Addressing Sunlight Reactivity in High Refractive Index Nano-Imprint Lithography Resins

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Abstract. High refractive index (RI) resins containing titanium oxide nano-particles (NPs) can be used to imprint features on high RI glass or plastic via UV-nanoimprint lithography (UV-NIL) for a wide field of view in VR/AR/MR devices. A limitation of this method is the photo-reactivity of the high RI resins which can result in rapid degradation in sunlight. We present a model for sunlight reactivity of titania-containing resins and a method for studying resin photo-degradation. We evaluate various techniques for stabilizing high RI resins including surface coating of the NPs, use of UV-blocking glass filters, and hermetic sealing. Ultimately, the stability of high RI TiO_2-containing NIL resins to average sunlight exposure can be increased from a few hours to months.

Keywords. UV-nanoimprint lithography (UV-NIL), high refractive index, titanium oxide, nano-particles, sunlight reactivity, hermetic sealing

Introduction. High refractive index (RI) glass or plastic provides a wide field of view for AR/VR/MR devices, and bulk materials with RI exceeding 2.0 exist. One can imprint features on the substrate via UV-nanoimprint lithography (UV-NIL) techniques where a resin is coated on a glass or polymer wafer, imprinted with a mold or stamp, and cured with UV light. To avoid reflections, the imprint resin should have an RI similar to that of the substrate, and imprint resins with RI exceeding 1.9 are available. Most of the high RI imprint resins contain titanium oxide (TiO_2) nano-particles (NPs) that are coated with organic capping agents. A limitation of these resins is that TiO_2 is photo-reactive, and the high RI organic phases can be rapidly degraded by sunlight. In this work, we present a procedure for following sunlight degradation of high RI imprint resins and evaluate methods for stabilizing TiO_2-containing resins.

Materials and Methods.

Samples. Glass coupons and wafers were spin-coated with either unmodified TiO_2 NP-containing resins or Addison Clear Wave's commercial high RI LuxNIL® U-series resins which are titania NP dispersions in proprietary UV binders. The coated coupons and wafers were heated at 100 °C for 1 minute to evaporate solvent. Coated coupons were cured in a nitrogen atmosphere with a 365 nm LED flood system (250 mJ/cm², 100 s). Coated wafers were imprinted and cured with EV Group's SmartNIL® process using POR conditions. The samples subsequently were conditioned at 150 °C for 4 hours. The resin thicknesses of the prepared samples were 600-900 nm.

Cut-on glass filters were 1 mm thick sheets of Schott GG400 and Schott GG420 glass.

Hermetic sealed samples. Coated coupons were encased in two pieces of glass (50 mm x 75 mm x 1 mm) using epoxy sealant A1705-TX (Addison Clear Wave Coatings, Inc.) in a dry nitrogen-filled glove box with an oxygen content of ≤ 0.1%. The epoxy was cured by 365 nm LED flood (250 mW/cm², 100 s) followed by heat (60 °C, 90 minutes).

Simulated sunlight. Sunlight exposure tests were conducted with a Q-Sun® xenon arc lamp tester (Q-Lab Corp.) fitted with a Daylight Q filter. The irradiance was set at 0.35 W/(m^2 nm) at 340 nm. The temperature was set at 45 °C.

Physical measurements. Refractive indices and film thicknesses were measured on a prism coupler (Addison Clear Wave) or an ellipsometer (EV Group). AFM studies were conducted at EV Group.

Background. Photo-reactivity of resins containing titania nano-particles (NPs) results because TiO_2 has a band gap of 3.0-3.2 eV, which corresponds to short wavelength visible light (<425 nm) and UV light in sunlight that reaches the surface of the Earth (300-400 nm). Absorbance of the sunlight promotes an electron from the TiO_2 valence band to the conductance band, and this excited state titania can react in redox reactions in addition to "recombining" back to the ground state.[1]

