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Nanoscale Characterization of Thin Film Coatings Using Annular Dark Field Scanning Transmission Electron Microscopy

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Abstract

When considering the optical performance of thin films in the Extreme Ultraviolet (EUV), developing an accurate physical description of a thin film coating is necessary to be able to successfully model optical performance. With the short wavelengths of the EUV, film interfaces and sample roughness warrant special attention and care. The surfaces of thin film samples are routinely measured by Atomic Force Microscopy, from which roughness can be determined. However, characterizing the quality of interfaces below the surface is much more challenging. In a recent study of scandium oxide thin films, High Resolution Transmission Electron Microscopy and Annular Dark Field Scanning Transmission Electron Microscopy (ADF STEM) were used to study the cross section of the samples. ADF STEM data analyzed along a path into the volume of the sample (normal to the interfaces) reveals information of sample density versus depth. This density-depth profile reflects the presence of subsurface film interfaces in the volume of the sample. Additionally, information from the ADF STEM profile can be used to gauge the roughness of the subsurface interfaces, which is used to refine the sample description during modeling. We believe this is the first use of ADF STEM in this capacity. This characterization technique may provide key insight to subsurface interface quality, which is particularly important when optimizing the performance of multilayer coatings in the EUV.

Introduction

Generally, optical studies are influenced only slightly by the nanoscale attributes of a material. However, in the EUV the wavelengths of photons are of the same scale as both the atomic dimensions and the structural features present in a coating [1]. In this energy regime, understanding a material's optical performance can be complicated by the nanoscale physical characteristics of the sample. To accurately model the performance of a thin film in the EUV, it is paramount that an accurate

description of the sample being studied be developed [2].

There are a variety of methods available which can be used to characterize a thin film sample and provide information about its composition and structure. Atomic Force Microscopy (AFM) and ellipsometry are two techniques which have become very popular, owing largely to their relative user-friendliness and speedy results. For many years, the Thin Films Group at Brigham Young University (BYU) has used AFM and ellipsometry in the analysis of thin film samples. Both AFM and ellipsometry can provide film parameters very quickly, however they each have their limitations. AFM can be used to determine the roughness of the surface of a thin film sample, and with proper sample preparation it can measure film thickness [3]. However, features below the surface, for example at a film interface, are not revealed in AFM analysis. Ellipsometry can be very fast and accurate for film characterization, provided that the correct optical constants for use in the modeling are available. Often, EUV studies are of novel materials, most of which have not been studied in depth as thin films and may not have optical constants determined for use in an ellipsometric model. Also, ellipsometry is an effective tool for modeling a sample with a known structure, but can become cumbersome when a film structure is unknown.

Less widespread, but also becoming more available, is the use of High Resolution Transmission Electron Microscopy to study thin films. Though sample preparation can be laborious, HRTEM of thin film sample cross sections can provide angstrom resolution. It can be difficult, though, to assign values to thin film parameters using these images if a sample exhibits less than ideal interfaces, or if a sample is polycrystalline.

In characterizing thin films, samples are measured using several techniques in an effort to be able to develop as complete and accurate a description of the film of interest. This study presents the use of Annular Dark Field Scanning Transmission Electron Microscopy (ADF STEM) as part of the characterization scheme, as it is able to illuminate the structure within the volume of a thin film sample. Film deposition, sample preparation, and sample imaging and analysis was all performed within the BYU Department of Physics and Astronomy.

Sample preparation

Thin films of interest are deposited on a variety of substrates, depending upon the use intended for a specific sample. In this report, the sample being studied is a thin film of reactively sputtered scandium oxide

