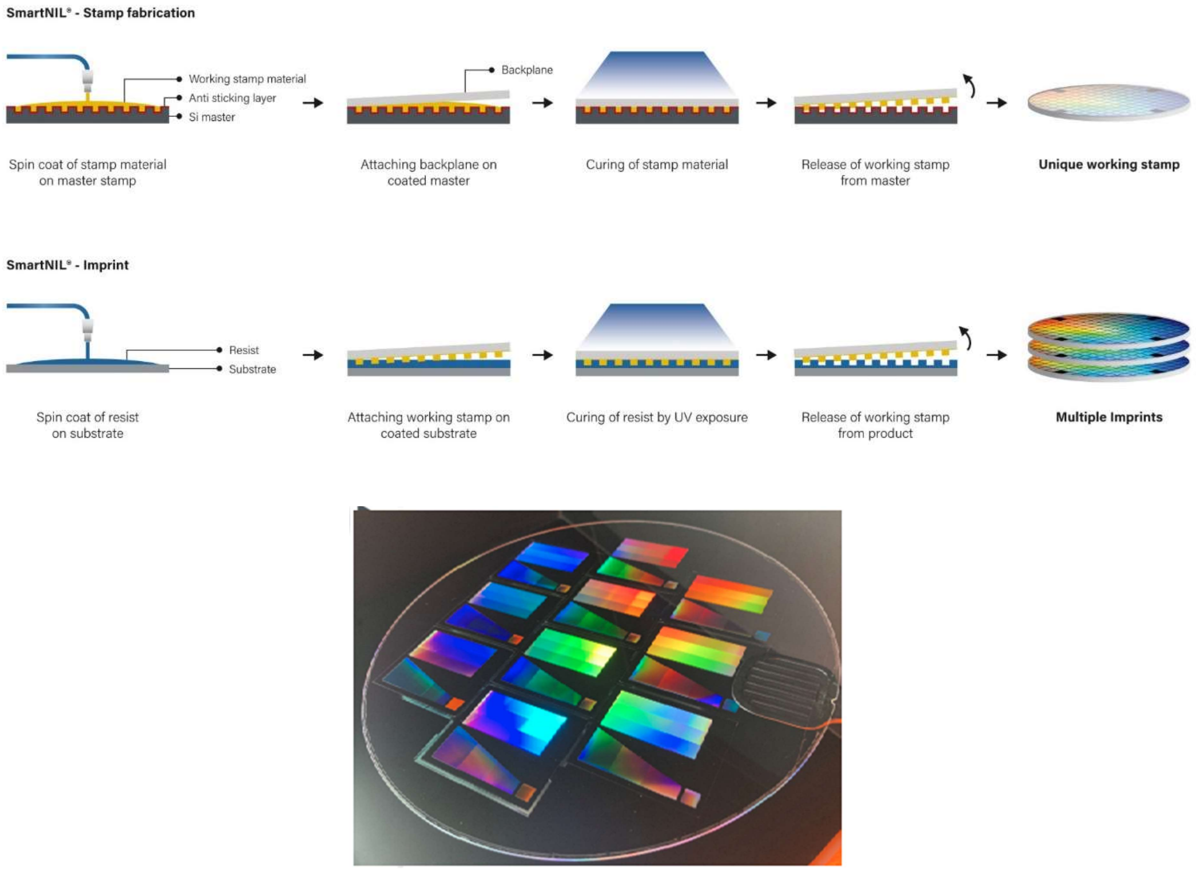

Figure 1. SmartNIL® replication process flow and a PixNIL® resin imprinted on 200-mm wafer

To ensure defect-free WS fabrication, the master is coated with an anti-sticking layer applied by spin coating. The WS material is then dispensed directly on the master, also by a spin coating process. Next, the transparent SmartNIL backplane is attached to the coated master. After curing the WS polymer using a UV LED, it is finally demolded from the master. Upon completing this process, the actual SmartNIL imprinting process begins, where a dedicated material is applied onto the substrate using the same process used for the WS fabrication, e.g., spin coating. The WS and the substrate with the dispensed material are then brought into contact. Similar to the WS fabrication, this step is followed by UV curing and demolding, allowing multiple imprints to be made with the final structures. Reusing the WS for multiple imprints during SmartNIL replication increases the process efficiency and has been well-proven in high volume manufacturing. Furthermore, even though the full SmartNIL imprint process described is split into two parts, the entire process can be implemented on the same equipment. This work is performed on the EVG®7300 SmartNIL system using 200 mm or 300 mm wafers.

