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Physical and chemical characterization of multilayered structures

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Abstract

It is important to know the physical and chemical properties of a multilayer if its performance is to be compared to theoretical predictions, or if guidance is needed for the production of superior multilayers. Accurate, nondestructive analytical methods, such as neutron activation analysis, are restricted to certain elements. Certain destructive methods, such as total carbon analysis by combustion, can be sensitive enough for use with very small samples. The method of choice depends upon sensitivity and specificity, both of which are discussed in this paper.

Introduction

To understand the performance of a multilayer, it is important to know its physical and chemical characteristics with adequate accuracy. Peak reflectivity depends upon (among other things) the materials from which the multilayer is made, their physical density (packing density), relative layer thicknesses, roughness, and interfacial diffusion. These properties can be measured by methods described below, or by combinations of these methods. Not all are nondestructive. Some are more precise than others, and certain materials may interfere with the analysis of others. The information presented here is intended as a basis for the selection of the best methods of characterization for common cases.

X-ray diffraction

Several subsequent methods rely upon knowledge of the d-spacing of a multilayer, which is obtained from the Bragg equation applied to x-ray diffraction data. The best accuracy can be obtained from the extended Bragg equation which takes into account the refractive

indexes of the layer materials. In favorable cases, reflections can be measured at several orders, and the reflectivities can be used to calculate γ , the ratio of a layer thickness to the thickness of the bilayer.¹ Roughness and interfacial diffusion affect the peak reflectance of the various orders to different extents and can both be estimated from a good diffraction spectrum and an appropriate model of multilayer reflectance.

If the multilayer contains randomly oriented microcrystals of adequate size, a powder pattern for that material will be observed.¹ For typical multilayers and diffractometer wavelengths, this pattern occurs at larger 2θ angles than the multilayer diffraction peaks. The rocking curves in the powder pattern can be used to estimate the crystallite size and the relative intensity indicates the degree of crystallinity if the optical environment experienced by the x-ray beam is known.² In some cases, it is also possible to estimate the degree of perfection of the crystallites. If the crystals are oriented because of epitaxial growth a more complex diffraction pattern will be generated with the multilayer being a superlattice.¹

Neutron activation analysis

One of the best methods for both qualitative and quantitative chemical analysis of multilayers is neutron activation analysis. For example, when tungsten is exposed to thermal neutrons, the naturally occurring ^{186}W is converted to ^{187}W which has a half-life of 24 hours, and can be qualitatively and quantitatively measured. The analysis is sensitive, nondestructive, and relatively easy to perform. Not all elements can be analyzed by this method. This is not totally without benefit, because some of these (such as silicon) are often used in substrates. Even a low activation of the substrate could overwhelm the signal from the relatively small amount of multilayer material (typically $50 \mu\text{g}/\text{cm}^2$ for a single 15A layer).

Because of these small quantities, neutron howitzers are inadequate for activation of most multilayer materials. Nuclear reactors are better: so much better they may even cause inconvenience by leaving the sample dangerously radioactive for weeks or months.

Gamma detection of the emissions from the activated sample is conveniently performed by scintillation detection using a thallium-doped sodium iodide detector. It is sensitive, but unable to distinguish emissions from two isotopes if they have similar energies. Semiconductor detectors (which are more expensive to purchase and maintain) will make the

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distinction and will probably yield higher sensitivity. Table 1 lists approximate detection limits for the most easily measured pure elements. The last line lists those which are not activated by thermal neutrons.

Table 1. Detection Limits of Selected Elements (ref. 3)

Micrograms	Elements
1-10	Mn, In, Eu, Dy
10-100	V, Rh, Ag, Cs, Sm, Ho, Lu, Hf, Re, Ir, Au
100-1000	Na, Al, Sc, Co, Cu, Ga, As, Br, Kr, Sr, Pd, Sb, I, Ba, La, Er, W, U
undetectable	H, He, Li, Be, B, C, N, O, P, S, Tl, Bi

It can be seen from the table that many elements of interest in the fabrication of multi-layers are easy to measure by neutron activation analysis, while others (such as carbon) are impossible. The latter fact rules out substrate interference for materials such as graphite, organic polymers, and silicon (detectable only at the 10 to 100 gram level). However, mica and glass may interfere because they contain large amounts of interfering elements. Both contain Si, O and H. In addition, Pyrex (borosilicate) glass contains Na, Al and B. Crown glasses are likely to contain K, Ca, and/or Mg. The following types of micas contain other elements: Muscovite, K and Al; Paragonite, Na and Al; Phlogopite, K, Mg and Al; Biotite, K, Fe, Mg and Al; and Lepidolite, K, Li and Al.

Interference occurs only if isotopic lifetimes are similar and the gamma peaks overlap. We have developed a computer code which indicates potentially interfering elements when scintillation detection is used. (Interference is rare if semiconductor detectors are used.) Table 2 lists potential interferences for several elements of interest in multi-layers. It is assumed the resolution is 100 KeV and irradiation is continued for several half lives of the longest lived isotope.

