The Fabrication of Antireflective Coatings by the Self-assembly of Silica Nanoparticle and Polycation Bilayers

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Abstract

This study examines several factors that affect the quality of antireflective coatings created by the self-assembly of alternating layers of silica (SiO_2) nanoparticles and poly(allylamine hydrochloride) or poly(diallyldimethylammonium chloride) (PAH and PDDA respectively) polycation on glass substrates. We employ a factorial experimental design to investigate the effects of the molarity of the nanoparticle solution, the size of the nanoparticles, the pH of the SiO_2 and polycation solutions, the number of silica-polycation bilayers, and the significance of an RCA cleaning process on the optical properties of the films. We examine the first order effects of these factors, as well as their interactions, on the reflectance, transmittance and uniformity of the coatings.

Contents

Antireflection Theory

An antireflective coating is a thin layer of material that is applied atop a substrate (typically glass) in order to minimize the reflection of light from that surface and thus increase the transmission of light through the substrate. Since glass is generally regarded as a transparent material, it may seem unimportant to increase its transmittance; however, the science of antireflection is actually a very important subject. It turns out that glass does reflect a significant portion of the light incident upon it. In fact, an untreated glass surface (like a normal window or a conventional lens) will actually reflect about 8% of the light incident normal to the plane of the glass: 4% when the incident ray encounters the glass medium initially, creating the first reflected ray, and another 4% when the transmitted ray exits the glass, creating the second reflected ray.[1] Figure 1 (below) depicts this occurrence with the two reflected rays each representing about 4% of the original light. Thus the transmitted ray represents about 92% of the incident ray.

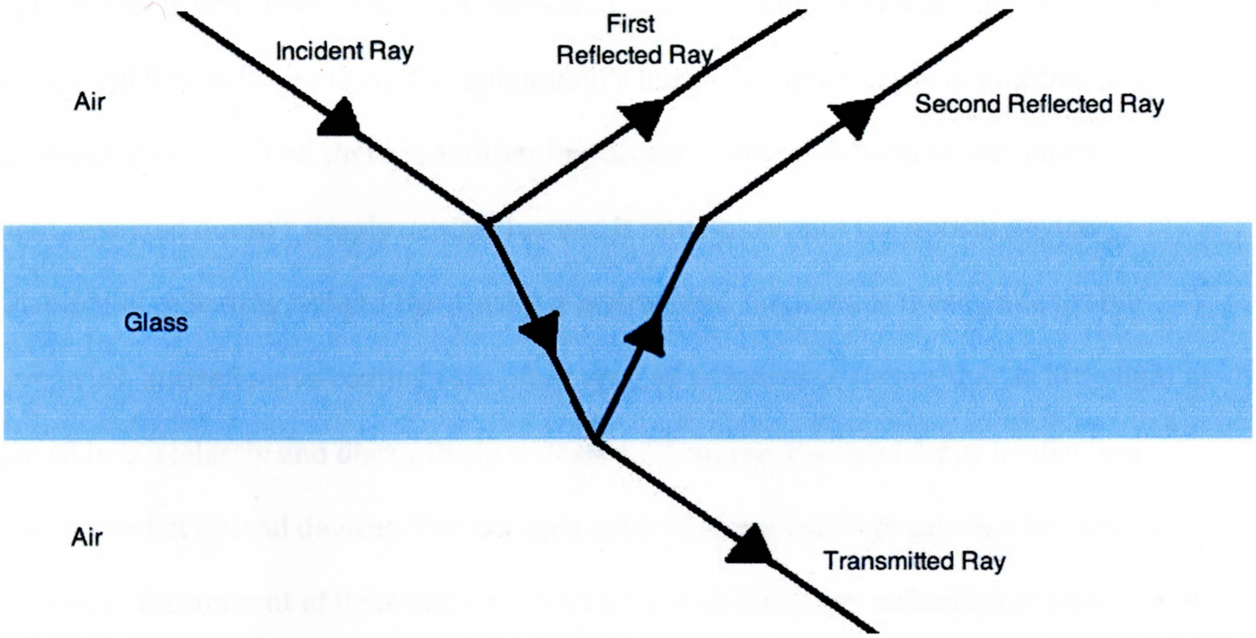

Figure 1: An incident ray of light strikes a glass surface. Roughly 4% is reflected in the First Reflected Ray, and the rest is transmitted through the glass. At the glass/air interface on the bottom another 4% of the light is reflected in the form of the Second Reflected Ray, while the rest leaves the glass as the Transmitted Ray.

In addition to exaggerated angles for clarity, Figure 1 contains two simplifications. First, it neglects the phenomena of scattering and absorption, which will be dealt with later, and assumes all incident light is either transmitted or reflected. Furthermore, when the second reflected ray is exiting the glass, there should be another reflection (as there is at every change in medium), but reflected rays beyond the first two deal with negligible energies for the purposes of antireflection and will hence be disregarded.

Although 8% might not seem like a great deal of loss, realistically it is a very significant amount for both scientific and commercial purposes. More light means clearer, sharper and better images produced by the lenses in devices such as microscopes, telescopes, cameras and binoculars. It is also important to note that many of these instruments are comprised of multiple lenses, so each untreated glass-air interface in the optical device will reflect 4% of the remaining light, causing an overall energy loss that can far exceed 8%, hence limiting the instrument's usability significantly. In addition to the problem of energy loss, there is another important matter that need be considered. The light reflected doesn't simply vanish; instead it remains within the optical device, chaotically reflecting around the sensitive instrument. To prevent these undesirable scenarios, antireflective coatings are often applied to lenses to insure that as little light as possible is uselessly and disruptively reflected. Of course, the need for antireflection doesn't end at optical devices. For example, antireflective coatings can also be used to maximize the amount of light that reaches a photocell for better collection of solar energy.[2]

The physical mechanism through which antireflection operates is thin film interference the very same phenomenon that causes oil slicks and bubbles to take on a rainbow tint. As in Figure 1, Figure 2 (below) depicts an incident light ray in air (with index of refraction n_i), that is now incident on a thin film (with index of refraction n_f) of thickness t abutting a glass substrate (with index of refraction n_t). Again there are two primary reflections, the first reflected ray coming from the air-film interface and the second reflected ray, which originates at the film-glass interface.

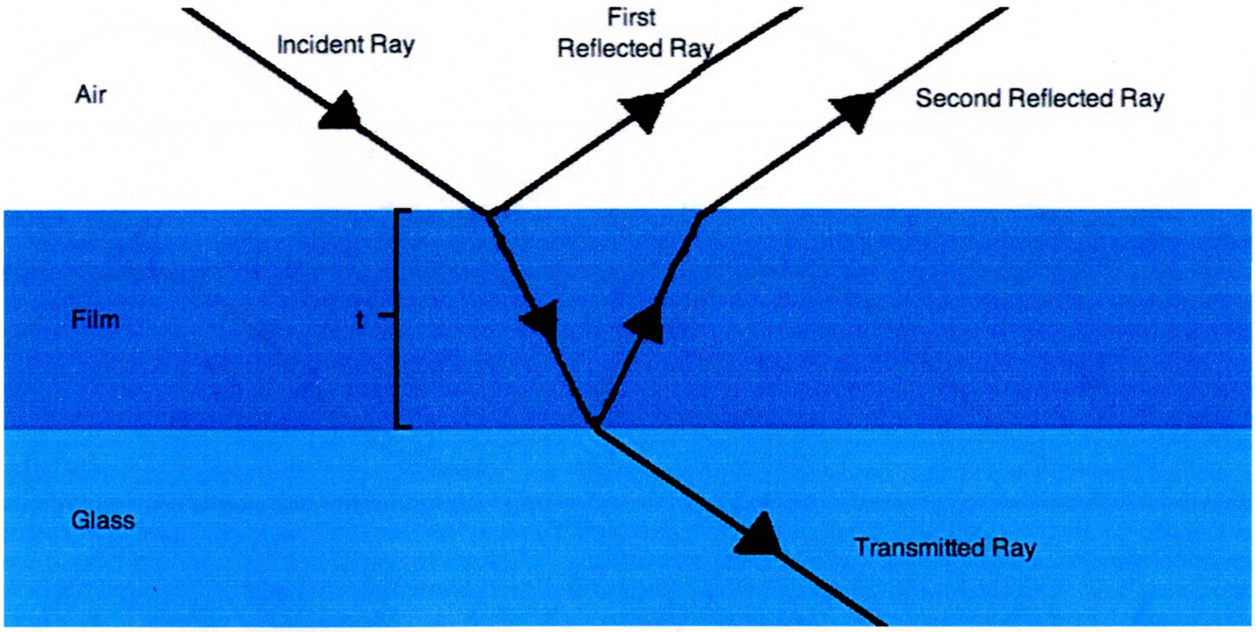

Figure 2: An incident ray of light undergoes two reflections (as in Figure 1) when traveling through a thin film of thickness t.

Again neglecting scattering and absorption and focusing solely on reflection and transmission for now, an antireflective coating needs to be a film that will minimize the sum of the light coming back in the form of the two reflected rays. This will maximize transmission by forcing as much light as possible into the transmitted ray.

In Figures 1 and 2, light has been treated as a ray, and in doing so a fact crucial to antireflection has been neglected. In order to minimize the sum of the first and second reflected rays in Figure 2, antireflective coatings take advantage of the fact that light possesses wave-like properties, in particular that it can *interfere* with itself. Wave interference works according to the superposition principle. Figure 3 shows two identical waves (they have the same amplitude, frequency and phase) being added together.

