Trends in High-Performance Optical Coatings with Advanced Materials

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I. Introduction

Evolution of the electronics and display industries, along with the need for innovative and advanced coatings, is a key factor driving advances in optical coating materials.[1,2] Where some industries need coatings for substrates that offer exceptional optical clarity, others require optical coatings that are transparent and excellent conductors of electricity. In a society where there is a drive to make devices smarter with improved capabilities, and where the impact of energy and technology is increasingly prevalent, optical coatings are playing a substantial role in products that are part of our everyday lives.

Since the demands placed on the optical coatings industry are high and varied, optical coating manufacturers are turning to advanced materials experts to assist in meeting such demands. Quantitative and qualitative enhancements have become evident through the incorporation of advanced and nano-sized materials into optical coatings. The coatings can be deposited onto a substrate from a dispersion to form a film or can be incorporated into hybrid coating materials. A number of factors impact incorporation of these materials into optical coatings, including material size and shape, cost, scalability, and stability and compatibility during formulation and processing. Those who are skilled in the art of nanoparticle engineering can create highly customized and optimized materials for specific (and often proprietary) optical systems, thereby allowing companies to introduce novel products to the market.

Coatings for optical surfaces have come a long way in recent years. Today's optical coatings are becoming increasingly sophisticated so they can address the demands of a variety of industries, from automotive, construction, and medical to electronics, solar and defense.[1,2] This non-confidential report details select properties and performance attributes of optical coatings that are in demand based on our extensive market research along with voice-of-customer interviews with leading companies in the optical coating industry. There are stand-out materials that have the potential to be industry disrupting, such as silver, titania, and zirconia, however there has been little progress optimizing materials such as these for optical coatings.[3] Moving forward, it will be critical to further optimize and customize these materials to bring about enhanced performance, as well as explore the multifunctional performance nanomaterials can contribute to further advance optical coatings.

II. Summary of Recent Research

High refractive index coatings

In optical coatings, control of refractive index (RI) is essential to achieve desired performance.[4] Specifically, we have seen there is demand for high-RI nanoparticles for incorporation into polymer-based optical coatings. By incorporating a high-RI coating on the light-emitting surface of a device, light can travel more productively in or out of the device, leading to improved efficiency and picture quality.[5] High-RI polymers are being developed for advanced optoelectronic applications in display devices, light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs), semiconductor image sensors, and a variety of lenses.[5,6,7] Typical optical polymers have RIs of 1.30-1.70, limiting the range of optical applications.[6] There is now increased interest in developing polymers with a RI greater than 1.7 with superior optical properties.[6] A promising approach to achieve these high-RI values is through the incorporation of metal oxide nanoparticles with organic polymers to create an organic-inorganic hybrid material.[5,6,7] The design of nanoparticles is an important consideration in their successful incorporation, specifically particle size and compatibility with the polymer matrix.[6] Individuals and companies who are skilled in the art of nanoparticle design, can synthesize small nanoparticles with surface modifications so aggregation is avoided. Two of the most popular nanoparticles for producing high-RI coatings are titania (TiO_2) and zirconia (ZrO_2).[5,6]

Zirconia is a well-known high-RI nanoparticle that, when incorporated into optical coatings, can bring about an increase in RI. Zirconia has shown success in increasing the RI of a coating when it is surface modified for compatibility with a polymeric system. For example, 6.1 nm ZrO_2 coated with gallic acid that was incorporated into a brush block copolymer showed an increase in RI with increasing ZrO_2 content, resulting in RI of the block copolymer increasing from 1.45 to 1.70 (Figure 1a and 1b).[8]

