Non-destructive Elemental Quantification of Polymer-Embedded Thin Films using Laboratory Based X-ray Techniques

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ABSTRACT Thin coatings are important for a variety of industries including energy (e.g., solar cells, batteries), consumer electronics (e.g., LCD displays, computer chips), and medical devices (e.g., implants). These coatings are typically highly uniform layers with thicknesses ranging from a monolayer up to several micrometers. Characterizing these highly uniform coatings for their thickness, elemental composition, and uniformity are all paramount, but obtaining these measurements can be more difficult when the layers are subsurface and must be interrogated

non-destructively. The coupling of confocal micro X-ray fluorescence (confocal MXRF) and nano-scale X-ray computed tomography (nano-CT) together can make these measurements while meeting these sensitivity and resolution specifications necessary for characterizing thin films. Elemental composition, atomic percent, placement, and uniformity can be measured in three dimensions with this integrated approach. Confocal MXRF uses a pair of polycapillary optics to focus and collect X-rays from a material from a 3D spatially restricted confocal volume. Because of the spatial definition, individual layers (of differing composition) can be characterized based upon the elementally characteristic X-ray fluorescence collected for each element. Nano-scale X-ray computed tomography, in comparison, can image the layers at very high resolution (down to 50 nm) to precisely measure the embedded layer thickness. These two techniques must be used together if both the thickness and atomic density of a layer are unknown. This manuscript will demonstrate that it is possible to measure both the atomic percent of an embedded thin film layer and confirm its manufacturing quality. As a proof of principle, a 1.5 atomic percent, 2 μm -thick Ge layer embedded within polymer capsules, used for laser plasma experiments at the Omega Laser Facility and National Ignition Facility, are measured.

1. INTRODUCTION

The non-destructive, elementally specific quantitative analysis of complex thin films is a challenging problem within the chemical, engineering, and materials sciences. Thin film analysis techniques such as secondary-ion mass spectrometry (SIMS) and glow discharge spectrometry (GDS) offer excellent limits of detection ($1 \mu\text{g g}^{-1}$ to $10^{-3} \mu\text{g g}^{-1}$) and depth analysis ($1 \mu\text{m}$ and $100 \mu\text{m}$, respectively), however, these techniques rely on erosion of the sample surface.[1] For the quantitative analysis of microscopically thick films (i.e., films of 0.1 to $100 \mu\text{m}$ thickness), these techniques are insufficient when non-destructive depth profiling of the sample is required.

Micro X-ray fluorescence (MXRF) spectrometry has been used as a non-destructive elemental analysis technique when the need to preserve a sample is desired, e.g., items of historical significance.[2, 3] Quantitative analysis of multilayered materials using MXRF has been conducted using fundamental parameter modeling techniques,[4] however, an inherent limitation of this method is that the layer densities must be known to derive a layer thickness. Typically, with MXRF instrumentation, a polycapillary lens is placed on the X-ray source, which creates a focused X-ray spot around 10 to 50 μm in diameter. This allows for excellent spatial discrimination of elements in the X and Y lateral planes; however, depending on the sample material, fluorescent X-rays can be detected from deep within the sample, making depth discrimination problematic.

These 2D limitations of MXRF can be overcome by using confocal MXRF, which uses a polycapillary lens on both the source and the detector which are arranged in a confocal configuration (typically 45° from the surface normal) (Fig. 1). This arrangement produces a spherical[5] or, depending on the source/detector geometry, ellipsoidal[6] excitation/detection volume at the point where the source and detector foci overlap and allows for spatial discrimination in the Z direction. Given the optic design and the fluorescent X-ray energy, lateral spatial resolution between $\sim 10\ \mu\text{m}$ to $\sim 200\ \mu\text{m}$ is possible. The X-ray source can either be synchrotron-based monochromatic excitation[7, 8] or a laboratory-based polychromatic X-ray tube excitation.[9]

Confocal MXRF (also referred to as 3D MXRF[10-15]) has been utilized by several laboratories for the qualitative analysis and 3D elemental mapping of semiconductor thin films[16], low density foams and aerogels[17], automotive paint chips[18], and lithium-ion battery cathodes.[19] Quantitative analysis of thickness and elemental composition of stratified

material has been conducted using synchrotron-based confocal MXRF by Mantouvalou et al. using a least-squares algorithm.[12] However, to date, no known studies have been published on the elemental quantitative analysis of materials using laboratory-based polychromatic confocal MXRF.

X-ray computed tomography is a non-destructive 3D imaging technique, in which a series of X-ray radiographs are collected as a sample is rotated. The radiographs are then reconstructed using software to create a series of 2D reconstructed slices which can be stacked and rendered as a 3D image; each voxel's gray scale in the reconstructed image (slice) corresponds to that volume's X-ray attenuation (electron density). Non-destructive 'micro'-scale (micro-CT) and 'nano'-scale X-ray computed tomography (nano-CT) have been utilized to characterize embedded layers within a variety of sample types. For example, laboratory-based micro-CT has been used to measure the width of Japanese oak tree rings[20] as well as dental enamel thickness.[21] Synchrotron-based nano-CT has been used by Yan et al. in the observation of sintering of 2 μm -thick Ni layers and 2.5 μm -thick BaTiO₃ layers within multi-layer ceramic capacitors, with 80 nm 2D resolution.[22] With the recent development[23] of commercially available laboratory-based nano-CT[24], our laboratory[25] can now acquire nano-CT of embedded thin film layers for an accurate measurement of the embedded thin film dimensions.