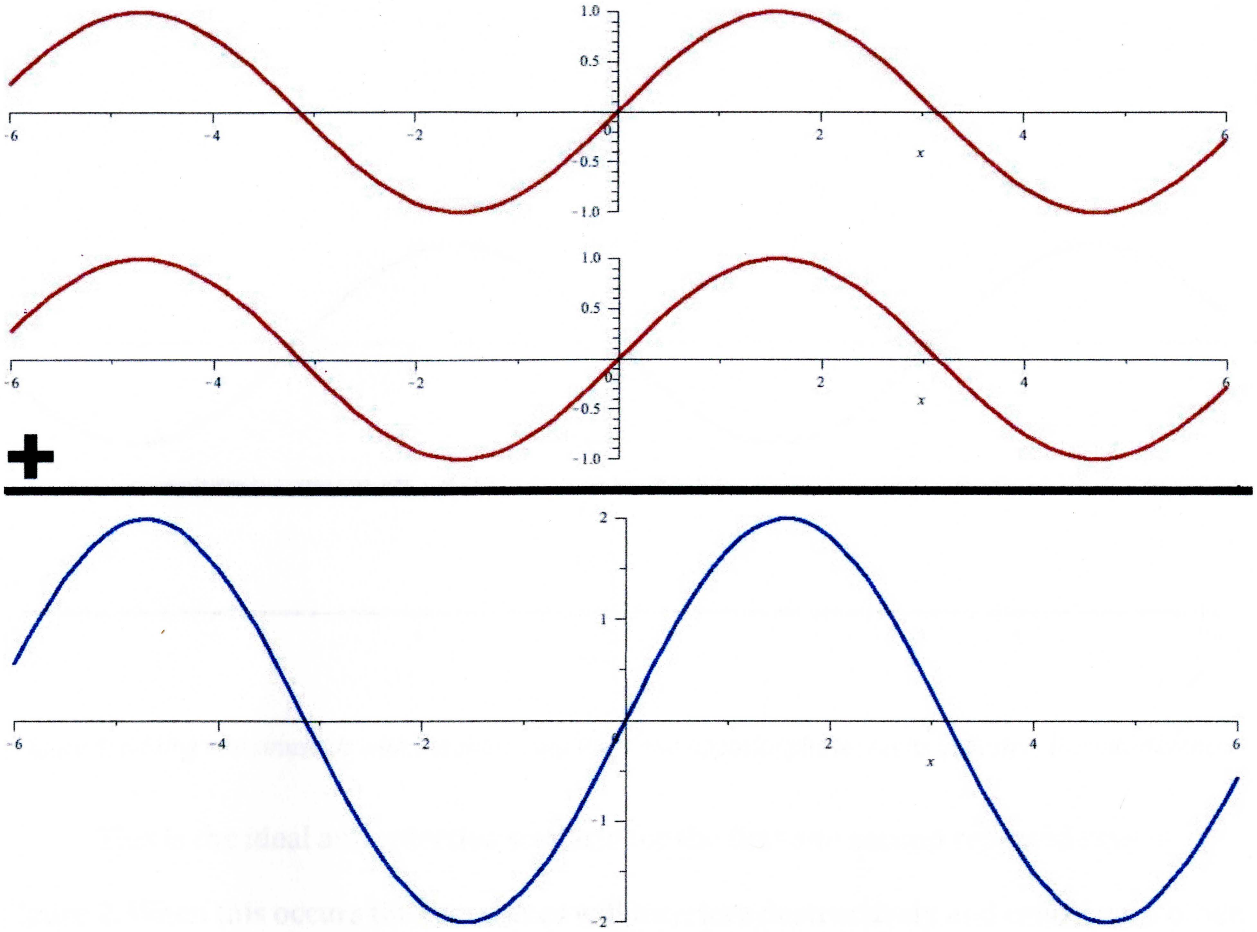

Figure 3: Adding two identical sinusoids produces another with twice the amplitude and the same phase. This is an example of constructive interference.

Note how the net result of the superposition of these identical waves produces a wave with the same frequency and phase but twice the amplitude. This is constructive interference, and it could be used to maximize reflection, producing a film much like what an astronaut would want on his visor. Of course, this is the exact opposite of antireflection. Figure 4 shows the superposition of two coherent waves with equal amplitudes and frequencies that are perfectly out of phase with each other (phase difference of π radians), meaning that they are identical in every way except that the second has been shifted by half of its wavelength.

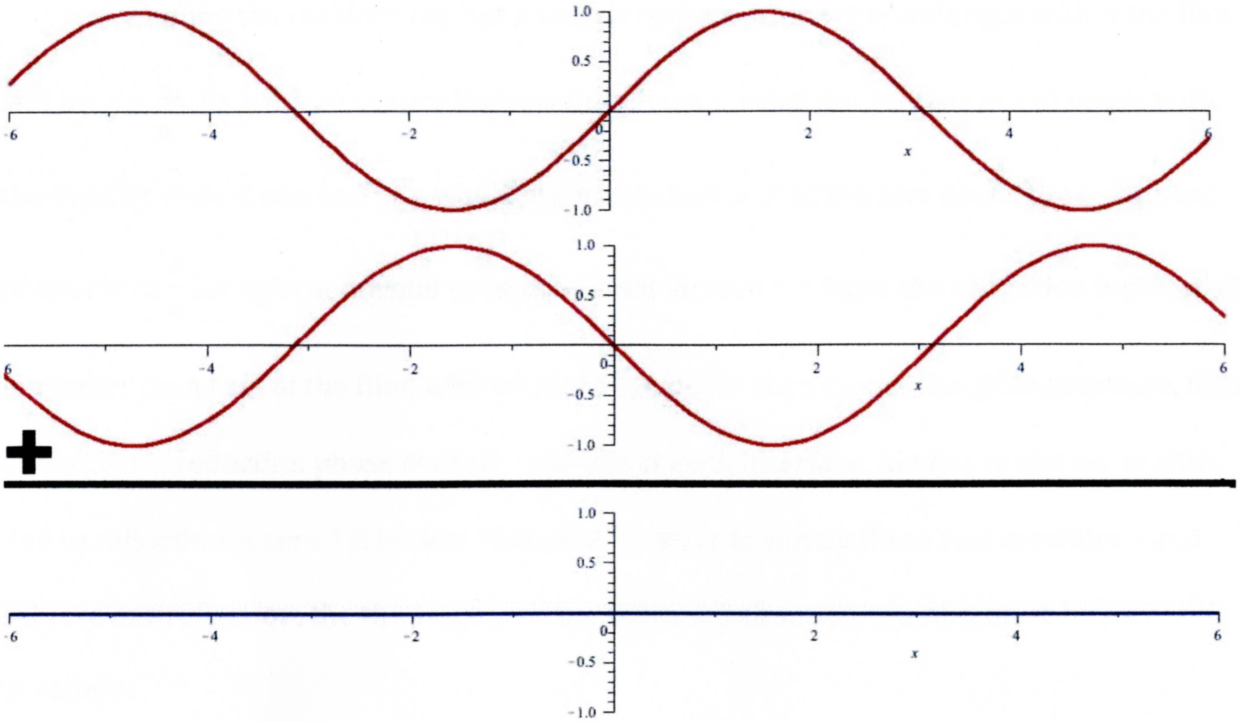

Figure 4: Adding two sinusoids with the same amplitude and opposite phase results in destructive interference.

This is the ideal antireflective scenario for the first and second reflected rays in Figure 2. When this occurs the two waves will interfere destructively and cancel each other out causing the total reflected wave to simply appear as no wave at all, as shown in Figure 4. Thus there is no reflection, and since the energy from the incident ray must be conserved, all the light must be in the transmitted ray.

As has been stated, the exact conditions for this cancelation to occur are for the amplitudes of the two reflected waves to be equal and for them to be π radians out of phase. To ensure the former condition, the Fresnel equations show that the index of refraction of the film n_f need be such that $n_f = \sqrt{n_i n_g}$, where, as before, n_i represents the refraction index of air (about 1.0) and n_g represents the refraction index of glass (typically 1.5).[3]

Assuming the incident ray has a wavelength $_0$ in air, its wavelength within the film will be $\lambda = \frac{\lambda_0}{n_f}$. In order to ensure the second reflected wave is radians out of phase with the first, or shifted one half of a wavelength, the thickness of the film needs to be adjusted precisely to $\frac{\lambda}{4}$ for light at normal or near-normal incidence.[4] Since the refraction index of air is smaller than that of the film, which in turn is smaller than that of the glass substrate, light undergoes a reflection phase shift of radians at each interface; hence the net phase shift due to reflection is zero.[4] It is clear then that in order to satisfy these two conditions and achieve antireflection, the thickness and the index of refraction of a film must be set precisely.

Materials

The 30nm diameter silica employed was purchased from Nanostructured and Amorphous Materials and is a 25% by weight SiO_2 dispersions in H_2O (CAS #1317-80-2).

The 15nm, 45nm, and 85nm diameter silica was all acquired from Nissan Chemical again as SiO_2 dispersions in water. The 15nm silica is the Snowtex-C brand and is 20% by weight, the 45nm silica is Snowtex-20L and is also 20% by weight and the 85nm silica is Snowtex-ZL and is 40% by weight.