deposited on a silicon wafer. The sample was prepared for HRTEM imaging using the wedge polishing technique [4]. Samples prepared in this was can also be used for ADF STEM and Energy Dispersive X-ray (EDX) analysis. As illustrated in Figure 1, at the tip of the wedge the sample will be thin enough for the electrons of the beam to pass through. Electrons passing through the sample will provide an image of the film and substrate volume versus depth.
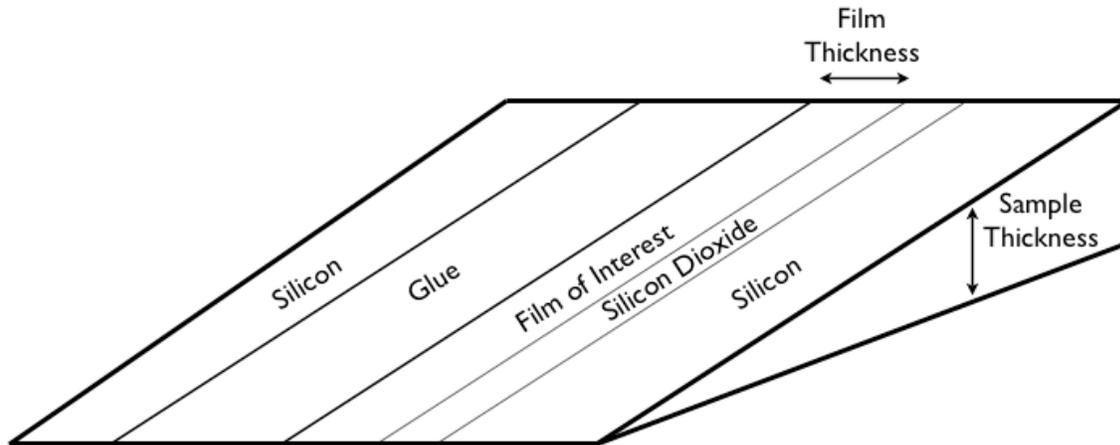

Figure 1. *A thin film prepared for imaging by the wedge polishing technique is similar to a piece of pie lying on its side. Note the distinction between film thickness and sample thickness, as they refer to two very different parameters.*

Analysis

Having prepared the sample, the HRTEM images were collected. An example of an HRTEM image is shown in Figure 2. Also shown in Figure 2 is an ADF STEM image. In each case, some features of the sample are more easily seen in one image, while not as apparent in the other. This is due to the different ways in which the images are generated. A HRTEM image is a phase-contrast image. As the electrons of the beam pass through the sample, their phase is altered, recording the electron-material interaction. These electrons are then focused onto a plane where they collectively form an image as a result of the phase variations the electrons have from interactions with different parts of the sample. In ADF STEM imaging, the electron beam is scanned across the surface of the sample. As the electrons of the beam pass through the sample, some are scattered by the sample's nuclei to a large angle from the specular path. An annular

detector below the sample collects these scattered electrons. The information from the detector can be used to construct the image since the beam position is known as it scans across the sample. In contrast to HRTEM images, the intensities of the ADF STEM image are proportional to the variations of the material density of the sample.
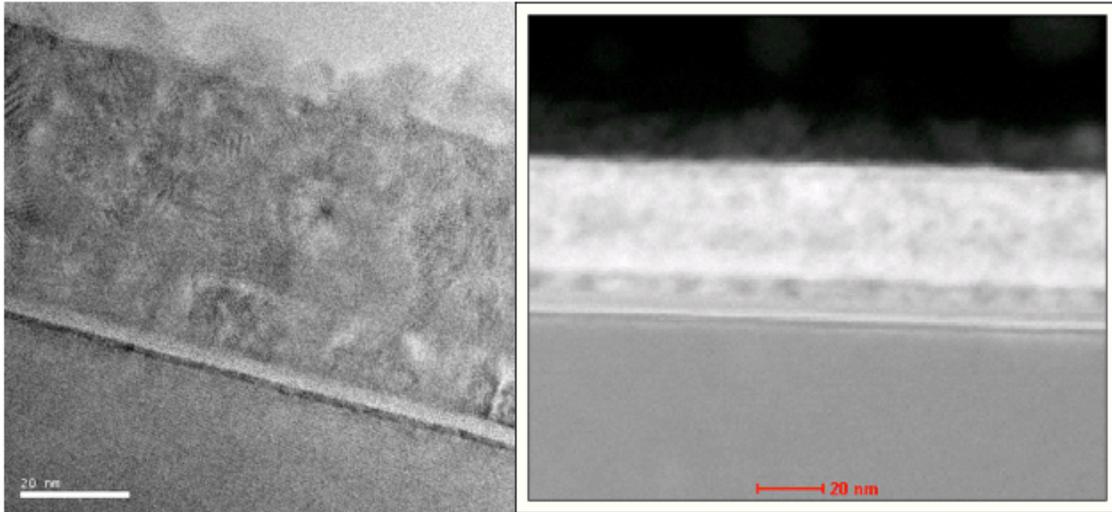

