ORNL/TM-2015/149
CRADA/NFE-14-05066

Oak Ridge National Laboratory

Pooran Joshi

March 24, 2015

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

ORNL/TM-2015/149
CRADA/NFE-14-05066

Materials Science and Technology Division
Advanced Manufacturing Office

Develop Roll-to-Roll Manufacturing Process of ZrO_2 Nanocrystals/Acrylic Nanocomposites for High Refractive Index Applications

Pooran Joshi
Brett Compton, Jianlin Li, Jay Jellison, and Chad Duty
Oak Ridge National laboratory

Zhiyun (Gene) Chen
Pixelligent Technologies, LLC

Date Published:
March 24, 2015

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

LIST OF FIGURES

ACKNOWLEDGEMENTS

This CRADA NFE- 14-05066 was conducted as a Technical Collaboration project within the Oak Ridge National Laboratory (ORNL) Manufacturing Demonstration Facility (MDF) sponsored by the US Department of Energy Advanced Manufacturing Office (CPS Agreement Number 24761). Opportunities for MDF technical collaborations are listed in the announcement “Manufacturing Demonstration Facility Technology Collaborations for US Manufacturers in Advanced Manufacturing and Materials Technologies” posted at http://web.ornl.gov/sci/manufacturing/docs/FBO-ORNL-MDF-2013-2.pdf. The goal of technical collaborations is to engage industry partners to participate in short-term, collaborative projects within the Manufacturing Demonstration Facility (MDF) to assess applicability and of new energy efficient manufacturing technologies. Research sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

ABSTRACT

The purpose of this Cooperative Research and Development Agreement (CRADA) was to develop and evaluate ZrO_2/acrylic nanocomposite coatings for integrated optoelectronic applications. The formulations engineered to be compatible with roll-to-roll process were evaluated in terms of optical and dielectric properties. The uniform distribution of the ZrO_2 nanocrystals in the polymer matrix resulted in highly tunable refractive index and dielectric response suitable for advanced photonic and electronic device applications.

1. DEVELOP ROLL-TO-ROLL MANUFACTURING PROCESS OF ZRO2 NANOCRYSTALS/ACRYLIC NANOCONTPOSITES FOR HIGH REFRACTIVE INDEX APPLICATIONS

This phase-1 technical collaboration project (MDF-TC-2014-025) was begun on May 01, 2014 and was completed on January 31, 2015. Pixelligent Technologies, LLC is a small business. The present investigation successfully demonstrates tunable refractive index and capacitance in ZrO_2 nanocrystal embedded polymer nanocomposites for integrated optoelectronic applications.

1.1 BACKGROUND

Pixelligent has developed a large-scale synthesis process and infrastructure to produce mono-dispersed sub-10 nm ZrO_2 nanocrystals with precisely engineered surface chemistry that is compatible with a large variety of polymer systems. Currently, the Pixelligent is capable of producing ~2 ton/year of nanocrystals and is working on further scaling up the productivity to ~25 ton/year. The small size and superb dispersability of these nanocrystals allow the nanocrystals to be added in high loading without significantly impacting the processability of the materials. High refractive index nanocomposites have broad applications as light coupling layers in light-emitting diode (LED), organic light-emitting diode (OLED), complementary metal–oxide–semiconductor (CMOS) sensors, photovoltaic, etc., to improve light utilization efficiency. Optimization of the process of the nanocomposite coating for a mainstream manufacturing process is an important milestone in the Pixelligent's commercialization pathway. Leveraging ORNL's roll-to-roll manufacturing setup and advanced material characterization capabilities, the Pixelligent-ORNL collaboration focused on establishing the nanocomposite coating characteristics critical for technology integration and defining the path-to-market.

1.2 TECHNICAL RESULTS

The key findings of the electrical and optical characterization of the ZrO_2-nc/acrylic nanocomposite films are highlighted in the following sections. The nanocomposites were processed on quartz substrates to analyze the optical transmittance and absorption characteristics while the dielectric response was evaluated on metal-film-metal (MFM) capacitors as a function of nanocrystal loading and applied small-signal frequency. The main focus of the present investigation was on establishing the impact of ZrO_2 nanocrystal loading on the resultant thin film properties for advanced lighting and integrated electronic applications.