The two polycations employed in the project are actually quite different. Both were purchased from Sigma Aldrich with the first being poly(diallyldimethylammonium chloride) (CAS #26063-79-3), or PDDA, being 35% by weight in water and the second being poly(allylamine hydrochloride), or PAH, being a solid with average M_w ~56,000, which was later dissolved in water (CAS #71550-12-4).

The RCA cleaning process used the following chemicals: 99.9% Acetone (CAS #67-64-1), 37% Hydrochloric Acid (CAS#7647-01-0), and Ammonium Hydroxide (CAS#1336-21-6), all from Sigma Aldrich.

Experimental Procedure

While the $\frac{\lambda}{4}$ thickness requirement for the antireflective coating is not too difficult to achieve using a homogeneous film, getting the perfect index of refraction is a little trickier. Because of the $n_f = \sqrt{n_i n_g}$ condition, the index of refraction of an antireflective film deposited on glass should be about 1.22. Unfortunately, there is no homogeneous material with this low index.[3] Using the ionic self-assembly of nanoparticle bilayers of SiO_2, groups such as Lee et al. have been able to create films with this low index of refraction that is necessary to get perfect antireflection.[3] The process involves forming a film that is composed of alternating layers of a polycation and silicon dioxide (SiO_2) on a glass substrate. Note that a bilayer is simply a layer of silica on top of a layer of polycation (Figure 5 has two bilayers).

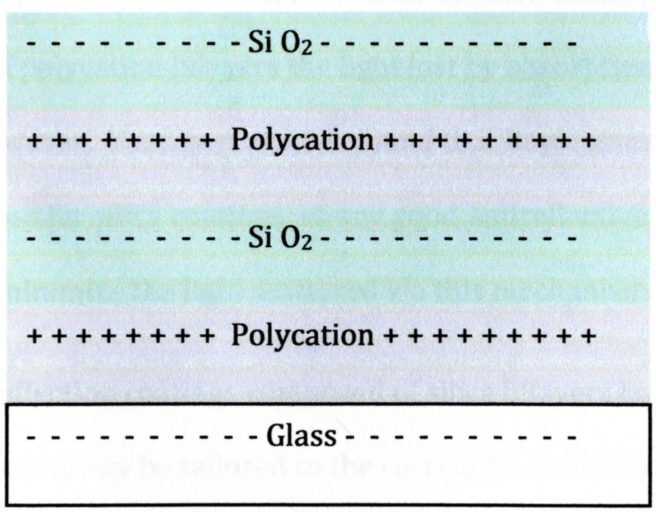

Figure 5: A glass medium with two polycation/silica bilayers applied as a coating.

Figure 5, while not at all to scale, shows how the process works by the ionic self-assembly of monolayers. Two materials are used to make the films. The first is the SiO_2 nanoparticles (very fine particles with diameters ranging from 10-100nm) that will determine the optical properties (the index of refraction) of the film and the second is a polycation (either PAH or PDDA). The polycation has no effect on the optical properties of the film and is only used as a "glue" to hold together glass and SiO_2.

This layer-by-layer deposition process takes place by ionic self-assembly: since the glass has a negative surface charge after it is cleaned, the positively charged polycation will adhere to it, forming the first layer of the coating. Next, a layer of SiO_2 is applied, which adheres to the first polycation layer due to their opposite charges. Using this process, films of any thickness can be created by adding the appropriate number of bilayers, thus causing the destructive interference necessary for antireflection.

Earlier, the assumption was made that all incident light was either reflected or transmitted when encountering a new medium. In fact, at each interface light can also be absorbed by the new material or scattered from it. In the case of antireflective coatings composed of silica and polycation bilayers the light lost by absorption is negligible in the visible spectrum.[5]. However, Yancey et al. have found that Rayleigh scattering is a significant source of loss for silica coatings, so any good antireflective coating made in this way will also need to minimize the light scattered via this mechanism.[3]

Although antireflection coatings composed of silica bilayers have the right index of refraction and can theoretically be tailored to the correct thickness to produce perfectly destructive interference for a chosen wavelength, many groups have had difficulty creating good, uniform coatings.[1,3] This project consisted of several separate experiments, each aimed at discovering how to make such uniform antireflection coatings more consistently by varying several factors during their deposition. The factors considered were: the pH of the SiO_2 and polycation solutions, the molarity of these solutions, the number of bilayers in the film, the type of polycation used, the size of nanoparticles used, and the time given for the solutions to adhere in the coating. Numerous and diverse sample coatings on glass slides were created and their optical properties were evaluated to see which combinations of factors produced the best films. Each of these experiments involved five major steps: RCA cleaning, experimental design, film deposition, measurement of optical properties and data analysis.

RCA Cleaning

RCA cleaning is a process whose goal is to remove any organic and inorganic contaminants that may be present on the manufacturer-direct glass slides.[6] First the slides were taken from their packaging and scrubbed using a lint-free cloth with acetone. Next they were placed in a strong base mixture, which was in turn placed in a water bath in order to heat the base to 80 degrees Celsius. The slides were left in this heated base for 20 minutes. Following this time period the slides were washed in de-ionized water and placed in a strong acid mixture for 20 minutes as well. Finally the slides were washed again, and then dried using flowing nitrogen gas to prevent any streaks or inhomogeneities that might appear from an air dry.

Experimental Design

A piece of statistical design software was used to design the factorial experiments for this project. A factorial experiment is one in which several factors, each with multiple levels, are tested to see which among them have an effect on any number of response variables. As opposed to a one-factor-at-a-time (OFAT) experiment, which allows only for testing many levels of a single independent variable, the factorial method permits the examination of several factors at once and, crucially, lets the experimenter check for interactions between different factors that may have been missed using OFAT. The number of factors, their levels and the type of factorial design are chosen by the experimenter and entered into the program, which then produces a randomized run order for the possible combinations using the chosen levels of the selected factors. For some experiments, a randomized block design was used in conjunction with the factorial approach in order to filter out extraneous sources of variability.

Film Deposition

After the experiment had been designed in this way, the coatings needed to be prepared on glass slides using the specifications required by the experimental design. The clean slides prepared with the RCA process described above were then taken through a layer-by-layer dipping process. First, each polycation and silica solution combination for the current block of samples was prepared through molarity calculations, mass measurements and pH adjustment. Next, each sample was dipped individually using the correct level of each factor.

Figure 6: A glass slide ready for deposition. It will be dipped into the polycation solution on the left, washed, then dipped into the nanoparticle solution on the right.

As shown in Figure 6, an RCA clean slide was first immersed in the polycation for the previously decided dipping time. It was then quickly rinsed in de-ionized water and placed in the appropriate silica nanoparticle solution for the same amount of time. Thus one bilayer was completed. This process continued until the correct number of bilayers was reached and the slide was dried with flowing nitrogen gas, labeled and stored. The dipping process was carried out for every slide in the current block of the experiment. Figure 7 (below) shows some glass slides after they have undergone deposition.

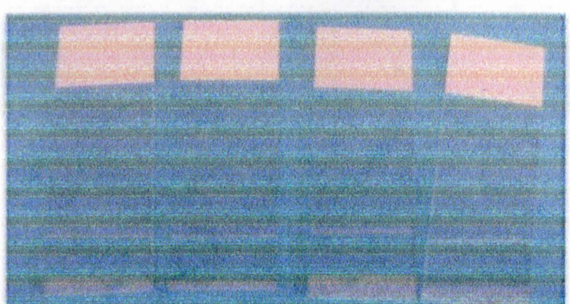

Figure 7: Some early coatings on glass slides.

Measurement of Optical Properties

Once every slide from each block of the experiment had been created, their optical properties were measured. The two most important measurements taken for each slide were its reflectance and its transmittance. The amount of light scattered by the film was then determined by calculation, using the conservation of energy. A Filmetrics F-20 thin film analyzer (Figure 8) was used to get this information from each coated slide. The instrument generated reflectance and transmittance spectrums for each antireflective coating for wavelengths of light between 200nm and 1000nm.

