

UV photon-counting CCD detectors that enable the next generation of UV spectroscopy missions: AR coatings that can achieve 80-90% QE

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ABSTRACT

We describe recent progress in the development of anti-reflection coatings for use at UV wavelengths on CCDs and other Si-based detectors. We have previously demonstrated a set of coatings which are able to achieve greater than 50% QE in 4 bands from 130nm to greater than 300nm. We now present new refinements of these AR-coatings which will improve performance in a narrower bandpass by 50% over previous work. Successful test films have been made to optimize transmission at 190nm, reaching 80% potential transmission.

Keywords: UV, Anti-reflection coatings, thin-films, CCDs

1. INTRODUCTION

Anti-reflection (AR) coatings have been used in a wide range of applications to increase transmission through a surface, including on CCDs at visible wavelengths. While CCDs have traditionally not been effective in the UV, treatments have been developed solve this problem. Backside illumination and Delta Doping can bring the quantum efficiency (QE) of treated devices up to the reflection limit of silicon at all wavelengths in a stable and consistent way;¹ in the UV this brings the QE to around 30%. This non-zero QE can then be increased to a much higher value with the selection of a good AR coating. Our initial work on single layer AR coatings at UV wavelengths has been successful at increasing QE to greater than 50% from 135nm and longer^{2,3}. While these coatings are a good start, they are indicative of what is possible with more complex designs.

The use of multi-layer AR-coatings at visible and IR wavelengths can provide near 100% transmission. Reaching that at UV wavelengths is a challenge due to the limited number of non-absorbing materials that can be used to make coatings. While adding a multi-layer coating to any surface can change the transmission through it, there are preferred configurations of thickness and index which will minimize reflectance.⁴ In this discussion, we restrict our work to those configurations dealing with high-index substrates, such as silicon, since these coatings are all designed for use on silicon CCDs. The first method to create AR coatings pairs a high and low index material, where both indices lie between the index of the substrate and 1.0, the index of air. Multiple layers (typically based on quarter wave thicknesses or multiples thereof) which alternate between the materials combine to minimize reflectance to nearly zero at a selected wavelength and usually twice that wavelength. Adjustment can be made to optimize the range of zero reflectance and to refine the film for best outcome. Here we do this using a computer program such as TFCalc. The quarter wave stack method works best when the index of refraction of the materials used (including the substrate) are not varying significantly over the wavelength range in question. Other limitations include the lack of a low index material lower than 1.37 (MgF₂).

A second method is to slowly vary the index of refraction from the substrate to air. This method uses layers of material that step down the index, all approximately a quarter wave thick. Films with highest index lie closest to the substrate, with each subsequent film having a lower index. Depending on the substrates and materials

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involved, these films will be optimized for large bandpasses and so can be an important component of imagers, which often require sensitivity over hundreds of nanometers. Typically, these broadband designs are made at wavelengths with a constant index of refraction for the substrate and layer materials. Silicon at UV wavelengths (100-300nm) has extremely variable optical constants, and so high QE, very broadband coatings like those made for optical wavelengths are not easily created. Instead, what we focus on in this paper is high QE at the expense of broad application and discuss only narrowband coatings for specific applications, made using multiple layers of high and low index material.

Lastly, there are more innovative AR-coatings which rely on 3-d nano structures to construct a pseudo-moth's eye film. These structures, often pyramids or cone shapes made out of the same material as the underlying substrate, are smaller than the wavelength of light observed. Their size and tapered shape cause a gradual change in the index of refraction from air to substrate in a smooth way. The light never encounters a "surface" to refract/reflect off, and so there is very little reflection. New techniques have attempted to apply this concept down to the NUV, but the cone size required is so small as to pose quite a challenge.⁵

Here we focus on multi-layer AR-coatings which are optimized for several UV wavelengths. Our first test multi-layers have focused on models centered near 200nm. This wavelength was selected since it is the location of an atmospheric window between O₂ and O₃ absorption bands,⁶ which allows for observation in the UV at balloon and rocket altitudes. A balloon experiment, the Faint Intergalactic Redshifted Experiment Balloon (FIREBall),⁷ is just such a mission. This balloon experiment is funded for a third launch, and is an ideal test bed for a delta-doped AR-coated CCD. With this in mind, we have selected several models as first tests.

