

Analysis of depth profiles of sol-gel derived multilayer coatings by Rutherford backscattering spectrometry and by cross-sectional transmission electron microscopy¹

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This paper describes the preparation and compositional analysis of multilayer thin-film coatings prepared using sol-gel techniques. Alternate layers were labeled with an iron tag, derived from hydrolyzed 1,1'-bis(triethoxysilyl)ferrocene. Iron-free layers were composed of SiO₂ derived from hydrolyzed tetraethylorthosilicate (TEOS). Analyses of these systems were based on Rutherford Backscattering Spectrometry (RBS) and Cross-Sectional Transmission Electron Microscopy (XTEM). The depth profile of iron, measured by RBS, yielded thicknesses (1000–1600 Å) for the individual layers that could be verified independently by XTEM.

I. INTRODUCTION

Multilayer ceramic coatings are important in applications in optics² and electronics.³ These and related applications require thin, defect-free layers.³ Sol-gel technology, combined with spin or dip coating, is an excellent method for the preparation of thin-film and multilayer ceramic coatings. The chemical composition of the precursors and the processing conditions control the properties of the final film, and it is relatively straightforward to control the porosity, composition, and index of refraction of these films.^{4–9} Multilayers made by the sol-gel route include antireflective coatings^{10,11,12–16} and wavelength-selective reflectors.^{17–19}

In this paper, we address the question of whether thin multilayers (<25 μm thick)³ of alternating chemical composition of inorganic (SiO₂) and organometallic layers can be produced by the sol-gel route without intermixing of the layers. We present the preparation and characterization of a model multilayer system using sol-gel suspensions derived from solutions of hydrolyzed 1,1'-bis(triethoxysilyl)ferrocene²⁰ and from hydrolyzed tetraethylorthosilicate (TEOS). This system is an ideal model for the building of multilayers. We employed RBS²¹ to measure the depth profile of iron, covalently incorporated as the ferrocenyl group, in the multilayer system. The signal for iron was a "tag" for the position of the iron-containing layers. This technique has previ-

ously proven useful in studying the depth profile and diffusion of iron in fused silica glass,²² and in studying layered systems in combination with TEM.²³ One objective of this work was to demonstrate the usefulness of RBS as a nondestructive technique, complementary to spectroscopic ellipsometry,^{24,25} for the analysis of multilayer ceramic coatings.

We verified the accuracy of the thicknesses of iron and iron-free layers, as measured by RBS, by independent examination using cross-sectional transmission electron microscopy (XTEM). We have also explored the extent of intermixing of the iron-containing layer with the iron-free layer during heating by monitoring the depth profile of iron by RBS as a function of thermal treatment.

The question of diffusion of components in gel structures is of general interest,^{26,27} and specifically relevant to thin-film structures requiring abrupt changes in composition.³ RBS has higher sensitivity to heavy elements than to light ones. The depth resolution of RBS is approximately 21 keV (~90 Å) at the surface of the sample due to the limits of the detector for the system we have studied. It is therefore an excellent technique for studying changes in the depth profile of iron as a measure of the diffusion of the iron species.

The limits to the resolution of RBS are set by the detector and by energy straggling. Detectors used for RBS analysis typically are surface-barrier, solid-state nuclear particle detectors. When a scattered helium ion passes through the detector, it creates electron-hole

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pairs in the depletion layer of the inverse Schottky barrier diode. These electron-hole pairs result in a voltage pulse, the height of which is proportional to the energy of the incident helium ion through the number of electron-hole pairs generated. Statistical fluctuations in the number of the electron-hole pairs generated from the scattered helium ions in the detector limit the resolution in the measurement of energy of the incident particle.

