UV-NIL Technologies

Hermetic Sealing for Preventing Sunlight Damage of High Refractive Index Resins in Augmented Reality Optical Devices

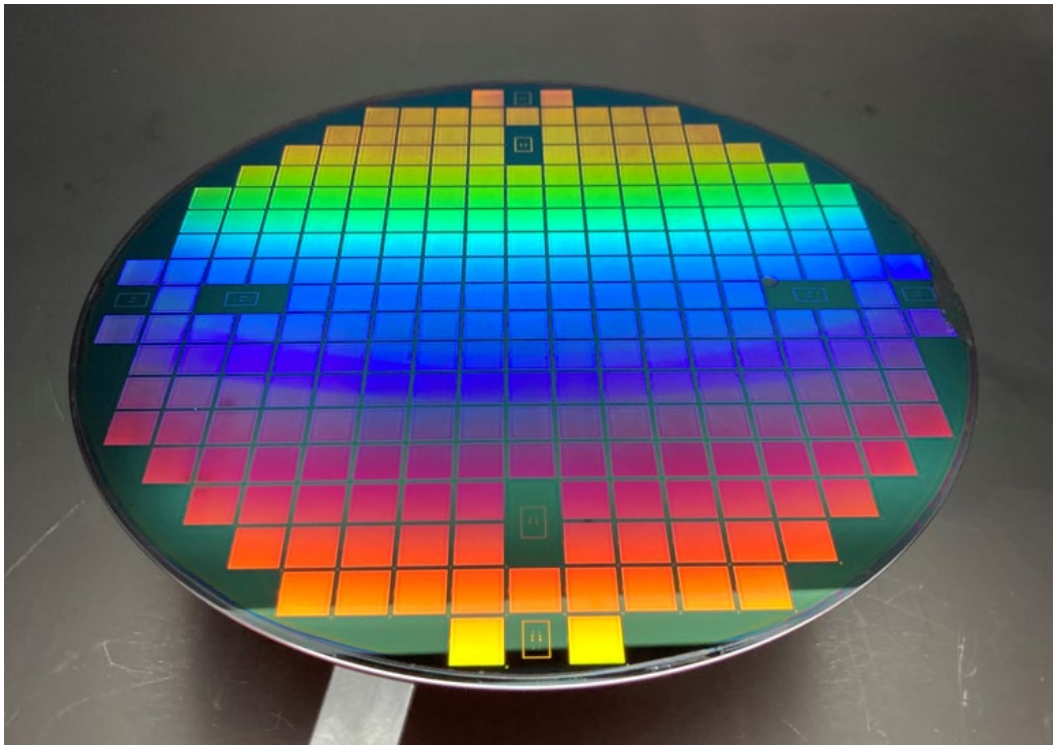

Image courtesy of EV Group (evgroup.com)

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Introduction

Augmented, Virtual and Mixed realities (AR/VR/MR) enable smart solutions in real time across a wide spectrum of industries from entertainment to communication to healthcare. AR/VR/MR devices bend and combine light to create virtual images that project onto the physical world. To provide the widest viewing angle and maximize the field of view (FOV), materials with refractive indices greater than 1.9 at 589 nm are employed. High refractive index glasses and plastics are available, and nanometer scale structures can be imprinted on these materials economically by UV- or photo nanoimprint lithography (UV-NIL or P-NIL); in this technique, a UV-curable resin is coated on the substrate, a working stamp with nanometer scale images is pressed onto the resin, the resin is cured photochemically, and the working stamp is removed.

Key points

- UV-nanoimprint lithography
- High refractive index resins
- Sunlight stability

High RI imprint resins are used with high RI base materials to avoid internal reflections, and many of these NIL resins achieve high RI by incorporating titanium dioxide (TiO_2, titania) nano-particles (NPs) in a curable organic resin. Titania provides high RI, but it is photo-active, and titania-containing resins can be degraded rapidly by sunlight. Here we demonstrate that high RI titania-containing resins are protected from sunlight by hermetic sealing encapsulation. We report sunlight stability enhancements of the resins exceeding three orders of magnitude and show that the nanostructures of irradiated materials remain unchanged even after 1000 hours of average sunlight irradiation.

