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Crystallographic Services and Technology Support for Industry

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Abstract: The activities of CSEM's XRD Application Lab are oriented towards the analytical support of technology and product development in the fields of materials sciences, microtechnology, physics, chemistry, nanotechnology and life sciences. Non-destructive X-ray diffraction methods are used for the structural investigation of materials, components and systems. New developments are made with a focus on *in situ* techniques to 'watch the action' – structural transformations in dependence of applied external fields such as temperature, humidity, magnetic fields or mechanical stresses.

Keywords: *in situ* XRD · Nanoparticles · Strain · Thin films · X-ray diffraction

The XRD Application Lab

The X-ray laboratory was created in 2006 at the Institute of Microtechnology of the University of Neuchâtel and was shared between the University of Neuchâtel and CSEM. A joint effort was conducted to the creation of this new analytical platform, the XRD Application LAB, which has been growing constantly over the last years. Initially active in three-dimensional (3D) structure determination for new compounds synthetized by chemists of different Swiss universities, mainly in the framework of BENEFRI (cooperation between the universities of Bern, Neuchâtel and Fribourg), the activities have been extended to the study of structural phenomena in various types of materials related to the rapidly developing fields of physics, materials sciences, biology and microtechnology. Since 2008, the XRD Application Laboratory (Fig. 1) is part of CSEM's Microsystems Technology Division. The laboratory has been certified with a quality management system ISO 9001:2008.

The laboratory provides support in technology and product development inside CSEM and for industrial clients, which is one of the main missions of CSEM as a Research Technology Organization (RTO). Strong partnerships have been established to national research institutes such as Swiss Universities, ETHZ, EPFL, Swiss Federal Laboratories for Materials Science and Technology (EMPA) and the Paul Scherrer Institute (PSI). The contact with industrial clients is established through direct mandates and within national projects through Public-Private Partnerships (PPPs) supported by the Commission for Technology and Innovation (CTI) or the Competence Centre for Materials science and technology (CCMX).

Technology progress is strongly connected to the usage and parallel development of state-of-the-art analytical tools. In a product development phase, the analytical support for the structural evaluation is of key importance as this important feature is responsible for the product's macroscopic physical properties and hence, its performance and functioning. A fine-tuning of the structure with respect to the product application is performed based on process developments, adaptations and optimizations (Fig. 2).

In our laboratory, we have developed a number of *in situ* techniques where structural analyses are carried out under applications of external stresses such as mechanical loads, temperature variations, humidity or magnetic fields. This enables us to investigate materials and systems properties under load related to their future working conditions and to do aging analyses.

Applications of XRD for Industrial Purposes

Single Crystal Structure Determination

Single crystal structure determination is the most important technique to characterize new compounds. No other analytical technique currently available can provide such complete and unambiguous information of molecular structure. The types of atoms, the crystal packing and the molecule's absolute structure configuration can be determined providing information on intra- and inter-molecular contacts.[1–3] Crystal phase transitions are investigated in collaboration with the University of Neuchâtel.

X-ray Powder Diffraction (XRPD)

X-ray powder diffraction is a rapid analytical technique primarily used for phase identification of crystalline pure and mixed phase materials, giving accurate information on the unit cell dimensions. Phase identification and quantification as well as an average crystallite size and strain deter-

Fig. 1. The XRD Application Lab at CSEM in Neuchâtel.

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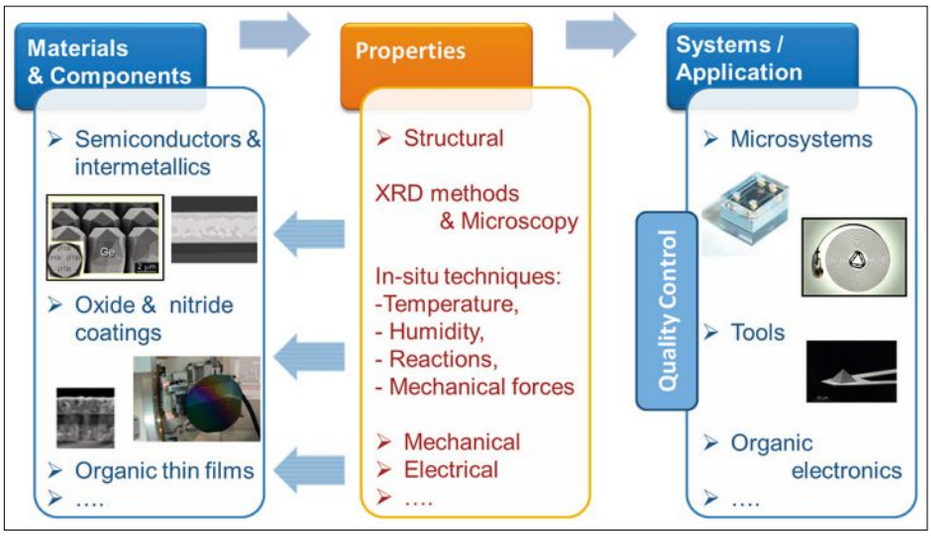

