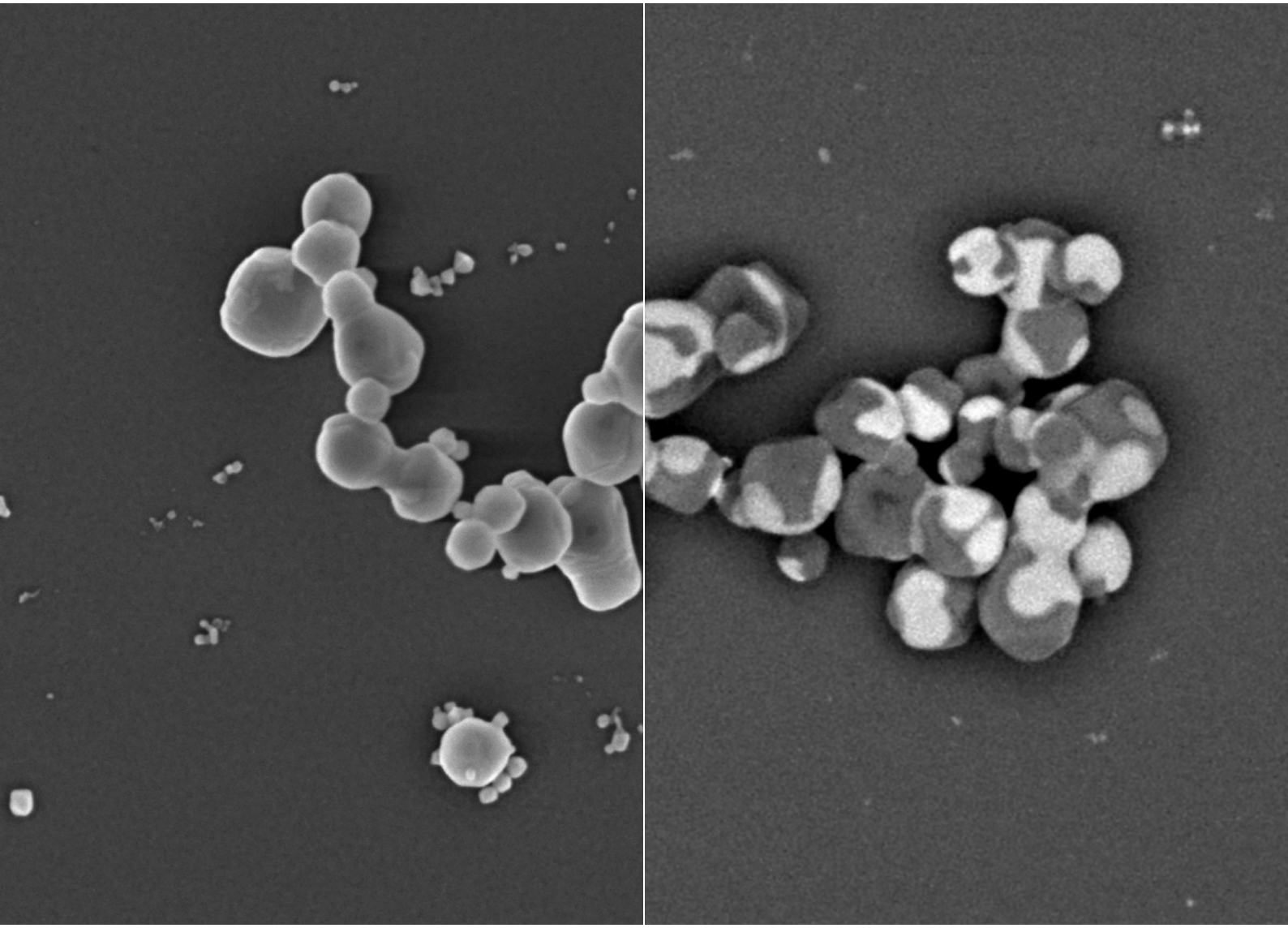

ZEISS GeminiSEM 500

Nanometer scale EDS Analysis using Low-kV FE-SEM and Windowless EDS Detector

ZEISS GeminiSEM 500

Nanometer scale EDS Analysis using Low-kV FE-SEM and Windowless EDS Detector

Author: Luyang Han[1], Simon Burgess[2], Fang Zhou[1], James Sagar[2], James Holland[2] and Xiaobing Li[2]

