

Anti-reflective optical coatings incorporating nanoparticles

Kevin C Krogman^{1,3}, Thad Druffel^{2,4} and Mahendra K Sunkara¹

¹ Department of Chemical Engineering, University of Louisville, Louisville, KY 40292, USA

² Optical Dynamics Corporation, 10100 Bluegrass Parkway, Louisville, KY, USA

E-mail: tdruffel@opticaldynamics.com

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Abstract

This paper presents a simple approach for forming anti-reflective film stacks on plastic substrates employing aqueous colloidal dispersions of metal oxide nanoparticles. Results demonstrate that it is possible to fabricate a polymeric thin film of continuously tunable refractive index over a wide range by loading the film with varying concentrations of metal oxide nanoparticles. Specifically, the refractive index for the polymer film was tuned from 1.46 to 1.54 using silica nanoparticle loadings from 50 to 0 wt% and from 1.54 to 1.95 using ceria nanoparticle loadings from 0 to 90 wt%, respectively. The low and high refractive index layers are then combined to create an anti-reflective coating which exhibits a reflectance spectrum, abrasion resistance, haze and transmission values that compare well with those produced using state-of-the-art vacuum based techniques. Furthermore, the results show that it is possible to begin with aqueous dispersions and then dilute them with organic solvents for use in a spin coating method to prepare the polymer–metal oxide nanoparticle composite films.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recent developments in the understanding of materials on the nanometre scale have allowed engineers to create new hybrid composites with enhanced mechanical, electrical, and optical properties over their undoped counterparts [1–4]. These new composites allow traditional plastic resins to be doped with a wide range of nanoparticles, wires, or tubes, thereby introducing the advantageous properties of the bulk particle while still maintaining the processability and low cost of the plastic at the macroscopic level. By careful selection of the nanoparticle dopant, the mechanical strength, electrical conductivity, optical refractive index, and countless other physical properties of the bulk resin can be controlled.

Of particular interest is a multi-layered thin film coating exhibiting lower spectral reflectance compared with the surface of the uncoated substrate. These anti-reflective coatings have

applications in ophthalmic lenses, solar cells, data storage, and other optical devices that require a reduced reflectance for an increase in optical efficiency. Oliviera *et al* were able to produce an anti-reflective effect using a sol–gel derived coating with tunable refractive indices and improved mechanical performance [5]. Belleville *et al* also reported using sol–gel coatings in high damage applications where anti-reflective coatings are necessary to maximize light intensity [6, 7]. Many of these sol–gel processes require either a thermal curing step or a chemical cure in the presence of NH₃ to carry out the necessary condensation reaction. These procedures add time and cost in the form of heat or chemical waste to the deposition process. The resulting sol–gel films often lack abrasion resistance as well. Early attempts to engineer anti-reflective coatings from a nanoscopic level resulted in fragile surfaces [8], but recently researchers have begun to develop thin film coatings using nanoparticles to enhance the abrasion resistance [1]. However, demand exists for a simplified coating method yielding good optical efficiency and abrasion resistance.

The spin coating method for depositing hybrid polymer nanoparticle composites has been widely studied [9–12] and

³ Present address: Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA.

⁴ Author to whom any correspondence should be addressed.

allows for a simple low cost deposition of thin films. Yu *et al* produced thin films of the order of several microns using a colloidal silica and acrylic monomer cured in the presence of heat [13]. Thicker films, i.e. of the order of several microns, present a greater degree of light scattering, often hampering their use in optical applications. Thin films less than half a micron thick, on the other hand, are difficult to keep uniformly thick, and in turn sacrifice mechanical strength. It is therefore necessary to find a way to deposit thin nanocomposite films that do not exhibit the light scattering seen in their thicker counterparts but still maintain the modified refractive index and mechanical strength. Spin coating presents a way to uniformly deposit sub-100 nm thick films, but it is unclear whether aqueous based dispersions can be utilized in such a process.

