Abstract. The development of monochromators and aberration correctors for transmission electron microscopes (TEM) has paved the way for a level of imaging and analysis that is unmatched by other methods. While current instrumentation does not permit the optimum spatial resolution of the microscope to be coupled with this high energy resolution, detailed spectroscopic analyses can be performed with ~1nm spatial resolution. Combined with ~0.1 eV energy resolution this is particularly useful for the analysis of the low-loss region of the spectrum, permitting quantum confinement effects and optical responses of individual nanostructures to be measured. Higher spatial resolution can be obtained from aberration corrected STEM, where spectral resolution of ~0.4eV can be coupled with a spatial resolution of <0.1 nm. Such resolution is particularly useful for analyzing core-loss signals at defects and interfaces, where localized structural and compositional modulations are expected to have a large effect on the structure-property relationships. Results from aberration corrected and monochromated systems will be presented to highlight the application of EELS to the study of Si3N4, GaN and extraterrestrial particles.

1. Introduction
The ability to use Z-contrast images in the scanning transmission electron microscope (STEM) to position the electron beam for electron energy loss spectroscopy (EELS) provides a powerful tool to characterize individual nanostructures, defects and interfaces [1-3]. Knowledge of the exact location of the beam (to ~0.1 nm precision) enables the local electronic structure to be correlated precisely with the atomic structure and composition of the feature being investigated. Although EELS has been used...
For decades to investigate the local electronic properties of materials [see for example 4], the recent development of monochromators and aberration correctors has significantly extended both the sensitivity of the method and its spatial resolution. In this paper, recent results from both monochromated and aberration corrected instruments will be presented that highlight the increases in sensitivity and resolution that have been achieved.

2. Instrumentation

2.1. Monochromated Schottky Field Emission FEI Tecnai F20

The results described here were obtained on the FEI monochromated Tecnai F20, operating at 200kV [5-8] in the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory (LBNL). Spectra are recorded on a post-column Gatan electron energy-loss spectrometer, with an insertable annular detector being used for STEM imaging. For the Tecnai F20 at NCEM an electron probe of 0.14 nm in diameter has been demonstrated [9]. In this high spatial resolution mode with the monochromator off, an energy resolution of 0.5 eV is achieved. The current system does not achieve such small probes when the monochromator is on (~0.5 to 1 nm probes have been achieved [10]). The reason is that the position of the virtual source does not allow the condenser lens system to achieve the level of demagnification necessary for the smallest probe. However, as the main benefit of the monochromator is for low-loss EELS, this is not a major limitation as the spatial resolution of EELS at energy losses below ~20 eV is hardly affected by the actual size of the probe [5].

2.2. Nion Aberration Corrected Cold Field Emission VG HB501

The ability to obtain high spatial resolution EELS (<0.1nm) has arisen through aberration correction of a VG dedicated STEM [11]. The high spatial resolution studies in this paper [12] were performed at the UK superSTEM laboratory on a VG HB501 dedicated STEM fitted with a 2nd generation spherical aberration corrector, a spectroscopy coupling module (both manufactured by Nion Co.) and a Gatan Enfina electron energy loss spectrometer. The spectroscopy-coupling module is necessary to compress the angular range of the bright field disk (which is large due to the convergence angle required for the 0.1 nm resolution) so that the 2mm entrance aperture to the spectrometer can collect a reasonable fraction of the electrons that pass through the sample while maintaining 0.4 eV spectral resolution. Particular care was taken with the environment, resulting in a spatial resolution of 0.1 nm with about 60 pA probe current and a drift stability of 0.05nm in 100s. The convergence semi-angle of the electron probe was 24 mrad for both imaging and spectroscopy. The collection semi-angle for the EELS spectra was 15 mrad and for the Z-contrast imaging was 70 to 200 mrad.