In Section 2, we describe techniques for model creation and the models themselves. In Section 3, we describe deposition recipes and techniques, along with growth rates for each material. In Section 4, we describe the reflectance and transmission measurements of the films on inert substrates.

2. MODEL DEVELOPMENT

Multi-layer films were modeled using TFCalc. Materials under consideration include MgO, MgF₂, Al₂O₃, SiO₂, and HfO₂. For uses below 220nm, we eliminate HfO₂ as a viable film layer due to absorption. Below 200nm, we eliminate MgO, and below 180 we eliminate Al₂O₃. For the shortest wavelength applications, multi-layers can be made of MgF₂ and SiO₂. The use of alternative fluorides, such as CaF₂ and LaF₃, can increase the options for high quality coatings at extreme UV wavelengths, although those options are not explored here. Optical constants come from Palik^{8,9} although in some cases constants used are from samples made at JPL and measured by J.A. Woollam using vacuum ellipsometry.

In previous work, we have used standard silicon optical constants to determine the expected reflectance and transmittance of film materials. However, further study has found that the optical constants of delta-doped Si are slightly different than undoped Si. Alternative optical constants for delta-doped Si were measured by the J.A. Woollam. While the difference is slight at most wavelengths, the reflectance can change by several percent at UV wavelengths, and so we include this layer in our calculations. As such, we use the following structure in our reflectance calculations: a bulk Si substrate, a 3.413nm thick delta-doped Si layer with alternative constants, and a 1.7nm thick native SiO₂ oxide. In this calculation, we determine the reflectance off of the stack and any added coatings. Absorption is not a concern for the delta doped layer, as any electrons created there are still detected in the CCD. Absorption calculations take into account the native oxide and any added coatings only. Anticipated transmission is calculated by subtracting reflectance and absorption from 100%.

We have developed a suite of sample films to increase QE above the reflectance limit of Si, in some cases reaching 90%, at a few test wavelengths. We present plots of expected transmission for films optimized at 155nm, 205nm (Figure 1), 255nm (Figure 2), and 305nm (Figure 3).

The most difficult range is certainly 155nm, where very few materials are available to create multi-layer coatings. Additionally, due to the limited range of optical constants, the maximum QE achievable is not much greater than that achieved with a single layer. At longer wavelengths, such as 205 and 255, there are more materials available and correspondingly more appropriate constants. Potential QE well above 80% is achievable with a few layers. Finally, films made above 300nm can achieve near perfect transmission, although truly wide

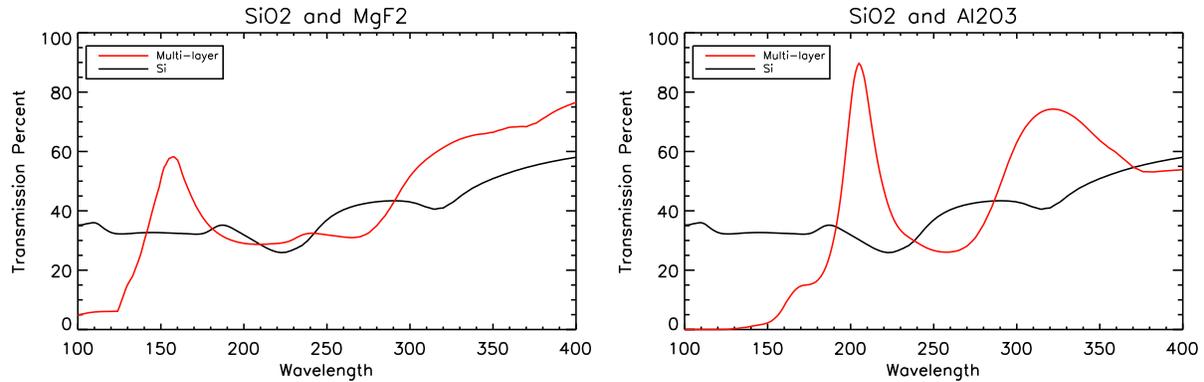


Figure 1. **At left:** Expected transmission for a multilayer model optimized for maximum transmission at 155nm using SiO₂ and MgF₂ as materials. **At right:** Expected transmission for a multilayer model optimized for maximum transmission at 205nm using SiO₂ and Al₂O₃ as materials.

bandpasses (hundreds of nm) with high QE (above 90% for the whole range) do not become possible until above 370nm.

