Low-loss EELS of 2D boron nitride

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Abstract. Electron energy loss spectroscopy provides a probe of the dielectric function of a material which can be affected by the size and morphology of a sample. In this paper, the effect on the loss function when hexagonal boron nitride is reduced to a single layer is investigated. The previously predicted red-shift of the spectrum is seen in experiment and reproduced by modelling using density functional theory. The dielectric function shows that, for a single layer, the lack of screening causes the real part of the dielectric function to tend to 1 so that the loss function resembles the imaginary part of the dielectric function.

1. Introduction
Many layered structures can be exfoliated down to 2D materials in a similar way to which graphene can be produced from graphite [1]. As in the case of graphene and graphite, these 2D materials can possess different properties to the related bulk materials and this has the potential to be exploited in a new generation of nanoelectronics. In order to reach this goal, understanding and characterization of these new 2D materials is vital. Low-loss electron energy loss spectroscopy (EELS) has already been used successfully to characterize graphene and to map the number of layers [2]. The EELS spectrum is related to the dielectric function of a sample, which in turn can be affected by size and morphology. Graphene and all 2D materials have been predicted to have a distinctive EELS spectrum [3]. In this paper we explore the low-loss spectrum of 2D hexagonal boron nitride and in order to understand the changes in the spectrum, we compare experimental data to simulated low-loss EELS spectra.

2. Experiment
Flakes of hexagonal BN were produced using liquid-phase exfoliation [1]. EELS spectra were then obtained using an FEI Titan 80/300 TEM/STEM operating in STEM mode. As BN suffers from beam irradiation in the same way as carbon materials [4], the microscope was operated at 80kV in order to minimize the damage. The energy resolution, defined by the full width half maximum of the zero loss peak, was 0.7eV.

A typical high angle annular dark field image taken from the BN sample is shown in Figure 1a. From the image, it can be seen that the thickness of the flakes vary. EELS spectra taken from a thick and a thin part of a BN flake are shown in Figure 1b. It can be seen that the reduction in thickness of the sample has a large effect on the low-loss EELS spectrum. The spectrum taken from the thin region shows a decrease in the peak at 26.5eV when compared to the spectrum from the thicker sample, as well as a shift of the peak at 8.5eV. This behaviour is similar to that seen for graphene [2].
3. Loss function simulations

The low-loss part of the EELS spectrum is described by the loss function, which is related to the dielectric function. There are several possible approaches to modelling the dielectric function of a composite material and the method used here is to calculate the dielectric function of the composite system using density functional theory (DFT). An alternative approach, which is also very popular, is to use an analytical expression to relate the bulk dielectric function to a specific geometry. Although that approach has been used to model the loss function of multi-walled carbon nanotubes [5], we have found that it is less successful for single BN layers.

DFT allows calculation of the ground state electronic structure. The dielectric function describes the response of a material to an external field, and is not a ground state property. The DFT ground state can be used as a starting point to calculate the dielectric function and some level of approximation must be made. All the simulations presented here have been carried out using the pseudopotential DFT code CASTEP [6] which uses the random phase approximation (RPA) to calculate the dielectric function. RPA has been shown to be adequate for EELS simulations due to cancellations between the quasiparticle shift and long range term near the plasmon energy [7]. Previous calculations on graphite [3] and BN [8] layered structures have shown that local field effects are negligible when the polarisation is in the plane of the material, but are required to accurately reproduce the spectrum from the out of plane polarisation. In this paper we are looking to explain the general trends, and so local field effects have not been included.

The simulations in this paper have been carried out using the PBE exchange-correlation functional and ultrasoft pseudopotentials. Plane waves up to a maximum of 340eV where included in the basis set, and the Brillouin zone was sampled using a regular grid with a maximum spacing of 0.03Å⁻¹. These parameters were checked so that any increases in cut-off energy or decrease in k-point spacing had no visible effect on the spectrum. The simulations have had a Gaussian broadening of 1eV applied.

Figure 2a shows the simulated loss function for bulk BN along with the experimental data from the thick region of the flake. There are several potential ways to stack the BN layers to produce bulk BN. Five different stacking geometries were simulated, and the results were all found to be very similar so only simulations from the AA’ structure (i.e. the atom type alternates along the c-axis) are shown here. As BN has an anisotropic structure, the dielectric function is also anisotropic. As a result the loss function varies with the direction of q. Figure 2a shows spectra simulated for q parallel to the c-axis (q||c), q perpendicular to the c-axis (q-c) and q averaged over all directions (poly). The experimental data in Figure 2a is reproduced relatively well by the spectrum simulated for an averaged q which tells us that the thick areas of the flake are bulk like.
In order to simulate single layers of BN, the $c$ parameter was increased to separate the layers. As the layers do not interact, the stacking is unimportant and an AA stacking is used for this calculation. The $c$ parameter was increased until the changes in the spectrum became very small and it was found that a spacing of 4.5nm was required. This is a larger value than would have been required to converge core-loss EELS spectra because in that case the initial state is very localised. Figure 2b shows spectra simulated for a single layer along with the previous bulk calculation. Only data for an average value of $q$ is shown.

4. Discussion

The simulated data shows that the main plasmon peak and the peak around 8eV move downwards in energy and that the plasmon peak decreases in intensity when the structure is reduced to a single layer. The differences between the single layer and bulk are in agreement with the generic changes predicted for 2D layered systems by Marinopoulos et al. [3].

The experimental data from the thick section of the BN flake has peaks at 8.4eV, 12eV, 18eV and 26eV. Figures 3a and c show the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric function for bulk BN with $q\parallel c$ (a) and $q\parallel c$ (c) along with the corresponding loss function. If $\varepsilon_1$ is zero and $\varepsilon_2$ is small, the loss function will show a peak, which is generally interpreted as a plasmon. The peak at 26eV in the experimental data corresponds to a zero-crossing of $\varepsilon_1$ for $q\parallel c$ and is the collective excitation of all the electrons (i.e. the bulk plasmon). Figures 3b and 3d show $\varepsilon_1$ and $\varepsilon_2$ for the layers with a spacing of 4.5nm (single layers). For $q\perp c$, the zero-crossing of $\varepsilon_1$ has disappeared which indicates a strong damping of the bulk plasmon. As seen by Marinopoulos et al. for graphite $\rightarrow$ graphene, as the interplanar distance in BN is increased $\varepsilon_1$ tends to 1 and the loss function tends towards $\varepsilon_2$. The plasmons have been damped to the extent that the loss function is dominated by single electron transitions. The situation for $q\parallel c$ is more complicated due to a strong coupling between plasmons and interband transitions. For a single layer, however, the damping of the plasmons again means that the loss function follows the form of $\varepsilon_2$. Comparison of the simulated data for a layer and the spectrum from the thin region of the flake suggests that the flake is thicker than a single layer.

5. Conclusions

When hexagonal BN is reduced to a single sheet, the low-loss EELS spectrum changes in the way predicted by Marinopoulos et al. [3]. DFT is able to model these changes and explain the behaviour of the loss function. As the layer separation is increased, the screening within the sample is reduced such
that the real part of the dielectric function tends to 1 and the loss function resembles the imaginary part of the dielectric function.

Figure 3: Real and imaginary parts of the dielectric function and loss function for bulk (a and c) and layer (b and d) BN with $q\perp c$ (a and d) and $q||c$ (c and d).

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