[1] *Carl Zeiss Microscopy GmbH, Germany*
[2] *Oxford Instruments NanoAnalysis, United Kingdom*

Date: March 2017

The investigation of morphology and chemistry of materials by combining scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) is a well-known method. Characterizing structures on a nano-scale, like quantum dots of GaInAs or nanoparticles of ferrocerium, is a challenge because the resolution of EDS analysis is typically limited to micrometers as it depends on the interaction volume of the electron beam with the sample. High resolution low kV SEM and a windowless EDS detector, used for this study, push the resolution down to 10 nm.

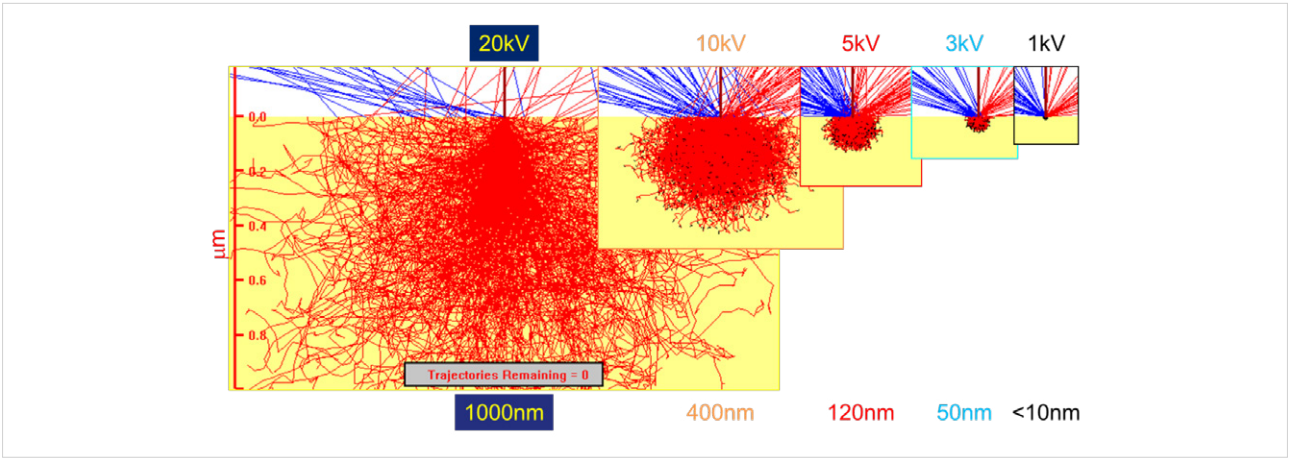

Figure 1 *Electron-sample interaction at different accelerating voltages modeled using Monte-Carlo simulations – Fe Lα in pure Fe.*

Introduction

Energy dispersive X-ray spectroscopy (EDS) is the routine technique in combination with a scanning electron microscope (SEM) to gain elemental information about a specimen. When the electron beam is scanned across the sample surface, elements in the specimen are ionized and emit characteristic X-rays. By detecting the energy spectrum of emitted X-rays, elements in the specimen can be identified. Measuring X-rays within a specific energy window across the scanned surface allows elementary maps to be obtained. Although the focused electron spot of a typical field emission SEM is around 1 nm, the resolution of EDS maps is fundamentally limited by the interaction volume of the electron beam with the sample. This is usually much larger than the focused electron spot when working at typical analytical conditions (beam energy > 15 kV). However, the interaction volume of X-rays can be reduced if the primary electron beam energy is decreased.
The influence of primary electron beam energy to X-ray interaction volume is illustrated in Figure 1. By reducing the energy of primary electrons to 1 kV, the size of interaction volume can be reduced to less than 10 nm, approaching the size of focused electron spot itself.

