

# Electron Energy-Loss Spectroscopy: Measuring Optical Properties at the Nanometre Scale

V. J. Keast\* and M. Bosman\*\*

\*University of Sydney, Sydney, NSW 2006, Australia, v.keast@emu.usyd.edu.au

\*\* University of Sydney, Sydney, NSW 2006, Australia, m.bosman@emu.usyd.edu.au

## ABSTRACT

Electron energy-loss spectroscopy (EELS) is widely used to study the composition and electronic structure of materials at the nanometre scale. The low-loss region of the EEL spectrum ( $< \sim 50$  eV) is of particular interest for the study of optical properties. Examples of the applications of EELS to measure the optical properties, and, in particular, of individual nanoparticles will be presented. Comparison to calculations of optical properties and EEL spectra using density functional theory will be given.

**Keywords:** dielectric function, electron energy loss spectroscopy, density functional theory, nanoparticles, surface plasmon

## 1 INTRODUCTION

Electron energy loss spectroscopy (EELS) measures the energy lost by high-energy electrons after they have passed through a thin section of a material. It is usually performed in a transmission electron microscope (TEM) or scanning TEM (STEM). The combination of TEM with EELS allows for the analysis of microstructural or nanostructural features in materials and for structure-chemistry-property correlations to be developed [1].

The energy lost by the incident beam of electrons will be determined by their interaction with the electrons in the material. The electrons in the material can undergo a variety of different excitation processes which appear as various features in the EEL spectrum. A spectrum from GaN is shown in Figure 1 as an example and will be briefly discussed below.

With a typical TEM specimen of 10-200 nm in thickness, most of the incident electrons do not lose any energy after passing through the material and are observed as a very intense peak at zero energy-loss called the zero-loss peak (ZLP). The width of the ZLP, usually at full-width half maximum (FWHM), is used to provide a measure of the energy resolution of the system.

The next most intense feature is the plasmon peak. Plasmons are collective oscillations of the valence electrons and their energy is usually in the range 10-40 eV. The energy of the plasmon peak is related to the density of valence electrons. The relative intensity of the plasmon peak can be used to measure the thickness of the TEM specimen and this is the most widespread application of the

plasmon peak. In cases where the changes in composition are associated with changes in the valence charge density the plasmon energy can be used to measure the composition. More recently, it has been recognised that a careful study of the plasmon energy, and hence valence charge density, could be used to assist our understanding of the physical properties of materials.

Also found in the low-energy region ( $< \sim 50$  eV) of the spectrum are features and peaks due interband transitions. These are single electron transitions from the valence band into the unoccupied states (or conduction band). They can appear both above and below the plasmon peak, as indicated in Figure 1. Indeed, in some materials, the low-energy region of the spectrum is dominated by interband transitions and it can be difficult to identify a strong plasmon related feature.

The low energy-region of the spectrum can be quite complex and it can be difficult to determine the origin of the various features. For this reason it has not found as widespread application as the higher energy features, to be described shortly. However, one way of interpreting the low-loss EEL spectrum is through a dielectric formulation. The intensity in the spectrum can be shown to be related to the complex dielectric function,  $\epsilon$ , of the material via the equation

$$\frac{d^2\sigma}{d\Omega dE} = \frac{1}{\pi^2 a_0 m_0 v^2 n_a} \left( \frac{1}{\theta^2 + \theta_E^2} \right) \text{Im} \left( \frac{-1}{\epsilon(\mathbf{q}, E)} \right)$$

where  $v$  is the speed of the incident electron,  $n_a$  is the number of atoms per unit volume and  $\theta_E$  is the characteristic scattering angle ( $\theta_E = E/\gamma m_0 v^2$ ). The term  $\text{Im}(-1/\epsilon)$  is often called the loss-function.

This means that the low-loss part of the EEL spectrum can be used to measure optical properties of the material. By determining the energy onset of interband transitions it is also possible to directly measure the bandgap of the material.

