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(71) Applicant (for all designated States except US): EUROPEAN COMMUNITY represented by COMMISSION OF THE EUROPEAN COMMUNITIES [—/LU]; Rue Alcide de Gasperi, L-2920 Luxembourg (LU).

(72) Inventor; and
(75) Inventor/Applicant (for US only): GIBSON, Peter, Neil [GB/IT]; Via delle Betulle, 7, I-21027 Ispra (IT).

(74) Agent: BOULT WADE TENNANT; Verulam Gardens, 70 Gray's Inn Road, London WC1X 8BT (GB).

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(54) **Title:** X-RAY REFLECTIVITY APPARATUS AND METHOD

(57) **Abstract:** A method and corresponding apparatus for determining one or more physical parameters, such as electron density, of a target surface of a sample are disclosed. The target surface is irradiated with X-rays of at least two different wavelengths over a range of angles of incidence, and the physical parameter is determined by combining measurements of the intensity of these X-rays following specular reflection. The X-rays at two different wavelengths may be simultaneously generated using a metal alloy anode.

X-RAY REFLECTIVITY APPARATUS AND METHOD

The present invention relates to a method and apparatus for determining a physical parameter of a sample in the vicinity of a target surface of the sample. In particular, the invention relates to a method and apparatus for making such a determination by measuring the intensity of X-rays reflected from said target surface.

X-ray reflectivity is one of a range of X-ray scattering techniques often used to probe the structure of matter. The technique consists of monitoring the intensity of X-rays reflected from a target surface, relative to the intensity of the incident beam, as a function of the scattering transfer vector. The technique can be used to study a variety of physical characteristics and parameters of a sample such as surface roughness, thin film thickness, interfacial roughness and density.

Specular reflection of X-rays occurs when the angle of reflection of the beam from the sample surface is the same as the angle of incidence. Since the index of refraction of solid and liquid materials at X-ray wavelengths is generally slightly less than unity, there exists a critical angle of incidence below which X-rays will be totally reflected from a sample surface. The critical angle varies depending on characteristics of the sample in the vicinity of the surface such as the mass density and electron density, and in particular on the atomic number density and composition, and is typically a few tenths of a degree. This means that specular X-ray reflectivity can be used, for example, to determine the density of a material in the vicinity of the sample surface. Specular X-ray reflectivity is described at length in Chason and Mayer, Critical Reviews in Solid State and Materials Sciences, 22(1):1-67(1997).

Conventional X-ray reflectivity systems generally use a well collimated X-ray beam, a well defined X-ray wavelength and one or more precise goniometers to separately vary the angles of the incident beam and of the detection equipment with respect to the target surface of the sample. A combined monochromator and collimator in the incident beam may be used to satisfy the first two requirements. The X-rays may be generated using a pure metal anode X-ray tube, which provides strong $K\alpha$ and $K\beta$ emission lines. The $K\alpha$ line is further split into the $K\alpha1$ and $K\alpha2$ lines, of which $K\alpha1$ is the strongest. For a copper anode the $K\alpha1$ line, with a wavelength of 1.5406×10^{-10}m, is commonly used for X-ray reflection measurements.

In some known X-ray reflectivity systems a knife-edge is positioned in close proximity to the target surface, and this effectively provides beam collimation as well as ensuring the positioning of the target surface in the beam. In known systems, accurate alignment of the system components and accurate positioning of the sample are of the utmost importance. Small errors in the assumed angular zero-point, which relates to the position of the goniometer in which the surface of the sample is exactly parallel to the incident beam, can result in significant errors in the subsequent data analysis, for example in the determination of sample density in the vicinity of the target surface. Such errors can easily result when samples are small or have slightly curved surfaces. In practice, much of the analysis software commercially available at present assumes no zero-point error, when, in reality, errors in alignment are strongly related to errors in parameters determined using the technique.

It is an object of the present invention to address these and other problems and disadvantages of the prior art.

According to a first aspect of the present invention there is provided a method of determining one or more physical parameters of a sample in the vicinity of a target surface of the sample, the method comprising the steps of irradiating the target surface with X-rays of at least first and second wavelengths, at two or more angles of incidence; taking measurements of the intensity of the X-rays following specular reflection from the target surface at each of the at least first and second wavelengths, and for each of the two or more angles of incidence; and combining said measurements of intensity of the reflected X-rays in order to determine said one or more physical parameters.

By combining measurements of the intensity of the reflected X-rays taken for two or more angles of incidence and more than one well-defined X-ray wavelength, the one or more physical parameters may be determined independently of errors in the assumed angular zero-point. Of course, the intensity may be measured indirectly through a number of different physical observables such as the total X-ray power, or a photon count, and using a wide variety of means familiar to the person skilled in the art.