Statistical fluctuations in the inelastic interactions between the helium beam and the electrons in the sample cause energy straggling as the beam particle passes through the sample. The Bohr value of energy straggling,²⁸ Ω_B^2 (eV²), is given by Eq. (1).

$$\Omega_B^2 = 4\pi Z_1^2 e^4 N Z_2 d \quad (1)$$

Here Z_1 is the atomic number of the ion in the ion beam; e ([eV Å]^{1/2}), the charge of an electron; N (Å⁻³), the atomic density; Z_2 , the atomic number of the atoms in the sample; and d (Å), the thickness. For a sample with a mixture of atoms, as in our sample, the average atomic number (7.25 ± 1.0 based on $70\% \pm 9\%$ C₁₀H₈FeSi₂O₃ and $30\% \pm 6\%$ SiO₂), based on a mass average, is used in Eq. (1). Straggling increases with depth; thus, peaks broaden from straggling with increasing depth into the sample. The theoretical Bohr value for energy straggling for our sample using a helium ion beam is 7.4 keV (30 Å) at 6000 Å.

II. EXPERIMENTAL SECTION

A. Materials

Ferrocene was purchased from Eastman Kodak Company. *n*-Butyllithium, tetramethylethylenediamine, and *p*-toluene sulfonic acid were purchased from Aldrich. Triethoxychlorosilane was purchased from Petrarch. Hexane was distilled from NaH. *n*-Butyllithium was titrated with 2,5-dimethoxybenzyl alcohol (Aldrich) immediately before its use.²⁹ Ethyl ether was purchased from Mallinckrodt. All reagents were used as-received unless noted.

B. 1,1'-bis(triethoxysilyl)ferrocene

1,1'-bis(triethoxysilyl)ferrocene was synthesized by the procedure of Wrighton and coworkers²⁰ in 18% yield: ¹H NMR (chloroform-d₁, 250 MHz, 25 °C) δ 1.25 (t, 18H), 3.88 (q, 12H), 4.22 (s, 4H), 4.41 (s, 4H).

C. Hydrolysis of 1,1'-bis(triethoxysilyl)ferrocene

Distilled water (0.63 mL, 33 mmol) was added to a solution of 1,1'-bis(triethoxysilyl)ferrocene (1.41 g, 2.90 mmol, 16.5 mmol of SiOR) in ethanol (14 mL) with *p*-toluenesulfonic acid monohydrate (0.01 g, 0.05 mmol) as catalyst. The solution was allowed to stir overnight prior to coating. "Thick" coatings (Fig. 3) were

made from a 10% [weight of 1,1'-bis(triethoxysilyl)ferrocene/volume] solution, and "thinner" coatings (Fig. 4) were made from a 1% (w/v) solution.

D. Pre-hydrolyzed TEOS

A solution containing tetraethylorthosilicate (TEOS) (43 mL, 193 mmol of Si), ethanol (43 mL), and aq HCl (14 mL of 0.15 M acid) was heated at 60 °C for 3 h. The solution was cooled and filtered through a 0.2 μ m filter, then diluted with additional ethanol (86 mL), and stored in a freezer (-8 °C).

E. Preparation of samples

We coated a silicon <100> wafer by pipetting enough solution (~3 mL) to cover the wafer and spinning the substrate at 1500 rpm for 2 min on a Headway model PWM 101ECR790 spin-coater. The samples were heated in a Fisher Scientific Isotemp Programmable Ashing Furnace Model 497 at 1 °C/min to 350 °C, held for 1 h, heated 1 °C/min to 500 °C, held for 1 h, and cooled at 1 °C/min to 30 °C. Coatings were rinsed with ethyl ether prior to applying the subsequent layer.

F. RBS analysis

RBS spectra were obtained using the CAMS (Cambridge Accelerator for Materials Science) facility. The CAMS consists of a tandetron accelerator that supplied a 2-MeV He⁺ beam. Backscattered particles were detected at 176° relative to the incoming beam, with a 150-mm² silicon surface barrier detector coupled to a multichannel analyzer and placed about 3 inches from the sample. Typical times for the acquisition of data were 10–15 min. Depth profiles of iron were calculated using "Spectrum Analysis".³⁰

Figure 1 shows a representative RBS spectrum²¹ of the three-layer coating (two iron-containing layers separated by a layer of SiO₂) derived from alternating coatings derived from hydrolyzed 1,1'-bis(triethoxysilyl)ferrocene and hydrolyzed TEOS on a silicon substrate.