Origin of Titania Sunlight Reactivity

Figure 1 illustrates the processes involved in titania's sunlight photo-reactivity. Titanium oxide's common crystal forms (anatase and rutile) have band gaps in the range of 3.0-3.2 eV which corresponds to light in the 380-415 nm range. Sunlight that reaches the Earth's surface contains UV light extending down to 300 nm. Absorption of high energy visible light and UV light by titania promotes an electron from the valence band to the conductance band leaving a positive hole in the valence band. The promoted electron can return to the valence band in a process termed recombination, or the excited electron in the conductance band and hole in the valence band can react in redox reactions.[1] Reduction of oxygen and oxidation of water can initiate radical reactions that lead to degradation of organic media.[1]

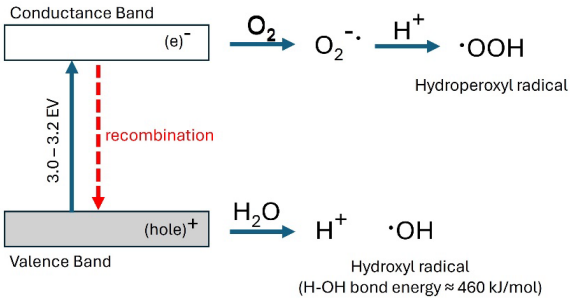

Figure 1. Processes in sunlight photo-reactivity of titanium oxide (after reference 1).

Design of the Study

Glass coupons (25 mm x 25 mm) were spin-coated with titania NP-containing acrylate resins, cured in a nitrogen atmosphere with 365 nm LED flood lamp system (250 mW/cm^2 for 100 s), and heated at 150 °C for 4 hours. Imprinted samples were prepared with the EV Group SmartNIL® process using an EVG® 7200 imprinting system; glass wafers were coated with titania NP-containing resin, imprinted, and subsequently diced into ca. 25 mm x 25 mm pieces. The coupons and wafer pieces were irradiated with artificial sunlight either open to the air or encased between two 75 x 50 mm glass sheets sealed in a nitrogen atmosphere with ACW's epoxy sealant A1705-TX. The artificial sunlight was produced in a Q-Sun® xenon arc lamp test chamber (Q-Lab Corp.) using a Daylight Q filter which closely mimics the irradiance spectrum of sunlight. The power level was 0.35 W/(m^2 nm) at 340 nm as recommended in ASTM Method D5071;[2] this power level is equal to 365 W/(m^2 nm) over the range 300-800 nm and is somewhat greater than twice the average power of sunlight reaching the Earth's surface. The temperature was 45 °C. The coupons' bulk properties (RI and thickness) were measured on a prism coupler. The diced wafer pieces were analyzed by AFM and SEM.

Bulk Property Evaluation

Figure 2A shows the RI behavior of several high RI resins containing unshielded titania NPs when irradiated open to air. The RI increased within a few hours of irradiation and then decreased rapidly. When the masses of similar samples were followed, a smooth loss of mass was observed (data not shown). Coupons coated with ACW's LuxNIL® resins behaved similarly when irradiated open to the air. This is shown in Figure 2B for LuxNIL® P285U resin which contains titania NPs that have a protective shield. In the case of P285U, the physical changes were slower than with the unshielded NP resins by about an order of magnitude, but the nature of the changes was the same. The RI initially increased but then decreased, and the thickness of the cured resin layer decreased smoothly over the course of the irradiation.