The invention provides for more rapid sample alignment than methods and apparatus of the prior art, because the need for absolute angular precision is reduced. Confidence in fitted parameters such as density, film thickness and interfacial thickness is increased, as the invention allows false minima in computer fitting programs to be more easily avoided. Target surfaces that are not perfectly flat may be analysed with increased accuracy using the present invention, because determination of the zero-point angle, in which the incident X-ray beam is parallel to the sample surface, is not as critical as in the prior art.

Preferably, the step of combining the measurements includes the step of fitting the measurements to a physical or mathematical theory or model relating the reflectivity of the target surface at a given wavelength and a given angle of incidence to the one or more physical parameters. By collecting X-ray reflectivity data from the same target surface at more than one wavelength and performing a simultaneous fitting procedure to an appropriate model for some or all of the collected data, the accuracy of the fitted solution, which may include a fit for the angular zero-point, is enhanced.

In particular, the one or more physical parameters may include refractive index, electron density and mass density. Various appropriate physical theories, mathematical models or mathematical expressions relating any of these parameters to expected X-ray reflectivity characteristics are well known to the person skilled in the art. Other physical parameters, such as surface roughness, thin film thickness and interfacial roughness may similarly be determined.

Preferably, the measurements are taken when the angles of incidence and reflection are substantially equal, in other words when specular reflection occurs. In such a situation the scattering transfer vector is substantially perpendicular to the target surface, and relatively simple models or expressions may be used to determine certain physical parameters such as refractive index or physical density.

Preferably, the target surface is simultaneously irradiated with X-rays of the at least first and second wavelengths. By simultaneously irradiating with X-rays of the two or more wavelengths, adjustments to the apparatus, which might otherwise be required between sets of measurements at each X-ray wavelength, may be avoided. This eliminates a potential source of error and also eliminates the need to either carefully realign the apparatus for a change of X-ray wavelength or to use a special monochromator set up.

Preferably, the measurements of the intensity of the reflected X-rays at the at least first and second wavelengths are taken simultaneously for any given angle of incidence. Any adjustments that might otherwise be required to adapt the apparatus used in order to change the detected wavelength would introduce a further source of error, as well as complicating the construction of the apparatus used and the carrying out of the method.

The X-rays for irradiating the target surface may be generated using a pure metal anode X-ray source, in which case the first and second wavelengths may be the Kα and Kβ lines of the pure metal anode.

Preferably, however, the X-rays are generated using a metal alloy anode X-ray source comprising at least first and second component metals, X-rays of the first wavelength being emitted by the first component metal and the X-rays of the second wavelength being emitted by the second component metal. The Kα and Kβ emission lines of most conventional pure metal anodes are rather close together in wavelength, and it may be difficult to obtain a very good split between their respective signals in the means used to detect the X-rays. In addition, for all practical applications, a larger separation of the two or more X-ray wavelengths used will result in an improved determination of, for example, the angular zero-point of the apparatus with respect to the target surface, or of the one or more physical parameters which the method and apparatus seek to determine.

Preferably, the metal alloy anode used is a nickel-chromium alloy anode. However, a variety of other elemental compositions will be suitable, as will be apparent to the person skilled in the art, including alloys of three or more metals. Indeed, any X-ray source capable of generating two or more wavelengths with sufficient wavelength separation may be used, such as a synchrotron or other source in combination with suitable monochromator means.

Preferably, the angles of incidence and reflection of the detected X-rays are in the range from zero to ten degrees. For typical solid and liquid samples, the critical angle for total external reflection of X-rays is in the range from 0.1 to 0.9 degrees. However, for layered surfaces, interference fringes may extend several degrees beyond the critical angle and can be used to determine the thicknesses of sub-surface layers.

According to a second aspect of the invention there is provided an apparatus for use in determining one or more physical parameters of a sample in the vicinity of a target surface of the sample, comprising an X-ray source adapted to generate X-rays of at least first and second wavelengths and arranged to irradiate the target surface with said X-rays; X-ray detection means adapted to take measurements of the intensity of X-rays following specular reflection from the target surface at each of the at least first and second wavelengths; and angle adjustment means arranged to allow the angle of incidence of the X-rays onto the target surface to be varied.

The apparatus may be arranged so that the angles of incidence, reflection and the orientation of the target surface may all be adjusted independently. It will be apparent to the person skilled in the art that useful X-ray reflectivity measurements may be taken by adjusting only one, or both of the angles of incidence and reflection.

The X-ray detection means may comprise two or more X-ray detectors. Reflected beam monochromator means may then be used to simultaneously or sequentially direct reflected X-rays of each of the at least first and second wavelengths to respective ones of each of said two or more X-ray detectors.

Preferably, however, the apparatus comprises an energy or wavelength-dispersive detector, so that the intensity of the X-rays at one or more of the at least first and second wavelengths can be measured simultaneously. For example, a semiconductor junction solid-state detector may be used. Alternatively, or additionally, the apparatus may comprise an adjustable monochromator arranged so that X-rays of only one of said at least first and second wavelengths impinge on the X-ray detection means at any one time.