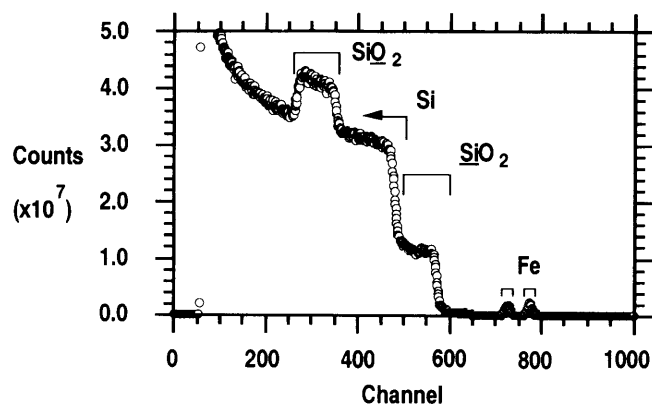


FIG. 1. RBS spectrum for a three-layer coating (two iron-containing layers separated by a layer of SiO₂) derived from alternating coatings derived from hydrolyzed 1,1'-bis(triethoxysilyl)ferrocene and hydrolyzed TEOS on a silicon substrate.

rated by a layer of SiO_2). At highest energy (\sim channels 800–700) in the plot of number of counts versus channel (linearly related to energy) were the signals from iron in the two iron-containing layers. Iron in the layer at the surface came at highest energy. The signal for silicon in the multilayer coating (\sim channel 575) was lower in intensity (number of counts) than that for silicon in the substrate (\sim channel 475) because it was “diluted” by the other components in the multilayer coating. The signal for oxygen at the surface of the sample (\sim channel 350) came at a lower energy than that for silicon at the surface because the mass of oxygen is lower than the mass of silicon.

Figure 2 shows the depth profiles of iron measured at two different regions on the sample analyzed in Fig. 3. The reproducibility of the data showed that no detectable variation of layer thicknesses existed in the sample within the resolution of RBS.

The diameter of the ion beam was 1 mm. Regions where the beam hit the sample exhibited a shiny spot, as did the silicon substrate with no coating. These spots are attributed to regions of beam-assisted deposition of hydrocarbons from the vacuum system. No major beam damage to the sample was apparent.

G. XTEM analysis³¹

Samples were prepared for XTEM by cutting a coated silicon substrate into 2 pieces ($1.5 \text{ cm} \times 1 \text{ mm}$ each) and gluing them together, coated face to coated face, with silver epoxy. The sample was thinned by grinding the exposed silicon faces on wet sandpaper until the sample was thin enough to fit into a molybdenum rod (4 cm in length, approximately 2.5 mm diameter) that had a slice removed from the center (through the diameter) through approximately 2 cm of the length. The sample was epoxied into the slice in the molybdenum rod and encircled with a brass sheath that

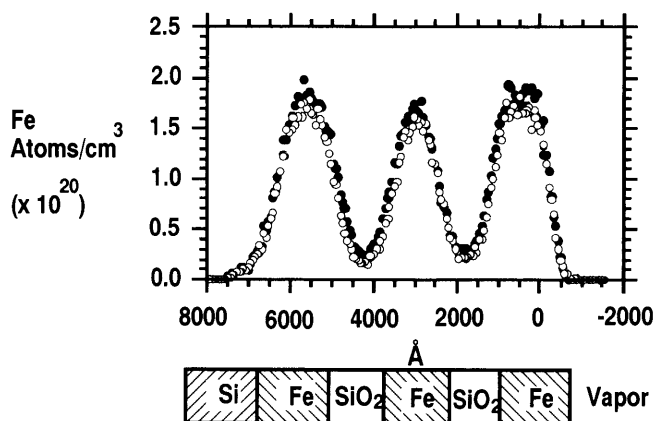


FIG. 2. Depth profiles of iron for the multilayer coating (analyzed in Fig. 1) with five layers measured from two different regions on the sample, in order to test the reproducibility of data.

