Large area Layer by Layer optical films: The power of reflection over absorption

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ABSTRACT

Layer by Layer Self Assembly can be used to deposit precise and uniform optical thin films using aqueous solution phase processing in an ambient environment. We have developed scaling capabilities for LbL that enable the rapid, high throughput deposition of NIR Bragg reflector structures on large area substrates. We integrated NIR Bragg reflectors with absorbing laminates to create a hybrid solar control film that sidesteps the existing disadvantages of purely absorbing technologies while delivering the solar control performance of sputtered films.

Keywords: layer by layer self assembly, energy efficiency, nanotechnology, industrial manufacturing, surface engineering

1 LAYER BY LAYER SELF ASSEMBLY

In the last two decades layer-by-layer (LbL) self-assembly has garnered significant interest as a simple, inexpensive and flexible technique for depositing nanostructured thin films with wide ranging applications from drug delivery to energy storage[1]. The process involves the sequential adsorption of colloidal materials (i.e. nanoparticles, polyelectrolytes) with complementary intermolecular interactions (electrostatic, hydrogen bonding, antibody-antigen interactions) onto a surface. Figure 1 highlights the electrostatically driven process beginning with step 1: a substrate is immersed into a bath containing positively charged species (Fig 1a) and allowed to incubate until the surface saturates and undergoes a charge reversal leading to self-limited adsorption and preventing further adsorption of the cationic material; step 2: the substrate is moved to a rinse bath (Fig 1b) to remove residual cations; step 3: the substrate is then immersed in a bath containing anionic species (Fig 1c) and allowed to incubate where the negatively charged materials adhere to the positively charged surface until saturation occurs and the surface charge is reversed again, step 4: the substrate is returned to the rinse bath (Fig 1b). The completion of this full cycle results in a composite layer, referred to as a bilayer, which has morphological characteristics (thickness, refractive index, porosity, surface area) defined by the solution conditions (ionic strength, pH, colloidal size) which mediate the intermolecular interactions. The combination of precision and uniformity which arise out of the self limitation, the creation of composite nanostructured multifunction, multilayer thin films, and the ability to do this under room temperature and ambient conditions has led to the widespread research adoption of the LbL technique.

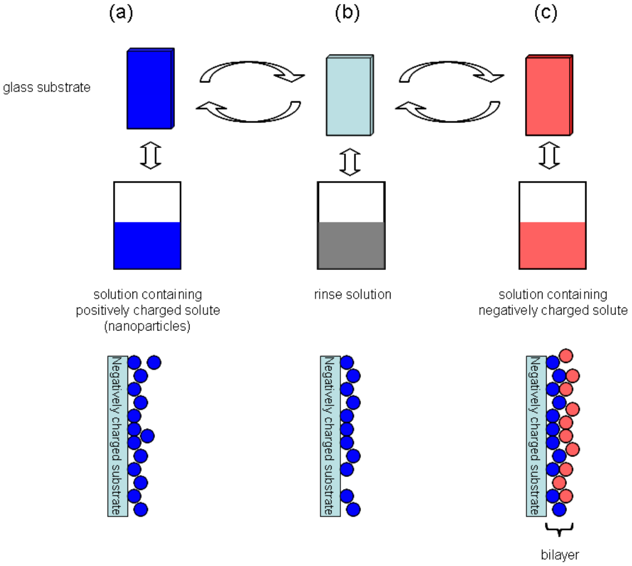

Figure 1. Illustration of the Layer-by-Layer assembly process.

However despite these advantages LbL has remained a slow and unforgiving for scale up and manufacture. The process is time consuming, with bilayer cycle times on the order of 5-60 minutes, with interesting films often requiring 10 – 100 bilayers. Schlenoff was among the first to consider the scale up challenges and investigated the use of commercial spray technology with LbL to reduce process time [2]. Krogman et al. advanced the art by creating an automated spray technique which resulted in reduction in bilayer cycle times by one to two orders of magnitude while creating comparable or improving the properties in the film, but limitations in size and continuous processing remained [3]. Building off of the innovations of Krogman et al. we have developed a spray based deposition platform and a series of prototype deposition tools that have focused on the critical scaling aspects of the LbL process speed and size.