Advantageously, the apparatus further comprises data processing means adapted to combine said measurements of the intensity of the reflected X-rays in order to determine said one or more physical parameters.

Preferably, the data processing means is adapted to fit the measurements to a physical or mathematical theory or model relating the reflectivity of the sample surface at a given X-ray wavelength and angle of incidence to the one or more physical parameters.

A number of embodiments of the invention will now be described, by way of example only, and with reference to the accompanying drawings, of which:

Figure 1 shows, schematically, apparatus for making multiple wavelength X-ray reflectivity measurements, employing a monochromator in the incident beam, and according to a first embodiment of the invention;

Figure 2 shows, schematically, apparatus for making multiple wavelength X-ray reflectivity measurements, employing a knife-edge collimator and a reflected beam monochromator, and according to a second aspect of the present invention; and

Figure 3 shows, schematically, apparatus for making multiple wavelength X-ray reflectivity measurements, employing an incident beam collimating slit, only a single goniometer and a solid-state detector, and according to a third embodiment of the present invention.

Turning now to Figure 1, there is shown an apparatus according to a first preferred embodiment of the present invention. X-rays are generated by a metal alloy anode X-ray source 1, for example a nickel/chromium anode source, although many other elemental combinations would be suitable. The nickel Kα emission line is at 1.659×10^{-10}m and the chromium Kα line is at 2.291×10^{-10}m, both these values being weighted averages of the Kα1 and Kα2 lines. Alternatively, the X-rays may be generated by a conventional single metal anode X-ray source.

The X-rays are passed through an adjustable monochromator 2 which also operates as a collimator. The monochromator is adjustable to select X-rays of a chosen one of two or more wavelengths, for example the nickel and chromium Kα lines generated by the metal alloy anode source, or alternatively, Kα1 and Kβ lines generated by a single metal anode. The X-ray beam emerging from the monochromator 2 is incident on the target surface 3 of the sample 4, defining an angle of incidence. The sample 4 is mounted on a first goniometer so that the target surface 3 is perpendicular to the plane of the goniometer, is precisely aligned with the rotational axis of the goniometer, and so that the angle of incidence of the collimated X-ray beam on the target surface may be adjusted with good precision. A slit 6 and X-ray detector 7 are mounted on a second goniometer 8 that is concentric with the first goniometer, in such a way that X-rays reflected from the target surface 3 may pass through the slit and onto the detector 7. The angle of reflection of the X-rays passing through the slit 6 may be adjusted by rotating the second goniometer 8 relative to the first goniometer 5.

The apparatus shown in Figure 1 may be used to carry out a method according to the invention in the following way.

The first and second goniometers 5 and 8 are adjusted to define an angular zero-point at which an X-ray beam emerging from the monochromator 2 grazes the target surface 3 at a zero angle of incidence and enters the slit 6 with a zero angle of reflection. The monochromator 2 is then adjusted to select X-rays of only a first wavelength, for example the nickel Kα line if the X-ray source is a nickel/chromium metal alloy anode source, or the Kα1 line at 1.5406×10^{-10}m wavelength if the X-ray source 1 is a conventional copper anode source. Measurements of X-ray intensity incident on the detector 7 following specular reflection at the target surface are then made for a number of angles of incidence, by adjusting the first and second goniometers 5 and 8 between each measurement.

The monochromator 2 is then adjusted to select X-rays of only a second wavelength, for example the chromium Kα line if the X-ray source is a nickel/chromium metal alloy anode source, or the Kβ line at 1.3922×10^{-10}m wavelength if the X-ray source 1 is a conventional copper anode source. The angular zero-point may be re-determined at this point, before proceeding to measure again the intensity of X-rays incident on the detector at a number of angles of incidence and corresponding angles of reflection.

An appropriately programmed computer is then used to simultaneously fit the data sets taken at the first and second X-ray wavelengths to a single physical model to yield a determination of one or more physical parameters, such as electron density or mass density. In general, however, the resetting of the monochromator 2 will change the exact path of the incident beam, and the system will need careful re-alignment for measurements at the second X-ray wavelength. Separate assumed errors in the zero-points determined for the two sets of measurements would need to be used during data analysis.

A number of variations in the described method and apparatus are possible. For example, the sample may be held in a fixed position while the source 1 and adjustable monochromator 2 are mounted on the first goniometer 5. Additional slits may be used, for beam collimation, and the monochromator may alternatively be positioned between the target surface 3 and the detector 7, in which case a single zero point error could be assumed for both sets of measurements.