The goal of this work was to study whether one can form sub-100 nm thin films of specific refractive index by varying the metal oxide nanoparticle loading in aqueous colloidal solutions. Also addressed is the question of whether one can engineer these films to form an anti-reflective stack on a plastic substrate. The mechanical and optical performances of the resulting anti-reflective films were evaluated. The work described here specifically uses silica and ceria nanoparticle dispersions and a UV-curable monomer to illustrate the applicability of nanoparticle dispersion chemistry in making anti-reflective films. However, the results could easily be extended to aqueous dispersions of other metal oxide systems. To the researchers' knowledge, there has been no prior report describing the use of colloidal dispersions of metal oxides entirely to form thin, anti-reflective films on any substrates at room temperature.

2. Experimental details

A spin coating technique was chosen for its simplicity and its efficiency in depositing thin, uniform films across a substrate. This technique is well understood and the thickness of the film is controlled primarily by the spin-off speed and the solution viscosity [14]. The repeatability of the thickness is high as long as the coating environment is controlled so as to not interfere with the evaporation of the volatile solvents. In this application a liquid phase colloidal suspension of metal oxide particles could be formed in a bulk solvent, which would also dissolve the chosen monomer sufficiently that the final viscosity of the solution is appropriate for spin coating to take place.

Several metal oxide nanoparticles are commercially available as colloidal suspensions in water. Among these, cerium dioxide, or ceria, and silicon dioxide, or silica, nanoparticles were chosen for their refractive indices. Cerium dioxide, which is available as a colloidal suspension from Sigma-Aldrich (Product No 289744), has a reported refractive index of 2.18 at 500 nm [15], and silicon dioxide, also available as a colloidal suspension from Sigma-Aldrich under the tradename LUDOX (Product No 420832), has a refractive index of 1.46 at 500 nm [15]. Using methods described by Macleod, a simple two-layer anti-reflective stack can be designed, such that a minimum of zero reflection can be achieved at 500 nm wavelength if the ratio of refractive indices is 0.8 [15].

In the case of the colloidal ceria, the mean particle diameter is 10–20 nm, which is sufficiently small not to scatter light in the visible region. However, the bulk solvent in the suspension is water. The water, which has been added to the solution, dissociates the acetic acid into acetate anions and hydronium cations. These acetate ions are attracted to the positive surface of the ceria particles, which creates the repulsive force necessary to stabilize the double-layer phenomenon around each colloid. Unfortunately, water is a very difficult solvent to use in a spin coating process because of its relatively low vapour pressure (0.0313 atm). The low vapour pressure makes it difficult to thoroughly evaporate the water present and can lead to a porous film. The acetate stabilized aqueous colloid is therefore introduced into a solvent with a greater vapour pressure such as methanol (0.128 atm) or ethanol (0.078 atm). Even though the bulk solvent is no longer water, the colloid particles are still stabilized by an electrical phenomenon because the water was never removed. Removal of the water reverses the acetic acid dissolution reaction which removes the stabilizing acetate anions from solution and results in agglomeration of the nanoparticles.

Diluting the aqueous solution with another solvent actually 'salts in' the colloid by gradually reducing the net concentration of stabilizing ions, increasing the net energy barrier described by the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory [16, 17]. It was found that only highly polar solvents, which most closely resemble water from a molecular standpoint, allow the colloid to remain stable. Therefore, methanol, with a dipole moment of 1.7 D (vapour pressure 0.128 atm), ethanol, with a dipole moment of 1.69 D (vapour pressure 0.078 atm), and 1-propanol, with a dipole moment of 1.68 D (vapour pressure 0.043 atm), were found to be successful bulk solvents. 1-butanol, with a dipole moment of 1.66 D [18], was marginally successful but required considerable ultrasonication to prevent the colloids from agglomerating. Ethanol, with its high availability and low toxicity, was selected as the solvent.

