Development and Characterization of Thin Film Reference Materials

Stephen W. Gaarenstroom

General Motors R&D Center, Analytical Chemistry & Instrumentation Dept.,mail code 480-106-320, 30500 Mound Road, Warren MI 48090-9055, USA

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Thin film reference materials are invaluable to the surface analyst for a number of tasks, such as verifying the operating performance of a spectrometer; determining the depth scale, depth resolution, and ion beam uniformity for sputter depth profiling; and for comparing unknown spectra to reference spectra for chemical characterization. Both single-layer films, such as an oxide film grown on an elemental surface, as well as multilayer reference films are used in surface analysis and electron spectroscopy. Good reference materials should have a number of positive attributes, like wide-spread usage in the analyst community, stable in the laboratory environment, and multiple usage purposes. Future trends for reference material usage will include more automated procedures for instrument calibration and more usage of reference materials among dissimilar instruments.

1. Introduction

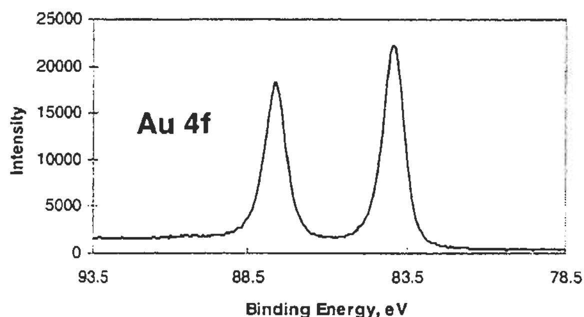
Reference materials are essential to the surface analyst for a number of critical tasks. In electron spectroscopy, both x-ray photoelectron spectroscopy and Auger electron spectroscopy, two of the most widely used surface analysis tools, they are used for energy scale calibration, signal intensity calibration, source size calibration, and depth profiling calibration. They may also be used for the chemical identification of unknown specimens. Common reference materials in electron spectroscopy include both homogeneous materials with clean surfaces (Au, Ag, Cu, graphite, poly(methyl methacrylate), etc.) as well as thin film reference materials (a single-layer SiO_2 film on Si, a multilayer Cu/Ni/Cu/Ni/... system, etc.). In this paper, I review the thin film reference materials most commonly employed in the electron spectroscopy laboratory. By understanding why certain reference materials are used, how they are used, and some pitfalls in their usage, we hope to be guided toward improved quality of our surface analysis results using today's reference materials and the development of even more useful reference film systems in the future.

2. Single-Layer Film Systems

Gold and Gold films

The most common use of reference materials by analysts for electron spectrometers is for the calibration and verification of electron energy scales. The typical materials used are foils of gold, silver, or copper. For this purpose, a thin film of one of these metals does not offer any advantage over a foil. However, frequently the analyst also uses these materials to examine the signal intensity performance of the spectrometer at the same time. Monitoring signal intensity variations is important for quantitation. Day-to-day variations in signal intensity in a spectrometer may be due to analyzer lens adjustments, stray magnetic fields, and detector aging. Fig. 1 shows peak-intensity and peak-width information for Au 4f peaks of a gold surface over a period of time. Unfortunately, some of the day-to-day variations in measuring the signal strength from a reference material may be due also to the surface cleanliness of the reference material or the positioning of the reference material in the spectrometer. In the past, some analysts have argued that a sputtered film of gold is a more reproducible surface than a cleaned gold foil and is superior for

monitoring changes in spectrometer signal strength with time.



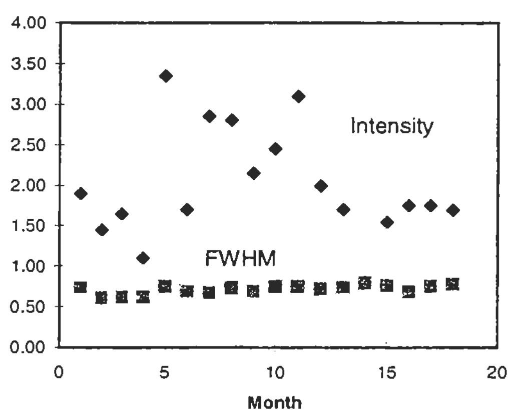


Figure 1. (upper) Au 4f spectrum from gold surface. (lower) Control chart showing variation in Au $4f_{7/2}$ peak intensity and peak width over a period of months.

