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C/ SiO_2 / Si thin film thicknesses using EPMA and a cold finger

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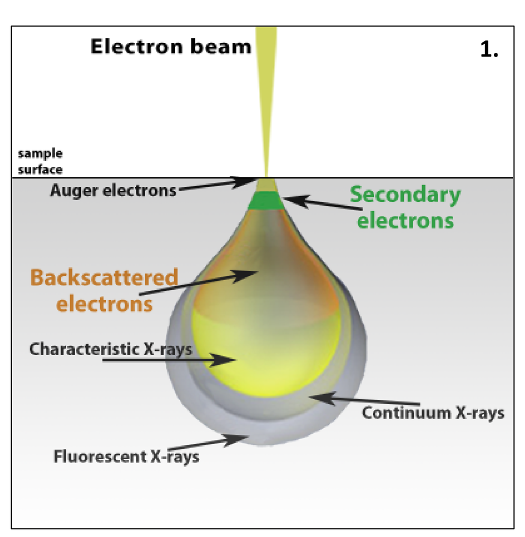
Backgroud:

Thin films generally consist of a nm-scale layer of metal or semiconducting material resting on a ceramic, glass, or metal substrate and are widely used in the optics and electronics industries. The thickness of a film often needs to be precise for the component in which the film resides to function properly. There are a variety of techniques which can be employed to examine the thicknesses of a thin film (profilometry, interferometry, ellipsometry, etc.), and each have benefits and drawbacks (exmp. Piegari and Masetti, 1984). In this investigation, we measure the thickness of C/SiO_2/Si thin-films with Electron Probe Micro Analyzer (EPMA) using a JEOL 8530 FE microprobe and newly published free BadgerFilm software (Moy and Fournelle, 2021a & b). Due to the small-scale lateral variations and fragile nature of the layers, the non-destructive EPMA technique is favored. During repeated or long analyses of the same spot, hydrocarbons within the chamber can concentrate on the sample surface and artificially raise [C]. To help in minimize surface contamination of hydrocarbons during the multiple-kV spot analyses we use a LN cold finger (see Yamashita et al., 2016 for more background reading).

C/SiO_2 alternating layers have recently been developed to mimic natural seashell structures and are desired for their thermal and mechanical properties (Xu et al., 2022). In this investigation we look at a range of samples (Fig. 1) to test for lateral coating variations for different deposition conditions in a non-destructive manner, in hopes to use it as a quality assurance method for future builds.

Thin film measurements by EPMA:



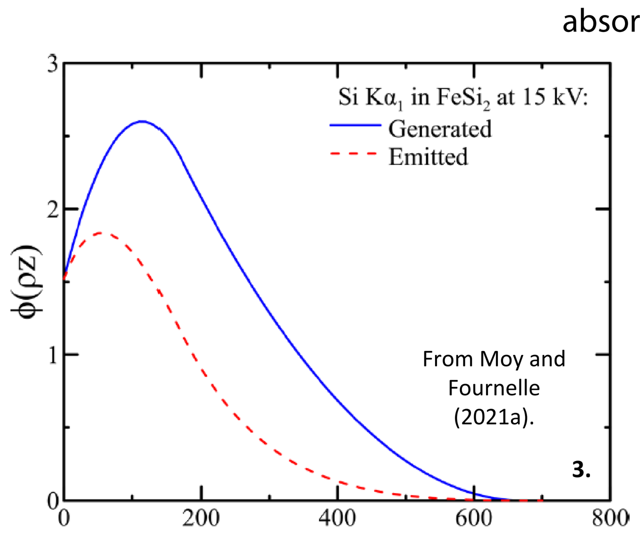
$$I_i = n_{el} \frac{N_A}{A_i} C_i \sigma_j(E_0)\omega_j \frac{\Gamma_{j-k}}{\Gamma_{j-\text{total}}} \lambda_j \int_0^{\infty} \phi_j(\rho z) e^{-\chi_i \rho z} d\rho z \, \varepsilon \frac{\Omega}{4\pi} + \mathcal{F}_c + \mathcal{F}_b$$