2 BRAGG REFLECTORS

Using this scaled process we demonstrate the ability to create large area multilayer optical films for use as selective reflective Bragg reflectors. A standard quarter wavelength optical thickness (QWOT) Bragg reflector operates through constructive interference of reflections generated at an interface between two QWOT layers with different refractive indices. When this interface is repeated, the reflectivity (R) is:

$$R = \left[\frac{n_0 (n_2)^{2N} - n_S (n_1)^{2N}}{n_0 (n_2)^{2N} + n_S (n_1)^{2N}} \right]^2 \qquad (1)$$

where n_0, n_1, n_2 *and* n_s are the refractive indices of the entering medium, two alternating materials and the exiting medium respectively and N are the number of material layer pairs. The width of the reflective band ($\Delta\lambda_0$) is:

$$\Delta\lambda_0 = \frac{4\lambda_0}{\pi} \arcsin\left(\frac{n_2 - n_1}{n_2 + n_1} \right) \qquad (2)$$

where λ_0 is the desired wavelength of the reflective band.

Bragg reflectors are typically deposited using physical vapor deposition, which can be expensive and technically challenging to do over very large areas. There has been extensive work in the LbL literature for creating selective reflectors. LbL delivers the required precision in optical thickness of each and every layer of a Bragg. Wang et al. demonstrated polyelectrolyte multilayers that leveraged localized domains of polyacrylic acid - silver nanoreactor chemistry to create a periodic variation in refractive index [4]. Zhai et al. were able to create tunable Bragg reflectors that would alter the reflective band based on pH gated porosity transitions [5]. Nogueira et al. used a spray based deposition technique to rapidly deposit non QWOT Bragg reflectors which yielded multi band narrow width reflectors in ultraviolet spectrum [6]. We have demonstrated the control and tunability of our process by demonstrating the ability to shift the reflective wavelength across multiple wavelengths as shown in Figure 2, demonstrating the flexibility and control of the LbL process.

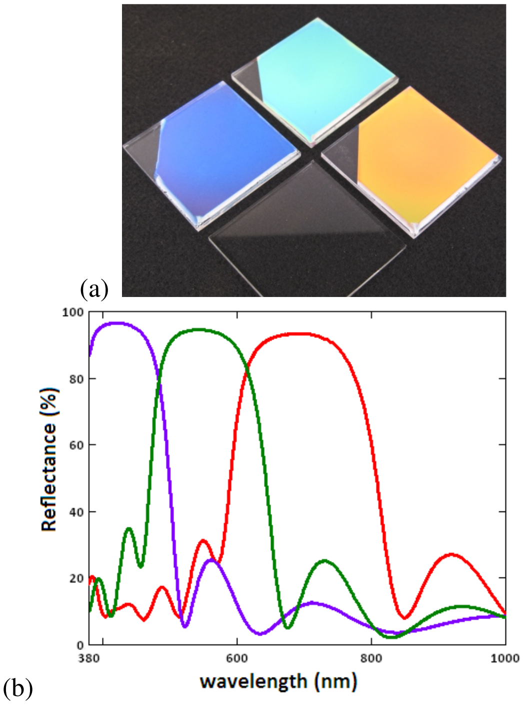

Figure 2. (a) 11 layer Bragg reflectors deposited onto 2” x 2” glass substrates and (b) the corresponding UV-Vis reflectance spectrum listed below. Alternating layers are constructed from titanium dioxide and silicon dioxide nanocomposite layers.

3 SOLAR CONTROL FILMS

By exploiting the precision and control of the native LbL process and coupling it with the size and speed of Svaya’s technology, Svaya is able to build highly selective Bragg reflectors for the near infrared radiation (NIR). This enables the production of solar control films that block heat in buildings or automobiles, while maintaining the required high visible light transmission for natural lighting or mandated visibility requirements.

3.1 Absorptive Solar Control

One form of existing solar control technologies, for applications which require high visible light transmission requirements, involve the use of IR absorbers (i.e. LaB_6 or ITO nanoparticles in a polyvinylbutyral interlayer for laminated glass). These are moderately effective in situations where there is airflow which promotes convective heat transfer. For example Solutia’s Saflex® PVB IR absorbing interlayer, laminated between two panes of clear glass, provide 82% visible and 52.5% solar transmittance [7]. However because the solar control is absorptive in nature, the laminated glass assembly can heat up and re-irradiate heat isotropically. Under air flow, this does not pose a problem because of convectively aided heat transfer. But for windshields in cars parked or stuck in traffic, or in buildings without sufficient wind flow, this “hot glass effect” can void window warranties or provide inadequate solar control. As a result IR absorbing solar control has not been rapidly or widely adopted by the market.