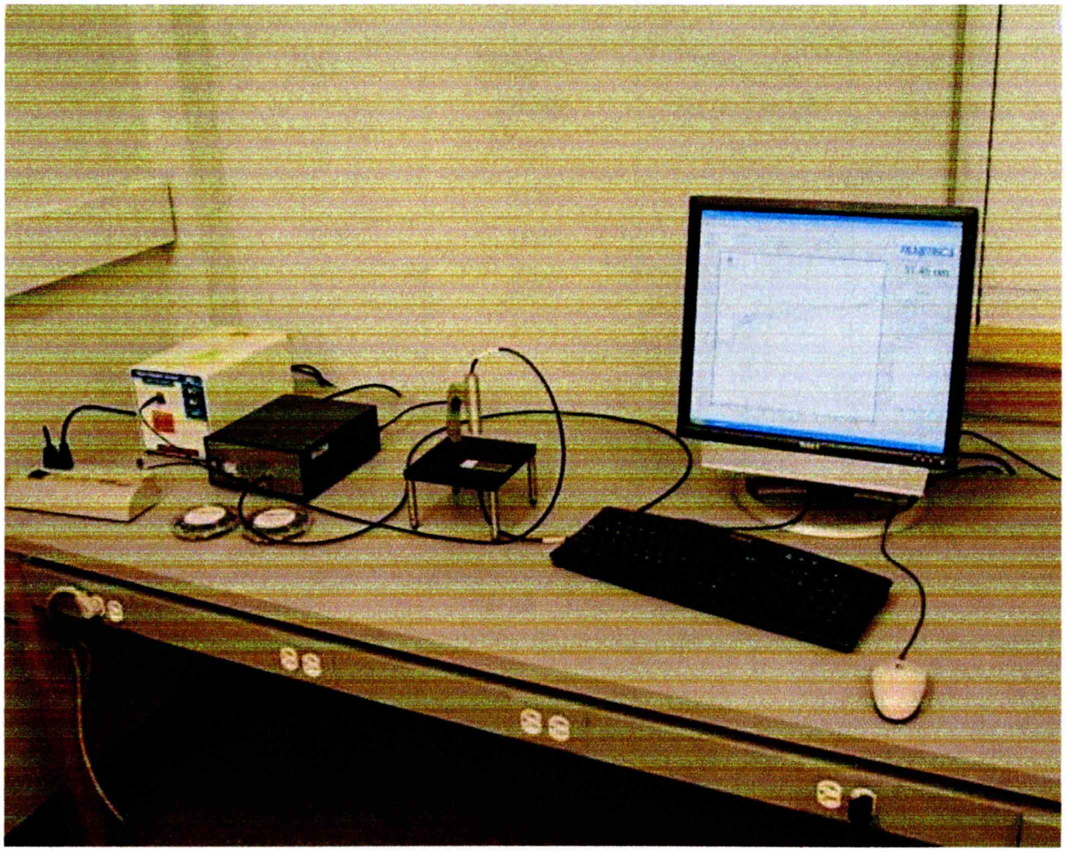

Figure 8: The Thin-Film Analyzer

Results and Data Analysis

Experiment 1

A first exploratory experiment was designed to investigate the influence of four deposition factors on the coating produced. The factors of this two level factorial were: the pH of the polycation solution and the silicon nanoparticle solution, the molarity of the silica nanoparticle solution, the amount of time the slide stayed in each solution per layer and the number of bilayers deposited. Table 1.1 shows the specifications for each deposited film. The molarity of the PDDA was 10mM.

Run Order	pH	Molarity (mM)	Dipping Time (min)	Number of Bilayers
1	9	40	1	8
2	9	100	1	4
3	7	100	4	4
4	9	100	4	8
5	7	100	1	8
6	7	40	1	4
7	7	40	4	8
8	9	40	4	4

Table 1.1: Experiment #1 coating specifics

Table 1.2 gives the measured optical responses for each coated slide. Note that for Table 1.2 and all subsequent response tables, the transmitted and reflected percentages are averaged over the visible spectrum (380nm to 750 nm). The extinction is calculated as the percent of the light in the visible spectrum neither transmitted nor reflected:

$$extinction\ (\%) = 100\% - [transmitted\ (\%) + reflected\ (\%)].$$

Since the absorption by the film and substrate is negligible within this range of wavelengths, the extinction is really a measurement of the amount of light scattered by the film. Rayleigh scattering [4] is proportional to $\frac{1}{\lambda^4}$. The slope of the best fit line of the extinction plotted against $\frac{1}{\lambda^4}$. (i.e., the Rayleigh slope) was used as a one of the responses in the factorial design. Lastly, the R^2 value represents how well this best fit line represents the extinction data.

Run Order	Transmittance (%)	Reflectance (%)	Extinction (%)	Rayleigh Slope	R^2
1	90.843	7.787	1.370	-0.0353	0.5907
2	79.635	9.064	11.301	0.2706	0.9440
3	90.330	7.701	1.969	0.0102	0.1512
4	80.469	9.087	10.443	0.2137	0.9548
5	90.850	7.475	1.675	0.0315	0.5894
6	92.168	7.795	0.037	-0.0069	0.0720
7	92.830	7.842	-0.672	0.0002	0.0001
8	91.798	7.787	0.416	-0.0149	0.2595

Table 1.2: Experiment #1 responses

Visual inspection revealed that the coatings in this experiment were very poor and non-uniform, and the optical measurements confirmed this fact. In fact, the average transmittance of nearly all of the slides was at or below the 92% for normal glass, meaning the films actually had no antireflective effect and in many cases caused *more* light to be reflected and scattered. Rayleigh slopes were quite small in most cases, so the scattering that did occur was likely not a result of Rayleigh scattering. Overall though, the poor quality of the fabricated films meant that little could be gleaned from this first endeavor.

Experiment 2

Experiment number two was another two level factorial design. A dipping time of two minutes of was used for each layer and the factors considered were the solution pH, silica molarity and number of bilayers deposited. Each factor/level combination was employed twice and the randomized block design was used to filter out extraneous variability. Table 2.1 lists the conditions under which each coating was created.

Run Order	Experiment Block	pH	Molarity (mM)	Bilayers
1	Block 1	9	80	12
2	Block 1	7	80	6
3	Block 1	9	80	6
4	Block 1	7	40	12
5	Block 1	9	40	6
6	Block 1	7	80	12
7	Block 1	7	40	6
8	Block 1	9	40	12
9	Block 2	9	40	6
10	Block 2	7	40	12
11	Block 2	9	80	6
12	Block 2	7	80	12
13	Block 2	7	40	6
14	Block 2	7	80	6
15	Block 2	9	80	12
16	Block 2	9	40	12

Table 2.1: Experiment #2 coating specifics

Run Order	Transmittance (%)	Reflectance (%)	Extinction (%)	Rayleigh Slope	R^2
1	91.691	7.537	0.008	0.0002	0.1941
2	91.817	7.636	0.005	0.000009	0.0003
3	90.893	7.319	0.018	0.0007	0.6179
4	91.759	7.600	0.006	0.0001	0.0257
5	89.729	7.180	0.031	0.001	0.7410
6	91.275	7.418	0.013	0.0002	0.1136
7	91.713	7.660	0.006	-0.0001	0.0274
8	83.153	8.160	0.087	0.0027	0.9354
9	91.098	7.426	0.015	0.0007	0.5973
10	91.812	7.561	0.006	-0.0001	0.0591
11	86.097	7.389	0.065	0.0019	0.9150
12	91.991	7.473	0.005	0.0003	0.2141
13	92.712	7.620	-0.003	0.00005	0.0096
14	88.757	7.593	0.037	0.0002	0.0839
15	85.391	7.137	0.075	0.002	0.9296
16	87.851	7.443	0.047	0.0007	0.6317

Table 2.2: Experiment #2 responses

Table 2.2 lists the measured and calculated optical responses for each of these coated slides. Despite the overall low transmittances of the films produced by this experiment (only slide #13 had a value greater than 92%), the slides scattered very little light. The statistical analysis revealed that the pH was as a very significant factor in determining the quality (amount of scattering) of the coating produced. Figure 9 shows the statistical significance of the pH with regards to scattering.

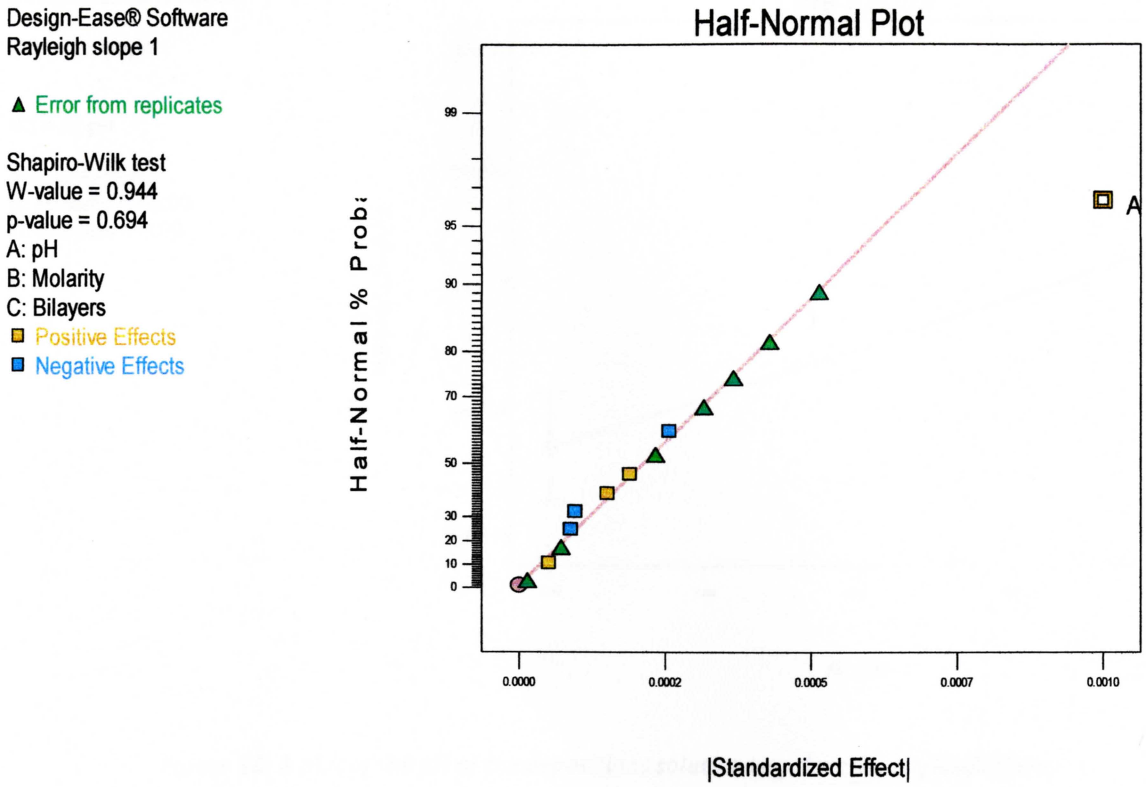

Figure 9: Half-normal plot for the factors of Experiment #2. Factor A, pH, is distinctly significant.

