Cosputtered composition-spread reproducibility established by high-throughput x-ray fluorescence

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We describe the characterization of sputtered yttria-zirconia composition spread thin films by x-ray fluorescence (XRF). We also discuss our automated analysis of the XRF data, which was collected in a high throughput experiment at the Cornell High Energy Synchrotron Source. The results indicate that both the composition reproducibility of the library deposition and the composition measurements have a precision of better than 1 atomic percent. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3478668]

High throughput characterization of thin film composition spreads is an important aspect of combinatorial materials science.[1] Synchrotron-based x-ray fluorescence (XRF) experiments at 10 keV have been developed for composition mapping of inorganic libraries.[2,3] We recently presented a combined high energy x-ray diffraction (XRD) and XRF experiment for high throughput characterization of composition spread thin films.[4] The 60 keV x-ray energy used for this experiment was chosen for the XRD measurements, and we note that this high excitation energy enables quantitative analysis of all elements in rows 4 to 7 of the periodic table. Here, we describe the capabilities of a high throughput analysis algorithm for the XRF experiment, which provides simultaneous determination of film composition and thickness. In addition, we present the characterization of two ZrO_2–Y2O_3 composition spread thin films prepared under the same sputter deposition conditions. The measured composition profiles for the two films coincide within 0.7 at.% over a broad range of composition, demonstrating the precision of both the synthesis and characterization techniques.

The composition-spread thin films were prepared by 90° off axis radio-frequency magnetron reactive cosputtering. Metal Zr and Y targets were placed in independently powered 2 in. magnetron sputter sources and operated in an atmosphere of 4 Pa of 40% O_2 in Ar. The Zr and Y sources were operated at 100 and 50 W, respectively. The two samples were deposited on different days and the deposition time for sample A was slightly longer than that of sample B. The 3 in. Si wafer with 500 nm SiO_2 diffusion barrier was maintained at 500 °C during deposition. The substrate was placed below and centered between the deposition sources, a geometry known to produce a deposition gradient from each source.[5]

The x-ray diffraction (XRD)/x-ray fluorescence (XRF) experiments were performed at the A2 beamline of the Cornell High Energy Synchrotron Source (CHESS). A 60 keV x-ray beam impinged on the back of the Si substrate with incident angle ~45° and 1 mm^2 spot size. The thin film was exposed to the direct beam on the downstream side of the substrate, and the XRF signal was obtained by a Rontec X-Flash detector oriented orthogonal to the direct beam. To preclude detection of fluorescence from other sources, a Mo and Pb shield was placed over the detector with an ~0.2 mm^2 hole aligned with the footprint of the beam on the thin film sample. For the $ZrO_2-Y_2O_3$ films, 11 substrate positions were characterized using equal-dose measurements of 6×10^{12} photons, requiring ~250 s exposures. A flux calibration was performed through XRF analysis of a Pt film of known thickness. The XRF spectra were acquired with 2048 channels from 0 to 80 keV.

The energy-dependent detection efficiency of the experiment is shown in Fig. 1. At low energy, the efficiency is limited mainly by attenuation of the fluorescence x-rays in the 22 mm air path from sample to detector. At high energy,

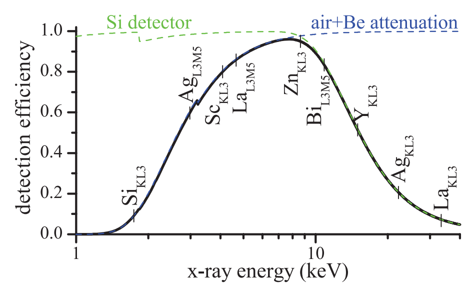

FIG. 1. (Color online) Detection efficiency of the XRF experiment with both air and Be window attenuation and detector efficiency components. To demonstrate detectability over rows 4–7 of the Periodic Table, select emission energies are noted.

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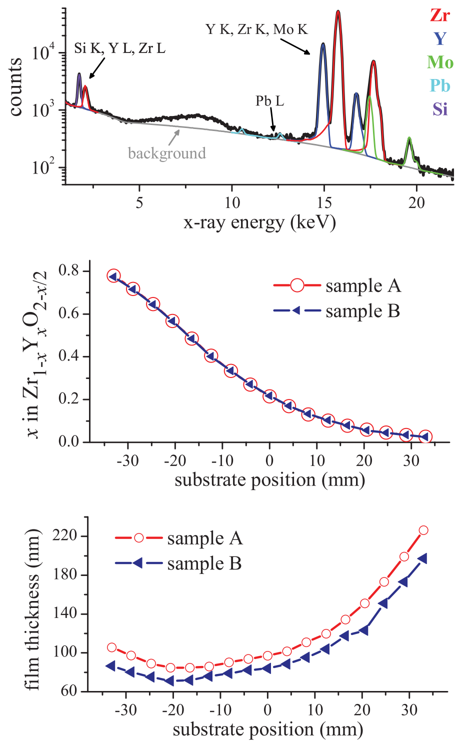