Using a set of thin films for calibration, this work presents the quantitative, non-destructive analysis of the Ge content of metal doped thin films within polymer capsules for both atomic density and film thickness. The capsules analyzed in this work are used to better understand ignition at the National Ignition Facility (NIF).[26] A comprehensive review of NIF is beyond the scope of this introduction; a brief, yet informative, review is given in reference 27.

The current technique for the quantitative analysis of the Ge content of these capsules is X-ray radiography, in which the X-ray transmission of a sample is plotted as a function of capsule radius and compared to a calibrated model.[28-31] Results from this characterization method agree well with results from other characterization techniques such as electron microprobe analysis and X-ray fluorescence spectroscopy. However, this method does not yield direct elemental information which is problematic if heavy element contamination is present within the sample.

The quantitative analysis of embedded metal doped thin films was conducted using laboratory-based confocal MXRF integrated with laboratory-based nano-scale X-ray computed tomography (nano-CT). Confocal MXRF fluorescent signal intensity from the metal doped thin film layers was used to measure the atomic density, while nano-CT provided ultra-high resolution 3D imaging of the samples to measure the layer thicknesses. When no assumptions can be made about the thickness and atomic percentage, these two techniques are required. With this method it is possible to characterize each of these capsules individually and non-destructively, such that the characterized capsules are then used in the physics experiment.

2. EXPERIMENTAL

2.1 Capsule Description

Approximately 2.2 mm in diameter, these capsules are sputter coated onto a poly(α -methylstyrene) (PAMS) mandrel. According to capsule design specifications, this mandrel is coated with a Ge/polystyrene layer approximately 2 μm -thick, a 3 μm -thick polystyrene separation layer, a Ga/polystyrene layer approximately 2 μm -thick, and an outer polystyrene layer (Fig. 2A). To remove the PAMS mandrel, the capsules are pyrolyzed, which unzips the polymer backbone after which the molecules volatilize and pass through a hole drilled in the

capsule wall, allowing the material to escape; however, the capsules analyzed in this work were received before the pyrolysis step. Two separate batches of capsules were received: Batch 1 consisted of capsules 1-3; Batch 2 consisted of capsules 4 and 5. Fig. 2A provides batch descriptions and manufacturer's design specifications and tolerances. The X-ray fluorescent energies of Ga and Ge present within these samples are far enough apart so that the confocal MXRF can adequately distinguish both the $K\alpha$ and $K\beta$ lines, as seen in Figure 2B.

2.2 Calibrant Preparation

A set of Ge thin films were deposited on polished carbon substrates by electron beam evaporation. The evaporation was performed at the pressure of 1.5×10^{-6} Torr and the deposition rate of 0.2 nm s^{-1} to 0.5 nm s^{-1} .

Geometrical film thickness was measured using a stylus profilometer (Veeco Dektak 6M). A total of 17 scans were performed on each thin film and the data averaged to reduce noise. The uncertainty of the thickness measurement is the propagation of the standard deviations of the mean of two $50 \text{ }\mu\text{m}$ -long portions of the profilometric scan, corresponding to the Ge thin film region and the carbon substrate region.

The Ge areal densities of the calibrants were determined by Rutherford backscattering spectroscopy (RBS) technique. RBS is inherently a standardless technique, thus requiring no reference material.[32] The RBS analysis was carried out at the Ion Beam Materials Laboratory (IBML) at Los Alamos National Laboratory using 2.3 MeV He^+ ions. The areal density values were calculated by fitting the experimentally measured spectra with the RUMP code[33] (RUMP is not an acronym-based name). The uncertainty of this measurement is taken as the inverse square root of the area under the Ge peak.

2.3 Instrumentation

2.3.1 Confocal Micro X-ray Fluorescence

A detailed description of the confocal MXRF microscope can be found in reference 34. Briefly, the confocal MXRF microscope, developed jointly by Los Alamos National Laboratories (Los Alamos, NM) and X-ray Optical Systems (XOS, East Greenbush, NY), is identical to a traditional MXRF instrument but that it uses a pair of monolithic polycapillary optics, developed by XOS, for both X-ray excitation *and* collection. A monolithic fused-silica polycapillary is placed on the Ag X-ray tube source to focus excitation X-rays onto the sample with a second polycapillary placed on the Amptek Si-PIN diode X-ray detector. Both the source and detector polycapillaries are positioned 30° from the surface normal, yielding a confocal focused spot on the sample. The microscope working distance is 10 mm. The excitation/detection volume thus is a prolate spheroid, in which the polar diameter is greater than the equatorial diameter. Confocal MXRF line scans and depth profiles were performed using a 45 kVp accelerating voltage and an applied current of 0.45 mA, a total of 20.25 W.

