Spectrochimica Acta Part B 101 (2014) 320–329

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Non-destructive elemental quantification of polymer-embedded thin films using laboratory based X-ray techniques

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ARTICLE INFO

Article history:
Received 2 June 2014
Accepted 13 September 2014
Available online 22 September 2014

Keywords:
Confocal micro-X-ray fluorescence
X-ray computed tomography
Embedded thin films

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.

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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 μg g^{-1} to10^{-3} μg g^{-1}) and depth analysis (1 μm and 100 μm, 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 μm 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 ~10 μm and ~200 μm 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

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http://dx.doi.org/10.1016/j.sab.2014.09.016
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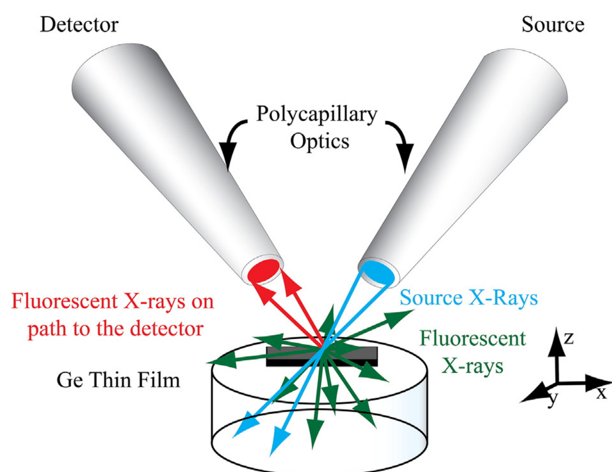

Fig. 1. Schematic of the confocal MXRF microscope, illustrating the concept of confocal micro-X-ray fluorescence. Source X-rays (blue) are focused onto the sample using a polycapillary optic. Detected fluorescent X-rays (red) travel through a polycapillary optic to the detector, while a significant portion of fluorescent X-rays do not reach the detector (green). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

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. [12] using a least-squares algorithm. 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 $BaTiO_3$ 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

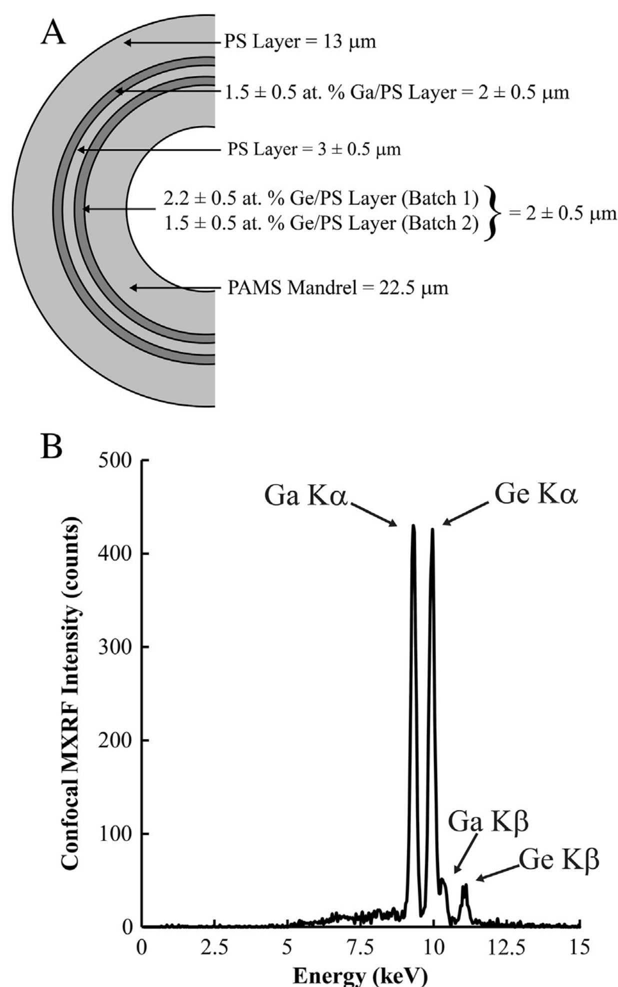

Fig. 2. (A) A schematic diagram of a metal doped polymer capsule showing capsule design specifications and tolerances. (B) Confocal MXRF spectrum of a metal doped polymer capsule exhibiting characteristic fluorescent lines of Ge and Ga.

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