In our model for titania photo-reactivity, we assume that the major reactions of the excited state species are reduction of oxygen and oxidation of water as illustrated in Figure 1. Reduction of oxygen gives the radical anion superoxide that is protonated to give a hydroperoxyl radical. Oxidation of water with concomitant proton transfer gives the hydroxyl radical which is an exceptionally high energy species that can react with any organic moiety. For the high RI titania-containing resins, redox reactions of the organic matrix and organic capping agents on the NPs also are possible. Following radical production, radical chain reactions are expected to degrade the polymer matrix forming low weight organic materials.
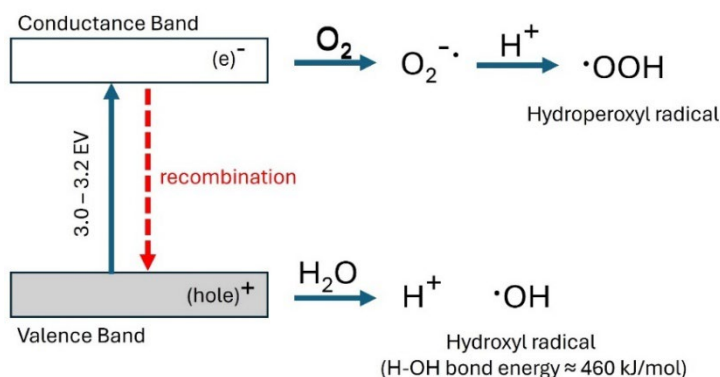

Figure 1. Model for titania photo-reactivity.

To the extent that the initial redox reactions of oxygen and water are the major processes resulting ultimately in degradation of the high RI titania-containing resins, one can envision reducing sunlight photo-reactivity by preventing these reactions. In principle, that can be accomplished by coating the titania NPs with a protective "shield", filtering out the high energy component of sunlight, or excluding water and oxygen from the high RI resins by hermetic sealing. In this work, we report results from sunlight exposure studies employing these various protective approaches.

Results and Discussion. The sunlight exposure test used here is similar to sunlight exposure specified in Cycle 1 of ASTM Standard D5071.[2] Specifically, a xenon arc lamp with a Daylight Q filter was used, which provides an irradiance spectrum that closely matches that of sunlight reaching the Earth's

surface. The irradiance was set at 0.35 W/(m² nm) at 340 nm which results in 365 W/(m² nm) over the range 300 to 800 nm light.[2] That amount is somewhat more than twice the average amount of sunlight reaching the Earth's surface. Thus, one hour exposure in our studies is equivalent to more than 2 hours exposure to average sunlight.

Unprotected nano-particles. Baseline studies were conducted with high RI resins containing titania NPs that were not protected. For samples with initial RI values of 1.80 to 1.95 at 589 nm, artificial sunlight exposure for 15 hours resulted in rapid increase of RI followed by fast decrease of RI (Figure 2). In similar irradiation studies, the mass of the samples was found to decrease smoothly with irradiation over a 15-hour period (results not shown). By the end of the 15-hour irradiation period, the resins were obviously highly degraded and were sticky to the touch.
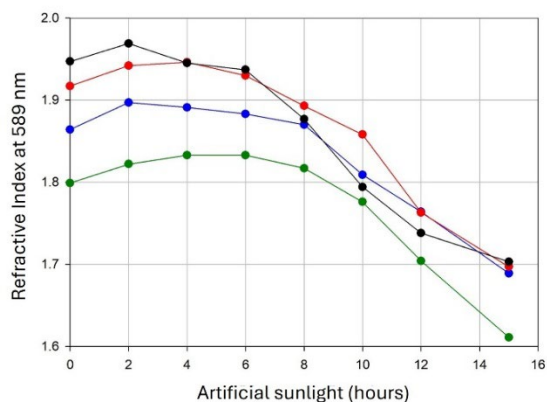

Figure 2. Refractive index response of high RI resins containing unprotected titania NPs to artificial sunlight exposure. The RIs in this group were measured at 589 nm.

Our interpretation of the behavior of the high RI resins is as follows. In the initial stages of irradiation, the organic components of the resin are degraded in radical reactions that produce volatile small molecules, and loss of organic material results in an increase in the RI. As the irradiation continues the NPs begin to aggregate, and the aggregated or pooled NPs display a reduced RI. We note as an example that increasing the diameter of the NPs by a factor of 2 would result in a reduction of the total cross-sectional area by a factor of 2 and hence a reduction in RI.

Shielded nano-particles. Addison Clear Wave's commercial high RI LuxNIL® U-series resins contain titania NPs that have a protective coating. The shield can block access of redox susceptible materials to excited state titania.