Finally, we summarize each model in Table 1. Listed characteristics are peak QE and at what wavelength, materials, and width of band at 50% QE. Typical FWHM for bandpasses are less useful here since the out of band QE is not zero, but typically closer to the reflectance limit of silicon. Therefore, we will just use the bandwidth at 50% to set a standard for comparison between film models in this paper.

3. DEPOSITION TECHNIQUES

All depositions were made using Atomic Layer Deposition (ALD) at NASA's Jet Propulsion Laboratory. ALD enables conformal, atomic-layer level control over film growth and allows well controlled, repeatable depositions. ALD recipes for Al₂O₃ came from Goldstein,¹⁰ MgO from a custom reaction developed at JPL by the authors, SiO₂ from Dingemans¹² and HfO₂ from Liu.¹³ Often growth recipes required modifications to accommodate the equipment used. Modified growth recipes were typically validated using either XPS, TEM, or both. Growths were typically conducted at 200 °C.

Films were grown on 1 inch <100> 1-20 Ohm-cm silicon wafers (to test reflectance) and on fused silica windows (to test absorption). As noted above, differing optical constants between un-doped and doped Si means the films tested here are slight modifications to the ones described above. All measurements (and corresponding models) plotted are based on a silicon substrate without the doped layer. We are still able to test the overall nature of the film, its behavior compared to modeled on normal silicon, and we expect few changes when grown

Table 1. Table summarizing characteristics of each film model pictured.

Model	Materials	Max QE %	λ of Max (nm)	Width at 50% QE (nm)
155	SiO ₂ & MgF ₂	58.1	158	14
205	SiO ₂ & Al ₂ O ₃	89.6	205	22
255a	SiO ₂ & Al ₂ O ₃	85.6	254	31
255b	HfO ₂ & Al ₂ O ₃	97.8	255	29
255c	MgF ₂ & Al ₂ O ₃	97.7	255	27
205a	MgF ₂ & Al ₂ O ₃	97.2	305	56
205b	HfO ₂ & Al ₂ O ₃	82.5	307	45
205c	SiO ₂ & Al ₂ O ₃	98.8	305	42