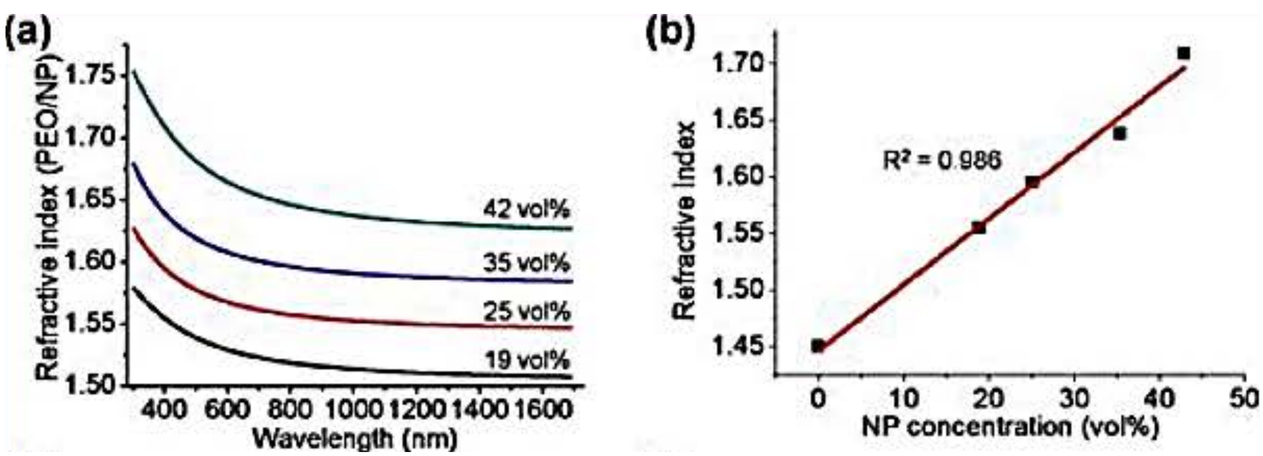

Figure 1. (a) RI of the poly(ethylene oxide)/ZrO_2 (PEO/NP) domain in a block copolymer over a wavelength range of 300-1690 nm, with different loadings of coated ZrO_2. (b) Effect of coated ZrO_2 concentration on RI (at 400 nm).[8]

Titania is a high-RI nanoparticle that can be incorporated into polymeric systems to produce high-RI optical coatings. For example, polyimide-nanocrystalline-TiO_2 coatings, with up to 50 wt% TiO_2, have been shown to form films with high optical transparency.[7] As shown in Figure 2, increasing TiO_2 content brought about an increase in the RI of the resulting film, allowing an RI of over 1.8 to be achieved with 50 wt% TiO_2.[7]

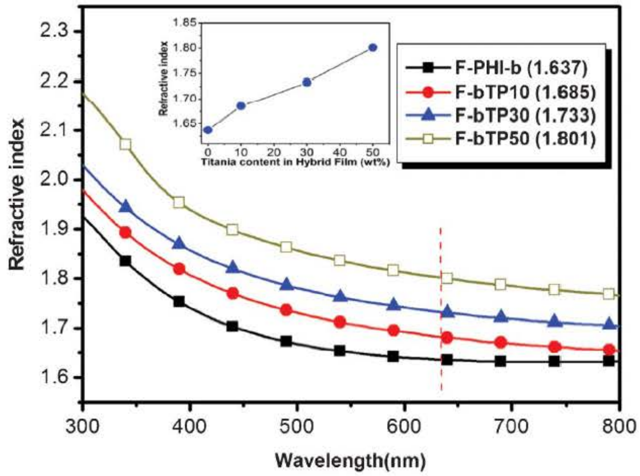

Figure 2. RI variation of polyimide-nanocrystalline-TiO_2 materials with wavelength, where F-PHI-b, F-bTP10, F-bTP30, and F-bTP50 contain 0 wt%, 10 wt%, 30 wt%, and 50 wt% TiO_2, respectively. Inset shows the variation of RI with increasing titania content for these samples at 633 nm.[7]