The farther from the central, model line on the half-normal plot a factor appears, the more likely it is that the factor is affecting the response. Above in Figure 9, pH stands out as a significant factor in the half-normal plot for the Rayleigh slope, meaning that changing the pH had a great effect on the scattering. Figure 10 shows that a lower pH caused a smaller Rayleigh slope, although neither coatings produced with the 7 nor the 9 pH scattered very much light.

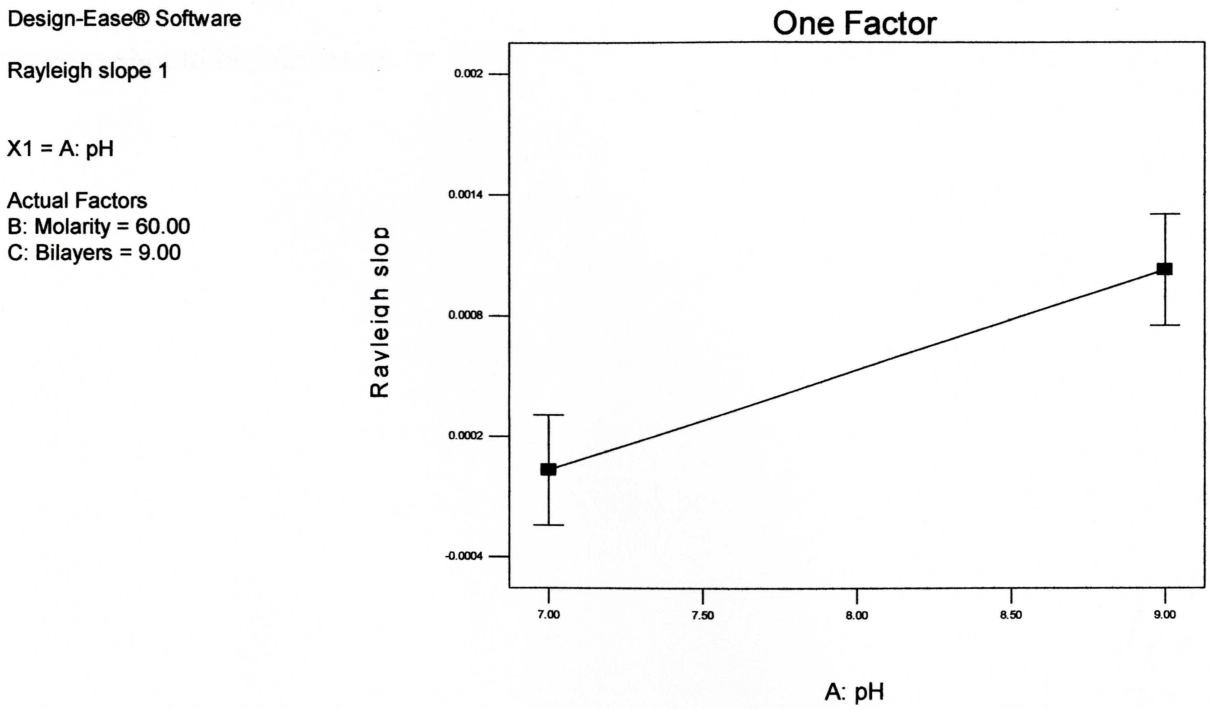

Figure 10: A plot of the pH of the depositions solutions against the Rayleigh slope.

The data also indicates that the number of bilayers is not significant to scattering. Since scattering happens at the contact surface of the coating and not in the bulk of the material, it makes sense that thickness, or the number of bilayers, does not affect the amount of light scattered. This is good news since it allows experimenters to tailor specific thicknesses to create destructive interference without worrying about causing more scattering.

Strangely, the molarity of the SiO_2 turned out to be not significant in this experiment, implying that perhaps the concentrations of nanoparticles used for the experiment (40 and 80 mM) were too small to cause a perceptible difference. This would account for the poor coatings and negligible scattering that the slides from experiment two exhibit. Visual inspection of the slides from this experiment, while qualitative, also seems to confirm that little deposition has occurred and that the molarity of the nanoparticle solutions should be increased.

Experiment 3

In order to improve the coatings, several drastic changes were made in experiment number three. This four-block factorial experiment increased the concentrations of the silica nanoparticle solutions from 40mM and 80mM to 0.5M and 2.0M, about a tenfold increase in the concentration. In addition to the familiar factors of pH, molarity and number of bilayers, the type of polycation used for deposition was also examined, as half of the coatings were made with PDDA (the polycation from experiments one and two) and half with PAH. Both of these polycation solutions were 10mM. Table 3.1 contains the pertinent information.

Run Order	Experiment Block	pH of Solutions	Molarity (M)	Number of Bilayers	Polycation
1	Block 1	9	0.5	4	PDDA
2	Block 1	7	0.5	4	PAH
3	Block 1	7	2.0	4	PDDA
4	Block 1	9	2.0	4	PAH
5	Block 1	9	2.0	12	PDDA
6	Block 1	7	0.5	12	PDDA
7	Block 1	7	2.0	12	PAH
8	Block 1	9	0.5	12	PAH
9	Block 2	9	0.5	4	PAH
10	Block 2	7	2.0	4	PAH
11	Block 2	9	0.5	12	PDDA
12	Block 2	9	2.0	12	PAH
13	Block 2	7	0.5	12	PAH
14	Block 2	7	2.0	12	PDDA
15	Block 2	9	2.0	4	PDDA
16	Block 2	7	0.5	4	PDDA
17	Block 3	7	0.5	4	PAH
18	Block 3	7	2.0	4	PDDA
19	Block 3	9	0.5	12	PAH
20	Block 3	9	0.5	4	PDDA
21	Block 3	7	0.5	12	PDDA
22	Block 3	9	2.0	4	PAH
23	Block 3	7	2.0	12	PAH
24	Block 3	9	2.0	12	PDDA
25	Block 4	7	2.0	12	PDDA
26	Block 4	9	2.0	12	PAH
27	Block 4	9	2.0	4	PDDA
28	Block 4	9	0.5	4	PAH
29	Block 4	7	2.0	4	PAH
30	Block 4	9	0.5	12	PDDA
31	Block 4	7	0.5	4	PDDA
32	Block 4	7	0.5	12	PAH

Table 3.1: Experiment #3 coating specifics

Run Order	Transmitted (%)	Reflected (%)	Extinction (%)	Rayleigh Slope	R^2
1	77.972	6.903	0.151	0.0045	0.9661
2	91.997	7.763	0.002	0.0001	0.0001
3	83.223	6.350	0.104	0.0022	0.9453
4	66.797	3.476	0.297	0.0076	0.9457
5	24.625	3.339	0.720	0.0062	0.8037
6	87.589	7.636	0.048	0.0014	0.9077
7	84.838	5.759	0.094	0.0033	0.9695
8	69.221	3.182	0.276	0.0071	0.9429
9	83.112	5.147	0.117	0.0044	0.9651
10	62.892	3.477	0.336	0.0095	0.9651
11	42.689	7.328	0.500	0.0080	0.8861
12	29.967	1.111	0.689	0.0098	0.8441
13	81.733	5.671	0.126	0.0039	0.9566
14	58.991	5.752	0.353	0.0092	0.9591
15	48.967	5.373	0.457	0.0093	0.9199
16	90.017	7.182	0.028	0.0013	0.9098
17	92.834	7.646	-0.005	0.0001	0.1145
18	83.982	5.280	0.107	0.0036	0.9603
19	51.398	2.638	0.460	0.0070	0.8818
20	84.868	6.938	0.082	0.0027	0.9489
21	89.201	6.728	0.041	0.0017	0.9369
22	80.769	4.494	0.147	0.0055	0.9676
23	48.289	2.012	0.497	0.0115	0.919
24	11.156	1.989	0.869	0.0032	0.6826
25	60.932	4.313	0.348	0.0076	0.9542
26	20.257	0.569	0.792	0.0080	0.7700
27	72.904	6.276	0.208	0.0062	0.9662
28	88.008	5.610	0.064	0.0026	0.9517
29	67.150	3.648	0.292	0.0078	0.9580
30	30.466	5.847	0.637	0.0067	0.8299
31	92.140	7.609	0.003	0.0003	0.3499
32	88.301	6.166	0.055	0.0022	0.9353

Table 3.2: Experiment #3 responses

Table 3.2 shows that the drastic changes in deposition certainly had a profound impact on the resulting coatings. In many cases the newly coated glass slides reflected far less than the 8% an untreated slide would, however the transmittance of many of the slides also decreased substantially, in some cases below 50%. Since the molarity of the nanoparticle solutions was significant in this experiment, it seems as though the concentrations were indeed too low in the first two experiments to be statistically different. The data holds that a higher molarity increases the Rayleigh slope and the scattering, which makes sense since a higher molarity should cause a rough and less uniform coating. The pH value of the solutions was also significant in this experiment, confirming the previous conclusion (from experiment two) that a lower pH yields a lower Rayleigh slope.

