doi:10.1017/S1431927621011442
Microsc. Microanal. 27 (Suppl 1), 2021

Oxidation of metallic glass thin films: a combined EPMA and XPS investigation into the composition and thickness of oxidized surfaces

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Metallic glass thin films (MGTFs) are a recently developed alternative to conventional alloy thin films that exhibit several unique material properties beneficial in applications from biomedical devices to electrical components [1,2]. The surface of MGTFs is characterized by ultra low coefficient of friction, and combined with Zr-based MGTFs' biocompatibility, makes them an advantageous coating material for minimally-invasive surgical devices and syringes [3]. Minimizing surface oxidation is critical to long-term utility of Zr-based MGTFs in biomedical applications and needs to be well understood for design considerations. We combined thin film analysis by electron probe microanalysis (EPMA) with X-ray photoelectron spectroscopy (XPS) to quantify the composition and thickness of surface oxidation layers of Zr-based MGTFs.

Thin films were deposited by employing an in-house built high vacuum direct current magnetron sputtering tool. An arc-melted alloy target with nominal compositions of $Zr_{55}Cu_{30}Al_{10}Ni_5$ (at. %) was commercially acquired. The base pressure of the vacuum vessel was better than 1×10^{-7} Torr. The operating pressure of process gas (Ar) was 4.3 mTorr during deposition as measured by a 275i Pirani-style pressure gauge made by Kurt J. Lesker Company.

Sputter deposited samples investigated in this study are comprised of three layers: (1) a substrate of Si < 001 > wafer, (2) two types of MGTF of base composition ZrCuAlNi with thicknesses ranging from 15-1500 nm, and (3) surface oxidation layer of composition ZrO_2 and unknown thickness. Three MGTF samples with nominal composition $Zr_{55}Cu_{30}Al_{10}Ni_5$ were fabricated for this study (nominally 50, 500, 1500 nm thickness), and two samples with the same nominal composition were used from a previous study (nominally 15 nm thickness). FE-SEM was used to measure cross sectional thickness of the MGTF from cleaved samples. XRD was used to confirm amorphous structure of MGTF samples used for this analysis. XPS analysis reveals high energy shifts in Zr 3d orbitals indicating that surface oxidation layers are dominantly ZrO_2. XPS data acquired in depth profiling mode are used as an independent constraint on layer thickness.

Analysis of characteristic X-ray emission from MGTF samples was performed using EPMA [4]. X-ray intensities for O-Kα (LPC0), Al-Kα (LTAP), Si-Kα (LTAP), Ni-Kα (LLIF), Cu-Kα (LLIF), and Zr-Lα (LPET) were acquired using a Cameca SX-Five Field Emission EPMA instrument equipped with Schottky Field Emission source and five wavelength-dispersive spectrometers (WDS). Experimental X-ray intensities were acquired from five unknown MGTF samples and a suite of standard materials (pure metals for Al, Si, Ni, Cu, Zr, and synthetic Fe_3O_4 for O). Measurements were acquired at 10, 12, 15, 20, 25, and 30 kV accelerating voltage.

X-ray intensities of all elements decrease with increasing accelerating voltage except for Si, which increases with voltage. This can be seen clearly upon inspection of data from the nominally 50, 500, and 1500 nm MGTF samples (Fig. 1). The increased activation volume at higher kV generates a larger proportion of X-rays from the substrate relative to the thin films. At low kV, Si k-ratios close to zero

indicate minimal interaction with the substrate for nominally 500 and 1500 nm samples. Trends in O k-ratios are independent of sample thickness and show no significant variation between samples.

Elemental composition and thickness of multi-layered samples was calculated using the *BadgerFilm* thin film analysis program [5,6]. *BadgerFilm* calculates theoretical k-ratios with the PAP phi-rho-z algorithm [7] and modified phi-rho-z matrix correction to calculate characteristic and Bremsstrahlung fluorescence effects. The program uses a non-linear fitting algorithm to match calculated k-ratios to experimental k-ratios acquired from a range of accelerating voltages to determine composition and thickness of stratified samples (Fig. 2). Input parameters include experimental k-ratios from multiple kV conditions and initial guesses for material composition/density and layer thickness. The program converges on a solution for the composition and thickness of both the MGTF and surface oxidation layer. The thickness of surface oxidation layers was found to range from 8-110 Å and correspond with time since sputter deposition.

