



**Pacific Northwest**  
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*

# Mickey Leland Energy Fellowship Report

## Development of Advanced Window Coatings

**July 29, 2014**

L Bolton  
KJ Alvine

AL Schemer-Kohn

## DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

*operated by*

BATTELLE

*for the*

UNITED STATES DEPARTMENT OF ENERGY

*under Contract DE-AC05-76RL01830*

Printed in the United States of America

Available to DOE and DOE contractors from the  
Office of Scientific and Technical Information,  
P.O. Box 62, Oak Ridge, TN 37831-0062;  
ph: (865) 576-8401  
fax: (865) 576-5728  
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service,  
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161  
ph: (800) 553-6847  
fax: (703) 605-6900  
email: orders@ntis.fedworld.gov  
online ordering: <http://www.ntis.gov/ordering.htm>



This document was printed on recycled paper.

(9/2003)

# **Mickey Leland Energy Fellowship Report: Development of Advanced Window Coatings**

MLEF Intern: LaDena Bolton  
Mentor: Kyle J. Alvine

L Bolton  
KJ Alvine  
AL Schemer-Kohn

July 2014

Prepared for the U.S. Department of Energy  
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory  
Richland, Washington 99352

# DEVELOPMENT OF ADVANCED WINDOW COATINGS

## INTRODUCTION

Advanced fenestration technologies for light and thermal management in building applications are of great recent research interest for improvements in energy efficiency.\* Of these technologies, there is specific interest in advanced window coating technologies that have tailored control over the visible and infrared (IR) scattering into a room for both static and dynamic applications. Recently, PNNL has investigated novel subwavelength nanostructured coatings for both daylighting, and IR thermal management applications.[1, 2] Such coatings are still in the early stages and additional research is needed in terms of scalable manufacturing. This project investigates aspects of a potential new methodology for low-cost scalable manufacture of said subwavelength coatings.

## BACKGROUND

Windows are divided into dynamic and static windows with regard to thermal management. Thermal management involves the transmission and blocking of infrared radiation into the room through coatings and or shading. Due to diurnal and seasonal cycling, dynamic windows have potential for significant primary heating and cooling energy savings of 1.45 Quad/yr. over static low-E windows. However, high cost for current dynamic window technologies forces the vast majority of current stock into the static category. Additionally significant tinting of the typical electrochromic or thermochromic window technologies limits natural daylighting.

Visible light redirecting films also offer significant potential improvements in energy efficiency through more efficient use of natural daylight. State of the art for advanced daylighting is defined as technologies that can redirect light significantly deeper into the room than the average 15 ft 1<sup>st</sup> zone perimeter.[3] Typical examples of daylighting technology are mirrored blinds and light shelves. However, current market penetration for advanced daylighting is exceedingly small due to high cost, high maintenance, low throughput, and in almost all such technologies, no view. There is a clear gap for technologies that can provide efficient light redirection through a simple coating, while still allowing for a view. Such daylighting technology has the potential for 1.2 Quad/yr. of primary lighting energy savings. Based on a recent study of daylighting[4], the associated potential for primary lighting energy savings for daylighting a 15ft perimeter space in US commercial buildings is ~20% or 0.7 Quad/yr. out of 3.7 Quad/yr. total usage.†

## SPECIFIC AIMS

To demonstrate partial proof-of-concept for a novel scalable process of manufacturing subwavelength nanostructured coatings, we set out to confirm the following specific aims:

1. Confirm that the wet deposition of a combination of metallic and template dielectric nanoparticles of markedly different sizes can lead to the fabrication of a subwavelength nanostructured film pattern foundation.

---

\* DOE Building Technology Office/Emerging Technology, Window and Envelops Roadmap 2014

† EERE's 2011 Buildings Energy Data Book/EIA's AEO 2012

2. Confirm that subsequent annealing of above said film can lead to sintering of the metallic nanoparticles to establish the subwavelength plasmonic film. This latter aim is a stretch goal.