1.2.1 Optical Transmittance

Fig. 1 shows the impact of ZrO_2 nanocrystal loading on the optical transmittance as measured by UV-VIS-IR spectrophotometer for two separate batches of nanocomposite samples. All the samples loaded with 20% and 80% ZrO_2 nanocrystals exhibited high transmittance (>80%) in the visible part of the optical spectrum, and a sharp optical absorption-edge at around 300 nm. The high optical transmittance even at a high ZrO_2 nanocrystal loading of 80% shows the suitability of the nanocomposite thin films for efficient light guiding and extraction applications.

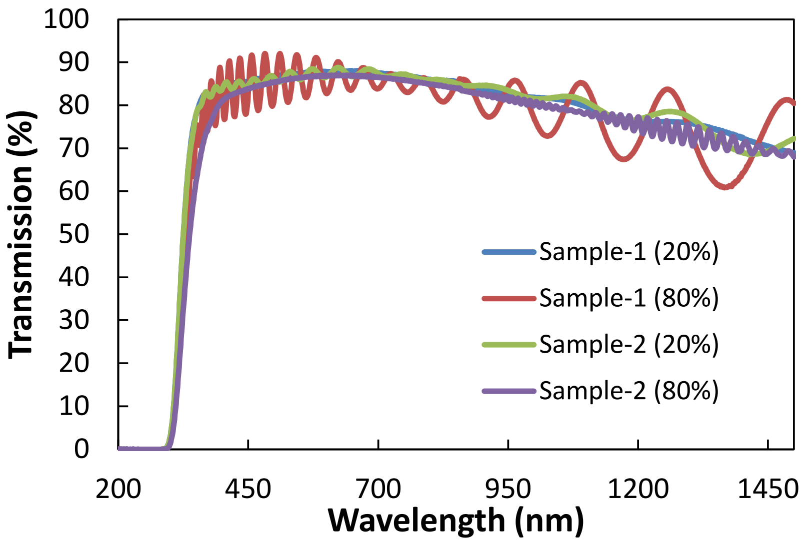
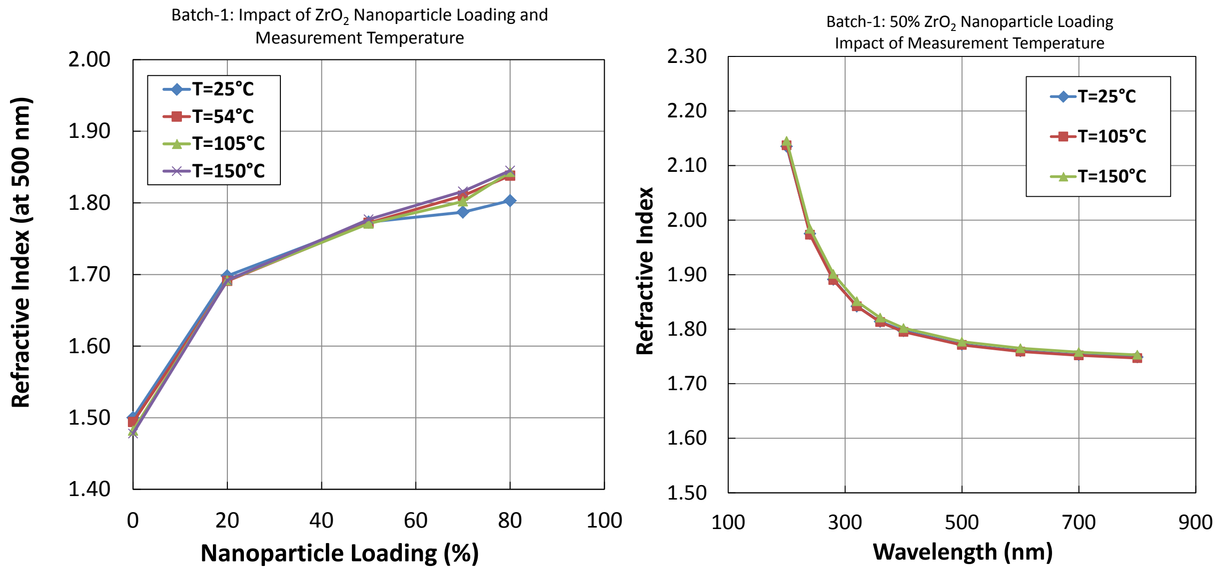