In Fig. 2, Au 4f signal strengths from 5 gold surfaces (freshly sputter-deposited, sputter-deposited and stored one month, electroplated, sanded foil, and CO_2-snow cleaned foil) are compared. The figure shows that a freshly sputter-deposited Au film has the strongest signal strength and is likely to have superior signal strength reproducibility compared to a gold foil cleaned *ex situ*. However, Fig. 2 also shows that ion sputter cleaning the specimens in the spectrometer improves the signal strength for all the gold surfaces. Since the signal strengths are nearly the same for all the surfaces, we conclude that any ion-sputter-cleaned gold surface may be used for monitoring spectrometer signal strength.

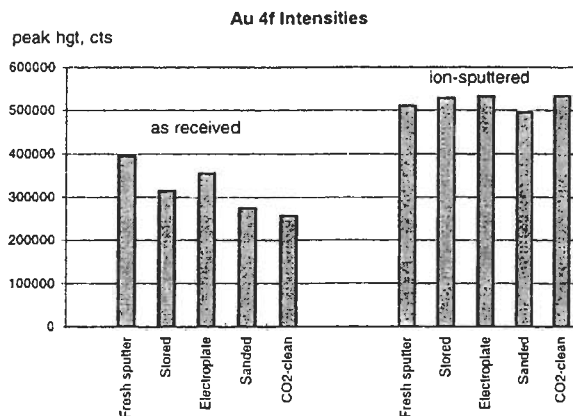


Figure 2. Au 4f signal strength from 5 gold surfaces (freshly sputter-deposited, sputter-deposited and stored one month, electroplated, sanded foil, and CO_2-snow cleaned foil). Results before and after ion-sputter cleaning are shown.

SiO_2/Si

The SiO_2/Si system is a popular thin film reference system because of the commercial importance of the system and because the oxide layer can be easily thermally grown on Si wafers. The interface is extremely sharp. The film thickness can readily be measured by ellipsometry and computed from well-known optical constants. Certified reference materials are available (NIST SRM's 2531-36, with film thicknesses from 10 nm - 200 nm) [1]. One drawback in some circumstances is that the SiO_2 is susceptible to electron-beam-stimulated oxygen desorption. For Auger depth profiling, this will have the effect of broadening the interfaces and giving an inaccurate depth, as shown in Fig. 3.

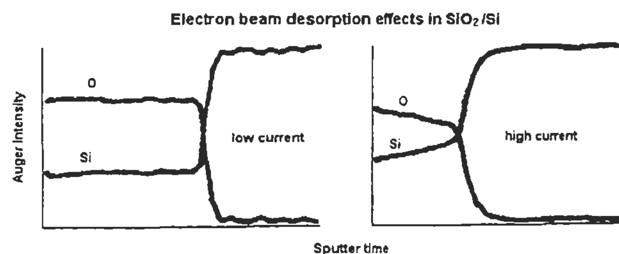


Figure 3. Electron-beam-stimulated oxygen desorption in SiO_2/Si. The electron beam reduces the oxide to a suboxide at high beam densities. Effects are measurable for the O/Si ratio, the time-to-interface, and the interface width.

Ta_2O_5/Ta

The Ta_2O_5/Ta system is the most popular thin film reference for electron spectroscopy and depth profile calibration. The initial popularity was because it is an easily-grown anodic film, but also because it had good characteristics for sputter depth profiling: (1) the amorphous film structure meant there was little ion-beam-induced topography, (2) the oxide-metal interface is abrupt, (3) the oxide film does not suffer charging problems under normal instrument conditions, (4) the Ta and O give strong analytic signals, (5) the oxide is dense, nonhydrated, and does not change with age. A widely used recipe for a 100-nm film is an anodic voltage of 66.6 V(dc) in 5.7% HNO_3 (although it has been found that this corresponds to more like 115-120 nm when compared to a Certified Reference Material). The Ta_2O_5/Ta system became even more popular when a certified reference material tantalum oxide film (BCR 261, consisting of 30 nm and 100 nm oxide films on Ta foil) was prepared and released by the UK's National Physical Laboratory [2,3]. Like the SiO_2/Si system, the Ta_2O_5/Ta system is also subject to electron-beam-stimulated desorption effects [4], but the effects are not as severe.

Al_2O_3/Al

The Al_2O_3/Al system is technologically an important oxide/metal system. Numerous surface-related processing phenomena involving aluminum metal, such as brazing, welding, bonding, stamping, plating, cutting, and rolling, are influenced by the surface oxide thickness and character. Because of this industrial importance, and also because the metal is readily available and the oxide surface film can be prepared inexpensively, Al_2O_3/Al is used as a reference film [5,6]. When the oxide film is anodically grown in an electrolyte in which the oxide layer is insoluble, the film is a barrier-layer type and is nonporous, amorphous, and uniformly thick. Shown in Fig. 4 is a transmission electron photomicrograph of barrier-layer oxide film grown in 4.5wt% aqueous tartaric acid solution, at pH 5.5, giving a film thickness of 1.3 nm/V. (The film is shown in cross section.)