Fig. 2. Technology development support provided from our analytical platform.

mination can be performed.[4,5] *Ab initio* structure resolution for crystalline powders can be done; the resulting structural parameters are Rietveld refined. Within the last years, especially *small-angle X-ray scattering* (SAXS) has been extensively used and developed in our laboratory for different application areas. In the following, an example is given for the study of gold nanoparticles with potential applications in medical diagnostics.

Quality Control for Nanoparticles by SAXS

It is well known that all physical and chemical properties are size-dependent. The size on the nano-scale has significant outcome on the properties of materials, which have found their application in different fields, especially in nanotechnology. SAXS[6] is a technique where the elastic scattering of X-rays by a sample, which has inhomogeneities in the nm-range, is recorded at very low angles (typically 0.1–10°). This angular range contains information about the shape and size of objects, characteristic distances of partially ordered materials, pore sizes, and especially the object size distribution. In addition, the surface-to-volume ratio can be determined. The materials can be solid or liquid and they can contain solid, liquid or gaseous domains of the same or another material in any combination.

The clear advantage of SAXS compared to other techniques is the better statistical quality in the particle size distribution obtained by one single SAXS measurement, because an ensemble of particles contributes to the diffraction. SAXS is applied for nanoparticles (or pore) size distribution in a range from 1 to 100 nm in nanopowders, colloidal suspensions, porous materials and nanocomposites with almost no sample preparation.

In order to demonstrate the power of SAXS methods, we present the analyses made on commercially available Klebosol's suspensions of silica (SiO_2) nanoparticles of 25 nm (**1**), 50 nm (**2**) and 80 nm (**3**).[7] Each suspension contained nanoparticles of a different mean size, which were characterized by a well-defined spherical shape and a narrow size distribution. In Fig. 3 the measured scattering curves of three samples are shown.

As an example of the particle size distribution analysis, the sample (**2**) will be discussed below. The volume-weighted particle size distribution $D_v(R)$ of the sample is shown in Fig. 4. This graph indicates that the sample contained particles having a radius predominantly in the range of 210–330 Å, with a volume-average of 275 Å and a relative standard deviation (size poly-dispersity) of 11%. The average diameter for the sample (**1**) was found to be 28(2) nm, while for the sample (**3**) about 84(3) nm was obtained. The distributions and the mean sizes of the suspensions containing the SiO_2 nanoparticles are in good agreement with the information from the producer.

As a next step, a mixture of three Klebosol's suspensions was prepared in the ratio 2:1:1 (25 nm : 50 nm : 80 nm) of SiO_2 nanoparticles. This experiment was carried out in order to demonstrate the ability of the SAXS method to distinguish three different distributions of the nanoparticles at once. As it can be seen from Fig. 5, the tri-modal size distribution can be obtained from SAXS data analysis. The obtained values are clearly in agreement with those measured for each suspension separately. Moreover, the distribution for the different systems can be distinguished.

