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Development of Nanostructured Antireflection Coatings for Infrared and Electro-Optical Systems

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Abstract: Electro-optic infrared technologies and systems operating from ultraviolet (UV) to long-wave infrared (LWIR) spectra are being developed for a variety of defense and commercial systems applications. Loss of a significant portion of the incident signal due to reflection limits the performance of electro-optic infrared (IR) sensing systems. A critical technology being developed to overcome this limitation and enhance the performance of sensing systems is advanced antireflection (AR) coatings. Magnolia is actively involved in the development and advancement of nanostructured AR coatings for a wide variety of defense and commercial applications. Ultrahigh AR performance has been demonstrated for UV to LWIR spectral bands on various substrates. The AR coatings enhance the optical transmission through optical components and devices by significantly minimizing reflection losses, a substantial improvement over conventional thin-film AR coating technologies. Nanostructured AR coatings have been fabricated using a nanomanufacturable self-assembly process on substrates that are transparent for a given spectrum of interest ranging from UV to LWIR. The nanostructured multilayer structures have been designed, developed and optimized for various optoelectronic applications. The optical properties of optical components and sensor substrates coated with AR structures have been measured and the process parameters fine-tuned to achieve a predicted high level of performance. In this paper, we review our latest work on high quality nanostructure-based AR coatings, including recent efforts on the development of nanostructured AR coatings on IR substrates.

Keywords: Antireflection coatings, nanostructured coatings, optical transmittance, optical reflectance, electro-optical infrared sensors.

1. Introduction

Electro-optical infrared (EO-IR) technologies are playing an increasingly important role in various defense and commercial system applications. EO-IR sensors and systems operating from the ultraviolet (UV) to long-wave infrared (LWIR) portions of the electromagnetic spectrum are being developed for defense and commercial security applications [1-9]. Development of multiband sensors with enhanced sensitivity is a critical requirement of next generation imaging systems. Antireflection (AR) coatings can eliminate or minimize reflection losses from the surfaces of sensor and optical components that limit the sensitivity and performance of the sensors and systems.

It has been known for some time that Fresnel reflection losses can theoretically be minimized between two media by grading the refractive index across the interface. However, the unavailability of materials with the desired refractive indices, particularly materials with very low refractive indices, has restricted the implementation of graded and step-graded refractive index designs. Recently, however, a new class of optical thin-film materials consisting of porous nanorods has enabled the realization of ultralow refractive index materials [10-19].

Nanostructured AR coatings were fabricated using a tunable self-assembly process on substrates that are transparent for a given spectrum of interest ranging from UV to LWIR. The nanostructured multilayer structures have been designed, developed, and optimized for various optoelectronic and imaging applications. The optical properties of AR-coated optical components and sensor substrates have been measured and the process parameters have been fine-tuned to achieve a predicted high level of performance. In this paper, we review our latest work on high-quality nanostructure-based AR coatings, including recent efforts on the development of nanostructured AR coatings on IR substrates.

2. Nanostructured Layer Growth

Porous nanostructured layers are fabricated using a scalable physical vapor deposition (PVD) method. It is a nanomanufacturable self-assembly process and the nanostructured layers can be processed on almost any type of substrate. In this process, a highly directional vapor flux is created, which can be implemented using a variety of optical coating materials. The formation of porous thin-films is enabled by surface diffusion and self-shadowing effects during the growth process. As illustrated in Fig. 1, random growth fluctuations on the substrate produce a shadow region that incident vapor flux cannot reach, and a non-shadow region where incident flux deposits preferentially, thereby creating oriented rod-like structures with high porosity and lower effective refractive index. The deposition angle, defined as the angle between the normal to the sample surface and the incident vapor flux, results in the formation of nanorod structures that are tilted relative to the sample surface.

The self-assembled nanostructured layer growth process can be applied to many different materials. For example, Fig. 2 depicts cross-sectional scanning electron microscope (SEM) images of two nanostructured thin-films: one employing silicon dioxide (SiO_2) and the other indium tin oxide (ITO). Both films were deposited at highly oblique angles (~80°), which resulted in the formation of well-defined nanorod structures.