Irradiation results for two LuxNIL® U-series resins, P283U and P285U, are shown in Figure 3. In these plots we show both RI and percent thickness of the resins as functions of hours of artificial sunlight irradiation. As with the unshielded NP resins, there is an initial increase in RI followed by a decrease in RI, whereas the thickness of the resins decreases smoothly. In comparison to the resins with unprotected NPs, the LuxNIL® U-series resins display apparent sunlight stability that is increased by about one order of magnitude.
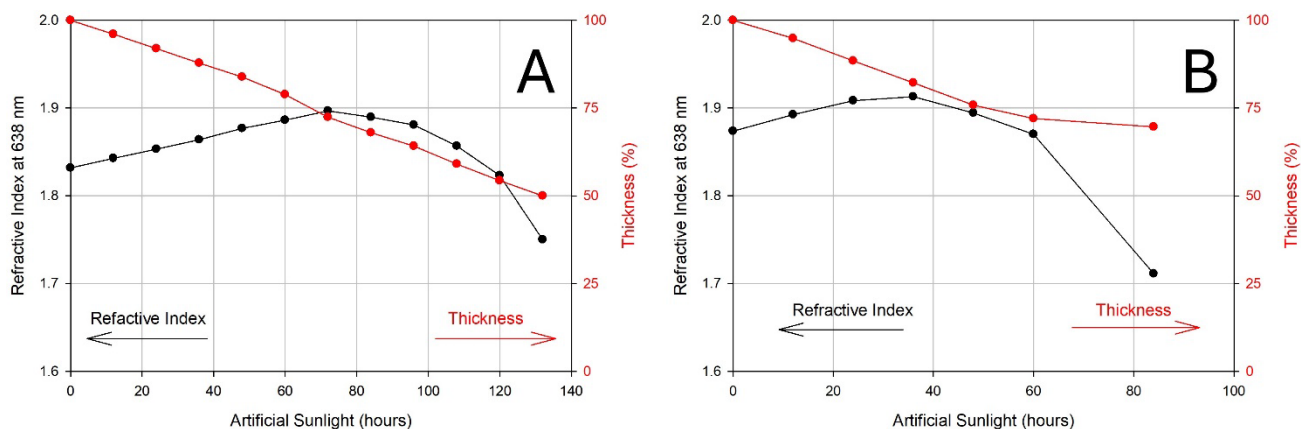
Figure 3. Response of (**A**) LuxNIL® P283U and (**B**) LuxNIL® P285U to artificial sunlight exposure.

Filtered light. It is possible to filter out the UV component of sunlight with doped or coated glass. This approach is expected to reduce or prevent photo-degradation of titania-containing resins, but there are some limitations. The UV absorbance of titania extends into the visible region, and 400 nm cut-on filters will "leak" a small amount of UV light. In addition, glass with a cut-on above 400 nm typically will have some yellow tint.

We report here studies with two glasses that transmit visible light but have 400 nm and 420 nm cut-on filter properties, Schott GG400 and Schott GG420 glasses. The results are shown in Figure 4. As expected, sunlight reactivity was markedly reduced by these glasses, but the growth and fall of the RI found previously remained. It is noteworthy that the thickness of the films was reduced to about 80% in 400 and 1000 hours, respectively, for GG400 and GG420.
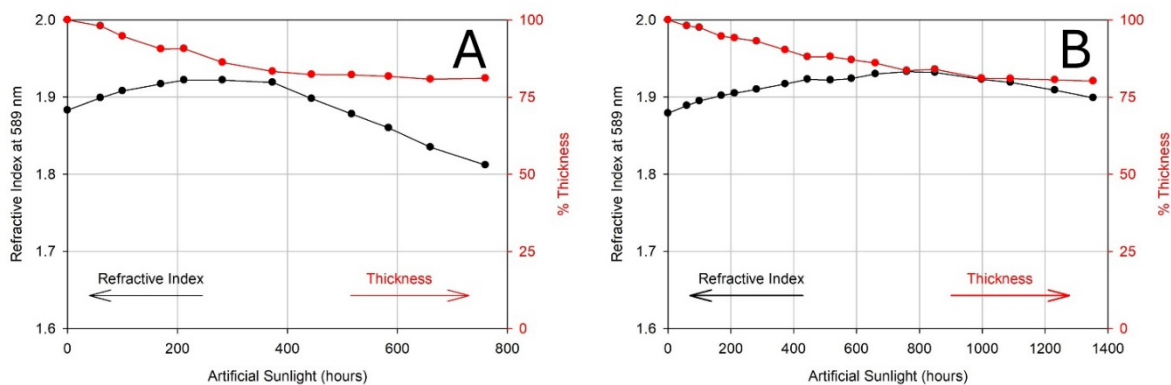

Figure 4. Behavior of LuxNIL® P285U when irradiated through 1 mm thick plates of (**A**) Schott GG400 glass and (**B**) Schott GG420 glass.

Hermetic sealing. Hermetic sealing in an oxygen- and moisture-free atmosphere should provide good sunlight stability to the high RI titania-containing resins if our reaction model is correct. Specifically, our model ascribes the photo-reactivity mainly to initial redox reactions of oxygen and

water. If the model is not correct and redox reactions of the organic components in the resin are more important than we anticipate, then hermetic sealing could have only a limited effect on the stability of the resins.