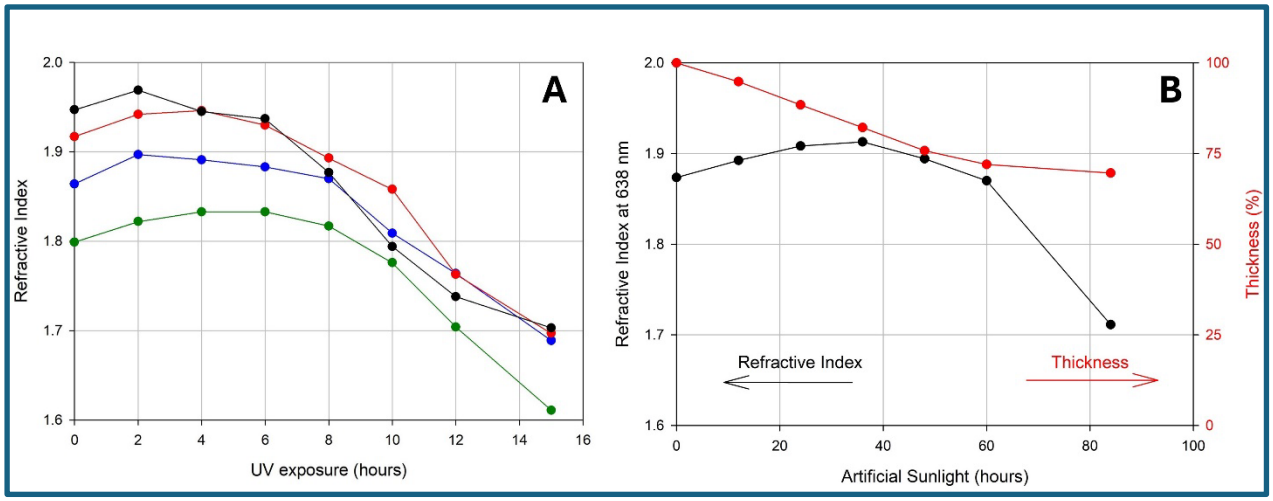

Figure 2. Artificial sunlight effect on (**A**) resins containing unprotected titania NPs and (**B**) LuxNIL® P285U resin.

The bulk property behavior of the titania NP-containing resins can be explained as follows. Sunlight initiated radical reactions resulted in cleavages of organic media to give low weight fragments that volatilized. In the initial stages of the irradiation, loss of organic material, which has low RI, resulted in an increase in the observed RI. As the irradiation proceeded further, degradation of the NP coatings permitted aggregation or pooling of the NPs, and an increase in the volumes of the NPs resulted in a reduction in the cross-sectional area and a decrease in RI. The mass and thickness of the resin decreased smoothly as the irradiation proceeded and organic material was lost.

Figures 3 and 4 show the bulk property behavior of titania NP-containing resins in sealed encasements. Resins with both unprotected NPs and shielded NPs were irradiated with artificial sunlight for 1000 hours. In each of the cases, a small increase in RI and a slight decrease in thickness were found. The amount of degradation was so small that one cannot accurately quantitate the improvement over the "open" samples other than to state that the stability apparently was increased by more than three orders of magnitude. Given that our irradiance is more than twice that in average sunlight, it is likely that these resins would survive for months of direct sunlight exposure.