A practical challenge of using EDS at low electron beam energy is the limited range of characteristic X-ray lines excited by the electron beam. This means that low energy X-ray lines such as M and even N lines must be used to identify heavy elements. These low energy X-ray emissions may have a low yield and peak/background ratio.
In Figure 2a, the photon energy of X-ray emission lines lower than 5 kV are shown for different atomic numbers.
For these X-ray emissions the corresponding fluorescence yields are usually below 0.1. Additionally, the overvoltage ratio is usually low in such conditions, further decreasing the production of X-ray photons. Thus the ideal EDS detector must maximize the efficiency for the collection of these low intensity X-ray lines.

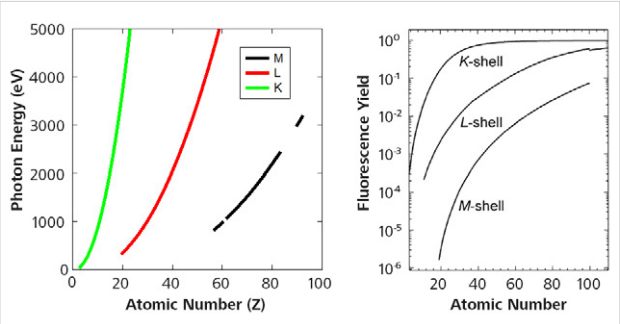

Figure 2 *Plot of characteristic X-ray energy (a) and corresponding yield (b) in different shells versus atomic number [1].*

Equipment

In the following examples, the X-Max Extreme detector is combined with ZEISS GeminiSEM 500, a field emission scanning electron microscope (FE-SEM).
ZEISS GeminiSEM 500 is especially suitable for high resolution low-kV EDS application: the resolution of around 1 nm at low-kV can be achieved without using sample biasing or immersing the sample within the magnetic field. The inlens EsB detector on ZEISS GeminiSEM 500 is an efficient BSE detector at low voltage, which gives almost pure material contrast. This material contrast image provides very useful information to compliment EDS analysis. The Oxford Instruments X-Max Extreme is an EDS detector specifically optimized for low-kV applications. With a 100 mm^2 detector area positioned very close to the sample and objective lens the detector solid angle is maximized.

The detector does not have a protective X-ray transparent window like conventional EDS detectors. Such windowless design minimizes the loss of low energy X-ray photons through absorption by this window. To improve sensitivity to low energy photon further this radical new geometry is combined with new low noise electronics.

Analysis

To demonstrate the practical resolution of low-kV EDS in combination with ZEISS GeminiSEM 500, particles from the sparks of ferrocerium collected on a silicon substrate were analyzed. The ferrocerium is a man-made flint containing Iron, Cerium, Lanthanum and many other trace elements. This material easily generates sparks when rubbed against a steel surface. Within these sparks a rich mix of particles with different sizes, from several micrometers to only a few nanometers, are produced. These particles are usually composed of multiple phases with quite different chemical composition. An example of these particles is shown in Figure 3.

