Abstract

This report focuses on a two-layered passivated anti-reflective coating, by combining randomly distributed nanostructures created on a transparent substrate with with a mesoporous silica coating. The nanostructures are subwavelength in size and create a gradient refractive index gradient between the mesoporous silica and the substrate and the mesoporous silica has a low refractive index which reduces the reflection at the surface. The fabrication process for both components is simple and inexpensive. Together these factors create an inexpensive resilient coating that is also anti-reflective to reduce glare for applications with touch screen technology.

The best prototype was constructed using a combination of nanostructures, imprinted into Norland Optical Adhesive 61, and mesoporous silica nano particles, dip coated with a 35% binder solution at 120 mm / minute. It was tested to determine the transmission and hardness characteristics. This prototype exhibited less then 2% combined reflection and absorption across most visible wavelengths. This is an improvement over the 8-9% reflection observed on baseline polished glass slides. It was also able to withstand mild contact, however adhesions issues with the mesoporous silica coating prevented accurate hardness measurements from being made.

In conclusion the prototype made outperforms both plain glass samples, plain nano structured samples and thin mesoporous silica anti-reflective coatings. While the hardness doesn't current compete with industry standards there is room for future research into better adhesion and stronger mesoporous silica coatings. In addition more research can be done to better mass produce the samples, through hot embossing and injection moulding of the nanostructures and spray coating the mesoporous silica solution.

Acknowledgements

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Glossary of Terms and Acronyms

ARC	Anti-reflective coating
FDTS	Anti-stiction coating
FE-SEM	Field Emission Scanning Electron Microscopy
MPS	Mesoporous silica
NS	Nanostructures
RIE	Reactive Ion Etch
SEM	Scanning Electron Microscopy
UV	Ultra-violet light
Arduino	Micro-controller capable of accepting computer input
Black silicon	Silicon that has etched using unmasked RIE and serves as the mould for the nanostructures
Dip coating	the process whereby a sample is coated by dipping it into a solution of particles and removing is at a controlled speed
Ellipsometry	Device used to measure the thickness and refractive index of a thin film
Hot embossing	the process whereby a pattern is transferred by pressing a heated polymer into a mould
Injection moulding	the process where a liquid polymer is injected into a mould in order to create the desired shape
Mohs Hardness	Scale from 1-10 to measure the hardness of a material
Norland Optical Adhesive	UV curable optical polymer
Ormacomp	UV curable optical polymer
Passivated	Protected from environmental effects
Reflectance	The amount of light that is reflected from a surface
Spray coating	the process whereby a sample is coated by spraying a solution of particles on the surface
UV curing	the process where a polymer is created due to the exposure to UV light

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1 Introduction, Motivation and Scope

Modern electronic displays reflect external light sources, resulting in visual discomfort and difficulties reading what is on the display. This phenomenon is perceived as glare by the user, and hence the pursuit of a solution has warranted large investments by many consumer electronics companies. Many current anti-reflective technologies are achieved with multiple layers of chemically deposited compounds. This approach is expensive and complex - requiring controlled vacuum conditions - as well as significant time allocation. These costs are transferred to the consumer.

This design project pursues the realization of structure-based anti-reflective surfaces in order to replace the currently-implemented multi-layer chemical vapor deposited coatings. It is desired that these structures replace the current coatings as a cheaper, easily producible, and superior anti-reflective solution. The most basic requirements consist of the creation of a product that is comparable to industrially-standardized coatings. Furthermore, batch production should be possible in order to attain the required throughput for mobile phone screens, laptop screens, large computer monitors, and television displays.

An anti-reflective coating is an optically transparent layer which is applied to an optical-grade surface in order to reduce reflection and hence increase transmission. The resultant transmission gains are industrially applicable in the design of displays for smart phones, laptops, and televisions. There are two relevant types of ARCs - those that reduce reflection through a gradual surface-to-substrate refractive index shift index, and those consisting of alternating high-low refractive indices. The former design minimizes reflectance at each virtual interface, whereas the latter design induces destructive interference patterns at the surface of the material, reducing reflectivity.

As it was shown in Figure 1, this system is comprised of a nanostructured surface that is passivated by a MPS coating. As a whole this product has certain requirements that a consumer would look for, but each of these requirements relate to a specific dimension or refractive index in either the nanostructures or MPS coating itself. Each of these specifications must first be simulated, to gain initial values, fabricated and measured to verify that these requirements have been met.

This report will detail the decision making process that lead to deciding on a nanostructured substrate coated with MPS. It will then detail the design process and testing plan and a description of how the prototype was fabricated. Finally the report will go through the results of the tests and present ideas for future work on this project.

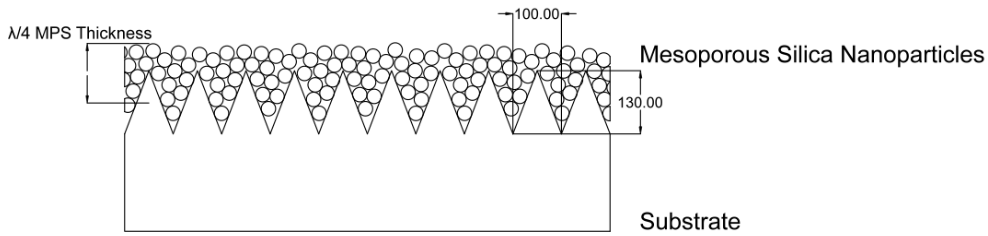


Figure 1: Overview of the two part Nanostructures / Mesporous Silica System

2 Requirements

From a consumer's point of view the requirements for this design project are threefold. Firstly it must be sufficiently anti-reflective, secondly it must be durable, and finally it must be inexpensive. From a manufacturer's point of view these requirements must be translated into actual values to be met. These requirements will be summarized here and are detailed in Appendix A of this report for consumer requirements and Appendix D for the functional specifications. The first two requirements are general requirements for any anti-reflective coating to be used for consumer electronics. The final requirement is particular to the design that is being investigated.

The antireflective properties of this coating are very important to its success. If there is a lot of light reflected from the coating then there will be significant glare and the coating will not be serving its purpose. For the reflectance tests the transmission will be measured and the maximum reflectance is:

$$Reflection_{max} = 1 - Tranmission$$

The primary requirements for transmission that is acceptable for the coating is 90% which corresponds to less than polished glass, The secondary requirement is the attainment of superior anti reflective properties of the developed coating relative to the nanostructure-deficient MPS-coated substrate which is around 96% transmission. The tertiary requirement is the reduction of coating reflectance values below perceivable ocular thresholds for all wavelengths within the visible spectrum which corresponds to greater than 99% transmission. All of these requirements apply from 0° to 45°.

The durability requirements of this coating are important for commercializing the product. If the coating cannot withstand rough contact then it is not suitable for a smartphone screen. If the coating cannot withstand occasional contact with a cleaning cloth then it is not suitable for the consumer electronic industry.

The durability of the coating will be measured in two ways, the hardness of the coating, and the coating's resistance to common solvents. The hardness will be measured using the Mohs hardness testing as a qualitative measurement to quickly determine the relative hardness of the coating compared to common objects. The Berkovich nano-indentor will be used to get a more accurate comparison of the hardness with respect to glass. The primary requirement for the durability of the coating is a Mohs hardness rating of greater than 4.0 which corresponds to the hardness of polycarbonate. The secondary requirement is a Mohs hardness rating greater than 6.0 which corresponds to that of glass. The tertiary requirement is a Mohs hardness rating greater than 9.0 which corresponds to Gorilla Glass, one of the toughest phone screens in the market today. Resistance to common solvents will be determined by their effect on the transmission values after the coating has been exposed to them. Resistance to water is a secondary requirement and resistance to acetone and isopropanol is a tertiary requirement.

The cost of the coating is the final requirement; if the coating is as expensive as current methods using CVD then it has not achieved its purpose. The cost of the coating will be determined by the fabrication method.

Using a UV curable polymer for the substrate is the least cost efficient method that will be attempted, however its success is required for testing prototypes, as such it is a primary requirement. Hot embossing is the secondary requirement for substrate manufacturing. Injection moulding the substrates would be the least expensive method and is the tertiary requirement. In order to coat the substrates dip-coating is a primary requirement and spray-coating is a tertiary requirement. Spray-coating is faster and less expensive than dip-coating which makes it more suitable for mass production of screens.

3 Project Description

As stated in Section 1.0, current antireflective substrates and coatings are relatively expensive for consumers. For example, antireflective coatings on a pair of glasses can cost anywhere from 30 to 100 dollars. This is in large part due to the technologies used to fabricate these coatings. As such, it would be valuable from a high level standpoint to look into these technologies and see ways in which fabrication costs can be reduced while maintaining similar or better antireflection levels.

3.1 Current Technologies

3.1.1 Index Matching

There are multiple ways of reducing reflection in a substrate. The simplest method is known as index matching, which uses a substrate that has a refractive index close to air. The cost of this method is the cost of the substrate itself, which can be low, but the main issue is that there are no solid substrates that have a refractive index that is even close to that of air.

3.1.2 Single and Multilayer Interference

Antireflection can also be achieved by means of destructive interference. If a layer is applied to a substrate in such a way that the light reflected off of the applied layer destructively interferes with the light reflected off of the substrate, reflection will be reduced. This is also known as single-layer interference.

Multilayer interference extends upon the concept of single-layer interference by adding additional layers of alternative refractive indices to create several levels of destructive interference.

The reflection from this method can be low, but the main issue is that the visible light spectrum is on the order of several hundred nanometers. Thus, to create a destructive interference layer, its thickness must be a fraction of the visible light range. More specifically, the thickness must be one quarter of light wavelength with a refractive index that is the square root of the substrate's refractive index. This is costly to manufacture because it requires vapour deposition to apply such a thin layer on top of the substrate.

Multilayer interference would be more antireflective, but even more costly to manufacture because of the additional layers.

3.1.3 Virtual Gradient Refractive Indices

Studying the moth-eye concept has reproduced antireflective coatings, and substrates. The moth eye removes the air-substrate interface by adding a gradient refractive index profiled-substrate in between. This has been achieved by adding multiple layers of increasing refractive indices. The main issue with this method is the fact that multiple layers need to be applied, and sometimes includes vapour deposition processes, which increases cost.

3.2 Nanostructures

Nanostructured substrates hold promise as an antireflection technology because its patterns can be similar to that of the moth-eye, which is an effectively perfect gradient refractive index.

It behaves as a gradient refractive index because the effective refractive index depends on the surface area ratio of air and substrate. By gradually increasing the surface area substrate/air ratio, a gradient refractive index will be produced.

3.2.1 Advantages

Nanostructures can be patterned by using maskless reactive ion etching, which is cheaper than using a mask. By reactively ion etching a silicon wafer, a black silicon wafer would be produced that contains the desired nanostructures. This nanostructures can be transferred onto plastic through means of conventional manufacturing processes like hot embossing and injection molding, which would be much cheaper than vapour deposition.

3.2.2 Disadvantages

While nanostructure fabrication would be straightforward, nanostructures on plastic are very easy to destroy, making them infeasible for practical consumer applications like touchscreen displays, glasses, or computer monitors and televisions. As such, another substrate would have to deposited on the nanostructures to provide passivation.

3.3 Mesoporous Silica

Mesoporous silica (MPS) is a form of silica, which is composed of silicon dioxide. MPS are also nanoparticles that are on the order of tens of nanometers in diameter, and are porous around the surface. This was chosen as our passivation layer because it has a tunable refractive index depending on how much binder solution we use, and how it is fabricated. By adding a passivation layer, destructive interference can be induced. MPS layers can be deposited on the antireflective structures by means of dip and spray coating.

3.4 Verification Plan

Before creating prototypes, a mathematical model is necessary in order to gain a quantitative comprehension of this anti-reflective system and to obtain desired design parameters. The Fresnel reflection and transmission equations, the Maxwell equations, and the Python electromagnetic library were all used to model our antireflective solution.

First, we have to note that the nanostructures incorporated within the design of the anti-reflective coating are of sub-wavelength size, they do not reflect light in the traditional sense; instead they act as a gradient of refractive indices, in which the effective refractive index may be obtained according to the following equation:

$$n_{effective} = n_1 \times \frac{V1}{V_{total}} + n_1 \times \frac{V2}{V_{total}}$$

The increased volume fraction of the higher refractive index material experienced by propagating light results in an optimized index gradient. This arrangement further decreases the reflectivity value of the anti-reflective coating [1].

Theoretically, this configuration provides a perfect interface between air and the reflective substrate, thus preventing reflection. This has been experimentally verified: black silicon, which contains randomized, sub-wavelength nanostructures, results in a 2% reflectance value at normal incidence. Conversely, typical silicon results in a 30% reflectance value at normal incidence [2]. The fragility of these structures requires their passivation for daily use. Substrate protection requires the deposition of another material. It is necessary to keep the refractive index of this material as low as possible in order to minimize its interface with air. MgF_2 - used in the chemical vapour deposition of anti-reflective coatings - has a refractive index of 1.38 - the lowest known solid refractive index [3]. The use of this material enables the attainment of a 2.5% reflectance value at normal incidence. This limits the potential of any anti-reflective coating comprised of this material.

MPS base refractive index of 1.12 can be increased - or tuned - by the addition of binding material [3]. By refining the MPS - binding solution ratio, the refractive index of the anti-reflective coating can be optimised while maintaining an adequate coating hardness. With the selection of a suitable refractive index, the thickness of this coating can be further engineered to decrease the surface reflectivity - thickness refinement to $\lambda/4n_2$ will reduce reflectance due to induced destructive interference.

Reflectance minimization requires the optimization of related process variables, such as the MPS-binder volume ratio, MPS film thickness, and MPS refractive index. Once an adequate model has been produced, these MPS parameters will be simulated - prior to prototype construction - in order to save time and expensive prototype tests. The model can also be utilized to determine error sources in previously-constructed prototypes. The reflection profiles of our substrate need to be simulated, but before that, the refractive index profile needs to be derived for our substrate. The substrate starts off with a thin-film of MPS, followed by a nanostructure. This nanostructure is essentially a periodic series of circular cones. In other words, the nanostructureâ cross-sectional radius linearly increases. It is also important to note that the nanostructures are fixed from the fabrication procedures to be $200nm$ [4]. The refractive index profile was derived based on the relative surface area of the nanostructure substrate and compared to the total surface are. Based on the assumptions above, the refractive index was derived to be:

For $r < \frac{P}{2}$:

$$n(r) = n_{MPS}\left(1 - \frac{\pi r^2}{P^2}\right) + n_{Plastic}\left(\frac{\pi r^2}{P^2}\right) \tag{1}$$

For $\frac{P}{2} \leq r \leq \frac{P}{\sqrt{2}}$:

$$A_{total} = \pi r^2 - 4\left[\frac{1}{2}r^2\left\{cos^{-1}\left(\frac{P}{2r}\right) - sin\left(cos^{-1}\left(\frac{P}{2r}\right)\right)\right\}\right]$$

$$n(r) = n_{MPS}\left(1 - \frac{A_{total}}{P^2}\right) + n_{plastic}\left(\frac{A_{total}}{P^2}\right) \tag{2}$$

Where r is the radius of the nanostructure, and P is the periodicity. Keeping this in mind, a refractive index profile was generated, as shown in Figure 2.

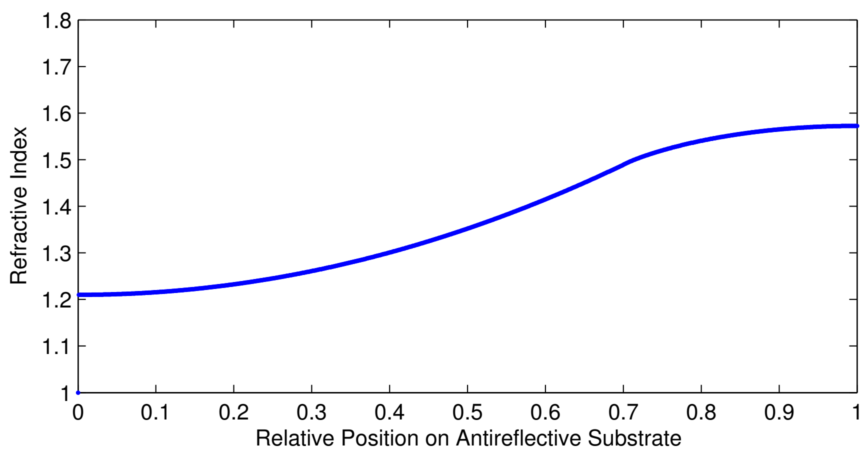


Figure 2: Refractive Index Profile of MPS - Nanostructure System

Next, a recursive reflection algorithm was derived from Davis [5] for light travelling through the substrate for both transverse electric and transverse magnetic modes.

$$\Re = |R_0|^2$$

where R_0 is a coefficient determined from

$$R_j = a_j \frac{F_j + R_{j+1}}{1 + F_j R_{j+1}} \tag{3}$$

starting from $j = N$, using $R_{N+1} = 0$, where j is the layer index. The coefficients a_j, and F_j are

$$a_j = e^{2ik_z^{(j)}d_j} \tag{4}$$

$$F_j = \frac{f_j - f_{j+1}}{f_j + f_{j+1}} \tag{5}$$

f_j is a constant that differs between TE and TE modes, given by

$$f_j = \begin{cases} \frac{k_z^{(j)}}{\mu_j} & \text{, TE mode} \\ (\frac{\mu_j c^2}{n_j^2})k_z^{(j)} & \text{, TM mode} \end{cases} \tag{6}$$

and

$$k_z^{(j)} = \frac{\omega}{c}\sqrt{n_j^2 - cos^2\pi - \phi} \tag{7}$$

where ω is the angular frequency of incident light, n_j is the refractive index of that particular layer, μ_j is the layer magnetic permeability, and ϕ is the incident light angle. Using this algorithm, reflectance profiles were produced.

3.4.1 Python Simulations

Simulations were performed in Python using the EMPY library [6]. After the validity of the library was confirmed by comparing the results to the analytical derivation, reflection profiles were verified for various cases.

The reflection profiles for various MPS thicknesses and refractive indices were investigated, and it was reported by Moghal et al that MPS refractive index can be tuned from 1.12 to 1.45 depending on the binder to MPS ratio used [3]. The engineering tradeoff for the binder to MPS ratio is that the MPS refractive index should be as low as possible, but a lower refractive index would require less binder, which means less nanostructure passivation. Moghal reports that an MPS refractive index of 1.28 is a good balance between anti-reflective properties and hardness/rigidity.

The reflection in the visible regions is minimized at $20nm$, but because this thickness is not possible (height of nanostructures is $200nm$), the next best profile would be at $220nm$.

3.5 Design Specifications

The protective MPS coating will be created with a binding solution with mesoporous silica beads suspended within it. The coating is strong and scratch-resistant, which enables it to be used in applications such as device displays. It also chemically-resistant, protecting it from environmental stresses.

3.5.1 Mesoporous Silica

The nanostructures reduce interfacial effects between the MPS coating and the substrate, increasing the anti-reflective properties of the system. The nanostructures also have a much higher surface area per unit area, which increases the adhesion between the MPS coating and the substrate, further strengthening the coating. Finally, the nanostructures are also inexpensive and simple to both fabricate and to transfer to the substrate. Testing began with an MPS:Binder ratio of 35%, as reported by Moghal et al [3], and an MPS layer thickness of 220nm from the python simulations in the previous section.

3.5.2 Nanostructures

The nanostructure shape and quality is of utmost importance concerning substrate antireflective properties. Functional requirements that are impacted by the final nanostructures in the substrate are substrate reflectance, substrate transmission, and substrate hardness. Functional requirements that are impacted by the pattern transfer process are the required nanostructure aspect ratios and nanostructure yields. These properties indirectly impact coating reflectance and transmission. The nanostructures impact the reflectance and transmission of the coating as they create a gradient refractive index throughout its entirety. From consultant professors at the University of Waterloo and Denmark Technical University, it was found that an aspect ratio of 1.3 and a structure height of 200nm yielded superior antireflection results in the visible spectrum [4].

