In situ and *Operando*

2

Chapter Preview

This topic is a very broad one since it involves everything that has been covered in W&C and then allows the specimen to change while you image it, record the spectra, and/or measure what changes are taking place. We are combining two topics that could be treated separately, namely in-situ experimentation and controlled-environment TEM (which we'll call an ETEM, but you'll also see E-TEM or eTEM). The reason for combining the two is that changes in the environment about the sample can change the material as we examine it in the TEM. With TEM, it's always an in-situ study! We're also including *operando* with *in situ*; *operando* implies that the material is behaving as it would do in "real life"; the translation is "working." For example, if a catalyst particle is actually acting as a catalyst when we observe it, it's an *operando* study; in general such a particle can't act as a catalyst unless there is something to catalyze! You are often measuring something (there is a metric) that relates to the performance of the materials – so that you know it's performing!

In the traditional TEM, the environment is always very reducing – traditionally we use the highest vacuum we can; historically we deposit a layer of carbon on the sample too (whether we wanted to or not). The reason for the clean vacuum is to prevent contamination of the sample and to avoid gases streaming up the column and degrading the vacuum of the electron gun or depositing on the window of the XEDS detector. Now we have two ways of changing the environment: we can use special holders, or we can actually modify the column around the specimen using extra apertures and differential pumping.

The field of in-situ TEM is changing rapidly for two reasons: nanotechnology is being used to build better, more flexible holders, and we have better, faster ways of collecting and recording the information from the changing specimen. Of course, the TEMs are also better and more stable, but that is not what is presently driving the progress.

So in this chapter we will outline what the holders can, and maybe can't, do. We'll discuss how the environment can be controlled, how we can record the changes, and how we can correct for drift when it is occurring. We'll also mention the cost of holders, why you might not have the one you want, and what you can do about it. There is no difference between an *in situ* experiment and an in-situ one – it's just grammar and both are correct.

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2.1 General Principles

If you are asking 'why do we want to do in-situ microscopy?' you should probably skip this chapter for now. The purpose of the chapter is to show you the potential of this type of microscopy and to give you an idea of how you can apply the techniques. For example, if you are processing nanoparticles, you might want to understand how they change during processing. Similarly, if you study catalysis, you know that the environment is a critical factor in determining and controlling the processes that take place; most catalysis does not take place in a vacuum, especially not in an ultrahigh vacuum (UHV). So we need to be able to change the environment around the specimen, but the atmosphere in a regular TEM is very reducing. Old TEMs tend to deposit carbon on the sample as the electron beam cracks oil vapor in the column. Of course, the vacuum can be an advantage if we want to study film growth *in situ*, e.g., for molecular beam epitaxy (MBE), because we are already close to the actual growth conditions. So the question then becomes, can you controllably change the environment if you must?

The realization that nanomaterials are important and that they often have properties differing from bulk materials has led to enormous interest in TEM characterization. Gradually, we have realized that it is not enough to be able to image these small particles because they change: nanoparticles of 'inert' materials can be very reactive. We want to understand how and why they change.

Now, it is not enough to synthesize a novel material, we must understand the origin of novelty. In order to understand the origin of novelty, it is important to understand how the atoms come together to form a cluster of atoms, and at a later stage, how they combine together to form the final novel material. This is where in-situ microscopy can play a unique role, using careful experimental design of the process in the TEM: in-situ TEM provides the link between structure, processing, and performance. Traditionally, in materials science and biology, a series of samples are synthesized by varying the processing parameters and then they are characterized under the microscope. What we want to do now is avoid this post-mortem approach by using in-situ studies and continuously vary the processing parameters while the material is still inside the microscope. This can allow us to analyze transition states that we wouldn't otherwise see! We say that in-situ experiments allow us to study the full parameter space. We will only give examples as illustrations, not as an end in themselves – we'll give references for you to pursue the applications.

Operando

You can read about the origin of the term *operando*. It is the ablative form of the gerund of the Latin verb *operari* so we italicize it and do not add 'in'! It has same meaning in Spanish and Italian. The other rule is that we stop using italics when the word or phrase is in common use. ◀

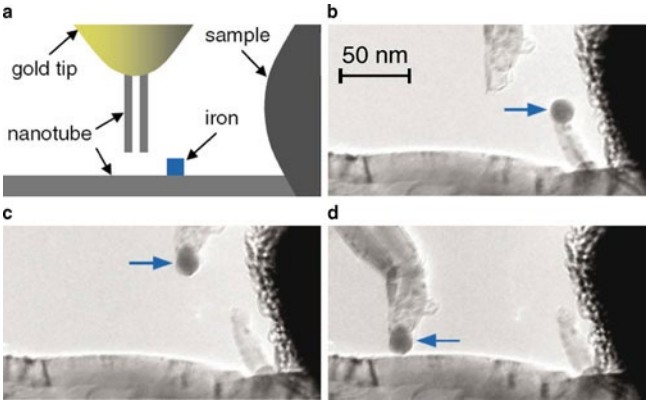

Fig. 2.1 The power of in-situ TEM: controlled manipulation of nanosized objects, and seeing what you are doing! Carbon nanotubes are being used to relocate iron nanoparticles

Materials change as they are used, often due to exposure to corrosive environments. The changes take place at the surface of the sample and propagate into the bulk material. If the material is a nanoparticle, there is no bulk! Atomistic mechanisms are involved whenever a material interacts with the environment. In-situ TEM can directly reveal how these processes occur – especially if you can obtain the necessary resolution (temporal and spatial).

In-situ manipulation of a nanoparticle is illustrated in Fig. 2.1; this figure really shows the power of in-situ experimentation – we can see what we are doing to a nanoparticle!

