In Situ Elastic Strain Measurements— Diffraction and Spectroscopy

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Abstract

Understanding the mechanical properties of materials is crucial for their reliable application as bulk materials as well as in a miniaturized form. The deformation of materials is usually non-uniform and, hence, needs to be characterized on a local level. The following article focuses on the *in-situ* determination of mechanical stresses in crystalline materials during deformation. This can be achieved by both diffraction as well as spectroscopical methods, where the elastic strain is the parameter measured, which is subsequently converted into stresses by the application of Hooke's law. As *in situ* measurements require rapid data acquisition in conjunction with reasonable penetration depths, we will focus on x-rays. However, the different techniques described can be applied to any other diffraction probe as well. The description of diffraction techniques, which span the range from averaging techniques to 2D and 3D strain mapping, is complemented by a section on Raman spectroscopy as an alternative method for stress determination for non-metallic materials. Local stresses also can be correlated to local defect densities.

Introduction

X-ray diffraction is a common tool to determine order in materials. Based on Bragg's equation, the average distance between nearest neighbors of atoms or molecules can be determined. In crystalline materials, a high degree of ordering results in very sharp diffraction peaks. The sharpness of these peaks allows for a highly accurate determination of atomic spacing and, consequently, of elastic strains (deviations from the equilibrium lattice spacing) and the calculation of stress tensors. In addition, any deviation from perfect periodicity, which exhibits itself in the broadening and asymmetry of diffraction peaks, renders information on the imperfections in materials, namely their microstructure. These imperfections range from grain boundaries, stacking faults, implantation defects over interfaces, and dislocations to the degree of disorder in amorphous materials. This article will demonstrate how both aspects of x-ray diffraction can be combined with *in situ* tests to gain insight

into the mechanisms of mechanical behavior of materials. In addition, a complementary technique of Raman spectroscopy is addressed, where similar concepts apply. X-ray diffraction concepts, in principal, also apply to electron and neutron diffraction. The latter, however, are omitted here for the sake of brevity.

X-Ray Diffraction Basic Principles of X-Ray Diffraction

The basis for x-ray diffraction is Bragg's equation

$$n\lambda = 2d \sin\theta, \quad (1)$$

where d is the lattice spacing, θ is the diffraction angle in a classical diffraction setup, λ is the wavelength of x-rays, and n is the order of reflection. Differentiation of Bragg's equation yields

$$\Delta\theta = -\frac{\Delta d}{d} \tan\theta, \quad (2)$$

which shows that measurements at a higher diffraction angle (usually high-order diffraction lines) are more accurate. In defect-free polycrystals, grain size can be determined by using Scherrer's formula:

$$\Delta 2\theta^\circ = \frac{\lambda}{D \cos\theta} \frac{180}{\pi}, \quad (3)$$

where $\Delta 2\theta$ is the full width at half maximum of the diffraction peak (measured in degrees) in addition to the instrumental broadening, and D is the grain size. If dislocations are also present, the peak shape and its change with the order of reflection need to be taken into account. This is elegantly done by obtaining the Fourier coefficients of each peak in the classical Warren-Averbach analysis.¹ The latter technique, however, requires the possibility of measuring high-order peaks, which is not always possible in an *in situ* setup.

Non-Local Measurements

Due to the spot size of laboratory x-ray sources, which is usually much larger than the grain size in typical polycrystalline materials, the diffracted signal originates from a polycrystalline ensemble, and powder-like spectra are acquired. The difficulty in the determination of elastic strains is that the measured lattice distance needs to be related to the equilibrium lattice spacing. Accurate elastic strain measurements require the equilibrium lattice parameter to be determined experimentally. The usual pathway is explained in the following.

Sin²ψ Technique. The angle ψ is defined as the angle between the normal of the diffracting planes and the surface normal of the material investigated (see Figure 1). Surfaces are stress free in their normal direction, and the material underneath can be stressed in tension or compression. If the elastic strain is probed at different angles to the surface normal (different angles ψ), it has to go through zero at a specific angle. Consequently, the reference is incorporated in the measurement. For an equibiaxial stress state in an elastically isotropic material, stress and elastic strain can be derived from the following equation:

$$\frac{d_\psi - d_0}{d_0} = \frac{1+\nu}{E} \sigma_b \sin^2 \psi - \frac{2\nu}{E} \sigma_b, \quad (4)$$

where d_0 is the unstrained spacing of a selected plane, d_ψ is the actual spacing of a plane oriented at an angle ψ relative to the surface normal, ν is Poisson's ratio, and σ_b is the equibiaxial stress. The angle for zero strain, consequently, depends on the elastic properties of the material investigated.