Of further importance is the spatial frequency of the nanostructures. A spatial frequency of 160nm (a nanostructure interspacing of 160nm) was found to provide minimal reflection [4].

As these idealities will not be entirely met by the attained nanostructures, a threshold variance needs to be determined to provide coherent antireflection for the substrate regardless of electromagnetic incidence angles. A variance of less than five percent is required.

In summary, Table 1 lists the recommended parameters that will result in optimal antireflection results when designing the nanostructures.

Table 1: Recommended AR Coating Parameters [4].

Parameter	Parameter Values
Spatial Frequency (Structure Interspacing)	$160nm$
Aspect Ratio	1.3
Structure Height	$200nm$
Spatial Frequency Variation	5
Aspect Ratio Variation	5%
Structure Height Variation	5%

3.5.3 Substrate

Substrate selection is important in order to achieve the required antireflective properties: Firstly, it is important that the substrates have high transmittance and low absorbance in the visible range. Currently-used industrial materials are preferred due to their ease of integration. Additionally, the substrate should be structurally rigid in order to withstand normal handling and nanostructure pattern transfer. Finally, material costs should be minimized.

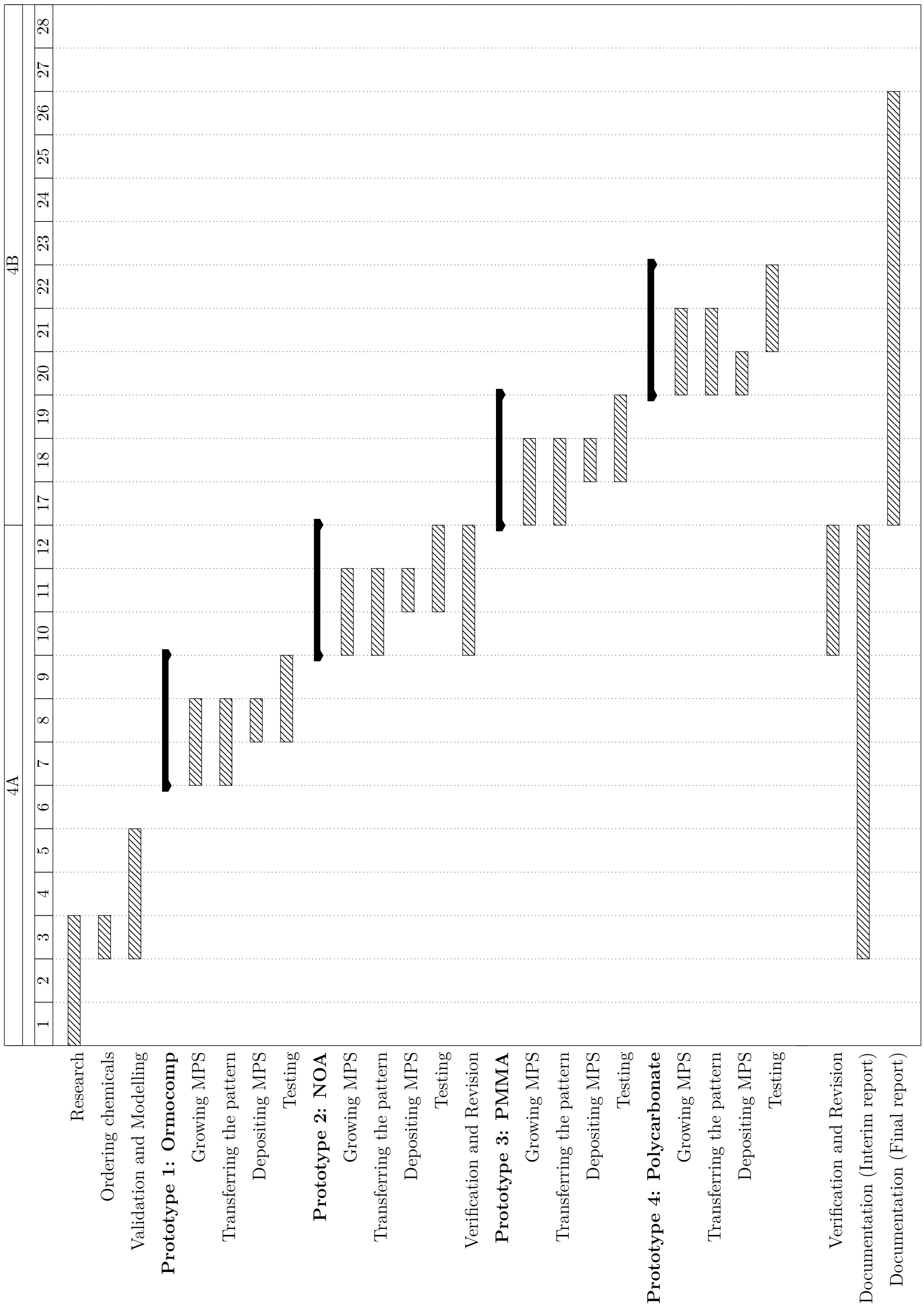
The selected substrates are functionally-verified industry standards. Firstly, ormocomp was chosen as a reference material as its successful pattern transfer has been well-documented. Secondly, Norland Optical Adhesive, another industry standard, will be utilized. It is used in the fibre optics industry as a UV cured clear polymer. Finally polycarbonate sample is considered, as the final integration into devices.

4 Design Project Plan and Milestones

The design plan for the project and the milestones set for the project are summarized below and detailed in Appendix B. The design flow diagram is shown in Appendix C.

In order to have sufficient time to accomplish the goals set out for this project the following project plan was proposed as shown below in Table 2. The time frame refers to which weeks the respective task would be performed during.

Table 2: Gantt chart showing time allocations



This project plan would allow ample opportunities for revisions to the design as problems became apparent.

The major milestones for this project are characterizing the black silicon, calibrating the dip-coater, UV curing a sample, hot embossing a sample, and testing the samples optical and physical properties. These milestones and their respective original dates are summarized below in table 3.

Table 3: Original project milestones

#	Milestone	Weeks
1	Calibrate dip coater	4 to 7
2	Characterize black silicon	5 to 6
3	Ormacomp plastic samples	7 to 9
4	AR coating: UV-cured Norland sample and MPS deposition via dip-coating	10 to 12
5	Hot embossed polycarbonate and MPS deposition via dip-coating	17 to 21
6	Spray coating MPS	18 to 22

These milestones were updated after four months of work to reflect the delays that had been encountered. The revised milestones and respective dates are shown below in Table 4.

Table 4: Revised project milestones

#	Milestone	Weeks
1	Calibrate dip coater	In Progress
2	Characterize black silicon	Complete
3	Ormacomp plastic samples	15 to 17
4	UV-cured Norland sample and MPS deposition via dip-coating	15 to 18
5	Hot embossed polycarbonate and MPS deposition via dip-coating	15 to 18
6	Optical and Hardness Testing	18 to 22

As can be seen there were significant alterations to the milestones due to unforeseen delays and difficulties.

4.1 Test Plan

In order to determine if the prototype has achieved the design specifications it needs to be tested. The testing procedures will be summarized below and are detailed in Appendix F of this report.

There are four different tests that will be performed on the samples to determine how well they fulfill the technical specifications. The tests are SEM imaging to determine pattern transfer and deposition profile, optical transmission testing using UV-Vis spectrometry, hardness testing using Mohs hardness, and physical hardness testing using Berkovich nanoindentation. As there are multiple types of samples to be tested the best will be combined for the final prototype.

SEM imaging will be the primary method of determining if the pattern transfer and coating functional requirements have been met. SEM imaging will be used to determine if the nanostructure pattern has been successfully transferred from the mould to the substrate with a high degree of fidelity for each pattern transfer method. Additionally SEM imaging will be used to determine if the dip-coating is successfully creating a uniform layer of MPS.

The optical testing will be the primary method of determining the anti-reflective properties of the coating and whether or not if fulfilled the functional requirements for transmission. The optical testing will be performed using a UV-Vis spectrometer to determine the transmission of light through the samples. The transmission of the samples will be measured because this is significantly easier to measure than the reflection. Each sample will be measured at four different angles. An Arduino will be used to angle each sample appropriately.

The scratch test will be the primary method for determining if the coating has met the functional specifications for physical hardness; the Berkovich nanoindentation will be used as a secondary test to determine the hardness of the coating relative to glass. For the Mohs hardness test each sample will be labelled with the numbers $1-9$ and then scratched under each number with materials of corresponding hardness. Afterwards the samples will be photographed and examined for damage. The Berkovich nanoindentation will be performed using the nanoindentor provided by Professor Ting Tsui. The results of the nanoindentation will be used to compare the hardness of the coating with that of glass.

5 Prototype Construction

The prototype constructed for this project was fabricated using a nanostructured transparent substrate coated with mesoporous silica nanoparticles, which were bound together using a binding solution. The process for creating this prototype starts with the fabrication of the nanostructures on a silicon wafer before transferring this pattern to a transparent substrate. Following successful pattern transfer the sample will than be coated with the mesoporous silica solution and allowed to dry to produce a uniform film.

5.1 Black Silicon Wafer Fabrication

The black silicon master molds, covered in the subwavelength nanostructures shown in Figure 3, were provided from DTU. These wafers were fabricated using an unmasked reactive ion etching process in an atmosphere of oxygen and sulphur hexafluoride. Before proceeding with anti-stiction coating and pattern transfer these structures were first imaged using a SEM to ensure they had survived transport. These structures have a mean height of $200nm$ and an aspect ratio of 1.3 and are randomly distributed across the surface of the mold[4].

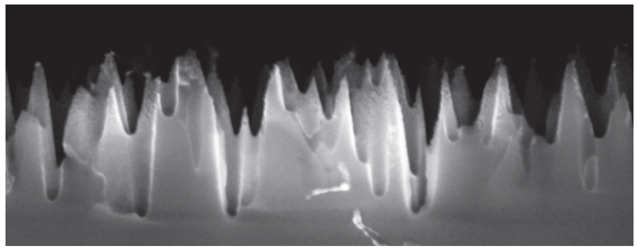


Figure 3: Cross-sectional view of the nanostructured silicon master mold [4]

5.1.1 Anti Stiction Coating

As it was mentioned, this nanostructure pattern must be transferred onto an optical substrate for it to function as an antireflective coating. The pattern transfer method used for this prototype was though UV curing of an optical grade polymer poured onto the nanostructures. In order to ensure accurate and easy pattern transfer the silicon master mold must first be coated to prevent stiction from the UV polymer. This is achieved by deposition of an FDTS anti-stiction coating, which will allow the sample to be easily removed from the substrate.

The film will be applied via molecular vapour deposition in which the mold and $0.5g$ of FDTS are placed into a vacuum chamber. The pressure of the chamber will then be reduced to, and maintained at, a pressure of 1 $mTorr$ for a maximal duration of $24hours$ to enable evaporation and the final deposition of the FDTS layer. Following deposition the FDTS coating must be hard baked at $150°C$ for 20 minutes.

5.1.2 Pattern Transfer of the NS into NOA

Following the anti-stiction coating of the master mold, the nanostructure pattern can be transferred by UV curing. The sample created will be a negative impression of the master mold, but should have the same antireflective properties of the initial positive structures. Two types of Norland Optical Adhesive, a UV curable polymer, were used to test pattern transfer of the nanostructures. Referred to as NOA 61 and NOA 68, these two polymers have different adhesion characteristics, chemical resistances and cure times. A summary of these differences is shown in Table 5.

Using the cure times listed in Table 5, $0.5mL$ of curable substrate, between 7-10 drops, will be deposited onto the mold and planarized using a glass slide. This sample is planarized

Table 5: Summary of NOA 61 and NOA 68 Properties[7]

	NOA 61	NOA 68
Adhesion Glass	Excellent	Excellent
Adhesion Metal	Excellent	Good
Adhesion Plastic	Fair	Good to Excellent
Viscosity at 25°C	300 CPS	5000 CPS
Shore D Hardness	85	60
Recommended Cure time with 100W UV	12 Minutes	3 Minutes

and leveled by using two glass slides on either side of the mold to support the main glass slide flattening the sample. Therefore all the samples created will have the same thickness, to ensure comparable and reproducible results. Following this the sample will be cured under the UV source for the calculated duration of time. After curing, the sample will be carefully separated from the mold using a scalpel and ensuring that the minimum amount of structures are affected during this process. This cured sample will be further exposed to UV after separation from the mold for 25% of the recommended cure time to ensure the samples are completely set. Samples of the NOA after pattern transfer are also characterized using SEM to ensure that complete transfer has occurred.

5.2 Mesoporous Silica Fabrication

Following the verification of the nanostructures after pattern transfer, the samples must to be coated with MPS to create the full dual anti-reflective coating. For this prototype the MPS was deposited via dip coating of the sample at a constant pull speed, using a MPS and binder solution. The ideal ratio of MPS solution to binder solution was determined through testing to be 65% MPS solution and 35% binder solution. The composition and preparation of these solution is discussed below. As for the mesoporous silica nanoparticles themselves, these particles were purchased from Nanoscape AG and donated by DTU. They were delivered as a 5.6wt% solution, suspended in isopropanol. The nanoparticles have a size distribution of 20-30nm, a pore size of approximately 3nm and a porosity of approximate 71% [3]. This gives the nanoparticles a base refractive index of 1.12, which can be increased by adding binder to the MPS.

5.2.1 Fabrication of the Binder Solution

Two solutions are used to fabricate the dip coating solution, the MPS solution and the binder solution. The MPS solution is a dilution of the initial MPS suspension (5.6wt%) down to

1.5$wt\%$ using HPLC grade isopropanol. The binder solution is prepared by mixing 1L HPLC grade isopropanol, 50mL of TEOS and 25mL of 0.1M hydrochloric acid [3]. These two solution were mixed at a ratio of 65% MPS solution to 35% binder solution for use in dip coating the samples.

5.2.2 Dip Coating Procedure

As it was stated earlier the MPS binder solution was deposited onto the prototype via dip coating, as it is capable of producing consistent film thicknesses onto our sample. This uniform thickness of material is achieved as the solvent evaporates and leaves a thin film of the material. The samples were dip coated using a Makerbot Reprap, and interfaced using the software Pronterface. Using a custom sample holder, each of the prototype samples were lowered into a beaker of the MPS binder solution and the Reprap was programmed to pull the samples at a constant speed. Determined through testing, the ideal speed for this MPS coating was found to be 120$mm/minute$. This pull speed was achieved using the code: G1 Z85.0 F120.0, which will pull the sample vertically 85mm at a speed of 120$mm/minute$. This sufficiently coated the NOA samples mounted on glass wafers, with the uniform deposition confirmed though SEM imaging.

Description of the types of samples fabricated and tested for this system The prototype was validated through the numerous testing procedures outlined earlier. This required the fabrication of a number of different samples for all parts of the prototype, in order to show improvements of the combined prototype over each of the components. The samples constructed for testing were:

1. Polished Glass Wafer
2. NOA 61 and NOA 68 unpatterned blanks
3. MPS coating on a polished glass wafer
4. Nanostructured NOA 61 and NOA 68
5. Nanostructured NOA 61 and NOA 68 with MPS coating

6 Prototype Verification

The prototype for this project was measured in a variety of ways to ensure that it met the customer requirements. A summary of the results will be presented here while a more detailed report is available in Appendix I of this report.

6.1 Nanostructures and MPS Verification

The successful creation of the nanostructures, and deposition of the mesoporous silica (MPS) as a continuous thin film was analyzed through the use of scanning electron microscopy (SEM). The successful creation of the nanostructures on a black silicon wafer can be seen in Figure 4.

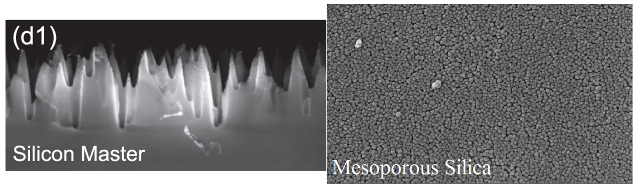


Figure 4: SEM image of black silicon and mesoporous silica

The MPS was characterized to determine an optimal combination of pull-speed and binder concentration. The characterization was done by measuring the transmission of samples with binder concentrations of 10%, 35% and 60% and pull speeds of 80$mm/minute$, 120$mm/minute$, and 240$mm/minute$. Figure 5 shows the results of this test.

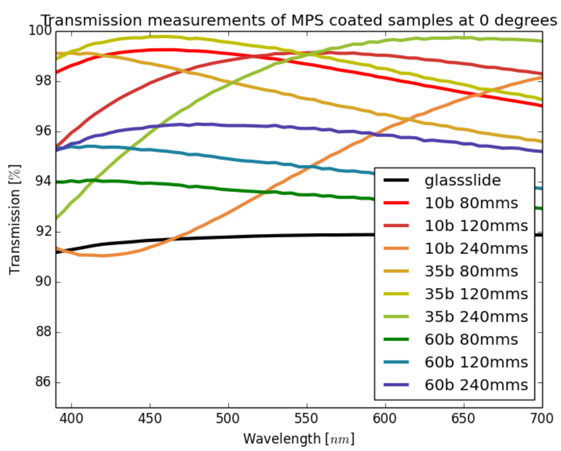


Figure 5: UV-Vis measurement of all MPS binder and pull Speed Combinations

As can be seen the best results were using a 10% binder concentration with a pull speed of either 80$mm/minute$ or 120$mm/minute$. Due to concerns about the final hardness of the coating a binder concentration of 35% was used.

6.2 Comparison between Theoretical and Experimental Results

Figure 6 below compares the theoretical results from the simulations and the actual results that were obtained by UV-Vis spectrometry. There is high agreeance with the theoretical transmission values expected.

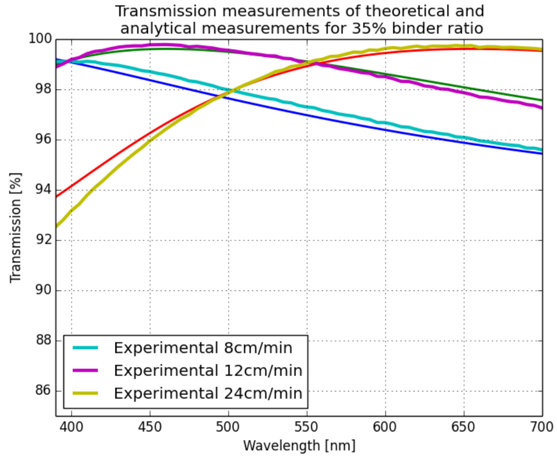


Figure 6: Comparison of theoretically derived reflection and experimentally derived reflection

6.3 Scratch resistance and Hardness testing

The other characteristic of the MPS film is the hardness, which was tested using a Mohs Hardness scratch test. Initial testing of a blank glass slide yielded a hardness of 6. A median pull speed of 120$mm/minute$ was chosen for scratch testing at each of 10%, 35% and 60% binder solutions. The results are shown below in Figure 7.