At higher energies in the spectrum ( $> \sim 50$  eV) we observe features called ionisation edges. These arise from the excitation of a core electron into the unoccupied electron states. They are entirely analogous to the absorption edges observed in X-ray absorption spectroscopy (XAS), except that electrons are used as the excitation source rather than X-rays. The energy of the ionisation edges identifies the elements present and the

relative intensity in the edges can be used to quantitatively measure the composition. The analysis of EELS spectra to provide qualitative and quantitative composition information using the ionisation edges has been its main application. In the past ~ 10 years, with the development of energy filtered imaging, mapping of compositional distributions has become widespread.

Looking closely at the ionisation edges, it can be seen that there are fine spectral details just above the edge onset. This is called the energy loss near edge structure (ELNES) and it is equivalent to the X-ray absorption near edge structure (XANES). The ionisation edges arise from transitions into the unoccupied states and the ELNES is a reflection of the energy distribution of these unoccupied states (the unoccupied density of states (DOS)). Thus the ELNES can provide information about the bonding environment of the atoms in the material. Studies of the ELNES have become reasonably commonplace in recent years and in many instances have been able to provide important information about the properties of the materials under investigation.

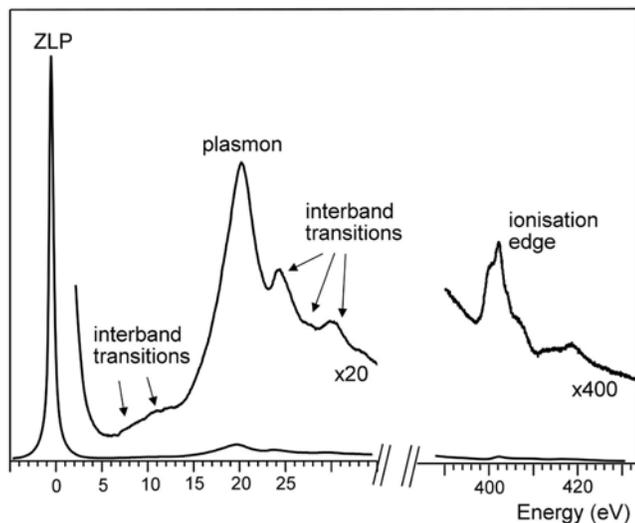


Figure 1. EEL spectrum from GaN illustrating the different spectral features.

## 2 MAPPING EELS

The focus of EELS has been moving away from single spectrum acquisition to mapping and imaging. This can be performed in two ways: energy filtered TEM (EFTEM) and spectrum imaging (SI). In EFTEM, the images are formed by only those electrons that have lost a user-defined amount of energy. By acquiring a large number of energy slices it is possible to improve the quantification and reliability of compositional imaging with EFTEM and this method is sometimes referred to as “image spectroscopy” (IS) [2].

With SI, a focused electron beam is scanned in a raster of pixels and at each pixel, an EEL spectrum is acquired [3]. In both SI and IS a three-dimensional data cube is acquired, with two spatial axes and one energy axis. It

allows the precise correlation between spatial and spectral features. Since each individual EEL spectrum can be used to determine the changes in chemistry and bonding states, the collection of spectra in the data cube has the potential to map these properties in a spatially resolved image. The two approaches to acquiring the data set have distinct merits, with SI sampling more finely in the spectral axis and IS sampling more finely in the spatial axes. As our interest is mostly in the very fine spectral details we will focus on the SI approach.

The key advantage of SI is that having the full spectrum available at each pixel means that the operator does not necessarily need to know what spectral features are present before performing the acquisition. Post-acquisition processing can reveal new and perhaps unexpected spectral features and phases in the materials. It also allows for the full and accurate processing of each individual spectrum and gives better quality and more accurate maps. The key disadvantage is that for a SI to be acquired in a reasonable amount of time, the acquisition time at each pixel must be very short. The individual spectra are very noisy.

The other challenge facing SI is that it produces a very large data set and extracting the important information from such a large dataset will be problematic, particularly when the spectral modulations are small. Whilst routines such as multiple least squares fitting of reference spectra can be used, they require prior knowledge from the operator as to what spectral features are expected. In a SI, which may contain many thousands of spectra and where all the possible spectral components are not known, there is a clear need for (semi-) automatic data processing procedures.