Depth profiles of Ge thin films were carried out by recording the intensity of the Ge K α X-ray fluorescence line, within the region of interest (ROI) of 9.61 to 10.08 keV (encompassing the Ge K α fluorescent line of 9.876 keV), scanning in the vertical (Z) direction. The thin film calibrants were placed perpendicular to the beam/detector and scanned using a 3 μ m step size with a dwell time of 5 s per step. This measurement was repeated five times for each thin film sample. In addition to the Ge thin films, a blank polished carbon substrate was measured, to account for scattering of X-ray photons by the carbon.

Line scans were recorded by placing the Ge thin films upright in a vice holder and aligning the Ge thin film/carbon substrate interface towards and parallel to the polycapillary optics. Line

scans were acquired by moving the sample perpendicular to the polycapillary optics (Y direction), using a 3 μm step size with a dwell time of 5 s per step.

For capsule analysis, five repeated measurements were taken at the top center (capsules 1-5) and bottom center (capsules 3-5) of each of the capsules, by moving the sample in the vertical (Z) direction. X-ray fluorescent energy was recorded within the energy range of 9.04 to 9.56 keV, to encompass the Ga $K\alpha$ fluorescent line (in addition to the previously mentioned Ge $K\alpha$ ROI) using a 3 μm step size with a dwell time of 5 s per step. Line scans of the capsules were also recorded as a function of sample rotation. The capsules were centered in the rotation axis and a line scan of the capsule wall was then performed. The sample was then rotated one degree and the line scan repeated. This procedure was repeated for two full rotations (720°).

Confocal MXRF data was acquired throughout a period of several days; however, repeated data acquisition for a single sample (i.e., a Ge thin film or capsule) was acquired during the same day. Prior to data acquisition, the Ag tube source was powered on for a minimum of 2 h to allow for thermal equilibrium. Gaussian functions were fitted to the confocal MXRF depth profiles and line scans with the Nonlinear Curve Fit Gauss function found in OriginPro 8.6.0 (OriginLab Corporation, Northampton, MA).

2.3.2 Nano-scale X-ray Computed Tomography

Nano-scale X-ray computed tomography was performed using an Xradia UltraXRM-L200 (Carl Zeiss Microscopy Inc., Pleasanton, CA). This system utilizes a Rigaku MicroMax-007HF (Rigaku Corporation, Tokyo, Japan) rotating Cu anode X-ray source operating at 1.2 kW, which emits an 8.04 keV beam focused onto the sample using a capillary condenser. A single capsule was imaged in absorption large field-of-view mode by collecting 1261 radiographs over 180° rotation (0.143° per radiograph) with a 100 s exposure per radiograph, and a 65 nm isotropic

voxel size. Analysis of the nano-scale CT data was carried out using Avizo Fire Edition version 8.0 software (FEI Visualization Sciences Group, Burlington, MA).^[25] Gaussian functions were fitted to the nano-CT line probe data by using OriginPro 8.6.0, with the Gauss function found in the Multiple Peak Fit module.

3. RESULTS

3.1 Calibration of Confocal MXRF

3.1.1 Determination of Confocal MXRF Excitation/Detection Volume of Ge

The confocal MXRF instrument was calibrated for the quantitative analysis of Ge, using four Ge thin films, with thicknesses (h_G) of 0.267 μm , 0.461 μm , 1.006 μm , and 1.310 μm (Table 1). The calculated atomic densities (ρ_G) of the Ge thin films, displayed in Table 1, are the product of profilometric thicknesses and RBS areal atomic densities (ρ_{RBS}), with uncertainty values calculated from the propagation of the uncertainties of these two measurements. The ρ_G of the thin films range from 90.9 % (calibrant 1) to 94.3 % (calibrant 3) of the full density value of bulk Ge (equal to $4.41 \times 10^{22} \text{ atoms cm}^{-3}$).

The calibration of the confocal MXRF is predicated on the principal that the Ge $K\alpha$ X-ray fluorescence intensity is directly dependent on the number of Ge atoms excited and then detected per unit volume. To accurately determine this value for each thin film calibrant, both the atomic density and the confocal MXRF excitation/detection volume of each thin film calibrant must be known. The confocal MXRF excitation/detection volume (V_G) is dependent on an element's fluorescent photon energy and thus must be determined for an individual element of interest. Therefore, it was necessary to measure the dimensions of the waist and height of the confocal MXRF excitation/detection volume at the Ge $K\alpha$ energy. Line scans of Ge thin films (five repeated measurements per calibrant) were recorded from the Ge $K\alpha$ line and Gaussian

distributions were fitted to the data (Fig. 3A), from which the full width at half maximum (FWHM) was calculated and taken as the width (in both the X and Y directions) of the confocal MXRF excitation/detection volume. The mean of these values was calculated and taken as the experimentally determined values for the waist ($\bar{d}_G$) of the confocal excitation/detection volume, which ranged from 30.3 to 31.0 μm (Table 2). Gaussian functions were also fitted to the depth profiles of the calibrants (five repeated measurements per calibrant), and the FWHM calculated, to determine the height of the confocal MXRF excitation/detection volume (Fig. 3B). This value, calculated from the mean of the FWHM ($n = 20$, where n is the number of measurements), was determined to be $55.4 \pm 0.1 \mu\text{m}$ (the uncertainty is the standard error of the mean).