Figure 1. Comparison of diffraction geometries of (a) the $\sin^2\psi$ technique: any x-ray energy can be used, and the sample needs to be tilted so that two sets of (111) planes with respect to the surface normal (ψ angle) can be used; and (b) the $\sin^2\phi$ technique: no tilt is required, and the x-ray energy needs to be tuned. A diffraction ring is monitored on an area detector, where its diameter is measured along an angle ϕ around the ring. The (111) reflection is chosen for fcc metal thin films as the x-ray intensity needs to be maximized. For higher accuracy in strain measurements, higher order peaks are usually advisable because they result in larger 2θ angles, which, in turn, results in increased strain resolution. L is the detector (charge coupled device) distance.

Noyan and Cohen² address more complex stress states and elastically anisotropic materials.

Several examples of *in situ* measurements can be found in References 3–5, where the first two show texture-resolved stress-strain curves of Cu thin films on polyimide, and the latter discusses the mechanical properties of nanocrystalline aluminum. However, the measurement time required is significant. This can be overcome by using synchrotron sources and/or using the following technique.

$\sin^2\phi$ Technique. The $\sin^2\phi$ technique, as described by Wanner and Dunand,⁶ is a relative technique and thus requires the determination of the residual stress state at the beginning of the experiment. This can be accomplished by the $\sin^2\psi$ technique. It is based on measuring the diameter of Debye-Scherrer rings by an area detector or two crossed linear detectors. If a strain is applied in the sample plane, the Debye-Scherrer rings are distorted into ellipses, whose ellipticity can be used to quantify the elastic strain. No change in diffraction geometry is required during an *in situ* experiment. If a textured material is investigated, the x-ray source needs to be tunable, and thus experiments are limited to synchrotron sources.⁷ Details of the

geometry can be found in Figure 1. On the top, the classical $\sin^2\psi$ technique is shown for two sets of (111) planes, which requires sample and detector movement, and on the bottom, the $\sin^2\phi$ technique with the tuning of the x-ray wavelength to the texture is indicated. For the latter technique, no sample rotation is required.

Recently, this method has been applied extensively to the investigation of scaling in the yield strength of thin films^{8,9} and arrays of metal nanowires.¹⁰ Stress-strain curves of metallic structures with feature sizes down to 20 nm could be investigated, shedding new light on the material deformation mechanisms: Nanocrystalline gold nano-interconnects exhibit lower yield strength in tension compared to a bending mode, they show temperature and strain-rate dependence at room temperature, and they are more ductile at lower temperatures (i.e., 120 K) than at room temperature. The first point can be explained by strain gradient plasticity, the second by a combination of surface and grain-boundary diffusion caused by the extremely short diffusion distances, and the last by predominant dislocation glide at low temperature. Strain-rate experiments by x-ray diffraction can only be achieved by short measurement times (e.g., 5 s per strain step) offered by the $\sin^2\phi$ technique.

An interesting example of the application of several *in situ* techniques—namely the $\sin^2\phi$ technique, scanning electron microscopy, and optical microscopy—can be seen in Figure 2. Here, the fracture and delamination behavior of thin brittle metal films (i.e., Ta) are investigated.¹¹ The onset of cracking can be determined as a stress drop in the stress-strain curve in the tensile direction (x direction), a change in slope in the stress-strain curve in the transverse direction (y direction), and the direct observation of first cracks. Cracking results in the buildup of compressive stress in the normal direction due to the relaxation of tensile stresses and consequently reduced Poisson contraction compared to the substrate. This, in turn, leads to thin-film delamination until finally most of the strain is carried by the substrate. Such experiments are used to determine both the fracture toughness of the thin films and the energy release rate of interfacial cracks. Further insights into the deformation mechanisms can be gained by focusing x-rays and resolving elastic strains at a more local scale.