It has been successfully shown that the SAXS technique is a beneficial tool for evaluating not only simple size distribution of the spherical particles, but also the size distribution of complex particle mixtures. We believe that the studies provided

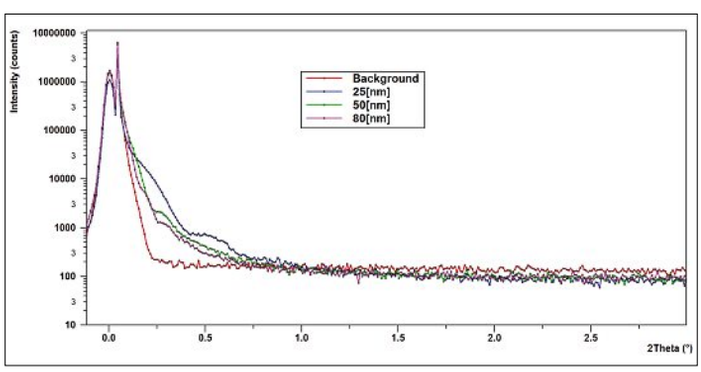

Fig. 3. Experimental scattering curves of the samples containing silica nanospheres with an average diameter of 25 nm (**1**) (blue), 50 nm (**2**) (green), 80 nm (**3**) (pink) and the corresponding background measurement of water (red).

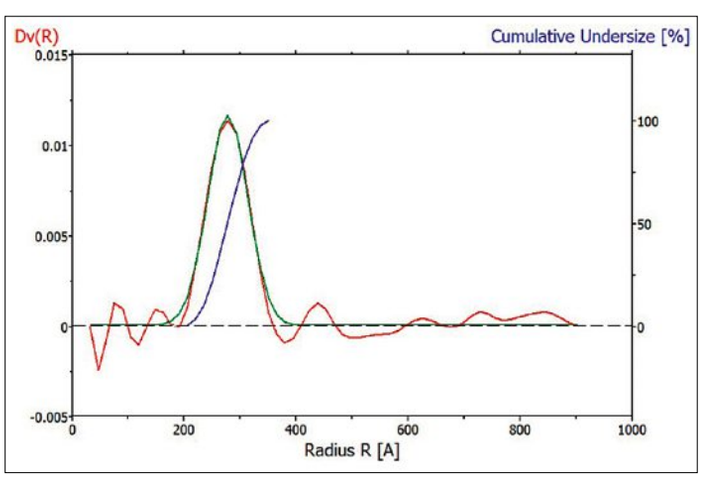

Fig. 4. The volume-weighted particle size distribution $D_v(R)$ curve (red) together with a Gaussian approximation (green) and with a cumulative undersize (blue) of the sample (**2**).

during this investigation can help industry to perform batch to batch reproducibility checks. Hence, a direct quality control can be offered on nanoparticle systems also on the industrial scale.

Wide-angle X-ray Diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) is often used to determine the phase composition of a thin film, coating or solid. The preferred crystallite orientation or texture of the thin film or bulk material, residual stresses and crystallite sizes can be determined. The great advantages of this technique are: the simplicity of sample preparation, the rapidity of measurement, and the ability to analyse mixed phases, and to do *in situ* structure determinations.

Our laboratory is active in technical and analytical support for the development of new coating together with the Swiss industry. One example is our collaboration with Oerlikon Balzers Coating AG for cathodic arc deposition of ternary oxides which can be used for a wide variety of applications, *e.g.* for thermal barriers, oxidation and chemical protective coatings, diffusion barriers, or for wear protection in tribological systems.[8–11] In order to achieve the required physical properties for such applications, the composition and the crystal structure of the deposited material are of primary importance. To control these parameters, it is necessary to understand the process related to the oxide synthesis. We are therefore active in analysing the phase transformation at the target (cathode) surface after the arc process and to correlate it with the phases obtained in the coating. One example is given in Fig. 6 for an Al-Hf composite target and the obtained respective coatings. 2θ scans with a 1° grazing incident angle are typically used to analyse the coating in order to avoid the signal from the substrate. Rietveld refinement on 2θ/ω scans is used to determine the phase composition of the cathode surface (Fig. 7).

WAXD *in situ* high temperature measurements up to 1300 °C (Fig. 8) are used to monitor in detail the oxidation process of the intermetallic in the layer and to probe the stability of the coating. An example is the transformation of Al-Cr intermetallics. It can be shown that solid solutions of $(Al_{1-x}Cr_x)_2O_3$ with corundum structure are formed and grow starting from 850 °C. The phase is stable up to 1300 °C, and thus acts as a thermal barrier.