Results and Discussion

One of the challenges of making successful nanocomposite materials is achieving uniform dispersions of the nanoparticles in specific resins. Pixelligent's PixCor™ core-shell nanocrystals have an average particle size of 20 nm with a narrow particle size distribution and unparalleled compatibility with solvents and monomers. Formulations with Pixelligent's nanocrystals offer long shelf-life stability under a range of storage conditions, long pot life for stability on a production line, and fast and facile UV curing for high-volume manufacturing.

The scope of this white paper will highlight the following aspects of the PixNIL® SCS1 resin:

1. Formulation Stability
2. Optical properties of flat films
3. Nanoimprinting Structures
4. UV Reliability

Formulation Stability

Shelf-life is an important feature for NIL resins, as the resin needs to remain relatively unchanged when used over many weeks to months. This storage stability is required to match not only customer storage preferences, but also to endure extreme shipping conditions (4C and 50C) used during standard shipping processes. Pot life stability is also important as the resins need to remain stable when utilized within a daily / shift time frame. Table 2 displays these four important stability criteria in terms of viscosity stability for the PixNIL® SCS1 formulation. Overall, the PixNIL® SCS1 formulation maintains comparable values to the initial viscosity (1.64 ± 0.03 cP) under the shelf-life, storage, and pot life conditions within the standard measurement error. This is a significant competitive advantage compared to other products in this market.

Table 2. Viscosity stability of PixNIL® SCS1 under various conditions (longer shelf-life test ongoing) (standard error in viscosity measurement = 1.7%)

25 C Shelf Life (cP)	4C Storage (cP)	50C Storage (cP)	25 C Pot Life (cP)
1.70 ± 0.03 (1 month)	1.67 ± 0.03 (48 hours)	1.66 ± 0.03 (48 hours)	1.69 ± 0.03 (24 hours)

Optical Properties of Flat Films

PixNIL® SCS1 was formulated to provide a range of film thicknesses between 200 and 500 nm based on typical waveguide structure feature sizes while providing best-in-class optics for both transmission and haze.

In Figure 2, film thickness is varied with spin speed. The one-step process shows PixNIL® SCS1 with film thicknesses ranging from roughly 150 to 330 nm at 4000 and 1000 RPM, respectively. Using a two-step process (i. e., a slow speed for 45 seconds followed by a faster speed for 15 seconds) that allows the liquid to gradually wet the substrate gives better film uniformity over a one-step process (i. e., one fast speed for 45 s). The two-step process produces about 200 nm thicker films at those spin speeds.

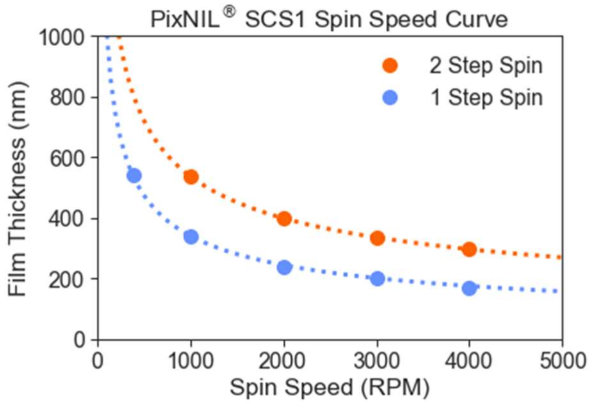

Figure 2. Spin curves for PixNIL® SCS1

Film refractive index and transparency (usually referred to as %Transmission or %T) are essential optical properties for waveguide applications. Figure 3 shows both the film refractive index curve in the visible and near IR wavelengths and %Transmission curve for PixNIL® SCS1 formulation. To avoid optical interference due to RI mismatch between the film and the substrate, %T measurement was measured on 1.9 RI Corning EXG glass and shows greater than 95% transmission above 400 nm.