Local Stress Measurements in 2D

Monochromatic Microdiffraction. When mapping local stresses at medium spatial resolution (a few tens of micrometers), monochromatic synchrotron x-rays can simply be restricted by slits to produce 2D maps of stress in transmission mode.¹² This is comparable to the $\sin^2\phi$ technique, but allows for the mapping of elastic strain states. Furthermore, this kind of diffraction experiment can be efficiently combined with 3D tomographic imaging (see also the section on Digital Volume Correlation in this article) to investigate the stress redistribution induced by the development of damage in a material under various experimental environments (applied load, temperature cycles). Such *in situ* experiments have been performed on Ti/SiC_f metal matrix composites, where the subscript *f* indicates that the Ti/SiC reinforcement phase is in fiber form.^{13,14} For this material, by combining 3D images of cracks in the SiC fibers and the diffraction profile recorded along the same fibers and in the neighboring matrix, it was possible to show the effect of elastic strain partitioning from the fibers to the matrix. It was also possible to evaluate the interfacial shear strength along the fibers, a key parameter for the modeling of the mechanical behavior of this kind of high-performance material.

When higher spatial resolution is needed, monochromatic x-rays can most easily be focused by Fresnel zone plates or refractive x-ray optics, the latter being less efficient at higher x-ray energies. In most cases, the x-ray beam then becomes smaller than

Figure 2. Fracture and delamination behavior of 100-nm-thin Ta films on a 125- μm -thick polyimide substrate investigated by x-ray diffraction (XRD) (without residual stress), optical microscopy, and atomic force microscopy. The different phases of deformation are the elastic regime (I), the onset of cracking (II), the steady-state cracking regime (III), the onset of delamination (IV), and the regime of predominant substrate deformation (V).

the grain size. Consequently, single-crystal diffraction has to be applied, and sample tilting is required. Measurements at a length scale of around one micrometer and less, however, are problematic due to the limited mechanical accuracy of currently available diffractometers. Consequently, successful *in situ* work has been limited to highly textured polycrystalline materials^{15–17} for monitoring the stress and composition evolution during electromigration, single crystals by microdiffraction topography¹⁸ for indirect measurement of stress in patterned thin films, and small-angle x-ray diffraction¹⁹ for monitoring the structure evolution in spider silk fabrication. All these experiments can be performed without sample tilt during the *in situ* experiment.

Laue Microdiffraction. Laue microdiffraction²⁰ solves the “tilt” problem described in the preceding section on Monochromatic

Microdiffraction for a randomly oriented polycrystalline specimen. In this technique, a white or pink x-ray beam—a small portion of the x-ray spectrum—is focused by achromatic Kirkpatrick-Baez mirrors to a spot size as small as 500 nm in diameter, which, in turn, renders this technique applicable to grain sizes of a minimal 200 nm. Sophisticated analysis of Laue patterns allows for the simultaneous detection of more than five patterns (grains) in a single Laue image. The locally single crystalline sample now acts as an analyzer for the polychromatic beam, resulting in a typical Laue pattern, where, in contrast to standard diffraction techniques, the wavelength rather than the diffraction angle is altered. A combination of well-calibrated area detectors and a reference pattern allows for the determination of the complete deviatoric strain tensor with a resolution of 10^{-4} .²¹ The lattice parameter, in principle, can be

determined by using a monochromator and scanning the wavelength or by analyzing the wavelength of the diffracted beam. The first approach is more accurate but has not yet reached the accuracy levels of the deviatoric strain determination. In addition to elastic strain, phases and defect densities also can be determined. Peak broadening in this technique is a direct measure of geometrically necessary dislocations or small-angle grain boundaries,²² similar to but more accurate than electron backscatter diffraction. Classical peak broadening would be reflected by a broadening in energy space.

Pioneered by the Advanced Photon Source at Argonne National Laboratory, several Laue microdiffraction beamlines have been set up worldwide (e.g., at the Advanced Light Source at Lawrence Berkeley Labs, the European Synchrotron Radiation Facility, the Swiss Light Source, and the Canadian Light Source). Broad beam *in situ* Laue diffraction has been demonstrated at the Karlsruhe synchrotron (ANKA).²³ Most *in situ* experiments have been carried out at the Advanced Light Source, as the first dedicated beamline was built there. Two examples will be described in the following.