High and low-RI nanoparticles can be used to form adjustable RI coatings. For example, nanoparticles of TiO_2 and silica (SiO_2) can be used to form TiO_2-SiO_2 composite solutions for stack coatings with RI ranging from 1.10-2.0 based on the content of SiO_2.[4] Composite layers can be deposited onto a substrate with decreasing RI and, as shown in Figure 3a and 3b, with increasing SiO_2 content, there is decreasing RI. The high-RI of TiO_2 nanoparticles contributes to this effect. This stack coating achieved reduced reflectance and high transmittance over the solar spectrum, with a maximum transmittance of 99.16% at ~550 nm.[4]

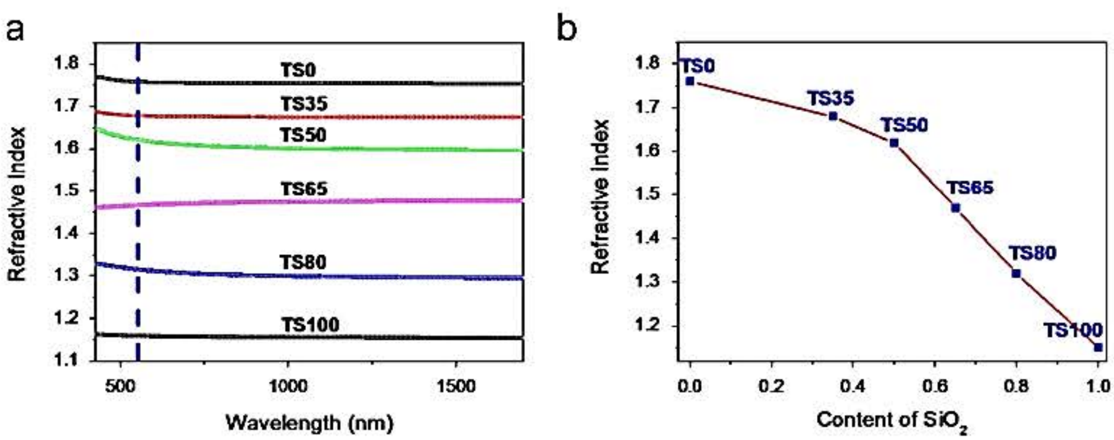

Figure 3. (a) Refractive index dependence on wavelength, where the vertical blue dashed line corresponds to wavelength of 550 nm; (b) Refractive indices of the composite layers versus SiO_2 content at wavelength of 550 nm. Where, TS0 (0% SiO_2), TS35 (35% SiO_2), TS50 (50% SiO_2), TS65 (65% SiO_2), TS80 (80% SiO_2) and TS100 (100% SiO_2).[4]

Anti-reflection (AR) coatings

Certain devices and surfaces, such as light emitting diodes (LEDs), liquid crystal displays (LCDs), and solar cells, require high transmittance while minimizing reflections of unwanted light from the surface.[9,10,11] One approach to creating anti-reflective surfaces is applying AR coatings to the substrate. Anti-reflection results from the destructive interference of light as it travels through thin films of differing refractive index (RI).[10] The tuning of RI and thickness of an AR coating is necessary for this purpose.[12] While obtaining near perfect AR coatings at research scale has been achieved, industrial scale production has been a challenge due to poor manufacturing robustness and contamination that impacts optical performance.[12] In addition, the need for multifunctional performance on surfaces such as these is growing.[9,10,11]

There have been a variety of materials explored for this purpose, two that seem ideal are nanoparticles of silica (SiO_2) and titania (TiO_2) due to their difference in RI (see Figure 4).[10] Thin films of SiO_2 and TiO_2 can be deposited onto glass substrates, as shown in the inset of Figure 4, to achieve improved transmittance and reflectance. As shown in Figure 5a, the transmittance of the glass is improved from 92% for the bare glass, to 95% and over 97% for glass coated on one side and both sides, respectively. Figure 5b shows the reduced reflectance of the coated samples as well. There is also multi-functional performance observed with this coating, as it absorbed UV light, was hydrophobic and oleophobic, and had very good scratch resistance and adhesion.[10]

