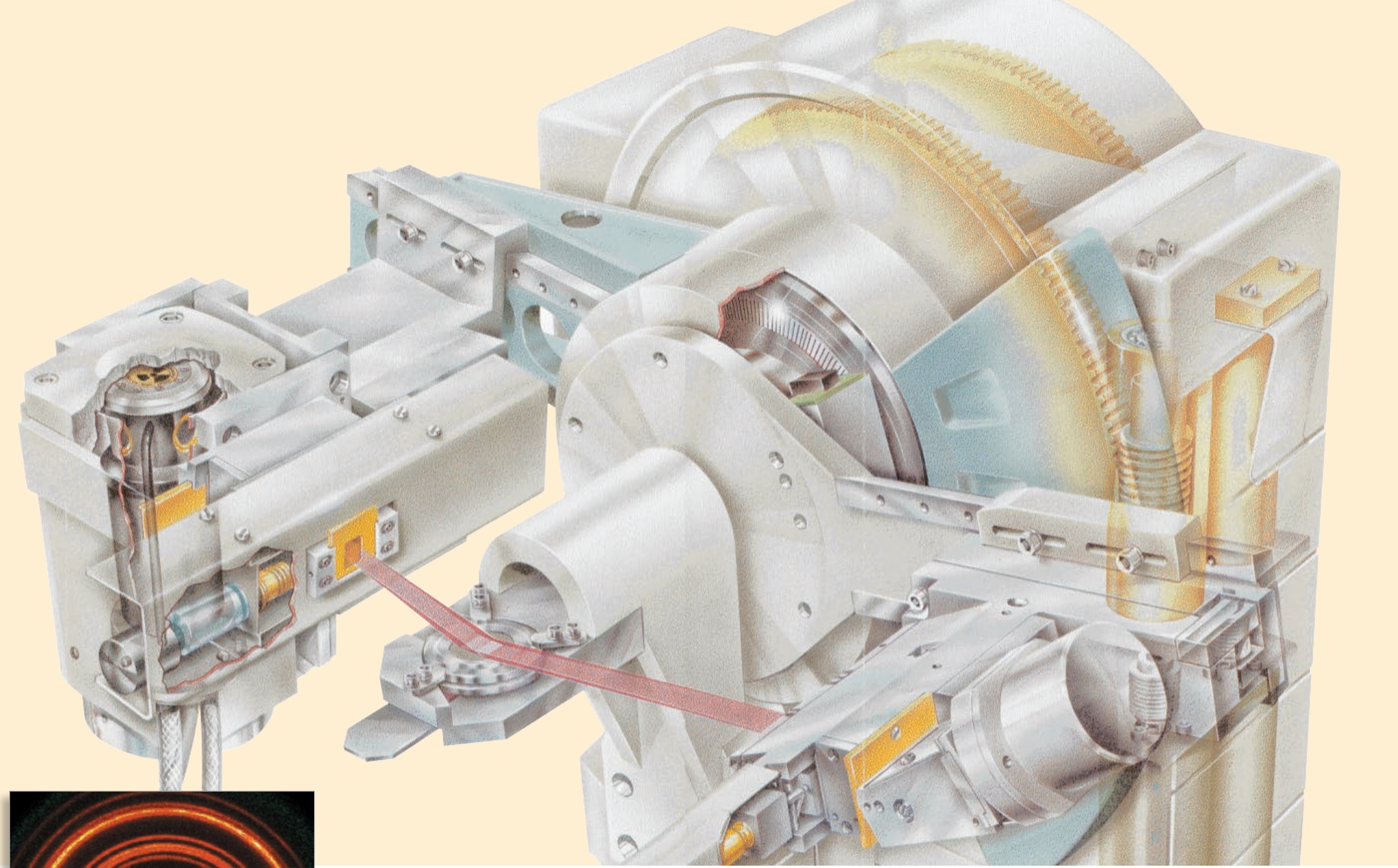

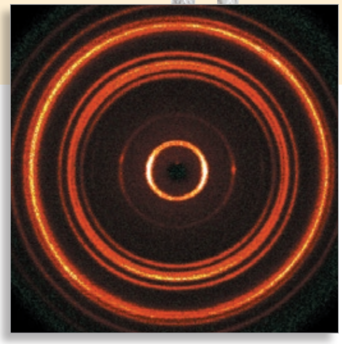

X-Ray Diffraction (XRD)