The easiest way of performing a mechanical *in situ* experiment involving thin films is depositing them on a substrate with a significantly different coefficient of thermal expansion. Stresses then can be induced by thermal cycling of the sample. Laue microdiffraction in such experiments revealed strong variations of stress from grain to grain (ca. 100 MPa) and significant stress gradients within a grain.²⁴ Recently, a novel mechanism for grain rotation, namely a combination of dislocation and disclination (an array of edge dislocations of equal sign) motion, has been elucidated.²⁵ As this mechanism only requires the rearrangement of defects in a grain boundary rather than long-range diffusion, it can act at significantly lower temperatures than conventional grain-boundary sliding mechanisms.

The directional transport of mass due to an electric current (electromigration) poses a reliability concern for microelectronic devices. *In situ* Laue microdiffraction was able to show that hillocks at the anode end of conductor lines are formed by dislocation climb.^{26–28}

3D Stress Measurements

Laue Microdiffraction. The concept of Laue microdiffraction can be extended from 2D to 3D by selective absorption of the diffracted beams. This can be achieved by scanning a highly absorbing wire (knife edge) over the sample surface in a 45° diffraction geometry.²⁹ This technique was used to study the deformation of copper

underneath a nanoindent;³⁰ however, the timescale for measurement is prohibitively long to allow for *in situ* observations. Defect structures were found to be aligned with the most easily activated glide systems.

3D Diffraction Microscopy. 3D elastic strain measurement techniques based on monochromatic x-ray beams can be subdivided into macroscopic (multigrain average) and microscopic (individual grain) approaches, similar to the 2D approaches.

In the first case, the sampled 3D volume element contains a large number of grains, giving rise to diffraction in well-defined directions described by cones. The analysis of the position and intensity distribution on the ring-like diffraction patterns observed on a 2D detector for several sample orientations gives access to components of the elastic strain state in the illuminated volume element. The localization of the diffracting volume element in three dimensions can be achieved by insertion of pinholes and/or beam-defining slits (e.g., conical slits for simultaneous observation of entire diffraction cones).

In the second case, only a limited number of grains are contained in the illuminated sample volume. One may now observe and analyze the position of individual diffraction spots on the detector. The latter methodology is termed 3D x-ray diffraction microscopy (3DXRD) and has been reviewed by Poulsen.³¹ Note that in this condition, the sample needs to be rotated over an extended angular range in order to record several reflections from each of the grains. With a suited combination of detector resolution and distance, the position, size, average orientation, and the full elastic strain tensor for each of the grains can be determined from such a set of diffraction images.³² The timescale for this kind of grain-resolved strain measurement is on the order of a few minutes using synchrotron radiation.

Placing an additional high-resolution detector system close behind the sample, one can analyze the 2D intensity distribution inside the diffraction spots. The intensity distribution in the diffraction spots can be assimilated as 2D projections of the grain volumes, and the use of tomographic or stochastic reconstruction approaches permit the reconstruction of 3D grain shapes (see Reference 31).

The use of advanced data analysis routines permits extraction of local lattice orientation *inside* individual grains and has been demonstrated recently for line beam illumination mode.³³ It can be speculated that further refinement of the methodology will eventually give access to the local deformation tensor (orientation and elastic

strain) at the subgrain level. The timescale for this kind of measurement depends on the dimensions of the sampled volume and varies from a few minutes to several hours for scanning a 2D section and a 3D sample volume, respectively.

3D Digital Volume Correlation and 3D Particle Tracking Techniques.