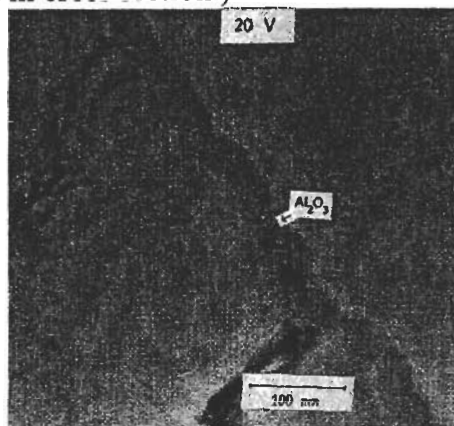


Figure 4. Transmission electron photomicrograph for anodic Al oxide film on Al metal. From Ref. 6. The film was prepared in cross section by microtoming.

These easily prepared barrier-layer oxide films can be grown in thicknesses from 30 nm to >200 nm and have the important characteristics required for reference films (sharp interfaces, amorphous, nonporous). They are also stable, with no observable changes after five years of storage, except for the very thinnest films [6]. Some XPS depth profiles are shown in Fig. 5.

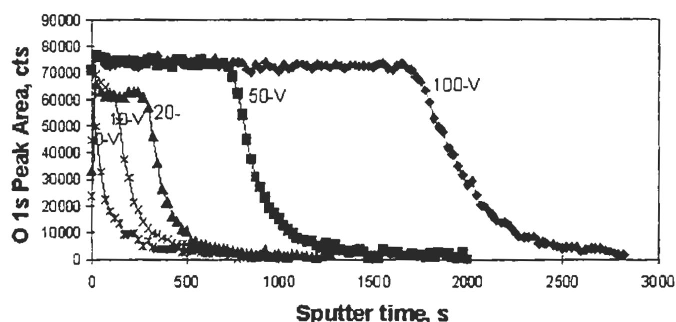


Figure 5. XPS sputter depth profiles for O 1s photoelectron line from anodic Al_2O_3 films. From Ref. 6.

TiN films

Titanium nitride films and coatings also have significant industrial uses, such as antiwear coatings for tools, diffusion barriers in

integrated circuit devices, and decorative coatings for consumer goods. The importance of TiN films has led to a number of activities to provide or characterize TiN reference films [7-10]. The reference films were typically made by reactive sputtering. A wide range of film thicknesses, from <100 nm to > 10 μm, have been prepared to represent all the applications of the film.

Ultrathin films

For ultrathin (<5 nm) films, both the film and the substrate are observed in an electron spectrum without ion sputtering. Both Al_2O_3/Al and SiO_2/Si systems can be used as ultrathin reference films. For Al_2O_3, a method consisting of mechanical polishing, electropolishing, rinsing, ion etching, and oxidation in pure oxygen (250°C, 5 hrs) has been described to produce a 23 Å Al_2O_3 film on Al [11]. A 20-laboratory international round-robin test with this material measured binding energies, photoelectron yields, and attenuation lengths. Also, the relative sputter rate of Al_2O_3 was measured as 0.72±0.14 of the sputter rate for Ta_2O_5, for argon ions with 2-3 keV energy. The Al_2O_3/Al system has also been proposed as a reference material for angle-dependent XPS [12]. An interlaboratory comparison for two reference thicknesses over a range of take-off angles of 40-120 gave differences of 10-20% in overlayer thickness computation. Peak fitting measurement was the principal cause of error in the study.

The SiO_2/Si system also has a described procedure [13] to obtain a film of reproducible thickness, 14 Å after cleaning. The procedure involves cleaning a <100> p-doped silicon wafer with 10:1 H_2O:HF to remove the native oxide, then sonically clean in H_2O_2:NH_4OH:H_2O, followed by water rinse and spin dry. As shown in Fig. 6, there is a steady-state increase in film thickness of 0.2 Å/month, but the original thickness is restored after cleaning.

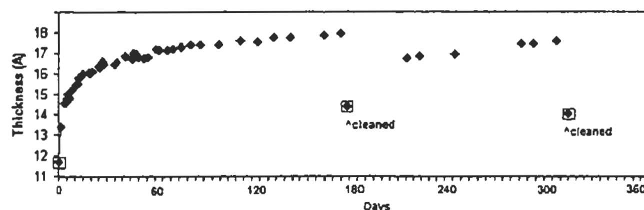


Figure 6. Measurements of SiO_2 film thickness by ellipsometry showing increases in film thickness and restorations after cleaning step. From Ref. 13.