Monomer, along with an appropriate photoinitiator, is then added to the bulk ethanol solution containing the colloidal ceria. Several acrylic monomers including dipentaerythritol pentaacrylate (available from Sartomer as SR-399), polyethylene glycol diacrylate (available from Sartomer as SR-344), and an ethoxylated trimethylolpropane triacrylate (available from Sartomer as SR-415) were tested. The pentafunctional monomer was selected for its strength and high degree of cross-linking, which is necessary for highly doped films containing very little monomer. It can be efficiently radiation cured using 2–4 wt% of Irgacure 184.

The solution was then spun onto an acrylic substrate and subsequently cured using an Optical Dynamics Corporation Table Top AR coater shown in figure 1. This apparatus consists of a HEPA clean air space surrounding a coating bowl, curing chamber, and cleaning bowl, and is designed to move a substrate through a complete coating process with no operator intervention. The coating bowl is equipped with a heated air inlet to minimize environmental effects and an outlet blower to enhance solvent evaporation. The self-contained environment is specifically designed to limit the contaminants that can be deposited onto the substrate during processing. The spin-off speeds are controlled to within 5 rpm for accurate repeatability.

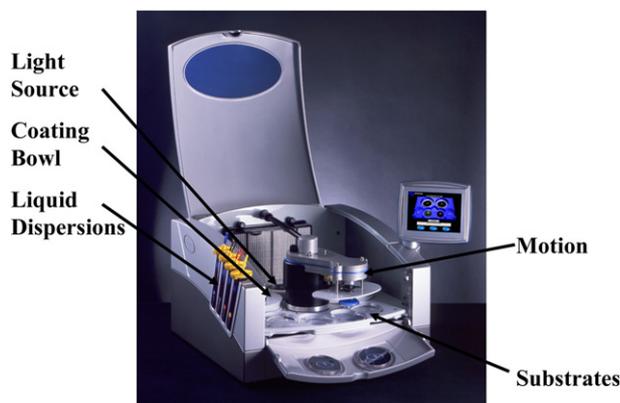


Figure 1. A photograph of the spin coating apparatus utilized in this research. The system eliminates most air-borne contamination by enclosing the entire casting process in a HEPA clean air space.

The curing bowl uses a low wattage UV germicidal bulb and an inert carbon dioxide atmosphere to minimize oxygen inhibition.

It is slightly more difficult to dilute the colloidal silica solution with an organic solvent because of the manner in which the colloid is stabilized. Silica particles have negatively charged surfaces, so they must be stabilized with an appropriate cation. In most cases, the cation is sodium. If a sodium stabilized solution is dispersed in an organic alcohol, the sodium ions will be consumed by the alcohol in the form of an organic alkoxide. In ethanol, for example, the sodium will react to form sodium ethoxide removing the stabilizing ions from solution. It is for this reason that a larger, more stable cation such as the ammonium cation must be used. Even then, the commercially available colloidal silica must first be diluted with water from 30 wt% to approximately 15 wt%. This process gradually decreases the net concentration of ammonium ions in solution and increases the net energy barrier stabilizing the colloids from agglomeration. This intermediate equilibrium allows the colloid to then be introduced into the bulk ethanol without loss of stability. Appropriate amounts of monomer and photoinitiator can then be added.

3. Results

Two parameters need to be defined in order to discuss the observed results effectively. The percentage of solids in the solution will be defined as the total weight of metal oxide nanoparticles and monomer divided by the total weight of the solution and is the ratio of nonvolatile substances to total weight. Since it is the competition between centrifugal forces and viscous forces that governs the spin coating process, the film thickness is strongly affected by the solution viscosity. The second parameter is the weight ratio of nanoparticles to total nonvolatile substances, which influences the optical and mechanical properties of the film. This ratio also plays an important role in the thickness of the film.