The presence of elastic strain in a material can be detected by measuring variations of the lattice parameter, as explained in the x-ray diffraction section of this article. The total strain (elastic plus plastic), on the other hand, can also be assessed, in principle, by measuring the displacement of elements of the microstructure between a reference and a deformed volume. Two different methods, called particle tracking (PT) and digital volume correlation (DVC), can be used. While the first one evaluates the displacements of microstructural features through the movement of their centers of mass, the second one uses correlation techniques to match the two volumes. Although the development of digital image correlation dates back to the 1980s,³⁴ its application to 3D tomographic images is more recent (see Reference 35). Both PT and DVC require the presence of markers within the images. Two different strategies have been employed so far: artificially introducing the markers in the studied material^{36,37} and directly using the material's microstructure.^{35,38–41} The first method, in principle, can be applied to a variety of materials, provided a suitable technique for homogeneously distributing the markers is found. However, the question of how much the presence of markers might affect the deformation process remains an issue. From that point of view, natural markers appear more attractive, but the number of materials presenting a relevant microstructure is restricted. So far, the deformation of quite different materials having natural markers (e.g., Al alloys, cast iron, trabecular bone, polystyrene foam, stone wool, and wood) has been studied. All these materials' microstructures exhibit features (nodules, intermetallic particles, fibers) that can be used as markers.

Both PT and DVC provide displacements at a subvoxel scale. In the case of DVC, the displacement uncertainty appears to be higher than that reported for 2D images,³⁵ probably because of the noise introduced in the images during the reconstruction process. This is likely to also be the case for PT, but to the authors' knowledge, a comparison between 2D and 3D accuracy has not been reported so far for PT. Values of uncertainties ranging from 10^{-1} to 10^{-2} voxels have been reported, depending on the material and the method used.³⁵ In the case of DVC, the level of uncertainty can be

reduced by using larger elements for correlation. However, this is done at the expense of the spatial accuracy of the measurement. If very short-range variations of the displacement field are to be captured, then a lower element size should be used, resulting in a higher uncertainty (and vice versa). For PT, the accuracy with which the displacement field is captured is dictated by the typical distance between markers.

One important application of kinematic measurements in the bulk of a material is the evaluation of the displacement field at the tip of a crack. This technique then gives a direct evaluation of the crack driving force via the extraction of the mixed mode stress intensity factor as explained, for example, by Rannou et al.⁴² This has been done in Al alloys using the tracking technique⁴⁰ and also in cast iron by using DVC.³⁵ Figure 3 shows an example of the results that can be obtained with DVC regarding the quantification of a 3D opening of a fatigue crack under load. It is important to note that the crack in Figure 3 does not immediately open as soon as a tensile load is applied but requires a threshold value. This phenomenon is called the crack closure effect; thanks to DVC, it can be measured *in situ* in 3D with a micrometer spatial resolution in an opaque material.³⁵

Merging the Concepts of Diffraction and Imaging.

For some classes of polycrystalline materials, the concepts of 3DXRD microscopy and tomographic imaging can be merged. The combined methodology, termed x-ray diffraction contrast tomography (DCT), provides simultaneous access to the 3D distribution of the x-ray attenuation coefficient as well as to the grain microstructure described in terms of shape, orientation, and elastic strain tensors for each grain.⁴³ Similar to the outlined 3DXRD methodology, the 3D reconstruction of grain shapes is achieved via analysis of the *shape* of the diffraction spots, observed on a high-resolution x-ray imaging detector positioned a few millimeters downstream from the sample. The DVC technique and associated analysis (see preceding section) can be applied to the 3D volume data provided by DCT. This opens interesting new possibilities to examine deformation processes in certain classes of polycrystalline materials, exhibiting microstructures amenable to DVC inspection.

Raman Spectroscopy Basic Principles

Figure 4a shows the experimental setup of a typical micro-Raman instrument.^{44,45} Light from the laser is focused onto a sample of interest, such as a micropillar

Figure 3. 2D map of the opening of a crack (mode I opening) in the interior of a cast iron sample obtained by digital volume correlation of tomographic images. The load is applied along the x axis (normal to the figure). The white line indicates the crack front (cracked surface above the line). For an applied load of 44 N, large black areas behind the crack tip (i.e., above the white line on the figure) indicate crack closure. When the load is increased, the crack gradually opens. Adapted from Reference 35.