In the event, hermetic sealing was found to impart excellent stability to the high RI titania NP-containing resins. Following multi-hundred-hour artificial sunlight exposures, we observed only small increases in RI and small decreases in resin thickness. Figure 5 shows results for two of the LuxNIL® U-series resins, and similar results were observed for resins containing unshielded titania NPs (results not shown). Given that our artificial sunlight is more than twice the intensity of average sunlight and our irradiation is continual, 600 hours irradiation in our apparatus is equivalent to average sunlight for 100 cloudless days or more than three months. It is possible that the resins will display limited degradation for the lifetimes of the hermetic seals; i.e, the quality of the hermetic seals may determine the ultimate lifetimes of the high RI resins.
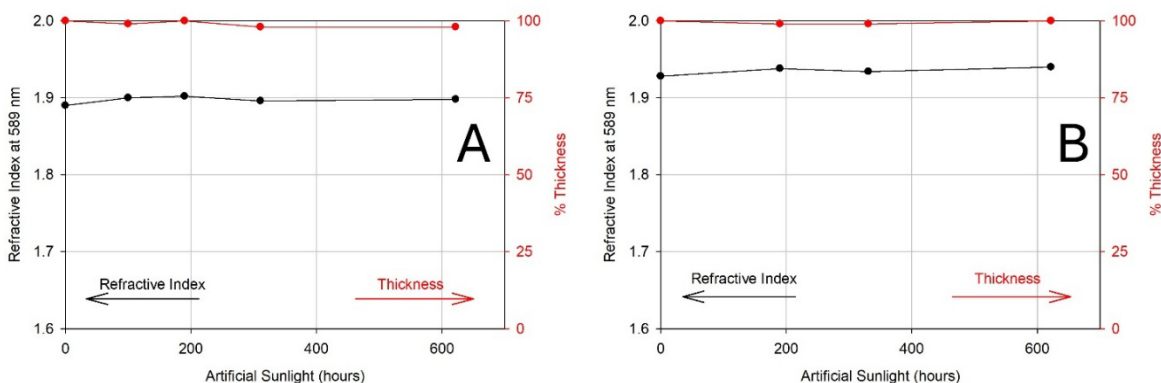

Figure 5. Response of hermetically sealed samples of (**A**) LuxNIL® P285U and (**B**) LuxNIL® P288U to artificial sunlight irradiation.

Nano-Structure Studies. The nano-structures of NIL resins exposed to sunlight were studied at EV Group. The LuxNIL® U-series resins P276U, P283U and P285U were readily imprinted using EV Group's SmartNIL® POR conditions, and we note that the LuxNIL® U-series resins are compatible with EVG®NIL UV/AS5 PFAS-free working stamp material.