Many other components of the TEM will be close to the in-situ holder, including the objective lenses, the objective aperture, the cold-finger, and possibly the XEDS detector(s). When designing a new holder, the proximity and interaction with these microscope components must be considered. The effect of the magnetic field (~2 T) of the pole-piece on the specimen has always created a challenge for imaging magnetic samples even if they are fixed tightly in the holder; many older TEMs have such samples decorating the interior of the column.

It takes time and effort to learn an in-situ technique; attention to detail and persistence is the key to success.

2.2 Some history

The history of in-situ TEM studies is relevant, because you will read and use reports that are in the literature. The in-situ specimen holders used to be top-entry and side-entry. Now they are nearly all side-entry. We often have two competing 'motivations': i) improve the vacuum so that there is less contamination, and ii) find ways to envelop the specimen in a liquid or a gas. A FEG source has to be in the best vacuum possible to maximize its stability and lifetime. Remember: the gun may

have to go back to the factory if the tip is destroyed. To minimize contamination and back-streaming to the gun, the vacuum within the column for a modern TEM is $\sim 1 \times 10^{-7}$ torr.

The traditional problems for in-situ TEM studies have always been specimen drift, contamination and alterations caused by the electron beam; and they still are! We can minimize the first two, but the third is unavoidable. Historically, we had three types of in-situ holders: straining, heating, and cooling, but we could generally only have one of these at any one time. Some in-situ studies were carried out in high-voltage (1 to 3 MV) machines so as to see through thicker specimens at high resolution, which more closely represent bulk material. Often these high-kV machines were used to simulate the effect of ion irradiation, which could be carried out in combination with straining, heating, or cooling. With the development of nanotechnology, new holders have become available; this allows us to be more quantitative and to combine stimuli.

The main emphasis in W&C was often to optimize all the components of the microscope to maximize the spatial resolution. We usually worked hard to obtain a high vacuum (aka a low pressure) and a contamination-free environment. But now our philosophy is going to be slightly different. We now want to observe changes in the specimen/thin foil as some external stimulus is changed.

The emphasis here is to be able to see things as they happen, and so, we may compromise on the resolution to be able to achieve this. While in a conventional TEM, we take elaborate steps to minimize thermal gradients (to minimize drift), we actually heat the specimen (often to fairly high temperatures) when we want to study thermal transformations *in situ*. Since the thermally induced transitions often depend upon the environment, we may also decide to deliberately contaminate the TEM by passing gases into the sample chamber. Of course, we try to do this in a controlled fashion such that this contamination is restricted to a region very close to the specimen.

The Stimulus

This stimulus could be chemical, the environment, a temperature change, stress or staining, laser illumination, an applied external electric or magnetic field, etc. ◀

The big challenge is how do we fit in-situ capabilities within the pole-piece gap of the TEM? In the future, we will see that one solution is to use aberration correction to increase the pole-piece gap without forfeiting the obtainable resolution. That's the future, but in many labs it is already here.

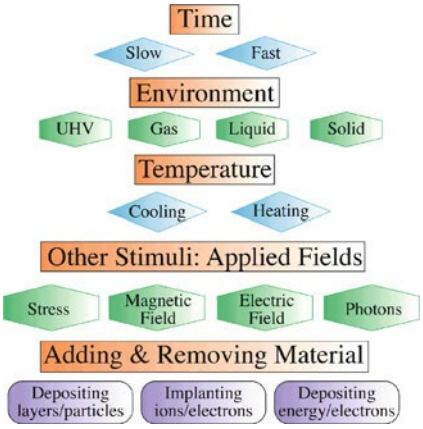

Fig. 2.2 Schematic summarizing the different sections of in-situ TEM

2.3 The Possibilities

Since this topic can take up several books itself, let's look at the scope of the topic first. The schematic in Fig. 2.2 summarizes the possibilities we are discussing. We may want to combine these topics. We may want to strain the sample while heating it. We may want to apply the strain locally (indentation) rather than globally (compress the specimen). We may even want to strain the specimen while heating it in a gas and irradiating it. We must also think about how fast or slow we want the stimulus to be, and for how long. How quickly do we need to record the specimen's reaction after stimulation?

TEM as a Lab

The basic idea is to use the TEM as an in-situ experimental laboratory with atomic resolution. ◀

Some points to keep in mind as we discuss this topic:

- Always keep safety in mind – both your own and that of the TEM and specimen holder.
- You will certainly be able to extract data from an in-situ experiment; the challenge becomes understanding the data and its relevance.
- Before you begin an experiment, think about what the sample will 'see' during the experiment; that includes the environment (chemical, pressure, temperature, stress, magnetic and electric fields), any grids, the holder, or anything else that might influence the reaction/mechanism.
- What accelerating voltage should we use in the experiments? For thicker samples, a higher accelerating voltage is preferable. For liquid-cell studies or indentation on bulk-like structures, a medium voltage is preferred. If we want to minimize the effect of the beam, a low voltage may be necessary. In any