High-resolution X-ray Diffraction (HRXRD) Analyses for Microsystems and Packages

Mechanical strains are at the source of varied failure modes of microsystems. In silicon-based micro-electromechani-

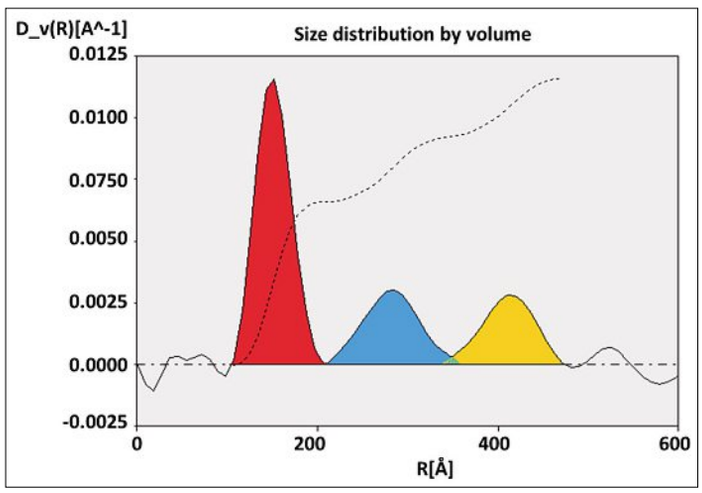

Fig. 5. Size distribution functions obtained by SAXS measurement of a mixture of 25 nm (red), 50 nm (blue) and 80 nm (yellow) nanoparticles, with a respective ratio of [2 : 1 : 1]. The coloured surfaces represent the areas of integration.

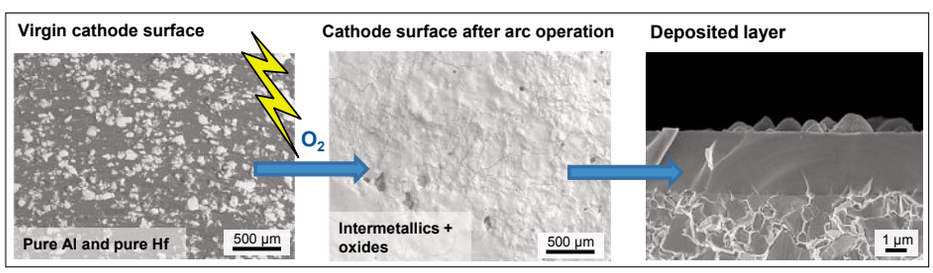

Fig. 6. SEM images of a composite Al-Hf cathode surface before (left) and after the arc operation (middle) and the associated deposited layer (right).