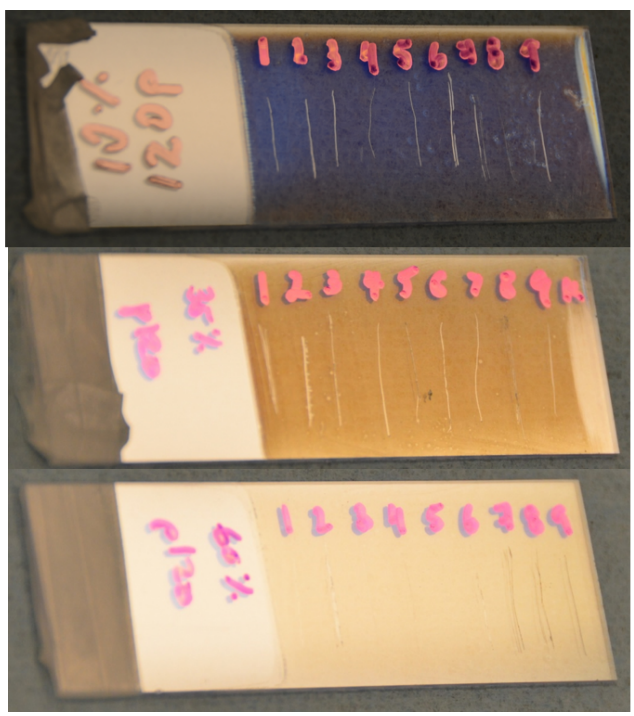


Figure 7: Mohs hardness testing on MPS thin films

The hardness of the samples was also evaluated using Berkovich nanoindentation. These results showed that our coating was less strong than glass and that the higher binder concentrations resulted in stronger coatings as expected.

6.4 Pattern Transfer Results

Successful pattern transfer was confirmed using SEM imaging of the NOA 61 and NOA 68 samples. The results are shown below in Figure 8.

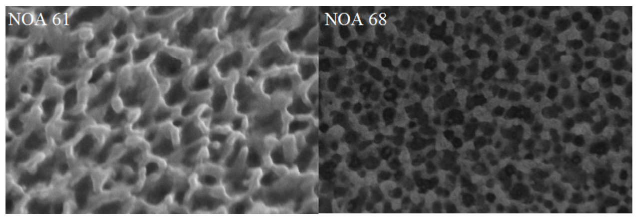


Figure 8: SEM Images of Nanostructure Patterns transferred on NOA61 and NOA68

After confirmation that the pattern was successfully transferred the transmission of the samples was measured. The UV-Vis results are shown below in Figure 9.

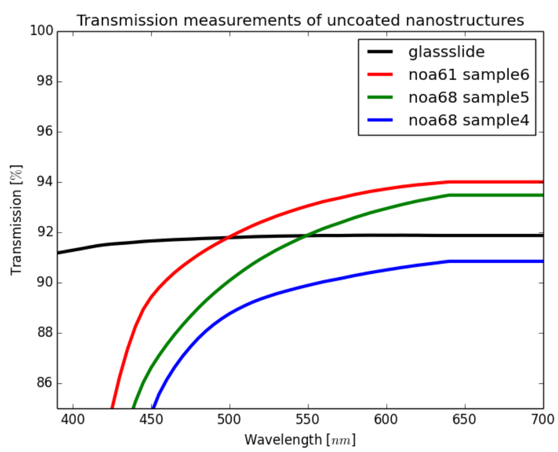


Figure 9: Transmission measurements Obtained for Various NOA Samples Containing Nanostructures without MPS

6.5 Prototype Optical results

The MPS transmission data, MPS hardness data, and the NOA transmission data was examined and a prototype using NOA and MPS with a 35% binder concentration and a $120 mm/minute$ pull speed was created. The optical properties of the prototype were then tested. The results are shown below in Figure 10.

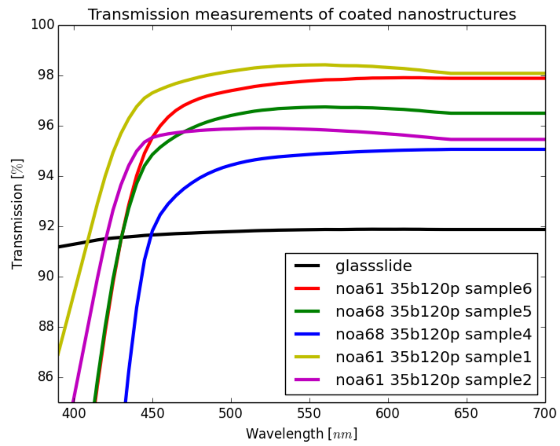


Figure 10: Transmission measurements obtained for various NOA samples containing nanostructures coated with MPS

6.6 Passivation results

Finally the passivation qualities of the coating were tested by exposing the coated samples to water, isopropyl alcohol, and a Kimwipe and then measuring the transmission values of these samples. Light touch had no visible effect on the samples, while the other methods reduced the transmission. The results of these experiments are shown below in Figure 11.

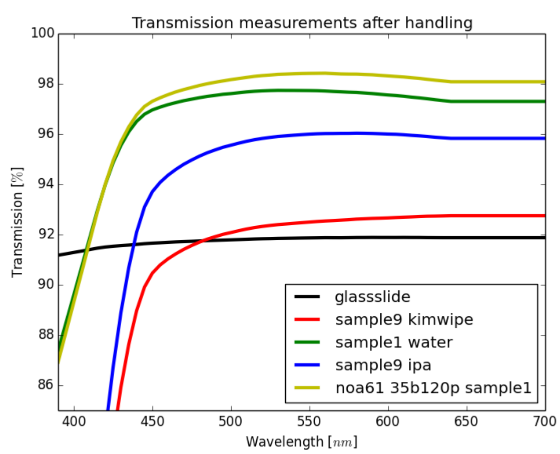


Figure 11: Transmission measurements after exposure to various elements and handling

7 Customer Requirement Design Deviations

Customer requirements pertaining to the practicality, functionality, and aesthetics of the nano-engineered antireflective system were identified, specifically regarding coating reflectance, transmittance, hardness, nanostructure pattern transfer effectiveness, and MPS dip coating uniformity.

7.1 Reflectance Customer Requirements

The primary customer requirement pertaining to coating reflectance was the attainment of reflectance values beneath 10% - corresponding to the reflectance of uncoated glass - between the angular ranges of $90° \pm 15°$ over the entirety of the visible wavelength spectrum, ranging from $390nm$ to $700nm$. This metric was selected in order to ensure that the developed anti-reflective coating provided superior anti-reflectance properties relative to uncoated glass. Figure 12 displays the obtained reflectance/absorbance/scattering data of the most advanced anti-reflective samples, which were obtained using a dip coating pull speed of $12cm/s$, a 35% binder-MPS ratio, and NOA 61 as the pattern transfer substrate. Independent reflectance measurements were unattainable due to equipment constraints.

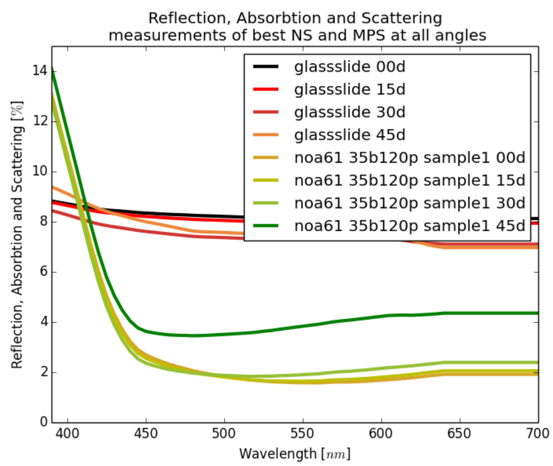


Figure 12: Combined reflection, absorption and scattering of most advanced anti-reflective samples.

Analysis of Figure 12 reveals that, for angular measurements of $90° \pm 0°$, $90° \pm 15°$, $90° \pm 30°$, and $90° \pm 45°$, the reflectance/absorbance/scattering values of the most advanced anti-reflective coatings were beneath 10% within the wavelength range of $450nm$ to $700nm$. The sudden, drastic reflectance/absorbance/scattering increase beneath $450nm$ has been attributed to ultraviolet light absorption exhibited by the utilization of NOA as the nanostructure-patterned substrate, as NOA is a UV-curable polymer. However, extrapolation of reflectance data between the wavelengths of $450nm$ and $700nm$ suggests that, in the absence of reflectance/absorbance/scattering intercorrelated data, the reflectance throughout the entirety of the visible spectrum is beneath 10%. Hence, the primary consumer requirement pertaining to coating reflectance was satisfied.

7.2 Transmittance Consumer Requirements

The primary consumer requirements pertaining to transmittance was the attainment of transmittance values above 85% between the angular ranges of $90° \pm 15°$ over the entirety of the visible wavelength spectrum. This metric was selected in order to ensure that the utilization of the developed anti-reflective coating provided superior transmittance properties relative to uncoated glass. Figure 13 displays the obtained transmittance data of the most advanced anti-reflective samples.

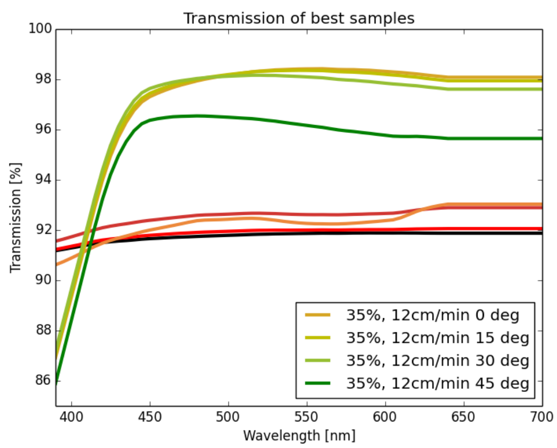


Figure 13: Transmission measurements of most advanced anti-reflective samples.

Analysis of Figure 13 reveals that, for angular measurements of $90°\pm0°$, $90°\pm15°$, $90°\pm30°$, and $90° \pm 45°$, the transmittance values of the most advanced anti-reflective coatings were above 85% within the wavelength range of $450nm$ to $700nm$. As previously mentioned within Section 7.1, the sudden, drastic transmittance reduction beneath $450nm$ has been attributed to ultraviolet light absorption from the patterned Norland Optical Adhesive substrate. Thus, transmittance extrapolation suggests that, in the absence of a UV-absorbing substrate, the transmittance values of the developed coating would exceed 85% throughout the entirety of the visible spectrum. Hence, the primary customer requirement pertaining to coating transmittance was satisfied.

7.3 Hardness Customer Requirements

The primary consumer requirement pertaining to the hardness of the anti-reflective samples was the attainment of a Mohs hardness value of 4.0, corresponding to the hardness of polycarbonate and steel. This metric was selected according to the attained Mohs hardness of the optimized MPS coating obtained by Moghal et al [3]. Following hardness testing, the most advanced anti-reflective sample yielded a Mohs hardness of approximately 1.0, which was evident by the abrasive contact of a Mohs hardness level 1.0 material upon it. This dissatisfying result may have been due to the patterned nanostructures, which, contrary to original expectations, may have reduced the hardness of the deposited MPS coating. However, Mohs hardness evaluations were also performed upon MPS deposited onto unpatterned glass microscope slides, also yielding a hardness of 1.0. This measurement contradicts the result obtained by Moghal et al utilizing identical binder-MPS parameters. However, whereas Moghal obtained this result via MPS spin coating, the most advanced anti-reflective samples were obtained via MPS dip coating, suggesting that dip coating may be insufficient in order to attain the desired Mohs hardness level. Consequently, alternative MPS deposition techniques, such as spin coating and spray coating, should be investigated. These techniques may result in enhanced coating hardness properties and should be considered for future tests.

7.4 Nanostructure Pattern Transfer Requirements

The primary consumer requirement pertaining to the nanostructure pattern transfer effectiveness was the attainment of a 90% pattern yield and consisting of identical aspect ratios relative to the master mould. Scanning electron microscopy (SEM) was originally intended to be utilized in order to evaluate this metric. However, upon further investigation it was discovered that, in order to obtain the desired SEM images, sample cleaving would be required which, when performed upon the fabricated NOA substrates, proved ineffective. However, it is possible that, once the anti-reflective coating is applied to the ultimately-desired substrate - polycarbonate - effective cleaving for SEM imaging analysis will be achievable. This should enable the evaluation of the nanostructure pattern effectiveness.

7.5 MPS Dip Coating Uniformity Requirements

The primary consumer requirements pertaining to the dip coating of the MPS film was the attainment of an overall thickness variation beneath 5%. DEKTAK profilometry was originally intended to be utilized in order to evaluate the metric. However, upon further investigation it was discovered that the available profilometer suffered from drastic hardware noise, severely limiting the measurement resolution, and hence measurement capability, of the deposited coating. Consequently, SEM imaging analysis was performed upon the MPS coating, enabling a qualitative description of this metric, as shown in Figure 14.

Analysis of Figure 14 reveals the apparent uniformity of the deposited MPS coating. However, in order to obtain a quantitative evaluation of this metric, profilometry should

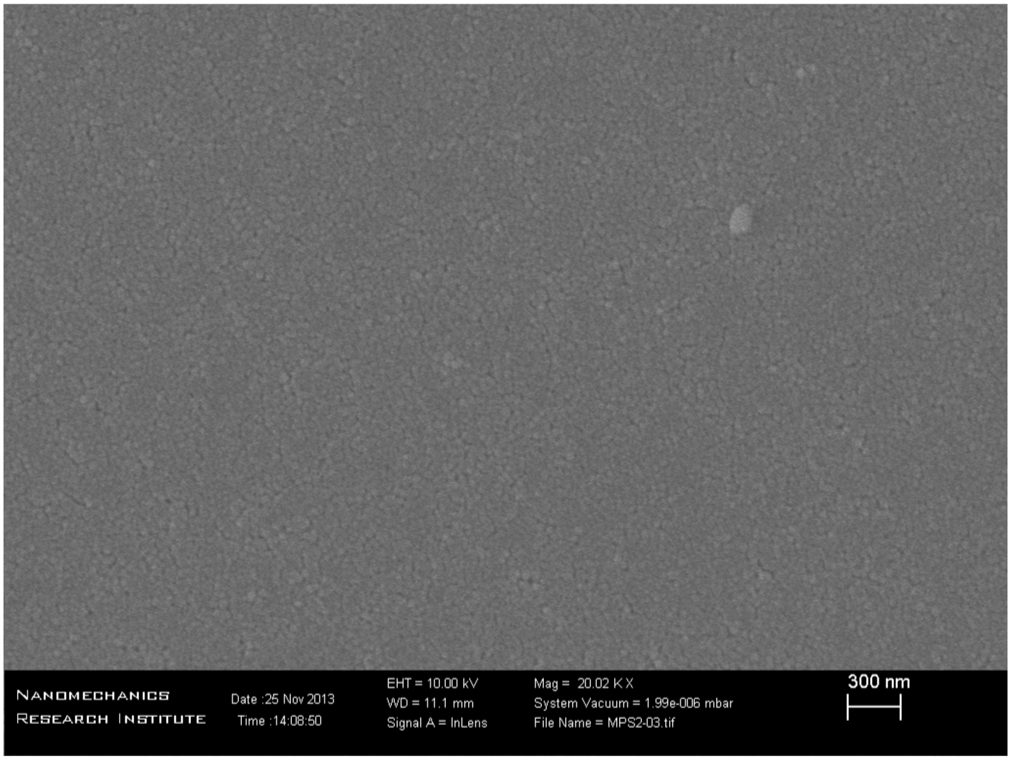


Figure 14: SEM image of deposited MPS coating.

be performed utilizing a device capable of attaining superior resolution than the machine within the Nanotechnology Engineering undergraduate clean room. This should enable the evaluation of the MPS coating uniformity.

8 Future Work

While the current prototype was able to meet the primary consumer requirements, there is still room for improvement and future research in this field. These improvements are focused in two area, the first being improvements to the antireflective and hardness characteristics of the coating itself, while the second area is improvements in the manufacturing and mass production of the samples themselves.

In order to improve the anti-reflective characteristics of the prototype more tests should be conducted with the nanostructured substrate. All the prototypes used in this report used the negative imprint of the structures, and the results did not quite meet those published in literature[4]. It is possible that the black silicon nanostructures are not symmetrical, and therefore more testing should be performed using a double pattern transfer process to imprint positive nanostructures onto the prototype substrate. These tests will indicate if there is a different fill profile between the two states, and therefore different reflection characteristics and possibly different adhesion to the mesoporous silica. This could help improve the anti-reflectivity of the sample.

While the current prototype met the primary consumer requirements for sample durability, the sample is still far too fragile for the target use in touch screen devices. Changing to positive nanostructure could improve the adhesion of the MPS coating, but it will not increase the hardness, and therefore durability of the coating itself. More tests should be conducted to explore a larger range of MPS solution to binder ratios to determine the trade-offs between the coating hardness and the reflectivity of the substrate. It would be useful to see the results of high binder ratio coatings on the nanostructured surface to see what effect the nanostructures have on improving the tougher, but more reflective, MPS coatings.

As for the production of the samples themselves, more research should be done to explore different production methods. The prototypes used in this research were produced though UV curing and dip coating, neither of which is able to mass produce samples, and therefore reduce the cost to compete with the currently established AR coatings in industry. The goals for future work would be to produce equivalent samples using different pattern transfer and MPS depositions methods.

Future research into pattern transfer should look into hot embossing and eventually injection molding the samples. With a suitable mold the nanostructures could be produced using polycarbonate or PMMA substrates, which are currently being used in industry for many lens applications. As for the deposition of MPS, future research should look into spray coating the MPS solution, as this will be able to produce samples in a continuous assembly line. With adaptations to the MPS binder solution the sample could be sprayed and cured using a heat source to deposit the uniform film over larger sample areas.

With this future research the product in this report could be able to compete with the current technologies on the market, as an inexpensive anti-reflective coating for plastic substrates.

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Appendix A Customer Requirements

A.1 Introduction

The objective of this design project is to create a passivated anti-reflective coating for use in the electronics industry. Modern electronic displays reflect external light sources, resulting in visual discomfort. This phenomenon is perceived as glare by the user, and hence the pursuit of a solution has warranted large investments by many consumer electronics companies. Many current anti-reflective technologies are achieved with multiple layers of chemically deposited compounds. This approach is expensive and complex - requiring controlled vacuum conditions - as well as significant time allocation. These costs are transferred to the consumer.

This design project pursues the realization of structure-based anti-reflective surfaces in order to replace the currently-implemented multi-layer chemical vapor deposited coatings. It is desired that these structures replace the current coatings as a cheaper, easily producible, and superior anti-reflective solution. The most basic requirements consist of the creation of a product that is comparable to industrially-standardized coatings. Furthermore, batch production should be possible in order to attain the required throughput for mobile phone screens, laptop screens, large computer monitors, and television displays.

A.2 Customer Requirements

A.2.1 Anti-reflective Properties

The anti-reflective properties of the coating - quantified in terms of reflectance value - are a high priority, as they are the principal focus of this design project. The reflectance value is the percentage of light reflected by a screen; a large reflectance value results in glare, reducing screen contrast. Primary, secondary, and tertiary design requirements have been identified. The primary requirement is the comparability of the coating to currently-implemented technology used within cellular devices. Hence, the maximum allowable coating reflectance value is 10%. The secondary requirement is the attainment of superior anti-reflective properties - principally the reflectance value - of the developed coating over the nanostructured deficient MPS-coated substrate. The tertiary requirement is the reduction of reflectance values below perceivable thresholds for all visible wavelengths and over all angles utilizing the developed anti-reflective coating.