One final point of note on this data is that the coatings made with PAH and those made with PDDA were not statistically different for any of the responses. The two polycations performed almost exactly the same, supporting the fact that the polycation will have no optical properties to contribute to the film.

Figure 11 on the following page shows the extinction data (in the visible spectrum) for the slides in the first block of this experiment graphed against $\frac{1}{\lambda^4}$. Rayleigh slopes for each sample were calculated from best-fit lines. The larger the slope, the more Rayleigh scattering is interfering with the antireflective coating.

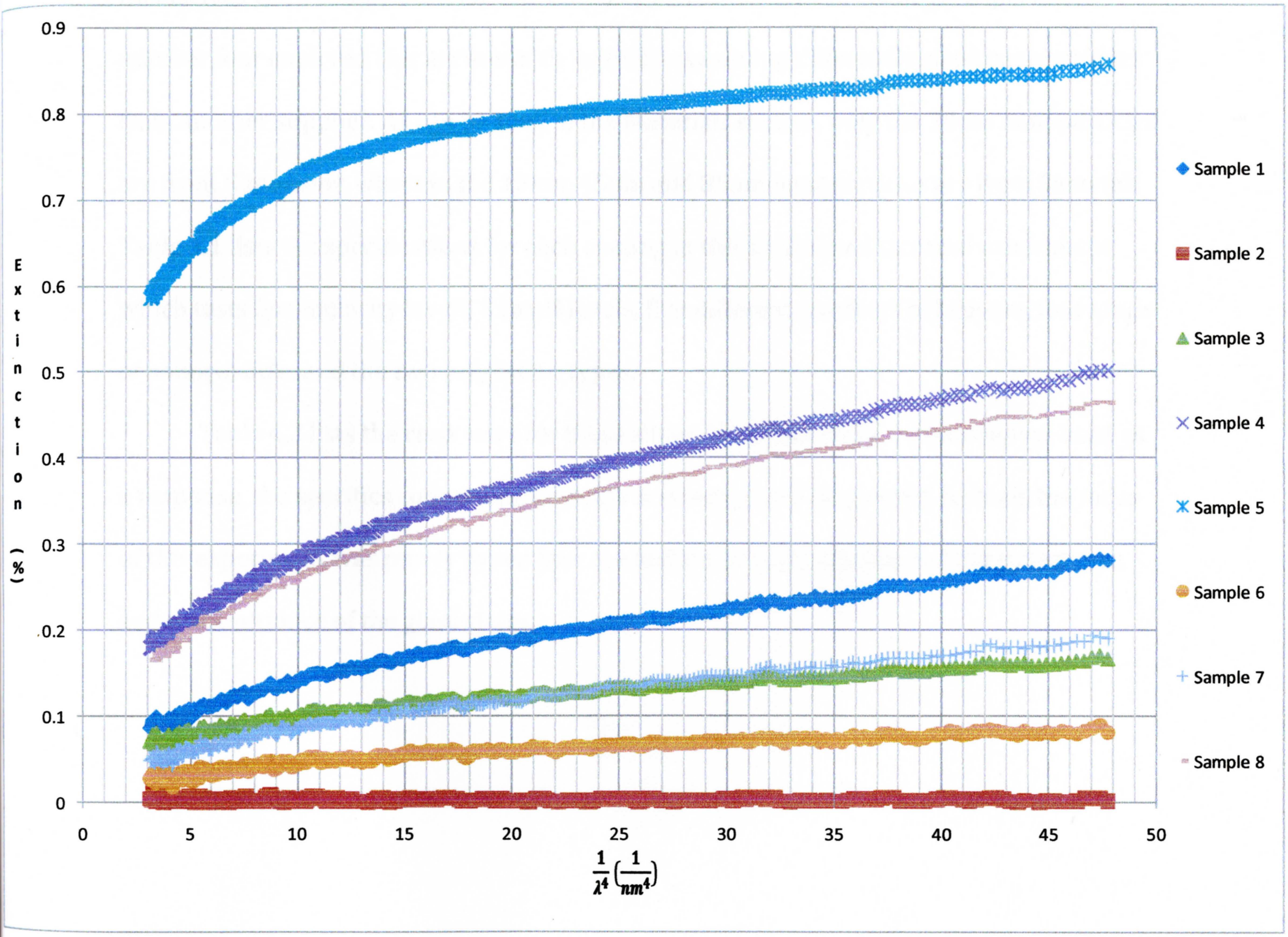

Figure 11: A plot extinction vs. $\frac{1}{\lambda^4}$ for the slides in block one of experiment three.

Experiment 4

Having increased the molarity of the nanoparticle solutions in experiment three without a corresponding increase in transmittance, it was possible that the nanoparticles themselves were simply unfit for the fabrication of antireflective coatings. Experiment number four explored this avenue of thought by examining differently sized nanoparticles from another supplier. As can be seen in the Materials section, only the 30nm nanoparticles are from Nanoamor, whereas the 15nm, 45nm and 85nm nanoparticles are from Snowtex. Table 4.1 lists the specifications for each coating in this multi-level factorial experiment which tests five molarity levels, five pH levels, five different numbers of bilayers, four kinds of nanoparticle, and the two polycation types.

Table 4.2 lists the responses for these slides. Note that while extinction was used as a response, the specifics concerning Rayleigh scattering were neglected. Instead, the focus of this experiment was purely to see how the factors in Table 4.1 affected the reflectance and transmittance of the glass slides.

Run Order	Block	Molarity (M)	pH	Number of Bilayers	Particle Size (nm)	Polycation
1	Block 1	1.8	7	20	15	PDDA
2	Block 1	1	7	12	45	PDDA
3	Block 1	1	7	4	30	PAH
4	Block 1	0.6	7.5	12	15	PAH
5	Block 1	1.8	8	12	85	PAH
6	Block 1	1.4	8.5	8	15	PDDA
7	Block 1	0.6	7.5	12	45	PAH
8	Block 1	1	7	4	30	PAH
9	Block 1	1.8	9	4	45	PAH
10	Block 2	0.6	7.5	12	30	PAH
11	Block 2	0.2	9	20	85	PDDA
12	Block 2	1.4	8	8	85	PDDA
13	Block 2	1.4	7.5	16	15	PAH
14	Block 2	0.2	8	4	15	PDDA
15	Block 2	1	7	12	45	PDDA
16	Block 2	0.6	7.5	12	85	PAH
17	Block 2	1	9	4	30	PDDA
18	Block 3	1	9	4	30	PDDA
19	Block 3	1.8	9	20	15	PDDA
20	Block 3	1.8	8	20	30	PAH
21	Block 3	1	7	12	30	PAH
22	Block 3	1.8	7	12	30	PDDA
23	Block 3	0.2	7	20	45	PDDA
24	Block 3	1.8	8	12	85	PDDA
25	Block 3	1	7.5	8	45	PAH
26	Block 4	1.4	7.5	8	15	PDDA
27	Block 4	0.6	8.5	16	85	PDDA
28	Block 4	1	9	20	15	PAH
29	Block 4	1.8	8	12	85	PAH
30	Block 4	0.2	7	12	45	PAH
31	Block 4	0.2	9	4	85	PDDA
32	Block 4	1.4	8.5	16	45	PAH
33	Block 5	0.2	7	4	85	PDDA
34	Block 5	1.4	7.5	12	30	PAH
35	Block 5	1	7	20	30	PDDA
36	Block 5	0.2	7	12	45	PAH
37	Block 5	1	9	12	85	PAH
38	Block 5	1.4	7.5	12	45	PDDA
39	Block 5	0.2	9	4	15	PAH

Table 4.1: Experiment #4 coating specifics

Run Order	Transmittance (%)	Reflectance (%)	Extinction (%)
1	93.544	4.613	1.843
2	55.827	2.232	41.941
3	89.917	7.071	3.012
4	93.090	0.778	6.132
5	89.520	3.918	6.562
6	66.885	0.852	32.263
7	92.938	4.211	2.851
8	79.778	4.656	15.566
9	93.474	2.186	4.340
10	83.707	6.354	9.939
11	84.512	4.913	10.576
12	82.296	2.773	14.931
13	94.341	1.886	3.773
14	92.886	6.237	0.877
15	76.184	2.765	21.051
16	91.880	5.296	2.824
17	69.072	5.471	25.457
18	71.411	6.324	22.266
19	52.273	0.963	46.764
20	44.183	3.147	52.671
21	83.671	6.137	10.191
22	89.889	7.533	2.578
23	85.901	4.232	9.867
24	92.299	4.220	3.481
25	85.784	3.310	10.907
26	96.322	3.487	0.191
27	84.425	4.556	11.019
28	93.921	3.594	2.485
29	88.934	3.451	7.615
30	92.348	4.079	3.574
31	91.995	3.265	4.739
32	90.260	3.428	6.312
33	91.468	1.779	6.753
34	84.760	6.034	9.206
35	69.174	5.615	25.211
36	89.641	3.291	7.068
37	89.698	3.987	6.315
38	92.245	3.880	3.875
39	91.652	7.156	1.192

Table 4.2: Experiment #4 responses

It is immediately clear from Table 4.2 that the Snowtex silica nanoparticles are much better than the Nanoamor particles for creating antireflective coatings. While all average reflectances were lower than that of untreated glass (at 8%), the Snowtex brand nanoparticle-based films had reflectances more than 2% lower than the inferior Nanoamor-based coatings. However, due to high amounts of scattering the average transmittances for the 15nm, 45nm and 85nm nanoparticle films were all higher than normal glass but they still surpassed that of the 30nm coatings by more than 10%. See Table 4.3 for these details.