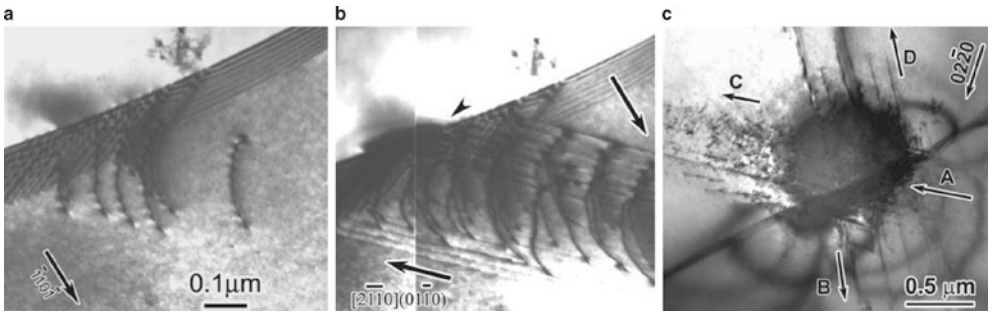

Fig. 2.3 A grain boundary in α-Ti building up dislocations during in-situ loading, followed by the eventual ejection of dislocations with several slip systems shown as **B**, **C** and **D**, where **C** was dominant. The initial **(a)** and final **(c)** states would not give a clear understanding of intermediate **(b)** state without in-situ observation

case, how long the beam irradiates the samples may well be critical. Beam control can be automated in STEM. Of course, you always want to know what the beam current is. Use a Faraday cup to check it.

- It almost goes without saying that we are always interested in the kinetics of processes; some changes, like the phase changes in phase-change materials (PCMs) are very fast, but we can now be quite quick too.
- What environment do we want or need? The environment will be critical for catalysis, but also the in-situ growth of thin films.
- What temperature will we need? We like room temperature because that is where the sample is generally most stable.
- We are often most concerned about how materials respond to stimuli – to applied fields – this is the basis of the electronics industry, the memory industry, etc. We'd like to be able to see directly the impact from an applied field.
- Whether we are growing thin films, simply depositing particles, or implanting atoms, we are often adding material. Of course, material will also be removed from a structure by sputtering or by displacement, such as bubble formation in a liquid cell.
- There is always an advantage to using energy-filtered imaging to decrease the effect of chromatic aberration.

We are not going to list every variant of every experiment, but we want to help you see the possibilities. The general question is 'how does the material change over time?

Keep in mind that we should always carry out the corresponding ex-situ analysis to be sure that beam effects have not completely changed the experimental response. Results from the ex-situ experiment will help us know whether or not the study can be completed *in situ* within the TEM. The experimental study on a microelectromechanical system (MEMS) heating stage could be carried out *ex situ* in an external vacuum chamber to reproduce the experimental conditions in the microscope without the electron beam. Overall, it might be easier to leave part of the specimen unexposed to the electron beam until the end of the test, to compare characterization with the exposed region.

2.3.1 Post-Mortem Characterization

Post-mortem analysis of deformation only provides the end result from a nanoindentation experiment. In-situ observation provides real-time imaging for a complete story of transition states that can be related to the stress-strain measurements. This can be seen in Fig. 2.3, where dislocation accumulation at a random grain boundary in α-Ti produced elastic distortion, until slip systems were activated to minimize the accumulated strain energy. This is why in-situ microscopy is so powerful. You see what happens and the order in which it happens, instead of trying to interpret what has happened during a reaction or process by comparing the initial and final states. We can view the processes as they occur within the microscope with nanoscale resolution (or better). Real-time imaging of dynamic processes enables us to view the effect that defects have on processes and structures. In a post-mortem analysis, you may overlook many factors. You could simulate the process, but hopefully you would remember to check what really happened. However, *post mortem* analysis is essential for many in-situ studies; e.g., a reactive environment might not allow you to analyze the specimen completely – you hope to stop the reaction and then probe it in a stable state. This is especially important when chemical analysis is not possible in the configuration you may be working with, such as older designs of liquid-cell holders.

2.3.2 Statistics

Before you perform in-situ TEM experiments, consider the statistical significance of the experiment and its reproducibility. Questions you should be asked at every presentation of your work will concern the set-up and control of your in-situ TEM experiment: the imaging conditions, beam effects, the defects in the material, especially when caused by specimen preparation, and how these considerations influenced your findings. It is so important to spend time with your experimental design so that you don't end up repeating all your hard work in an effort to confirm your interpretation, but you need to be able to when necessary for the scientific process! Reporting the complete characterization of the parameters defining your experiment will leave a legacy for