- phase identification
- texture or preferential orientation
- crystallite size
- residual stress
- in-situ temperature and pressure studies
- high resolution diffraction
- layer thickness measurements

X-rays are electromagnetic waves with a wavelength in the range of interatomic distances (0.1-10 Å). This match of length scales makes them suitable for the study of crystalline materials. For single-phase materials the crystal structure can be obtained directly using X-Ray diffraction (XRD). With the help of a database of known structures XRD can be used for phase identification. Also crystal size, strain and preferred orientation of polycrystalline materials can be measured. The related technique of X-ray reflection enables accurate determination of film thickness.

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Principles

When X-ray radiation is directed on a sample, the X-rays are scattered ("diffracted") by electrons present in the material. If the atoms in the material are arranged in a regular structure, i.e. if the material is crystalline, this scattering results in maxima and minima in the diffracted intensity. The signal maxima follow Bragg's law $n\lambda = 2d\sin\Theta$. Here n is an integer, λ is the X-ray wavelength, d is the distance between crystal lattice planes and Θ is the diffraction angle (see fig. 1). Thus, for each lattice spacing d, Bragg's law predicts a maximum at a characteristic diffraction angle Θ. During an X-ray diffraction (XRD) measurement the angles of incidence and detection are scanned. When the intensity of detected X-rays is plotted as a function of angle Θ an X-ray diffraction pattern is obtained, which is characteristic for the sample material.

The usual information depth of XRD measurements ranges from a few micrometers to a few hundred micrometers, depending on the density of the material.

By using a very small, fixed incidence angle of the X-rays (so-called grazing incidence measurement) also thin layers of only a few nanometers can be investigated.

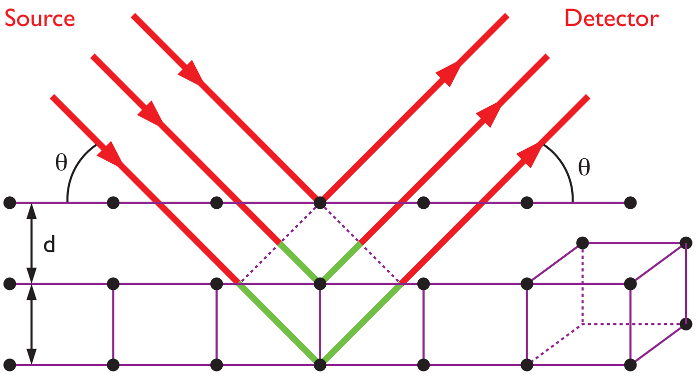


Fig. 1: Schematic representation of diffraction of X-rays in a crystalline material. Bragg's law is satisfied when the pathlength difference of the X-rays (indicated in green) is equal to $n\lambda$. The diffraction angle Θ is half the angle between the incident and diffracted X-rays.

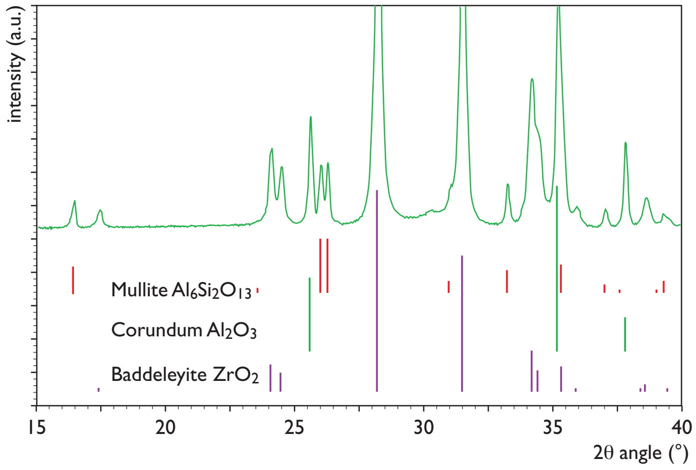


Fig. 2: XRD pattern of furnace material and reference patterns of identified components.