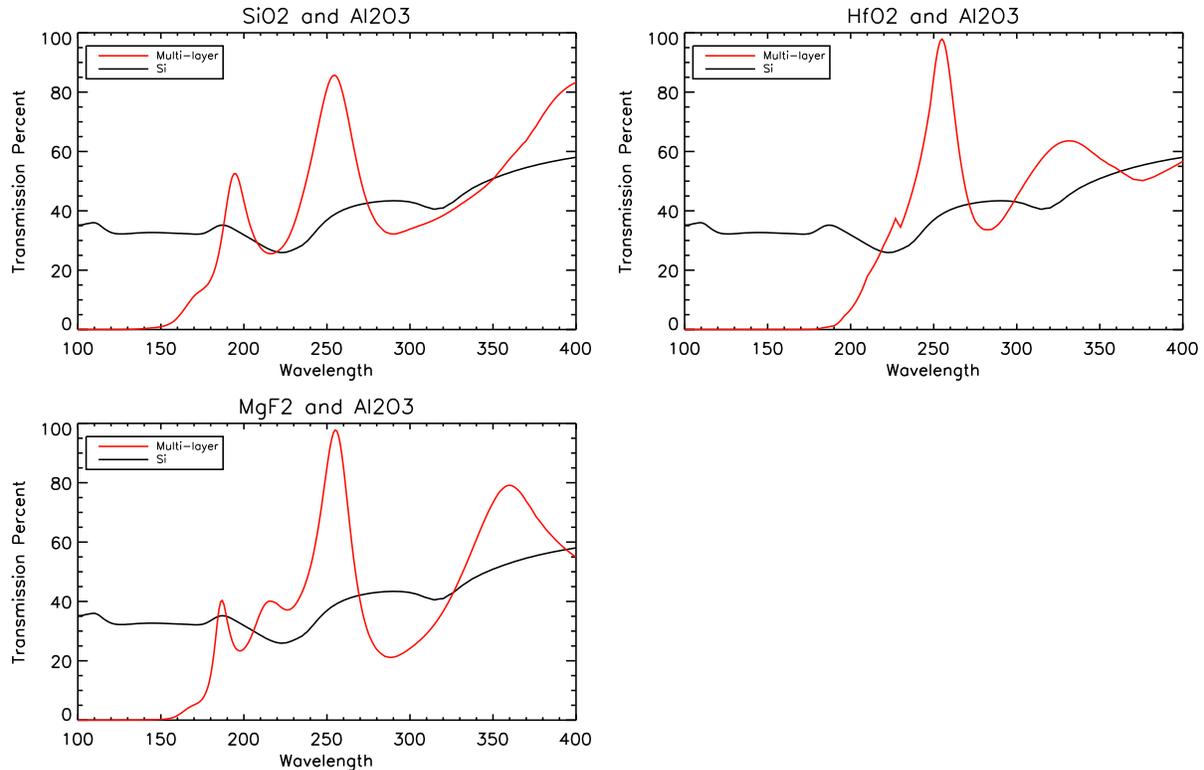


Figure 2. Expected transmission for three possible multilayer models optimized for maximum transmission at 255nm using SiO₂, Al₂O₃, HfO₂, and MgF₂ as materials. Each film uses only two materials, listed above each plot.

on delta-doped CCDs. Previous work on delta-doped CCDs has shown good fidelity to model predictions. Thicknesses were verified in an ellipsometer.

4. TESTING AND RESULTS

Tests were conducted at a reflectance set-up at Columbia University. The samples were placed in a vacuum chamber maintained at less than 1×10^{-4} torr for the duration of the measurement. An Acton monochromator fed by a focused deuterium lamp provides light from 120nm to 600-700nm. The light then is then reflected off samples at any angle of incidence from nearly normal (5°) to straight through, in the case of transparent substrates. In testing films grown on Si substrates, reflectance was at 10° from normal. For transparent substrates, usually fused silica, the light was able to pass directly through the sample. Current measurements were taken in using a PMT with a scintillator, from McPherson. For each sample the following set of measurements were made: direct emission from the lamp, reflected emission from the sample, reflected emission from a bare Si standard, reflected ambient light not directly in the path of the light. These measurements were then used to calculate direct reflectance from the sample and Si (as a standard).

Samples measured are as follows:

1. 5-layer film of Al₂O₃ and SiO₂ optimized at 190nm. See Figure 4.
2. 3-layer film of Al₂O₃ and SiO₂ optimized at 190nm. See Figure 5.

5. DISCUSSION

We find that films made with ALD are able to match expected values for reflectance and absorption with great accuracy. Both 3 and 5 layer films match the model very closely, without additional absorption which can

