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Complementary techniques for the characterization of thin film Ti/Nb multilayers

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ABSTRACT

An aberration corrector on the probe-forming lens of a scanning TEM (STEM) equipped with an electron energy-loss spectrometer (EELS) and X-ray energy-dispersive spectrometer (XEDS) has been employed to investigate the compositional variations as a function of length scale in nanoscale Ti/Nb metallic multilayers. The composition profiles of EELS and XEDS were compared with the profiles obtained from the complementary technique of 3D atom probe tomography. At large layer widths ($h \geq 7$ nm, where h is the layer width) of Ti and Nb, XEDS composition profiles of Ti/Nb metallic multilayers are in good agreement with the EELS results. However, at reduced layer widths ($h \approx 2$ nm), profiles of EELS and atom probe exhibited similar compositional variations, whereas XEDS results have shown a marked difference. This difference in the composition profiling of the layers has been addressed with reference to the effects of beam broadening and the origin of the signals collected in these techniques. The advantage of using EELS over XEDS for these nanoscaled multilayered materials is demonstrated.

1. Introduction

As thin film materials used in many areas of nanotechnology, such as in electronic and optical applications continue to decrease in layer widths to the nanoscale, marked changes in properties of these materials are expected to occur due to changes in crystal structure and composition [1,2]. Indeed, such multilayers have been of considerable interest due to the ability to control properties by engineering the structure of materials at these length scales. Improved characterization tools allow direct imaging and analysis of such materials in order to link the performance variations with crystal structure and composition variations. The techniques that are used for the characterization of nanoscale multilayers include high-resolution TEM (HRTEM) and high angle annular dark-field (HAADF) STEM for *imaging*, 3D atom probe tomography and TEM and/or STEM fitted with XEDS and EELS for *microanalysis* [3–6].

Traditionally, HRTEM has been applied for morphology, defect and crystal structure analysis of these materials and has the great advantage of yielding local information on the atomic arrangements projected along the direction of the electron beam at a resolution comparable to the interatomic distance. HAADF-STEM is another proven technique where the images are free from any delocalization effects and directly interpretable due to the incoherent nature of the imaging process [7]. At sufficiently high scattering angles (>50 mrad half-angle) the intensity variations in HAADF STEM image are atomic number dependent (Z-contrast imaging). Therefore in material systems, where such atomic number difference is significant, HAADF STEM is a convenient technique to examine the bulk and interface structure at the nano- or atomic scale [8].

Lateral dimensions in nanolayered structures are typically in the range of 1–5 nm, thus there is a real need for determining the chemical and electronic information at the nanometer regime. TEM characterization of nanoscale multilayers has been often

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achieved by the use of fine probe STEM imaging combined with XEDS and EELS microanalysis. Specimen thickness, incident electron energy and probe size are the key experimental parameters that define the ultimate spatial resolution of TEM microanalysis. Among these, thickness of the specimen has been the dominant factor limiting the resolution of X-ray analysis due to both elastic and inelastic scattering of the electron beam within the material, manifested as beam broadening or spreading [9]. The effect of beam broadening is more pronounced for XEDS than EELS, since for the latter technique the electrons that enter the spectrometer originate from a volume defined by the entrance aperture and the foil thickness, whereas for XEDS X-ray generation occurs in the volume of material irradiated by the broadened electron beam.

Atomic column resolution in STEM EELS has been successfully demonstrated [10,11]. There have also been many attempts to detect and quantify very small amounts of material using STEM XEDS. Microanalysis better than 2 nm and even at atomic-level have been reported using STEM XEDS, but in some cases deviations from the expected chemical composition were noted, and these deviations were attributed to the effect of broadening of the electron beam within the relatively thick TEM specimens ($t \geq 100$ nm) [12–18]. It is very clear that the thickness of the TEM foil still remains the most important factor limiting the spatial resolution in STEM XEDS analysis.

Because it is important to determine composition with accuracy and precision, it is necessary to validate compositional measurements using independent techniques. Therefore, a study has been conducted to determine the composition of individual layers in nanoscale Ti/Nb metallic multilayers using probe aberration corrected STEM with both XEDS and EELS, and these results have been compared with atom probe analyses conducted previously. The reliability of composition profiles is discussed in the light of the limits and capability of each technique.