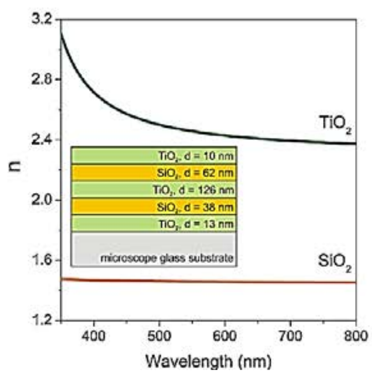

Figure 4. RI (n) variation of single layers of SiO_2 and TiO_2 with wavelength. Inset shows schematic of the AR multilayer coating.[10]

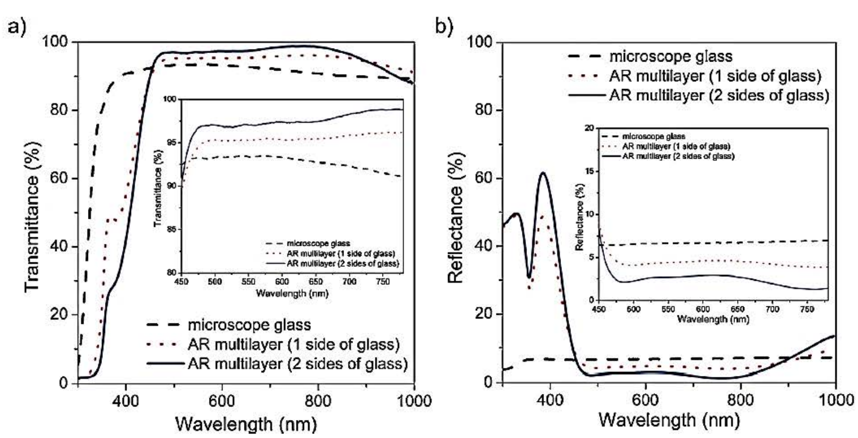

Figure 5. Transmittance (a) and reflectance (b) spectra of bare glass, and glass with AR coating on one & both sides.[10]

AR coatings with self-cleaning functionality have also been explored. TiO_2 is often used in this application due to its photocatalytic properties, as it can degrade organic contaminants, while maintaining anti-reflective performance.[12] This can be seen for modified 4 nm anatase TiO_2 nanoparticles that were incorporated into a block copolymer (BCP) and processed into a thin film that can be coated on glass or plastic.[12] The RI of the AR coating excluding TiO_2 is particularly low. This allows for the incorporation of 37.5 wt% TiO_2 to achieve the optimal RI of 1.22 for an AR coating on glass (Figure 6a). As shown in Figure 6b, 50 wt% TiO_2 incorporated into the AR coating had a maximum transmittance of about 99.3%, maintaining the high transmittance of the coating. These AR coatings also showed excellent photocatalytic and self-cleaning properties, which should improve the long-term performance of their substrates.[12]

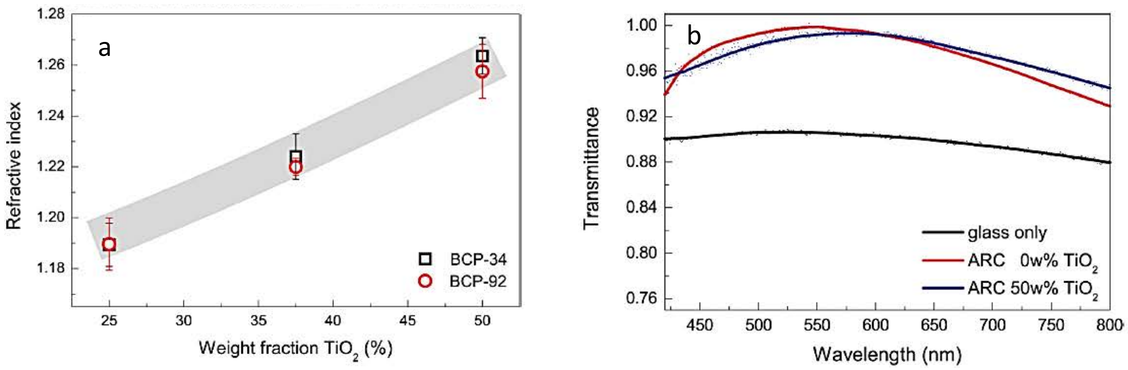

Figure 6. (a) RI as a function of TiO_2 wt% for two different BCPs, with molecular weights of 34.4 kg/mol and 91.9 kg/mol. (b) Transmittance of bare glass, and glass coated on both sides with AR coating containing 0 & 50 wt% TiO_2.[12]