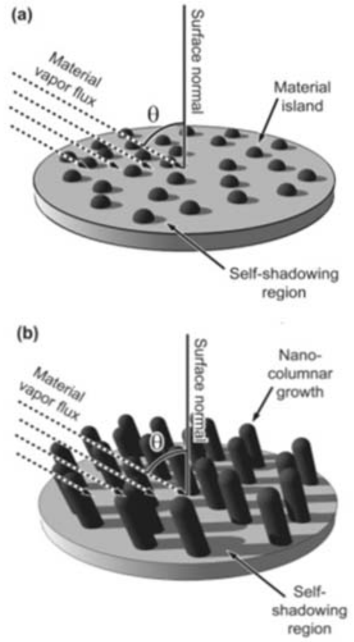


Fig. 1. Simplified schematic of the self-assembly process for synthesizing porous, nanostructured films, showing (a) the initial formation of material islands at random locations across the substrate, followed by (b) the formation of self-shadowed regions and nano-columnar growth when material vapor flux arrives at a non-normal deposition angle (θ) to the substrate.

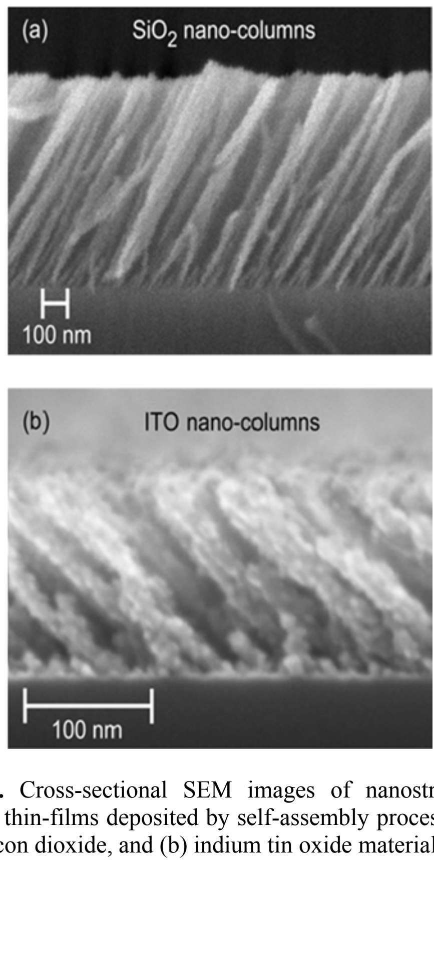


Fig. 2. Cross-sectional SEM images of nanostructured optical thin-films deposited by self-assembly process using (a) silicon dioxide, and (b) indium tin oxide materials.

Because the gaps between the nanorods are typically much smaller than the wavelengths of visible and IR radiation, the nanostructured layers act as a single homogenous film having a refractive index intermediate in value between the ambient air and the nanorod material that decreases with increasing porosity. Fig. 3 presents the measured refractive index dispersion curve as a function of wavelength from a layer of nanostructured SiO_2 deposited at a highly oblique angle [11]. This low-index nanostructured SiO_2 film was deposited on a silicon substrate and measured by ellipsometry. Also shown is a comparison of experimental reflectivity data with theoretical calculations. These results demonstrate that nanowires and nanorods grown by the self-assembly process provide a pathway for fabricating high-quality broadband AR coatings for a variety of nanosensor applications.

Figs. 4 and 5 demonstrate the use of SiO_2 and TiO_2 nanowires and nanorods to achieve high-performance, step-graded AR coatings on AlN substrates. The feasibility of this technology has been demonstrated for UV light-emitting diode (LED) applications [11]. In the next section, we summarize our recent efforts to extend this technology to different substrates and other bands of interest over the visible, near-infrared (NIR), and mid-wave infrared (MWIR) spectra for next generation EO/IR sensors.