A.2.2 Coating Lifetime

Anti-reflective coating lifetime is another crucial consumer concern, as it relates to the evolution of coating degradation as well as costs related to materialistic replacement. It describes the period over which the coating performs above a specified threshold, including reflectance, transmission, and aesthetic properties. Hence, in order to achieve a practical and marketable product, coating lifetime maximization is desirable. Additionally, as the defined anti-reflective coating is intended for display applications within the consumer electronics market, display categorization is required. Displays are employed for two principal user-based interactions: Touch-based interactions - such as those utilized for tablets - involve extensive and frequent contact. Visual-based interactions - such as those utilized for televisions and laptops - involve infrequent, periodic contact, which typically occurs during cleaning and maintenance. Based upon these considerations, primary, secondary, and tertiary coating lifetime objectives were identified. The primary objective is the complete retainment of transmission, reflectance, and aesthetic properties following mild surface contact, such as during gentle display wiping. This should ensure adequate coating integration within displays intended for visual-based interactions. The secondary objective is the complete retainment of transmission, reflectance, and aesthetic properties following extensive surface contact. This should ensure adequate coating integration within displays intended for touch-based interactions. Lastly, the tertiary objective is the complete retainment of transmission, reflectance, and aesthetic properties following abrasive surface contact, such as the extensive, repeated application of steel wool.

A.2.3 Application cost of the coating

The final consumer requirement entails the production costs associated with these anti-reflective coatings. As the principal consumer will implement this product within manufacturing lines, it is imperative that the antireflective coating application process is simple, consistent, and inexpensive. Furthermore, in order to reduce error and curtail costs, it is desirable that this process minimizes human intervention. This is a requirement for the mass production of current display technologies. Therefore, various procedures are proposed in order to transfer the nanostructures and apply the mesoporous silica.

Three pattern transfer methods are proposed: UV curing, hot embossing, and injection moulding. Since UV curing is the simplest of these procedures, it satisfies the primary transfer requirement. However, due to its inconsistent and irreproducible nature, it is generally impractical. Hence, the two proposed alternatives are hot embossing and Injection moulding. These are the secondary and tertiary requirements, respectively.

Regarding mesoporous silica application, the primary requirement consists of the attainment of a topographically-uniform coating. This can be achieved in a simple manner via dip coating. However, industrial application demands high throughput, whereas dip coating is a slow and tedious process. Hence, spray coating is proposed as an alternative deposition process. This method will enable continuous, high throughput coating application.

A.3 Summary of Customer Requirements

	Primary	Secondary	Tertiary
Reflectance	10 percent reflectance	Less reflectance for nanostructured surface compared to simple MPS coated substrate	No visible reflectance for all visible wavelengths and all angles
Lifetime	Withstand occasional light contact with soft material	Withstand frequent light contact with soft material	Withstand frequent contact with abrasive material
Cost	Dip Coating UV curing	Hot embossing	Spray coating Injection moulding

Appendix B Project Plan and Milestones

B.1 Introduction

This section aims to quantitatively and qualitatively describe the steps and requirements that will be taken to ensure a successful project completion. This includes a detailed description of the design challenges that will likely be encountered, a timeline chart of each week's tasks, group member responsibilities and expertise, and costs, such as equipment, chemicals, lab space requirements and software. The timeline detailing the project flow will start with week 1 as September 9th, 2013, and will span over the 4A and 4B terms (28 weeks in total).

This project is different from other fourth year projects in that many iterations of our anti-reflective surface will be fabricated with different substrates and techniques, each with unique advantages over the previous. As such, our main milestones will be the completion of fabrication and characterization of each anti-reflective surface. As such, many of the anti-reflective surface fabrication and characterization steps required will be shared among each milestone.

The timeline outlining our procedure illustrates the latest time each project will be finished with potential difficulties taken into account. At the end of our timeline we have included another milestone, spray coating, that is a stretch goal for our group, and will be addressed time and budget permitting.

Table B.1: Project milestones

#	**Milestone**	**Weeks**
1	Calibrate dip coater	4 to 7
2	Characterize black silicon	5 to 6
3	Ormacomp plastic samples	7 to 9
4	AR coating: UV-cured Norland sample and MPS deposition via dip-coating	10 to 12
5	Hot embossed polycarbonate and MPS deposition via dip-coating	17 to 21
6	Spray coating MPS	18 to 22

B.2 Milestones

What follows is a breakdown of each milestone in our project. Each of these milestones is comprised of a series of tasks that must be performed, and many of these tasks are repetitive.

Each of the task requirements will be written out once, and repetitions of the task will refer back to this original task requirements.

B.2.1 Calibrating the Dip Coater

Requirements for Calibrating Dip Coater

Tasks	Mix binder and MPS solution, Create Test Concentrations, Test Pull Speeds, Measure Film Thicknesses, Correlate concentration and Pull Speeds to Film Thickness, Test Silicon Wafer
Total Hours	31.5 hours
Total Budget	$356.8
Timeframe	September 30 - October 31
Special Needs	Black silicon wafers from DTU

The protective film used on our nanostructures is created with a combination of binder solution and mesoporous silica nanoparticles (MPS). By varying the pull speed and the concentration of the MPS in the binder solution the thickness of the coating can be controlled. Before calibrating the dip coater the MPS binding solution needs to be mixed together. To enable the creating of various concentrations of MPS binding solution we will fabricate a stock of binder solution that can be mixed with MPS when needed to produce precise concentrations.

Mix binder and MPS solution

Milestone	Week 5
Lab Space	Dr Tsui's Lab
Equipment	Glassware, pipettes
Hours	1 hour
Budget	$336.80 HPLC IPA($137.50)(4L) HPLC HCl ($75.30)(500mL) TEOS ($124.00))
Software	None
Special Needs	None

Initially three concentrations of MPS will be used, 1%wt, 2%wt, and 4%wt. The concentration of the MPS will be refined based on the results of the first test to further optimize the thickness of the MPS coating. Each of these concentrations is created by mixing precise amounts of the 10%wt MPS stock solution with the stock binder solution.

Create Test Concentrations

Milestone	Week 5-6
Lab Space	Dr Tsui's Lab
Equipment	Glassware, pipettes
Hours	5 hours
Software	None
Special Needs	None

Initially three pull speeds will be used to calibrate the MPS film thickness 60mm per min, 120mm per min, and 240mm per min. The pull speeds will be refined based on the results of the first test to further optimize the thickness of the MPS coating. Each of these pull speeds will be tested with each different concentration of MPS solution.

Test Pull Speeds

Milestone	Week 6-7
Lab Space	Dr Tsui's Lab
Equipment	3D Printer - Dip Coater
Hours	9 hours (2x (3 concentrations x 3 pull speeds) samples x 15 minutes) x 2 people
Budget	$10 (18 glass slides)
Software	None
Special Needs	None

The thickness of the MPS film is important to the design, so it will be measured using SEM cross-sectional imaging. It is also important for there to be little or no variations in the thickness of the MPS coating, so additional SEM images of the top of the sample will be taken to look or any surface height variations.

Measure Film Thickness

Milestone	Week 6-7
Lab Space	Dr Tsui's Lab
Equipment	FE-SEM
Hours	18 hours (18 samples x 30 minutes) x 2 people
Budget	$10 (18 glass slides)
Software	None
Special Needs	None

In order to refine the MPS concentration and the pull speeds the data obtained from the first test will be analysed and new concentrations and pull speeds will be generated for the second test.

Correlate concentration and Pull Speeds to Film Thickness

Milestone	Week 7
Lab Space	Dr Tsui's Lab
Equipment	Laptop, Dip Coater
Hours	30 minutes
Budget	$10 (18 glass slides)
Software	Excel
Special Needs	None

This project will be comparing the antireflective coating created on a number of different materials, and it is important that each material can be calibrated to create precise film thicknesses. Samples from a silicon wafer will be used to test whether the concentrations and pull speeds vary between materials; it will also allow us to determine the refractive index of the MPS coating.

Test Silicon Wafer

Milestone	Week 6-7
Lab Space	Dr Tsui's Lab
Equipment	FE-SEM
Hours	2 hours (30 minutes prep wafer + 30 minutes Dipcoat + 30 minutes SEM + 30 minutes contingency)
Budget	$10 (1 silicon wafer)
Software	Excel
Special Needs	None

Design Challenges

The primary concern for the MPS coating is optimizing its thickness, which may prove difficult as temperature and humidity will all factor into the solvent evaporation that determines film thickness. In addition if we determine any major changes in film thickness across different materials it may require performing a calibration on every new material tested. Refining the film thickness is one of the most important aspects to this project, as only precise thicknesses of a uniform MPS coating will create an antireflective coating.

B.2.2 Characterizing Black Silicon

Characterize Black Silicon

Milestone	October 7th - October 18th
Lab Space	Dr Tsui's Lab
Equipment	FE-SEM
Hours	5 hours
Budget	None
Software	Excel
Special Needs	None

Denmark Technical University (DTU) has supplied our group with the initial black silicon wafer samples that contain the antireflective nanostructures. These structures were fabricated using an unmasked reactive ion etch process. Before these structures are transferred to our plastic antireflective samples, the nanostructures must be characterized to ensure that the required quality and aspect ratio is present. These wafers will be characterized, via SEM cross-sectional imaging and SEM aerial imaging, to determine the height and width of the structures as well as the larger periodicity in the distribution of structures.

SEM Cross section / SEM Aerial analysis	
Milestone	Week 5-6
Lab Space	Dr Tsui's Lab
Equipment	FE-SEM
Hours	5 hours ((4 Samples x 30 min)+30 min contingency) x 2 people
Budget	None
Software	Excel
Special Needs	None

Design Challenges

Verifying the quality of these nanostructures is very important to our project, as they form the basis of our anti-reflective coating. If any major variations in these structures, or damaged structures, is observed then these black silicon wafers may have to be recreated, creating substantial delays to our schedule.

B.2.3 Ormocomp Plastic Samples

Ormocomp Plastic Samples	
Tasks	Characterization of Nanostructures, MPS Film Deposition via Dip-Coating, Characterization of Film Thickness and Uniformity, Optical Transmission and Reflectivity Evaluation via Spectroscopy and Lifetime Evaluation
Total Hours	200 hours
Total Budget	None: Materials Included in Other Milestones
Timeframe	October 25 - December 1 (1 month)
Special Needs	None

For the ormocomp testing there are three samples that need to be created. A blank substrate to serve as a comparison sample for both the plain coated sample and the nano-structured and coated sample. Before proceeding it is necessary to characterize the Ormocomp patterned samples to ensure that the structures are intact. This SEM characterization will include a horizontal cross-section to verify the aspect ratio of the structures, and an aerial view to examine the surface coverage of these structures.

Following the verification of the nanostructures, the three different ormocomp samples need to be coated with MPS before undergoing testing. For these samples the MPS will be applied via dip coating of the samples at various pull speeds and pull concentrations as covered above in the Dipcoat calibration milestone.

MPS Film Deposition via Dip-Coating

Milestone	Week 7-8
Lab Space	Dr Tsui's Lab
Equipment	3D Printer and Dip coater
Hours	10 hours
Budget	None
Software	None
Special Needs	None

Now that the structures have been coated with the MPS solution they must undergo a variety of testing to measure the physical and optical properties of the coating. The first measurement is of the thickness and uniformity of the MPS coating. The thickness will be measured using a cross-section of the sample imaged using the SEM. The uniformity will be measured using several line scans on height profilometer. These height measurements will be taken multiple different directions on the sample to ensure a uniform coating in every direction. This task has been outlined in Milestone 2.3: Ormocomp Plastic Samples.

Once the samples have passed the thickness and uniformity testing, they must then undergo optical testing to measure the transmittance and reflection for the coating. These measurements will be taken at a 90 degree angle of incidence to measure transmittance, and to determine the intensity that is lost to internal scattering. Following this the reflectance will be measured at a variety of different angles in order to plot the intensity of the reflected light versus the angle of incidence. At a direct angle of incidence this antireflective coating should reduce the percentage of light reflected compared to the blank substrate. This optical testing will be performed before and after the lifetime evaluation of the substrate. It is one of the main measurements of the lifetime of the coating, as if the coating is destroyed the substrate should reflect additional light.

Optical Transmission and Reflectivity Evaluation via Spectroscopy

Milestone	Weeks 8-9
Lab Space	Dr Tsui's Laband Not Assessed
Equipment	Multiwavelength Light Source, Photodetector, Arduino and Electronics
Hours	10 Hours
Budget	Free
Software	None
Special Needs	None

After the initial optical testing, the samples must now undergo a lifetime evaluation to determine the hardness of the coating. This testing is performed by pulling a weighted test material over the sample at a constant rate. By testing with a microfiber cloth at a low applied weight up to a fine sandpaper with a larger weight the hardness and durability of the coating can be analyzed. Each of these tests will be verified by a visual inspection for scratch marks or other damage, as well as optical testing to determine if the level of reflection has changed.

Lifetime Evaluation

Milestone	Weeks 8-9
Lab Space	Not assessed
Equipment	Microfiber cloth, sandpaper, selection of weights
Hours	10 Hours
Budget	Free
Software	None
Special Needs	None

Upon completion of the physical and optical testing for the ormocomp samples, the results from each characterization can be analyzed to determine the success of the substrate and coating thickness. A design review will be performed for each of these characteristics to obtain an optimized anti-reflective ormocomp sample.

Ormocomp Fabrication Optimization

Milestone	Not assessed
Lab Space	Dr Tsui's Lab
Equipment	Previously mentioned
Hours	170 Hours
Budget	Free
Software	None
Special Needs	None

Design Challenges

The main design challenge that has been identified for the Ormocomp samples is calibrating the thickness of the MPS coating to coincide with the nano-structured surface for the best anti-reflection characteristics. Obtaining a precise thickness of the MPS coating on a new material will require some calibration, in addition to how the nanostructures will affect the thickness of the coating. Another challenge may be that these nano-structures could create a surface roughness in the MPS coating, with these thickness variations compromising the reflection of the surface. Evaluation of these characteristics will only be possible once the samples have been created and tested.

B.2.4 Norland Optical Adhesive Samples

Norland Optical Adhesive Samples

Tasks	FDTS Application, Nanostructure Pattern Transfer via UV-Curing, Characterization of Nanostructures, MPS Film Deposition via Dip-Coating, Characterization of Film Thickness and Uniformity, Optical Transmission and Reflectivity Evaluation via Spectroscopy and Lifetime Evaluation
Total Hours	350 hours
Total Budget	$530
Timeframe	December 1, 2014 - January 15 (1.5 months)
Special Needs	None

Norland Optical Adhesive was selected as an inexpensive alternative to Ormocomp, enabling the production - and hence optimization - of a large quantity of samples. It is UV-curable and thus pattern transfer will be performed in this manner. Subsequent MPS deposition via dip-coating will be employed in order to fabricate the final anti-reflective coating. Lastly, sample optimization will be performed following SEM imaging analysis, transmission and reflection quantification, and the lifetime evaluation.

FDTS-deposited black silicon wafers are required in order to attain anti-stiction properties, which will ensure the nondestructive removal of the mould from the Norland sample. This will be performed in a non-standard manner, employing a vacuum dessicator and acute FDTS application. The following resources are required in order to pursue this endeavor:

FDTS Application

Milestone	Week 10
Lab Space	Not assessed
Equipment	Vacuum dessicator
Hours	10 Hours
Budget	$230
Software	None
Special Needs	None

Following FDTS deposition, nanostructure pattern transfer will be achieved via UV-curing. This involves the deposition of Norland Optical Adhesive onto the black silicon mould and its subsequent exposure to ultraviolet radiation. This will cure the sample, after which it will be extracted, resulting in the desired pattern transfer. The following resources are required in order to pursue this endeavor:

Nanostructure Pattern Transfer vis UV-Curing

Milestone	Week 10-11
Lab Space	Not assessed
Equipment	UV lamp
Hours	10 Hours
Budget	$100
Software	None
Special Needs	None

SEM imaging will then be performed in order to analyze the characteristics - namely aspect ratio and quality - of the transferred nanostructures.

Characterization of Nanostructures

Milestone	Week 11
Lab Space	Dr Tsui's Lab
Equipment	SEM
Hours	50
Budget	Free
Software	None
Special Needs	None

MPS deposition will then be achieved via dip-coating, which should result in a uniform surface coating. The subsequent testing for this dip-coated sample is identical to the process described above in Milestones 2.3: Ormocomp Plastic Samples. Refer to those task descriptions for the process of Characterization, Optical Testing and Lifetime Evaluation.

Ormocomp Fabrication Optimization

Milestone	Not assessed
Lab Space	Dr Tsui's Lab
Equipment	Previously mentioned
Hours	170 Hours
Budget	Free
Software	None
Special Needs	None

Design Challenges

Three principal design challenges have been identified in the fabrication of the Norland anti-reflective coating via UV-curing and subsequent dip-coating. Firstly, the attainment of adequate nanostructure pattern transfer could prove difficult, as black silicon is extremely fragile. Hence, structural fracture may arise during this process, resulting in inadequate results. Additionally, a non-standard and untested FDTS application procedure will be utilized, which may result in unexpected consequences, such as non-uniform deposition. Lastly, the optimization of the Norland sample is expected to be highly tedious and time-consuming.

B.2.5 Polycarbonate Samples

Polycarbonate Samples

Tasks	FDTS Application, Nanostructure Pattern Transfer via Hot Embossing, Characterization of Nanostructures, MPS Film Deposition via Dip-Coating, Characterization of Film Thickness and Uniformity, Optical Transmission and Reflectivity Evaluation via Spectroscopy and Lifetime Evaluation
Total Hours	350 hours
Total Budget	$200
Timeframe	January 15, 2014 - February 25 (1.5 months)
Special Needs	None

Following FDTS deposition, nanostructure pattern transfer will be achieved via hot-embossing. This involves preheating the black silicon master mould along with the polycarbonate plastic sample. Following this the polycarbonate sample and silicon mould are loaded into a heated press and the temperature is increased to above the glass transition temperature of polycarbonate, but below the melting temperature. Once the sample has reached this temperature a force is applied by the press to imprint the nanostructures into the plastic sample. This required force will be determined through trial and error until the nanostructure pattern is successfully transferred.

Nanostructure Pattern Transfer via Hot Embossing	
Milestone	Weeks 17-20
Lab Space	Not assessed
Equipment	Vacuum desiccator
Hours	10 Hours
Budget	Free: Materials Included in Previous Milestones
Software	None
Special Needs	None

After a successful transfer of the nanostructures, these polycarbonate samples will undergo the same characterization, MPS deposition and testing as the Norland Optical Adhesive samples.

Design Challenges

Three principal design challenges have been identified in the fabrication of the polycarbonate anti-reflective coating via hot embossing and subsequent dip-coating. Firstly, the attainment of adequate nanostructure pattern transfer could prove difficult, as black silicon is extremely fragile. Hence, structural fracture may arise during this process, resulting in inadequate results. Additionally, a non-standard and untested FDTS application procedure will be utilized, which may result in unexpected consequences, such as non-uniform deposition. Lastly, the optimization of the polycarbonate sample is expected to be highly tedious and time-consuming.

B.2.6 Spray Coating MPS

Spray Coating MPS

Tasks	Designing the Spray Coating System, Calibration of Spray Coated Film Thickness, Spray Coating a Sample Material, Characterization of Film Thickness and Uniformity, Optical Transmission and Reflectivity Evaluation via Spectroscopy and Lifetime Evaluation
Total Hours	113.5 hours
Total Budget	Budget Allowing
Timeframe	February 10-March 10 (4 weeks)
Special Needs	None

One of the time permitting milestones in this project is to design and implement a spray coating system to deposit the MPS. This spray coating system is another step towards proving this technology can be easily mass produced. For a proof of concept system a small spray coating system needs to be designed for coating single samples at a time in a reproducible manner. This system will have a pressurized reservoir that will hold the MPS solution, and control the flow rate of the system. This will feed through a valve, to activate or deactivate the spray, into the nozzle which will provide a uniform spray of the liquid. This milestone will only be addressed and completed if the other milestones in this project finish ahead of schedule.