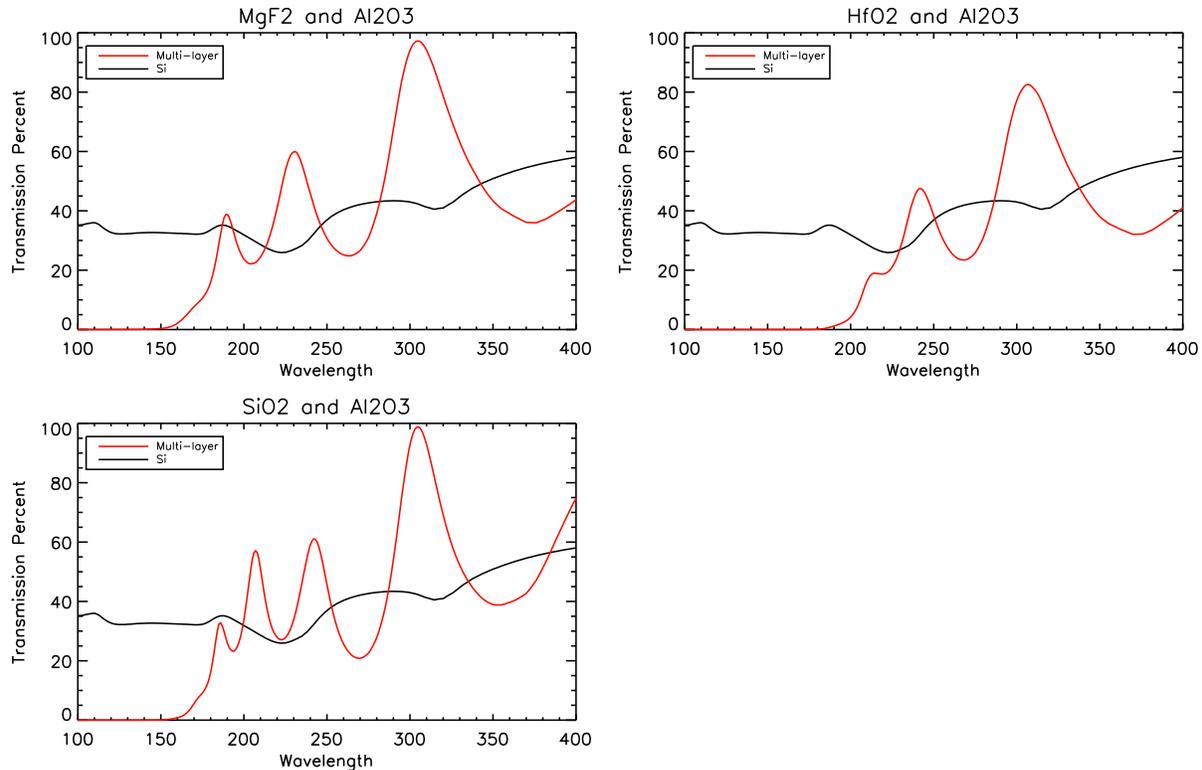


Figure 3. Expected transmission for three possible multilayer models optimized for maximum transmission at 305nm using SiO₂, Al₂O₃, HfO₂, and MgF₂ as materials. Each film uses only two materials.

indicate interaction between the silicon substrate and coating layers. We are able to achieve greater than 80% transmission for the 5-layer film, and expect higher QE with more carefully grown layers. This is a greater than 50% improvement over the measured QE for a single layer film from our previous work.

In all of our films, we had standard errors related to ALD growth. Typically deposition errors result from inaccurate growth curves for new materials (i.e. thickness of growth per cycle), and these errors are easy to correct with accurate characterization. Typical growth curves are also calculated by growing samples on Si test wafers. But in our multi-layers, for example, SiO₂ is grown on existing layers of Al₂O₃, which appears to modify the growth of SiO₂. Still, once characterized, the growth is highly repeatable, and we expect a good ability to hit thickness targets in the future.

Despite these small errors, achieving extremely high QE at UV wavelengths is now possible. Application of these films on live devices will proceed soon, starting with an SiO₂/Al₂O₃ multi-layer optimized for 205nm. The bandwidth of such a film can be narrowed by increasing the number of layers in the coating. These types of films (high QE, but narrow bandwidth) have many uses. Laser applications, in particular, do not require a wide band. A spectrograph that operates over a narrow range, or one with many detectors each observing a narrow range, could also use these types of coatings to achieve overall high QE. A further solution for a spectrograph consisting of one detector would be to build a ramped AR-coating such that the correct thickness AR-coating was applied to the correct region where a certain wavelength will be detected. At the blue end of the spectrograph detector, the AR coating would be thin, while at the red end, the coating would be proportionally thicker.

Widening the bandwidth, however, and achieving high QE over many tens of nanometers in the UV, is a challenge that still needs to be worked on. Creative use of ALD to create meta-materials, more careful index matching, and the innovative use of 3-d nano-structures (bumps, pyramids, etc.) or ramps, could all be harnessed to create a wide bandwidth, high QE detector.