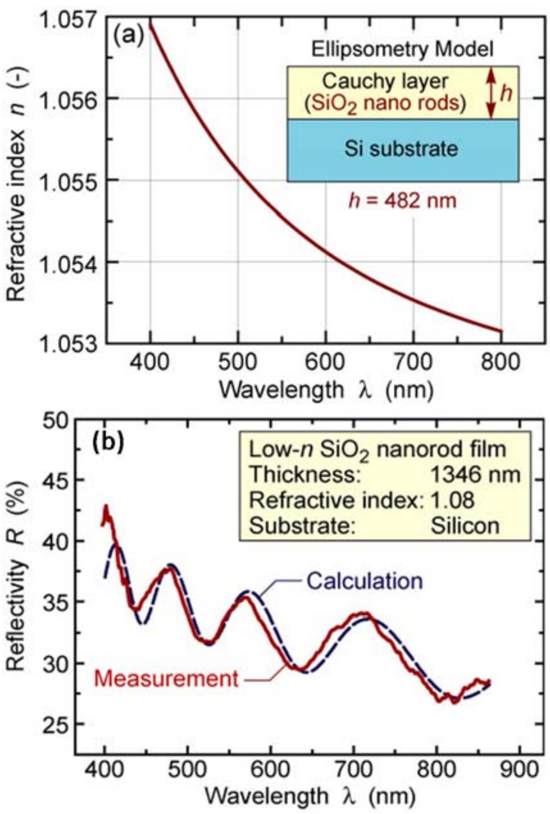
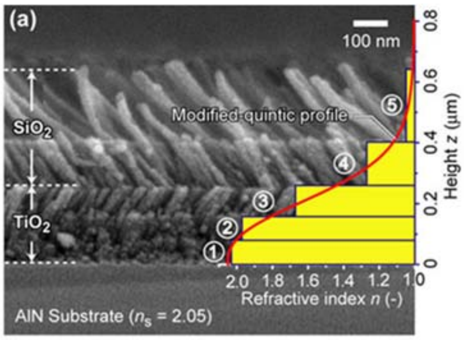


Fig. 3. (a) Refractive index dispersion curve of a low index SiO_2 nanorod thin film on silicon substrate as measured by ellipsometry, with (b) comparison of the measured and calculated reflectivity spectra.



(b) Layer No.	1	2	3	4	5
Source		TiO_2		SiO_2	
Deposition angle	25°	40°	65°	−68°	−87°
Thickness (nm)	77.4	80.2	99.3	145.0	223.0
Refractive index, *n*	2.03	1.97	1.67	1.27	1.05

Fig. 4. (a) Cross-sectional SEM image of TiO_2 and SiO_2 step-graded index nanowire/nanorod coatings that approximate a modified quintic profile. Graded-index coating consists of three TiO_2 and two SiO_2 nanorod layers. (b) Physical targets for each layer, including deposition angle, thickness and refractive index.

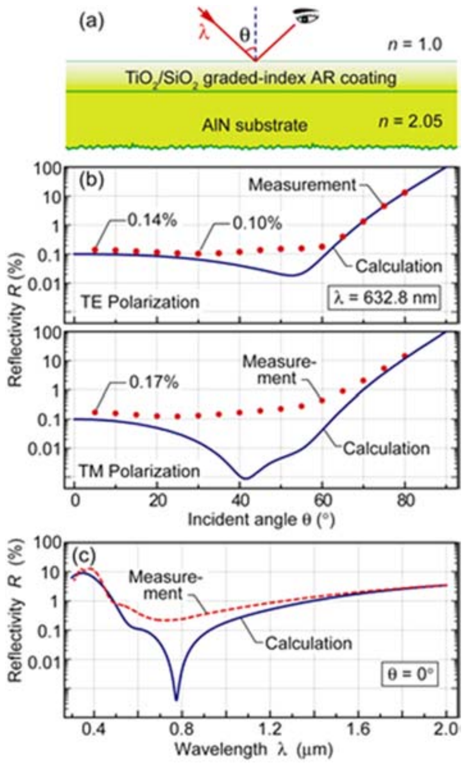


Fig. 5. Reflectivity of graded-index coating on AlN substrate summarized above in Fig. 4, including (a) schematic of the reflectivity measurement; (b) theoretical (solid line) and measured (dotted line) reflectivity of polarized light vs. incident angle; and (c) wavelength dependence of theoretical (solid line) and measured (dashed line) reflectivity at normal incidence. Further details can be found in Ref. [11].