Nanoparticles of silica (nano-silica) have also been used to produce AR coatings. Nano-silica thin films can be produced via sol-gel processing and coated on glass to bring about significantly reduced light reflection.[13] As shown in Figure 7, deposition time and cycles impact film morphology, and therefore anti-reflection properties as well. The uncoated glass substrate had a maximum transmittance of 91.5%, and when comparing the results for one deposition cycle, a highest maximum transmittance of 96% was achieved with 60 s deposition time. With two deposition cycles of 30 s each, the maximum transmittance reached was 97.5%, due to a more homogeneous and dense SiO_2 layer.[13]

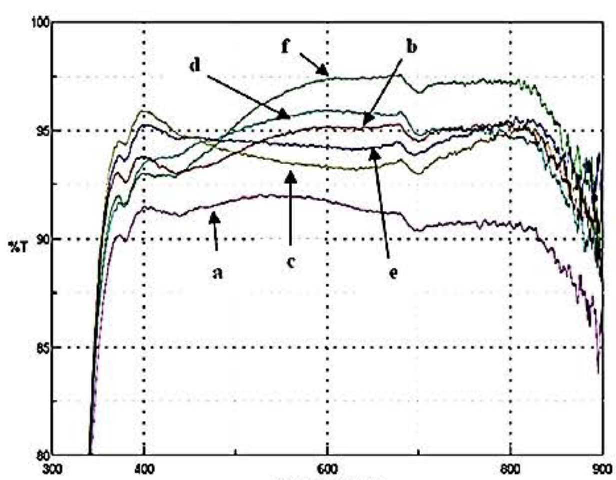

Figure 7. Transmittance spectra of (a) uncoated glass and glass that was coated with AR silica thin films that had deposition times of (b) 5 s, (c) 30 s, (d) 60 s, (e) 120 s and (f) 30–30 s (two deposition cycles).[13]

High reflective coatings

There has been wide interest in producing high reflective coatings for applications ranging from decorative to construction, military and defense, and telecommunication. This can be achieved through deposition of metal or metal oxide nanoparticles on various substrates.[2,14] Some reflective surfaces find application in buildings, heat dissipation in electronics, and solar cell cooling.[15]

Silver-based coatings are the ones of choice for several applications because silver offers the highest reflectivity from VIS to IR of all metals.[16] Silver (Ag) nanoparticles, for example, present in low amounts in a polymer matrix can form metal mirrors with exceptional light reflectivity, in addition to electric conductivity.[14] As shown in Figure 8, when measured from 250 nm to 950 nm, the Ag polymer coating showed reflectance surpassing 90%. Interestingly, this material also demonstrated the ability to self-heal defects. This coating can be applied to a range of substrates, from flexible substrates like textiles, to glass, wood, plastic, and steel (Figure 9).[14]

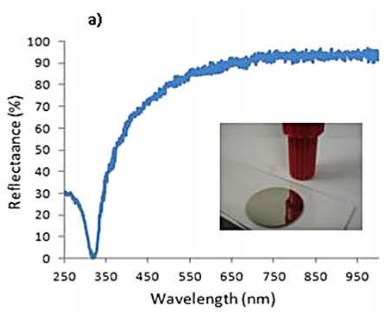

Figure 8. Reflectance spectrum of silver polymer coating, with image of sample featured.[14]

Figure 9. Images of silver polymer coating applied to a range of substrates.[14]