Fig. 1. Impact of ZrO_2 nanocrystals on optical transmittance of various nanocomposites at 20% and 80% loading levels.

1.2.2 Refractive Index Tunability

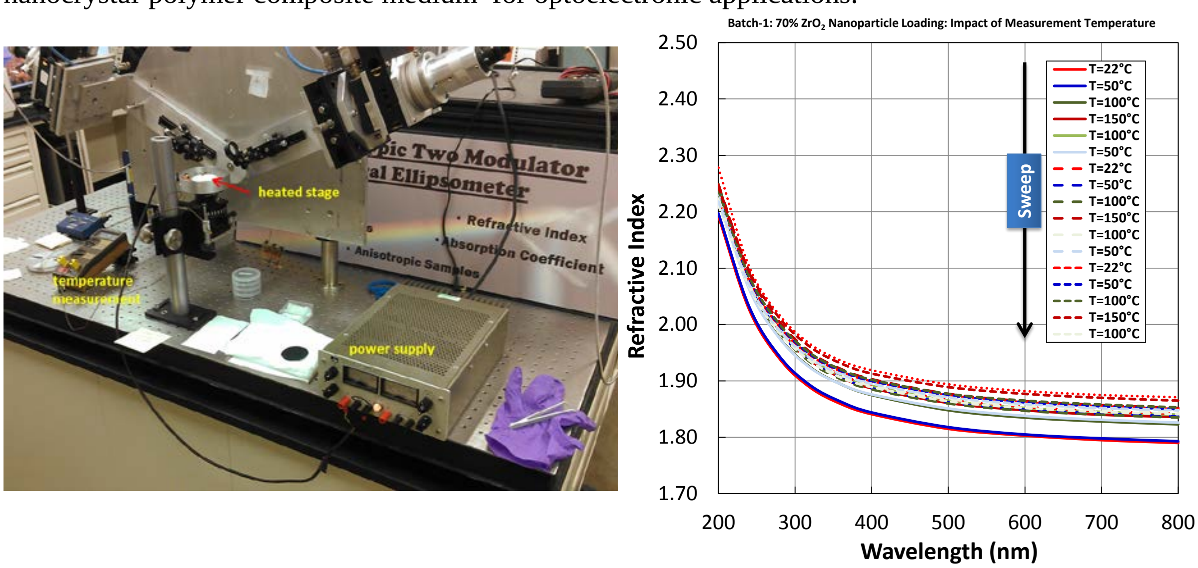
The refractive index of the ZrO_2 nc-embedded composite thin films was evaluated by spectroscopic ellipsometry technique in the wavelength range of 200-850 nm. The ellipsometry data was found to fit the Tauc-Lorentz dispersion model well. The impact of ZrO_2 nanocrystal-loading on the refractive index is shown in Fig. 2(a). The refractive index value was found to increase with an increase in the nanocrystal concentration indicating uniform loading in the acrylic matrix. The measurement temperature did not show any appreciable influence on the refractive index in the temperature range of 25-150°C. The n-k dispersion characteristics were also established from the ellipsometry data, and a typical curve for a ZrO_2 nanocrystal embedded polymer film (50% loading) on Si substrate is shown in Fig. 2(b). The dispersion curve was well-behaved and a refractive index value of 1.78 was obtained at 500 nm. The observed increase in refractive index with an increase in ZrO_2 nc-concentration coupled with thermal stability of the refractive index shows promise for enhancing the light extraction efficiency of solid state lighting devices.