The percentage of ceria in the film will be defined as the weight of nanoparticles divided by the total weight of nonvolatile solids (i.e. nanoparticles, monomer, and photoinitiator) present after spin coating. This ratio should directly control the refractive index of the film (as it is directly

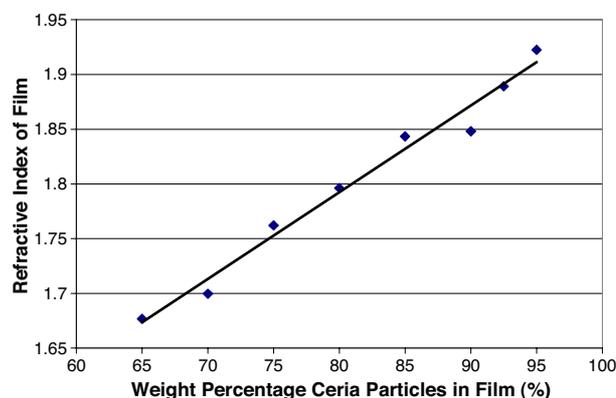


Figure 2. Linear relationship between the weight percentage of ceria particles in the film and the resulting refractive index observed at a wavelength of 550 nm. The observed linearity across a broad range supports the conclusion that the refractive index is, in fact, tunable.

related to the volume ratio). To test this hypothesis, eight solutions were formulated by varying the percentage of ceria in the film, and holding the percentage of solids in the solution constant at 3 wt%. Each film was deposited on a three-inch silicon wafer and cured with ultraviolet radiation. The film thickness was measured using a Dektak Profilometer. This thickness was then used in conjunction with a reflectance spectrum measured by a Filmetrics F20 Spectrometer to calculate the refractive index. These films were also cast onto optically clear lenses, and the measured clarity of the coated substrate was not changed as measured using a BYK Gardner Hazegard.

As hypothesized, the relationship in figure 2 is linear with an interpolation R^2 value of 0.98. If this linear relationship is extrapolated, the limit at 100% loading would correspond to a refractive index of 1.95, which is less than the reported bulk refractive index of ceria. However, the aqueous ceria solution has been treated with a mild acid, and its surface properties have undoubtedly been affected by this procedure. Even with this residual organic acid present, the refractive index is continuously tunable from the refractive index of the pure polymer (1.54) to the refractive index of the treated ceria particles (1.95).

Figure 3 shows the observed influence of ceria loading on the thickness of the thin films. The percentage of solids in each of the formulations was held constant at 3 wt%. Therefore, an increase in the loading of ceria particles in the film must be accompanied by a decrease in monomer added to the solution. The exchange of rigid ceramic particles for tacky monomer molecules has an acute effect on the viscosity of the monomer solution to be spin coated. As the viscosity of the solution increases, i.e. at lower ceria loadings and higher monomer loadings, the balance of viscous to centrifugal forces changes yielding thicker films.

It was also speculated that an increase in the nanoparticle loading in the film would increase the mechanical strength of the film. Introducing ceramic nanoparticles, noting that ceria has a Mohs' scale hardness of 6, into the polymer matrix should increase the abrasion resistance of the film considerably since the nanoparticles will also act as a binder. Six of the previous formulations were coated onto acrylic substrates

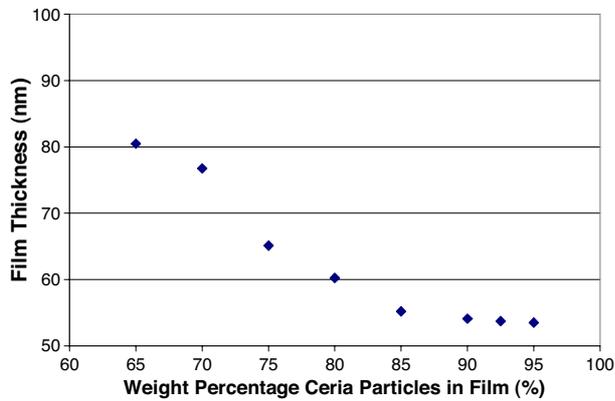


Figure 3. Observed relationship between the weight percentage of ceria particles in the film and the thickness of the film. The curve clarifies the condition that the percentage of solids was held constant at 3 wt%. The exchange of solid particles for tacky monomer molecules has a profound effect on the viscosity of the solution.