Multivariate statistical analysis (MSA) is a useful technique to analyze large datasets which contains many known and/or unknown variables. This family of techniques has been used in a wide range of research applications to gain insight into spectral data. Principal component analysis (PCA) is one of the most popular MSA approaches and is also widely performed as a first step of other advanced MSA approaches.

The general concept of PCA is to reduce the dimensionality of an original large dataset by finding a minimum number of variables, which describe the original dataset without losing any significant information. PCA extracts the variables as “abstract components”, which are uncorrelated with one another and without any prior knowledge of the dataset [4].

Figure 2 shows an application of EELS SI and PCA analysis to a C nanotube. There is a peak in the C-K ionisation edge due to transitions to unoccupied  $\pi^*$  bands, with the other features are due to transitions to the  $\sigma^*$  bands. The  $\pi^*$  bands in the  $sp^2$  bonded graphene sheets of nanotubes are highly directional in nature. The intensity of the  $\pi^*$  peak can be related to the orientation of the planar sheets in the structure, relative to the electron beam. In the experimental conditions used here the momentum transfer is primarily perpendicular to the electron beam and we see,

as expected, that the  $\pi^*$  peak is more intense when the planes are oriented perpendicular to the electron beam.

The first loading spectrum is the average spectrum. The second loading spectrum contains spectral information that differs from the average spectrum and in this example contains the orientation information. It shows an anti-correlation between the  $\pi^*$  and  $\sigma^*$  features and the corresponding score image reflects the orientation of the bonding. Importantly the residual spectrum, shows only noise indicating that those two components describe all of the non-noise information in the spectrum information. A reconstruction of the spectrum image using only the non-noise components is a very effective way to remove noise from SI datasets.

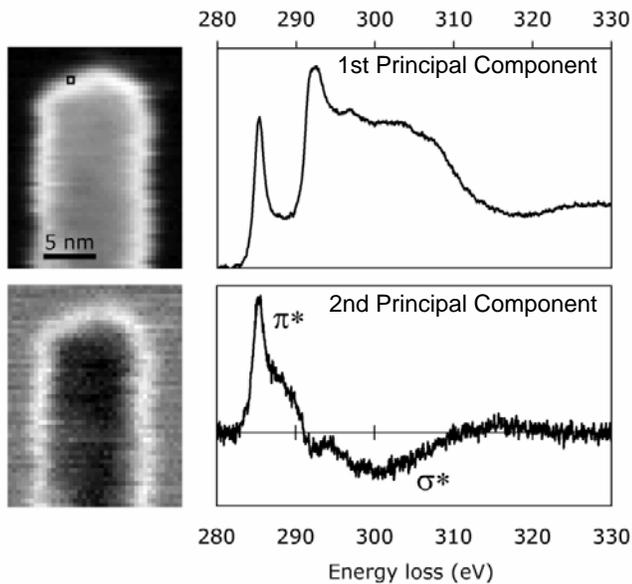


Figure 2. 1st and 2nd principal components from the PCA analysis of an EELS spectrum image from a Carbon nanotube, The 1st component is the average spectrum and the 2nd component shows the orientation of the bonding.

### 3 CALCULATION OF EELS

It follows from the equation in Section 1 relating the loss function to the dielectric function that, if we want to use an *ab initio* method to calculate the low-loss EELS, we must first calculate  $\epsilon$ . The dielectric function describes the response of the material to a time-dependent electromagnetic field and the underlying theory is well developed [5]. In many cases the random phase approximation (RPA), also called the independent quasiparticle approximation, is made. The RPA approximates the polarizability of the system as a sum over independent transitions. This approach has been implemented in the OPTIC routine within the WIEN2k code [6].

There has been a significant amount of work done previously on the calculations of the dielectric function and optical properties, but very little of this in the electron

microscopy and EELS communities; an exception being the work of Moreau and others [7,8]. A previous publication of this author applied DFT bandstructure calculations of the electronic structure, dielectric functions and loss-functions to a wide variety of simple materials in order to examine how well low-loss EELS can be predicted [9]. Very good agreement was observed for most materials. For example, Figures 3 and 4 show the experimental and a calculated spectrum for Ag and Au.