Turning now to Figure 2 there is shown an apparatus according to a second preferred embodiment of the invention. X-rays are again generated by a nickel/chromium metal alloy anode X-ray source 11. These X-rays, however, are neither well collimated or passed through a monochromator before being incident on the target surface 13 of sample 14. The sample 14 is mounted on a first goniometer 15 so that the target surface 13 is perpendicular to the plane of the goniometer, is precisely aligned with the rotational axis of the goniometer, and so that the angle of incidence of the X-ray beam onto the target surface may be precisely adjusted. Collimation of the beam is provided by a knife-edge collimator 12, which comprises a fine edge positioned very close to the sample surface 13, and close to the rotational axis of the first goniometer 15. A slit 16, reflected beam monochromator 19 and X-ray detector 17 are mounted on a second goniometer 18, concentric with the first goniometer 15, in such a way that X-rays reflected from the target surface 13 may pass through the slit, and be directed onto X-ray detector 17 by the monochromator 19. The reflected beam monochromator 19 selects X-rays of a particular but adjustable wavelength, and directs the selected X-rays onto X-ray detector 17. The angle of reflection of the X-rays from the target surface that pass through the slit 16 may be adjusted by rotating the second goniometer 18.

The apparatus shown in Figure 2 may be used to perform the method of the invention in a similar way to that described above in relation to the apparatus shown in Figure 1. However, because the monochromator is located between the slit 16 and the detector 17, there is no need to re-determine the angular zero-point of the first and second goniometers 15 and 18 between successive sets of measurements, made using X-rays at two or more different wavelengths by adjusting the monochromator 19. Therefore, a single zero-point error may be assumed when the two or more data sets at different X-ray wavelengths are analysed by simultaneous fitting to a physical or mathematical theory or model. However, in using a single assumed zero-point error there remains a likelihood of small variations in the actual zero-point error between scans, for example due to temperature variation or mechanical interference with the system.

A number of variations in the method and apparatus of the described second preferred embodiment will be apparent to the person skilled in the art. For example, the X-ray source may be mounted on the first goniometer 15 instead of the sample 14 and knife-edge collimator 12. Additional slits may be mounted in the incident beam to reduce the amount of scattered radiation.

The arrangement shown in Figure 2 may be adapted by providing a reflected beam monochromator that simultaneously selects X-rays of each of two or more wavelengths and directs the X-rays of each selected wavelength to a separate X-ray detector. If such an arrangement is used then the intensity of each selected wavelength can be simultaneously measured, so that only a single scan over the desired range of angles of incidence and reflection is required. The same result could be achieved by using a motorised monochromator to select each wavelength in turn for each angle of incidence and reflection. Because only a single scan is performed only a single assumed zero-point error is required during analysis of the intensity measurements.

The arrangement shown in Figure 2 may also be adapted by replacing the reflected beam monochromator 19 and conventional X-ray detector 17 with a wavelength-dispersive detector such as a semiconductor junction solid-state detector. Electronics connected to the detector may then be used to record scans over a range of angles of incidence and reflection, simultaneously at the two or more desired X-ray wavelengths.

Turning to Figure 3, there is shown an apparatus according to a third preferred embodiment of the invention. The X-rays generated by the nickel/chromium metal alloy anode X-ray source 21 are collimated by a slit 22 before being incident on the target surface 23 of sample 24. The X-ray source 21 and slit 22 are mounted on a single goniometer 25 in such a way that the X-ray beam emerging from the slit is directed towards the rotational axis of the goniometer 25. The sample is fixed in position, rather than being mounted on the goniometer, in such a way so that the target surface 23 is perpendicular to the plane of the goniometer, and is precisely aligned to pass through the axis of rotation of the goniometer. The angle of incidence of the X-rays onto the target surface 23 is adjusted by moving the source 21 and slit 22 using the goniometer 25. A solid state energy or wavelength dispersive detector 27 is provided in a fixed position relative to the sample 24, with the active surface of the detector located so that X-rays reflected from the sample with an angle of reflection of between zero and the required upper limit are incident on the active surface. The distance of the active surface from the target surface 23 may be changed to ensure that the solid-state detector is large enough to always intercept the X-ray beam for desired angles of reflection. A knife-edge 26 is provided to prevent the X-ray beam from impinging directly on the detector 27 without first reflecting from the sample surface, when the angle of incidence is very small. Two or more single channel analysers are connected to the detector 27 to discriminate between the two or more X-ray wavelengths the intensities which are to be measured, although a motorised monochromator together with a more standard detector could be used.

The apparatus of Figure 3 may be used to perform the method of the invention by making measurements of the intensities of the reflected X-ray beam at two or more wavelengths over a range of angles of incidence and reflection, by adjusting the goniometer 25. No precise determination of the zero-point is required, as the zero-point angle can be determined during the data processing stage, although approximate alignment is clearly desirable. The use of a single goniometer also simplifies operation of the apparatus considerably.

The use of a metal alloy anode X-ray source means that two or more emission lines may be used with a better separation than could be achieved with a single metal anode source. For example, the nickel and chromium Kα lines discussed above are easy to differentiate in electronics used to process the signals from the solid-state detector. For similar reasons, a metal alloy anode X-ray source may advantageously be used in place of the other described sources in any of the X-ray reflection apparatus described, or indeed any apparatus embodying the invention.