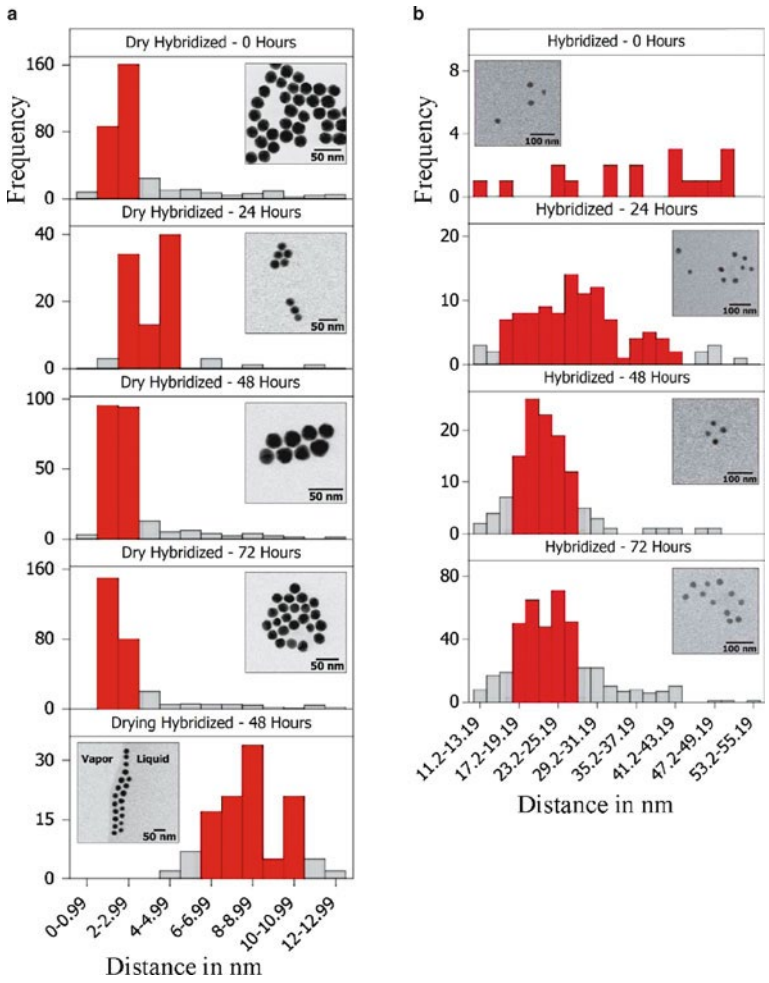

Fig. 2.4 Measurement of hundreds of inter-nanoparticle spacings of DNA-assembled Au nanoparticles, where the samples dried configured to spacing far below that which was predicted by the DNA attachment in solution. Rows show the time that particles were allowed for attachment. **a** Hybridized Au nanoparticles imaged on a dry surface in vacuum. **b** Hybridized Au nanoparticles imaged in a continuous liquid

your published results, even if your printed interpretation turns out to be incorrect.

Give some thought to the relevance of the properties observed within the TEM to the bulk materials that we are trying to characterize. The electrical, mechanical, magnetic, optical, and reaction properties of materials measured *in situ* will all be affected by the free surfaces available, particularly when in contact with gas/liquid. This is especially important when you consider the substrates used to support small catalyst particles or reactive species. In TEM, we cannot avoid having relatively large surface areas (especially of heavy elements like metals), since the samples are thinned to electron transparency or are nanoscale to begin with. The advantage TEM provides is location-specific detail. Specific test cases could be set up to determine the effect of defects, grain boundary orientations, doping, and crack dependence on the nanostructure in comparison to an averaged response in bulk studies. As an example, many researchers have used conventional TEM analysis on carbon grids to study nanostructured assemblies, though it has been shown through controlled experiments that during drying, the free surfaces cause these assemblies to have smaller inter-nanoparticle spacing than those you would observe if the arrays were in solution, Fig. 2.4. This systematic approach provided enough statistical evidence to prove the conclusion, though reproducibility in the experimental design was required.

We do not want to introduce artifacts that will affect our in-situ measurements; otherwise we are only studying sample-preparation artifacts. Pay attention to the preparation of the specimen – it's at least as important for in-situ analysis as it is in conventional characterization. An example is in preparation of a semiconductor specimen for characterizing the electrical properties of the material: if you use an ion mill to thin the sample, you will implant ions into the material. You may not see these dopants in the image or detect them in a spectrum, but they will highly influence the electrical behavior of the material. Therefore, once again, the success of the TEM experiment for in-situ analysis will be based on how well the specimens are prepared before you put them in the TEM. We have to apply statistics to in-situ studies so that we can compare them to other measurements; you may find the article by Spitzer et al. (2014) interesting. (Remember the meaning of 'typical image'.)

2.4 Time

The experiment defines the temporal resolution required to capture the events of interest happening in a material. For example, atom migration and transient states during phase transitions require sub-microsecond timeframes to capture those events, whereas corrosion and radioactive decay occur on much longer timescales of hours to months. So, when approaching the characterization of a material process or mechanism within the TEM, we should first define the process duration and then choose the instrumentation.

2.4.1 Recording the Data

The first in-situ experiments were captured by pointing a video camera directly at the phosphor screen in the viewing chamber. The first videos of dislocations moving were recorded in this way. There could well be a situation where this will still be the best approach! In this case, you will be limited by how fast your phosphor can respond to changes in the intensity of the electron beam and what resolution it can give. You record changes in your specimen as they take place to prove to others that you understand how the changes occurred. Recording technologies have changed, along with the development of microscopy instrumentation.

Of course, you have to record useful and correct data while actually doing the in-situ experiment. You will often be looking at one particular region of a sample while the most interesting things are happening at the other end of the specimen. This could be due to a beam effect, non-uniformities in the environment across your specimen, or just luck. So you need to keep your eyes open for anything that you are not seeing! We can use several different approaches. One comes with experience. You can switch from the CCD camera to the microscope screen for a wider field of view, but this may interrupt the video recording. During in-situ microscopy, the sample and the environment may be changing continuously; the focus condition also keeps on changing. You need to keep adjusting the focus while recording the images.

The ideal recording media would have a detector quantum efficiency (DQE) of 1, with a large number of pixels and rapid readout rate. As more data is recorded, storing and processing the data becomes challenging; TEM is now a producer of 'big data'. With the new high-speed 2k-by-2k cameras, 60 seconds of images acquired at 400 frames per second (FPS) produces ~160 gigabytes of data. To convert this data from DM format to individual tiffs would require a full day using the DM batch convert software. (See Chap. 6 for more on DM – digital micrograph.) With the new direct detection cameras, described in Sect. 2.4.3, 15 minutes of recording can produce up to 5 terabytes of data. Do the calculation: even 30 FPS at 1k by 1k per frame for 15 minutes produces around 27 GB of data. Researchers and companies are addressing this issue of too much data (big, but redundant, data). The goal is to use computers to identify the data that you are looking for without manually searching through thousands of images. Still, it is important to plan the experiment well before you start recording it, as you can quickly create more data than a person is able to examine. While doing the experiments, you store data directly onto the TEM's computer and then transfer it to a removable drive; many managers don't want their TEM directly connected to the internet.