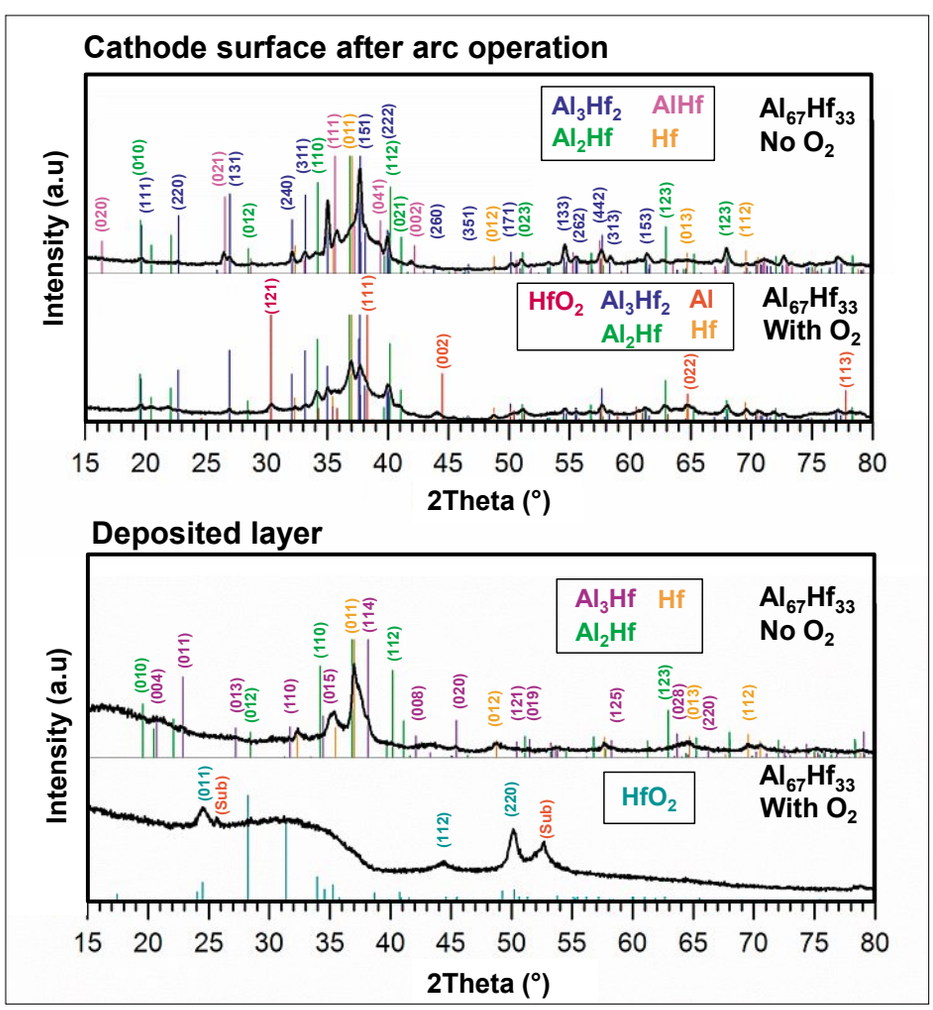

Fig. 7. WAXD phase analyses of an $Al_{67}Hf_{33}$ cathode surface after arc operation with and without oxygen atmosphere (top) and the associated deposited layers (bottom).

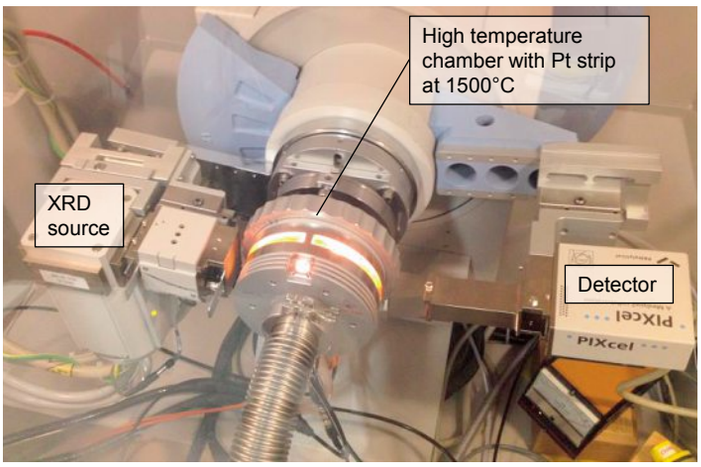

Fig. 8. XRD chamber heated up to 1500 °C (1300 °C at the layer).

cal systems the two main symptoms of ageing and failure related to mechanical strains are (instantaneous) fracture, (slow) drift and degradation of the device performance. These are induced by mechanical loads to which a system is exposed in operation or by residual strains built up during fabrication, packaging and assembly. Early detection of strains during fabrication and quality control of ready-for-use devices is crucial in guaranteeing the desired functionality. High-resolution X-ray diffraction (HRXRD) is an accurate, non-destructive experimental method to evaluate strains, defects and deformation of device parts and is therefore very well suited for quality control during the full device life-cycle.[12]