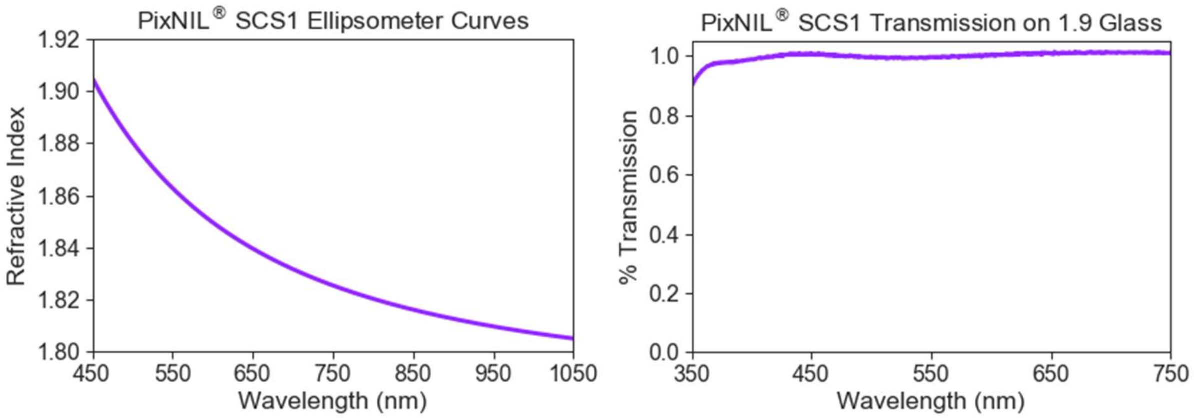

Figure 3. Film RI and %T versus wavelength for PixNIL® SCS1 at 200 nm thickness.

Nanoimprinting Structures

Imprintability

As described in the Methodology section, the nanoimprinting process comprises the following steps: spin coat, soft bake, and stamp/cure. An optional post-bake process can also be applied for certain applications. Two important factors that determine imprint quality are:

1. Soft bake conditions: Once the desired film thickness has been deposited (Figure 2), the softbake is applied. Soft bake removes the solvent to prepare the formulation for imprinting process. For PixNIL®SCS1, softbake conditions covering temperature ranges of 25 to 80°C and time ranges of one to five minutes were tested. The best imprinting results at 200-nm film thickness were obtained at 50°C/1 min softbake.
2. Wait time before imprint process: It is essential to know the maximum time a film can sit prior to imprinting, while still showing perfect resolution. Ideally, manufacturers prefer materials that survive longer wait times, enabling inexpensive batch-type processing. The SEM images for PixNIL® SCS1 in Figure 4 show that the two imprints produced within a minute after soft bake (a) versus a 24-hour wait time after soft bake (b) are nearly identical.

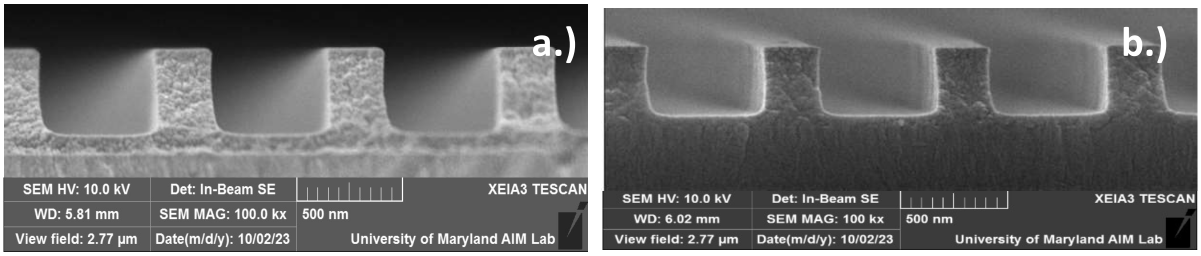

Figure 4. Wait time between Softbake and UV Cure (400-nm binary gratings). PixNIL® SCS1: a.) Initial and b.) 24-h wait.

Refractive index uniformity within the imprinted structures is crucial for device efficiency in XR devices. When imprinting resins that contain nanoparticles into grating structures on the order of 100 nm or less, concerns arise about the ability of the nanoparticles to distribute evenly within the structures. Utilizing the capping materials that have been optimized to surround the PixCor™ nanoparticles, combined with careful resin component selection, the PixNIL® SCS1 exhibits excellent nanocrystal uniformity throughout the structure after imprinting. Figure 5 illustrates this result, showing close packing of the nanoparticles within the imprint structures including sharp edges, without any indications of phase separation between the nanoparticles and resin. These observations provide additional evidence of the dispersion quality of the nanoparticles within the resin system after imprinting. As mentioned earlier, the ability to properly fill the structures and distribute evenly along the edges and corners is a highly attractive benefit of Pixelligent's nanocomposite systems. This result is evidenced in Figure 6, a 15x15 um AFM scan across an imprinted surface prepared for PixNIL® SCS1 demonstrates an impressively low surface roughness values (Rq) of 1.44 nm.