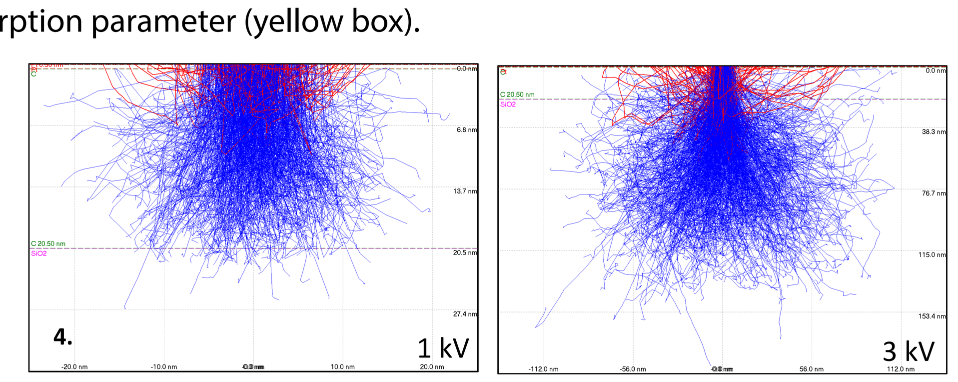
Atoms per atomic weight; Weight fraction in sample; Relaxation parameters (self fluorescence, subshell transitions, production cross section, etc.); Absorption parameter; Detection efficiency; Primary and Secondary fluorescence

2.

1. Characteristic x-rays generated during e-beam-sample interaction

2. The amount of x-rays that make it to the detector is governed by complex physics and modeled with the above equation. We will focus on the absorption parameter (yellow box).

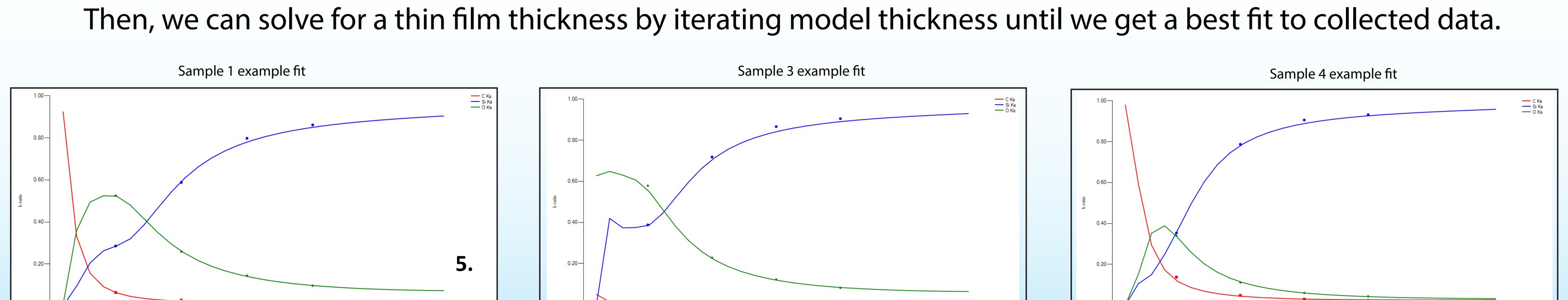




3. The amount of x-rays generated and absorbed varies with depth into the sample

4. Beam interaction volume and penetration depth varies with beam energy.

5. We can model how many x-rays should be produced at different beam energies using Monte Carlo simulations. Then, we can solve for a thin film thickness by iterating model thickness until we get a best fit to collected data.