A variation of the apparatus shown in Figure 3 that may often be more convenient to arrange is to mount only the sample 23,24, or the sample and the detector 27, on the goniometer, keeping the X-ray source 21 fixed.

Various degrees of automation may be used with each of the described embodiments. For example, the operation of the goniometers may be automated and controlled by a computer, as may be the operation of the X-ray source and the determination of the angular zero-points. Clearly, the signals from the X-ray detector or detectors used will typically require some electronic post processing, which may be rather complex for solid state energy or wavelength dispersive detectors. Data from the detectors, and also from the goniometers, X-ray source, monochromators and so on will be typically fed to a computer for storage and further processing.

While the embodiments have generally been described with specular reflection in mind, it will be clear to the person skilled in the art that the intensity of X-rays reflected at non-specular angles may also be measured by the described apparatus, although some minor modifications that will be apparent to the person skilled in the art may be necessary for one or more of the described embodiments. Accordingly, while the measurements of intensity may be processed using known theories or models of specular reflection, for example to determine the refractive index, mass density, electron density, film thickness and interfacial roughness in the vicinity of the target surface, other parameters may also be determined.

The data analysis may be performed by computer apparatus directly connected to or apart from the system, using standard software or software written or adapted for the purpose. The data may be analysed by performing a least-square type fit using the multiple wavelength data, in order to reduce or eliminate alignment errors, to identify or eliminate false minima or maxima in parameter space, and to increase confidence in the results.

Further variations that could be made in each of the described embodiments will be apparent to the person skilled in the art. For example, other X-ray sources such as synchrotron or rotating anode sources could be used with appropriate monochromating means. The described arrangements and alignments of the goniometers, sample, X-ray source and detector arrangements are merely exemplary, and other arrangements for carrying out the invention could equally be used.

For determining physical parameters such as atomic number densities and surface roughness parameters, reflectivity models such as those given in Crabb et al, Computer Physics Communications 77 (1993) 441-449 may be used, with suitable modifications to allow fitting of the zero point angle using data sets obtained at two or more wavelengths. The recursion formula of Parratt may be used in the reflectivity model to allow for a number of homogenous layers with plane-parallel interfaces.

A simplified expression for the X-ray reflection coefficient R of a flat surface in air, just above the critical angle, is given by

$$R(\phi) = \frac{(\phi - A)^2 + B^2}{(\phi + A)^2 + B^2}$$

where $$2A^2 = [(\varnothing^2 - 2\delta)^2 + 4\beta^2]^{1/2} + (\varnothing^2 - 2\delta)$$

and $$2B^2 = [(\varnothing^2 - 2\delta)^2 + 4\beta^2]^{1/2} - (\varnothing^2 - 2\delta)$$

In the above expression, $\varnothing$ is the angle of incidence and reflection of the X-rays, δ is essentially a function of the electron density of the sample and β describes absorption in the material of the sample. Coefficients δ and β are components of the index of refraction n of matter at X-ray wavelengths, which may be expressed as:

$$n = 1 - \delta - i\beta$$

The coefficients depend on atomic number density and composition, and can be calculated using these expressions:

$$\delta = \frac{\lambda^2 e^2}{2\pi mc^2} \sum_i N_i(z_i + f_i')$$

$$\beta = \frac{\lambda^2 e^2}{2\pi mc^2} \sum_i N_i(f_i'')$$

Here, λ is the X-ray wavelength, m and e are the mass and charge of an electron, c is the speed of light, N_i is the atomic number density of atoms of species i, Z_i is the corresponding atomic number, and f' and f'' are the real and imaginary components of the anomalous dispersion correction to the atomic scattering factor.

For a sample of known composition but unknown mass density (or equivalently, electron density), for example, coefficients δ and β essentially become functions of the X-ray wavelength λ and the sample density ρ. The X-ray reflection coefficient R may then be written as a function of incident angle, X-ray wavelength and sample density, $R(\varnothing,\lambda,\rho)$. If the incident angle includes a measured component θ and an unknown zero point error angle $\Delta\theta$, and measurements of R are made at two or more wavelengths, then the expression for $R(\theta+\Delta\theta,\lambda,\rho)$ can be fitted to the data to yield values for $\Delta\theta$ and ρ.

Because the critical angle $\varnothing_c$ of total external reflection of X-rays is typically small, it can be approximated by

$$\varnothing_c = (2\delta)^{½}$$

If $\varnothing_c$ is measured, with an unknown zero point error angle of $\Delta\varnothing$, then the measured value of $\varnothing_c$ can be expressed as a function of the X-ray wavelength λ, the electron or mass density ρ based on

$$\sum_i N_i(z_i + f_i')$$

and the zero point error $\Delta\varnothing$, as $\varnothing_c(\lambda,\rho,\Delta\varnothing)$. Thus, measurements of $\varnothing_c$ at two or more wavelengths λ may also be fitted to the data to yield values for density and zero point error angle. However, the more limited amount of data resulting from a measurement of the critical angle is likely to provide a less accurate determination of the desired physical parameters and zero point angle error than a method of analysis based on reflectivity data points at a range of angles of incidence greater than the critical angle.