While the height of the confocal MXRF excitation/detection volume is a useful measure and is easily obtained from Gaussian fits of the Z depth profiles, it is not truly indicative of the probed calibrant volume. In this calibration, h_G ranges from 0.267 μm to 1.310 μm , in comparison to the confocal MXRF beam height, which is 55.4 μm (Fig. 4). Therefore, in the calculation of the confocal MXRF excitation/detection volume, the h_G of each thin film calibrant is considered rather than the excitation/detection height. A key advantage in using thin films of these dimensions for calibration is this difference in spatial dimensions (i.e., the difference between the thin film thicknesses and the confocal MXRF excitation/detection height) allows for a linear calibration which requires no corrections for sample absorption of fluorescent X-rays. For the calculation of the number of Ge atoms (N_G) probed during the calibration of the confocal MXRF microscope, a cylindrical beam/sample interaction volume geometry was assumed (Eqn. 1).

$$N_G = \rho_G V_G = \rho_G \left(\pi h_G \left(\frac{d_G}{2} \right)^2 \right) \quad \text{Equation 1}$$

In this calculation, the curvature of the excitation/detection volume was considered to be negligible. The values used to calculate N_G are presented in Table 2.

3.1.2 Calibration of Confocal MXRF Signal and Number of Ge Atoms

The intensity of the Ge signal from the confocal MXRF thin film calibrants was recorded as a function of depth by raising the thin films into the confocal MXRF excitation/detection volume. The resulting depth profiles, presented in Fig. 5, display a direct increase of the confocal MXRF Ge K α ROI intensity as a function of Ge thin film thickness, as was expected. From these depth profiles, the maximum intensity (in counts) was recorded and the mean ($\bar{I}_G$) of five measurements per calibrant (Table 2) was used as the response of the calibration plot (discussed below). The precision of this method was evaluated using the Cochran Test,[35, 36] which compares a single estimate of the variance of a mean to a group of estimated variances from a group of means. From this test, the g statistic is used (in place of the F statistic for the comparison of only two estimated variances) and compared to a critical g value. For the sake of brevity, the equations for the Cochran test have been omitted; the reader is referred to reference 37. The calculated g value was determined to be 0.608. This is compared to the critical g value at the 95% confidence level ($g_{0.05,5,4}$), equal to 0.629. The calculated g value does not exceed the critical g value and the null hypothesis is accepted (i.e., the estimated variances of the means are equal) and it is concluded that there is no statistical evidence of difference in the precision of the confocal MXRF depth profile measurements for each thin film calibrant.

The calibration plot of $\bar{I}_G$ as a function of N_G , presented in Figure 6A, shows a linear relationship. The calibration equation, from the least-squares linear regression of the data, is presented in Equation 2.

$$\bar{I}_G = YN_G + \bar{I}_C \quad \text{Equation 2}$$

In Equation 2, Y is the elemental yield, expressed as $I N_G^{-1}$ (equal to 9.54×10^{-11} counts per number of atoms probed); $\bar{I}_C$ is the mean of the maximum intensity (in counts) of X-ray scatter of a blank carbon substrate. Experimentally this value is 42 ± 1 (uncertainty is the standard error of the mean), the linear regression value is equal to 49.

The R^2 value of the least-squares linear regression is equal to 0.99995. The plot of the residuals (i.e., observed $\bar{I}_G$ – calculated $\bar{I}_G$) in Figure 6B contains only five data points, too few to exhibit a distinguishable pattern. A distinguishable pattern in the residuals plot indicates either a systematic departure from the linear regression, non-constant variances, or a poor model fit; references 36 and 38 provide examples of distinguishable patterns in residual plots.[36] A more rigorous approach to evaluating the linear regression is the analysis of variance (ANOVA) with repeated observations.[36, 38] This analysis takes into account the error from lack of fit as well as pure error, enabling a statistical approach to evaluating the appropriateness of the regression equation. The equations for the ANOVA are omitted for brevity; the reader is referred to reference 39. The result of the ANOVA is presented in Table 3. The calculated $F_{\text{Regression}}$ value, equal to 107167, exceeds the critical F value of 4.28 at the 95% confidence level; therefore, the null hypothesis (i.e., the variance due to regression is equal to the variance due to error) is rejected and it is concluded that there is a linear relationship between $\bar{I}_C$ and N_G . The calculated value for $F_{\text{Lack of Fit}}$, equal to 1.87, does not exceed the critical F value of 3.10 at the 95% confidence level. From this result, the null hypothesis (i.e., the variance due to lack of fit is equal to the variance due to pure error) is accepted and it is concluded that the linear regression equation (Eqn. 2) of the calibration plot appropriately fits the data.

To summarize, the calibration equation (Eqn. 2) is found to be appropriate for this calibration by using rigorous statistical methods. This statistical examination allows for the quantitative

analysis of Ge using the confocal MXRF instrument with certainty. While the R^2 value is often cited to show the “goodness of fit” of a calibration equation to experimentally observed data, even small deviations from unity can mean significant lack of fit which can lead to erroneous calibration equations.[38]

It is also recognized that there is uncertainty in the independent variable N_G of the calibration plot, which may impact the least-square linear regression. It has been proposed by Cornbleet and Gochman[40] that significant error is present in the least-squares slope estimation when the ratio of the standard deviation of an individual measurement (here, this is taken as the uncertainty of an individual N_G) and the standard deviation of the mean of the independent data set (in this case, the standard deviation of the mean of N_G) exceeds 0.2. This ratio was calculated for each N_G and found to be less than 0.03; therefore, it is assumed that any uncertainty in the calculation of N_G from experimental measurements is considered negligible and does not introduce significant error in the least-squares estimation of the calibration slope.