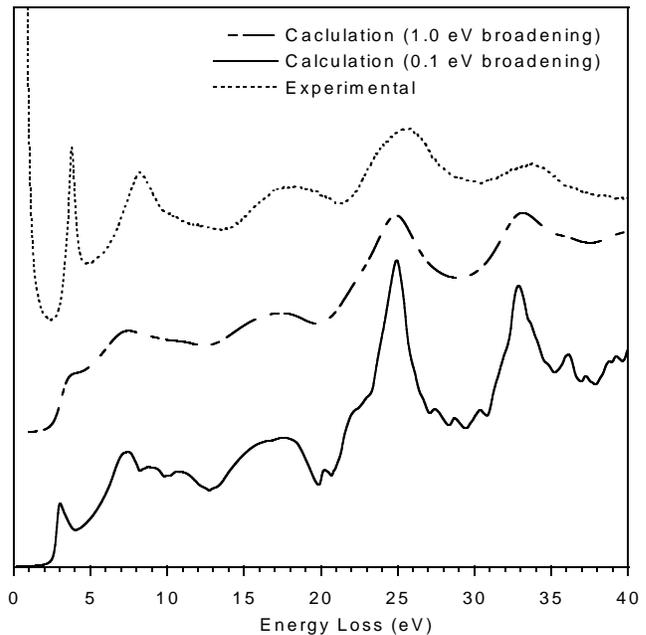


Figure 3. Calculated and experimental low-loss EELS for Ag. Good agreement is observed between the two spectra.

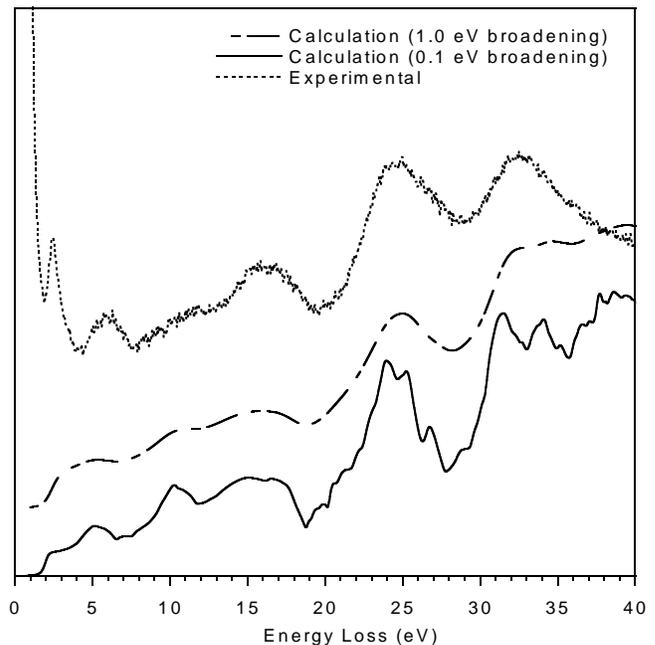


Figure 4. Calculated and experimental low-loss EELS for Au. Good agreement is observed between the two spectra.

The first peak in the Ag spectrum is the bulk plasmon response. The higher energy peaks can be attributed to transitions from the d-band to unoccupied states. The results for Ag contrast with those for Au, where in Au, an interband transitions appear at an energy below the bulk plasmon energy, thus explaining the different colour of Au to Ag.

#### 4 NANOPARTICLE SURFACE PLASMONS

It is well known that small metallic spheres (< 50 nm) have a markedly different optical absorption to that of the bulk metal. The classic example being that of Au nanospheres, found in some ancient glasses and now finding new applications in a variety of areas. The different optical response of nanostructured metallic materials can be explained by the excitation of surface plasmons.