## **METHODS & MATERIALS**

A Laurell Technologies spin coater (model WS400BZ-6NPP/LITE) was used for proof-of-concept monolayer deposition of polystyrene nanoparticle films and partly for drying of Au nanoparticle layers. The silicon wafers were pre-cleaned prior to wet deposition using an oxygen plasma cleaner. SEM images were captured using a JEOL scanning electron microscope (SEM) at various magnifications.

Polystyrene nanospheres with diameter of 210nm, suspended in aqueous solution, (Bangs Laboratories Inc.) were used after pre-filtering. Au nanoparticles (AuNP, Sigma Aldrich) of diameters 5, 15, 30, and 60nm in a citrate stabilized citrate buffer solution were used after pre-concentration via evaporation at 60C. The resulting Au nanoparticle solutions ranged from 10 to 20 times the concentration of the original solutions of  $10^{12}$  to  $10^{13}$  particles/ml.

## **TECHNICAL APPROACH**

It was previously decided by the PNNL team that the desired photonic structure was that of a plasmonic so-called “fish-net” structure comprised of a metallic matrix with an array of regular nanoscale holes. Typically, such structures created by e-beam lithography form square holes, but for our purposes, circular holes are significantly easier to obtain. It is expected that the resultant resonant properties will be different with respect to a square-hole array, but not drastically so. Such a pattern could also be adapted to form photonic structures through the substitution of a dielectric for the metal.

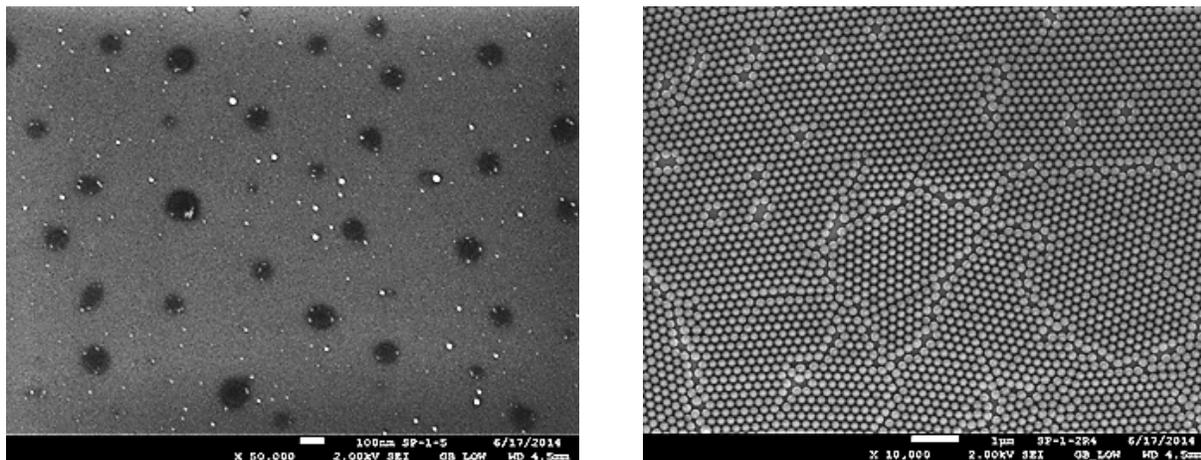
In order to fabricate the fish-net structure, we have adopted a templating approach where the polystyrene (PS) nanoparticles form a close-packed monolayer and the Au nanoparticles fill in the interstitial valleys in between the particles. We have tried both wet deposition of a mixture of Au and PS nanoparticles and a two-step coating process and found that the two-step process is preferable. In both cases, the Au nanoparticles are significantly smaller than the PS nanoparticles in order to fit the packing requirements.

Typical Au nanoparticle (AuNP) patterned films were prepared by spin coating a monolayer of 210nm PS NPs at 5000-6000 rpm with high acceleration onto a pre-cleaned silicon wafer. The organic films were annealed at 107 C for 2-3 minutes. A few drops of concentrated AuNPs were then added to the PS covered wafer and spun at 300rpm with low acceleration until dry.