3. Nanostructured Antireflection Coatings on Rigid Substrates

We have fabricated and tested a number of different step-graded antireflection structures on glass substrates [13-15]. In particular, multilayer structures comprising nanostructured SiO_2 have been incorporated using the self-assembly process. These multilayer AR structures have been deposited on both sides of a glass substrate, and the transmittance characterized as a function of wavelength and incident angle.

Fig. 6 compares the measured broadband performance of an uncoated glass slide to one coated on both sides with a multilayered, nanostructured SiO_2 coating. The nanostructured coatings were prepared with electron beam evaporation using different deposition angles to form distinct layers with a step-graded refractive index profile. The inset in Fig. 6 shows a representative cross-sectional SEM image of a two-layer structure. The transmittances of the coated and uncoated glass slides were measured using an angle-dependent transmittance measurement setup consisting of a xenon lamp light source and Ando AQ6315A optical spectrum analyzer calibrated to detect transmitted photons over a broadband spectrum (400-1800 nm). The measured peak broadband transmittance at normal incidence of the uncoated glass slide is 92%, in line with the expected approximate 4% reflection loss at each glass/air interface. The peak transmittance increases to 98.3% for the double-sided, nanostructured coated glass, implying an average broadband reflection loss of less than 1% at each glass/air interface. As shown in Fig. 6, the transmittance through the nanostructured SiO_2 coated glass is also significantly higher than the uncoated glass across a wide range of incident angles. While the transmittance of the uncoated glass slide falls below 80% at an incident angle of 65°, the glass slide with the double-sided coating still maintains transmittance above 95%.

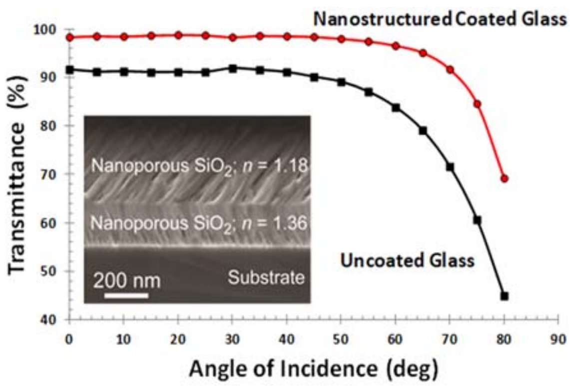


Fig. 6. Incident angle dependent broadband transmittance measurement through a glass slide coated on both sides with a step-graded, nanostructured SiO_2 AR structure. Also shown is the measured broadband transmittance of an uncoated glass slide, and a cross-sectional SEM image of a two-layer nanostructured coating.

The transmittance of coated and uncoated glass slides has also been measured as a function of wavelength at normal incidence using a JASCO V-570 spectrophotometer. As seen in Fig. 7, the measured transmittance through a glass slide is dramatically improved over the entire 400-1800 nm spectrum by the application of the nanostructured AR coating. In particular, the average measured broadband transmittance between 350-1800 nm increases from 92.2% for the uncoated glass to 98.6% for the double-sided, nanostructured coated glass. Moreover, the transmittance through the glass with a nanostructured SiO_2 coating exceeds 97.8% at all wavelengths between and 440 nm and 1800 nm, implying a glass-air interface reflectivity below 1.1% over a wide range of wavelengths. These optimized nanostructured antireflection coatings have been shown to outperform an ideal quarter-wavelength MgF_2 coating over all wavelengths and incident angles [15].