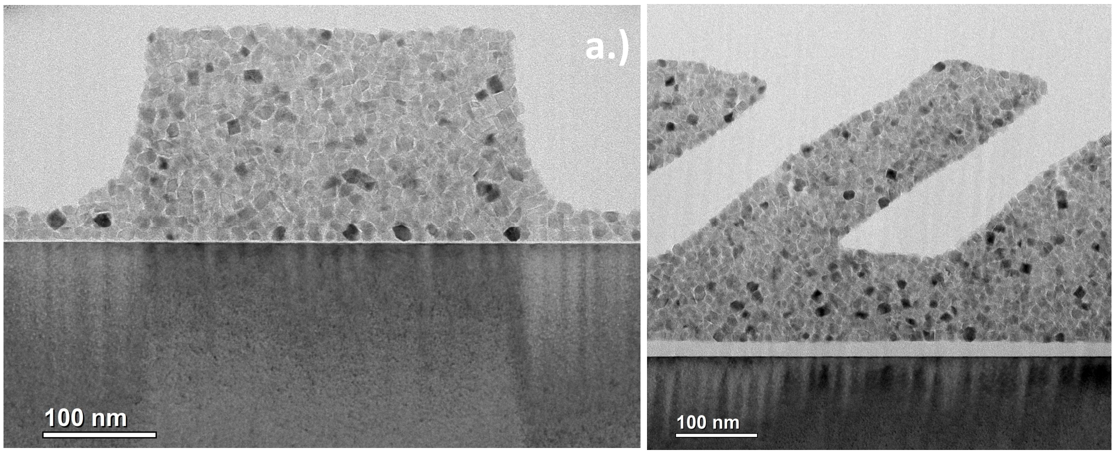

Figure 5. Images of PixCor™ nanoparticles in PixNIL® SCS1 imprints: a.) binary and b.) slanted features.

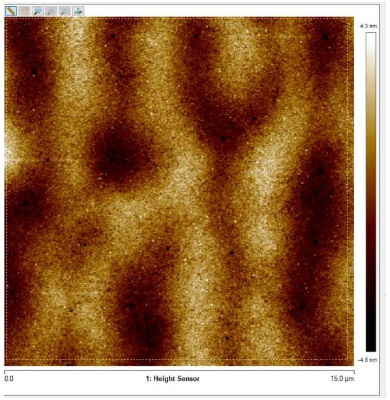

Figure 6. AFM images of PixNIL® SCS1 with low surface roughness (Rq = 1.44 nm)

The versatility of imprinted structures prepared from PixNIL® SCS1 formulation were evaluated by comparing side-by-side to a reference 1.5 RI imprint nanoparticle-free resin (EVGNIL UV/A2) as seen in Figure 7. Key highlights are: 1) well-defined, slanted gratings with consistent heights (roughly 337 nm) and clean, sharp edges; 2) high-aspect ratio gratings at 6:1 height-to-width (433 nm:70 nm); and, 3) small, blazed gratings with 130-nm heights. It is important to note that the features and trenches do not show any adverse roughness due to the presence of the nanoparticles.