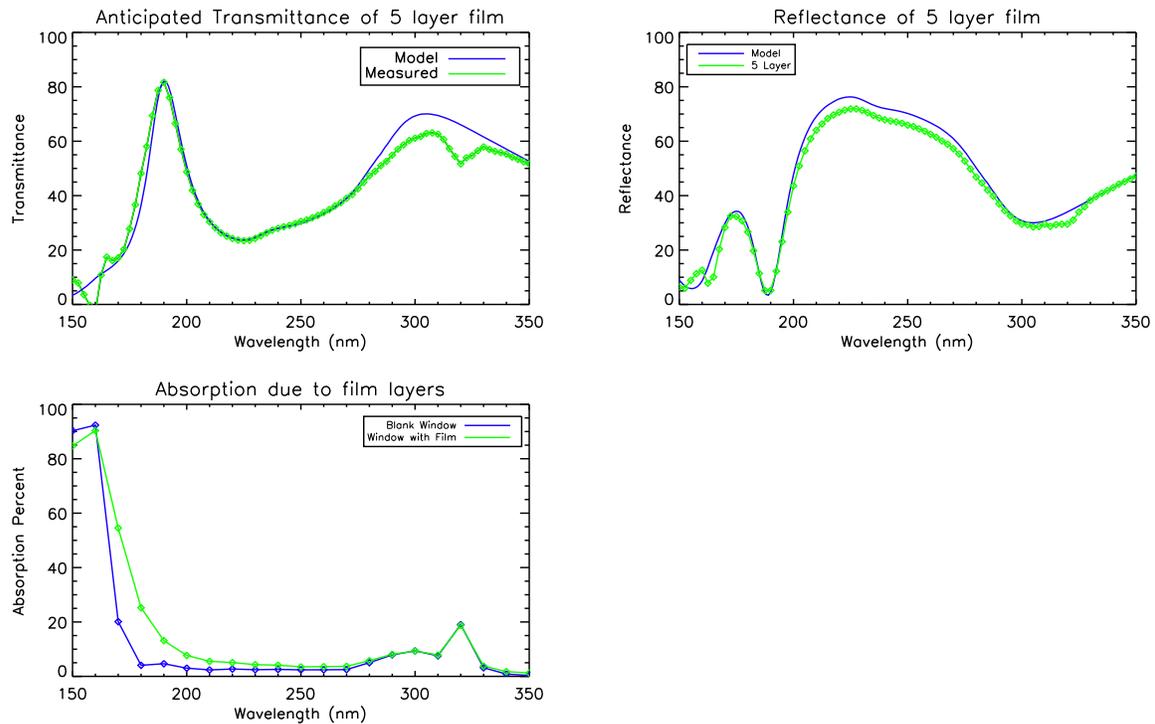


Figure 4. **Top Left** Estimated transmission for a 5-layer film of SiO_2 and Al_2O_3 . Peak transmission is at 190nm, and far exceeds previous work at this wavelength (approximately 60% transmission). This transmission was determined by subtracting the reflectance and absorption from 100 %. **Top Right** Measured reflectance for a 5-layer film of SiO_2 and Al_2O_3 . Minimum reflectance is at 190nm. **Bottom Left** Measured absorption for 5-layer film on fused silica window. Absorption is due to both the fused silica substrate, as well as the film itself. The film absorption can be measured by the difference between the two lines. Film absorption is rising at shorter wavelengths, but is still minimal at 190 nm and higher.

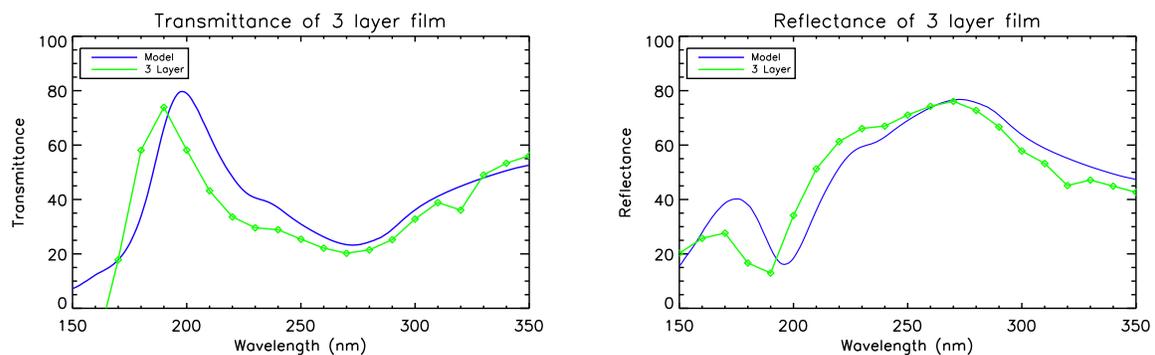


Figure 5. **Left** Estimated transmission for a 3-layer film of SiO_2 and Al_2O_3 . Peak transmission is at 190nm, slightly below the target of 200nm. A thinner than expected SiO_2 layer is responsible for the discrepancy. The width of the transmittance peak is significantly thicker than that of the peak for a 5-layer film in Figure 4, while the absolute height of the peak is slightly shorter. **Right**. Measured reflectance for 3-layer film. Minimum reflectance is at 190nm, slightly below the target of 200nm.

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