3.2 Sputtered Solar Control

State of the art solar control is achieved through thin optical films on PET or glass, created using vacuum sputtering processes. Typically, one or more thin films of silver is sandwiched between several metal oxide layers to form a Fabry-Perot etalon. Today Southwall’s XIR 70® solar control film is the best in class product for automotive applications with visible light transmission of greater than 70% and solar transmittance of less than 50%, rejecting IR primarily through reflection[8]. However the use of silver films suffers from several drawbacks which include an absorptive component of solar control, interference with radiofrequency signals and corrosion upon exposure to saline conditions. Of all challenges, RF interference has provided the largest impedance to adoption due to the increasing use of communications in automotive environments.

3.3 Hybrid Reflective Solar Control

NIR Bragg reflectors, produced using the LbL process, have the ability to sidestep the limitations in existing solar control technologies. Because Bragg reflectors are reflective in nature, they do not give rise to hot glass effect of absorptive technologies. If Bragg reflectors are created from metal oxide materials, they do not interrupt long wavelength RF signals or suffer from oxidative degradation. The challenge for NIR Bragg reflectors is described by Equation 2 and shown in Figure 2, where the reflective bandwidth is relatively narrow. Because a substantial portion of the solar irradiance spectrum spans the range from 700 – 1800 nm, a NIR reflector, when designed effectively, can realistically cut out only a portion of that without creating a highly complex film structure with dozens or hundreds of alternating layers.

To improve the solar control characteristics, of the NIR Bragg reflectors, we created a laminated window structure where the reflector is place in front of a material which contains IR absorbing materials, as shown in Figure 3(c). In this configuration, the reflector blocks a substantial portion of the IR, between 700 – 1100 nm with the higher wavelength, less intense remaining radiation is absorbed. Because the reflector is effective at rejecting the bulk of the heat by redirecting it back to the environment, the absorbers take on less energy and heat. Meanwhile, RF transmission is not impeded because neither the absorbers or the material in the reflector interfere. Correspondingly, the combination of these two solar control technologies enables the creation of a hybrid solar control film that brings the effectiveness of reflection at wavelengths where it is most needed and couples it with the efficiency of absorption over the very broad range of IR frequencies. The convolution of the two technologies is shown in Figure 3. The result is a laminated window that provides visible light transmission of greater than 70% while providing total solar energy rejected of 55%, as measured by ASTM 9050.

As a measure of the efficacy of the hybrid solar control windows, two scaled model cars were built and outfitted with and without the window structure shown in Figure 3(c). The model cars, shown in Figure 4(a) were loaded with thermocouples and placed in our parking lot. The thermocouples reported temperatures over the course of a day with the data shown in Figure 4(b). The stationary model car with the hybrid solar control windows demonstrated nearly 20 degree (F) reduction in temperature.