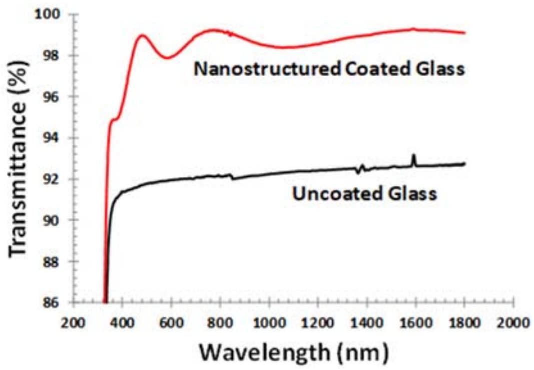


Fig. 7. Wavelength-dependent transmittance measurement of a step-graded, nanostructured SiO_2 AR coating on a glass substrate.

4. Nanostructured AR Coatings on Flexible Substrates

Broadband and high-performance AR coatings have been demonstrated on flexible substrates such as polycarbonate films. Polycarbonate is an excellent plastic for display filters, plastic lenses, and face shields, and is thus commonly utilized in commercial and defense applications. Polycarbonates also provides high impact resistance combined with an excellent flammability rating.

Nanostructured SiO_2 multilayer AR coatings having an optimized step-graded index profile have been deposited on both sides of polycarbonate sheets. The AR coatings eliminate nearly all the reflection loss and yield ultrahigh optical transmittance. Fig. 8 compares the optical transmittance spectra of AR-coated and uncoated polycarbonate sheets. The expanded transmittance spectrum over the visible band is plotted in the inset of Fig. 8. As seen in the inset, the uncoated polycarbonate sheet shows approximately 90% transmittance over the visible spectrum (~400-800 nm). The AR coating on the polycarbonate sheet increases the transmittance to almost 100%, nearly a 10% enhancement in optical transmittance. The enhancement in the optical transmittance is observed for the entire visible and part of the NIR band. Ultrahigh AR performance over the entire visible spectrum makes the nanostructured AR coatings potential candidates for multicolor complementary metal oxide semiconductor (CMOS) sensors.

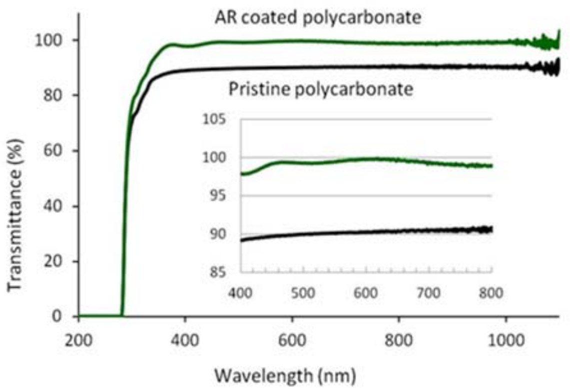


Fig. 8. Optical transmittance spectrum of a transparent polycarbonate sheet (5 mil thickness) before and after application of the large-area AR coating. The AR coating yields nearly 100% transmittance.

5. Nanostructured AR Coatings on Curved Surfaces

The ultrahigh performance of the nanostructured AR coatings has likewise been successfully demonstrated on curved surfaces such as optical lenses. Converging and diverging lenses are key components in an EO-IR system that manipulate the optical pathway through the system. Light passing through a lens suffers from reflection losses at both surfaces of the lens. These losses add up and can limit the performance of an EO-IR system. Demonstration of AR coatings on curved lens surfaces extends the benefits of the AR coating to EO-IR systems and their applications.

AR coatings have been designed and optimized with step-graded index profiles for n-BK7 lenses. Nanostructured SiO_2 layers featuring the desired refractive indices were deposited on the surface of the optical lenses by the self-assembly process. Multilayer step-graded index profiles were created and optimized by controlling the refractive indices and thicknesses of the individual layers. Fig. 9 compares the transmittance of uncoated and nanostructured SiO_2 multilayer-coated n-BK7 lenses. The nanostructured AR coating significantly improved optical transmittance through the lens from 94% to almost 100%.