Having determined coefficients δ and β, other physical parameters such as the refractive index may be easily calculated.

The analysis discussion presented above is, of course, very simplified. It will usually be desirable to incorporate a roughness model into the procedure, and more complex crystallographic or multi species composition models may of course be used. Reflectivity data may be fitted to the model using, for example, least squares techniques.

CLAIMS

1. A method of determining one or more physical parameters of a sample in the vicinity of a target surface of the sample, comprising the steps of:

irradiating the target surface with X-rays of at least first and second wavelengths, at two or more angles of incidence;

taking measurements of the intensity of the X-rays following specular reflection from the target surface at each of the at least first and second wavelengths, and for each of the two or more angles of incidence; and

combining said measurements of intensity of the reflected X-rays in order to determine said one or more physical parameters.

2. The method of Claim 1 wherein the step of combining the measurements includes the step of fitting the measurements to a physical or mathematical theory or model relating the reflectivity of the target surface at a given X-ray wavelength and a given angle of incidence and reflection, to the one or more physical parameters.

3. The method of any preceding claim wherein the one or more physical parameters include at least one of mass density, electron density and refractive index.

4. The method of any preceding claim wherein the sample is simultaneously irradiated with X-rays of the at least first and second wavelengths.

5. The method of Claim 4 wherein the measurements of the intensity of the reflected X-rays at the at least first and second wavelengths are taken simultaneously for any particular angle of incidence.

6. The method of any preceding claim wherein the X-rays are generated using a pure metal anode X-ray source.

7. The method of any of Claims 1 to 5 wherein the X-rays are generated using a metal alloy anode X-ray source comprising at least first and second component metals, X-rays of the first wavelength being emitted by the first component metal and X-rays of the second wavelength being emitted by the second component metal.

8. The method of Claim 7 wherein the metal alloy anode is a nickel-chromium alloy anode.

9. The method of any preceding claim wherein the angle of incidence of the measured X-rays is in the range from zero to ten degrees.

10. Apparatus for use in determining one or more physical parameters of a sample in the vicinity of a target surface of the sample, comprising:

an X-ray source adapted to generate X-rays with at least first and second wavelengths and arranged to irradiate the target surface with said X-rays;

X-ray detection means adapted to take measurements of the intensity of X-rays following specular reflection from the target surface at each of the at least first and second X-ray wavelengths; and

angle adjustment means arranged to allow the angle of incidence of the X-rays onto the target surface to be varied.

11. The apparatus of Claim 10 wherein the X-ray source comprises a metal alloy anode X-ray source, the metal alloy comprising at least first and second

component metals, the X-rays of the first wavelength being emitted by the first component metal and the X-rays of the second wavelength being emitted by the second component metal.

12. The apparatus of Claim 11 wherein the metal alloy anode is a nickel-chromium alloy anode.

13. The apparatus of any of Claims 10 to 12 further comprising an adjustable monochromator arranged so that X-rays of only one of said at least first and second wavelengths impinge on said X-ray detection means at any one time.

14. The apparatus of any of Claims 10 to 12 wherein the X-ray detection means comprises two or more X-ray detectors, and further comprising reflected beam monochromator means adapted to simultaneously or sequentially direct reflected X-rays of different ones of said at least first and second wavelengths to different ones of said two or more X-ray detectors.

15. The apparatus of any of Claims 10 to 14 wherein the X-ray detection means comprises one or more energy or wavelength-dispersive detectors.

16. The apparatus of Claim 15 wherein the one or more wavelength-dispersive detectors are semiconductor junction solid-state detectors.

17. The apparatus of any of Claims 10 to 16 further comprising data processing means adapted to combine said measurements of the intensity of the reflected X-rays in order to determine said one or more physical parameters.

18. The apparatus of Claim 17 wherein said data

processing means is adapted to fit the measurements to a physical or mathematical theory or model relating the reflectivity of the sample surface at a given X-ray wavelength and angle of incidence to the one or more physical parameters.

19. The apparatus of any of Claims 10 to 18 wherein the one or more physical parameters include at least one of electron density, mass density and refractive index.