You may even just want to use video to allow you to correct for drift of the sample. To do this you'll need to find the software that is compatible with your TEM. But remember, our repeated warning: having the beam on so that you can see the specimen may be enough to change what happens to your specimen! So, blank the beam for various intervals upon repeating the experiment to check how bad the beam effects are.

2.4.2 The CCD Camera

CCD cameras are now attached to all research-grade TEMs. The CCD cameras may be side-entry or bottom-entry. With a side-entry camera, we do not compromise on the field of view. The bottom-entry camera does compromise on the field of view, but the magnification is ~10× larger. In either case the data is stored digitally. The parameters you should know for in-situ microscopy imaging are the digital size of the camera, the sensitivity of the pixels, the threshold electron dose that a pixel can tolerate, and the lifetime electron dose per pixel of the camera. Cameras traditionally use an optical-fiber-based stack technology with multiple read-out ports for high-contrast resolution. While doing the in-situ microscopy, you will always work to optimize the camera parameters. Better image quality usually means poorer time resolution. Of course, the exposure time depends on the quality of the sample, conditions of the experiment, etc.

2.4.3 Direct-Detection Cameras

Direct-detection cameras are quite new and currently very expensive. The principle is rather like the operation of a secondary-electron detector in SEM. CCD cameras work by converting an electron signal into photons using a scintillator; direct electron detectors detect each electron that reaches each pixel, so the DQE is much higher. Examples (2015) are the DE-series (up to 67.1 megapixels) from Direct Electron, Falcon II (16 megapixels) from FEI, and the K2 (57 megapixels) from Gatan. Since the DQE is higher (in principle, it is 1, but in practice between 0.35 and 0.8), the 'exposure time' can be much shorter. The first users were those in the biosciences, where low dose is recognized as being critical and money is more plentiful. Now these cameras are being applied to materials science questions, such as understanding the interface structure between silicon and a $NiSi_2$

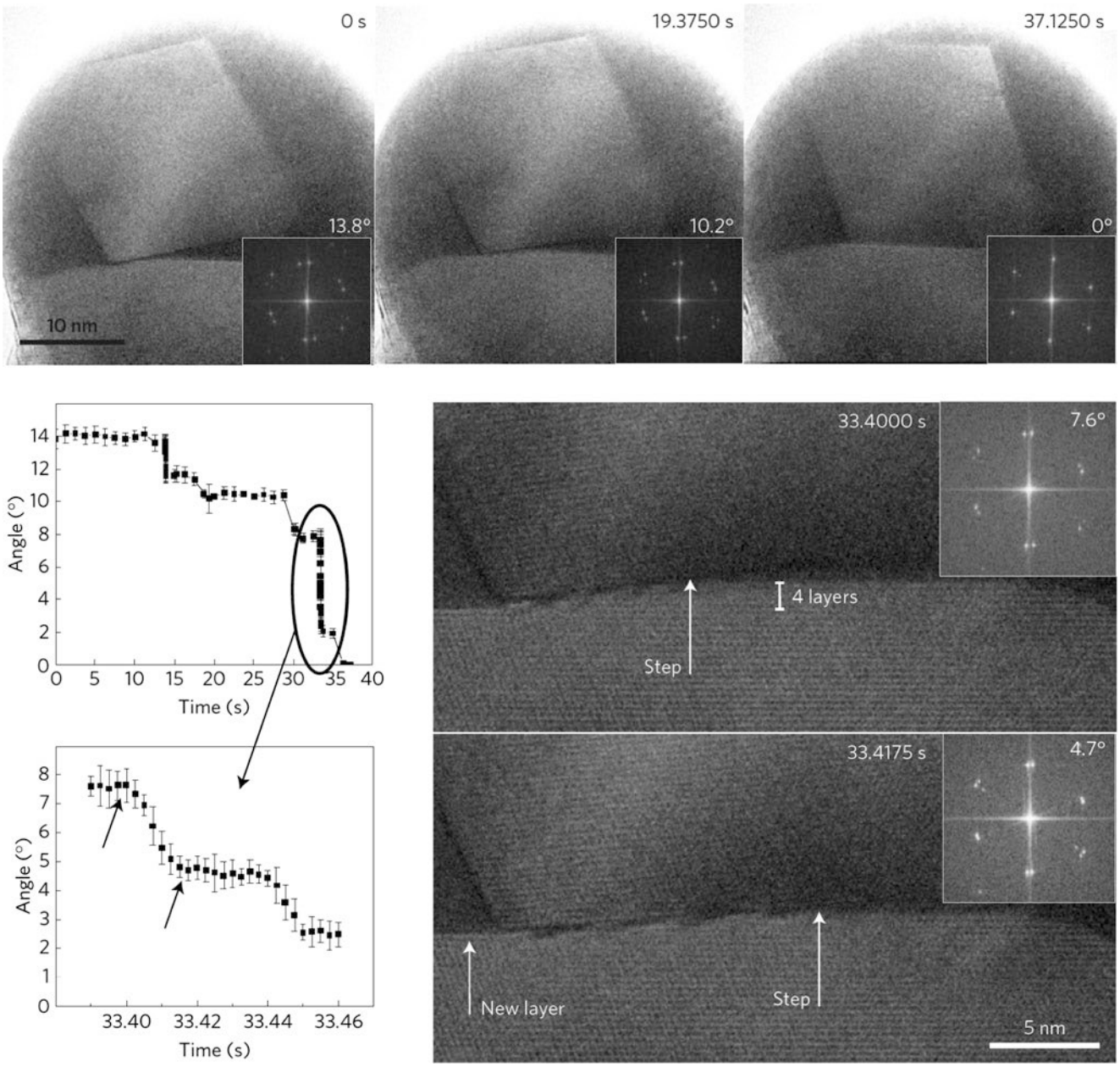

Fig. 2.5 Si nanowire growth at an interface with $NiSi_2$ nanocrystal at 400 °C, images acquired at 400 frames per second. Angle between crystals is indicated, where rotation for epitaxial alignment is achieved over the 37.1-s period. These high-speed cameras can resolve atomic-scale information when using 'enough' electrons