The optical transmittance enhancement has been preserved over the entire visible, and majority of the NIR, spectra. Hence, the AR-coated lens can transmit the near-total optical signal to a sensor over a broader spectrum by eliminating the vast majority of unwanted reflections, enabling significantly higher responsivities in detector devices and thereby enhancing their effectiveness. This approach can be expanded to various EO-IR components and significantly improve imaging, sensing and detection capabilities of EO-IR systems.

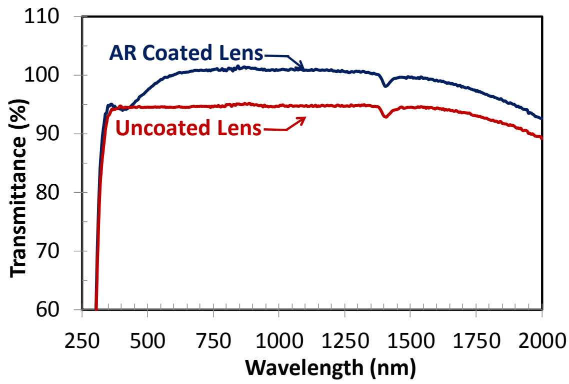


Fig. 9. Measured wavelength-dependent transmittance of a nanostructured SiO_2 coated lens compared to an uncoated lens. The AR coating yields nearly 100% transmittance. The ultrahigh transmittance was preserved for a wider spectrum of light.

6. IR-Band AR Coatings on Silicon Substrates

In order to extend the application of the nanostructured AR coatings to the IR spectral bands, nanostructured AR coatings on silicon wafers have been fabricated and successfully demonstrated ultrahigh AR performance over the 3-5 µm and 10-12 µm spectral bands. The measured wavelength-dependent reflectance of multilayer AR-coated and uncoated Si substrates are shown in Fig. 10. The multilayer AR coating has been synthesized by sequentially growing multiple layers of nanostructured Si and SiO_2 layers with a desired graded-index profile for the 3-5 µm MWIR band. The index profile is achieved by controlling the tilt angle. The average measured reflectance for the multilayer AR-coated Si wafer is less than 1.5%, while the average measured reflectance for the uncoated silicon <211> wafer is approximately 30% over the 3-5 µm MWIR spectral band.

Fig. 11 shows the measured wavelength dependent reflectance of two-layer AR-coated and uncoated Si <211> substrates. The AR coating index profile has been specifically designed for the 8-10 µm LWIR spectral band. The two-layer AR coating has been synthesized by sequentially growing two nanostructured Si layers at different tilt angles. The average reflectance at the 8-10 µm spectral band for the two-layer AR-coated Si wafer is approximately 1.5%, while that of the uncoated Si<211> wafer is 29%.

These results clearly demonstrate that the multilayer AR coating significantly minimizes the loss of incident IR signal in both spectral bands. Ongoing efforts are focused on further improving performance by fine-tuning process parameters.

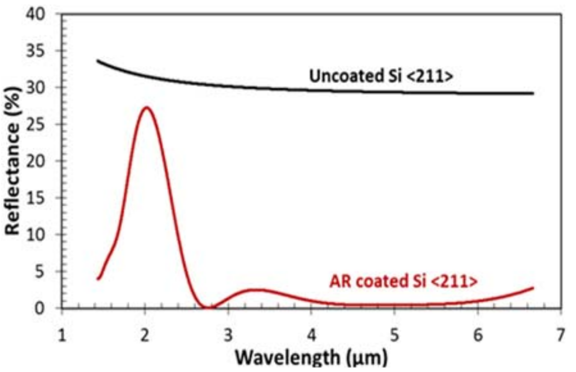


Fig. 10. Measured wavelength-dependent reflectance of multilayer AR-coated and uncoated Si<211> wafers. The multilayer AR coating on Si<211> shows average reflectance of 1.43% over the 3-5 µm spectral band.