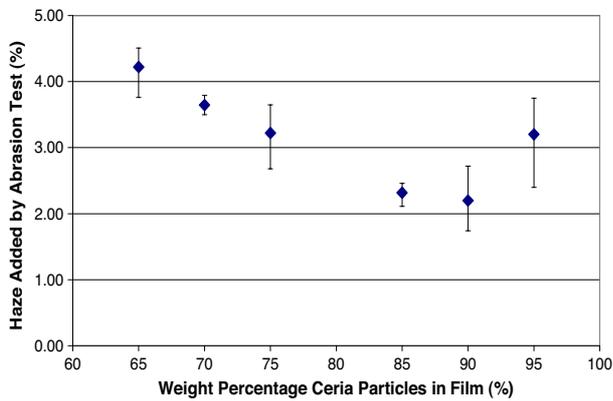


Figure 4. Observed relationship between the weight percentage of ceria particles in the film and the abrasion resistance of the film. Simply a measure of how strongly the particles and monomer matrix hold together, the failure of the film is quantified by measuring the degree to which the film becomes scratched.

and subjected to a physical abrasion test used in the optical industry [19]. This tumble test was chosen as opposed to the Taber abrasion test, which would be too aggressive and would be influenced too much by the plastic substrate. The tumble test

simulates abrasive wear on AR coated samples and measures the increase in haze (light scatter caused by scratches on the surface). Lenses exhibiting more scratches have a higher haze value. The test is sensitive, but can quickly sample a large population of lenses, so a large sample size was chosen for each formulation.

Using a BYK Gardner Hazegard the light scattered from an incident beam was measured before and after administering the test. The increase in scattered light, measured in the form of haze, was then recorded in figure 4. As expected, the increase in nanoparticle dopant increased the abrasion resistance of the film, appearing as a decrease in added haze. This increase in abrasion resistance reaches an optimum point, however, around 90 wt% loading in the film. Beyond this loading there is simply not enough monomer available with which to form a continuous matrix around the nanoparticles. The nanocomposite properties are lost and a decrease in mechanical strength is noticed.

The two cross-sectional micrographs shown in figure 5 were taken with a transmission electron microscope. Therefore, the atomically heavier ceria particles appear darkest in the images because they affect the transmitted intensity the most. Two films of different thicknesses, controlled by varying the percentage of solids in the bulk solvent, have been created.

In both cases the dispersion of ceria particles is uniform across the matrix. The particles do not appear to have condensed near the substrate interface, but have formed a homogeneous nanocomposite. On evenly distributing nanoscale particles homogeneously throughout the film, the wavelength of the incident light is great enough that the light is not affected by individual particles. The light is not scattered but effectively 'sees' only a single phase with constant refractive index rather than patches of low index and patches of high index. This allows the film to maintain its macroscale applications and processability, while tuning its physical properties such as refractive index and mechanical strength on the nanoscale.

The curves displayed in figure 6 present an ideal application of these tunable nanocomposite films. By coating an acrylic substrate with a high index ceria doped thin film, followed by a low index silica doped thin film, it is possible to create a two-layer anti-reflective coating which can now be tuned for optimal performance. By varying the percentage