3. Results

3.1. Si$_3$N$_4$ Grain Boundaries

As an example of the use of the FEI Tecnai F20 in the high spatial resolution mode, here we discuss results from the analysis of grain boundaries in Si$_3$N$_4$. Bulk Si$_3$N$_4$ ceramics are currently limited by a brittleness that reduces their reliability. Such properties can be improved by the incorporation of an intergranular phase. An understanding of how this phase governs the macroscopic mechanical properties has been limited because the amorphous morphology of the phase and its small dimension makes analysis difficult. However, the ability of the scanning transmission electron microscope to probe the interface structure offers the potential to understand the atomic scale phenomena occurring in these materials. Figure 1 shows the interface between the intergranular phase and a Si$_3$N$_4$ matrix grain for each of four sintering additive types, Sm$_2$O$_3$, Er$_2$O$_3$, Yb$_2$O$_3$ and Lu$_2$O$_3$ [9]. The bright spots that appear at the interface in the amorphous intergranular phase, are attributed to columns of Sm, Er, Yb and Lu atoms, respectively. These images clearly show that the atomic bonding of those atoms along the Si$_3$N$_4$ prismatic plane is periodic and occurs at very specific atomic sites. Sm atoms bond in single-atom configuration to both positions, A and B. This changes with the slightly heavier, but
smaller, atoms Er, Yb and Lu, as they bond in pairs at position A with the pair-axis oriented parallel to the prismatic plane. The atom-pairs of Lu, Yb and Er appear to be separated differently; Lu: 1.43±0.07 Å, Yb: 1.46±0.05 Å and Er: 1.48±0.04 Å. This growing pair separation can be related to the increase of the valence shell radius from Lu to Er and demonstrates that the bonding of the rare-earth elements to the interface is controlled by atomic size.

Figure 1. Chemically-sensitive, atomic resolution STEM images: Sm, Er, Yb, and Lu-doped Si$_3$N$_4$. The matrix grain is oriented along the [0001] zone axis such that the open Si$_3$N$_4$ crystal structure is clearly visible at the atomic level.

Figure 2. Precise EELS measurements from Si$_3$N$_4$ containing Sm. The results for (A) the Si L$_{23}$ and (B) the Sm N$_{45}$ edges identify the individual bonding characteristics at positions A and B. The Si L$_{23}$ edge shows a double peak at position A but not at position B.

Precise EELS measurements to identify specific atomic bonding configurations were performed on the Sm-containing sample. The results in Figure 2 show the electron loss spectra for the Si L$_{23}$ and the Sm N$_{45}$ edges measured at positions A and B along the interface. There is no difference between the spectra at the Sm N$_{45}$ edge, suggesting that the atomic environment and bonding characteristics are the same for the Sm atoms at both locations. The difference in the electron loss spectra from position A and B is at the Si L$_{23}$ edge. A double peak (102 eV and 103.5 eV) appears in the spectrum taken from atom position A. The first peak can be identified with a Si-N bond while the second peak is associated with a Si-O. This indicates that the atomic environment around the terminating Si atoms on the Si$_3$N$_4$ prism plane that surround position A is most likely an oxygen atom. In contrast, the atomic environment of the Si atoms on the prism plane that surround position B appears to be nitrogen.
3.2. Interplanetary Dust Particles (IDPs)

As an example of the use of the monochromated electron beam in the Tecnai F20, we present the analysis of a series of interplanetary dust particles [10]. Here the advantage of the monochromator is that the zero loss peak can be accurately subtracted from the spectrum and precise low-loss EELS analysis performed. This is possible as apart from the narrow energy spread, another advantage of a monochromated electron beam is its symmetric energy distribution. This symmetry (Figure 3) allows for an accurate subtraction of the zero-loss and a detailed interpretation of the low-loss spectrum.

![Figure 3](image)

**Figure 3.** (a) Comparison of the zero-loss peaks of an unfiltered Schottky field emission microscope (200 kV), a cold field-emission microscope (100 kV) and a monochromated Tecnai F20 (200 kV). (b) Spectrum of a CdSe particle (dotted), the zero-loss peak (dashed) and the energy-loss function (full).