The limit of detection (LOD) of the confocal MXRF microscope, with respect to this particular analysis, was calculated using the following equations (Eqn. 3 and 4)[41], where S_m is the minimum distinguishable confocal MXRF intensity signal, $\bar{I}_C$ is the mean confocal MXRF maximum intensity of a blank carbon substrate from depth profiles (here, equal to 37 counts from $n = 17$ measurements), k is equal to 3,[42, 43] and s_C is equal to the standard deviation of $\bar{I}_C$ (equal to 5 counts).

$$S_m = \bar{I}_C + ks_C \quad \text{Equation 3}$$

From Equation 3, S_m was calculated to be 51 counts. The LOD was then calculated using the elemental yield (Y) presented in Equation 2 and $\bar{I}_C$ using Equation 4.

$$\text{LOD} = \frac{S_m - \bar{I}_C}{Y} \quad \text{Equation 4}$$

From Equation 4, the LOD was calculated to be 1.48×10^{11} Ge atoms. The limit of quantification (LOQ), calculated by using Equation 5,[41] was determined to be 4.78×10^{11} Ge atoms.

$$\text{LOQ} = \frac{10s_c}{Y} \quad \text{Equation 5}$$

Assuming the mean of the calculated atomic densities (i.e., the mean of each ρ_G) presented in Table 1 and the mean of the individual confocal MXRF spot diameters (equal to 30.5 ± 0.3 , where the uncertainty is the standard error of the mean) , the LOD and LOQ translates to a Ge thin film with an approximate thickness of $5.1 \text{ nm} \pm 0.1 \text{ nm}$ and $16.3 \text{ nm} \pm 0.2 \text{ nm}$, respectively. Uncertainties were calculated from the propagation of the standard error of $\bar{I}_C$, the standard error of the mean of N_G , and the standard error of the mean of the confocal MXRF excitation/detection waist.

3.2 Quantitative Analysis of Ge Content of Metal Doped Polymer Capsules

3.2.1 Confocal MXRF Analysis

The Ge content of the metal doped polymer capsules was determined by recording the maximum fluorescence peak intensity of the Ge $K\alpha$ ROI using confocal MXRF and calculating these values using the calibration equation (Eqn. 2). The maximum fluorescence intensity was recorded by performing depth profiles of the capsules, with the confocal MXRF excitation/detection volume positioned at the top-center of the capsule. As can be seen in both the line scan (Fig. 7A) and depth profile (Fig. 7B), the confocal MXRF instrument adequately differentiates the Ga/PS and Ge/PS layers. From the maximum confocal MXRF peak intensity of

the depth profiles of the metal doped polymer capsules, the number of Ge atoms probed was calculated using Equation 2. This value ranges between 3.32×10^{12} atoms (capsule 2) and 3.87×10^{12} atoms (capsule 4, see Table 4).

Capsules 3-5 were evaluated for self-absorption of fluorescent X-rays by recording depth profiles (five repeated measurements) at the bottom-center of the capsule. The fluorescent photons reaching the detector thus had to travel through the overlying PAMS mandrel and another section of the capsule shell. The $\bar{I}_G$ recorded at the bottom-center of each capsule was as follows: capsule 3 = 357 ± 6 ; capsule 4 = 386 ± 8 ; capsule 5 = 390 ± 5 , where the uncertainties are the standard errors of the mean. For each capsule, the $\bar{I}_G$ acquired from the top-center and bottom-center were subjected to the F test for homogeneity of variances. The experimental F value of each capsule (capsule 3 = 1.10; capsule 4 = 3.31; capsule 5 = 4.62) was less than the critical F value ($F_{.05/2,4,4}$) of 9.60; therefore, the null hypothesis (i.e., that the estimated variance of $\bar{I}_G$ recorded at the top-center of the capsule is equivalent to the estimated variance of $\bar{I}_G$ recorded at the bottom-center of the capsule) of the F test is accepted at the 95% confidence level. Student's t test was employed to evaluate the homogeneity of $\bar{I}_G$ recorded from the top-center and bottom-center of each capsule. The experimental t value for capsule 3 ($t = 0.76$) and capsule 4 ($t = 2.04$) were less than the critical t value ($t_{.05/2,2,8}$) of 2.31; therefore, the null hypothesis is accepted (i.e., that the $\bar{I}_G$ recorded from the top-center and bottom-center of the respective capsule is statistically equivalent) at the 95% confidence level. However, the experimental t value of capsule 5 ($t = 2.36$) was greater than the critical t value, indicating a statistically significant difference in the two means. This result indicates that the PAMS mandrel of capsules 3 and 4 have minimal absorption effects on the Ge fluorescent X-rays and the capsules may be considered homogeneous in Ge at.%. For capsule 5, the $\bar{I}_G$ recorded from the

bottom-center of the capsule is statistically greater than that taken from the top-center of the capsule, despite the fact that the fluorescent photons travel through the PAMS mandrel. This result may indicate heterogeneity in the Ge at.% of capsule 5.