Designing the Spray Coating System

Milestone	Week 18
Lab Space	Dr Tsui's Lab
Equipment	3D Printing System
Hours	Time Allowing
Budget	Budget Allowing
Software	None
Special Needs	None

Once the spray coating system has been designed, it must be calibrated to determine the pressure and time needed to coat our sample with the required thickness of MPS solution. By testing the system at several different pressures and spray coating for several different times a calibration curve for the system can be developed. Finally it may be necessary to test a few different nozzles to achieve uniform coating of the final solution. The thickness of the coating will be analyzed by SEM imaging of the cross sectional height of the coating.

Calibration of Spray Coated Film Thickness

Milestone	Week 20
Lab Space	Not assessed
Equipment	Spray Coater
Hours	Time Allowing
Budget	Budget Allowing
Software	None
Special Needs	None

Once the thickness of the spray coated MPS has been calibrated it can now be tested on a nanostructured sample. This sample will be coated with several thicknesses of MPS and tested to determine which settings produce the most anti-reflective sample.

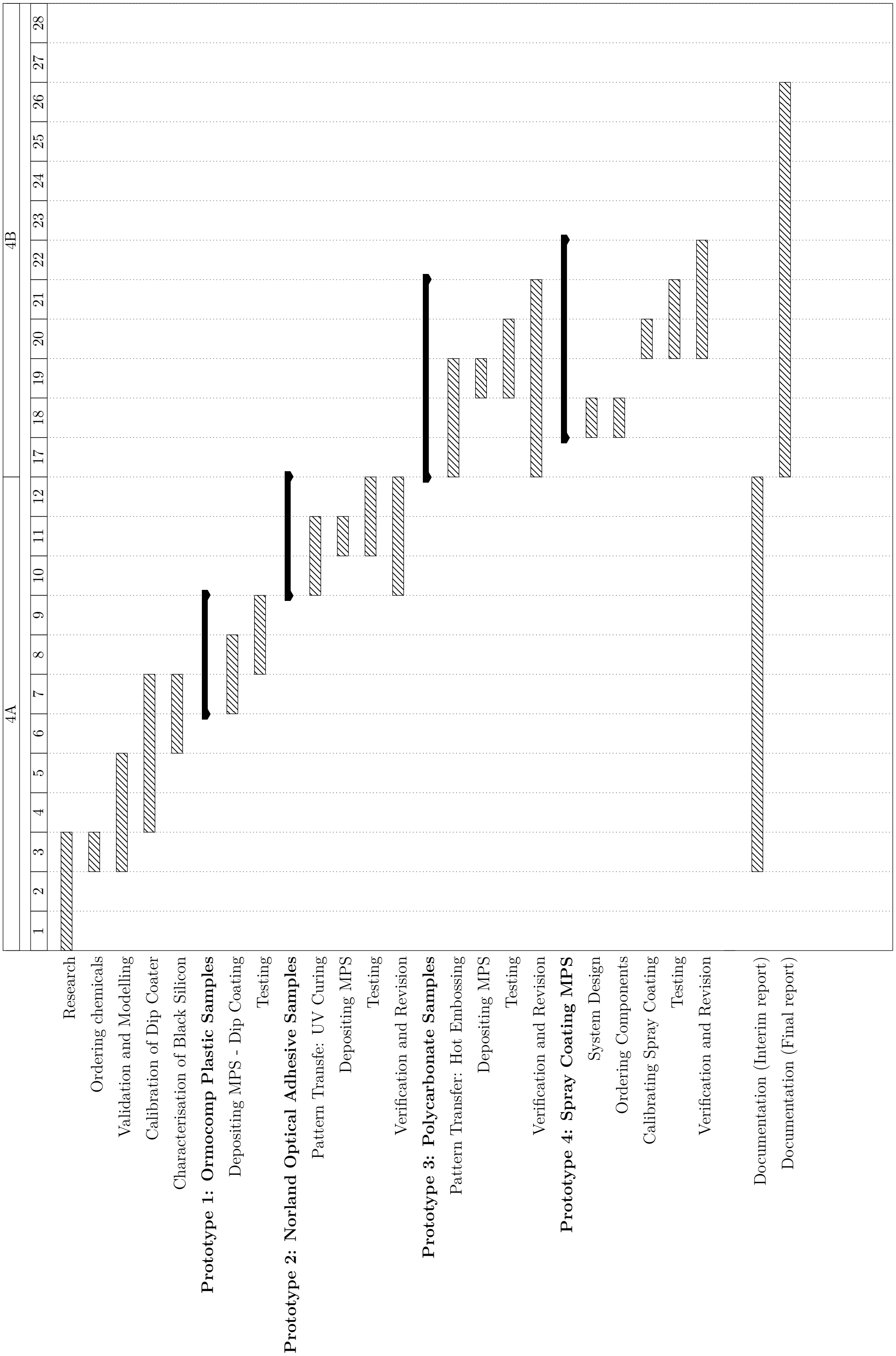
Spray Coating a Sample Material

Milestone	Weeks 20-21
Lab Space	Not assessed
Equipment	Spray Coater
Hours	Time Allowing
Budget	Free
Software	None
Special Needs	None

After spray coating the nanostructured materials, these samples will undergo the same process for measuring the film thickness, optical testing and lifetime evaluation. These tasks are outlined above in Milestone 2.3: Ormocomp Plastic Samples.

Design Challenges

The challenges associated with spray coating are obtaining a uniform thickness of MPS coating across the entire sample in a reproducible manner. Compared to dip coating, when the thickness is controlled by the pull speed, in spray coating the pressures in the system must be precisely controlled, so that the deposition rate is consistent, and the spray times must be precisely controlled so that the total deposition is consistent. Finally the spray pattern on the nozzle must be uniform such that the entire surface is evenly coated, and this uniformity must also apply to the times where the spray is just starting and ending. This is a lot of difficult features that must be optimized in order to achieve a reproducible spray coating system.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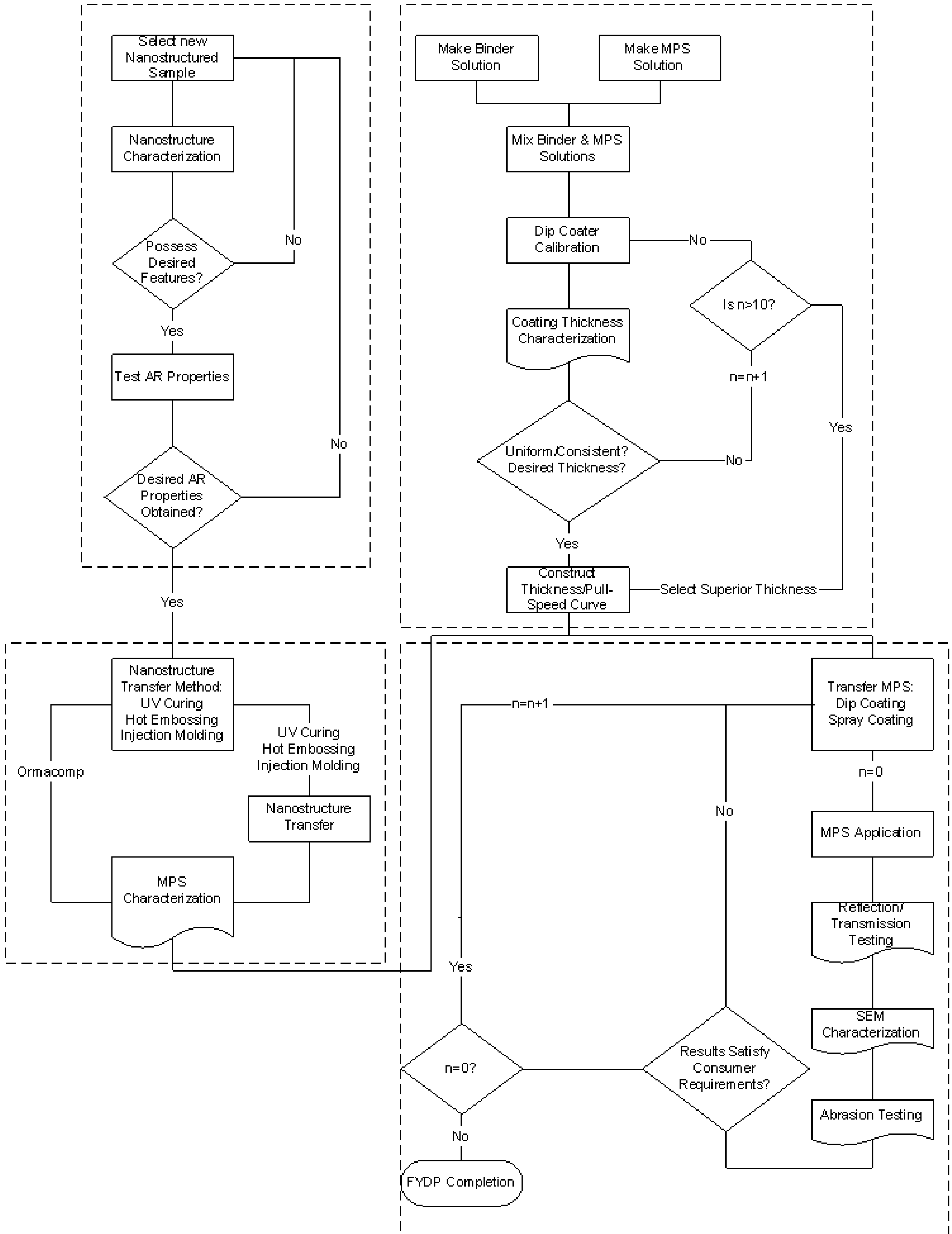
Research
Ordering chemicals
Validation and Modelling
Calibration of Dip Coater
Characterisation of Black Silicon
Prototype 1: Ormocomp Plastic Samples
Depositing MPS - Dip Coating
Testing
Prototype 2: Norland Optical Adhesive Samples
Pattern Transfe: UV Curing
Depositing MPS
Testing
Verification and Revision
Prototype 3: Polycarbonate Samples
Pattern Transfer: Hot Embossing
Depositing MPS
Testing
Verification and Revision
Prototype 4: Spray Coating MPS
System Design
Ordering Components
Calibrating Spray Coating
Testing
Verification and Revision
Documentation (Interim report)
Documentation (Final report)

Appendix C Design Flow



Appendix D Functional Specification

D.1 Introduction

This anti-reflective passivated coating is comprised of two separate components. First is the nanostructured substrate, which is the primary antireflective effect in this product. While serving as an anti-reflective coating these nanostructures also provide the structural rigidity for anchoring the Mesoporous Silica coating (MPS). This MPS coating provides a secondary anti-reflective effect that also serves as a protective coating for the fragile nanostructures. This two-part system is shown below in Figure D.1.

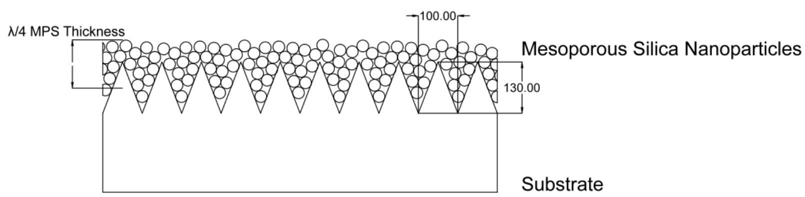


Figure D.1: Overview of the two part Nanostructures / Mesporous Silica System

This high-level design, as summarized above, satisfies the primary objective of creating contact-resistive antireflective coating. A more detailed list of functional requirements is summarized below in Table D.1.

Table D.1: Data sheet: Minimum functional requirements (Priority 1) and supplementary requirements (Priority 2 and 3)

Function or Property	Performance Specification	Priority
Reflectance	$< 10\%$ reflectance at $90° \pm 15°$ for all visible wavelengths	1
	$< 5\%$ reflectance at $90° \pm 30°$ for all visible wavelengths	2
	$< 2\%$ reflectance at $90° \pm 60°$ for all visible wavelengths	3
Transmission	$> 85\%$ transmission at $90° \pm 15°$ for visible wavelengths	1
	$> 90\%$ transmission at $90° \pm 30°$ for visible wavelengths	2
	$> 95\%$ transmission at $90° \pm 60°$ for visible wavelengths	3
Hardness	Mohs Hardness value of 4.0 (Polycarbonate)	1
	Mohs Hardness value of 6.0 (Borosilicate Glass)	2
	Mohs Hardness value of 9.0 (Sapphire Glass)	3
Passivated Coating	No reaction to Water or Water+Surfactant Solutions	2
	No reaction to Isopropanol or Acetone Solutions	3
UV Curing Fidelity	Successful pattern transfer of structures with correct aspect ratios and 90% structure yield	1
Dip Coating	Reliable and reproducible MPS film thickness, with a variation of less then 5°	1
Hot Embossing	Successful pattern transfer of structures with correct aspect ratios and 90% structure yield	2
Spray Coating	Reliable and reproducible MPS film thickness, with a variation of less then 5°	3
Transfer Lifetime	Achieve greater then 10 successful pattern transfers with a single master mould	3

D.2 Background

There are currently three different fabrication approaches to anti-reflection coatings; the single layer, double layer and the infinite layer (continuous). Reflections occur when light travels and encounters a discontinuous refractive index. Using Fresnel equations, the reflection can be determined for an interface where the refractive index changes. For a incident beam travelling from refractive index n_1 to refractive index n_3, the reflection, R is given by

$$R = \left[\frac{n_1 - n_3}{n_1 + n_3}\right]^2$$

For non-incident light, the reflection is separated into p-polarized and s-polarized waves. The reflections are as follows:

$$r_{\perp} = \frac{cos\theta_i - \sqrt{n^2 - sin^2\theta_i}}{cos\theta_i + \sqrt{n^2 - sin^2\theta_i}}$$

$$r_{\parallel} = \frac{\sqrt{n^2 - sin^2\theta_i} - n^2 cos\theta_i}{\sqrt{n^2 - sin^2\theta_i} + n^2 cos\theta_i}$$

Thus, it can be seen that a higher the mismatch in refractive index results in higher reflection. One approach to minimizing the reflection is the single-layer anti reflective coating (ARC), by using a material of refractive n_2 in between n_1 and n_3. Thus, the reflection from the both the interfaces combined would be less than a single interface. Furthermore, by making the ARC thickness equal to $\lambda/4n_2$, we can take advantage of destructive interferences and further reduce the reflection. For a , $\lambda/4n_2$ interface, the reflection is now

$$R = \left[\frac{n_2^2 - n_1 n_3}{n_2^2 + n_1 n_3}\right]^2$$

In order to minimize the reflection, it can be seen calculated that the best choice for n_2 is $\sqrt{n_1 n_3}$. However the drawback of single coatings is that they are wavelength selective. One approach to increase to bandwidth is by going to multiple layer system.

By using more layers, it will result in lower total reflectance. Therefore, another way to achieve zero reflection is by creating a gradient from n_1 to n_3. Theoretically this would also result in a 0 reflectance values of zero, however is impractical as there is a lack of materials with such refractive indices.

Our solution takes advantage of both the anti-reflective systems described above. The mesoporous silica provides a tuneable refractive index depending on the binder-particle ratio; and thus can be tuned in the range of $n = 1.2$ to 1.35. This will allow us to reach the $\sqrt{n_1 n_3}$ condition. Furthermore, as the nanostructures are sub-wavelength sizes, they act as a gradient, greatly minimizing the interface, and thus the reflection.

D.3 Detailed Functional Specifications

D.3.1 Reflection, Transmission and Substrate Angle Requirements

To quantify reflectance, transmission, and substrate tilt requirements, a multi-wavelength spectrometer and Arduino will be used to measure these values. The spectrometer will obtain the reflectance and transmission values of the substrate, and the Arduino will be used to tilt the substrate. The obtained values of reflectance and transmission at various tilt angles for different substrates will be compared against the calculated values of reflectance using the Fresnel equations to then obtain a measure of how well the sample was fabricated, and to verify the consumer requirements. The reflection and transmission values will be taken at the 2 boundary incident angles plus a normal incident specified by the customer requirements.

Based upon the customer requirements, the anti-reflective substrate needs to reflect no more than 10% at an 75 to 105 degree incident light angle, and transmit more than 85%(primary requirement). It should reflect no more than 5% at an 60 to 120 degree incident light angle, and transmit more than 90%(secondary requirement). If time allows, it would be desirable to reflect no more than 2% at an 30 to 150 degree incident light angle, and transmit more than 95%(tertiary requirement).

D.3.2 Coating Hardness, Durability and Lifetime

The anti-reflective coating lifetime will be evaluated according to the primary, secondary, and tertiary objectives outlined within the Consumer Requirements section of this report. The primary objective is the complete retainment of transmission, reflectance, and aesthetic properties following mild surface contact, which has subsequently been defined as the attainment of a Mohs hardness value of 4.0. This quantity corresponds to the approximate hardness of polycarbonate, which the mesoporous silica is intended to protect [8].

The secondary objective is the complete retainment of transmission, reflection, and aesthetic properties following extensive surface contact, which has subsequently been defined as water exposure in addition to the attainment of a Mohs hardness value of 6.0. This quantity corresponds to the approximate hardness of many glasses [9].

The tertiary objective is the complete retainment of transmission, reflectance, and aesthetic properties following abrasive surface contact, which has subsequently been defined as isopropanol exposure in addition to the attainment of a Mohs hardness of 9. This quantity corresponds to the approximate hardness of Gorilla Glass, which is employed in the displays of a vast quantity of electronic devices, such as tablets and smartphones [10].

The Mohs hardness test involves the frictional, abrasive exposure of the sample to various specimens of differing hardnesses, followed by subsequent sample analysis. The presence or lack of visible scratches upon the sample following this test is indicative of the sample hardness and thus the retainment of transmission, reflection, and aesthetic properties. For instance, if the anti-reflective coating withstands abrasive polycarbonate exposure, then its hardness value is superior to that of polycarbonate and its transmission, reflectance, and aesthetic properties will have been retained.

D.3.3 Coating Fabrication Methods

In order to create the anti-reflective coating the nanostructure pattern must be transferred from the master mould to the substrate. For this design project the transfer is being done through two methods. The first pattern transfer method is UV curing; with UV curing the substrate is a liquid initially and is poured into the mould and then cured. Once cured the substrate is a solid and can be removed from the mould with the pattern transferred to its surface. The second pattern transfer method is hot embossing; with hot embossing the substrate is heated to beyond its glass transition temperature and then the nanostructured mould is pressed into the surface, the substrate is then left to cool and when the mould is removed the pattern has been transferred to its surface.

Once the pattern has been transferred to the surface it is fragile and must be protected. A layer of mesoporous silica (MPS) is being used to protect the nanostructures. In order to coat the nanostructures with MPS two methods are being investigated, with a heavy emphasis on the first method. The first method is dip coating; in dip coating the sample is submerged in the MPS solution and then drawn out slowly to produce a uniform coating of the desired thickness. The second method is spray coating in which the sample is sprayed with the MPS solution to create a uniform coating.

In order to judge the success of our pattern transfer the substrate must exhibit similar anti-reflectance properties to the mould, this will be evaluated visually by looking for areas that are reflecting light. The samples will also be tested with a spectrometer for a more analytical evaluation of their anti-reflective properties. This criteria will be judged successful if there are no visible areas of reflectance and the reflectance values are within 25% of the master mould.This criteria is a priority 1 criteria. In order to judge the success of our coating procedure the thickness and uniformity of the coating will be examined using cross-sectional SEM and aerial SEM respectively. This criteria will be judged successful if the coating is uniform $\pm$ 5%. This criteria is a priority 1 criteria.

Appendix E Verification Plan

E.1 Introduction

As described within the Functional Specifications, this anti-reflective system is comprised of two separate components: a nano-structured surface and a deposited mesoporous silica film. This combined coating will result in a passivated, contact-resistant anti-reflective surface. Prior to prototype construction, the creation of a mathematical model is necessary in order to gain a quantitative comprehension of this anti-reflective system and hence to obtain desired design parameters.

