The method of calculation can in fact be applied to any angle as is shown in FIG. 6. Curve 72 shows the ratio of th overlayer peak height to the substrate peak height calculated over a range of angles instead of for a single angle for an overlayer thickness of 0.5 nm. Curve 74 shows the same ratio for an overlayer thickness of 1.0 nm. Curve 76 shows the same ratio for an overlayer thickness of 1.5 nm. Curve 78 shows the same ratio for an overlayer thickness of 2.0 nm. A measurement of the overlayer thickness of an actual sample can be made by obtaining the ratios of the heights of the photoemission peaks from the overlayer and the substrate for a series of incidence angles and comparing them to the calculated ratios shown in FIG. 6. The calculated curves in FIG. 6 would serve as standards against which the actual sample would be compared.

Alternatively, a series of known standards having known thicknesses of oxide layers or other thin films on known substrates can be prepared. Then the photoelectron emission of an unknown sample would be compared to the known standards.

There are a number of reasons why the method of the invention, employing a grazing angle of x-ray incidence has advantages over prior art methods employing measurement of photoelectron emission using a large angle of x-ray incidence. In comparing photoelectron emission for a large takeoff angle versus photoelectron emission for a grazing takeoff angle, the former electrons can escape atoms at a greater depth beneath the surface, while the latter electrons must come from atoms near the surface owing to the greater amount of matter which they must otherwise penetrate in order to escape. In both cases the depth which is sampled is limited by the quantity of matter which the electrons must traverse in order to escape, and there is always an attendant energy distortion to the spectral line due to inelastic collisions in making their way out of the sample.

In FIG. 7 a calculated curve provides a comparison of the photoelectron energy spectra where x-ray penetration depth is limited by means of prior art near normal (85 degrees) and large, but reduced, takeoff angles (45 degrees) which result from changing the angle of the sample with respect to the electron spectrometer. The x-ray photoemission spectrum is calculated for photoelectrons limited to near normal and reduced takeoff angles from the metal tungsten, using as a source the characteristic radiation of 1253.6 eV from an x-ray tube with a magnesium target. The method of calculation is that described by S. Tougaard in Surface and Interface Analysis, vol. 11, p .453–472, (1988). The calculated photoemission lines are normalized to the same height for the purposes of comparison. In both cases the spectral lineshape shows a distribution of photoelectrons at lower kinetic energy (from about 975 ev to 993 ev) than the main peak (at approximately 1,000 eV) due to inelastic scattering as the photoelectrons escape from the surface. Such photoelectrons that have a lower kinetic energy than the main peak would cause significant distortion of a separate peak due to an overlayer.

An additional distortion in the photoemission lines has been documented when carrying out a process of rotating the sample with respect to an x-ray source and an electron spectrometer whose orientation are held constant with respect to each other, as is conventionally the case. See N. E. Erickson and C. J. Powell, Journal of Vacuum Science & Technology A4, 1551–1556 (1986). This distortion is due to the change in sample position relative to the focal point of the electron spectrometer.

The above-mentioned distortions in photoelectron emission are greatly reduced by employing the apparatus and method of the invention. Evidence for the reduced lineshape distortion that results from using the invention is provided by FIG. 8 in which a comparison is easily made between calculated photoelectron energy spectra where penetration depth is limited by means of x-ray incidence angles above and below the critical angle at the surface of the sample. In FIG. 8, the x-ray photoemission spectra are calculated for the system in which the sample is held fixed with respect to the electron spectrometer; and depth variation, obtained by varying the angle of incidence of the collimated x-ray beam from normal incidence to just below the critical angle as described, is provided with the invention. It is seen that the distortion of the photoemission lines for a small grazing angle of incidence in FIG. 7 is considerably reduced (see curve 80) compared to a normal angle of incidence (see curve 82). The reduced distortion with the grazing angle of incidence is due to the fact that the penetration depth is limited partially by the x-ray penetration depth rather than totally by the escape depth of the photoelectrons.

Thus it can be seen that by employing the principles of the invention, measuring the depth distribution in a multilayer sample does not suffer the disadvantages of prior art methods. More specifically, by using the principles of the invention, energy distortion which has been documented due to change in the relative motion of the sample with respect to the spectrometer is eliminated. Furthermore, energy distortion due to a large angle of incidence is considerably reduced with the invention.

Moreover, with the invention, for photoemission lines in which the changes due to chemical environment are small and must be distinguished by means of fitting peaks with the variation of binding energy, the diminished distortion provided by employing the principles of the invention provides a distinct advantage.

What is claimed is:

1. An x-ray photoelectron emission analyzer apparatus for analyzing a sample in an evacuated chamber, the apparatus comprising:

- an x-ray source;
- collimating means for collimating x-rays from the source for providing a collimated x-ray beam which interacts with the sample within the evacuated chamber;
- incidence angle adjustment means for adjusting the collimated x-ray beam for permitting the collimated x-ray beam to interact with the sample with an adjustable grazing incidence angle;
- electron detector means, maintained in a predetermined, fixed orientation with respect to the sample, for detecting photoelectron emission from the sample;
- fixed sample support means for maintaining the sample in the evacuated chamber in a predetermined, fixed orientation with respect to said electron detector means; and
- means for monitoring the grazing incidence angle of the collimated x-ray beam that interacts with the sample.

2. The apparatus described in claim 1 wherein said x-ray source includes an x-ray tube.