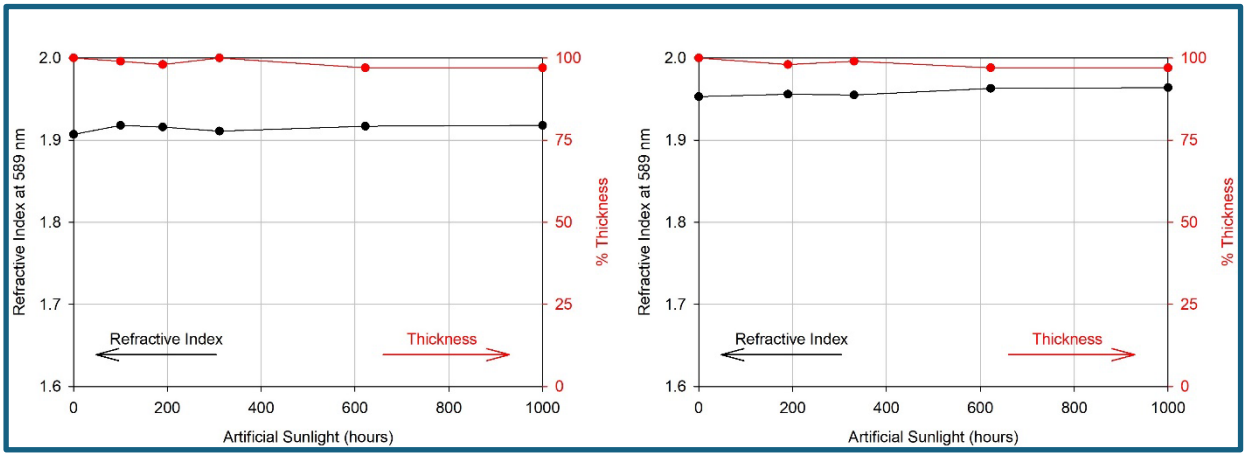

Figure 3. Artificial sunlight effect on hermetically encased resins containing unprotected NPs

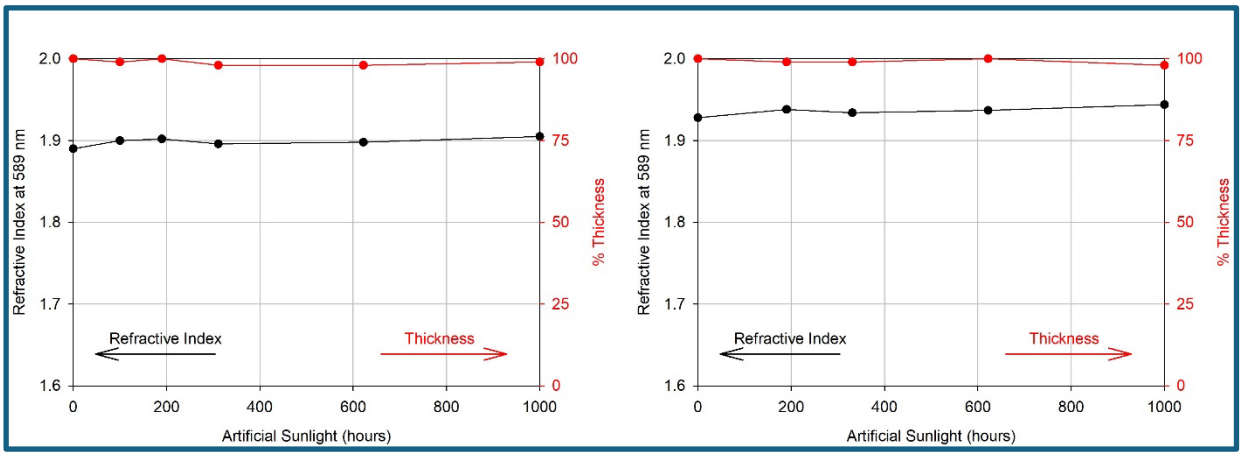

Figure 4. Artificial sunlight effect on hermetically encased LuxNIL® resins; left: P285U, right: P288U.

Nano-scale Evaluation

AFM and SEM studies reveal the effect of sunlight on titania NP-containing resin LuxNIL®P285U on the nanometer scale. Figure 5 shows a wafer imprinted with LuxNIL® P285U. The average grating height measured by AFM at five positions was 403 nm. The grating width was 300 nm.