## **RESULTS**

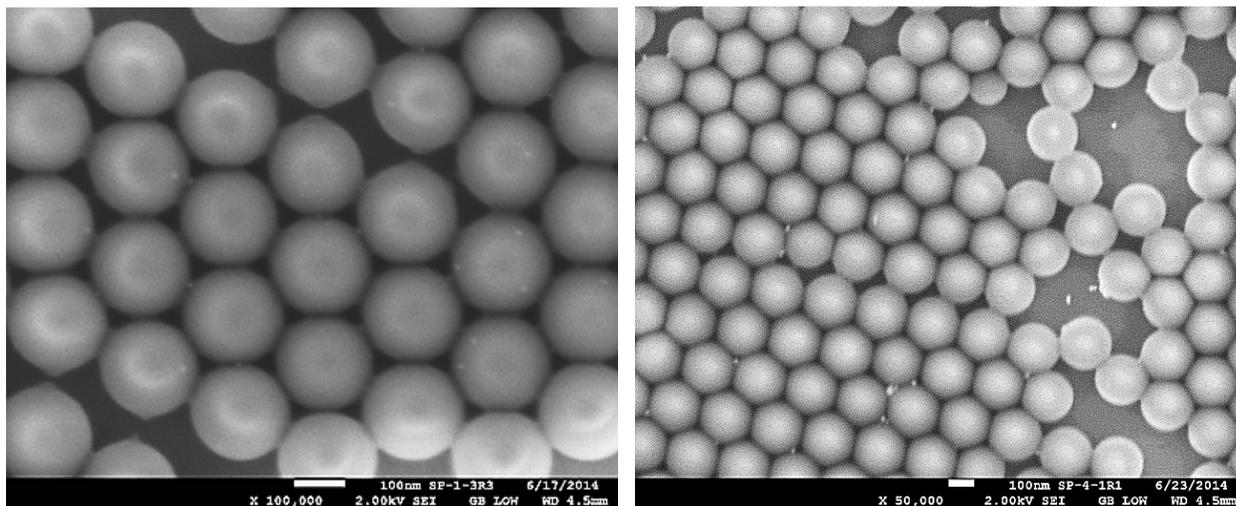
As shown in Figure 1(left), pristine AuNPs were spun to determine the most favorable spin parameters for forming a gold film prior to incorporating the PS nanospheres. Though a dense uniform film was not obtained, the most favorable results to date were reached using a spin speed of 300rpm and slow acceleration for 60 seconds. Neat PS nanospheres were also spun to

determine the optimal spin properties for preparing a dense monolayer. See Figure 1(right). The parameters were determined to be a range from 5000-6000rpm at high acceleration. When spun, Au particles do not form a dense monolayer due to low concentrations, while PS NPs at the much higher concentrations available commercially do. In addition, the optimal spin rates for the formation of a monolayer of each are quite different due to the vastly different sizes and concentrations.



**Figure 1:** Scanning electron micrographs of spin-coated monolayers of (left) 5nm AuNPs at 300rpm and (right) PS nanospheres at 4000rpm.

Preliminary investigations revealed that pre-mixing the as-received 5nm AuNPs with PS nanospheres results in Au partially decorating (Figure 2-left) the surface of the PS layer rather than filling the interstitial sites between each nanosphere. The more concentrated larger NPs, however, shown in Figure 2-right, start to successfully fill the spaces between the PS nanospheres as will be shown later. Initially, the as received PS and AuNPs were pre-mixed containing volume fractions of AuNPs at 0.25, 0.50 and 0.75.