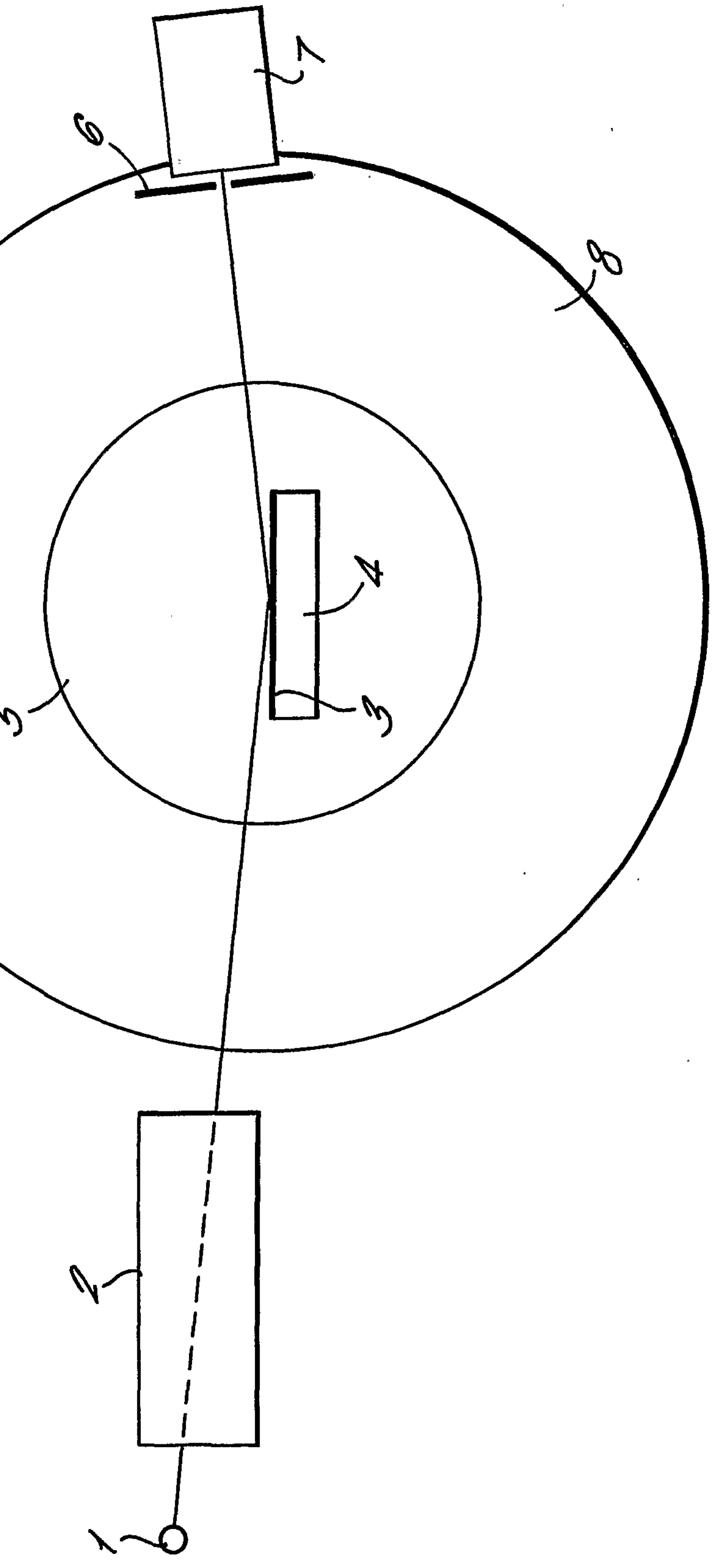

FIG. 1.