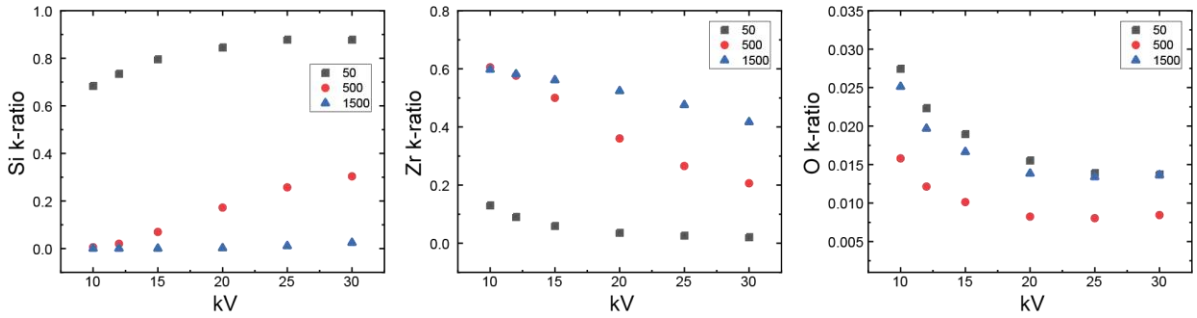

Figure 1. Experimental k-ratios for Si, Zr, and O from nominally 50, 500, and 1500 nm metallic glass thin films.

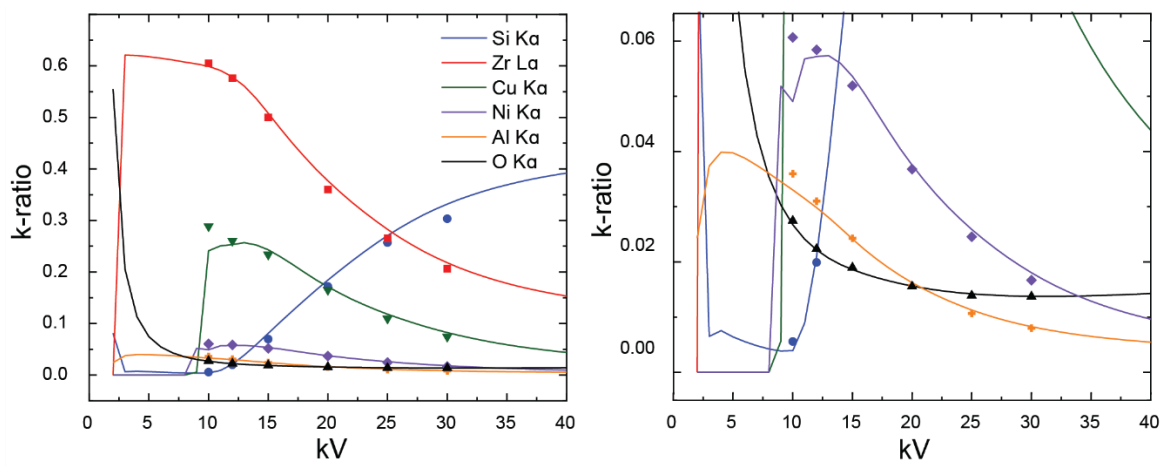

Figure 2. The *BadgerFilm* program uses a non-linear fitting algorithm to match calculated k-ratios to experimental k-ratios acquired from a range of accelerating voltages, enabling quantitative determination of composition and thickness of stratified samples. This plot shows results from a 470 nm MGTF of composition $Zr_{53}Cu_{30}Al_{10}Ni_7$ with 71 Å ZrO_2 surface layer.

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https://doi.org/10.1017/S1431927621011442 Published online by Cambridge University Press

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