(a) (b)

Fig. 2. Refractive index of ZrO_2 nanocrystal embedded acrylic films as a function of (a) nanocrystal loading concentration and (b) optical wavelength.

The spectroscopic ellipsometry setup was modified, as shown in Fig. 3(a), to evaluate the impact of thermal cycling on the refractive index dispersion characteristics. A heating stage was added to the setup for temperature dependent ellipsometry measurements up to 150 °C. The refractive index was found to increase as a function of thermal cycling as shown in Fig. 3(b). The typical refractive index value, for a sample containing 70% ZrO_2 nanocrystals, increased from 1.82 to 1.89, as measured at 500 nm, after four thermal cycles in the temperature range of 22-150°C. The observed results suggest that more detailed investigation is necessary to understand the nanocrystal distribution in the polymer matrix and establish the factors dictating the observed refractive index variation, and find optimum nanocrystal-polymer composite medium for optoelectronic applications.



(a) (b)

Fig. 3. (a) Modified ellipsometry setup for temperature dependent optical measurements, and (b) the impact of measurement temperature on refractive index dispersion characteristics.

1.2.3 Dielectric Response

High-k polymer nanocomposites have the potential to meet the performance demands of energy storage and flexible thin film transistor (TFT) applications. The nanocomposite approach offers a practical solution exploiting the high breakdown strength of polymers coupled with high dielectric constant of metal-oxide nanomaterials. The dielectric properties of the nanocomposites were evaluated in metal-film-metal (MFM) configuration. The MFM capacitors were fabricated by evaporating Au top electrodes on nanocomposite coatings processed on n^+-Si substrates. The typical dielectric response of a Au/Nanocomposite (20% ZrO_2-nc)/n^+-Si capacitor, measured at room temperature, is shown Fig. 4. The measured low dissipation factor of 0.048 at 100 kHz (Fig. 4) indicated the formation of a dense nanocomposite coating with good film/electrode interface characteristics. The low-frequency dielectric dispersion, which is typically dictated by the film-electrode interface, can be further improved by optimization of the surface microstructure and metal-electrode deposition process. Aside from a low dielectric loss, the ZrO_2 nanocrystal embedded acrylic films showed a highly tunable dielectric response (Fig. 5) as a function of nanocrystal concentration. The dielectric constant increased with an increase in the concentration of ZrO_2 nanocrystals in the acrylic matrix indicating uniform nanocrystal distribution, and a value of 7.9 was obtained at 80% loading-level. The observed high dielectric tunability in ZrO_2-nc/acrylic nanocomposite represents a promising dielectric system for integrated electronic applications.

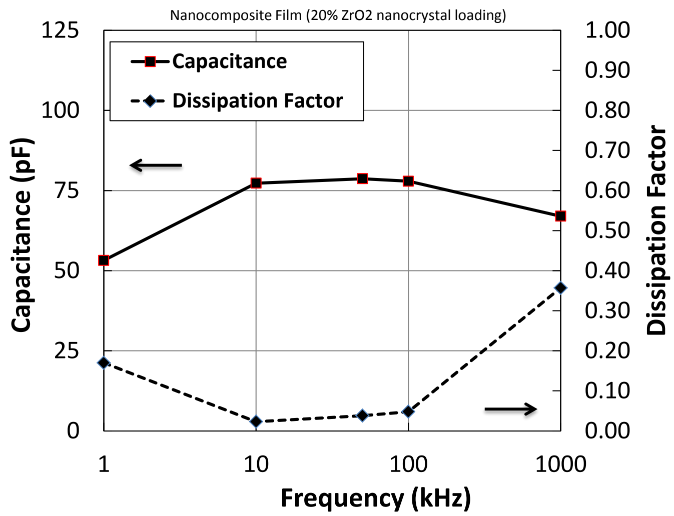


Fig. 4. Dielectric response of ZrO_2-nc/acrylic nanocomposite as a function of frequency.