2. Experimental

2.1. Sample preparation

Ti/Nb metallic multilayers were grown by DC magnetron sputtering on {111} Si wafers with a native surface oxide. The oxide surface and low deposition temperature (~25 °C) prevented any epitaxial orientation relationship between the film and the substrate. The films were grown over a 2-in. diameter wafer and at a total multilayer film thickness of 0.5 μm. Ultra-high-purity Ar was used as the working gas at a pressure of 2–4 mTorr and the optimum base pressure of the chamber was $\sim 4 \times 10^{-9}$ Torr. An FEI Helios^{TM} FIB system with a Ga^+ ion source was used for TEM sample preparation. The surfaces of the multilayers were first sputter coated with a 100 nm thick Au film in order to preserve the thin film from further damage during the subsequent FIB specimen preparation steps. After the alignment of the surface to the electron beam and to the Ga^+ ion source, a 30 μm × 2 μm × 1.5 μm Pt layer was deposited to serve as a sacrificial layer during milling. This Pt layer was used as a protective barrier to minimize Ga implantation into the sample. Trench milling of the samples was done using 30 kV FIB Ga^+ ions. For the final milling stage, all the trenched foils were welded to Mo Omniprobe^{TM} grids and milled to electron transparency at Ga^+ ion energy of 5 kV. The cross-section TEM specimens were then transferred to a low energy concentrated Ar^+ ion beam (CIB) system (Fischione Nanomill^{TM}) to remove the residual Ga^+ ion damage from the foil surfaces and milled from both sides of the TEM foils at an Ar^+ ion energy of 500 V. The details of the atom probe sample preparation of Ti/Nb multilayers were described elsewhere [19].

2.2. Compositional profiling

All the TEM imaging and microanalysis were conducted using a FEI TITAN^{3,TM} 80–300 S/TEM equipped with a CEOS probe aberration corrector and operated at 300 kV accelerating voltage. STEM images were obtained using a Fischione HAADF detector at a collection semi-angle range, β_1 of 46–325 mrad. All XEDS and EELS line profile spectra were acquired in the STEM mode, and drift correction was applied. For the XEDS experiment, the sample configuration was set such that the interfaces along the layers were parallel to the line of sight of the XEDS detector. This sample configuration was intended to minimize the effect of variation in the absorption path length of the layers. The TITAN^{3,TM} S/TEM is fitted with both an EDAX energy-dispersive spectrometer, a windowless Si (Li) detector with a collection solid angle, β_2 of 0.18 sr and take-off angle of 18°, and a GATAN ultra-high resolution imaging filter, 0.12 eV full width half maximum (FWHM) energy resolution at an acquisition time of 1 s. The size of the electron probe (d_{FWHM}) upon aberration correction at a convergence angle, α of 18 mrad, was ~0.1 nm and the probe current was 40 pA. For analytical purposes, this probe size at full-width tenth maximum (FWTM) was approximated to be 0.18 nm ($d_{FWTM} = 1.8 \times d_{FWHM}$).

The TEM specimen-detector geometry and important characteristic signals and their angular ranges for the analysis of an A/B multilayer system are shown in Fig. 1. Table 1 is a list of the individual layer widths and corresponding techniques involved in the characterization of the Ti/Nb multilayers. The XEDS and EELS spectra of the Ti/Nb multilayer, labeled as Ti/Nb multilayer #1, were simultaneously acquired at a probe dwell time of 15 s and step size of 0.15 nm/step. XEDS and EELS line scan of the Ti/Nb multilayer #3 were collected separately to optimize the

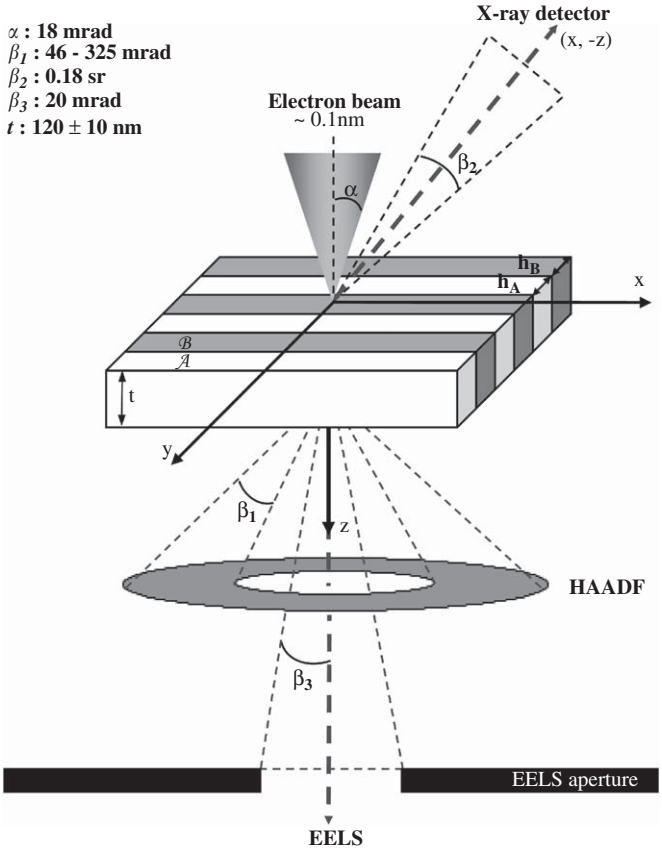

Fig. 1. A schematic showing the specimen geometry of the TEM analysis of an A/B multilayer system and also emphasizing the important angular ranges of the signals used.