Figure 2. *On the left is an HRTEM image of a scandium oxide thin film deposited on a silicon wafer substrate, on the right is an ADF STEM image taken from the same sample. From bottom to top in both images are silicon, a thin band representing the silicon/silicon dioxide strain layer (approximately 1-2 nm), silicon dioxide (2 nm), and the deposited scandium oxide (40 nm), followed by the glue layer from the sample preparation. In the ADF STEM image, the intensities of the layers is proportional to the density of the material, revealing that within the volume of the scandium oxide layer there are actually two layers of scandium oxide. In the HRTEM image, the evidence of this bimodal quality is subtly present.*

In the HRTEM image of Figure 2, silicon and silicon dioxide layers of the substrate are at the bottom of the image. The silicon dioxide layer is the light grey layer immediately above the dark grey stripe, which is the strain layer between the crystalline silicon and the amorphous silicon dioxide. Above the silicon dioxide is the scandium oxide layer. The polycrystalline nature of this layer is evident in this image.

The ADF STEM image of Figure 2 is of the same scandium oxide sample. Again, the bottom of the image is the silicon substrate, above which is the

silicon dioxide and the scandium oxide thin film. Most striking in this image is the fact that the scandium oxide coating is actually a bilayer. Above the thin, light grey stripe of the silicon dioxide, there are two layers of scandium oxide. Both layers were confirmed to be scandium oxide using EDX, shown in Figure 3. This bimodal quality of the deposited film was unexpected, though there is an explanation. During the deposition of this film there was