Limited sunlight degradation of the nano-structures in hermetically sealed samples was expected based on the small RI and thickness changes found in the sunlight exposure studies in Figure 5, and AFM studies confirmed this behavior. Figure 6 shows AFM results for binary features of LuxNIL® P285U imprints exposed to artificial sunlight open to the atmosphere and in hermetically sealed encasements. Open samples irradiated for relatively short periods of 22 and 76 hours displayed significant degradation with approximately 13% and 19% reductions in grating heights, respectively; such results are consistent with the degradation found in the studies shown in Figure 3. For the hermetically sealed samples, however, the grating heights displayed essentially no reductions after 211 and 328 hours of irradiation.
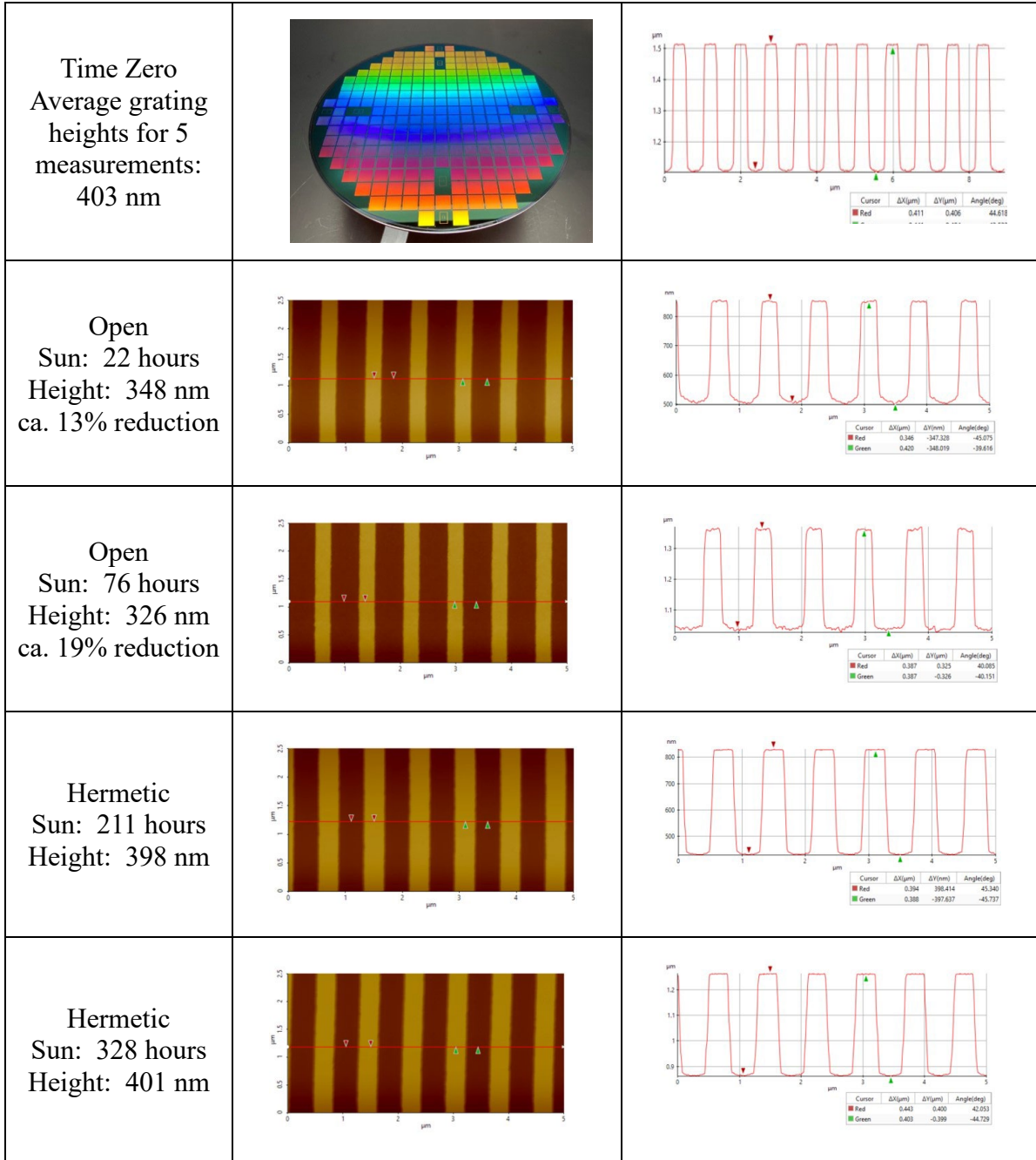
Time Zero Average grating heights for 5 measurements: 403 nm		
Open Sun: 22 hours Height: 348 nm ca. 13% reduction		
Open Sun: 76 hours Height: 326 nm ca. 19% reduction		
Hermetic Sun: 211 hours Height: 398 nm		
Hermetic Sun: 328 hours Height: 401 nm		

Figure 6. AFM results for diced sections of a wafer coated with LuxNIL® P285U that were irradiated with artificial sunlight either open to the atmosphere or in hermetically sealed encasements. The height reduction values for the gratings of the open samples are based on the initial height measurements for the positions on the wafer and the final height measurements for the diced samples after irradiation.

Conclusion. This work has shown that high RI titania-containing resins can be protected from sunlight by various methods. Coating titania nano-particles with a shield offers modest protection, and further improvement in this area might be expected. Filtering sunlight to the edge of the visible-UV boundary provides good protection. Hermetic sealing provides exceptionally good protection with sunlight stabilities increased by several orders of magnitude.

The studies reported here were performed with ACW LuxNIL® resins that are comprised of titania NP dispersions in proprietary UV-curable acrylate binders. We cannot be certain that similar results will be found with titania-containing high RI resins of others, but we believe that the stabilizing effects we found in this work will prove to be general.

Hermetic sealing to protect high RI materials in optical devices from sunlight damage is especially noteworthy given that we found essentially no degradation in high RI resins with exposure to the equivalent of months of normal sunlight. Hermetic sealing is a well understood and widely used process, and applications of UV-NIL methods with high RI resins for commercial devices might be widely employed when this technique is incorporated into the manufacturing processes.

References
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