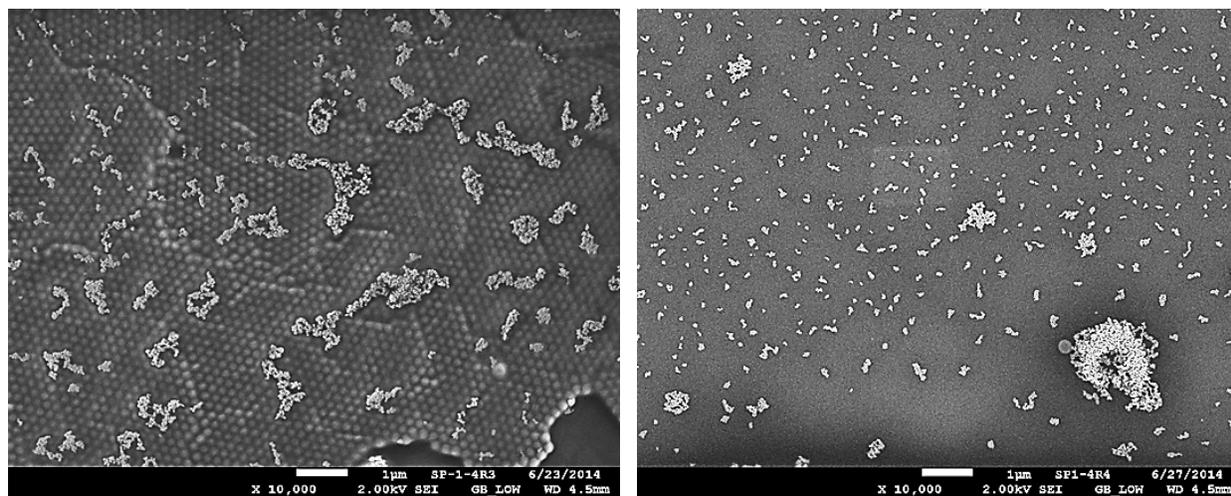


**Figure 2:** Representative scanning electron micrographs of PS/Au mixture containing 75% v/v (a) as received 5nm AuNPs and (b) 10x concentrated 15nm AuNPs.

Following mixing, the samples were sonicated for 10 minutes to ensure homogenous dispersion of each component and equilibrate the sample temperature to near ambient. The mixtures were then spin coated onto a plasma cleaned silicon wafer. Spin speeds were decreased from 4000rpm to 1500rpm as the fraction of AuNPs in the mixture decreased. For all AuNP sizes investigated and for colloids that were concentrated up to 10x, pre-mixing resulted in sparse distribution of the Au throughout the PS layer.

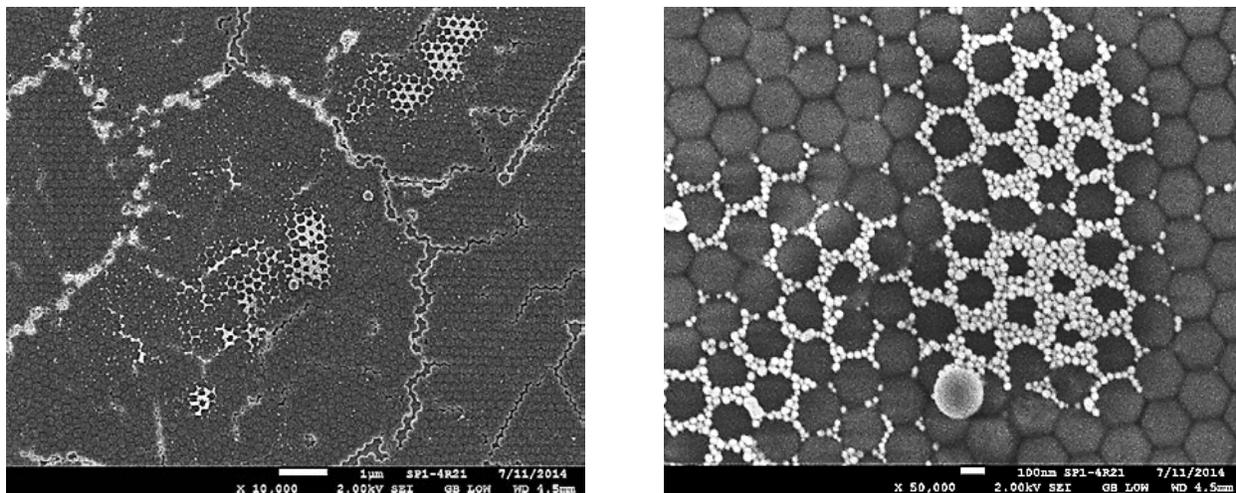
Ultimately, it became clear that good AuNP coverage required a different approach. To this end, we investigated: (1) larger AuNPs, (2) instead of premixing the components, prepare a PS film then drop cast the Au onto the surface followed by air-drying and (3) concentrate the AuNP samples by a factor greater than 10. The aqueous solvent was evaporated by in a glass vial with a large surface area in increments of 10-15mL. Solutions of AuNP were concentrated by annealing at 60 C under flowing Ar gas. After about 3 hours of annealing, the AuNP solution was concentrated 15 to 20 times. As a result of increasing the concentration and particle size, the particles covered a larger surface area of the film and began forming a percolated network.