nanocrystal during Si nanowire growth, Fig. 2.5. These cameras generally will cost over 500,000 (2015) US dollars. For our in-situ studies, the video frame rate of 1,600 FPS is the enormous improvement, but the amount of data that you must store and transfer is correspondingly large. (Think about this challenge!) A recent advance using these high-speed cameras is the ability to collect full tomographic data from a structure within seconds, though stability of the holder and focus conditions are the key factor in the quality of images obtained.

2.4.4 Software and Data Handling

The most important part of in-situ TEM is often considered as an afterthought! You know you will use an electronic device to record the image, but what software will you use? We list some of the manufacturers at the end of the chapter. (Notice we are already no longer saying CCD camera.) One important aspect that we have to discuss is the computer and its processing

time. Image recording, processing, and saving, depends on the computer that you are using. The computers that are generally interfaced with the microscope should be state-of-the-art and fit the hardware configuration when the instrument is purchased. Shortly after it's purchased, it will no longer be state-of-the-art; it will still be adequate for running the microscope – but not for doing state-of-the-art image processing, etc.

Many in-situ experiments require the use of multiple computers to operate the TEM separately from the holder or external stimulus controller. Currently, there are ways to use both hardware (master clock) and plotting software (LabVIEW, Python, Matlab, Mathematica, Igor, Origin, and Excel) to synchronize the quantitative property measurement from the holder with the video/images collected on the TEM. To correctly overlay the video onto the plot, it becomes necessary to input the exact moments each image/data point was acquired at. If you are working on this analysis, you should refer to the website spacetime.uithetblauw.nl (08/2015) to synchronize your external data with your image. Camera software can usually place a timestamp directly on the image, so that this information cannot be separated from the data during the time it takes between collecting the results and publishing them. At present, we usually use LabVIEW to control laser beams and ion beams incident on the specimen. Many use Comsol® software to model the various in-situ systems, processes, and environments.

The camera you use will have its own image-grabbing software package, but you'll find that different users have different philosophies. In practice, you'll optimize the camera parameters and then start the auto image-grabbing software: record images continuously. The negative part of this is that you can only see the images while they are being recorded! If your microscope does not have software to record videos, you can load software onto the microscope control computer (with consent of the instrument manager) to collect screen captures of the search screen or scanning frames. Examples include VirtualDub and CamStudio, which allow you to select a region of the monitor to collect a screen shot with a predetermined capture rate (usually synched with the frame rate while searching).

Post-processing of the videos and images can be completed using the same software you use for conventional TEM images. ImageJ, Fiji, Python and DM are free; Matlab, Mathematica, Camtasia Corel are not. (Check out youtube.com for instructional videos on using the software, especially for ImageJ.) For example, you can use image registration to correct for drift in an image series or group of video frames. Scripts can also be found through various sources; there are collections for DM or for Matlab such as Smart Align (lewysjones.com (08/2015)). Some image-processing techniques may be tricky for in-situ experiments when the background is not constant, such as with bowed membranes in liquid-cell experiments. In such images, it may be useful to apply more specialized algorithms to gain information from the experimental data, such as adaptive threshholding. Images recorded on high-frame-rate cameras may require their own software to be able to convert the bulk data into a format that is compatible with more conventional image-analysis software.

Processing Data

You must report any changes that are not just correcting levels (brightness/contrast) or cropping the image, even in video. Be sure to record and report any modification done to the video data just as you would for images. ◄

2.4.5 Drift Correction

Depending on the task at hand, you have to set the working range of magnification. If you're working in nanoscience and technology, the magnification is generally high. This worsens the drift problem for in-situ microscopy. General methods to reduce drift in a series of images include using different support grids, piezo-controlled goniometers, drift-corrected holders, and automated drift-correction software. Hardware may use electronic drift compensation with piezo-driven stage control or image-shift deflection coils to correct for drift in the images (Banhart 2012), though the drift-correction software and drift-corrected holders on the market are not really drift-corrected for in-situ microscopy. The sources of drift for in-situ microscopy are expansion or contraction of the sample, specimen charging, temperature variations induced by the beam, reaction of the samples with the environment, flowing water inside the holder for cooling, and occasional bubble burst inside the cooling channels; or the sample may change and thus move in most in-situ experiments.