Figure 8 presents the mean maximum peak intensity of a series of Y line scans of a metal-doped polymer capsule as a function of sample rotation. A noticeable variation of the maximum peak intensity of the Ge $K\alpha$ signal is observed, which can be attributed to precession due to the sample being slightly off the center axis of rotation. However, this precession was not observed in a previous study involving confocal MXRF measurements of Cu/Be capsules composed of a 60 μm -thick Cu layer, which is thicker than the ~ 30 μm beam width.[44] In light of this result, this measurement method proved inadequate in discerning the uniformity as a function of rotation around the circumference of the Ge/PS and Ga/PS layers, which would be better measured with a confocal beam size that is closer in dimension to the thin film thickness.

3.2.2 Nano-CT Imaging Results

The thickness of the Ge layer within the capsules was determined by measuring the thickness of the Ge/PS layer using nano-CT. Due to the small 2D field of view required by nano-CT (65 μm x 65 μm), only a partial volume of the capsule was imaged; however, this method proved more than adequate in resolving the Ge/PS and Ga/PS layers. Figure 9 presents a reconstructed nano-CT slice image of the metal doped polymer capsule in which the Ge/PS layer, Ga/PS layer, PS outer and separation layers, and PAMS mandrel are observed. The thicknesses of the Ge/PS and Ga/PS layers were measured by taking a line probe through the capsule shell (Fig. 10A) using Avizo software, which yielded peaks corresponding to the metal doped layers. The line was drawn at 20 different locations on the CT data. A Gaussian function was fitted to the data (Fig. 10B), with the FWHM calculated from the fits and taken as the thickness of the respective

layers. From the Gaussian fit, the thickness of the Ge/PS layer was calculated to be $2.20 \mu\text{m} \pm 0.01 \mu\text{m}$; the Ga/PS layer was calculated to be $1.50 \mu\text{m} \pm 0.01 \mu\text{m}$ (the uncertainties are the standard errors of the means). Due to the time required for data acquisition, only one capsule (capsule 3) was analyzed using nano-CT; therefore, only one Ge/PS layer thickness measurement was used in the calculation of the Ge at.%. Based on the manufacturer's specifications and the slow Ge/PS layer coating rate ($\sim 0.5 \mu\text{m h}^{-1}$)[45] of the capsules, it was assumed for this work that the thickness of the Ge/PS layer is consistent for each capsule.

3.2.3 Combination of Confocal MXRF and nano-CT

In the calculation of the confocal MXRF excitation/detection volume of the capsules, the mean of the individual waist diameters measured from each calibrant were used. The mean waist diameters were tested for homogeneity of variance using the Cochran test, with an experimental g value of 0.509 and critical g value ($g_{0.05,5,4}$) of 0.629, indicating that the variances of the means were equivalent at the 95% confidence level, thus suitable for the individual measurements to be averaged. From the thickness of the Ge/PS layer of the metal doped polymer capsule, determined from nano-CT, and the mean of the waist diameters (equal to $30.5 \mu\text{m} \pm 0.3 \mu\text{m}$, where the uncertainty is the standard error of the mean), the confocal probed volume of the Ge/PS layer was calculated to be $1606 \mu\text{m}^3 \pm 14 \mu\text{m}^3$ (the uncertainty is the product of the propagation of the uncertainty of the nano-CT Ge/PS layer thickness measurement and the uncertainty of the confocal MXRF excitation/detection waist diameter).

It was assumed that the Ge/PS layer consisted of PS with a molar composition of $\text{C}_1\text{H}_{1.35}$ and a density of 1.01 g cm^{-3} .[45] It is understood that this is a considerable assumption for this analysis; however, these values are used by the manufacturer in the quantitative analysis of Ge content using contact radiography. The number of C (N_C) and H (N_H) atoms within the Ge/PS

layer was calculated using these values and the calculated confocal MXRF excitation/detection volume of the capsules. The Ge at.% of the Ge/PS layer of metal doped polymer capsules was then calculated using Equation 6.

$$\text{Ge at. \%} = \left(\frac{N_G}{N_G + N_C + N_H} \right) \times 100 \quad \text{Equation 6}$$

The result of this calculation for each capsule is presented in Table 4. From this analysis, the Ge content of metal doped polymer capsules differ slightly from that of the manufacturer's target specifications. The capsules analyzed from Batch 1 (capsules 1-3) fall within the 2.2 ± 0.5 Ge at.% requirements. At 2.14 Ge at.%, capsule 4 falls outside of the target specification of 1.5 ± 0.5 Ge at.%; whereas, capsule 5 barely meets the target specifications.

4. DISCUSSION

Unlike typical MXRF quantitative studies, the analysis of metal doped polymer capsules using a confocal MXRF microscope is fairly straightforward with respect to calibration. The excitation/detection volume of the confocal MXRF microscope, being greater in height than the thickness of the thin films (and with no overlying highly absorbing materials) allows for a linear calibration plot within this spatial regime, as shown using a thorough analysis of the linear regression calibration equation with respect to the data acquired. The precision of this technique was shown to be adequate through statistical analysis of the repeated measurements of the thin film calibrants.