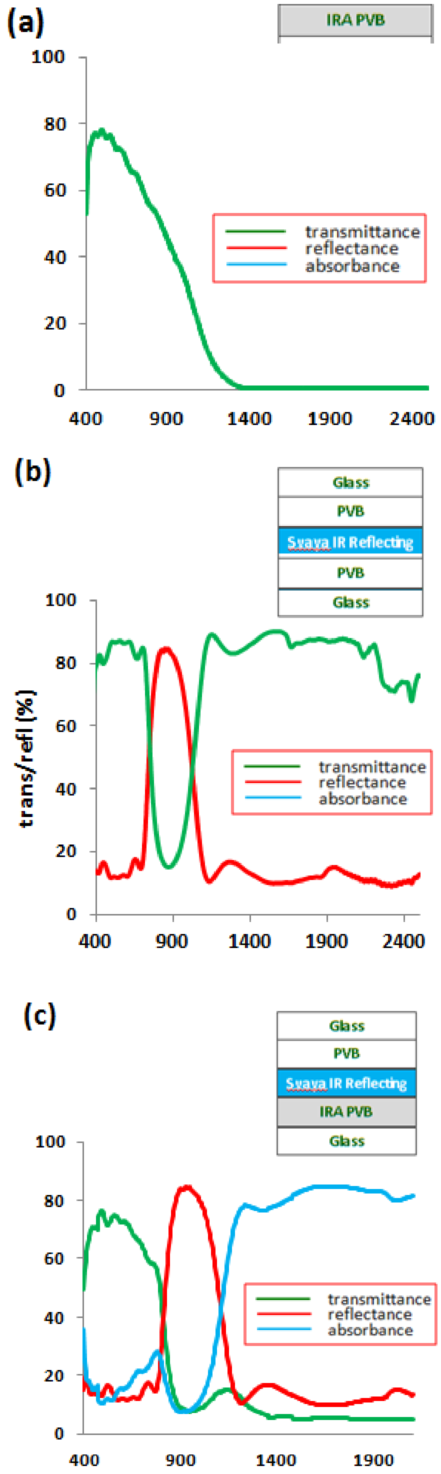

Figure 3. (a) Transmittance of absorbing laminating material PVB. (b) Optical measurements of NIR Bragg reflector (c) Optical measurements of convoluted NIR Bragg reflector with absorbers.

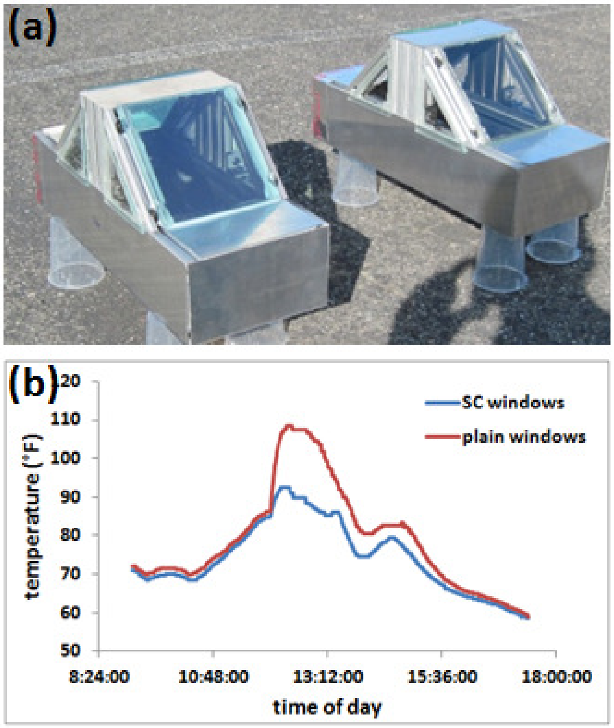

Figure 4. (a) Model cars outfitted with hybrid NIR Bragg reflector windows. (b) Temperature measured in model cars throughout the day. Solar control windows kept the model car 20°F cooler than plain windows.

4 MATERIALS AND METHODS

4.1 LbL Deposition

Bragg reflectors were assembled from solutions containing polydiallyldimethyl ammonium chloride (PDAC, 100-200,000 MW, Sigma Aldrich),
silicon dioxide nanoparticles (SiO_2, LUDOX® TM-50, WR Grace) and titanium dioxide nanoparticles (TiO_2, Photocatalyst sol X-500, Titan PE) using Layer by Layer spray deposition, based on the apparatus described by Krogman et al. Rinse solutions were deionized water with pH adjusted using NaOH to 10.0. NIR Bragg reflectors consisted of nine alternating refractive layers $(HL)^4(H)$, where H and L indicate high and low index, respectively.

4.2 Measurements

Optical measurements were performed on a Shimadzu 3101 UV-Vis spectrophotometer.

5 SUMMARY AND CONCLUSIONS

LbL has the potential to revolutionize optical thin film production. The advantages of uniformity and precision of LbL, coupled with Svaya's spray technology for high throughput deposition onto large areas using aqueous solution processing in an ambient environment, enables the volume production of multilayer Bragg reflectors at a cost effective price point. Solar control films can be created from these Bragg reflectors by reflecting NIR radiation. By combining these Bragg reflectors with exisiting absorbing technology in a hybrid solar control window, we have demonstrated compelling solar control characteristics. These Bragg reflectors are an enabling technology and can be integrated into many applications, including high intensity lighting applications, where existing absorbing technologies lead to thermal durability challenges.

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