Nanoparticle Size (nm) and Supplier	Average Transmittance (%)	Average Reflectance (%)
15, Snowtex	86.102	3.285
45, Snowtex	85.461	3.361
85, Snowtex	88.703	3.816
30, Nanoamor	76.556	5.834

Table 4.3: The average transmittance and reflectance for the coatings in experiment #4. The Snowtex brand nanoparticles proved to be much better for the fabrication of antireflective coatings.

The silica nanoparticle coatings indeed caused antireflection to occur, but the deposition process still seemed to create non-uniform, rough coatings that caused too much scattering, much more so than normal, untreated glass and causing the antireflection to be ineffective. As other experimenters have found, it is indeed difficult to consistently produce smooth, uniform coatings on the glass that will cause destructive interference but not scattering.[1]

The molarity of the nanoparticle solution used in the deposition process was also a significant factor in this experiment. Neglecting the 30nm particles, the data shows that molarity is negatively correlated with both transmittance and reflectance, meaning the greater the molarity of the nanoparticle solution, the lower the percentage of the incident light that is transmitted through and reflected back off of the glass. This of course means that higher molarity results in more scattering, as seen in the extinction data.

Interestingly, the factorial experiment did reveal an interaction between the particle size and the pH with regards to the scattering. While the 15nm and 85 nm nanoparticles had more extinction for higher pH values, the 45nm silica coatings actually scattered less light at higher pH values.

Lastly, as in the previous experiment, the type of polycation used to form the bilayers was not a significant factor for any of the responses.

Experiment 5

One final experiment was performed to test the effectiveness of the RCA cleaning process. The only independent variables for the films were the size of the particle employed (given the results of the previous experiment, only Snowtex particles were used) and the type of cleaning process. Half of the slides for this experiment underwent an RCA cleaning as described in the experimental procedure section and the other half only received a wipe with acetone before being used. All other factors were kept constant for the deposition: the dipping time was two minutes, all solutions were set to pH 7, all films were composed of eight bilayers, the molarity of the silica solution was 1.5 Molar, and PDDA (10mM) was used as the polycation. Table 5.1 outlines the details for each slide. Note that each possible combination of factors and levels was used three times.

Run Order	Cleaning Process	Particle Size (nm)
1	Acetone	15
2	RCA	85
3	Acetone	85
4	Acetone	15
5	RCA	85
6	RCA	15
7	RCA	85
8	RCA	45
9	Acetone	45
10	Acetone	15
11	Acetone	45
12	RCA	15
13	Acetone	85
14	Acetone	45
15	Acetone	85
16	RCA	45
17	RCA	15
18	RCA	45

Table 5.1: Experiment #5 coating specifics

The experiment was conducted in two blocks, with coatings one through nine being deposited in the first block and those numbered 10 through 18 being deposited in the second block. Table 5.2 lists the data from this last experiment.

Run Order	Transmittance (%)	Reflectance (%)	Extinction (%)
1	95.929	4.019	0.052
2	96.160	0.909	2.931
3	96.350	0.744	2.906
4	96.389	3.851	-0.240
5	97.207	0.771	2.022
6	95.063	4.177	0.760
7	93.550	1.653	4.797
8	91.998	6.677	1.326
9	93.040	6.376	0.583
10	73.486	0.964	25.550
11	52.401	2.301	45.298
12	96.933	1.952	1.115
13	92.236	3.372	4.392
14	84.734	3.020	12.245
15	87.620	3.032	9.349
16	90.152	4.139	5.709
17	95.615	2.412	1.973
18	91.866	4.439	3.695

Table 5.2: Experiment #5 responses

Despite the RCA cleaned slides having higher average transmittances and lower average reflectances than their acetone-wiped counterparts, the cleaning method turned out not to be a statistically significant factor for magnitude of transmittance or reflectance. However, the RCA cleaned slides in Figure 11 have a far smaller spread of transmission values than the acetone cleaned ones in Figure 12, implying that while an RCA cleaning may not improve the quality of the slides significantly, it does improve the consistency of the deposition process, allowing for the creation of many films with similar properties.

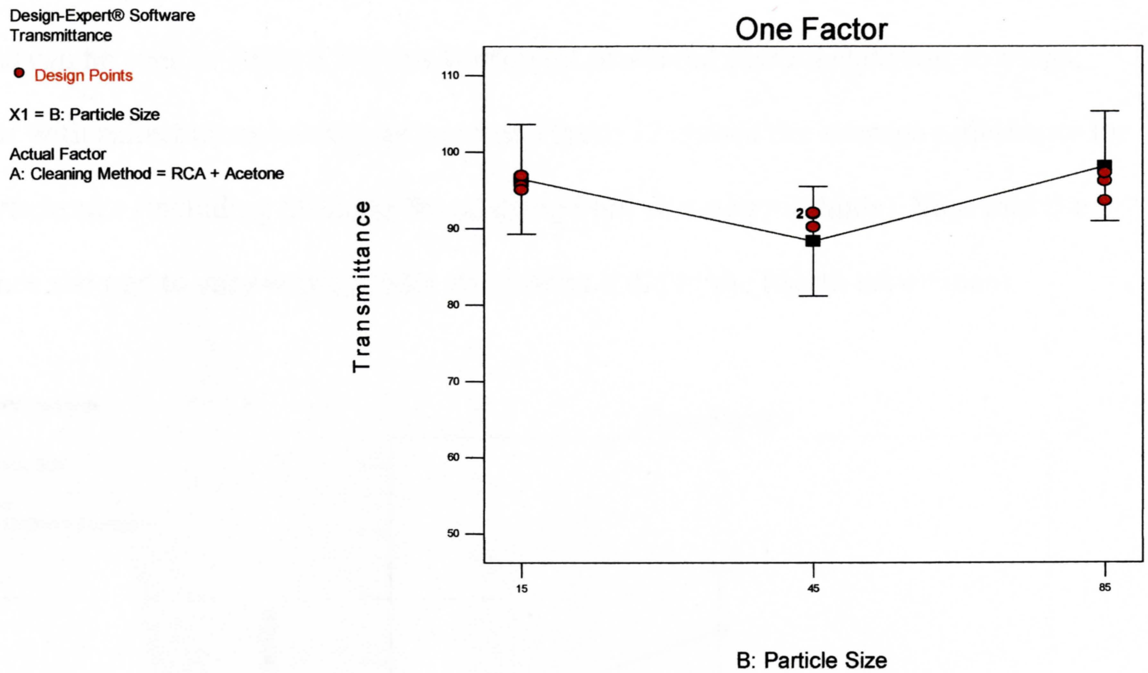

Figure 11: Particle size vs. transmittance for the coatings deposited on RCA cleaned slides

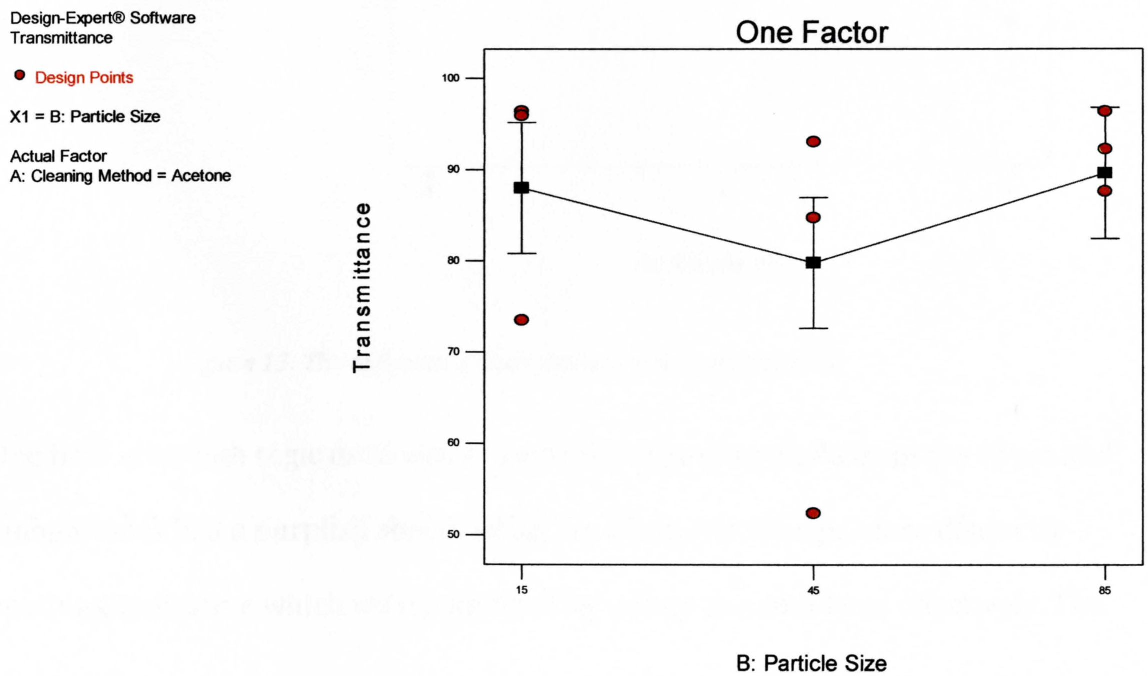

Figure 12: Particle Size vs. Transmittance for the coatings deposited slides that received only an acetone wipe

As can be seen in Table 5.2, this experiment produced several excellent coatings, even four with reflectances below one percent. Figure 13 shows the average reflectance for each particle size (including films produced using both cleaning methods). Note that the reflectance seemed to vary with particle size just as it did in the fourth experiment.