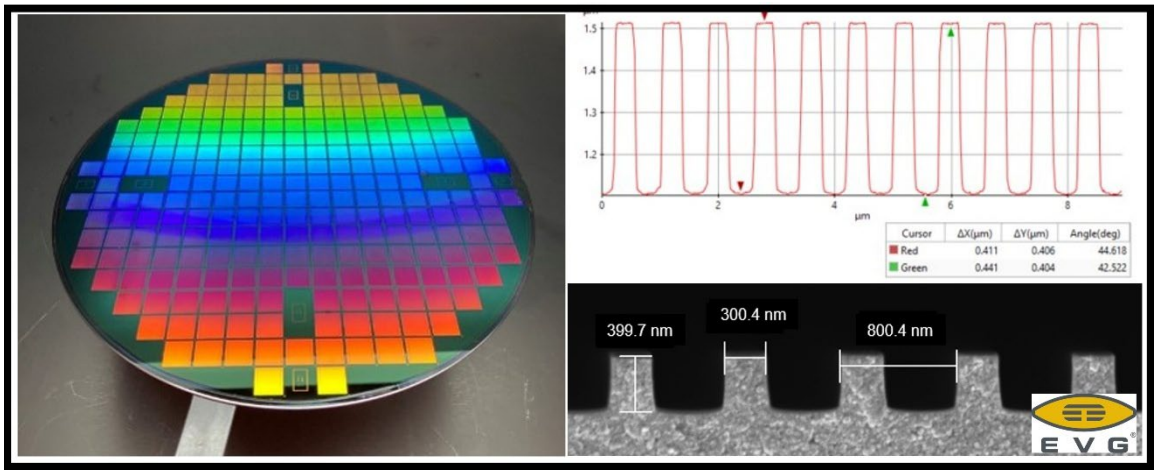

Figure 5. Wafer imprinted with LuxNIL® P285U. Images courtesy of EV Group (evgroup.com).

Fragments of the wafer were irradiated in the open air and in hermetically sealed encasements, and figures 6 and 7 show the results of AFM and SEM analyses. Samples irradiated in open air displayed significant damage; the grating height was reduced to 350 nm in 22 hours (13% reduction) and to 320 nm in 76 hours (21% reduction), and the grating width at 76 hours was reduced to 246 nm (18% reduction). Consistent with the bulk property behavior, the nano-structures of hermetically sealed fragments that were irradiated for 328 and 512 hours were essentially unchanged.