![Image of an IDP sample](image)

**Figure 4.** (a) Image of an IDP sample. (b) Low-loss spectra from various forms of carbon and GEMS in the IDP samples. These types of samples all show a peak at 5.7 eV.

It is this ability to observe transitions in the low-loss region of the spectrum that is vitally important in the analysis of IDPs. Much of what is known about grains in space comes from spectral features observed in emission, polarization and absorption. The strongest feature by far in the ultraviolet (UV)-visible (VIS) wavelength range is the “~217.5 nm bump” (corresponding to an energy of 5.7 eV) that can be observed along almost every galactic line of sight. Forty years after its discovery, the origin of the feature and the nature of the carrier(s) remain controversial. The feature is
enigmatic because although its central wavelength is almost invariant its bandwidth varies strongly from one sightline to another, suggesting multiple carriers or a single carrier with variable properties. Using the monochromated beam, a series of IDP samples was investigated (Figure 4) [12]. Here it can be seen that the samples are found to consist of various forms of organic and inorganic carbon and silicate glasses embedded with metals and sulphides (GEMS). All of these compositions show a feature at 5.7 eV with a width that is dependent on the material present. Using the TEM to select a specific area and the monochromator to look at a particular low-loss transition, the composition of interstellar matter giving rise to the 217.5 nm bump (and the different materials that give it its width) can thus be identified.

3.3. Dislocations in GaN

To highlight the level of spatial resolution obtainable with aberration corrected systems, here we discuss results from MOCVD-grown GaN on a sapphire substrate. These samples are n-type doped materials, with an approximate Si-dopant concentration of 5x10^{17}. From superSTEM images of ~50 mixed dislocations, the core structure of the undissociated mixed dislocation was determined to be an 8-atom ring core, just like the edge dislocation (Figure 5) [13,14]. It is possible to distinguish this dislocation from edge dislocations due to the large amount of strain present from its screw component. The level of strain (and large Burgers vector) present at mixed dislocations is generally not favorable in crystals, and it might be expected that it would structurally re-order to reduce its energy. Figure 5 shows a mixed dislocation that has split into two partial dislocations with a stacking fault in between. This stacking fault lies along the [110] direction and in the (021) habit plane (i.e. the a-plane).

Figure 5. Aberration-corrected Z-contrast image of (a) a full-core mixed dislocation, with the core of the dislocation outlined in the box and (b) a dissociated mixed (partial dislocation), showing a stacking fault in between the (edge and screw) dislocation cores of approximately 3 nm length.

This dissociation of dislocations into partials separated by a stacking fault is known to occur in many materials, but has never been observed on the atomic scale in materials with hexagonal crystal symmetry. The structure of the core appears to be a screw dislocation at the left end and an edge dislocation at the right end with a stacking fault between the two. The screw component causes a distortion in the z-direction, which gradually decreases as the stacking fault widens to accommodate the strain of the edge component. The assignment of these features can be confirmed by EELS. Figure 6 shows spectra obtained from various parts of the partial dislocation compared to a bulk spectrum. The spectrum from the 9-atom ring shows a fine structure that is very similar to that of the bulk, while the spectra from the 8-4 atom rings in the stacking fault and the 7-atom ring show a fine structure that is dramatically different. The intensity in the first peak far exceeds the second peak, meaning that there is now an increase in the density of unoccupied states at the conduction band minimum. Based on the previous results and analysis of the other two types of dislocation cores [13,14], we can see that this change in fine structure is related to the screw component of the mixed dislocation. A similar fine structure to the bulk (in the 9-atom ring) was observed in the edge dislocation. The 8,4 atom rings also contain distortions in the c-direction and exhibit a fine structure similar to the screw dislocation.
4. Conclusions

Monochromators and aberration correctors have significantly increased the sensitivity of energy loss spectroscopy, its applicability to the low-loss spectroscopy and its spatial resolution for core-loss spectroscopy. When monochromators and aberration correctors are incorporated into the same instrument in the future, spatial resolution of 0.1 nm and energy resolution of 0.1 eV can be expected.

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