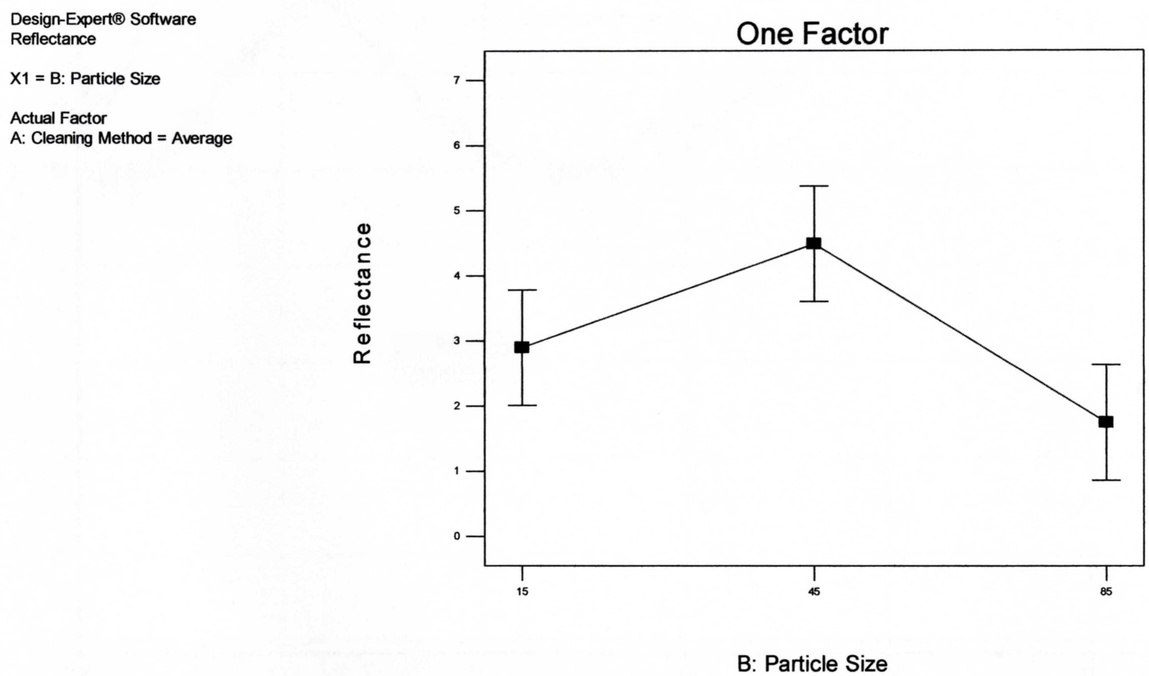

Figure 13: The reflectance data for each size of nanoparticle

One final note with regards to visual inspection: coatings made from the 15nm and 85nm nanoparticles had a purplish sheen, while the 45nm particles produce distinctly yellow coatings, indicating which wavelengths of light they transmit least effectively. The optical analysis confirmed these results as Figure 14 depicts.

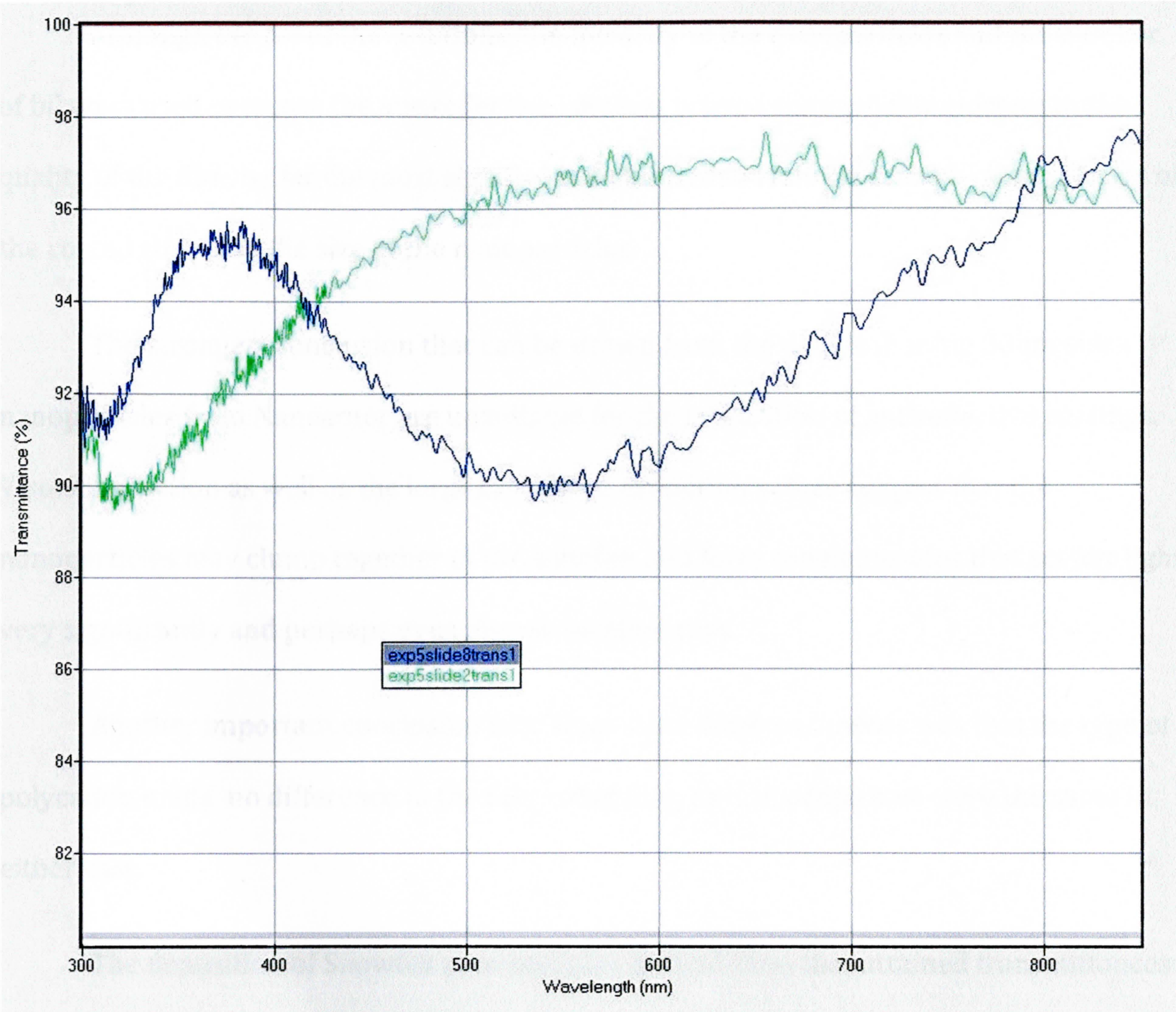

Figure 14: Transmittance vs. wavelength for coated slides 2 and 8 from experiment 5. Note that slide 8, whose coating was composed of 45nm silica, transmits best on the outer ends of the spectrum, whereas slide 2 transmits best at the center of the visible spectrum.

Summary and Conclusions

Although the pH of the solutions, the molarity of the nanoparticles and the number of bilayers used to create the antireflective coatings proved somewhat important to the quality of the film, by far the most significant factor in determining the optical properties of the coated slide was the size of the nanoparticles.

The strongest conclusion that can be drawn from the data is that the 30nm silica nanoparticles from Nanoamor are unsuitable for the fabrication of antireflective coatings. Visual inspection as well as the large calculated extinction values suggest that the nanoparticles may clump together in the solution and form conglomerates that scatter light very significantly and perhaps even absorb incident rays.

Another important conclusion that arose from the experiments was that the type of polycation made no difference in the fabricated film; optical properties were the same in either case.

The deposition of Snowtex nanoparticles created films that attained transmittances as high as 97%. In fact, across all the experiments, only nine coatings had average transmittances higher than 95%, and every one of those was fabricated using either the 15 or 85nm silica. The 45nm nanoparticle coatings proved to be superior only at the very ends of the visible spectrum (as seen in Figure 14).

There are numerous directions for this research to go from here. Primarily though, since the Nanoamor silica particles have proven to be ineffective for making antireflective coatings, the next steps should concentrate on the nanoparticles from the Snowtex supplier. Experiments could even concentrate solely on the 15nm and 85nm particles, as the films they composed had higher transmittances.

Other factors could also be examined. For example, the washing method used between layers during the deposition process and the drying method employed after the bilayers are in place could definitely influence the fabricated coatings.

More long-term directions include trying out titanium dioxide particles and examining antireflection in the infrared region. Also, given the differing wavelengths that they transmit, better broadband antireflection across the entire visible spectrum could possibly be achieved by using a combination of different nanoparticle sizes in the fabrication of the film.

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