3. Multilayer Film Systems

Ni/Cr multilayers

An early certified reference material issued for sputter depth profile calibration was a Ni/Cr multilayer film on a silicon wafer, SRM 2135 from NIST [1, 14]. The film has five 53-nm-thick layers of Cr and four 66-nm-thick layers of Ni. The Ni/Cr relative sputter rate (nm/s) was measured as 1.09 for a 3-kV argon ion beam. The Ni/Cr reference material proved to be so popular that it has sold out. A replacement reference film is in preparation.

An advantage of a multilayer reference material over a single-layer reference material is that sputter rates and depth resolutions can be calibrated at a number of depths. As shown in Fig. 7, a multilayer film can also be used to determine the shape and location of an ion beam in the plane of a specimen. In the photomicrograph, the ion beam gave a distorted peak shape which will likely result in a loss of depth resolution during an Auger depth profile. Alignment of an electron beam and the ion beam for Auger sputter depth profiling is an especially critical procedure. Even small misalignments can give measurable loss of depth resolution.

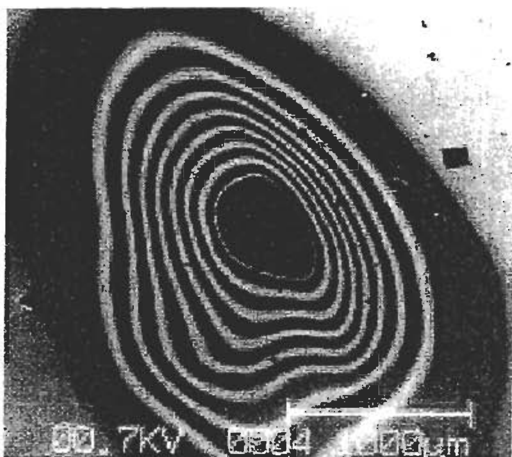


Figure 8. Scanning electron photomicrograph of a ZrN/AlN multilayer film used to determine shape of a sputter-ion beam and the alignment of the electron beam and the ion beam in an Auger spectrometer.

Other multilayers

Another certified reference multilayer system is a chromium/chromium oxide thin film depth profiling standard from NIST, SRM 2136 [1]. The material has seven individual Cr films, separated by thin marker layers of chromium oxide. The choice of having thin, marker layers for a multilayer reference material for depth profiling has both advantages and drawbacks compared to full-layer pairs. The chief advantage is that the material can be modeled like a single material with only single sputter yield. Typically bilayers must be treated as having two different sputter yields, which leads to asymmetries in profiling the solid interfaces and complicates the fitting procedure and determinations of thicknesses.

Thin film and microelectronics manufacturing has created demands for thin film measurements to support numerous manufacturing processes, involving conductors, insulators, and semiconductors. Some notable proposed multilayer reference systems include conducting Ti/Al [15], insulating SiO_2/Si_3N_4 [15], and semiconducting GaAs/AlAs superlattices [16]. These materials systems are not only useful for electron spectroscopy, but also for other measurement methods such as ellipsometry, glow discharge optical emission spectroscopy, secondary ion mass spectrometry, and electron microscopy. A standards document related to the GaAs/AlAs system is under active consideration currently by ISO Technical Committee TC201 on Surface Chemical Analysis.

4. Future trends

One future trend in electron spectroscopy is increased automated procedures for instrument calibration. It is likely this will involve the use of thin film reference materials during a process to automatically verify operating conditions such as binding energy scale, signal intensity, image magnification, ion sputter rate, and depth resolution. The analyst would prefer that only one or two reference materials be used to speed this procedure. The analyst would also wish that reference materials used for electron spectroscopy also be suitable for calibration of other instrumentation, such as electron probe microanalysis, infrared spectroscopy, electron microscopy, etc., to make comparisons of results from different techniques easier.

Another trend encourages the proliferation of reference materials, as the analyst seeks references that are as closely matched to his or her current materials analysis request as possible. In these cases, the reference material supports the quantification of an analysis directly, more so than simply verifying the operating performance of the instrument and optimizing the analysis conditions. Many common bulk materials (pure metals, minerals, common polymers) are available in supplier catalogs, but thin film materials are much less common.

A final trend is the increased availability of not only reference materials but also reference data. With access to peer-reviewed surface spectroscopy data from the entire surface science community, the need for individualized reference materials may be less. A number of surface spectroscopy databases are becoming

available, including activities by the American Vacuum Society and the Surface Analysis Society of Japan. Currently, the databases are mostly of homogeneous materials, and not thin films, but that will change with time. For instance, a focused-topic collection on Oxide Surfaces was published in the AVS database [17]. The collection contains 45 oxides, of which 15 are ultrathin oxide films.

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