The method is based on precise mapping of the diffraction peaks in reciprocal space. The position, shape and background of the Bragg peaks contain information on the strain distribution, orientation and quality of the crystal. From Bragg's equation ($n\lambda = 2d\sin(\theta)$) it is apparent that the smallest detectable strain, *i.e.* the variation in the lattice parameter d, depends on the dispersion and divergence of the incident X-rays and the spatial resolution of the detector. By using beam-shaping elements such as X-ray mirrors and monochromators to enhance the quality of the incident beam and by applying a secondary monochromator in front of the detector the resolution in reciprocal space can be increased so that a strain sensitivity of 10^{-4} can be achieved routinely in laboratory X-ray instruments. Besides the excellent strain sensitivity HRXRD offers additional distinctive advantages for material and system investigations. As diffraction is only dependent on the spacing between atomic planes, single elements of the strain tensor can be assessed. The penetration depth of X-rays (on the order of 100 µm in semi-conductors) allows the investigation of sub-surface structures in a nondestructive way. The limits of the spatial resolution in HRXRD are influenced by the beam size and the X-ray penetration depth as the whole illuminated volume contributes to the diffracted intensity. Areas with different crystallographic properties can nevertheless be discerned because of the differing diffraction angles. Simulations of the strain distribution by Finite Element Methods (FEM) are used to compare the experimental diffraction patterns with system models, supporting the interpretation of the data.[13] For product and process development and quality control, laboratory X-ray instruments offer excellent conditions in accessibility, cost, speed and data quality.

In the following the use of X-ray diffraction measurements for quality control and process qualification in example processes used in microsystems technology are reviewed and discussed to illustrate the benefits HRXRD offers for industrial research and development activities.

Microelectromechanical Systems (MEMS) Packaging and Assembly

Miniaturization and densification of functional elements leads to a continuous reduction of the separations between structures, and thus stresses built up in one place can radiate and affect the surrounding. Encapsulation and especially wafer-level packaging (WLP) can provide protection from environmental hazards and gains in processing speed and cost due to parallelization. On the other hand, packaging-induced residual stresses can pose a serious threat to the long-term functioning of microsystems. In addition, the packaging can directly influence the functioning and performance of the system. Residual stresses by packaging are induced by mechanical pressure during bonding, by a mismatch of the coefficient of thermal expansion of adjoined materials or from shrinkage of (polymer) encapsulants. Rocking curve measurements have been made to evaluate strain gradients close to bonding interfaces and to correlate the degradation during accelerated aging tests with changes in the strain level of MEMS components.[14,15] The distortions induced by attaching MEMS on a printed circuit board (PCB) have been investigated.

We have investigated the wafer-level packaging stress in MEMS resonator devices.[15–17] The system was based on silicon-on-insulator (SOI) wafers where the active structure was etched into the device layer. SOI wafers consist of a thin (10–100 µm) device layer and a thick (~500 µm) handling wafer, *i.e.* two different monocrystals which are separated by a thin silicon oxide layer. They are not perfectly aligned and thus their diffraction peaks are offset in reciprocal space, so the handling wafer can be used as an internal reference. In Fig. 9, a comparison of the measured reciprocal space maps of the resonator MEMS prior to bonding (Fig. 9b) and after packaging (Fig. 9c) are shown. The diffraction of the device layer was split into two distinct peaks, corresponding to the interfaces to the buried oxide and to the devices surface to which the cap was bonded. Small changes were observed after packaging, showing that the applied packaging method establishes a bonding but influences the device only in a minor manner.

Epitaxial Growth of 'Incompatible' Materials

The epitaxial growth of germanium on silicon allows standard electronic devices to be created with the superior properties of germanium as high electron density and high electron mobility. However, due to the large mismatch of unit cell size and thermal expansion coefficient, the two materials are virtually 'incompatible' and internal stresses are relaxed by formation of defects already after the growth of only few monolayers. New approaches to grow defect-free germanium on silicon using a process which is compatible with standard complementary metal oxide semiconductor (CMOS) technology have been studied[18–20] and significant improvements of the crystal quality have been made by growing the germanium on micro-structured silicon. During the development of the process HRXRD was used to determine the stresses, distortions and defects in the germanium and the silicon with highest precision. The diffraction experiments confirmed that stress-free and low-defect germanium layers can be grown on silicon with high thicknesses of tens of micrometres (Fig. 10).