For a simple substrate, the maximal reflection at normal incidence experienced by a propagating electromagnetic wave from its transition from a material with refractive index n_1 to a material with refractive index n_3 may be calculated as

$$R = \left[\frac{n_1 - n_3}{n_1 + n_3}\right]^2 \tag{8}$$

The maximal reflection at normal incidence following the introduction of a surface coating layer with an intermediate refractive index, n_2, may be expressed as

$$R = \left[\frac{n_2^2 - n_1 n_3}{n_2^2 + n_1 n_3}\right]^2 \tag{9}$$

Note that the above formulae does not incorporate destructive interference, which occurs for an intermediate film thickness of $\frac{\lambda}{4n_2}$; hence, the true normal incidence reflectivity values will be of lower magnitude than those obtained from these equations. It is evident from these equations that increasing the quantity of materialistic layers within the coating reduces its reflectivity value. As the nano-structures incorporated within the design of the anti-reflective coating are of sub-wavelength size, they do not reflect light in the traditional sense; instead they act as a gradient of refractive indices, in which the effective refractive index may be obtained according to the following equation:

$$n_{effective} = n_1 \times \frac{volume_1}{volume_{total}} + n_2 \times \frac{volume_2}{volume_{total}} \tag{10}$$

Hence, the increased volume fraction of the higher refractive index material experienced by propagating light results in an optimized index gradient. This arrangement further decreases the reflectivity value of the anti-reflective coating [1].

Theoretically, this configuration provides a perfect interface between air and the reflective substrate, thus preventing reflection. This has been experimentally verified: *black silicon*, which contains randomized, sub-wavelength nanostructures, results in a 2% reflectance value at normal incidence. Conversely, typical silicon results in a 30% reflectance value at normal incidence [11]. However, the fragility of these structures requires their passivation for daily use.

Substrate protection requires the deposition of another material. It is necessary to keep the refractive index of this material as low as possible in order to minimize its interface with air. MgF_2 - used in the chemical vapour deposition of anti-reflective coatings - has a refractive index of 1.38 - the lowest known solid refractive index [3]. According to Equation 9, the use of this material enables the attainment of a 2.5% reflectance value at normal incidence. This limits the potential of any anti-reflective coating comprised of this material. The second section of this system comprises mesoporous silica nanoparticles (MPS), which also exhibits anti-reflective properties [3]. Its base refractive index of 1.12 can be increased - or tuned - by the addition of binding material [3]. By refining the MPS-binding solution ratio, the refractive index of the anti-reflective coating can be optimised while maintaining an adequate coating hardness. With the selection of a suitable refractive index, the thickness of this coating can be further engineered to decrease the surface reflectivity - thickness refinement to $\frac{\lambda}{4n_2}$ will be reduce reflectance due to induced destructive interference.

Reflectance minimization requires the optimization of related process variables, such as the MPS-binder volume ratio, MPS film thickness, and MPS refractive index. Once an adequate model has been produced, these MPS parameters will be simulated - prior to prototype construction - in order to save time and expensive prototype tests. The model can also be utilized to determine error sources in previously-constructed prototypes.

E.2 Simulations

There are several simulations that need to be performed to verify the anti-reflective properties of the coating before proceeding to prototype trials. The first simulations are back of the envelope calculations using the equations presented above, not accounting for destructive interferences. Next, analytical solutions Maxwell's electromagnetic equations will be explored that will cover the reflection, absorption, and transmission of different polarizations and wavelengths of light at different incident angles. Finally, simulations will be run using COMSOL and will be cross-correlated with the analytical solution. The first simulation will be of a simple single layer substrate to establish a baseline of reflection for a blank substrate. After this baseline has been established it is now necessary to bring insert the nanostructures to determine their effect on the reflection.

E.2.1 Nano-structure Simulations

In stepwise progression, these nanostructures will be modelled to determine the effect they have over a plain substrate. The first test will approximate these structures as a 130 nm thick coating with a refractive index equal to the average between the substrate and air. The next simulation will then approximate these structures as several discrete layers forming a rough gradient between substrate and air to determine the effect of multilayer approximation. Finally this model will be expanded to a large number of extremely thin layers to model the true gradient effect present with these structures. This final model will also be used to examine the effect of the mesoporous silica coating on the overall reflection.

E.2.2 Mesoporous Silica Simulations

After examining the reflective properties of the nanostructured substrate, it will be necessary to optimize the characteristics of the mesoporous silica coating used to protect these structures. Using an average refractive index for mesoporous silica, the first simulation will examine the effects of a mesoporous silica layer on top of the nanostructured surface. Once again this will progress from the simple three layer system of substrate, nanostructures and mesoporous nanoparticles to the gradient system with a large number of extremely thin layers representing the true behaviour of the nanostructures. These simulations can be compared using different refractive indexes for the mesoporous silica, as well as different film thickness, which will change the destructive interference properties. Initial test thickness for the first prototype runs will be extracted from the most anti-reflective simulations tested here.

E.3 COMSOL Simulations

The final test will be to model this system using COMSOL, and finite element analysis. Using the electromagnetic wave module it will be possible to examine the true interference effects created by the interaction between layers of different refractive indices. This model will be the final test for this anti-reflective system and it should indicate any fringe effects that were not seen in the mathematical models. Initial results shown in Figure E.2 demonstrate that transmission is increased using the multi layer system, even with thickness's not equal to $\lambda/4$, confirming the back of envelope calculations. Further refining of the model should increase transmission, as $\lambda/4$ conditions are met and more layers of nanostructures are simulated. Also, after validating our model against our experiments, we will be able to use COMSOL to calculate quickly reflections at different angles to ensure we meet our customer requirements. After each run we will refine the model to match the results obtained and can optimise various parameters, such as refractive index, and thickness before proceeding to the following production run.

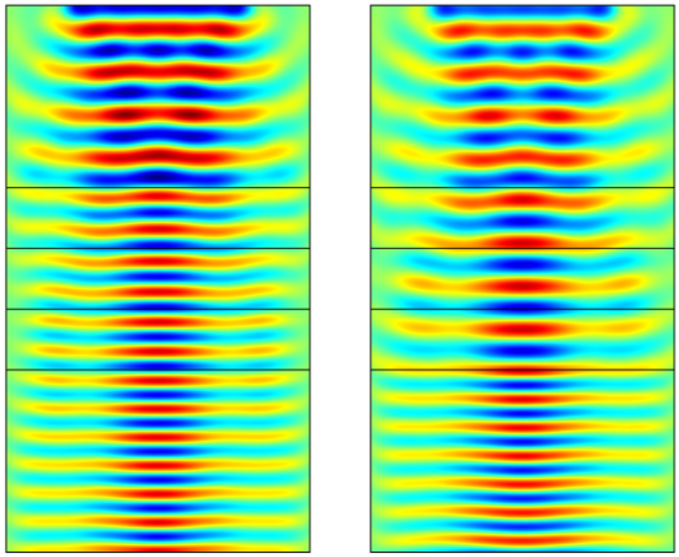


Figure E.1: COMSOL simulation showing the proposed solution on the left and just an air-glass interface on the right

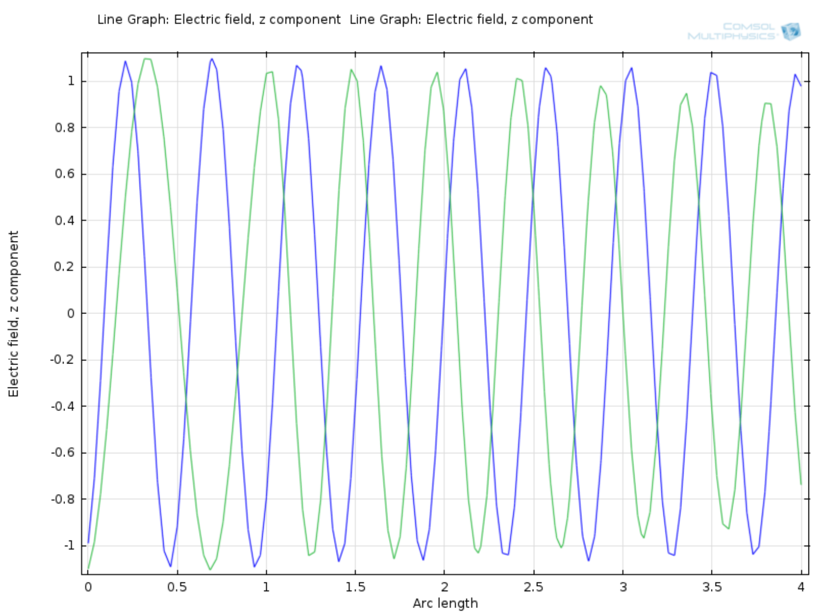


Figure E.2: COMSOL results of the electromagnetic wave that is transmitted. The left system is in blue and the right system in green.

Appendix F Test Plan

F.1 Introduction

This document will serve as a reference test plan to verify that the prototype passivated anti-reflective coating meets all the performance standards. These requirements, detailed in Consumer Requirements, and stated more specifically in Functional Specifications, should be met by the final prototype in order to verify a successful design. This document outlines the performance testing methods for each aspect of the prototype in order to validate the final performance specifications.

For our prototype there are a number of sample iterations, namely: Ormocomp, Norland Optical Adhesive and Polycarbonate that all need to undergo similar tests to quantify their associated pattern transfer method, namely: Mesoporous Silica (MPS) film thickness, optical reflection and transmission characteristics, and hardness values. While the exact specifications for each of these tests on each of these substrate may vary, the target specifications and testing procedures will all be the same. Therefore the final functional prototype will be assembled using the best material from these different sample tests.

The required test procedures can then be broken down into four categories, with a more detailed breakdown of each category with respect to sample materials. Each sample will be required initial nanostructure analysis, and post pattern-transfer nanostructure analysis to ensure that the required specifications for these nanostructures are maintained throughout the construction phases. These structure analysis tests, as will be detailed later, will be quantified through Field Emission Scanning-Electron Microscopy (FE-SEM) Imaging. The next test procedure will measure the film thickness and film uniformity of the MPS coating. Precise film thicknesses are required to produce an anti-reflective destructive interference effect at the surface of the sample. These film thickness tests, as will be detailed later, will also be quantified through FE-SEM imaging and ellipsometry measurements. The next test procedure will measure the optical characteristics of the dual anti-reflective coating present in each of the different samples. These reflection and transmission optical tests, as will be detailed later, will be quantified using a broad spectrum light source and a light intensity photodetector to determine the intensity of transmitted or reflected light at different wavelengths and across different incident angles. Finally the last test procedure will measure the physical characteristics of the sample coating, more specifically the hardness of the coating and it ability to withstand various environmental conditions. These physical tests, as will be detailed later, will test the hardness of the material with a Mohs hardness test, and the ability to withstand various liquids without destroying the surface coating. The results will be quantified with the specific Mohs hardness value, visual inspection of the surface for scratches or defects, and additional optical testing to ensure that the reflection and transmission has not changed.

F.2 Testing Procedures and Qualitative Requirements

Detailed below are the specific testing procedures and qualitative specifications required to verify the prototype for each test procedure. As it was previously mentioned, the final prototype will be constructed using the most successful material based on these test procedures.

F.2.1 Optical Testing

Since this project entails the development of an anti-reflective coating, transmission maximization and reflection minimization are desired. However, these properties must be independently assessed, as there exists a third optical phenomenon - absorption - that transpires when electromagnetic radiation is incident upon a surface.

An additional objective is the parameterization of these aforementioned properties as functions of incident angle and wavelength (i.e. the reflection and absorption of these nanostructures are functions of wavelength and incident angle). Angular transmission maximization and angular reflection minimization are desired. Wavelength transmission maximization and wavelength reflection minimization are desired.

A multi-wavelength spectrometer will be used to test the optical transmission and reflection of the samples that undergo this procedure. Furthermore, a servo motor and a sample holder will be incorporated into the set-up to measure transmission and reflections over several incident light angles.

The initial transmission and reflection evaluation of the nanostructured materials will occur at normal incidence (0°). The samples will be inserted into the designated spectrometer and subsequently subjected to the broadband wavelength spectrum. Next, the obtained reflection and transmission data will be parametrized - and graphically displayed - as functions of incident wavelength.

Following this process, angular transmission and angular reflection evaluation will be performed within the broadband wavelength spectrum. The samples will be mounted upon the sample holder, which will be connected to the servo-motor and driven by the Arduino board. They will subsequently be subjected to the broadband wavelength spectrum across a myriad of angles (0° to 90°). Next, the obtained reflection and transmission data will be parametrized - and graphically displayed - as functions of incident wavelength and incident angle.

The optical testing plan will verify if the customer requirements for reflectance is satisfied, namely: a primary, secondary, and tertiary requirement that the reflectance and transmission is at <10% and >85%, <5% and >90%, and <2% and >95% each respectively with an incident angle variation of 15, 30, and 60 degrees relative to a normal incident angle for all visible wavelengths each respectively.

F.2.2 Physical Testing

A Mohs hardness value of 4.0 is desired as the primary consumer requirement, corresponding to the hardness of polycarbonate. A Mohs hardness value of 6.0m is desired as the secondary consumer requirement, corresponding to the hardness of borosilicate glass. Finally, A Mohs hardness value of 9.0 is desired as the tertiary consumer requirement, corresponding to the hardness of sapphire.

The testing procedure for the Mohs hardness is to scratch the surface of our samples with the samples of known hardnesses to determine the harness of our sample. The inability of a test material to scratch our sample is indicative of the superior hardness of our sample; if the test material can scratch our sample then our sample is softer than the test material.

Physical testing will employ various test materials of differing Mohs hardnesses in addition to the anti-reflective sample. Visual inspection will subsequently be conducted in order to evaluate sample hardness.

F.2.3 SEM Testing

The primary imaging mode will employ the use of secondary electron imaging mode. As the sample is primarily constituted of glass, there will be little material composition contrast available. Instead, secondary electron imaging will offer the best imaging resolution for the desired purposes.

Both aerial and cross-sectional imaging methods will be utilized. The requirement for successful aerial imaging will be the attainment of complete coating surface homogeneity, such that visible discontinuities are not present.

Cross-sectional imaging will be used to gauge the uniformity and thickness of the samples fabricated. Initially, a nanostructure height of 130 nm is desired, which represents a transfer of 90% of the original nanostructures from the mold. A variation tolerance of no more than 10% is desired throughout the sample. Similarly, an initial mesoporous silica film thickness of 120 nm at a refractive index of 1.28 is desired; however, these values will be fine-tuned in order to minimise the reflectance and maximise the transmittance.

This imaging method requires a 90% height transfer of the nanostructures from mold to substrate. Additionally, it is required that the variance in the height of the nanostructure is no greater than 10% of their 130 nm average height. Furthermore, it is required that the MPS thickness variance should also be no greater than 10% of desired 120 nm coating thickness [3].

F.2.4 Refractive Index Determination by Ellipsometry

Following the thickness determination from SEM cross sectional analysis, the refractive index can be determined by ellipsometry.

	Uncoated	MPS Dip-coated	MPS Spray Coated
Blanks		Sample 1	Sample 2
UV Cured	Sample 3	Sample 6	Sample 9
Hot Embossing	Sample 4	Sample 7	Sample 10
Injection molded	Sample 5	Sample 8	Sample 11

The black silicon master molds (sample 0) will undergo the following tests: SEM testing and optical testing in order to determine if the patterns have remained intact.

The MPS coated slides (samples 1 and 2) will undergo the following tests: SEM testing, ellipsometry and optical testing in order to optimize the dip coater pull speed and to have a reference to show that the NS improve the anti-reflective properties of the MPS.

The uncoated patterned samples (samples 2 through 5) will undergo the following tests: SEM testing and optical testing in order to determine the fidelity of the pattern transfer and to show that the NS provide anti-reflective properties.

MPS coated samples (samples 6 through 11) will undergo the following tests: SEM testing, optical testing, and physical testing in order to determine the thickness of the MPS coating, to determine the anti-reflective properties of the coated sample, and to determine the passivation effects of the MPS coating.

Appendix G Design Specifications

G.1 Introduction

There are three principal requirements of our anti-reflective coating. Firstly, as the name would suggest, that it is antireflective; secondly, that the coating is resilient to environmental and physical stresses; and thirdly that the coating is relatively inexpensive.

The coating is comprised of three distinct parts, the protective mesoporous silica (MPS) coating, the nanostructures on the substrate, and the substrate itself. Each of these components contributes to the requirements of our coating in different ways.

The protective MPS coating will be created with a binding solution with mesoporous silica beads suspended within it. The coating is strong and scratch-resistant, which enables it to be used in applications such as device displays. It also chemically-resistant, protecting it from environmental stresses.

The nanostructures reduce interfacial effects between the MPS coating and the substrate, increasing the anti-reflective properties of the system. The nanostructures also have a much higher surface area per unit area, which increases the adhesion between the MPS coating and the substrate, further strengthening the coating. Finally, the nanostructures are also inexpensive and simple to both fabricate and to transfer to the substrate.

The substrate should be utilized extensively within industry so that the antireflective coating is not restricted in its applications and remains inexpensive.

G.2 Antireflective Coating Components

G.2.1 Mesoporous Silica Film

The mesoporous silica nanoparticle coating is critical to the functionality of an anti-reflective passivized substrate. These particles act as a material with a tunable refractive index, capable of antireflection at specific film thicknesses, while also providing surface hardness to the final prototype. The requirements for this coating are a tradeoff between anti-reflectance and coating strength, while maintaining adhesion to the nanostructures. The specifications listed in this section act as initial conditions, and are subject to simulation results and practical testing, as the tradeoffs between surface hardness and anti-reflectance, subject to MPS: Binder ratio, film thickness and deposition technique.

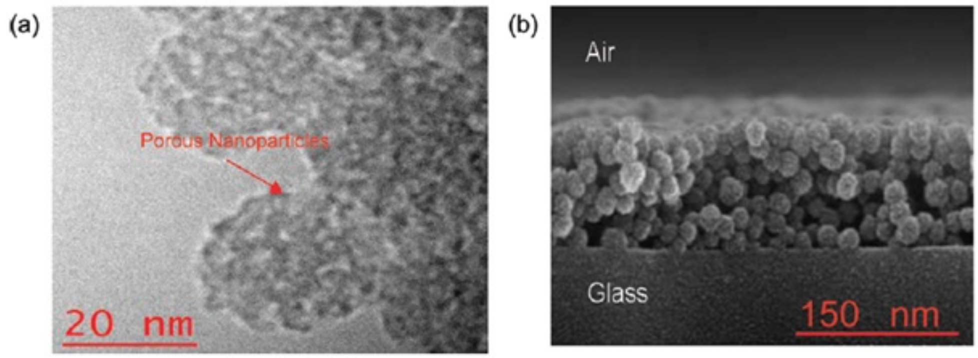


Figure G.1: Individual mesoporous silica nanoparticles (a) imaged using high-resolution TEM, and (b) particles deposited into a film imaged by SEM [3]

The MPS used for this anti-reflective coating was purchased from NanoScape AG as a $10wt\%$ solution suspended in isopropanol. This solution will be further diluted down to 1.5% before mixed in with the binder solution. The main properties of interest with respect to the MPS is the average particle size, pore size and porosity of the individual silica nanoparticles. These characteristics all impact the refractive index of the resultant MPS film, and therefore the anti-reflective properties. The nanoparticles used here have an average diameter of $25nm$ and a pore size of $2-4nm$. Images of these nanoparticles seen in literature are also shown below in Figure G.1 both as high-resolution TEM images, and SEM cross-sectional images of the resulting particles as an anti-reflective coating. The specific characteristics of this MPS creates a minimum refractive index of 1.12, which can be increased by changing the ratio of binder in the system. The porosity of the particles, or the ratio of pore to particle volume, controls the refractive index of the particle, and should be as high as possible to allow the maximum loading of binder between particles to match the refractive index and give mechanical strength. Initial testing will focus more on the surface hardness, as discussed later, but the exact value for the MPS refractive index will be determined through simulation, and then verified in the working prototype.