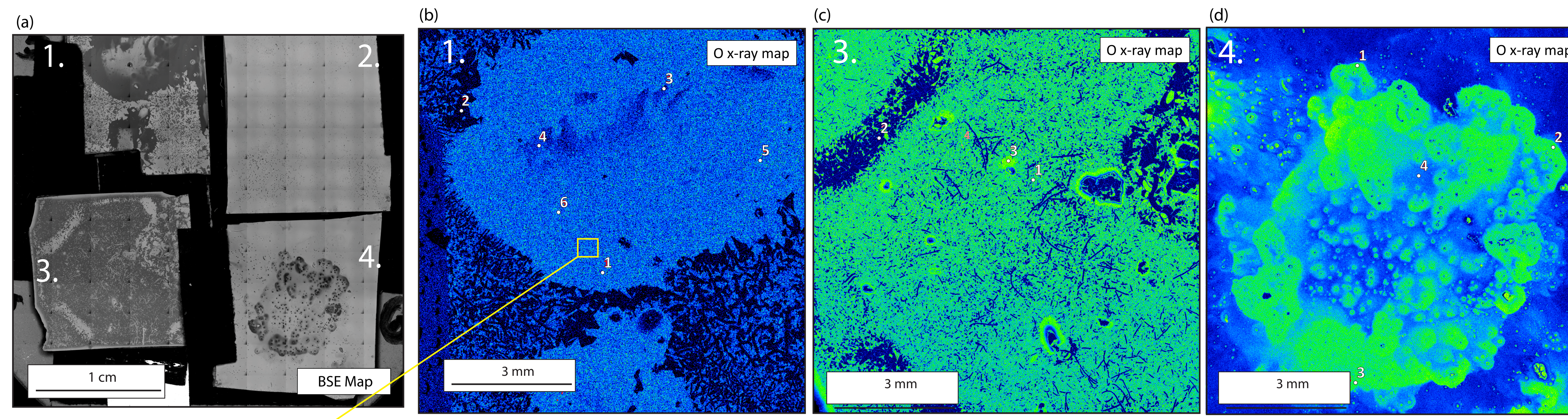
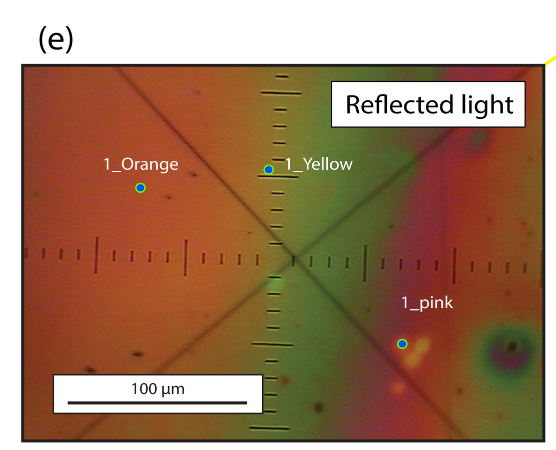


Table 1

Sample	Coating:
1	C/SiO2/Si
2	Blank/Si
3	SiO2/Si
4	C/SiO2/Si

Table 2

Thickness (nm)		
Sample	C	TEOS
1_1	22.5	382
1_2	0.34	2
1_3	17.1	780
1_4	4.5	182
1_5	14.3	542
1_6	19.8	319
1_Orange	16.9	700
1_Yellow	16.4	652
1_Pink	16.3	549
3_1	3.9	1050
3_2	1.2	330
3_3	3.7	1092
4_1	57	278
4_2	43.8	193
4_3	48.6	265
4_4	10	39



SiO_2/C/Si Samples:

Samples were made by spin-coating Tetraethyl orthosilicate (TEOS) and/or sugar-water solutions onto Si wafers at varying coating ratios and spin speeds, which were then heat treated to leave behind SiO2 and C. The layers present in each coupon are shown in table 1. The four figures above from left to right are (a) BSE images of individual coupons. (b-d) O x-ray maps of the coupons. O highlights the areas in which TEOS coating was present, and thus were target areas for analyzing coating thickness. The dark areas in sample 1 and 4 show where C deposition was present. Sample 3 has TEOS only, and sample 2 had C only, but was lost during the heat treatment, suggesting that the TEOS layer helps preserve C during the heat treating. Using varrying beam energies of 5, 10, 15, and 20 kV, a pure C, Si, and SiO2 standard, and the free software, Badgerfilm, we determined the thickness of C and SiO_2 layers for the various samples. The results are presented in Table 2; the corresponding numbers link to the lables on the images. The C and SiO_2 layers vary in thickness, but the C layers appear to have the most agreeability for any individual sample, whil while the SiO_2 layer varies significantly even for a single sample. Badgerfilm calculates the C layer to be 100% C, the SiO2 layer on average to be stochiometric, and the Si layer to be 100% Si.