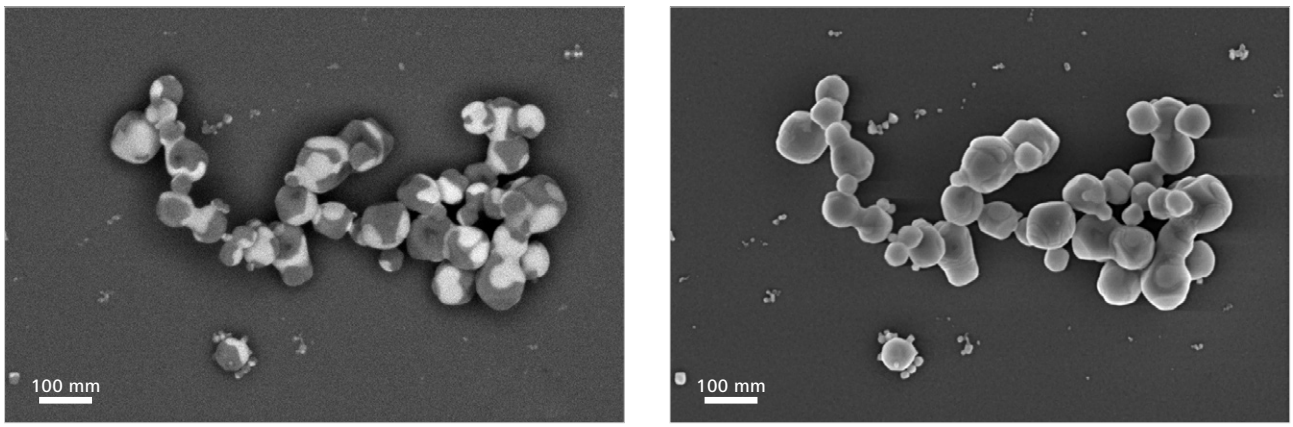

Figure 3 *SE image (a) and BSE image (b) of particles produced during sparking of ferrocerium. The BSE image shows strong material contrast variation within the particles, indicating that each particle is composed of multiple phases. Images were obtained at 2 kV beam energy with Inlens SE and Inlens EsB detectors.*

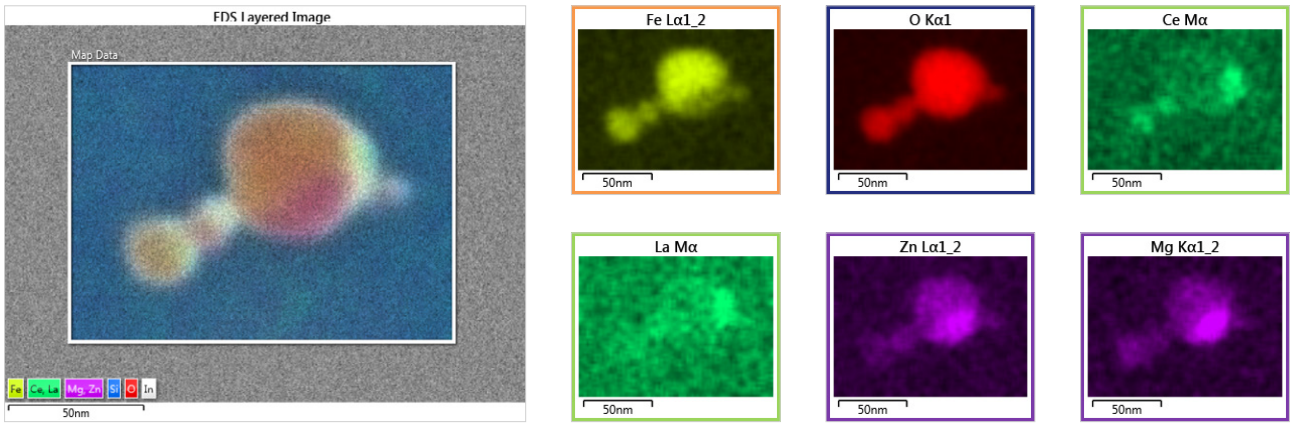

Figure 4 *EDS element mapping of ferrocerium particles. The composite elementary map (left) and colored maps of individual elements (right) are shown.*

The BSE image, figure 3b, clearly shows that particles are composed of phases with quite different atomic numbers.

Several of the nanoparticles are analyzed in detail using low-kV EDS. The results of elemental mapping performed at 2 kV beam energy are shown in Figure 4. Due to the low excitation energy, the L and M lines are used to identify the heavier elements. The phase separation within a small particle is clearly identified. The 50 nm diameter particle is composed of an iron oxide region (orange), a zinc / magnesium oxide region (purple) and a cesium / lanthanum oxide region (green). Similar phase separation can also be observed in the two smaller particles, where the size of the resolved phase is well below 10 nm.