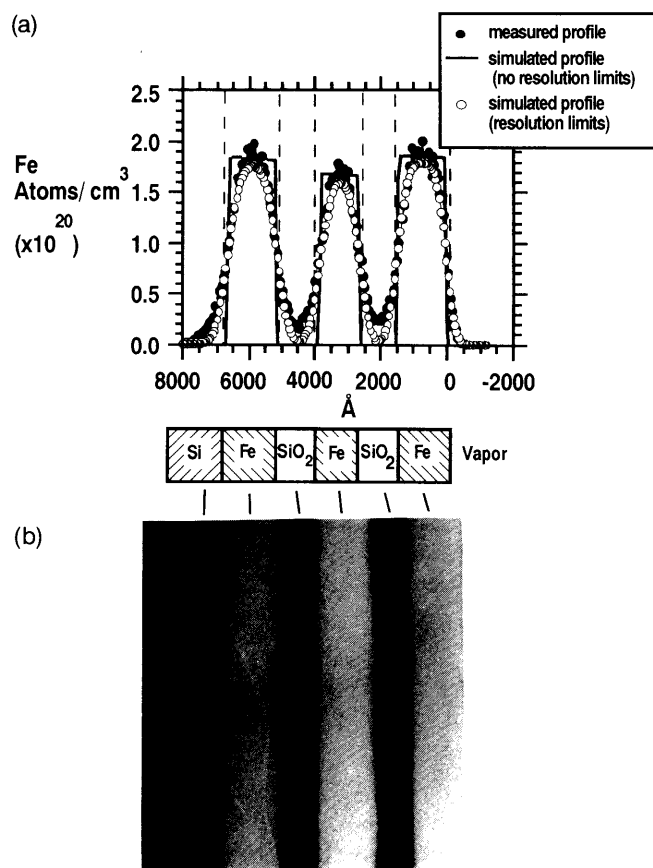


FIG. 3. (a) Measured and simulated depth profiles of iron for a multilayer coating (derived from alternating coatings of hydrolyzed 1,1'-bis(triethoxysilyl)ferrocene and hydrolyzed TEOS). The depth profile of iron measured by RBS (\bullet) is compared with a simulated depth profile with neither detector resolution nor straggling effects ($-$), and a simulated depth profile of iron with energy resolution limitation from the detector and energy straggling taken into account (\circ). Thicknesses of layers are measured at half of the peak height in the RBS depth profile of iron. (b) Imaged layers from XTEM analysis for the same multilayer coating as in (a).

covered about 2 cm of the rod. Approximately 1-mm thick slices were cut from the rod (at the end with the sample) using a Slurry Drill (South Bay Technology Inc., Model 350) equipped with a diamond blade. The center ($\sim 1 \text{ mm}$) of the slice was thinned to approximately $25 \mu\text{m}$ with a dimpler (South Bay Technologies Inc., Model 515). Further thinning was achieved using a Gatan Dual Ion Mill (model 600) until the sample had a small hole in it. The thinned sample was analyzed along the edge of the milled hole in a Philips EM 420T Transmission Electron Microscope. One source of error in XTEM analysis is in the uncertainty in the microscope magnification ($\leq 5\%$). We assumed the error was 5%. The thickness values reported in Table I are the average of six measurements taken at different locations in the sample. The error reported in the table reflects both the variation in the thickness measurement and the error in magnification of the microscope. The

TABLE I. Thicknesses of layers of a multilayer coating as measured by RBS and XTEM.

	Layer thickness (Å)	
	RBS	XTEM
Vapor		
↑ Fe	1600 ± 200	1660 ± 170
SiO ₂	1050 ± 200	1070 ± 80
Fe	1450 ± 200	1780 ± 160
SiO ₂	1200 ± 200	1130 ± 70
Fe	1600 ± 200	1800 ± 110
Si substrate		

layers were analyzed by electron microprobe analysis,²¹ in the electron microscope, to verify the composition (iron-containing or SiO₂) of the layers.