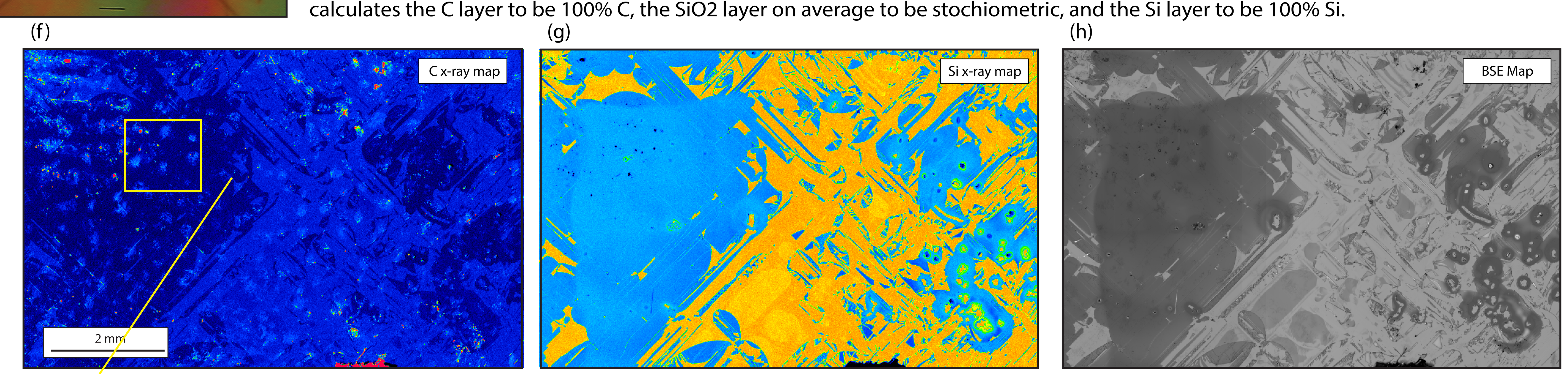
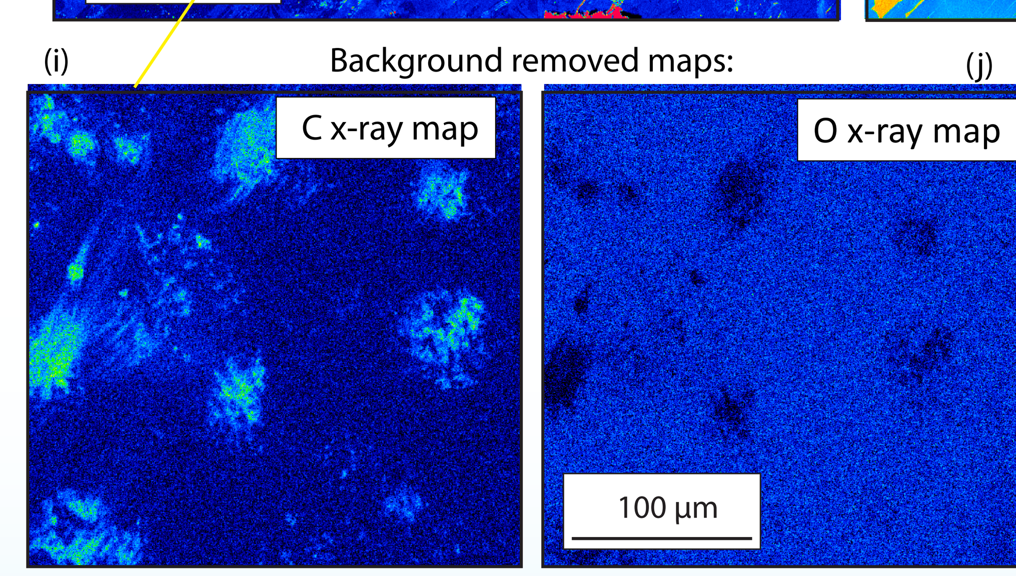
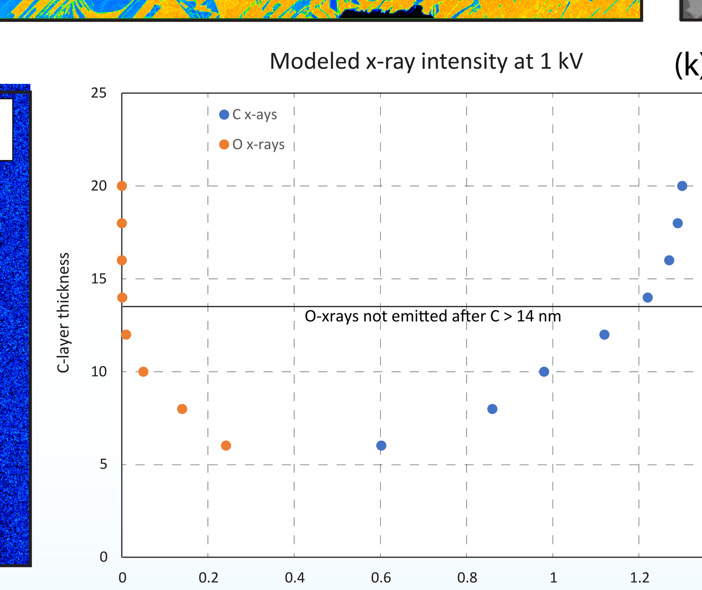