Figure 4. (a) Principle of Raman spectroscopy: the laser is focused on the sample for excitation (diffraction-limited spot $\sim 1 \mu\text{m}$), then the scattered light is collected through the same objective and dispersed into a spectrum by the spectrometer. (b) *In situ* micro-Raman for dynamic stress sensing: spectra are collected simultaneously during compression. (c) Tip-enhanced Raman spectroscopy for nanoscale residual stress analysis: the metal tip localizes the excitation beyond the diffraction limit.

under load, using microscope objectives and sample micropositioners. The scattered light is collected and directed into a premonochromator and a Raman spectrometer for detection by a charge coupled device system. If a 100 $\times$ objective (numerical aperture of 0.9) is used, a probing spot with a diameter of 300–500 nm can be obtained, depending on the optical system and on the wavelength of light. A further reduction of spot size can conventionally only be achieved by the use of wavelengths in the UV range or the application of oil immersion objectives. The probe depth ranges from a few nm to mm, depending on the optical properties of the materials, and can be limited to the submicron range via a confocal setup.

Raman scattering arises from an inelastic interaction between photons (light of the incident laser) and phonons (vibrations of the crystal lattice). Spectral analysis of the scattered light reveals distinct peaks that are related to particular optical phonon modes (zone center optical phonons [i.e., wave vector $k = 0$ selection rule]) in the crystal, providing a unique fingerprint of the probed material. Spectra from amorphous materials exhibit broad bands that can be rationalized by considering all possible phonon modes in a crystal ($k = 0$ selection rule relaxed). Raman-active materials (i.e., materials that give rise to Raman scattering), in this sense, are many semiconductor and ceramic materials. Pure metals do not exhibit Raman scattering because of the presence of free electrons screening the interaction between light and nuclei and because many have no optical-branch zero wave vector vibrational modes. Raman-active samples also include many types of molecules, nanotubes, and polymers due to molecular vibrations, where different selection rules apply.⁴⁶ The difference between the frequency of the scattered and the incident light is called the Raman shift, expressed in wave numbers (cm^{-1}). The number of Raman peaks that can be observed depends on the crystal symmetry, the polarization directions of the incident and detected light, and the propagation directions of the incident and detected beams with respect to the crystal axes. For instance, silicon in the stable phase at ambient conditions (i.e., the diamond cubic structure) exhibits a single peak around 520 cm^{-1} (one-phonon mode) and additional weak two-phonon mode peaks. During an unloading from high hydrostatic pressure—for instance during unloading of a nanoindentation experiment—a sequence of other crystal structures and amorphous silicon can form below the contact area, each exhibiting a characteristic number of peaks at different wave numbers.⁴⁶

The finite size of crystalline grains in the nanometer range significantly alters the Raman spectrum; selection rules derived from the assumption of infinite crystals relax, leading to an asymmetric peak broadening in most cases, as phonons with lower or higher frequencies participate in the scattering process. Crystal defects, such as dislocations formed during plastic deformation, generate microstrains, resulting in a symmetric peak broadening.

Elastic strain changes the frequency of lattice vibrations and, therefore, will shift the Raman peaks. Peak shifts vary linearly with stress components, and the related coefficients are well documented for many materials.⁴⁷ Some prior knowledge of the stress distribution, however, is required, since in many cases the stress tensor leads to shifts and shape changes of a single peak only. In many cases, simple uniaxial or biaxial stress states are studied.

If Raman spectroscopy is combined with a micromechanical testing setup, phase transformations or changes in the microstructure, such as an increase of dislocation density during loading, would alter the spectrum or peak shapes, respectively. The stress field can be probed with 1 μm resolution through monitoring the peak positions. When the nature of the stress state is known through the loading conditions, the observed peak shifts can be converted easily into local stress values (i.e., the Raman spectrum serves as a microscopic elastic strain gauge on the sample). A small change in wave number of $\sim 0.02\text{ cm}^{-1}$ can be detected using state-of-the-art equipment, which translates to a stress resolution of roughly 10 MPa for most materials. An example of uniaxial loading—an *in situ* microcompression experiment—is shown schematically in Figure 4b.⁴⁸ Elastic and plastic deformation as well as fracture events can be analyzed. During the uniaxial compression of silicon (001) oriented pillars, good agreement between the stress measured by the micro-indenter load cell and the stress deduced by the Raman peak shift in the elastic region was found. Small shoulders at lower peak frequencies are evidence of crack propagation and corresponding stress relaxation prior to brittle fracture of the silicon pillars. *In situ* Raman microcompression experiments on (001) GaAs pillars of similar size demonstrated the capability of this technique in determining the onset of plastic deformation. While the Raman peak undergoes monotonically positive shifts linearly proportional to the increase in elastic strain, the onset of plasticity and the corresponding load drop is seen as a sudden negative shift. During plastic deformation, the peak broadens

due to increased dislocation density and inhomogeneous plastic deformation localized with well-defined glide bands emanating from the contact edge between flat punch and micropillar.