III. RESULTS AND DISCUSSION

Figure 3 presents three depth profiles of iron. Along with the measured depth profile of iron for a multilayer coating [derived from alternating coatings of hydrolyzed 1,1'-bis(triethoxysilyl)ferrocene and hydrolyzed TEOS] are two additional depth profiles: a simulated depth profile with neither detector resolution nor straggling effects, and a simulated depth profile of iron with energy resolution limitation from the detector (~ 90 Å) and energy straggling [the Bohr value calculated at the depth of each datum point using Eq. (1)] taken into account. This figure also presents a cross-sectional view by XTEM of the layers of the same sample. We simulated RBS spectra using the program RUMP,³² based on values of the measured thicknesses from the RBS analysis, and calculated the depth profiles of iron from the RBS spectra using the program "Spectrum Analysis".³⁰ The simulated profile of iron without resolution limits has a flat compositional distribution within the iron-containing layers; this profile contrasts with the other two profiles where the detector and straggling effects transform the step-function distribution of iron into peaks resembling gaussian distributions (the areas of these peaks are approximately the same). The simulated profile with limitations of the detector (~ 90 Å) and straggling [calculated from the Bohr value from Eq. (1)] taken into account is almost superimposable on the data. Thus, it appears that the differential broadening of the deeper peaks is due to energy straggling.

The thicknesses determined from these techniques are compared in Table I, and within experimental error, they are the same. We conclude that RBS is an accurate technique for the nondestructive analysis of sol-gel derived multilayer coatings.

In the profiles, the iron peaks appear shorter and broader with increasing depth into the sample. Some

degree of broadening for deeper layers is expected from energy straggling.²⁸ Additional broadening could be due to interdiffusion of the iron species with SiO₂ between the deeper layers which have been through more thermal treatments than those layers at the surface. To test this hypothesis, and to test the validity of the simulated spectra in Fig. 3, a multilayer coating consisting of three layers was analyzed by RBS, heated six times to 500 °C for 6 h each, and analyzed by RBS again. These results are presented in Fig. 4—Fig. 1 presented the RBS spectra for the sample heated only once. The indistinguishable depth profiles indicate that no detectable (± 200 Å) diffusion occurred during the thermal treatments.

IV. CONCLUSIONS

We have prepared multilayers, with modulated composition, derived from the hydrolyzed sol-gel precursors 1,1'-bis(triethoxysilyl)ferrocene, and TEOS. These multilayers have sharp interfaces and exhibit no detectable intermixing of the layers after coating.

RBS is a quick and nondestructive tool for the analysis of heavy-atom tagged multilayer systems obtained by sol-gel methods. The iron profile was easily measured by RBS in the Ferrocenyl/SiO₂ system for up to five layers (~ 6700 Å). Thicknesses were in good agreement with values determined by XTEM. RBS exhibits straggling which broadens the peaks as a function of depth.

In this system, interdiffusion of species in the iron-containing layer with species in the iron-free layer (SiO₂) after thermal treatment was not detected by RBS.

In general, we have demonstrated that RBS is a useful and relatively quick technique—compared to XTEM—for the analysis of multilayers made by the

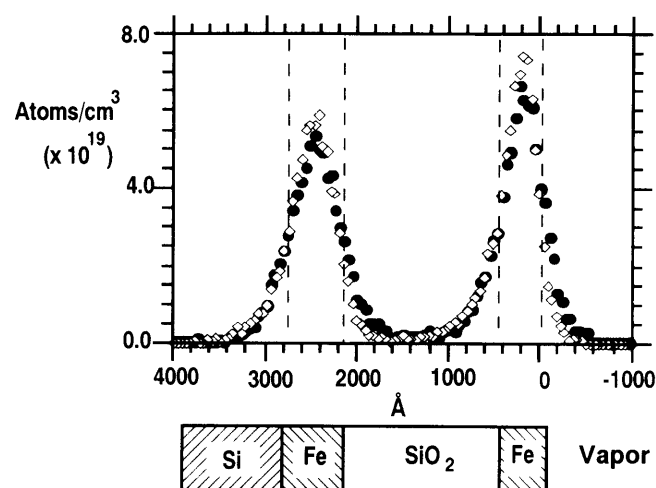


FIG. 4. The depth profiles of iron for a multilayer which has been heated at 350 °C and 500 °C for 1 h each (●), and heated six additional times to 500 °C for 6 h each (◇).

sol-gel route. Furthermore, since RBS is nondestructive, it may be used for the analysis of a device, made by the sol-gel route and whose optimum properties may depend on sharp interfaces, to monitor the presence or lack of interdiffusion of the layers.

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