Due to the very low penetration depth of low energy electrons, low-kV EDS is also sensitive to chemical information close to the sample surface. To demonstrate this surface sensitivity, $In_xGa_{1-x}As$ quantum dots on the GaAs substrate were analyzed. The secondary electron image (taken with the Inlens SE detector) and sketch of the sample is shown in Figure 5.

The $In_xGa_{1-x}As$ quantum dots were grown by molecular beam epitaxy (MBE) on a single crystal GaAs substrate.
The difference in lattice parameters between the two materials causes the spontaneous growth of pyramidal structures. The width of the base of these pyramids is around 20 nm and their height is less than 10 nm.

To achieve the required surface sensitivity, the EDS analysis was performed at 1 kV and 2 kV electron beam energy. Comparing the EDS spectra on the quantum dot and the substrate shows the presence of Indium and also a decrease of Gallium signal on the quantum dot, while the Arsenic signal on the quantum dot is similar to the substrate (Figure 6). This observation is consistent with $In_xGa_{1-x}As$ being a pseudo-binary alloy composed of InAs and GaAs. The corresponding elemental maps shown in Figure 7 further confirm that the quantum dot show a deficiency of Ga, and increased In-Mz signal with respect to the substrate. The maps also show that the quantum dots are preferentially oxidized with respect to substrate.

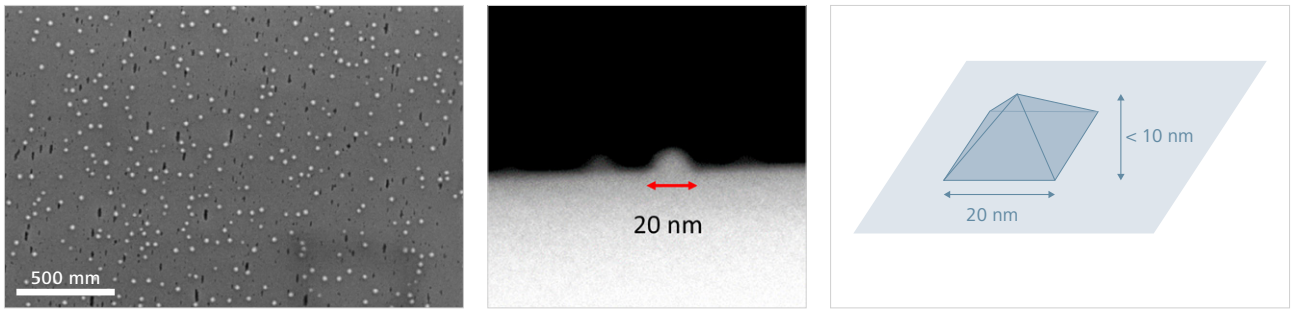

Figure 5 *Top view (a) and cross section (b) of $In_xGa_{1-x}As$ quantum dots on a GaAs substrate. A schematic view of the quantum dot is also shown (c).*