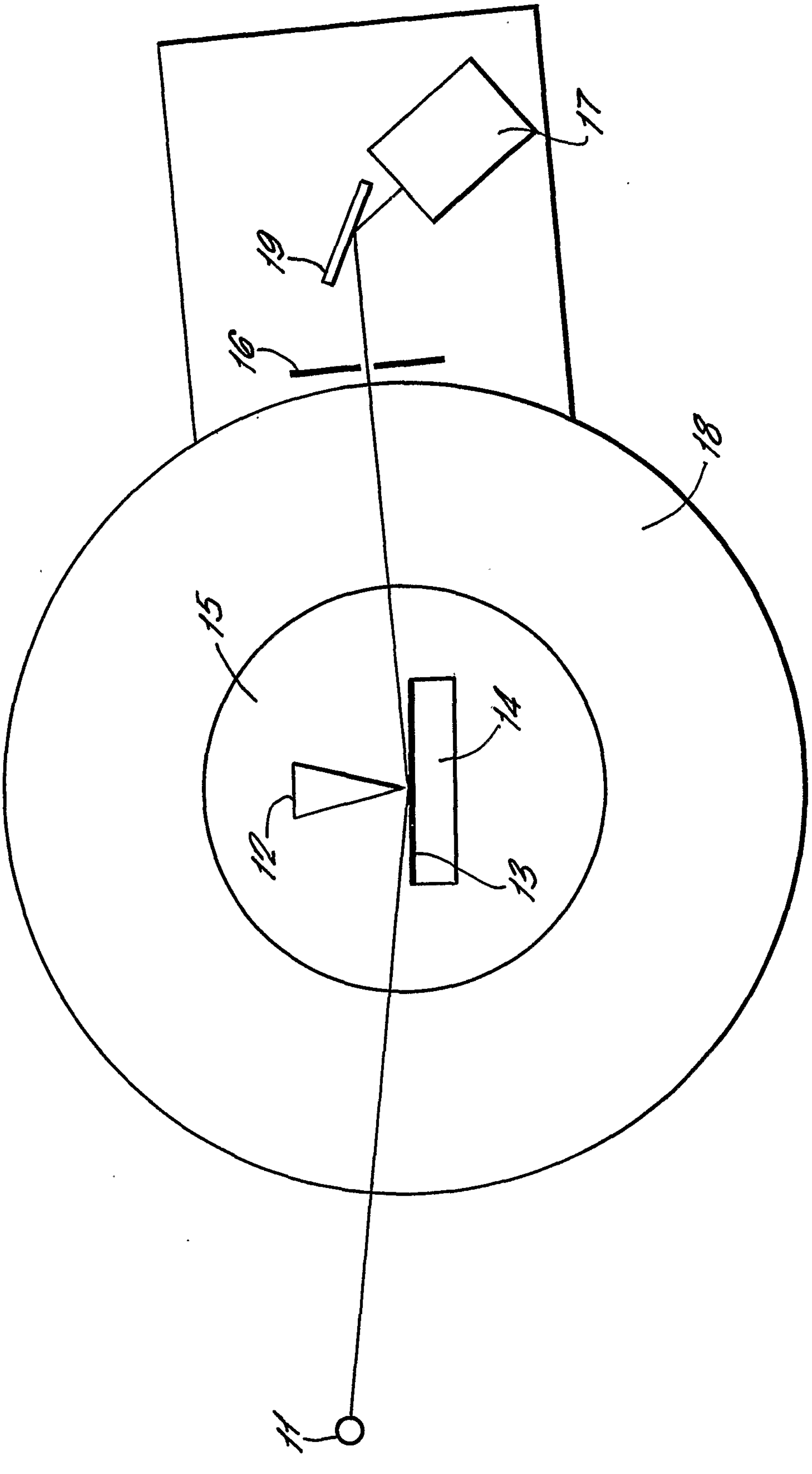

FIG. 2.

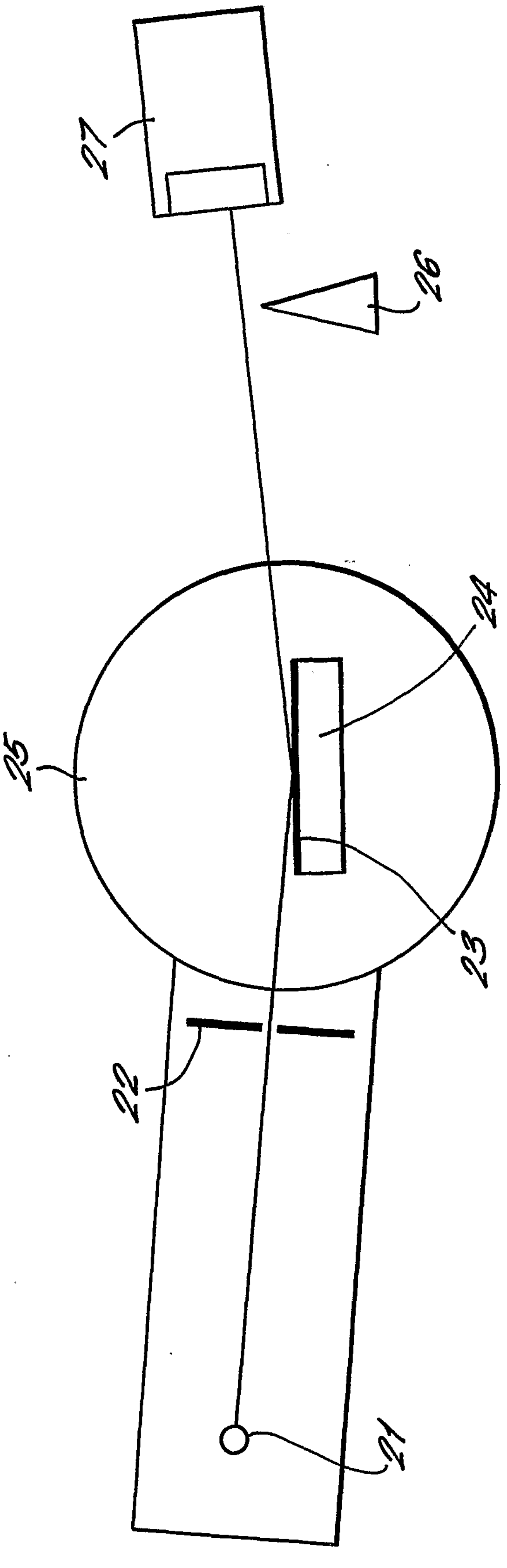

FIG. 3.