Techniques and applications

Phase Identification

In an X-ray diffraction pattern the position and intensity of the maxima are characteristic for the crystallographic structure and the atomic composition of the material. In case of a multi-phase composition, the resulting pattern is a combination of the patterns of all structures present. Phase identification can be done by matching the XRD pattern with reference patterns of pure substances.

Fig. 2 shows an example of an XRD pattern of a temperature-resistant material used in the construction of a high temperature furnace. In this particular case the reaction between the furnace wall and the furnace content has been studied. The XRD pattern (dark green) can be matched with a mixture of the crystallographic structures of mullite (red bars), corundum (green bars) and baddeleyite (purple bars). Each colored bar of a reference pattern corresponds to a characteristic interatomic spacing (d) of the crystallographic structure.

Quantitative information on single phase and multi-phase materials can be obtained using pattern calculation and pattern fitting methods (so-called Rietveld refinement). In combination with the use of standard materials this approach can supply accurate values for sample composition, crystal symmetry, unit-cell dimensions, atom positions, site-occupancy factors, etc.

Preferential Orientation, Texture

In powder samples the number of crystalline grains ("crystallites") is large. Their orientation is usually random. However, preferential orientation of the crystallites can occur. In such a case the sample is called "textured". Especially in thin films and rolled metal sheets, texture can be found. The presence of preferential orientation is already visible in a standard diffraction pattern. This is illustrated in fig. 3, where two diffraction patterns of crystalline MgO are shown. Although the MgO crystal structure is identical in both samples, the orientation distribution is different. This difference manifests itself in the relative intensities of the diffraction peaks. The pattern of an MgO powder (purple curve) represents a sample with randomly oriented crystals, whereas the pattern of the oriented thin MgO layer on a glass substrate (red curve) displays a textured polycrystalline layer.

The accurate description of the texture present can be determined by measuring diffraction in three dimensions. By rotating and tilting the sample with respect to the X-ray beam an orientation distribution of the crystallites can be calculated.

Crystallite size, micro-strain and residual stress determinations

XRD can also supply information about deformation of a crystalline sample. Deformation (also referred to as strain) of a crystal lattice will result in a change in the inter-atomic distances. The effect on a diffraction pattern depends on whether the deformation occurs on a local (microscopic) or on a global (macroscopic) scale. Microscopic deformation, i.e. local variation of the interatomic distances in a sample, is referred to as micro-strain. In this case, XRD analysis of an entire sample will display a range of deviations from the expected inter-atomic distances (d). This leads to peak broadening. The width of a diffraction peak is also influenced by the crystallite size: a large crystallite size causes sharp reflections, whereas a small size leads to broad reflections. Although size and strain both result in peak broadening, their effects can be separated since their angular dependence is different. The effect crystal size can have on an XRD pattern is shown in fig. 4.

Deformation on a macroscopic scale, i.e. more or less homogeneous in a sample, causes diffraction peak shifts. These shifts reflect the change in interatomic distances in the material. The deviation in the peak position can be translated into macroscopic strain and into a residual stress if mechanical material constants are known.