Interestingly, confocal MXRF is capable of discerning the Ga/PS outer layer and Ge/PS inner layer of metal doped polymer capsules, as seen in the confocal MXRF line scan and depth profile presented in Figure 7A and 7B, even though these layers are separated by only a 3 μm -thick PS

layer. This is only achievable due to the fact that the Ge and Ga X-ray fluorescent ROIs do not overlap and that the Ga layer does not significantly absorb the Ge fluorescent X-rays.

The key component of this study is the coupling of nano-CT with confocal MXRF to determine an accurate layer thickness while simultaneously measuring the atomic percentage of the capsules in a non-destructive manner. Modeling of the confocal MXRF data would provide approximate layer thickness of these capsules, similar to the work by Mantaouvalou et al.[12], who were able to derive the thickness of Zn-containing polymer layers using data acquired from synchrotron-based monochromatic confocal MXRF. However, the approach here provides direct and accurate spatial information, eliminating the need for complex algorithms to derive spatial information from confocal MXRF data. This is the key point of this work: the coupling of these two non-destructive measurements to achieve an empirical measurement without relying on modeling.

The demonstrated integration of nano-CT and confocal MXRF for the quantitative analysis of Ge content of polymer embedded thin films shows that this method would be valid for the quantitative analysis of other complex thin film systems, provided that the upper thin film layer does not significantly attenuate the fluorescent X-rays from the buried layer. Certain limitations exist with the current laboratory-based confocal MXRF microscope, namely in that it cannot detect X-ray fluorescent photons of low atomic number elements ($< \text{Ca}$) due to absorption of low energy X-ray photons by ambient air. This limitation has been overcome by Smolek et al.[5] and Nakazawa et al.[18], who have developed laboratory-based confocal MXRF microscopes under vacuum which allows for the detection of low atomic number elements, down to Na. Currently, a similar laboratory-based vacuum chamber confocal MXRF microscope is being developed at Los Alamos National Laboratory, which will extend our capabilities to detect low atomic number

elements within samples. Another limiting factor with this method is the fabrication and analysis of thin films needed to calibrate the confocal MXRF microscope, which is not possible for pure Ga due to its low melting point (29.76 °C).

5. CONCLUSIONS

In this work we have presented the non-destructive quantitative analysis of both the thickness and atomic percentage of the Ge content of metal doped polymer capsules using laboratory-based confocal MXRF coupled with laboratory-based nano-scale X-ray computed tomography. These results have shown that this technique is applicable in the characterization of metal thin films which are embedded in a low Z matrix. Due to the complex nature of these capsules, adequate spatial and elemental discrimination of the Ge/polystyrene and Ga/polystyrene layers was required to accurately provide quantifiable data, which would not be possible using conventional MXRF instrumentation. Using nano-CT to measure the metal/polymer layer thicknesses enabled a simplistic calibration and quantification approach, as there was no need to calculate the layer thicknesses using confocal MXRF data, which would have required exhaustive modeling of the instrument.

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FIGURE CAPTIONS

Figure 1. Schematic of the confocal MXRF microscope, illustrating the concept of confocal micro X-ray fluorescence. Source X-rays (blue) are focused onto the sample using a polycapillary optic. Detected fluorescent X-rays (red) travel through a polycapillary optic to the detector, while a significant portion of fluorescent X-rays do not reach the detector (green).

Figure 2. A A schematic diagram of a metal doped polymer capsule showing capsule design specifications and tolerances. **B** Confocal MXRF spectrum of a metal doped polymer capsule exhibiting characteristic fluorescent lines of Ge and Ga.

Figure 3. Confocal MXRF line scan (**A**) and depth profile (**B**) of the Ge $K\alpha$ X-ray fluorescent intensity of a 1.310 μm -thick Ge thin film and the Gaussian fits of the confocal MXRF data. From this, the measured height and diameter of the confocal MXRF excitation/detection volume is 55.4 μm and 30.5 μm , respectively, for the Ge X-ray fluorescent energy.

Figure 4. Schematic diagram of the confocal MXRF volume encompassing a region of the thin film, illustrating the calculated volume of the thin film excited/detected by the confocal MXRF polycapillary optics. The Z direction is the direction in which the sample is moved during depth profiling, as seen in Figure 3B. The diagram is not drawn to scale.

Figure 5. Confocal MXRF depth profiles of the Ge K α X-ray fluorescent intensity of Ge thin films with thicknesses of 0.267 μm , 0.461 μm , 1.006 μm and 1.310 μm .

Figure 6. A Calibration plot of mean confocal MXRF maximum intensity of Ge thin film calibrants (squares) as a function of the number of Ge atoms present in the confocal MXRF excitation/detection volume. Dashed lines are the 95% confidence interval of a mean fluorescence intensity measurement. The linear regression line is omitted for clarity. Inset: A magnified view of the data corresponding to calibrant 3, showing the linear regression line (black line), the 95% confidence interval of the mean fluorescence intensity measurement (dashed line), and the 95% confidence interval of the linear regression (dotted line). **B** A plot of the residuals of the calibration.