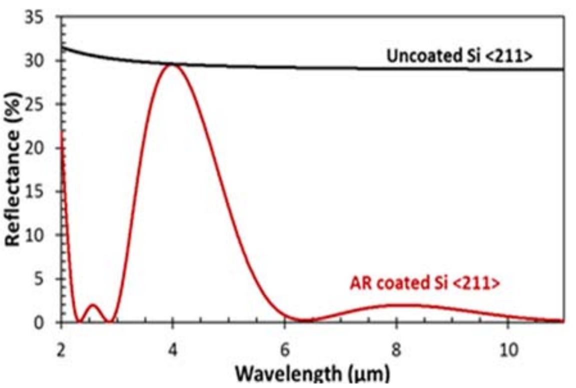


Fig. 11. Measured wavelength-dependent reflectance of two-layer AR-coated and uncoated Si<211> wafers. The two-layer AR coating on Si<211> shows average reflectance of 1.5% over the 8-10 µm spectral band.

6. Summary

This paper has sought to demonstrate that the growth of porous nanostructured layers offers an innovative approach for developing high-quality antireflection coatings for use on next-generation sensors and optical windows to minimize reflection losses for both defense and commercial applications. Step-graded multilayer AR technology has been shown to be both broadband and omnidirectional in nature. Continued efforts are underway to demonstrate nanostructure-based AR coatings for spectral bands from the UV to the IR for next-generation sensors, and to extend their functionality to larger area substrates.

References

[1]. Gopal G. Pethuraja, John W. Zeller, Roger E. Welser, Ashok K. Sood, Harry Efstathiadis, Pradeep Haldar, Priyalal S. Wijewarnasuriya, and Nibir K. Dhar, Development of Nanostructured Antireflection Coatings for Electro-Optic Infrared Technologies, Paper presented at: *TechConnect World Innovation Conference*, May 14-17, 2017, Washington, DC, USA.

[2]. A. K. Sood, R. A. Richwine, Y. R. Puri, S. Horn, and R. S. Balcerak, Design Considerations Using APD Detectors for High Resolution UV Imaging Applications, *Proceedings of SPIE*, Vol. 7419, 2009, pp. 74190V.

[3]. M. J. Cohen, T. J. Martin, J. C. Dries and M. J. Lange, InGaAs Sensor / Focal Plane Arrays for SWIR Applications, *Proceedings of SPIE*, Vol. 5406, 2004, pp. 38-45.

[4]. A. K. Sood, R. A. Richwine, Y. R. Puri, N. DiLello, J. L. Hoyt, T. I. Akinwande, S. Horn, R. S. Balcerak, G. Bulman, R. Venkatasubramanian, A. I. D'Souza, and T. G. Bramhall Development of Low Dark Current SiGe-Detector Arrays for Visible-NIR Imaging Sensors, *Proceedings of SPIE*, Vol. 7298, 2009, pp. 72983D1.

[5]. M. Davis, J. Devitt, M. Greiner, R. Rawe, A. Timlin and D. Wade Advanced InSb FPA Sensor Development at CMC Electronics, *Proceedings of SPIE*, Vol. 5563, 2004, pp. 62- 73.

[6]. A. K. Sood, R. A. Richwine, Y. R. Puri, N. K. Dhar, D. L. Polla, and P. S. Wijewarnasuriya Multispectral EO/IR Sensor Model for Evaluating UV, Visible, SWIR, MWIR and LWIR System Performance, *Proceedings of SPIE*, Vol. 7300, 2009, pp. 73000H.

[7]. P. W. Norton, M. Kohin, M. Dovidio and B. Becker Commercialization of Uncooled Infrared Technology, *Proceedings of SPIE*, Vol. 5563, 2004, pp. 55-61.

[8]. A. K. Sood, R. A. Richwine, Y. R. Puri, D. L. Polla, N. K. Dhar, Z. L. Wang, J. M. Xu, P. S. Wijewarnasuriya, N. Goldsman, M. B. Soprano, and B. Lineberry EO/IR Sensors Development Using Zinc Oxide and Carbon Nanostructures, *Proceedings of SPIE*, Vol. 7318, 2009, pp. 731804.