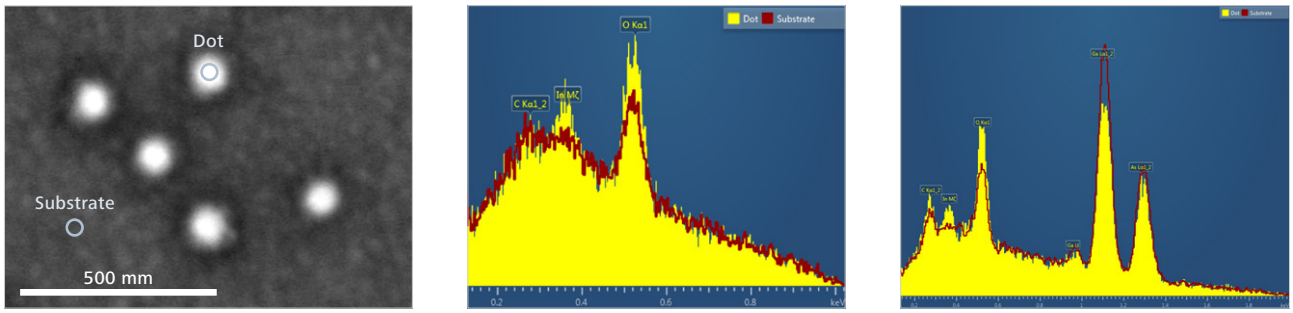

Figure 6 *EDS spectra of InxGa1-xAs quantum dot on GaAs substrate measured at 1 kV and 2 kV energy. On the quantum dot the presence of Indium can be identified by its M line.*

Conclusion

The combination of X-Max Extreme with ZEISS GeminiSEM 500 provides a uniquely convenient and powerful imaging and analysis tool for investigating the morphology and chemistry of nano-structures down to less than 10 nm.

Using the example of ferrocerium nano-particles and GaInAs quantum dots this capability has been demonstrated in practice. This combination shows the potential of state of the art technology, for high resolution imaging and elemental analysis of bulk samples.

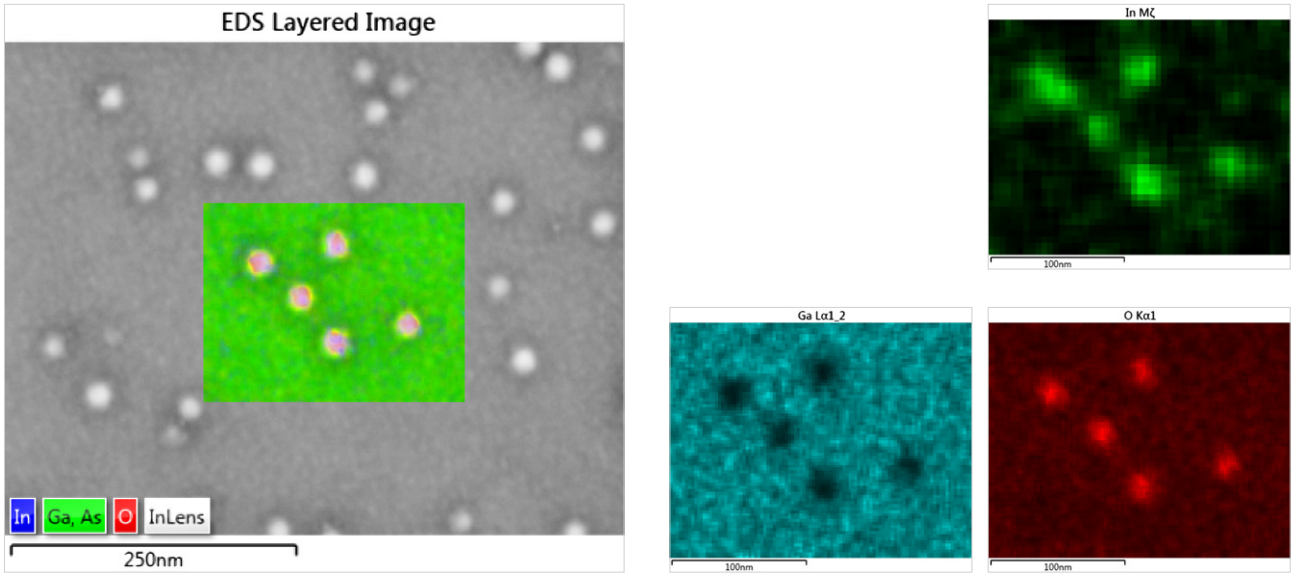

Figure 7 *EDS elemental mapping (left: composite, right: elementary for In, Ga and O) of InGaAs quantum dot on GaAs substrate.*

References:

[1] X-RAY DATA BOOKLET, Center for X-ray Optics and Advanced Light Source, Lawrence Berkeley National Laboratory

Carl Zeiss Microscopy GmbH
07745 Jena, Germany
microscopy@zeiss.com
http://www.zeiss.com/geminisem