Update to New Homogeneous Standards by Atomic Layer Deposition for Synchrotron X-ray Fluorescence and Absorption Spectroscopies. A. L. Butterworth[1] N. Becker[2,3], Z. Gainsforth[1], A. Lanzirotti[4], M. Newville[4], T. Proslier[2], J. Stodolna[1], S. Sutton[4], T. Tyliszczak[6], A. J. Westphal[1] and J. Zasadzinski[3], [1]University of California, Berkeley, Space Sciences Laboratory, 7 Gauss Way, Berkeley, CA, 94720-7450 [2]Material Sciences Division, Argonne National Laboratory, [3]Illinois Institute of Technology, Chicago, IL, [4]Dept. Geophys. Sci., University of Chicago, [5]CARS, University of Chicago, [6]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA.

Introduction: We reported last year [1] on a coordinated effort to produce new homogeneous quantification standards compatible across multiple analytical techniques, including Synchrotron X-ray Fluorescence (XRF), Synchrotron X-ray Absorption Spectroscopy (XAS) using Scanning Transmission X-ray Miscroscopy (STXM) and Transmission Electron Microscopy (TEM). Here, we provide an update on the availability of new thin film standards.

Mutli-technique campaigns of coordinated non-destructive quantitative analyses are essential for understanding small, unique samples such as returned NASA Stardust cometary or interstellar samples. Cross calibration standards are vital to support these efforts.

The most critical requirement of a standard is homogeneity; the typical NIST SRM 1832/1833 thin film standards vary on small scales at the tens of percent level. New thin film standards must be homogeneous at scales from ~100 µm to suit XRF beamlines, down to ~1 nm, to be useful for STXM and TEM.

We are synthesizing new homogeneous multi-layer standards on silicon nitride membranes and on pure silicon substrates using the Atomic Layer Deposition (ALD) technique [2] and characterizing them using multiple analytical methods, including ellipsometry, Rutherford Back Scattering (at Evans Analytical), Synchrotron X-ray Fluorecence (SXRF) at Advanced Photon Source (APS) Beamline 13-ID; and Synchrotron X-ray Absorption Spectroscopy (XAS) at Advanced Light Source (ALS) Beamlines 11.0.2 and 5.3.2.1 and by electron microscopy techniques at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory.

Atomic Layer deposition (ALD) is a sequential, self-limiting synthesis technique that has the crucial advantage over classical deposition techniques of conformally coating arbitrarily large areas and complex substrates. The uniformity of the grown film properties (density, thickness and chemical composition) is controlled down to the atomic scale on surface areas up to 100 m^2. As the ALD technique has matured, a large number of synthetic routes have been developed over the last 20 years [2], allowing combinations of compatible alloys of many different elements to be grown into multi-layer structures.

Methods: In a reactor chamber at Argonne National Laboratory, ALD layers were grown simultaneously on 0.5 by 0.5 mm square silicon nitride membranes (50 nm thick on 3-mm diameter Si frames, Norcada, Inc.) and pure silicon wafer substrates. These Si_3N_4 membranes are mechanically robust and are compatible with synchrotron STXM and XRF, and with TEM. A number of different substrates were included in the reactor at the same time, taking advantage of the uniform large area growth. The new homogeneous standards may be optimized for different beamline capabilities, accurately synthesizing multiple element layers tens of nanometers thick.

Some of the ALD coatings were grown on Norcada holey silicon nitride membranes substrates, which conveniently provide the necessary blank region for signal normalization during STXM acquisition.

A new membrane design from Norcada now features 40% area of holey silicon nitride and a 250 µm by 500 µm area of homogeneous Si_3N_4 providing optimal compatibility between XRF and STXM beamlines. We will use this substrate style for future production.