Unfortunately, as the particle sizes increased, the drop casted nanoparticles tended to migrate toward and settle in the holes in the PS layer or areas where the silicon surface was exposed. This is attributed to both differences in hydrophobicity of PS and the Si wafer, as well as the difficulty for larger particles to fit in small spaces without disrupting the film. In figure 4-left, the PS layer was annealed for 5 minutes (rather than the usual 2-3 minutes) at 107 C, to try to prevent the PS particles from being displaced from the wafer surface during AuNP drop casting. The nanospheres began to fuse into a large thermoplastic mass eliminating the fine boundaries around the individual particles. As a result, the AuNPs collected on the PS surface as small agglomerates. Where concentrated 30nm particles were used, the majority of the AuNPs were found dispersed on the exposed regions of the Si wafer (figure 2-right).



**Figure 4:** Scanning electron micrographs of PS film containing droplet(s) of (left) concentrated 15nm AuNPs and (right) concentrated 30nm AuNPs.

To control the AuNP agglomeration, and to redirect deposition from the exposed Si regions of the PS film, the method for drying Au droplets was modified from air-drying to slowly spin drying (in the spin-coater) for several minutes. The desired effect was more uniform distribution of AuNPs over a large surface area of the PS layer. Figure 5 shows highly promising results from 30nm concentrated AuNPs that were drop casted onto an annealed PS film. The AuNP droplets were spun at 300rpm until dry. The structure in Figure 5 clearly shows the formation of a fish-net pattern as desired. Clearly additional research is needed to increase the coverage and to determine appropriate sintering methodology for these patterns.



**Figure 5:** SEMs of PS film containing droplet(s) of concentrated 30nm Au NPs at (a) 1μm and (b) 100nm

## CONCLUSIONS

In this work, we identified a potentially scalable fabrication process for preparing subwavelength plasmonic or photonic coatings. The most favorable results were produced from a multistep method by coating a monolayer of PS nanospheres onto a pre-cleaned Si wafer followed by drop casting concentrated 30nm AuNPs onto the PS layer. The Au was then dried on the spin coater resulting in a fine fishnet microstructure. Slow dry spinning of Au droplets on PS film forms small areas of microporous-like Au films. This project can be advanced by enhancing the surface area coverage of the Au film. This may potentially be done by further increasing the concentration of the Au colloids or substituting drying the Au droplets with a flow coater. Alternatively, adding an additional step such as pre-casting an organic PS solution onto the wafer prior to coating the PS nanospheres layer may assist in annealing. After reproducing the fishnet Au film, sintering studies of the AuNP need to be performed and the samples optical properties will be measured and analyzed.

## REFERENCES

- [1] K. J. Alvine *et al.*, *Applied Physics Letters* **102**, 201115 (1 (2013)).
- [2] K. J. Alvine *et al.*, in *Conference on Micro- and Nanotechnology Sensors, Systems, and Applications V*, edited by T. George, M. Islam, and A. DuttaBaltimore, MD 2013), pp. (87252H).
- [3] N. Ruck, (Lawrence Berkeley National Laboratory, Berkeley, CA 94720, 2000).
- [4] D. Arasteh *et al.*, *Proc. ACEEE Study on Energy Efficiency in Buildings* (2006).