Resolution Beyond the Diffraction Limit

Elastic strain is very important in the semiconductor industry because it can boost the speed and reduces the power consumption of electronic devices. Focusing the exciting laser on the sample surface gives, at best, probing spots on the order of $\sim 1\text{ }\mu\text{m}$. Developments in near-field Raman spectroscopy have produced novel measurement techniques that allow nanoscale lateral resolution. One approach is to guide laser light onto a tip with a very small aperture of diameter 50–200 nm. The tip is held at a distance of $\sim 10\text{ nm}$ above the sample in near-field scanning optical microscopy (NSOM). NSOM has been used to analyze elastic strain in crystalline samples.⁴⁹ The spatial resolution is restricted to $\sim 150\text{ nm}$ due to significant power losses in small apertures. An alternative approach to circumvent the optical diffraction barrier was proposed by Wessel⁵⁰ based on a discovery by Fleischmann.⁵¹ The Raman scattering cross-section is enhanced by many orders of magnitude by placing a metal in contact with the sample surface.⁵² This so-called surface-enhanced Raman scattering effect is mainly due to an electromagnetic field-enhancement occurring near surface irregularities through the excitation of localized surface plasmons by light.^{53,54} By replacing the metal grains with a metallic nanometer-sized tip (see Figure 4c), the enhancement can be localized.^{55–57} Provided that the scattering comes predominantly from the contact area, a resolution of several tens of nanometers can be achieved. The resulting tip-enhanced Raman spectroscopy (TERS) seems therefore to be capable of measuring Raman spectra with high spatial resolution, effectively overcoming the diffraction limit. A successful TERS experiment depends heavily on the ability to fabricate metallic tips with the appropriate shape and size, which is still a challenging process.^{58–60} An ultimate goal for the future would be to integrate the TERS experiment (i.e., nanoscale mapping capabilities) into an *in situ* micromechanical testing setup like a tensile or compression test on a microscopic sample.

Stress and Microstructure

An addition to the determination of stress during an *in situ* experiment is also the monitoring of microstructural changes. The peak width returned to its original value after deformation and subsequent unloading for

nanocrystalline Al below a grain size of 80 nm, indicating the absence of dislocation storage mechanisms.⁵ Maass et al.^{61,62} were able to correlate the peak broadening and peak shift in *in situ* Laue microdiffraction compression experiments to the glide systems present. In Laue microdiffraction, peak broadening is not indicative of a reduced periodicity as caused by a reduction in grain size or an increase in dislocation density, but of the rotation of grains by an excess of dislocations of one sign. These rotations are directly linked to the active glide systems. Consequently, in the metal pillar compression, the mechanical behavior of small volumes is mostly determined by the microstructure rather than the absolute value of pillar diameter.

Complementary application of transmission electron microscopy and micro-Raman spectroscopy on the same sample area allows for direct imaging of the residual stress field of lattice defects, such as dislocations and disclinations,⁵⁴ and of crystal structures formed due to phase transformations during a nanoindentation experiment.^{63,64} TEM alone would only allow for the visualization of defect structures. The stress fields will have been changed by sample fabrication. Raman microscopy allows for the direct imaging of the residual stress field without sample modification.

Future Directions

Future challenges of *in situ* elastic strain measurements will involve

- Improved spatial resolution: Focusing of probes down to the 10 nm length scale (e.g., by zone plates) will also pose challenges for spatial stability, as measurement time will increase.
- Quantification of defect structures: Direct correlation between atomistic modeling and complementary experimental techniques is required to quantify the character and magnitude of defects and their changes during deformation.
- Reduction in measurement time for dynamical experiments: Here a compromise will have to be found between timescale and spatial resolution.
- Solving space constraints of *in situ* experimental setups: A quantitative analysis of defect structures requires large scattering angles or sample tilts. This would require a miniaturized design of *in situ* test equipment.
- The interpretation of coherency effects in small-scale diffraction (see Reference 65).

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