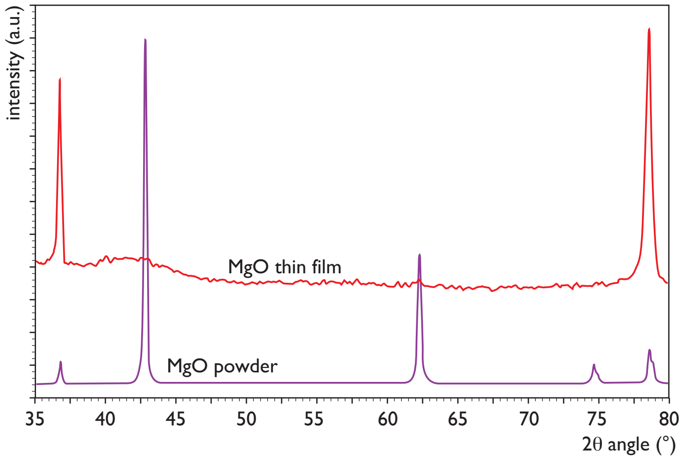


Fig. 3: XRD patterns of a thin MgO film with a preferential orientation and of randomly oriented polycrystalline MgO powder.

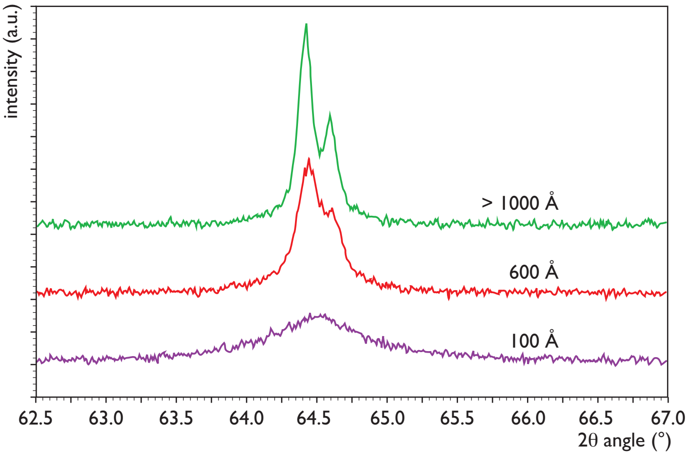
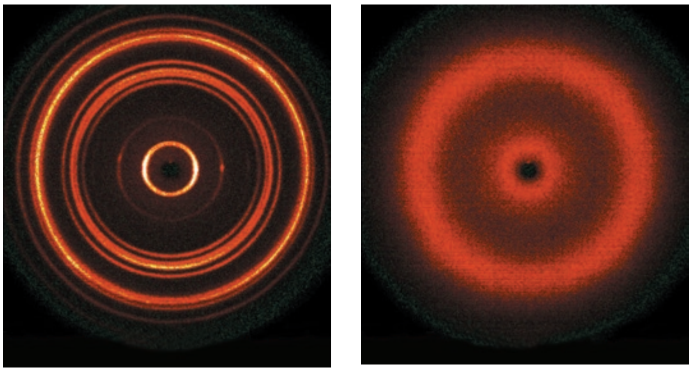


Fig. 4: XRD peak profiles of polycrystalline silver with different crystallite sizes.

Non-ambient and in-situ XRD

For XRD studies under non-ambient conditions (gas pressures up to 60 bar and/or temperatures up to 1600°C) a special vessel can be attached to an instrument. This allows the study of phase transformations induced by temperature, crystallization, and/or incorporation of interstitial atoms in a material, e.g. hydrogen absorption.
For qualitative analysis of materials with relatively large lattice spacings, e.g. polymers and liquid crystals, and for studying changes in such materials a special X-Ray detector and a sample heater are available. The two-dimensional nature of the detector permits the rapid collection of diffracted and scattered X-rays and provides this way the unique capability of directly imaging phase transformations and orientation changes in a diffraction pattern. An example is given in fig. 5, which shows 2-D patterns of a liquid crystalline material. In the pattern recorded at 200°C a broad diffuse ring can be seen, indicating that the material has no crystalline structure, i.e. it is a liquid. The pattern recorded at room temperature shows discrete rings, which means that the material is crystalline. The intensity differences that are visible along some of the rings indicate that the crystallites have certain preferred orientations.

Fig.5: 2-D diffraction images of a liquid crystalline material recorded at room temperature (left) and at 200°C (right).