The drift thus caused can only be corrected manually by observing the images while they are being recorded, Fig. 2.6. Automated image-drift correction works by keeping a pre-selected reference region (fiducial) in the field of view. The amount of

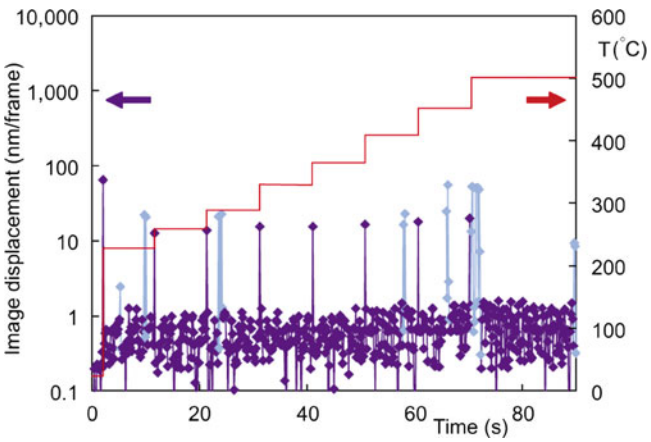

Fig. 2.6 Tracking of the thermal-drift velocity, as the displacement rate between consecutive images (*dark blue*), of a heating experiment from room temperature to 501 °C (*red*). *Light-blue points* show the manual drift corrections during the series of images. Displacement spikes observed at each step increase in temperature, larger displacement values for larger steps

drift in an image may be related to the electrical conductivity of the specimen/grid and the beam dose on the specimen (related to beam-induced heating). Remember, when only a small region of the sample is exposed at one time, charge build-up is limited and beam-induced movement is reduced. Drift performance for in-situ holders should have been tested and recorded for your instrument when they were installed, but that might have been 10 (or 30) years ago!

Good Practice

For all TEM, *in situ* or not, keep the o-ring on the specimen rod properly lubricated. Tap the base of the holder to seat the o-ring and improve contact between the holder and goniometer, but be aware of when you shouldn't! ◀

Note: be careful when tapping to seat the o-ring! Don't tap the holder if doing so will move your carefully aligned specimen or probe tip (e.g., if you're using an STM-TEM holder). Drift or mechanical vibrations may be caused by the cabling connected to the base of the holder (common for in-situ and double-tilt holders). Pay careful attention to stabilizing this cabling and avoid moving cables during the experiment. Electrical experiments can be destroyed if static discharge from moving the cables causes a sharp pulse to flow through a nanomaterial sample.

2.4.6 Ultrafast Electron Microscopy

What happens when we want to observe dynamic events in materials that occur in very short times? For example, phase transformations, transient states, or nanostructure nucleation can happen in millisecond or shorter times. We need to be able to acquire images in series that are representative of the timescale upon which the dynamic events are taking place.

During TEM imaging, images can be acquired at standard video frame rates of 33 ms per frame (30 FPS), or with an advanced high-speed camera down to 625 µs per frame (1,600 FPS as we saw in Sect. 2.4.3). Even the fastest cameras still limit the kinds of dynamic processes in materials that we can study using nanometer-resolution real-space imaging, and we always need to consider the electron beam dose necessary to collect enough information from the sample with the high-frame-rate cameras. A change in electronic states and atomic-scale fluctuations in materials can occur within a femtosecond (1 fs is 10^{-15} s), which is much too fast for standard TEM imaging. Ultrafast electron microscopy (UEM) has set out to overcome these barriers and to increase the temporal (time) resolution for TEM imaging/diffraction down below the nanosecond time regime. The key development in UEM is that the camera speed no longer defines the temporal resolution; instead the beam is limited to emit electrons for a very short defined pulse. The camera records the data over a much longer timescale by leaving the shutter open to wait for the pulse, but the temporal resolution is determined by the duration of the acquired pulse.

Fast vs Ultrafast

This high-speed electron microscopy has come to be known as ultrafast electron microscopy. (1,600 FPS is fast but not ultrafast!) ◀

The development first targeted imaging and diffraction at high temporal resolution by Bostanjoglo in 2000, framed in the use of laser pump-probe measurements. In this design, an external stimulus induced a modification to the specimen; the imaging signal, has a predetermined timed delay, allowing us to collect the information of the sample's response. In this experimental design, the temporal resolution is only limited by the pulse duration. Based on this pump-probe approach, two methods have been developed where repeated diffraction or imaging compiles single-electron pulse events for reversible processes – this is the *stroboscopic* UEM, or an individual packet of electrons is used to produce a single image or diffraction pattern for irreversible processes – this is *single-shot* UEM (commonly known as dynamic TEM (DTEM)). The single-electron pulse actually consists of 1–10 electrons, whereas the packet of electrons is generally ~10^9 electrons. Although the DTEM is a *single-shot* process, we can record a series of such images with a defined time delay to make a short video!

Using the *stroboscopic* approach, a femtosecond pulse continuously collects information from events that occur on an ultrafast (< 1 ns) timescale. For this to work, the specimen must return to the unperturbed state prior to interaction with the next pulse. In the *single-shot* approach, a single packet of electrons collects information from a sample in the nanosecond time regime (the time needed to fit in enough electrons without significant repulsion), which is important for irreversible processes to produce an image/diffraction pattern with reduced noise. In both of these methods, the pulse duration of the incident laser is about the same as the emitted electron pulse. Bostanjoglo's single-shot DTEM was able to collect an image using 7- to 11-ns pulse duration, with times between pulses of 20 ns to several microseconds, producing an image with ~100-nm spatial resolution. This microscope was also the first to use an electrostatic beam-shift, located after the specimen, to deflect a pulse train onto different regions of a CCD to produce a 'movie', i.e., a short sequence of images, of the irreversible process. The TEM modifications of the *stroboscopic* and *single-shot* systems are similar, though the number of electrons released from the gun differs. The *single-shot* approach uses greater laser beam energy with a low repetition rate; the *stroboscopic* mode uses the opposite. The photoelectron source can be used as a thermionic emitter, providing conventional TEM imaging when desired.