As it was previously mentioned, the strength of this anti-reflective coating is subject to numerous factors, and trades off with the anti-reflection of the substrate. In principle increasing the hardness of the coating increases the amount of material present in the coating binding it together. This therefore increases the relative refractive index of the coating, therefore increasing the reflection, as there is a more abrupt transition from air to the coating. This tradeoff is already seen in literature, with the results shown in Figure G.2. The main design consideration is anti-reflectance so long as the coating can withstand mild contact.

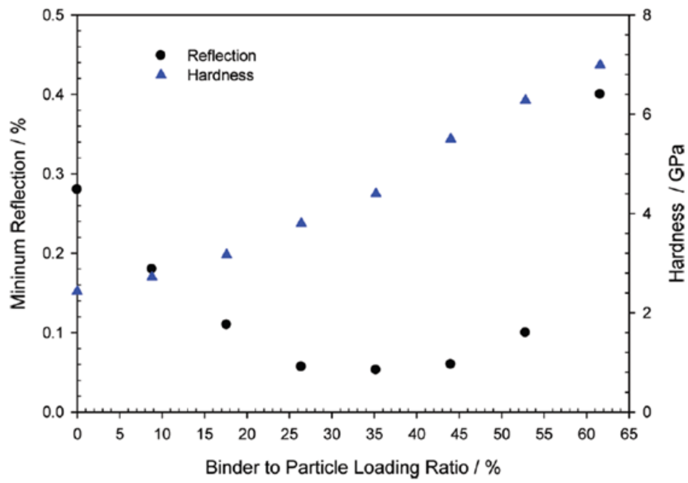


Figure G.2: Reflection and hardness as a function of mesoporous silica to binder ratio [3]

Therefore, as per Figure G.2, testing will begin with a MPS:Binder ratio of 35%, as reported by Moghal et al. [3]. A study will be conducted to verify the behaviour seen in literature. The refractive index of this material will can then be measured for the optimized coating.

Another design consideration for this system is the thickness of the MPS film. For specific film thicknesses another anti-reflective effect can be created by destructive interference between the two film interfaces. This effect is maximized for thicknesses of $\frac{\lambda}{4n_2}$ where n_2 is the refractive index of the film. This thickness is difficult to calculate, as λ is not a fixed constant, but the range of visible wavelengths. In addition the thickness of the coating requires a reference to the nanostructures, and it is unknown if this formula applies to the top, middle or base of the nanostructures. Finally, as stated in Functional Specification, this coating will have to remain anti-reflective at various incident angles. Therefore the target thickness will have to be considered at multiple angles. The initial film thickness will be $120 \pm 5nm$, as the value seen in literature, with optimization to be performed based on the numerical models and experimentation [3].

G.2.2 Nanostructures

The nanostructure shape and quality is of utmost importance concerning substrate antireflective properties. Functional requirements that are impacted by the final nanostructures in the substrate are substrate reflectance, substrate transmission, and substrate hardness. Functional requirements that are impacted by the pattern transfer process are the required nanostructure aspect ratios and nanostructure yields. These properties indirectly impact coating reflectance and transmission. The nanostructures impact the reflectance and transmission of the coating as they create a gradient refractive index throughout its entirety. From consultant professors at the University of Waterloo and Denmark Technical University, it was found that an aspect ratio of 1.3 and a structure height of 200nm yielded superior antireflection results in the visible spectrum [4].

Of further importance is the spatial frequency of the nanostructures. A spatial frequency of 160nm (a nanostructure interspacing of 160nm) was found to provide minimal reflection [4].

As these idealities will not be entirely met by the attained nanostructures, a threshold variance needs to be determined to provide coherent antireflection for the substrate regardless of electromagnetic incidence angles. A variance of less than five percent is required.

In summary, Table G.1 lists the recommended parameters that will result in optimal antireflection results when designing the nanostructures.

Table G.1: Recommended AR coating parameters.

Parameter	Parameter Values
Spatial Frequency (Structure Interspacing)	160nm
Aspect Ratio	1.3
Structure Height	200nm
Spatial Frequency Variation	5
Aspect Ratio Variation	5%
Structure Height Variation	5%

G.2.3 Substrate

Substrate selection is important in order to achieve the required antireflective properties: Firstly, it is important that the substrates have high transmittance and low absorbance in the visible range. Currently-used industrial materials are preferred due to their ease of integration. Additionally, the substrate should be structurally rigid in order to withstand normal handling and nanostructure pattern transfer. Finally, material costs should be minimized.

The selected substrates are functionally-verified industry standards. Firstly, ormocomp was chosen as a reference material as its successful pattern transfer has been well-documented. Secondly, Norland Optical Adhesive, another industry standard, will be utilized. It is used in the fibre optics industry as a UV cured clear polymer. Finally polycarbonate sample is considered, as the final integration into devices.

Appendix H Verification Data

H.1 Introduction

In order to optimise the anti reflective properties of the coating, lumped element modelling (LEM) was performed. The ideal properties and thicknesses where obtained from LEM, and experimental results where compared to the models in order to improve the reliability and accuracy of the models.

H.2 Analytical reflectance derivation

Reflectance and transmission were first analytically derived from first principles, namely, that of the Maxwell equations. Starting with the SI forms of the Maxwell equations, given as:

$$\nabla \cdot \overrightarrow{B} = 0 \tag{11}$$

$$\nabla \times \overrightarrow{E} = -\frac{\partial \overrightarrow{B}}{\partial t} \tag{12}$$

$$\nabla \cdot \overrightarrow{D} = \rho \tag{13}$$

$$\nabla \times \overrightarrow{H} = \overrightarrow{J} + \frac{\partial \overrightarrow{D}}{\partial t} \tag{14}$$

The anti reflective structure was represented by a multilayer surface composed of N parallel layers with a thickness corresponding to each of the layers. The refractive index of these layers increase linearly from the refractive index of MPS to the refractive index of the substrate used. The entire refractive index model is described to have a semi-infinite layer of vacuum, followed by the anti-reflective substrate which is composed of a thin-film of MPS, the gradient refractive index layer where the refractive index of MPS transitions to the dielectric layer of choice used, followed by a semi-infinite layer of the dielectric layer of substrate.

From the Maxwell equations, Davis[5] derived a recursive algorithm for the light travelling through the substrate for both transverse electric (TE) and transverse magnetic (TM) modes. The recursive algorithm was found to be as follows:

$$R = |R_0|^2 \tag{15}$$

where R_0 is a coefficient determined from

$$R_j = a_j \frac{F_j + R_{j+1}}{1 + F_j R_{j+1}} \tag{16}$$

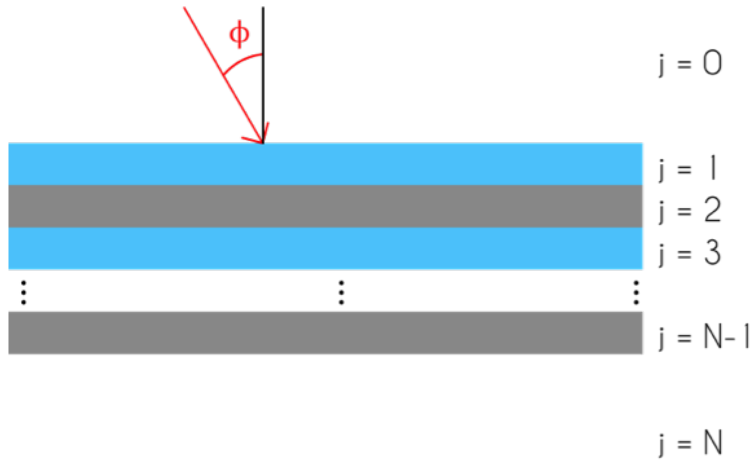


Figure H.1: Antireflective substrate refractive index sketch

starting from $j = N$, using $R_{N+1} = 0$, where j is the layer index. The coefficients a_j, and F_j are

$$a_j = e^{2ik_z^{(j)}d_j} \tag{17}$$

$$F_j = \frac{f_j - f_{j+1}}{f_j + f_{j+1}} \tag{18}$$

f_j is a constant that differs between TE and TE modes, given by

$$f_j = \begin{cases} \frac{k_z^{(j)}}{\mu_j} & \text{, TE mode} \\ (\frac{\mu_j c^2}{n_j^2})k_z^{(j)} & \text{, TM mode} \end{cases} \tag{19}$$

and

$$k_z^{(j)} = \frac{\omega}{c}\sqrt{n_j^2 - cos^2\pi - \phi} \tag{20}$$

where ω is the angular frequency of incident light, n_j is the refractive index of that particular layer, μ_j is the layer magnetic permeability, and ϕ is the incident light angle. Using this algorithm, reflectance profiles were produced.

H.3 Refractive Index Profile Derivation

The next step was to calculate the anti-reflective substrate's refractive index profile. The substrate starts off with a thin-film of MPS, followed by a nanostructure. This nanostructure is essentially a periodic series of circular cones. In other words, the nanostructure's cross-sectional radius linearly increases. Keeping this in mind, a refractive index profile was generated, as shown in Figure H.2.

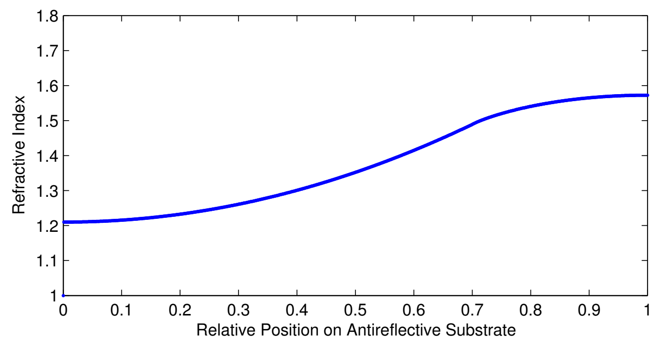


Figure H.2: Antireflective substrate refractive index function

H.4 COMSOL Simulations

Results obtained in COMSOL are heavily dependant on the mesh selection, and in order to converge the model a high mesh size was needed. It was decided that the time required to solve the models was not economical and thus not pursued any further. Also, due to the simple model required and the wave nature of light, analytical and LEM simulations provided to be much more powerful tools then finite element analysis.

H.5 Python Simulations

Simulations were performed in Python using the EMpy library[6]. The validity of the library was first determined by comparing the results to those obtained from the methods described above. After validating the model, various cases were investigated.

First the base case is simulated. This is the single anti-reflective coating. In Figure H.3, we can see that the reflection is very high for all wavelengths other than the desired wavelength.

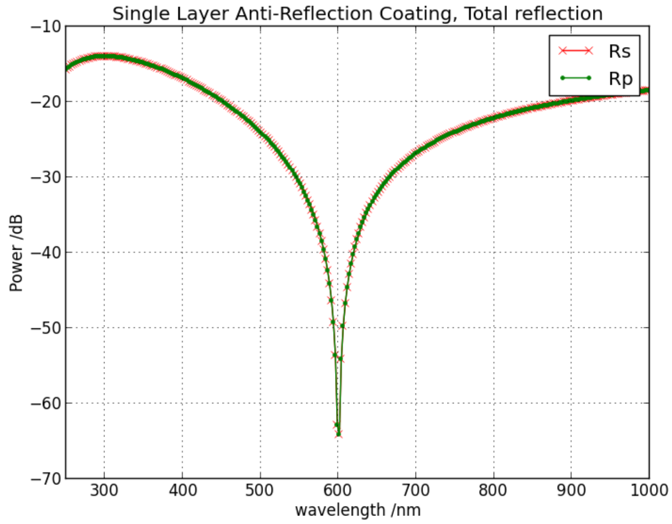
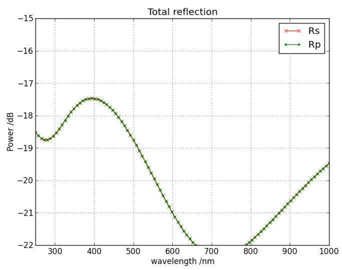


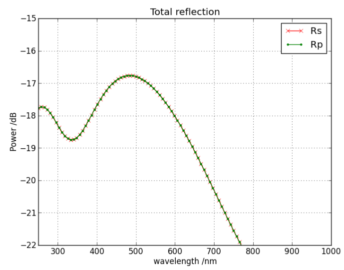
Figure H.3: Total reflection of a single layer anti-reflective coating designed for 600nm

The height of the nanostructures are fixed from the fabrication procedures to be 200nm [4]. The thickness, as well as the refractive index of the mesoporous silica layer need to be fine tuned to minimize total reflection.

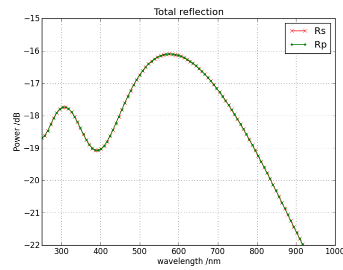
First, the ideal thickness was determined. Using the refractive index of 1.38 obtained from [3], the mesoporous silica height was varied from 20nm to 340nm, which roughly correspond to the upper and lower bounds achievable using dip coating. It can be seen in Figure H.4 that the reflection in the visible regions (roughly 350nm to 750nm) is minimized at 20nm, however that is unpractical, and thus the next best is at 220nm and thus this value was used for further tests. Because in the variation, the mps thickness should be determined experimentally by trial and error rather than by simulations.



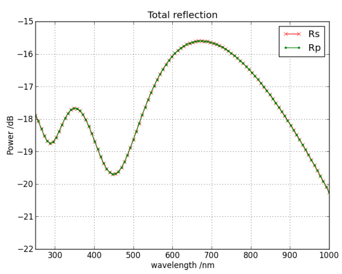
(a) $t_{MPS} = 20nm$



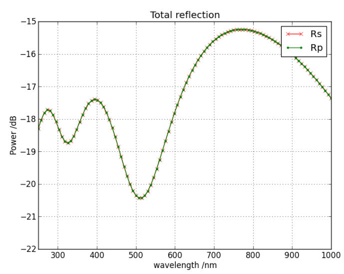
(b) $t_{MPS} = 60nm$



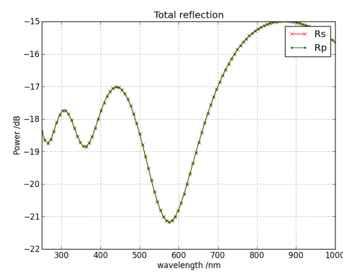
(c) $t_{MPS} = 100nm$



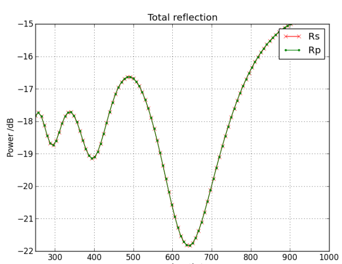
(d) $t_{MPS} = 140nm$



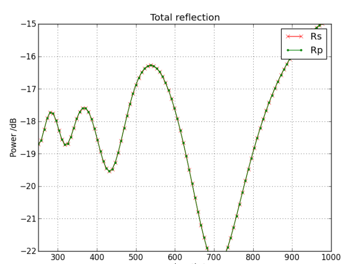
(e) $t_{MPS} = 180nm$



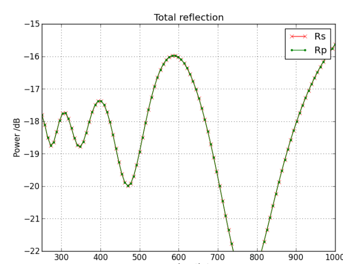
(f) $t_{MPS} = 220nm$



(g) $t_{MPS} = 260nm$



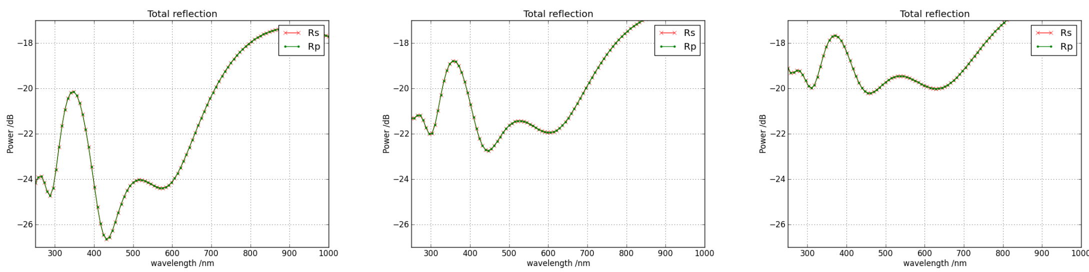
(h) $t_{MPS} = 300nm$



(i) $t_{MPS} = 340nm$

Figure H.4: Total reflection with varying MPS thickness

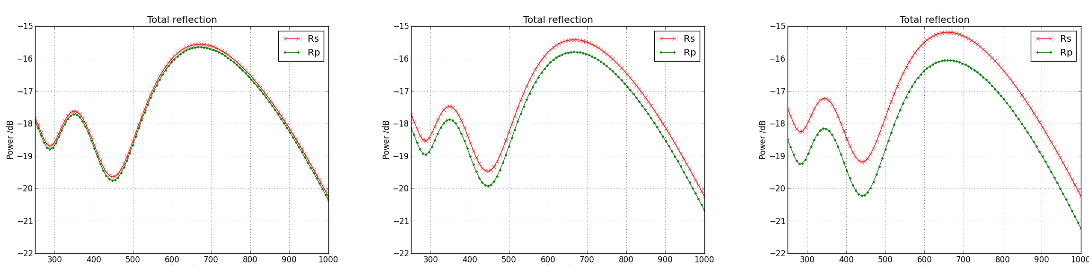
Next, the refractive index is examined. Moghal et al [3] report being able to tune the refractive index anywhere from 1.12 to 1.45, depending on the binder to MPS ratio used. Figure H.5 shows the reflections obtained for various MPS refractive index. The optimal refractive index was determined to be as low as possible. Obviously, if it was a continuous gradient from air to substrate would be ideal. However, that is not practical as the structures need to be protected. Instead, the refractive index will be tune according to the strength data that we will obtain. Moghal reports 1.28 being a good balance between anti-reflective properties and rigidity/hardness.



(a) $RI = 1.15$ (b) $RI = 1.20$ (c) $RI = 1.25$

Figure H.5: Total reflection with varying MPS refractive index

Finally, the LEM model was used to simulate the reflection obtained at various angles. As seen in Figure H.6, the total reflection is increased at angles off incidence, as predicted from Fesnel's Equations.



(a) $\theta = 5°$ (b) $\theta = 10°$ (c) $\theta = 15°$

Figure H.6: Total reflection with varying angles

H.6 Conclusions

The results confirm that the proposed project should reduce the reflection by a significant amount. It can be seen that the total reflection of the proposed solution to be around $-17dB$ to $-20dB$, whereas for an untreated surface, the reflection is $-12dB$. Similarly, the reflection for the simple mesoporous silica case, the reflection is $-12dB$ to $-15dB$, except at the desired wavelength where reflection drops to $-40dB$. Thus by adding the refractive index gradient obtained from the nanostructures the antireflective coating is more broadband and decreases the overall reflection.

Appendix I Prototype Test & Measurement Data

I.1 Introduction

The prototype for this project was measured in a variety of ways to ensure that it met the customer requirements. The successful creation of the nanostructures, and deposition of the mesoporous silica (MPS) as a continuous thin film was analyzed though the use of scanning electron microscopy (SEM). The successful creation of the nanostructures on a black silicon wafer can be seen in Figure I.1A. Following this several tests were performed to calibrate the dip coating process for MPS onto polished glass slides. Verification of a uniform deposition though dip coating can be seen by SEM in Figure I.1B.