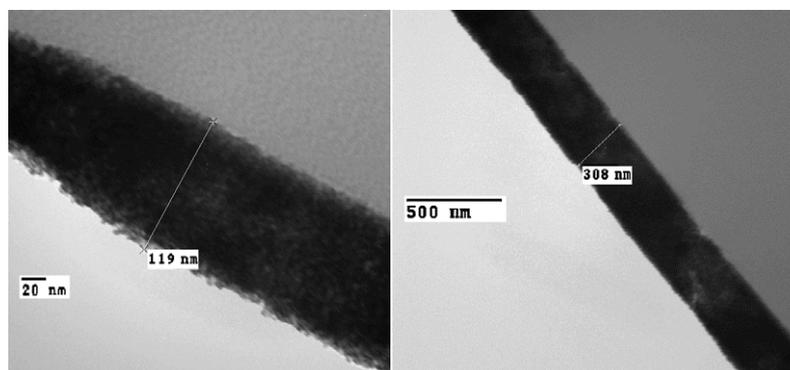


Figure 5. Transmission electron micrographs taken from cross sections of two differently doped thin films. The darker grey region is the plastic substrate, the black layer is the doped film and the light grey region is the epoxy into which the sample was embedded for cross-sectioning. The ceria distribution appears to be homogeneous across the polymer matrix.

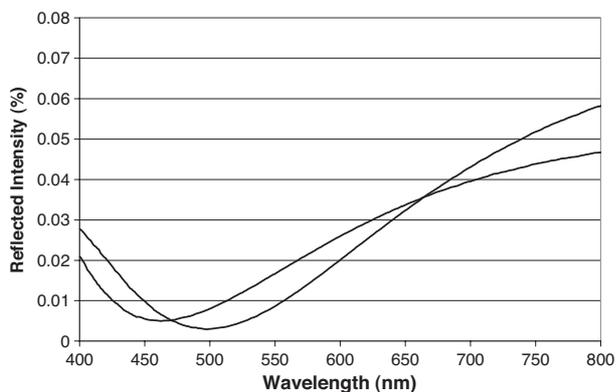


Figure 6. Reflected intensity across wavelengths in the optical spectrum taken from two different coated substrates. The minimum has been shifted by manipulating the thicknesses and refractive indices of the high and low index doped films.

of solids in each layer the thicknesses can be controlled, and by varying the nanoparticle loading the refractive indices can be controlled. The following reflectance spectra were taken from two acrylic substrates coated with such an anti-reflective coating.

By manipulating the thickness and refractive index of the high and low index layers, it is demonstrated that the minimum wavelength can be tuned to a desired value. This manipulation changes the reflected colour and intensity of light from the lens. Using only two layers these samples exhibit a 96.3% and 97.6% transmission, an increase from the 90% transmission achieved from an uncoated acrylic substrate. In the optical lens industry thin film coatings are subjected to a series of standardized tests meant to objectively measure the ability of the coatings to withstand mechanical abrasion as well as extreme humidity [20]. The industry benchmark for an acceptable coating is a score of 3.25 out of 5.0. Coatings deposited in the previously described method routinely score above 4.0, thereby comparing very favourably with films made in more expensive and complex vacuum based systems.

4. Conclusions

This research presents a method for making optically transparent polymer nanocomposite thin films from liquid colloidal solutions. Specifically, the results show that the index of refraction of the polymer films can be tuned from 1.46 to 1.54 using silica nanoparticles and from 1.54 to 1.95 using ceria nanoparticles. Combining the high and low refractive index films in layers creates an anti-reflective coating whose performance is comparable to or better than those produced using sol-gel and vacuum based techniques. The procedure described in this work provides an inexpensive and safe method of effecting AR coating compared to others that require an evacuated environment or high temperatures.

The method of surface treatment to stabilize the colloids followed by addition of an organic solvent for eventual spin coating and photocuring can easily be adapted for several other metal oxide nanoparticles. Results also indicate that it is not necessary to begin with organic dispersions of nanoparticles when creating polymer nanocomposites. It is possible to begin with aqueous solutions, taking advantage of

the colloidal phenomenon to stabilize the nanoparticles, and modify them to maintain the efficiency in spin coating observed with organic solvents. This opens many doors for future research. Similar techniques may be used to incorporate other interesting materials into nanocomposites. Aqueous colloidal suspensions of titania, alumina, zirconia or zinc oxide could be reliably cast using this procedure, broadening the range of refractive indices further and improving the reflectance spectra obtained in this work using ceria and silica.