A standard TEM can actually be retrofitted to become a UEM by adding at least one laser system to the microscope column that is deflected onto the tip of the photoemission gun. A second laser is commonly used to induce synchronized heating or ablation of

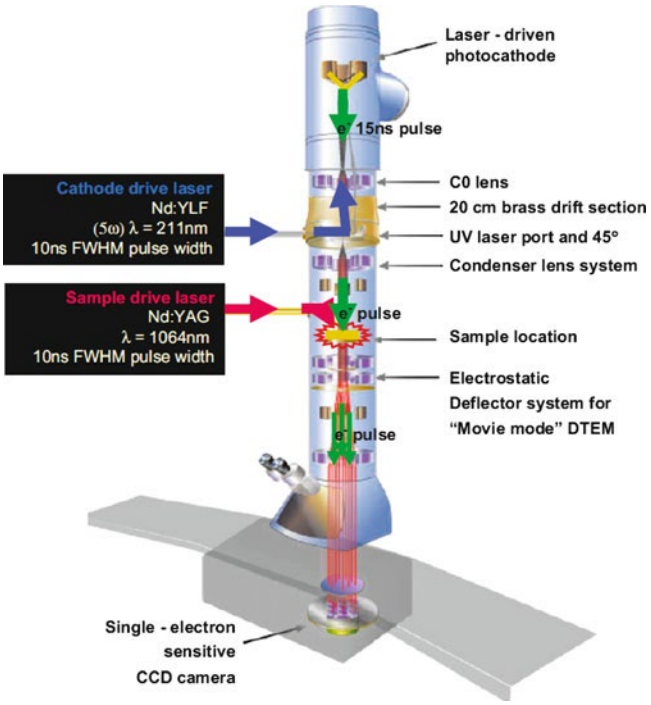

Fig. 2.7 Bringing laser beams into the TEM; the experimental set-up. One laser system is incorporated above the condenser lens system to deflect onto a photoemission cathode, while a second laser is directed with mirrors onto the specimen to stimulate processes in the material

the sample. This modification is now commercially available, Fig. 2.7. It's easy to bring light into the TEM – we can use windows – and not affect the vacuum!

During an experiment, the laser that is directed onto the sample can stimulate a reaction or change in the sample. After a predefined time delay, the second laser is directed onto a photoemission source producing emitted electrons, which are then focused to interact with the specimen and form the image/diffraction pattern. In contrast to high-speed cameras, which still require a high electron dose to provide enough contrast in an image, UEM is inherently a low-dose technique, evidenced by the fact that only a relatively small number of electrons are emitted to interact with the specimen and the time of this interaction is limited. UEM thus combines a relatively high spatial and temporal resolution with low-dose imaging! The information transferred from the sample is a result of the laser-initiated process, not an electron-beam effect (Fig. 2.8).

Irreversible Processes

The *single-shot* UEM (or DTEM) can be used to study phase transformations, crystallization, and nanowire growth. Currently (in 2015), the record for the temporal and spatial resolution is a 15-ns pulse with 9-nm features resolved. The size of the electron packet is related to the bias on the cathode and the laser pulse duration. A 15-ns packet will contain ~10^9 electrons from the photoemission source. Synchronizing the sample- and cathode-drive lasers provides the ability to observe changes occurring within 1 ns from its stimulated initiation. If we increase the rate of image acquisition, we'll degrade the coherency of the beam and lose high-resolution information; it's a trade-off between spatial and temporal resolution.

It's interesting to think about the physics of the *single-shot* UEM. The number of electrons that can be emitted from the surface of the cathode within a short pulse is limited by the Child-Langmuir effect (the space-charge-limited emission of electrons from a source). As the emitted packet of electrons travels down the electron column, individual charges repel one another, so the packet is broadened, causing the spatial resolution to degrade. This space-charge effect limits the number of electrons collected by the condenser system. To reduce these space-charge effects, we sacrifice some of the temporal resolution and extend the pulse duration. This should increase both the number of electrons contributing to the image and the spatial resolution. The original *single-shot* UEM used a Ta disk cathode that emitted ~3–4 × 10^7 electrons per 10-nm pulse from a 200-μJ laser. Remember, mass-thickness and diffraction-contrast imaging modes are less dependent on coherence.

Irreversible processes, such as the melting of thin metal films (Al, Cr, Ni, Ni-P, Co, and Pt) and phase transformations, have been studied with the DTEM (Fig. 2.9). We can use laser-heating to reach high temperatures within short pulse durations. Dark-field imaging has provided temporally resolved images of grain boundary, stacking fault, and dislocation motion.

We can expect improvements in the design of photoemission guns as DTEMs become more popular. Already we see brighter sources, and plans for back-illumination of the gun to remove the aperture created by the mirror. As in any gun, the material used for the photoemission source used can greatly affect the brightness and current density of the emitted electron pulses. Materials that have already been considered include a combination of photoelectron emitters (CeB_6, LaB_6, CeS, ZrC, Ce, Tb, Ti, and Zr) on hairpin metals (Ir-W, Nb, Re, Ta, and W). A Zr-coated Re hairpin cathode is producing the highest electron current densities and is operating as a thermionic emitter. Photo-excitation would allow the cathode material to be optimized for quantum efficiency without worrying about stability at high temperatures.

You can make movies using a high-speed electrostatic deflector to deflect a defined number of pulses on different regions of the CCD; In 2015, the number of frames is 9, but that's just the beginning (Fig. 2.10**)**. (If you're interested, check how many frames can currently be collected with an SEM using parallel beams.) An arbitrary waveform generator (AWG) for microsecond pulsed imaging, aberration correction, and more control over the parasitic electron–electron interactions within the electron packet are planned (or hoped for). The AWG can extend the pulse duration of the laser on the photoemission source to vary from 10 ns to several microseconds. With an increase in the pulse

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