[9]. A. K. Sood, Y. R. Puri, L. Becker, M. Z. Tidrow, R. S. Balcerak, G. Brill, P. Wijewarnasuriya, N. Dhar, P. Boieriu, C. Fulk, S. Sivananthan, J. Yehoda, and S. Finke, Development of High-Performance Radiation-Hardened Antireflection Coatings for LWIR and Multicolor IR Focal Plane Arrays, *Proceedings of SPIE*, Vol. 6206, 2006, pp. 620615.

[10]. D. J. Poxson, M.-L. Kuo, F. W. Mont, Y.-S. Kim, X. Yan, R. E. Welser, A. K. Sood, J. Cho, S.-Y. Lin, and E. F. Schubert High-Performance Antireflection Coatings Utilizing Nanoporous Layers, *MRS Bulletin*, Vol. 36, 2011, pp. 434-438.

[11]. J. Q. Xi, M. F. Schubert, J. K. Kim, E. F. Schubert, M. Chen, S.-Y. Lin, W. Liu, and J. A. Smart Optical Thin-Film Materials with Low Refractive Index for Broadband Elimination of Fresnel Reflection, *Nature Photonics*, Vol. 1, 2007, pp. 176-179.

[12]. M. F. Schubert, F. W. Mont, S. Chhajed, D. J. Poxson, J. K. Kim, and E. Fred Schubert Design of Multilayer Antireflection Coatings Made from Co-sputtered and Low-Refractive-Index Materials by Genetic Algorithm, *Optics Express*, Vol. 16, 2008, pp. 5290-5298.

[13]. R. E. Welser, A. W. Sood, A. K. Sood, D. J. Poxson, S. Chhajed, J. Cho, E. F. Schubert, D. L. Polla, and N. K. Dhar Ultra-High Transmittance through Nanostructured-Coated Glass for Solar Cell

Applications, *Proceedings of SPIE*, Vol. 8035, 2011, pp. 80350X.

[14]. S. Chhajed, D. J. Poxson, X. Yan, J. H. Cho, E. F. Schubert, R. E. Welser, A. K. Sood and J. K. Kim, Nanostructured Multi-Layer Tailored-Refractive Index Anti-Reflection Coating for Glass with Broadband and Omni-Directional Characteristics, *Applied Physics Express*, Vol. 4, 2011, No. 052503.

[15]. R. E. Welser, A. W. Sood, G. G. Pethuraja, A. K. Sood, X. Yan, D. J. Poxson, J. Cho, E. Fred Schubert, and J. L. Harvey, Broadband Nanostructured Antireflection Coating on Glass for Photovoltaic Applications, in *Proceedings of the 38th IEEE Photovoltaic Specialist Conference*, No. 525, 2012.

[16]. Gopal G. Pethuraja, Roger E. Welser, John W. Zeller, Yash R. Puri, Ashok K. Sood, Harry Efstathiadis, Pradeep Haldar, and Jennifer L. Harvey Antireflection coatings for solar panel power output enhancement, *MRS Proceedings,* 1771, 2015, pp. 67-72.

[17]. Ashok K. Sood, Gopal Pethuraja, Roger E. Welser, Yash R. Puri, Nibir K. Dhar, Priyalal S. Wijewarnasuriya, Jay Lewis, Harry Efsthadiatis, Pradeep Haldar, and E. F. Schubert Development of large area nanostructured antireflection coatings for EO/IR sensor applications, *Proceedings of SPIE,* Vol. 9609, 2015, pp. 96090D.

[18]. Gopal G. Pethuraja, Roger E. Welser, John W. Zeller, Yash R. Puri, Ashok K. Sood, Harry Efstathiadis, Pradeep Haldar, Nibir K. Dhar and Priyalal Wijewarnasuriya Nanostructured Antireflection Coatings for Optical Detection and Sensing Applications, *MRS Proceedings*, 1805, 2015, mrss15-2137947.

[19]. Gopal G. Pethuraja, Roger E. Welser, John W. Zeller, Yash R. Puri, Ashok K. Sood, Harry Efstathiadis, Pradeep Haldar and Jennifer L. Harvey, Antireflection coatings for solar panel power output enhancement, *MRS Proceedings*, 1771, 2015, pp. 67-72.