a plasma failure midway through the coating period. The fault was inadequate gas flow, which was quickly corrected without breaking vacuum. As a result of the interruption, the deposition was performed under two slightly different sets of sputter parameters, leading to the film deposited having two different densities. During the imaging session, the HRTEM images were collected first, at which time the scandium oxide coating was presumed to be a single layer. This bimodal quality does appear in the HRTEM images, though its presence is subtle and easily overlooked. The sensitivity of ADF STEM to sample density revealed a key feature which most likely would have gone undiscovered without use of this characterization method.
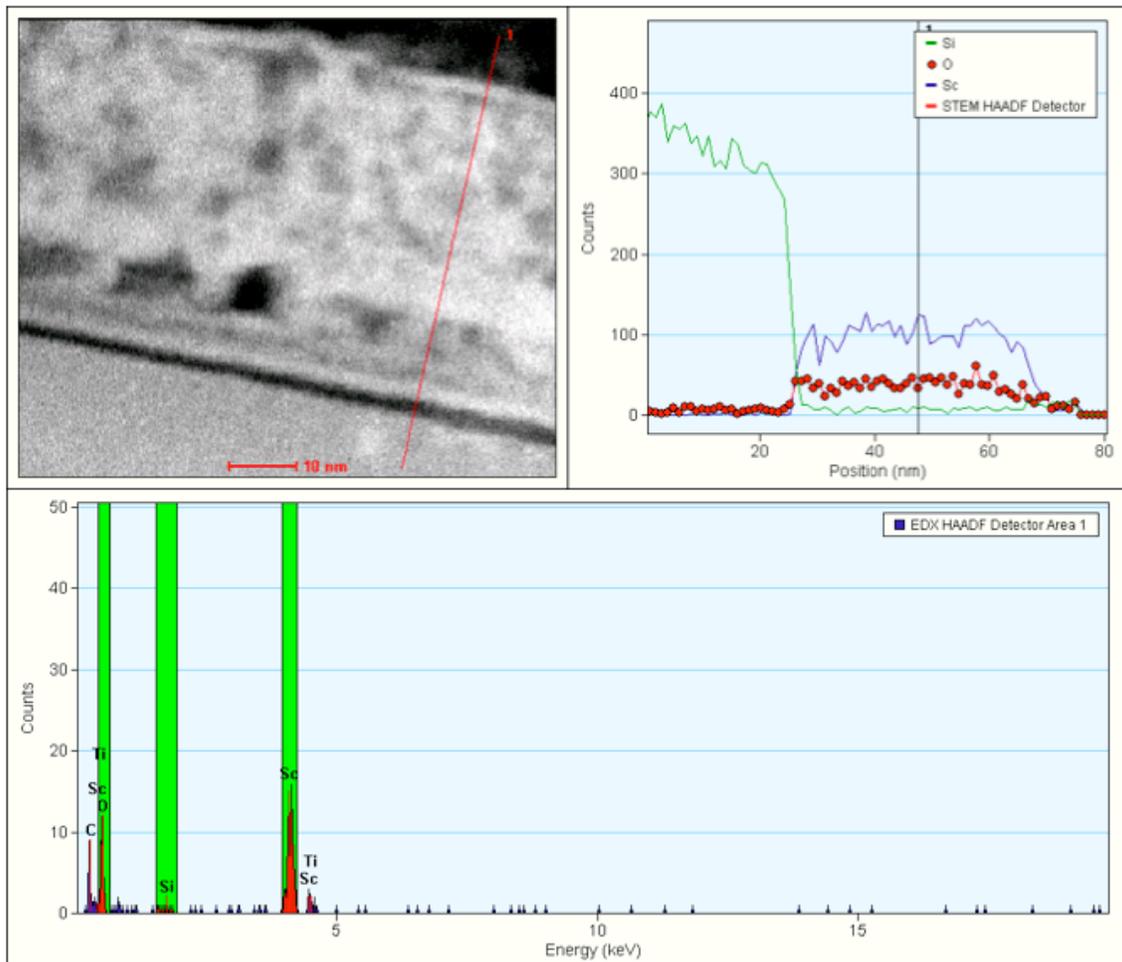
Figure 3. *Here, an EDX scan performed along the path selected in the image confirms the sample is composed of silicon, oxygen and scandium. In the spectra, titanium and carbon have a slight presence, attributed to the sample holder (titanium) and hydrocarbon contamination from ambient exposure.*
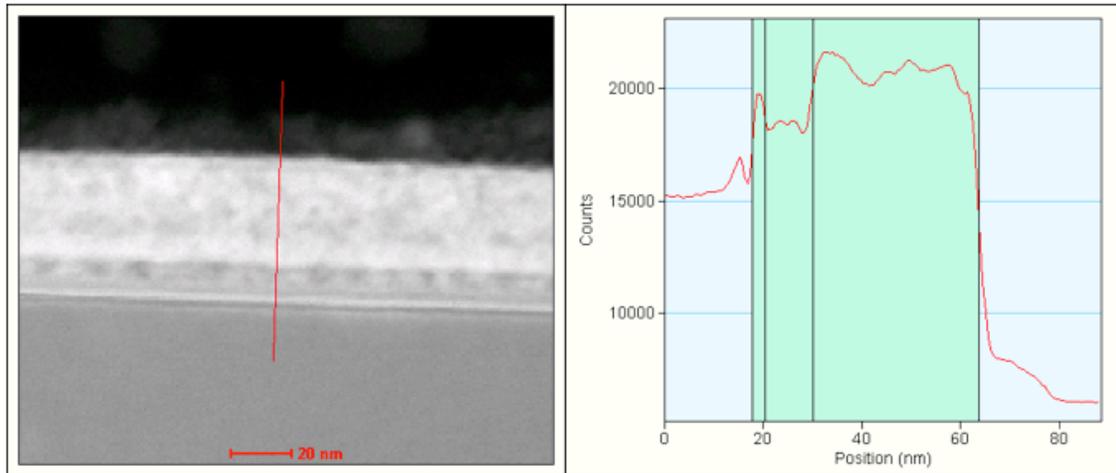
Figure 4. *A path normal to the film interfaces is selected in the ADF STEM image. The intensity profile to the right is calculated by averaging the intensities of the image from 30 nm on either side of the selected path. In the intensity profile, the interfaces between the layers of the samples are represented by transitions between intensity values. Vertical markers are placed at the midpoint of these transitions, and the individual layers of the sample can be measured. Here, from left to right, the thicknesses are: silicon dioxide, 2.6 nm; low density scandium oxide, 9.67 nm; and high density scandium oxide, 33.56 nm.*