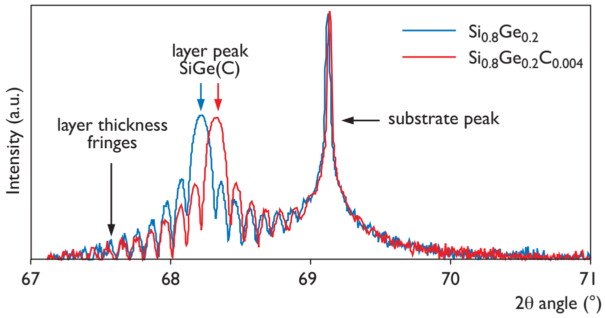


Fig. 6: High resolution measurement of $Si_{0.8}Ge_{0.2}$ and $Si_{0.8}Ge_{0.2}C_{0.004}$ layers on <001> Si-wafers.

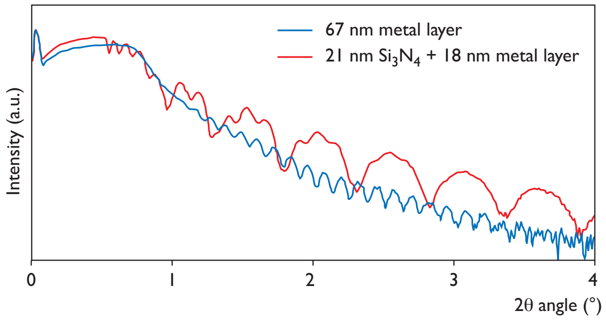


Fig. 7: Layer thickness determination of a single and double layer-stack.

High Resolution X-ray diffraction

Thin layers are often grown epitaxially on a crystalline substrate. Epitaxy implies a perfect match between the crystal lattices of the substrate and the crystalline layer that is grown on top of it. With an extremely well defined X-ray beam it is possible to measure minor changes in the degree of epitaxiality of the thin layer or the crystal quality. The thickness of thin layers and very small changes in crystal lattice dimensions resulting from differences in composition are also measurable.

As an example, in fig. 6 high-resolution diffraction patterns of a SiGe layer and a SiGeC layer on top of a silicon substrate are displayed. Si_xGe_y is a semiconductor material with superior electrical properties in comparison to pure silicon, but has the disadvantage of introducing strain and defects into the device. $Si_xGe_yC_z$ is used to reduce this lattice mismatch between the thin layer and the substrate without significant loss of electrical properties. In fig. 6 the broad peak of the thin SiGe layer (blue curve) appears at a different angle (inter-atomic spacing) than the sharp peak from the silicon substrate. The peak shift observed is caused by the larger Ge-atoms incorporated in the silicon lattice leading to a larger lattice parameter. Due to the addition of carbon a peak shift to a larger angle (smaller lattice parameter) is seen in the red curve. The smaller difference in lattice parameter between the substrate and the thin layer reduces the strain in the thin layer.

X-ray Reflectivity (XRR)

X-ray reflectivity measurements are used to determine the thickness of thin layers and layer-stacks (3 to 300 nm) on a flat and smooth substrate. In the case of a single thin layer, reflection occurs at the surface of the thin layer and at the interface with the substrate. Interference of these two reflections results in a characteristic wave pattern of the reflected intensity as a function of the angle of incidence. In the case of a multi-layer, the reflected intensity is the result of the addition of the wave pattern of each layer. In fig. 7 examples of such X-Ray reflectivity curves of a single and a double layer are shown. The absolute layer thickness is obtained from the difference in angular position of the visible fringes.

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Phone: +31 40 27 40455
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Characteristics

Sample type

- solid substance as bulk (e.g. powders) or thin film (on a substrate)

Sample size

- few mm² to several cm²; few mg for powders

Resolution

- spot dimensions typically 10*10 mm², penetration depth ranging from 2 μm (Au) to 120 μm (Al_2O_3)

Detection limit

- minority phases are detectable from approx. 1 wt% (phase identification), depending on the elements present
- XRR: Layer thickness 3-300 nm, roughness up to 3 nm

Advantages

- fast technique
- non-destructive
- small sample amount required
- in most cases no elaborate sample preparation necessary

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