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References

- [1] Perrin F X, Nguyen V and Vernet J L 2002 Mechanical properties of polyacrylic-titania hybrids—microhardness studies *Polymer* **43** 6159–67
- [2] Que W, Zhou Y, Lam Y L, Chan Y C and Kam C H 2000 Optical and microstructural properties of sol-gel derived titania/organically modified silane thin films *Thin Solid Films* **358** 16–21
- [3] Elim H I, Ji W, Yuwono A H, Xue J M and Wang J 2003 Ultrafast optical nonlinearity in poly(methylmethacrylate)-TiO₂ nanocomposites *Appl. Phys. Lett.* **82** 2691–3
- [4] Xu J F, Czerw R, Webster S, Carroll D L, Ballato J and Nesper R 2003 Nonlinear optical transmission in VO_x nanotubes and VO_x nanotube composites *Appl. Phys. Lett.* **81** 1711–3
- [5] Oliveira P W, Krug H, Frantzen A, Mennig M and Schmidt H K 1997 Generation of wet-chemical AR coatings on plastic substrates by the use of polymerizable nanoparticles *Sol-Gel Optics IV* ed B S Dunn, J D Mackenzie, E J A Pope, H K Schmidt and M Yamane (San Diego, CA: SPIE) pp 452–61
- [6] Pégon P M, Germain C V, Rorato Y R, Belleville P F and Lavastre E 2004 Large-area sol-gel optical coatings for the Megajoule Laser prototype *Advances in Optical Thin Films (Proc. SPIE vol 5250)* ed C Amra, N Kaiser and H A Macleod (Bellingham, WA: SPIE Optical Engineering Press) pp 170–81
- [7] Floch H G and Belleville P F 1997 Proc. Sol-gel laser coatings at CEA, Limeil-Valenton *SPIE* **3136** 275–83
- [8] Spiller E, Haller I, Feder R, Baglin J E E and Hammer W N 1980 Graded-index AR surfaces produced by ion implantation on plastic materials *Appl. Opt.* **19** 3022–6
- [9] Flack W, Soong D, Bell A and Hess D 1984 A mathematical model for spin coating polymer resists *J. Appl. Phys.* **56** 1199
- [10] Schroeder H 1969 Oxide layers deposited from organic solutions *Phys. Thin Films* **5** 87–141
- [11] Haas D E, Quijada J N, Picone S J and Birnie D P 2000 Effect of solvent evaporation rate on skin formation during spin coating of complex solutions *Sol-Gel Optics* (Bellingham, WA: SPIE Optical Engineering Press) pp 280–4
- [12] Rehg T J and Higgins B G 1992 Spin coating of colloidal suspensions *AIChE J.* **38** 489–501
- [13] Yu Y-Y and Chen W-C 2003 Transparent organic-inorganic hybrid thin films prepared from acrylic polymer and aqueous monodispersed colloidal silica *Mater. Chem. Phys.* **82** 388–95

-
- [14] Meyerhofer D 1978 Characteristics of resists films produced by spinning *J. Appl. Phys.* **49** 3993–7
- [15] Macleod H A 2001 *Thin Film Optical Filters* (London: Institute of Physics)
- [16] Verwey E J W, Overbeek J T G and Van Ness K 1948 *Theory of the Stability of Lyophobic Colloids—The Interaction of Soil Particles Having an Electrical Double Layer* (Amsterdam: Elsevier)
- [17] Krogman K 2004 Anti-reflective coatings incorporating nanoparticles *MS Eng. Thesis* University of Louisville
- [18] *CRC Handbook of Chemistry and Physics* 1980 (Boca Raton, FL: CRC Press)
- [19] Colts Laboratories 1997 *Tumble Abrasion* SOP No. L-11-13-06
- [20] Colts Laboratories 1997 *Real Life Simulation Test* SOP No. L-24-11-03