the sample includes a third layer that underlies the second layer;

the third layer has a third-layer critical angle;

the grazing incidence angle is at an angle greater than the second-layer critical angle and less than the third-layer critical angle, whereby photoelectron emission intensity from the second layer is enhanced; and

determining thickness of the second layer based on the intensity of photoemission peaks corresponding to the chemical species of the second and third layers.

28. The method described in claim **21** wherein:

the sample includes an "n"th layer that underlies an "n-1"th layer;

the "n"th layer has an "n"th-layer critical angle;

the "n-1"th layer has an "n-1"th critical angle;

the grazing angle is at an angle greater than the "n-1"th-layer critical angle and less than the "n"th-layer critical angle, whereby photoelectron emission intensity from the "n-1"th layer is enhanced: and

determining thickness of the "n-1"th layer based on the intensity of photoemission peaks corresponding to the chemical species of the "n-1"and "n"th layers.

29. The method described in claim **21** wherein the collimated x-ray beam has an energy range from 100 to 10,000 electron volts.

30. The method described in claim **21**, further including the step of:

determining an interface between the first layer and the second layer by detecting a total x-ray field, at the interface, which is stronger than an x-ray field at a layer surface, for angles of incidence that are less than or equal to the second layer critical angle and greater than the first-layer critical angle.

31. A method for analyzing a multilayer sample having a first layer and a second layer, wherein the first layer is a top layer and has a first-layer critical angle, and wherein the second layer has a second-layer critical angle, the method comprising the steps of:

supporting the sample in a evacuated chamber with a predetermined, fixed orientation with respect to an electron detector, wherein the sample is a semiconductor and has an optically polished first layer;

directing a collimated x-ray beam to the sample at a grazing incidence angle with respect to the sample;

monitoring the grazing incidence angle of the collimated x-ray beam with respect to the sample by detecting x-rays reflected off of the sample with an x-ray detector and generating data representing the grazing incidence angle;

controlling the grazing incidence angle with respect to the sample such that the incidence angle includes angles greater than the first-layer critical angle and less than the second layer critical angle;

detecting photoelectron emission from the sample with the electron detector and generating data representing the quantity of electrons at each kinetic energy;

evaluating the data representing the energy distribution of the detected photoelectron emission to determine peaks in intensity corresponding to photoemission from different chemical species; and

determining thickness of the first layer based on comparing the intensity of peaks due to photoemission from the different chemical species at different incidence angles.

32. A method for analyzing a sample, comprising the steps of:

supporting the sample in a evacuated chamber with a predetermined, fixed orientation with respect to an electron detector;

directing a collimated x-ray beam at a grazing incidence angle with respect to the sample;

monitoring a grazing exit angle of the collimated x-ray beam with respect to the sample by detecting x-rays reflected off of the sample with an x-ray detector:

controlling the grazing incidence angle of the collimated x-ray beam with respect to the sample based on the monitored grazing exit angle of the x-rays reflected off of the sample;

detecting photoelectron emission from the sample with the electron detector; and

evaluating the detected photoelectron emission to determine different chemical species in the sample.

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