The high strain sensitivity of HRXRD in high-quality monocrystalline materials such as silicon, germanium and sapphire makes it a powerful tool for precise analysis of the stress distribution in microsystems. In complex structures the crystalline material can also be used as a strain gauge for interfacing materials and nearby structures. In addition, the diffuse scattering al-

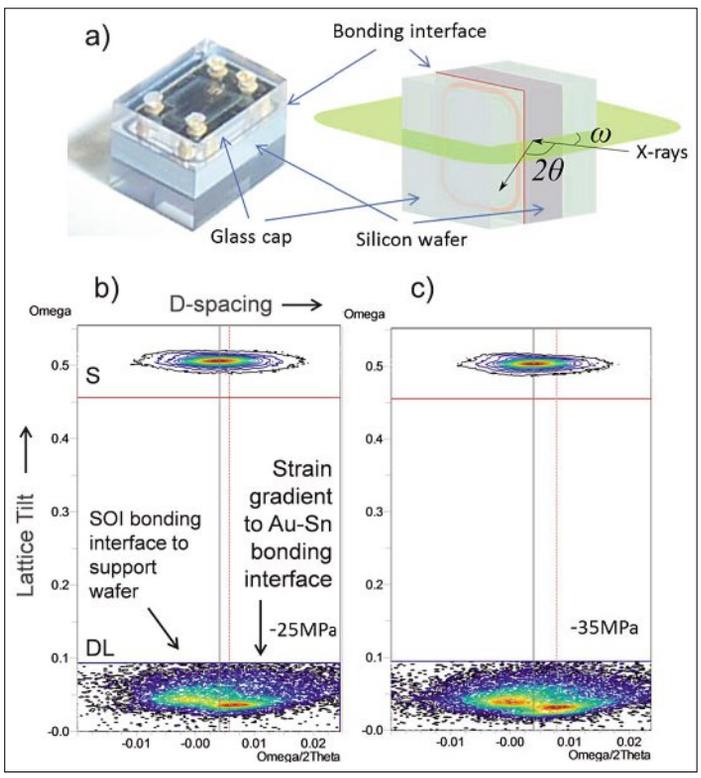

Fig. 9. HRXRD RSMs of the bonding interfaces of resonator MEMS (adapted from ref. [17]): a) encapsulated resonator with a schematic view of the HRXRD experiment. The scattering plane is highlighted in green. b) RSM of packaged resonator giving details on structural observations; c) RSM of an un-packaged resonator. ω and ω/2θ axes show degrees on a relative scale. The change in the stress level reflects the influence of bonding. The upper peaks (S) are the diffraction peak of the handling wafer and the peaks at lower ω values (DL) are the diffraction signal of the device layer.

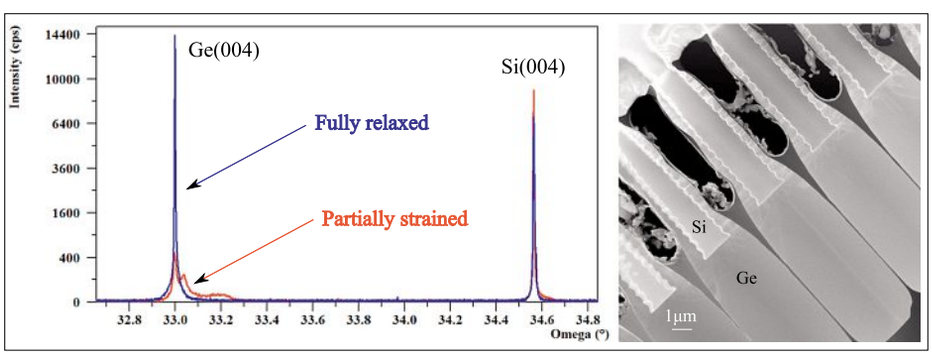

Fig. 10. High-resolution X-ray diffraction for 8 µm thick Ge layers on Si pillars (right). The red line shows a sample that is partially strained which results in the splitting of the Ge(004) diffraction peak. The blue line shows a fully relaxed germanium layer of the same thickness using an optimized process. Si pillars with Ge grown on top are shown in the left picture (STEM view of 8 µm Ge towers on Si pillars, adapted from ref. [20]).

lows the investigation of process-induced defects.

These examples illustrate that it is possible to access detailed information about the strain distribution, defects and distortions in MEMS materials, devices and packages by high-resolution X-ray diffraction techniques. By revealing such features, these methods support the quality control during the development, fabrication, packaging and testing of microsystems.

Conclusion

The CSEM's XRD Application Lab successfully answers the industrial demands on structural characterizations of a broad range of materials, components and systems for various applications. The parallel development of state-of-the-art analytical tools fosters technology progress directly for industry or by public private partnership (PPP) driven projects.

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