Results: We reported previously [1], that we found differences in the expected thickness of ALD layers grown simultaneously on the two different substrates: Si substrates have a single ALD coating on one side, but Si_3N_4 membranes should have exactly twice the film thickness from the ALD coating grown on both sides. Ellipsometry and Rutherford Back Scattering measurements on the Si substrate were consistent with expected values, but we found by STXM and XRF measurements, that the ALD coatings on Si_3N_4 membranes were depleted.

This problem was solved by updating the reactor chamber at Argonne, and by first growing a very thin layer of Al_2O_3 before growing Fe_2O_3 or ZnO layers on top. Grown this manner, the ALD layers on Si_3N_4 membranes were exactly twice the thickness of layers grown simultaneously on Si, as expected.

We report here the availability of several thin film standards, including Fe, Zn, Er, Mg, Al, Y. We have verified the standards using STXM at ALS Beamline

11.0.2: we analysed Fe and Zn L-edges, Mg and Al K-edges, and Er has both M- and N-edges accessible within the energy range. We analysed Y L-edge at ALS beamline 5.3.2.1. We analyzed Fe and Zn on Si and Si_3N_4 substrates at ALS beamline 10.3.2 XRF, we expect complementary XRF analyses at APS. RBS measurements will also be available.

NB041912-1: Fe_2O_3 grown from 600 cycles of $FeCl_3$ + H_2O on top of a thin pre-coating of Al_2O_3. We measured 7.1 $\mu g/cm^2$ Fe on Si (XRF) and 14.2 $\mu g/cm^2$ on Si_3N_4 (STXM).

NB042012-1: ZnO grown from 360 cycles of DEZ + H_2O on top of a thin pre-coating of Al_2O_3. We measured 55.3 $\mu g/cm^2$ on Si (XRF).

NB082812-1: Er_2O_3 grown from 100 cycles of $Er(MeCp)_3$ + H_2O resulting in 19nm thick Er_2O_3 on Si and 38 nm thick Er_2O_3 on Si_3N_4 substrates, giving an expected 30 $\mu g/cm^2$ Er on Si_3N_4.

NB091212-2: Multilayer Al_2O_3, Fe_2O_3, ZnO, shown in Fig. 1, grown from 1000 cycles of Trimethylaluminum (TMA) + H_2O, 1000cy $FeCl_3$ + H_2O at 275C, and 362cy DEZ + H_2O. We measured 25.7 $\mu g/cm^2$ Al, 20.9 $\mu g/cm^2$ Fe and 42.2 $\mu g/cm^2$ Zn on Si_3N_4 (STXM).

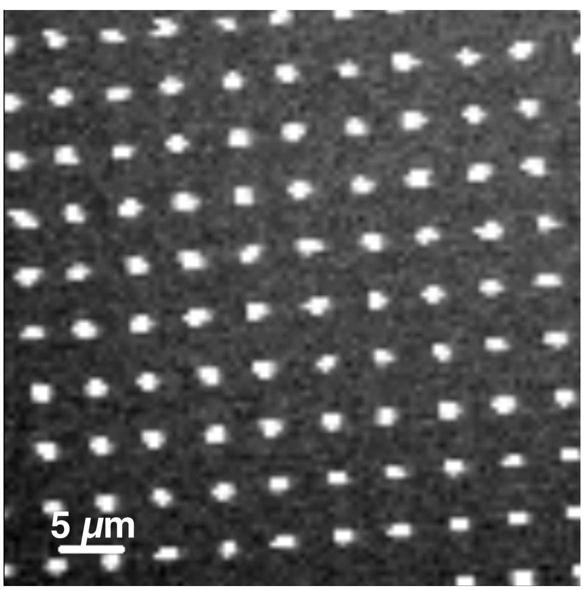

Figure 1. STXM X-ray Absorption Image acquired at 718 eV of a holey Si_3N_4 membrane sample *NB091212-2*, showing Fe homogeneity over a wide area.

References: [1] Butterworth A.L. (2012) LPS, XLIII, Abstract #2666. [2] R. L. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005).

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