Film thickness values are a chief concern when modeling the EUV performance of a thin film. ADF STEM images can be analyzed to provide a thickness value for either the total film thickness or the thickness of the individual layers. In Figure 4, a path leading into the depth of the film normal to the film interfaces has been selected in the ADF STEM image. The image intensity along this path creates a profile of the sample versus depth. In Figure 4, the profile shown is generated by averaging the image intensities from 30 nm on either side of the chosen path. There is an advantage to creating the profile in this way, since the irregularities of the interface surfaces can make it difficult to determine a film thickness value. By averaging the intensities of the image over a relatively wide area along the path, the singular peaks and valleys along the interfaces balance each

other and appear as an interface which is easier to interpret. In the intensity profile of Figure 4, regions of the profile are selected between vertical markers. The markers are placed at the midpoints of the interfaces, and the software used provides the distance between the markers, thereby giving the thickness of the individual layers.
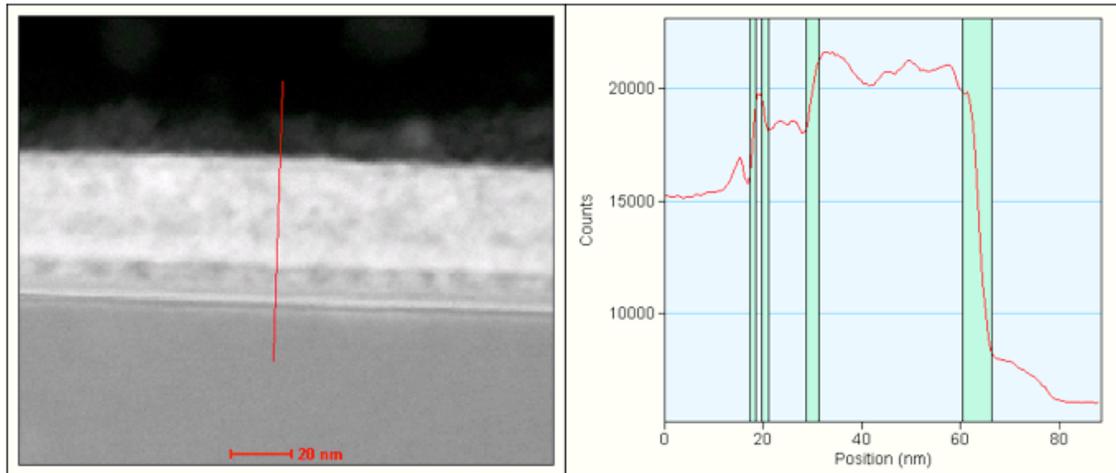
Figure 5. *Further analysis of the intensity profile can provide information about the film interfaces. Vertical markers are used to highlight the portions of the profile which correspond to the following interfaces (from left to right): silicon/silicon dioxide, silicon dioxide/low density scandium oxide, low/high density scandium oxide, and scandium oxide/ambient (or glue, in the case of the prepared sample). The width of each interface region is proportional to its roughness.*

The intensity profile versus depth used in the analysis of the ADF STEM image also contains information about the relative roughness of film interfaces. Roughness is a parameter often overlooked, though it can be particularly important for proper modeling of EUV data. With AFM, it is not difficult to measure the roughness of substrates, or of the surface of a thin film. However, until now the roughness of film interfaces within the volume of a sample had been a parameter that would have to be guessed at, if included in the model at all. In the intensity profile versus depth, interfaces between layers appear as transitions between regions of different intensity. The widths of the profile transitions can be used to assign roughness values.

In Figure 5, the portions of the intensity profile which correspond to the silicon/silicon dioxide, silicon dioxide/low density scandium oxide, low density/high density scandium oxide, and scandium oxide/ ambient

interfaces are highlighted (from left to right). From AFM analysis, the roughness of scandium oxide thin films of this nature are expected to have an rms roughness of 1.6-2.0 nm. Also from AFM measurements, the substrate being used is expected to have an rms roughness of 0.1-0.2 nm at the silicon dioxide surface before it is coated. By comparing the widths of the highlighted transition regions of the intensity profile, the relative roughness of the interfaces within the volume of the film can be gauged. The rms roughness values found through AFM measurements can be related to the widths of the corresponding interfaces in the ADF STEM profile as an elementary calibration, from which the rms roughness of interfaces within the sample volume can be determined. In this case, the low density/high density scandium oxide interface was assigned an rms roughness value of 0.6 nm.

This is a preliminary use of the ADF STEM intensity profile in this capacity. There are a number of conditions which can be imagined in which the slope of the intensity profile in the vicinity of an interface should not be entirely recognized as due to interfacial surface roughness. For example, if the mating materials at an interface are active and the formation of a new compound occurs, this analysis would not be appropriate. However, we believe that an ADF STEM intensity profile of novel interfaces would be valuable in providing insight into interdiffusion, compound formation, and/or interfacial roughness.

Conclusion

ADF STEM imaging has been used to study thin films. Used in conjunction with other characterization techniques, an accurate description of the physical nature of a coating with nanoscale attributes can be developed. Initially, analysis of ADF STEM images was to provide film thickness values. Additionally, though, information about the subsurface interfaces of the thin film coating and their relative roughness was gained. The results of this ADF STEM characterization were incorporated into the modeling of the EUV reflection and transmission data of a scandium oxide thin film coating, in which calculation and measurement ultimately agreed very well.

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