Figure (e) shows a reflected light optical microscope image of the sample 1 surface. The rainbow color pattern is common amoungst these samples. Thickness measurements indicate that the C layer is fairly homogenous in this region at ~16-17 nm, while the SiO_2 layer thickness varies, and may potentially be contributing to the color. If this is confirmed in more testing, this may provide a quick and useful way for quality assurance of the thicknes of the SiO_2 layer in future builds.

Background removed maps:





Si/C/SiO_2 Sample:

Figures (f)-(k) refer to a sample with different coating ordering. In these samples, a substrate of SiO2 was coated in sugar, and then coated in pure Si. The C x-ray map in Figure (f) shows splotchiness in the coating. The areas in higher C that correlate with Si are due to an increase in the Bremsstrahlung because of the pure Si present in those locations. Figures (i) and (j) are 1kV background removed maps which shows C and O (as a proxy for SiO2). Monte Crlo simulations using CASINO for varying C layer thicknesses are shown in figure (k). At C thicknesses >14 nm at 1 kV, O x-rays don't leave the sample. and thus indicate that the darkest areas in Figure (j) have C layer thicknesses >14 nm. Future work here will aim at correlating pixel intensities with background removed maps and BadgerFilm measurements to make 'thickness maps'.

Conclusions and future work:

1. We have demonstrated the use of Badgerfilm and a cold finger in EPMA to accurately calculate the thicknesses of samples in a non-destructive manner which would prove challeneging to analyze with other thickness measurement techniques.
2. We find that C is highly correlated to SiO2, and we may need the SiO2 layer to be present to survive the heat treatment step.
3. The C coat is generally uniform for a given sample, while the SiO2 layer varies greatly over a samples surface.

In the futrue we will:

1. continue to develop better coating methods to get a uniform surface thickness so we can characterize the sample using other thickness measurements and create an in-house standard.
2. Correlate background removed count intensities with thickness measurements to create thickness maps.
3. Try to resolve more complex layering, such as C/SiO2/C/SiO2.

References:

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