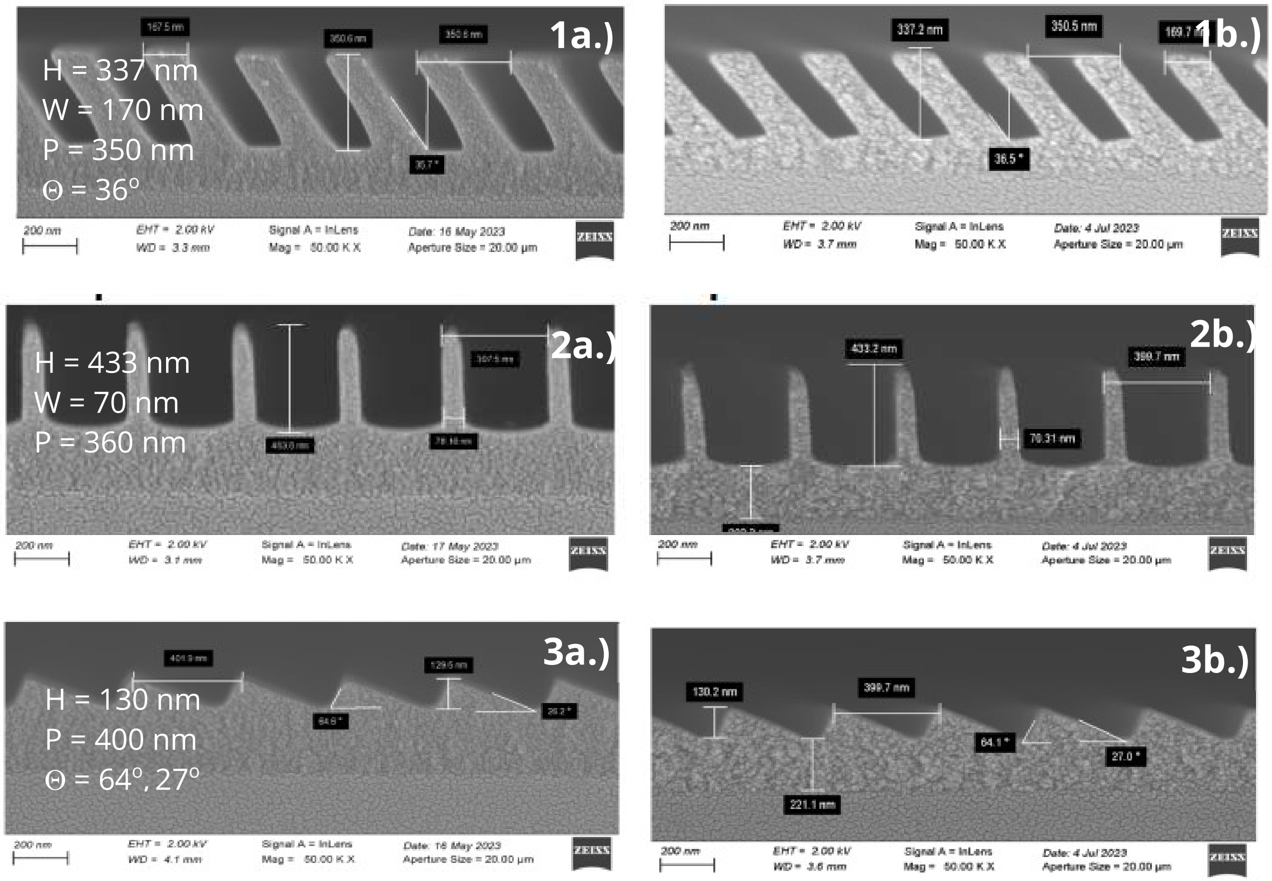

Figure 7. Using EVG's Moldnano master various imprinted structures compared with reference 1.5 RI NIL resin "EVGNIL UV/A2" (1a to 3a) compared to SCS1 (1b to 3b) with slanted (top), high aspect-ratio binary (middle), blazed gratings (bottom)

Demonstration of Low Residual Layer Thickness (RLT)

Residual layer thickness is a critical parameter in cases where there is a mismatch between the RI of the substrate and the resin, resulting in an undesirable effect on image quality. When the refractive indices of the substrate and imprint are better matched, then thin RLTs are less necessary. Pixelligent's PixNIL® formulations are commonly selected as index-matching materials for specific RI grades of glass and PC wafers. Regardless of the required index, PixNIL® SCS1 can deliver RLT of < 40 nm. Figure 8a demonstrates imprints with 200 nm heights, 360 nm widths, and 800 nm pitches, that can achieve RLTs close to 30 nm. RLT values of this magnitude are approximately twice the size of the PixCor™ nanoparticles themselves, and yet exceptional imprinting is still achieved. Figure 8b demonstrates the uniform distribution and close packing of the nanoparticles within the residual layer of these imprints.

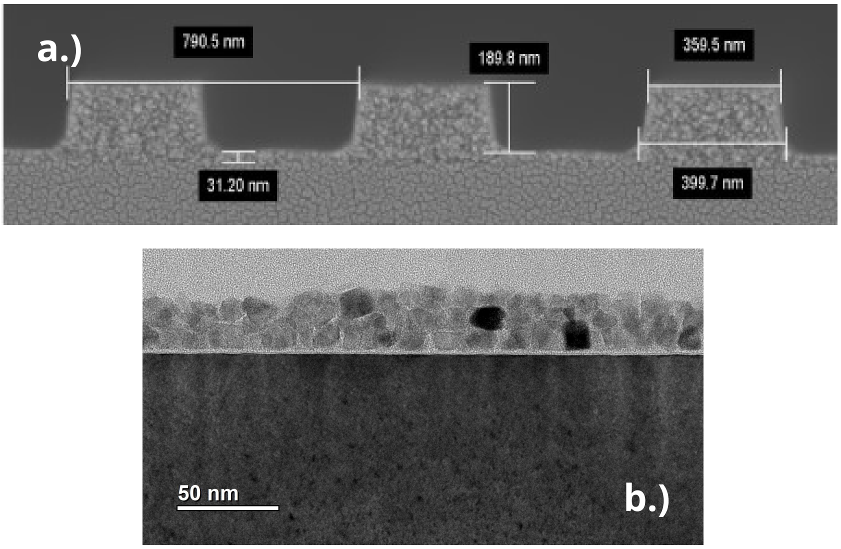

Figure 8. a.) Binary gratings of PixNIL® SCS1 with 31 nm RLT and b.) Close up TEM of residual layer with close packed nanocrystal distribution