FIG. 2. (Color online) Low-energy portion of the XRF spectrum from the center position of sample A with fitted peaks (top). The Si *K* peak from the substrate is detected but has low intensity considering its substantial thickness (see Fig. 1). Mo and Pb are detected from excitation of the detector shroud. The Zr *K* and Y *K* fitted areas are used for quantitative analysis, providing the composition profiles (middle) and thickness profiles (bottom) for the two samples.

the efficiency is limited by absorption in the 300 μm Si detector. As indicated by the noted elemental lines, the experiment allows characterization of thin films comprising elements with atomic number Z greater than Z_K. We have successfully characterized 100 nm films with <1 wt % Sc. For $Z_{Ag} \leq Z \leq Z_{La}$ both K and L shell x-rays can be analyzed, while K (L) shell x-rays are analyzed for elements below (above) this range.

A program for automated analysis of a set of XRF spectra was developed in the PYTHON programming language using routines from the PYMCA software package.[6] For a given spectrum, profile fitting is performed, and the resulting peak areas are used in an iterative routine to determine the film composition and thickness.

The $Zr_{1-x}Y_xO_{2-x/2}$ film was modeled as a two layer sample with the Si layer having fixed density and thickness. The thin film layer was modeled with a composition-dependent density $\rho(x)=(6.14-1.2x)$ g/cm^3 (Ref. 7) and thickness d. Using the initial values $x=0.5$ and $d=100$ nm, the elemental mass fractions of Zr and Y in the thin film layer, f_{Zr} and f_Y, were calculated using PYMCA. A self-consistent model of the XRF spectrum requires the sum of the calculated mass fractions to be equal to the corresponding mass fraction of the model layer:

$$f_{Zr}+f_Y=f_{model}\equiv\frac{(1-x)M_{Zr}+xM_Y}{(1-x)M_{Zr}+xM_Y+(2-x/2)M_O}, \quad (1)$$

where M is the respective atomic mass. The self-consistent solution for x and d was found by iterative PYMCA analysis by modeling the film for iteration i using $\rho_i=\rho(x_{i-1})$ and $d_i=(f_{i-1,Zr}+f_{i-1,Y}-f_{model})d_{i-1}$. Typically, the routine converges to within 10^{-4} discrepancy in mass fraction in $\lesssim 20$ iterations.

The XRF-determined composition and thickness of two $Zr_{1-x}Y_xO_{2-x/2}$ composition-spread thin films are shown in Fig. 2. The composition profiles are essentially identical with maximum deviation in x of 0.7 at. % and mean absolute deviation of 0.1 at. %. The thickness profiles are also nearly identical with sample A measured to be $14\pm1.5\%$ thicker than sample B due to a corresponding difference in deposition time. The reproducibility of the $Zr_{1-x}Y_xO_{2-x/2}$ composition profile in this work indicate that both the XRF-determined compositions and cosputtered compositions have phenomenal sub-at. % precision. In this article, we do not discuss absolute accuracy or the possible introduction of systematic error in the interpretation of the XRF data. These topics are discussed in Ref. 8, where we established that this standardless XRF technique can provide ~3 at. % accuracy in film composition.

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[1]Z. H. Barber and M. G. Blamire, Mat. Sci. Tech. **24**, 757 (2008).
[2]S. Vogt, Y. Chu, A. Tkachuk, P. Ilinski, D. Walko, and F. Tsui, Appl. Surf. Sci. **223**, 214 (2004).
[3]B. Xia, Y. S. Chu, and W. L. Gladfelter, Surf. Coat. Technol. **201**, 9041 (2007).
[4]J. M. Gregoire, D. Dale, A. Kazimirov, F. J. DiSalvo, and R. B. van Dover, Rev. Sci. Instrum. **80**, 123905 (2009).
[5]R. B. van Dover and L. F. Schneemeyer, Macromol. Rapid Commun. **25**, 150 (2004).
[6]V. Solé, E. Papillon, M. Cotte, P. Walter, and J. Susini, Spectrochim. Acta **B62**, 63 (2007).
[7]JCPDS Card Nos. 4-010-3273 and 30-1468.
[8]J. M. Gregoire, D. Dale, A. Kazimirov, F. J. DiSalvo, and R. B. van Dover, Rev. Sci. Instrum. **80**, 123905 (2009).