Figure 7. Confocal MXRF line scan (**A**) and depth profile (**B**) of the Ga K α and Ge K α signals of a metal doped polymer capsule. Data presented is the mean of five line scan recorded using 1 μm steps (**A**) and 3 μm steps (**B**) with a dwell time of 5 s per step. Peak height positions are separated by 5 μm (**A**), showing excellent spatial resolution in the Y direction, and 9 μm (**B**).

Figure 8. The mean ($n = 2$) of the confocal MXRF maximum peak intensity of the Ge K α signal of a metal doped polymer capsule as a function of theta. The capsule was scanned in the Y direction then rotated one degree. This was repeated for two full rotations. The mean run-to-run error is equal to 2.6%.

Figure 9. Reconstructed nano-CT slice of a metal doped polymer capsule. Isotropic voxel size is 65 nm with 150 nm 2D resolution. The outer layer of higher absorbance (left side of image) cannot be identified even with a vacuum MXRF instrument.

Figure 10. A line probe profile taken from the nano-CT slice image presented in Figure 8 (A). Gaussian fit of the Ga/polystyrene layer signal and Ge/polystyrene layer signal (B).

Table 1. Ge thin film thicknesses, areal densities, and calculated atomic densities.

Calibrant	h_G (μm)	ρ_{RBS} (atoms cm^{-2})	ρ_G^a (atoms cm^{-3})
Blank	0	-	-
1	$0.267 \pm 1.9\%$	$1.07 \times 10^{18} \pm 0.2\%$	$4.01 \times 10^{22} \pm 1.9\%$
2	$0.461 \pm 1.5\%$	$2.02 \times 10^{18} \pm 0.2\%$	$4.12 \times 10^{22} \pm 1.5\%$
3	$1.006 \pm 0.5\%$	$4.33 \times 10^{18} \pm 0.2\%$	$4.16 \times 10^{22} \pm 0.5\%$
4	$1.310 \pm 1.0\%$	$5.36 \times 10^{18} \pm 0.2\%$	$4.12 \times 10^{22} \pm 1.0\%$

^aThe uncertainty is calculated from the propagation of the uncertainties associated with h_G and ρ_{RBS} .

Table 2. Experimentally determined number of Ge atoms within the confocal MXRF spot volume for Ge thin films and mean confocal MXRF maximum peak intensities of Ge thin films.

Calibrant	$\bar{d}_G^a$ (μm)	V_G^b (μm^3)	N_G^c (atoms)	$\bar{I}_G^a$ (counts)	95% Confidence Interval of $\bar{I}_G$ (counts)
Blank	-	-	-	42 ± 1	0 - 98
1	$30.4 \pm 0.3\%$	$193.7 \pm 1.9\%$	$7.76 \times 10^{12} \pm 2.70\%$	784 ± 4	743 – 833
2	$30.3 \pm 0.8\%$	$332.2 \pm 2.2\%$	$1.46 \times 10^{13} \pm 2.65\%$	1450 ± 6	1392 – 1479
3	$31.0 \pm 0.3\%$	$757.1 \pm 0.8\%$	$3.26 \times 10^{13} \pm 0.93\%$	3161 ± 14	3106 - 3199
4	$30.3 \pm 0.9\%$	$947.1 \pm 2.0\%$	$3.88 \times 10^{13} \pm 2.26\%$	3728 ± 9	3691 – 3789

^aThe uncertainty is the standard error of the mean.
^bThe uncertainty is the product of the propagation of uncertainty associated with $\bar{d}_G$ and h_G .
^cThe uncertainty is the product of the propagation of uncertainty associated with ρ_G and V_G .

Table 3. Analysis of variance (ANOVA) of the calibration plot of confocal MXRF intensity as a function of the number of Ge atoms probed.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares		
Regression	49046092	1	49046092	$\frac{F_{\text{Regression}}}{107167}$	$\frac{F_{\text{Critical}} = F_{0.05,1,23}}{4.28}$
Total Error	10526	23	458		
Lack of Fit	2303	3	768	$\frac{F_{\text{Lack of Fit}}}{1.87}$	$\frac{F_{\text{Critical}} = F_{0.05,3,20}}{3.10}$
Pure Error	8223	20	411		
Total	49056619	24			

Table 4. Mean confocal MXRF maximum peak intensities; calculated number of germanium atoms probed, and experimentally determined germanium atomic percent of metal doped polymer capsules.

Metal Doped Polymer Capsule	$\bar{I}_G^a$ (counts)	N_G^b (atoms)	Ge at.% ^c
1	362 ± 5	3.29x 10 ¹² ± 1.5%	1.88 ± 0.05
2	357 ± 8	3.24 x 10 ¹² ± 2.7%	1.85 ± 0.08
3	363 ± 5	3.29 x 10 ¹² ± 1.6%	1.88 ± 0.05
4	405 ± 4	3.74 x 10 ¹² ± 1.6%	2.14 ± 0.05
5	387 ± 2	3.46 x 10 ¹² ± 0.6%	1.97 ± 0.04

^aThe uncertainty is the standard error of the mean.
^bThe uncertainty is taken from the standard error of $\bar{I}_G$.
^cThe uncertainty is the product of the propagation of uncertainties associated with N_G and $\bar{d}_G$.

Figure(s)

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