There has been interest in creating coatings with high reflectivity in the solar spectrum and high emissivity in the "sky window" region for radiative cooling and thermal management applications.[15] Two-layer coatings consisting of a top reflective layer, containing titania nanoparticles, for instance, and a bottom emissive layer, such as one consisting of silica or silicon carbide nanoparticles, have demonstrated reflective and cooling performance on substrates.[15] Simulations have shown that coatings based on these materials on an aluminum substrate achieved reflectivity of 90.7% in the solar spectrum. Measurements obtained from rooftop studies showed that these coatings can cool an aluminum substrate to ambient temperature when exposed to direct sunlight.[15]

Optical filter coatings

There are specialized coating applications that require selective filtration of certain wavelengths of light. For example, certain plastics are not resistant to UV light, and in turn suffer from aging and degradation.[17] Another surface that can benefit from this is windows, where near-infrared solar energy could be blocked to improve solar-driven cooling.[3] There is interest in approaches that can modify surfaces like these that would allow them to effectively absorb certain wavelengths of light.[17] A current approach focuses on tuning nanomaterials to selectively absorb damaging or unwanted wavelengths and transmitting those that are preferred.[3] There are a variety of nanoparticles that can be utilized, such as titania and zinc oxide.[3] The choice of nanoparticle and the stability of the nanoparticle in the coating solution are important considerations in achieving the desired performance.[3]

Titania (TiO_2) nanoparticle solutions can be used to form thin films on glass. As shown in Figure 10, these films transmit visible light and strongly absorb UV radiation. Coatings such as these can be used to protect surfaces and devices from UV light.[18]

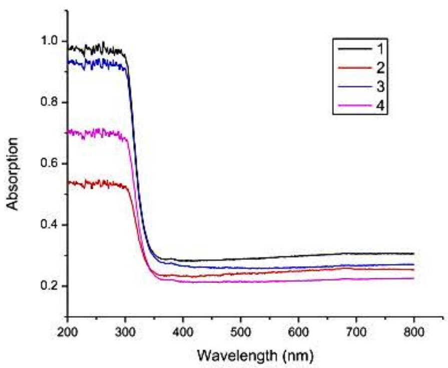

Figure 10. UV-Vis absorption spectra for 1, 2, 3, and 4 layer TiO_2 thin films coated onto glass.[18]

Zinc oxide (ZnO) is known for the broad-spectrum protection it can provide against UV radiation and it more effectively scatters UV radiation when in nanoform.[17] Zinc oxide nanoparticles can be used in coatings to selectively filter UV-A radiation, for example.[17] An aqueous suspension of 28 nm ZnO nanoparticles can be coated on a substrate, such as a polyethylene terephthalate (PET) film, to increase UV light absorbance. As shown in Figure 11, when applied as a single coating, the coating that contained 500 mg/L ZnO performed best. Also, increasing the number of coatings on the PET substrate brought about increased UV absorbance. The coatings did not impact the aesthetics of the original substrate and it remained transparent.[17]

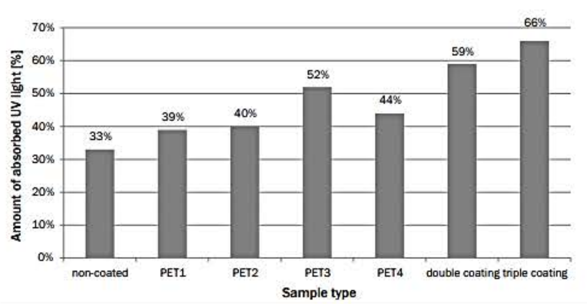

Figure 11. UV light absorptivity at UV wavelength 340 nm, with ZnO concentrations of 200 mg/L (PET1), 350 mg/L (PET2), 500 mg/L (PET3) and 1000 mg/L (PET4). Repeated coatings were carried out with 500 mg/L ZnO.[17]