Surface plasmons can also be excited by an electron beam and are observed as low-energy peaks in the EEL spectrum. Figure 5 shows the region of the EELS spectrum containing surface plasmons for three different nanostructured Au materials: a thin film, a sphere and a hemispherical cap. The energy of the surface plasmon for these different geometries is observed at a different energy.

The advantage of the EELS measurements over optical measurements is that, as shown in the example given, the plasmon response from an individual nanosphere or nanocap can be measured. We have also observed that different regions in a nanoporous Au film have a different surface plasmon responses.

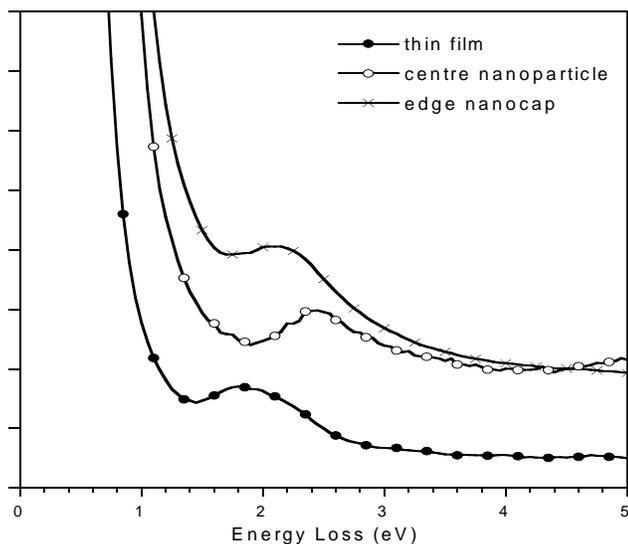


Figure 5. Low-Loss EELS from different structures of gold. The energy of the surface plasmons are seen to shift depending on the geometry of the material being studied: 2.2 eV for a 10 nm thin film, 2.5 eV for a 30 nm spherical nanoparticle and 1.9 eV for a hemispherical cap.

#### 5 SUMMARY

EELS is an experimental technique that can measure electronic structure at the nanometer scale. By implementing spectrum imaging (SI) it is possible to map features in the spectrum and so, in principle, map materials properties at the nanometer scale. The low-loss region can be related to optical properties, and in particular, as shown here, the optical response of individual nanoparticles can be readily examined. A thorough understanding of the EELS spectrum requires *ab initio* simulations of the spectra and it has been shown that for many systems that DFT calculations within the RPA approximation work very well.

#### REFERENCES

- [1] Egerton RF., "Electron Energy Loss Spectroscopy in the Electron Microscope". New York and London: Plenum Press, 1996.
- [2] Thomas PJ, Midgley PA. "Image-spectroscopy -I. The advantages of increased spectral information for composition EFTEM analysis". *Ultramicroscopy* 88:179-186, 2001,
- [3] Jeanguillaume C, Colliex C. "Spectrum-image: the next step in EELS digital acquisition and processing." *Ultramicroscopy* 28:252-257, 1989.
- [4] Bosman M, Watanabe M, Alexander DTL, Keast VJ. "Mapping chemical and bonding information using multivariate analysis of electron energy-loss spectrum images." *Ultramicroscopy*, In press.
- [5] Onida G, Reining L, Rubio A. "Electronic excitations: density-functional versus many-body Green's-function approaches" *Reviews of Modern Physics* 74:601-659, 2002.
- [6] Schwarz K, Blaha P, Madsen GKH. 2002 "Electronic structure calculations of solids using the WIEN2k package for material sciences". *Computer Physics Communications* 147:71-76, 2002.
- [7] Launay M, Boucher F, Moreau P. "Evidence of a rutile-phase characteristic peak in low-energy loss spectra". *Phys. Rev. B* 69:035101, 2004.
- [8] Moreau P, Cheynet MC. "Improved comparison of low energy loss spectra with band structure calculations: the example of BN filaments." *Ultramicroscopy* 94:293-303, 2003.
- [9] Keast VJ. "Ab Initio Calculations of Plasmons and Interband Transitions in the Low-Loss Electron Energy-Loss Spectrum" *Journal of Electron Spectroscopy and Related Phenomena* 143:97-104.