Table 2. Potential Interferences in Neutron Activation Analysis

Isotope	Detection KeV	Interfering Elements and Comments
Ti 51	320.07	K, Zn, Ge, Zr, Mo, Pd, In (avoid glass and mica)
V 52	1433	Na, Ga, Ge, Pd, In, Ba (avoid glass and mica)
Cr 51	320.08	Hf only
W 187	685.72	As, Br, Mo, Sb (other good detection energies avail.)
Ag 108	633.2	Tl, Zn, Ga, Ge, Br, Pd

We used neutron activation analysis to demonstrate that certain multilayers contained vanadium. The emission energies and half life were characteristic of vanadium. We have also used this method to determine the packing density of tungsten in a W/C multilayer of known structure. The number of layer pairs (138) was known from the record of fabrication, and layer dimensions were known from x-ray diffraction (1.09 nm tungsten). A small sample was irradiated for 10 hours at a neutron flux of about 10^{12} neutrons/cm² in a TRIGA reactor and counted a day later. (The sample remained too radioactive to transport without protection for several weeks.) A small piece of pure tungsten was used as a calibration standard. The calculated density was 19, as compared to 19.35, the literature value for the crystal density. Neither the silicon substrate nor the carbon of the layers interfered with the analysis.

Carbon analysis

Carbon can be burned in a stream of oxygen at 1,000°C, and the resulting CO₂ cleaned and titrated coulometrically. A commercial instrument based on this principle has a sensitivity of 0.1 µg of carbon.⁴ Combustion was performed on a 2.89 cm² piece of the multilayer described in the previous paragraph, and the amount of carbon determined to be 70.0 µg. From this the carbon density was calculated to be 2.0.

Chemical analyses

Other chemical analyses can be used for materials which do not lend themselves to neutron activation analysis or combustion analysis. An example is the fluorimetric analysis of Al using morin reagent.⁵ This method is sensitive to submicrogram quantities of Al, but, as with other wet chemical methods, is more subject to contamination than the previously described methods. There are a host of other methods which are generally less sensitive than fluorimetry. They include electrochemical analyses of various types (including the use of ion-selective electrodes), colorimetric methods, titrimetry, and gravimetric methods.

Special techniques must be developed to distinguish chemical compounds from their constituent elements (e.g. determination of tungsten carbide in the presence of elemental tungsten and carbon). Differences in solubility (possibly electrochemical oxidation) can be exploited to remove the metal, and the compound can be identified by infrared spectroscopy. The Mossbauer effect can be used with a few isotopes (e.g. ⁵⁷Fe and ¹¹⁹Sn to disclose chemical binding.

Physical characterization

The roughness of the substrate and/or the completed multilayer can be measured using a sensitive profiler, such as the WYKO NCP-1000M, as discussed in a previous paper. An example of such use is shown in Figures 1 through 3. It can be seen that the silicon substrate is not very rough (6.5 Å rms). Sputtering 1000 Å of carbon causes roughness with pits or scratches, and overcoating with evaporated aluminum further increases the roughness with hillocks being present.

a) SURFACE PROFILE

b) HISTOGRAM OF SURFACE HEIGHTS

Figure 1. a) Surface profile of a silicon substrate. b) Histogram of surface.

a) SURFACE PROFILE

b) HISTOGRAM OF SURFACE HEIGHTS

Figure 2. a) Surface profile after sputtering with 1000A of carbon. b) Histogram showing negative deviations from gaussian profile.

Figure 3. a) Surface profile after overcoating the carbon with evaporated aluminum. b) Histogram showing positive deviations from gaussian profile.

This instrument also indicates the curvature of the substrate (nominally infinite in the previous cases). Other devices can also be used to measure curvature.⁶

There seem to be no sophisticated tests for multilayer adhesion. Common practice is to apply a piece of pressure-sensitive tape, peel it off, and observe the effect on the multilayers.

The multilayer may be under compression or tension on the substrate. If a hole can be etched through the substrate, the multilayers will be stretched like a drum membrane (tension), or else appear wrinkled over the hole (compression). A 30% w/w solution of potassium hydroxide in water will etch silicon that is not heavily doped with inhibitors such as boron. At room temperature the etch rate is approximately 2.2 $\mu\text{m}/\text{h}$. The rate increases dramatically as the temperature is raised. This solution does not attack C, W, Ti or several other metals, so a multilayer can be left intact. However, the membrane will be thin and fragile. A slight differential pressure across it will tear it, particularly if its lateral dimensions are large. For this reason, it is advisable to constrain the diameter of the etched hole using a small "O" ring and an alkali-resistant grease.

Conclusions

Because of the numerous materials used in multilayers, it is impossible to describe a concise set of methods for physical and chemical characterization. However, the above analyses can provide a starting point for the selection of appropriate methods.

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