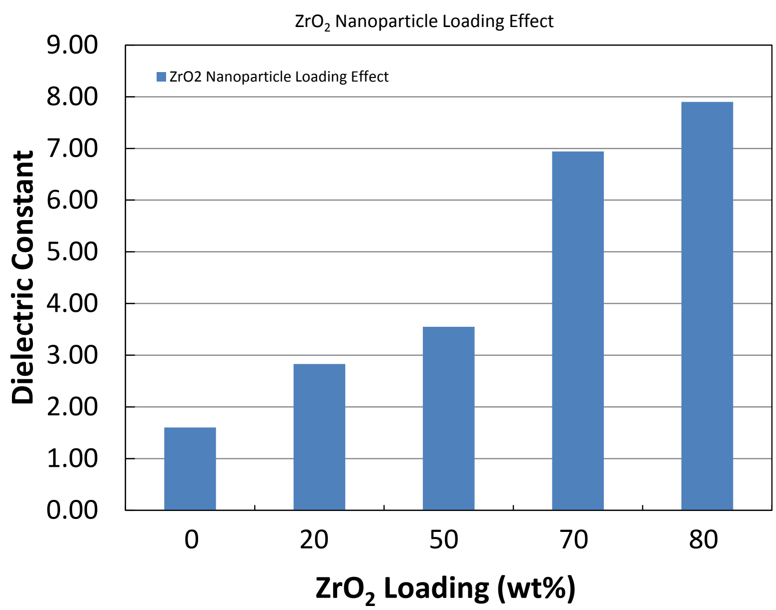
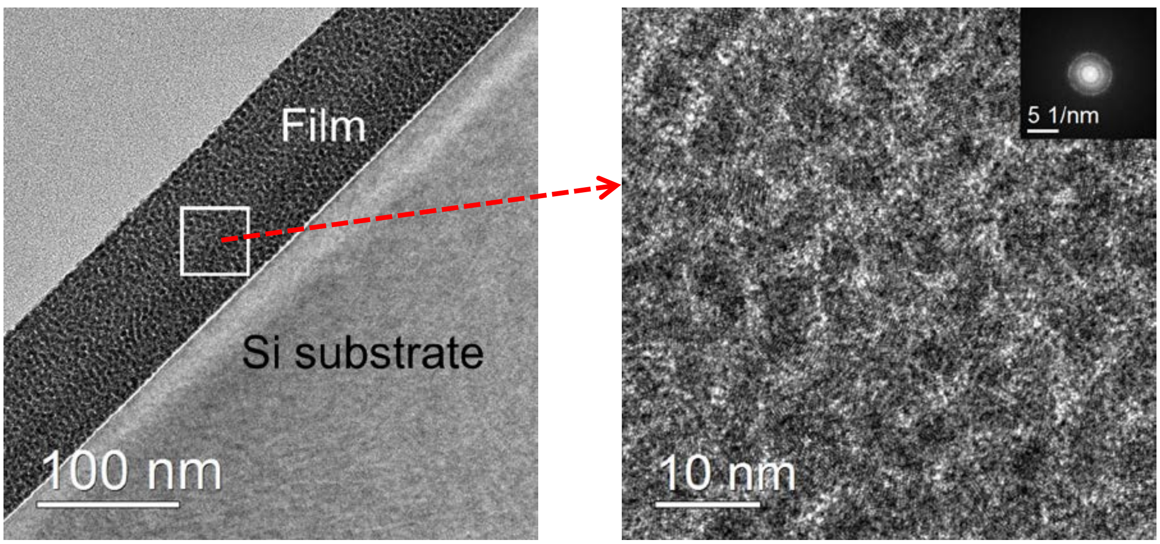


Fig. 5. Impact of nanocrystal loading on the dielectric response of ZrO_2-nc/acrylic nanocomposite.