UV Reliability

Under a 405-nm UV exposure test (25 mW/cm^2 for 148 hours), the color, film thickness and refractive index were measured for the PixCor™ containing PixNIL® SCS1 when compared to PixClear® ZrO_2 and TiO_2 nanocomposite films to show the UV stability benefit of the PixCor™ nanoparticles. Figure 9 displays how the SCS1 performs in between the ZrO_2 and TiO_2 in these three ways. The ZrO_2 nanocomposite has virtually no color change while the ΔE^* of TiO_2 is greater than 1.0, indicating a noticeable color evolution, while the ZrO_2 shell of the PixCor™ nanoparticles passivates the TiO_2 core, reducing the impact of color formation under UV exposure by <85%. Similarly, the photo-active TiO_2 causes significant changes in film thickness and RI, due to photo-degradation. Again, the SCS1 film changes much less in these properties by maintaining better stability under UV light at 405 nm.

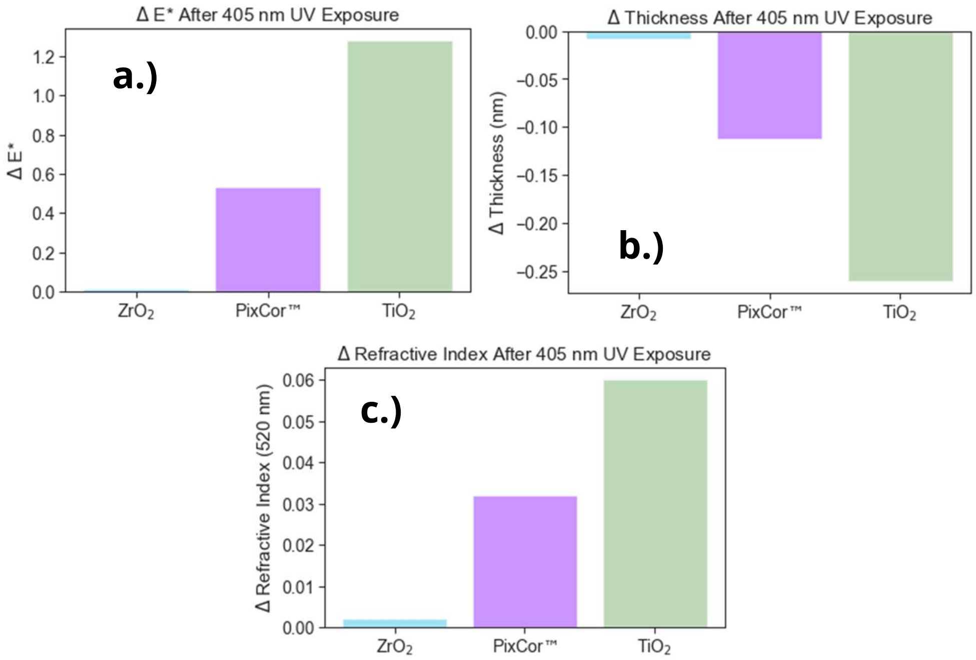

Figure 9. 405-nm UV exposure behavior of PixNIL® SCS1 with changes in a.) ΔE*, b.) film thickness, and c.) refractive index

Conclusions

The importance of high refractive index materials for advancements in the Extended Reality market is essential for delivering both the largest field of view possible as well as highly efficient devices. These materials must meet stringent NIL requirements, including: the highest optical clarity; high refractive indices that match the glass substrate; optimized fluidity to allow proper filling of binary and slanted grating structures; all while delivering a fully uniform dispersion of nanoparticles throughout the structures; and the highest degree of UV and product stability. Pixelligent's PixNIL® SCS1 has demonstrated the ability to meet all these stringent requirements with 1.86 RI at 589 nm, >95%T in the visible wavelengths, the ability to print a wide range of complex nanoimprinted structures, UV stability close to that of ZrO_2 performance, and robust shelf-life properties.

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