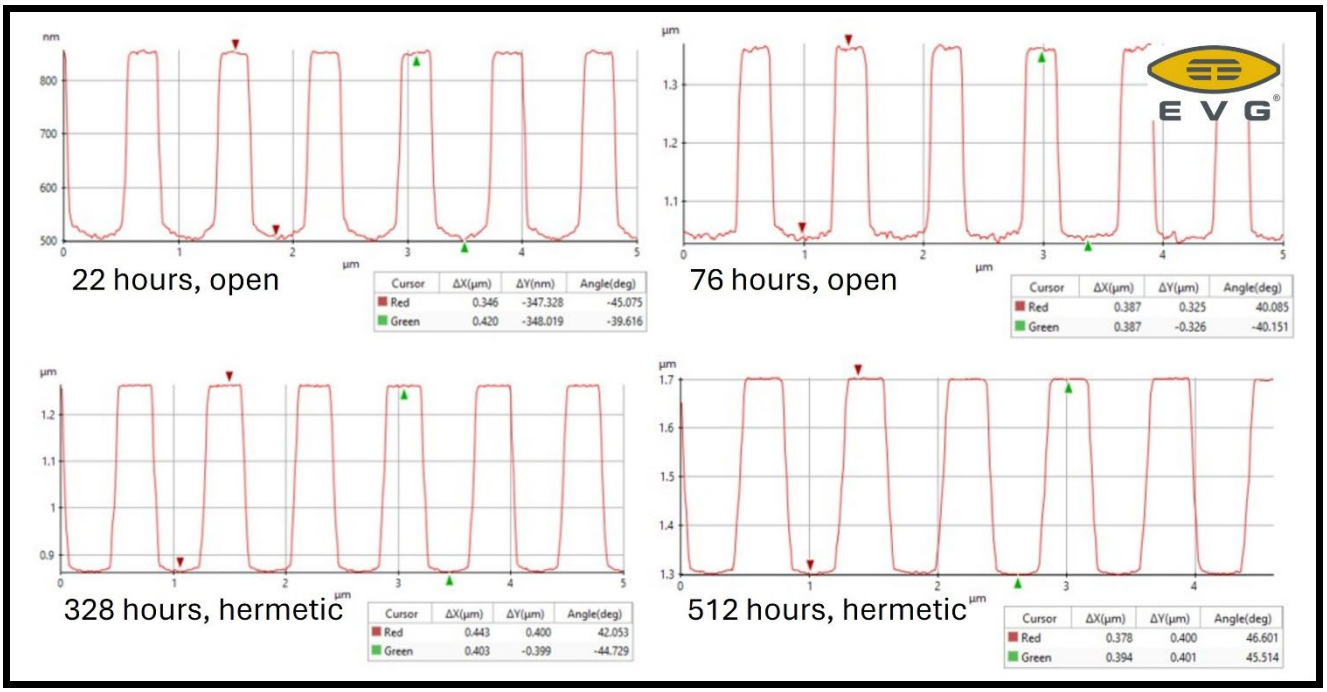

Figure 6. AFM images of irradiated wafer fragments. Images courtesy of EV Group (evgroup.com).

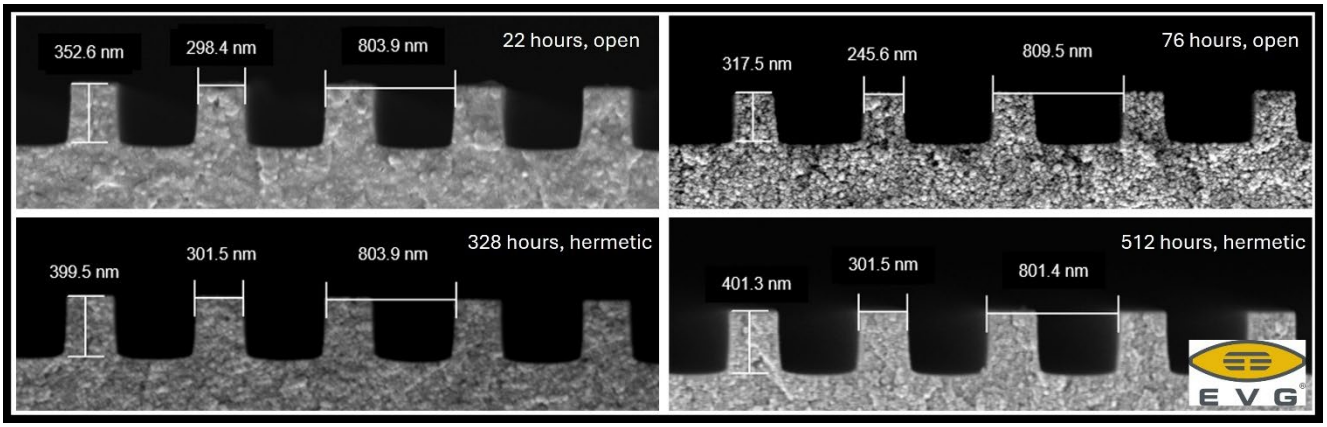

Figure 7. SEM images of irradiated wafer fragments. Images courtesy of EV Group (evgroup.com).

Conclusion

Hermetic sealing provides excellent sunlight protection for high RI titania NP-containing resins, but the limit of protection afforded is difficult to quantitate. The AFM and SEM studies with imprinted LuxNIL® P285U showed no apparent damage in 512 hours of irradiation, and the bulk property studies with both unprotected NP-containing resins and LuxNIL® resins with shielded NPs revealed only minor changes in RI and thickness with 1000 hours of irradiation. Recalling that the irradiation power in the artificial sunlight in these studies was more than twice that of average sunlight, one can reasonably conclude that the encased resins would be stable for up to half a year of direct sunlight exposure. It is conceivable that the limiting factor in the resin stability is the integrity of the hermetic seals and that well-sealed devices containing titania NPs will be stable in sunlight for years.

Acknowledgement

ACW thanks EV Group (evgroup.com) for imprinting the wafer with their master and analyzing the wafer fragments by AFM and SEM.

References

1. Ohtani, B. "Titania Photocatalysis beyond Recombination: A Critical Review," *Catalysts* **2021**, *3*, 942-953. DOI: 10.3390/catal304942.
2. ASTM Standard D5071-06(2021), "Exposure of Photodegradable Plastics in a Xenon Arc Apparatus," ASTM International, West Conshohocken, PA, 2021, DOI: 10.1520/D5071-06, www.astm.org.