Transparent conductive coatings

The market for transparent conductive coatings has exploded because of the increased demand and development of touch screen displays, thin-film solar cells, and light emitting devices.[19] There are now trends towards making flexible devices and larger touch screens.[20] Indium tin oxide (ITO) is almost exclusively used in transparent conductive coatings, however, due to its high cost, high temperature needed to deposit films, brittleness, and yellow tint when deposited at certain thicknesses, a reliable replacement is being sought.[20,21] A variety of replacement materials have been investigated, from carbon nanotubes to graphene to conductive polymers, but there have been challenges in achieving similar performance of ITO.[21] Silver nanowires (AgNW) have recently emerged as an exciting substitute because of their high transparency and conductivity, low-cost deposition, resistance to cracking, high dc conductivity and optical transmittance.[20,21,22]

The design of AgNWs is a critical factor in the performance of the resulting coating. Longer nanowires decrease sheet resistance because there are fewer connections between them, and because of this, there is a pressing need for the development of ultra-long nanowires.[21] This is demonstrated in Figure 12, which shows the relationship between transmittance and sheet resistance of AgNW dispersions varying in size that have been deposited onto glass.[20] Promisingly, the AgNW dispersion with the smallest diameter (27 nm) and longest length (18 µm) showed results comparable to that of commercially available ITO.[20]

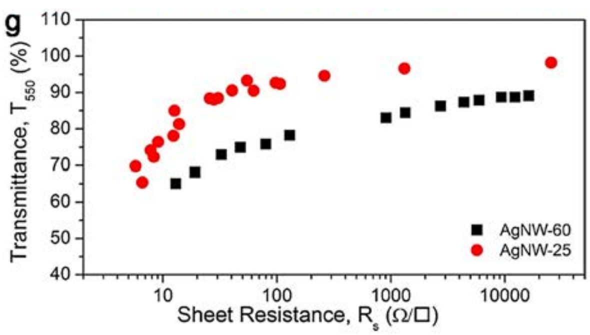

Figure 12. Transmittance at 550 nm plotted against sheet resistance of AgNWs with two different sizes, where AgNW-60 has average diameter 54 nm and average length 9.4 µm, and AgNW-25 has average diameter 27 nm and average length 18 µm.[20]

AgNWs can also be combined with other nanomaterials to improve performance for certain applications. For example, a film of AgNWs with a diameter and length of 60 nm and 30-40 µm, respectively, with a thin over layer of ZnO (AgNW(ZnO)) offer improved connectivity between nanowires and improved adhesion with low-lying surface.[22] When compared to ITO, AgNW(ZnO) and AgNW showed comparable and acceptable transmittance and sheet resistance, and when applied to Cu(In,Ga)Se_2 (CIGS) solar cells, the enhanced performance of AgNW(ZnO) can be seen (Table 1). With a solar cell efficiency of 13.50%, the solar cell coated with AgNW(ZnO) was significantly higher than that for AgNW and slightly higher than that for ITO. It is thought that the improved adhesion contributed to the superior performance.[22]

TCE	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	eff (%)	R_s (Ω cm^{-2})	R_{sh} (Ω cm^{-2})
AgNWs	0.2	0.54	33	0.05		
ITO	30.7	0.65	65	13.04	0.92	147
AgNW(ZnO)	33.7	0.64	62	13.50	0.65	299

Table 1. Parameters of CIGS solar cells with AgNW(ZnO), AgNW, and ITO as transparent conductive electrodes.[22]

III. Conclusion

Market research and voice-of-customer interviews indicated the optical coating industry has a growing need for products that demonstrate enhanced performance to meet customer needs in a variety of end-use applications. Because of the promise inorganic advanced and nano-sized materials have in optical coatings, many industry leaders are focusing research and development efforts on incorporating these materials into their optical coatings. There are, however, existing challenges in producing these materials cost-effectively and to scale, as well as a need to dedicate more research into the optimization/customization of these materials. In order to overcome these and other hurdles, partnering with inorganic materials experts will enable industry to supply their customers with innovative and high performance optical coatings.

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