1.2.4 ZrO_2 Nanocrystal Distribution

The ZrO_2 nanocrystals need to be dispersed homogeneously in the selected matrix for stable and reliably device development. The transmission electron microscopy (TEM) was used, as shown in Fig. 6, to establish ZrO_2 nanocrystal distribution in the polymer matrix. For a nanocomposite film with 20% ZrO_2 nanocrystal loading, the TEM analysis established an average nanocrystal size of 3.0±0.5 nm. The nanocrystals were found to be uniformly distributed in the polymer matrix (Fig. 6(a)). The magnified image of the in-boxed region in Fig. 6(a), as shown in Fig. 6(b), clearly establishes the presence of crystalline ZrO_2 nanocrystals in the polymer film. The fast Fourier transform (FFT) image in the inset shows a ring pattern indicating random orientation of the ZrO_2 nanocrystals in the polymer matrix. Overall, the TEM analysis indicated the formation of well-dispersed nanocomposites. The observed results are consistent with the ellipsometry and dielectric data showing highly tunable optical and dielectric responses as a function of nanocrystal loading.



(a) (b)

Fig. 6. (a) Cross-sectional TEM image of the ZrO_2-nc/acrylic nanocomposite, and (b) a magnified image of the in-boxed region in Fig. 6(a).

1.3 IMPACTS

The availability of high volume production for high refractive index nanocomposite will have significant impact on the energy efficiency of the US. In 2010, lighting in the United States consumed nearly 10 quads of primary energy. One of the key applications of the Pixelligent's nanocomposite is to provide a light coupling layers for Solid State Lighting such as LED and OLED. A nationwide move toward Solid State Lighting (SSL) for general illumination could save a total of 16 quads of primary energy between 2010 and 2030. The goal of DOE's efforts is to produce a SSL system that is 50% efficient by 2025. If this goal were attained, SSL could save the country $30 billion in annual energy costs, or the equivalent of 200 million barrels of oil. The current project demonstrates the potential for increasing the light extraction efficiency to meet DOE's light extraction goal for 2020. This could have a significant impact on not only general lighting applications, but also LEDs and OLEDs for various display and communication applications. In addition, inclusion of the Pixelligent's ZrO_2 nanocrystals in a polymer system also leads to significantly improved scratch and corrosion resistance enabling efficient material usage and high performance device development. The tunable dielectric response of nanocomposite capacitors, a key finding of the present investigation, offers a promising dielectric system for integrated electronic applications. The present findings strengthen Pixelligent's continued investment in the commercialization of leading-edge nanocomposites for integrated optoelectronic applications, including solid state lighting, displays, and integrated thin film capacitors.

1.4 CONCLUSIONS

Highly transparent ZrO_2-nc/acrylic nanocomposites have been developed on bare silicon and quartz substrates. The nanocomposites show efficient loading and distribution of ZrO_2 nanocrystals even at a high loading-concentration of 80%. The ZrO_2 nanocrystal embedded acrylic coatings exhibited excellent optical transparency in the visible range, and highly tunable refractive index and dielectric response for novel optoelectronic applications. The Au/nanocomposite/n^+-Si capacitors exhibited a low dielectric loss at a frequency of 100 kHz indicating the formation of a dense nanocomposite microstructure. Aside from a low dielectric loss, the ZrO_2 nanocrystal embedded acrylic films showed a highly tunable dielectric response as a function of nanocrystal loading. The observed high dielectric tunability represents a promising dielectric system for integrated electronic applications. The present findings will significantly impact the business decision to exploit advanced nanocomposite manufacturing technology to realize more efficient solid state lighting and integrated electronic devices.

2. PARTNER BACKGROUND

Pixelligent develops applications with leading-edge technology firms, as well as Fortune 500 companies. Pixelligent Technologies, producer of PixClear™, is an advanced materials company that delivers next generation materials for demanding applications in solid-state lighting, flat panel displays, and optical components & films. Pixelligent leverages its proprietary nano-dispersion and manufacturing technology and processes to create innovative materials that significantly improve existing products. Pixelligent's proprietary methodology for delivering uniform nanocrystal dispersions is the best in the world. This is the key enabling technology required to deliver the highest performance in a wide range of demanding applications. Pixelligent's Zirconia nanocrystals are used to magnify and optimize the optical, electronic, thermal, and mechanical properties of numerous families of polymers, from acrylics and epoxies to silicones and spin-on glasses. Pixelligent is a US small business.