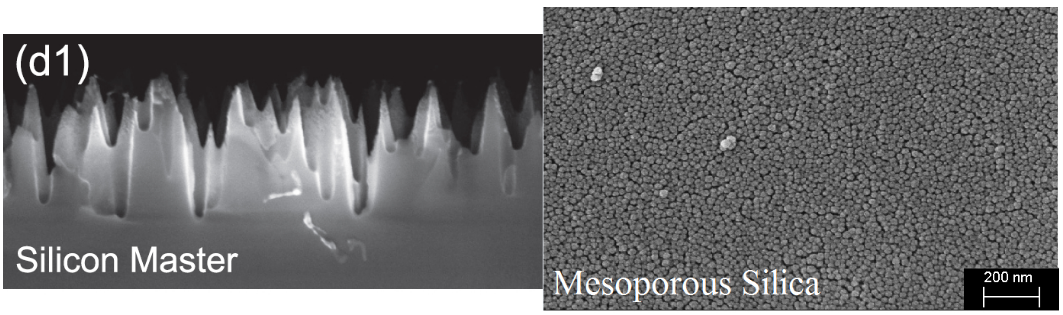


Figure I.1: Overview of the two part Nanostructures / Mesporous Silica System

I.2 Mesoporous silica

I.2.1 Transmission test

Before proceeding with the nanostructure pattern transfer, off of the black silicon wafer and onto our transparent samples, it is first important to characterize and optimize the MPS coating. The important characteristics that needed to be considered were the MPS to binder ratio and the pull speed used for dip coating. From literature it is known that higher binder ratios have a higher mechanical strength, and a higher reflection. It is also known that increasing the pull speed for dip coating produces a thicker MPS film. With this in mind nine samples were created to fully characterize the MPS coating. MPS to binder ratios of 10%, 35% and 60% binder were prepared, with samples created for each of these solutions at pull speeds of 80, 120 and 240$mm/minute$. All nine of these samples were measured using a UV-Vis Spectrometer to measure the transmission for each sample at a variety of angles. The angles used for the measurements were 0, 15, 30 and 45 degrees. The maximum transmission for each sample is usually at an angle of 0 degrees, so a comparison of the nine samples, versus a blank glass slide, is shown in Figure I.2. As for the angle measurements, the results for each of these samples at Red ($640nm$), Green ($510nm$) and Blue ($475nm$) wavelengths is shown in Figure I.3(a)-(c) .

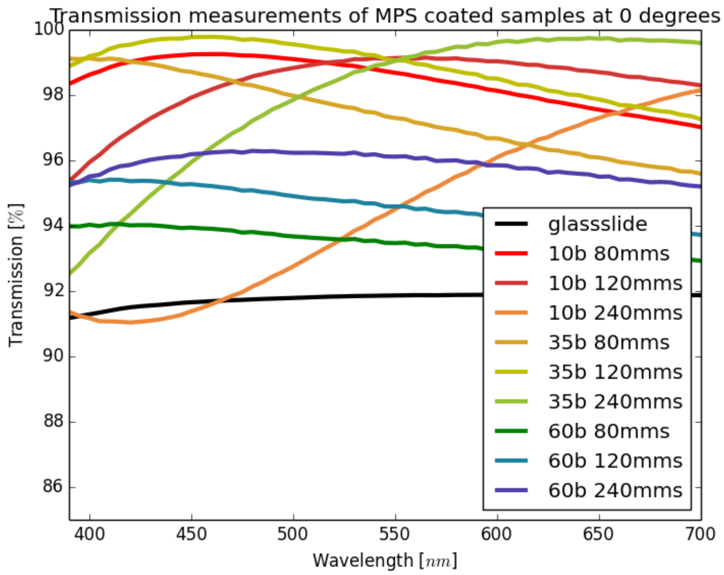
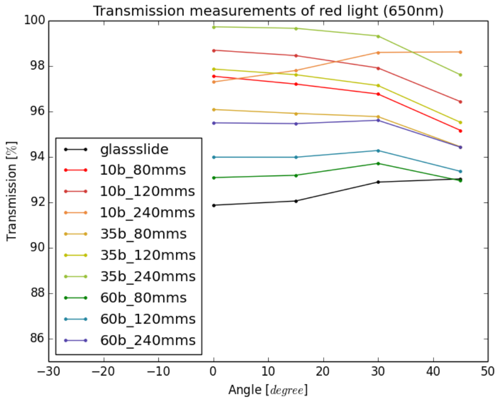
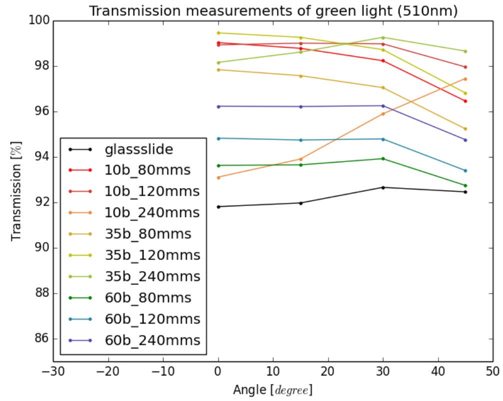


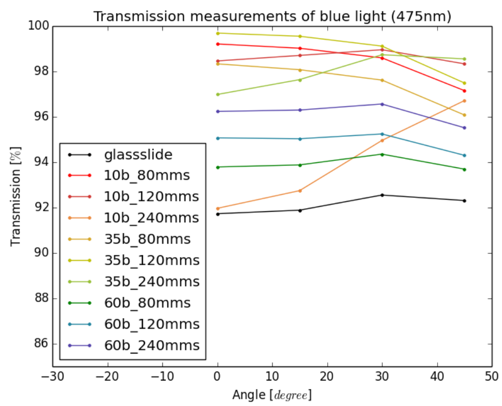
Figure I.2: UV-Vis Measurement of all MPS Binder and Pull Speed Combinations



(a) Transmission of red light ($650nm$)



(b) Transmission of green light ($510nm$)



(c) Transmission of blue light ($475nm$)

Figure I.3: Transmission obtained by UV-Vis for various samples obtained at different binder and pull speed ratios

I.2.2 Hardness test

The other characteristic of the MPS film is the hardness, which was tested using a Mohs Hardness scratch test. Initial testing of a blank glass slide yielded a hardness of 6. A median pull speed of $120mm/minute$ was chosen for scratch testing at each of 10%, 35% and 60% binder solutions. The results are shown below in Figure I.4. All of the samples were scratched using the softest mineral present (hardness = 1) which likely means that the adhesion forces between the coating and the substrate are not high enough to take a proper measurement. In subsequent testing the coating was resilient to light touch, but could be polished off using a kimwipe. This meets primary requirements, but should be further optimized for ideal film hardness.

As a different validation test for the MPS film, samples of 10%, 35% and 60% binder ratios at 120 mm/min were tested using a Nanoindentor. This measured the Hardness and

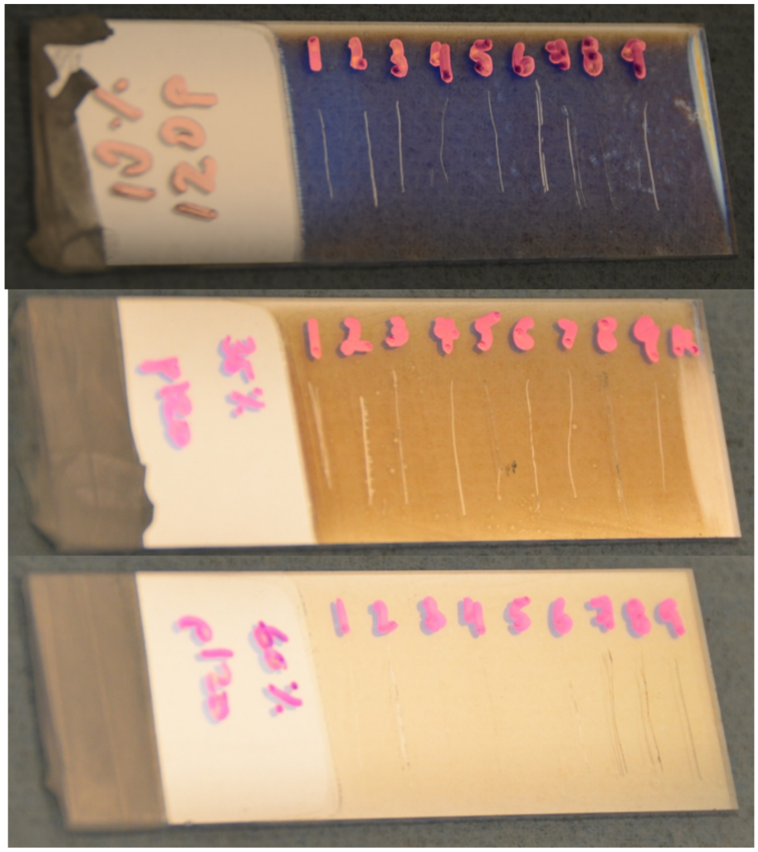
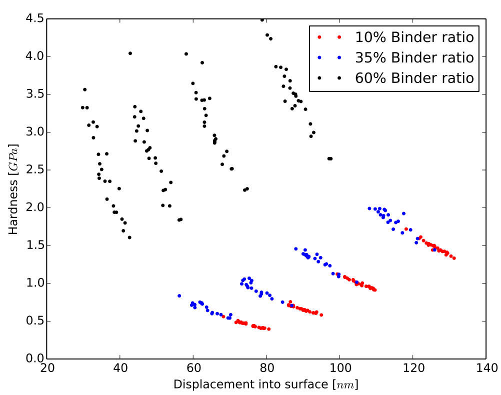
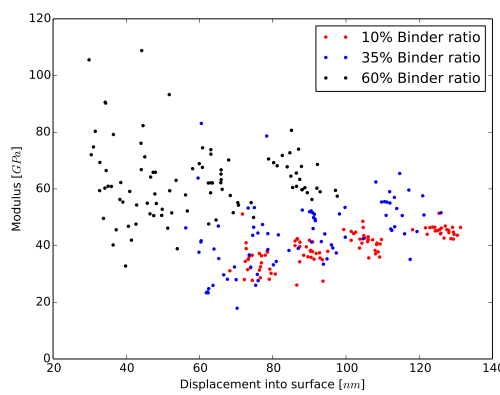


Figure I.4: Mohs Hardness testing on the MPS thin films

Elastic Modulus for the given film at varying depths into the substrate. The Nanoindentor results are shown below in Figure I.5a and Figure I.5b for the hardness and elastic modulus respectively.



(a) Sample Hardness



(b) Sample Modulus

Figure I.5: MPS Thin film properties of various binder ratios obtained by a nano-indenter using a Berkovich Tip

I.3 Nanostructures

I.3.1 Transmission test

After establishing the ideal MPS film composition, as a tradeoff between antireflection and film hardness, the next stage of testing was to transfer the nanostructure pattern from the black silicon onto the transparent medium for the final prototype. For ease of sample production initial tests used Norland Optical Adhesive (NOA), as it is a UV curable substrate so it can be poured over the black silicon and cured to make a sample. Two types of NOA were tested, NOA 61 and NOA 68, each with different curing times and chemical resistant properties. Verification of the pattern transfer was done using SEM. The results are shown below in Figure I.6. Figure I.6a shows the pattern transferred into NOA 61, while Figure I.6b shows the results for NOA 68. Both of these patterns are the negative impression of the structures, but still serve as an antireflective substrate.

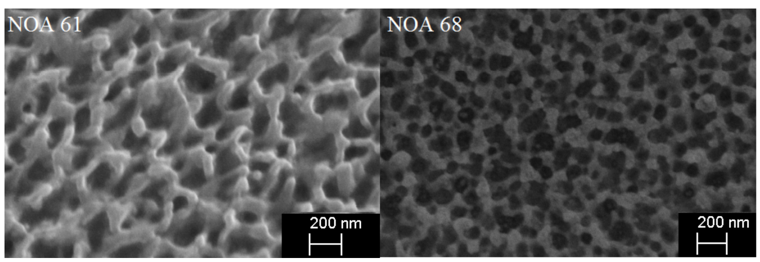


Figure I.6: SEM Images of nanotructure patterns transfered upon NOA 61 and NOA 68

After successful pattern transfer these sample were subsequently tested using the UV-Vis spectrometer to measure the transmission though each of these samples. The transmission for each of NOA 61 and 68 is shown below in Figure I.7.

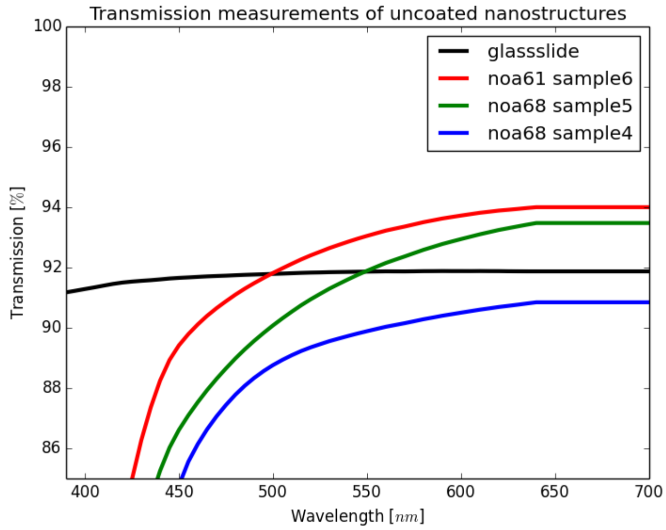


Figure I.7: Transmission measurements obtained for various NOA samples containing nanostructures without MPS

I.4 Combined test

I.4.1 Transmission test

Now that both the nanostructured NOA substrate and the MPS film characteristics have been established they must be combined to produce the final prototype. The ideal MPS characteristic were determined to be a binder ratio of 35% at a pull speed of 120 $mm/minute$. Given that the NOA 61 and 68 were so similar both were used to make combined prototypes. These samples were measured to determine the transmission at angles of 0, 15, 30 and 45 degrees. The maximum transmission for each sample is at an angle of 0 degrees, so a comparision of the samples versus a blank glass slide, is shown in Figure I.8. As for the angle measurements, the results for each of these samples at Red (640nm), Green (510nm) and Blue (475nm) wavelengths is shown in Figures I.9(a)-(c) respectively.

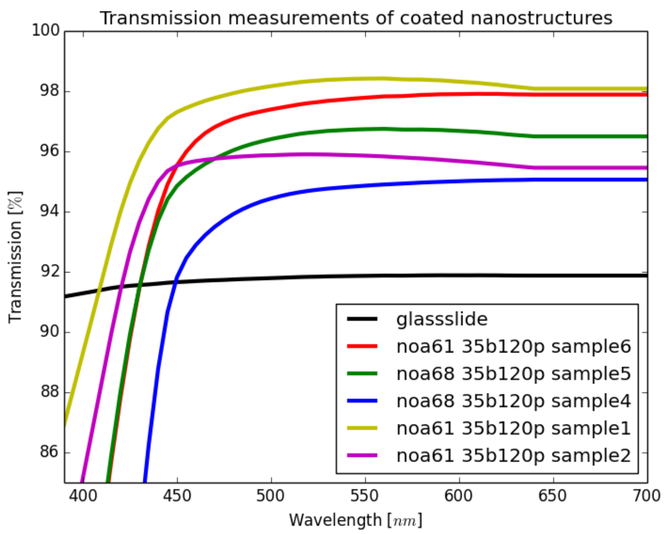
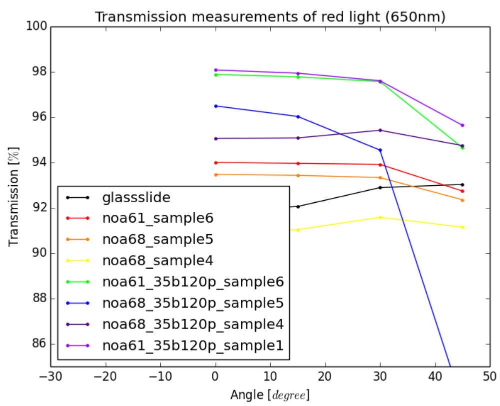
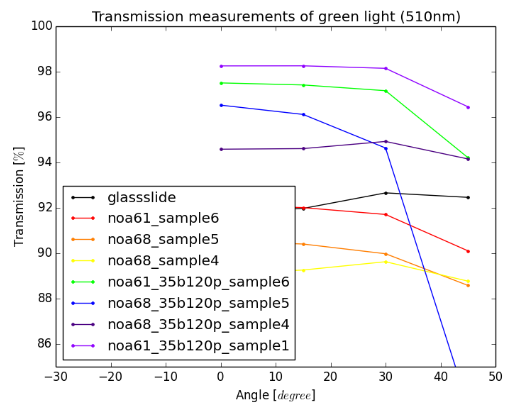


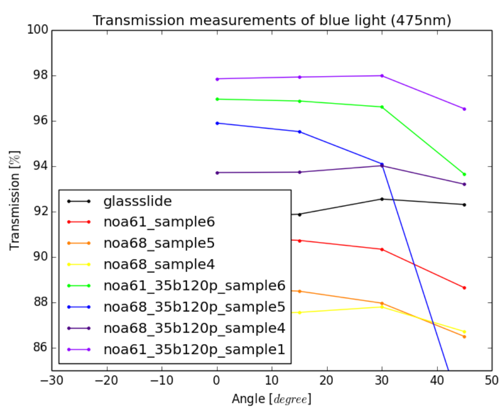
Figure I.8: Transmission measurements obtained for various NOA samples containing nanostructures coated with MPS



(a) Transmission of red light (650nm)



(b) Transmission of green light (510nm)



(c) Transmission of blue light (475nm)

Figure I.9: Transmission obtained by UV-Vis for various NOA samples both coated and uncoated with MPS obtained at different binder and pull speed ratios

I.4.2 Handling test

Given the final prototypes the hardness of the combined product must be measured again. Instead of taking scratch test measurements, the sample were tests for light touch, which had no visible effect, and wiping with a $KimWipes^{TM}$. In addition to the hardness the passivation of the prototype was also tests, by submerging the sample in water and isopropanol (IPA) to determine if there was any effect on the transmission results. The results of these three tests are shown below in Figure I.10 for the maximum transmission results at 0 degrees.

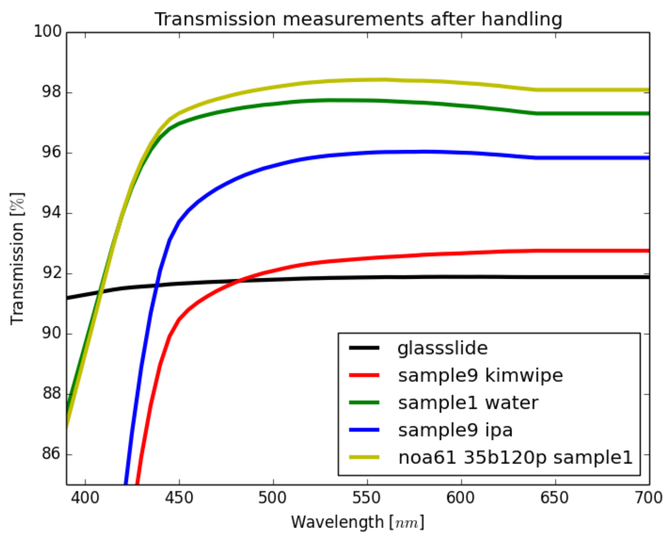


Figure I.10: Sample transmission after exposure to various elements and handling