Sub-nanometer resolved measurement of the tunnelling effective mass using bulk plasmons

V. Stolojan\textsuperscript{1}, P. Moreau\textsuperscript{2}, M. J. Goringe\textsuperscript{3} & S. R. P. Silva\textsuperscript{1,}\textsuperscript{*}

\textsuperscript{1} Advanced Technology Institute, University of Surrey, Guildford, GU2 7XH, UK
\textsuperscript{2} Institut des Matériaux Jean Rouxel, Université de Nantes-CNRS, Laboratoire de Chimie des Solides, 44322 Nantes, France
\textsuperscript{3} School of Engineering, University of Surrey, Guildford, GU2 7XH, UK
\textsuperscript{*} e-mail: s.silva@surrey.ac.uk; Fax. +44 (0)1483 686081

KEYWORDS : superlattice, EELS, tunnelling mass, plasmon delocalisation.

Superlattices are periodic structures where the constituents alternate between low and high band gap materials; the resulting quantum confinement tailors the resulting device’s properties and increases their operating speed. To understand the properties of such structures on the nanoscale, the electronic structure needs to be sampled with high spatial resolution. Here we show that, in layered structures, the bulk collective oscillation of the sample’s electrons can be defined for ‘sandwiched’ layers as thin as 5Å, due to the very effective screening at the ‘sandwiched’ layer’s interfaces, well below the bulk plasmon extinction distances. Using this, we measure the quantum confinement in diamond-like carbon superlattices as a function of well width, as derived from the plasmon energy, and show that it is well described by the ‘particle-in-a-box’ model. We
also find the effective tunnelling mass $m^* = 0.067m_e$, using the ‘particle-in-a-box’ model, which makes diamond-like carbon films as feasible candidates for electronic devices.

DLC films have optical band gaps from 1.2-4.0 eV controllable through the deposition parameters, such as plasma power\textsuperscript{[1]}. They are an attractive option for the semiconductor industry due to the inexpensive, fast and reliable manufacturing method. When the deposition parameter is varied cyclically during deposition, we obtain a band gap modulation in an essentially homogenous material system\textsuperscript{[2, 3]}, leading to higher device speeds and controllable electronic properties. The confining potential of a bandgap-modulated artificial structure on the electron wavefunction leads to the quantization of the particle momentum and energy. The resulting energy levels are controlled by the well’s width and depth\textsuperscript{[4, 5]}. When the artificial structure consists of several alternating barrier and well layers, the resulting quantized energy levels can degenerate into bands, depending on the tunneling through the barriers and implicitly on the barrier width and height\textsuperscript{[5]}. This can lead to the tailoring of devices for specific applications, such as frequency generators for the mobile phone industry.

In an electron microscope, it is possible to image the barrier and well layers constituent of a superlattice, even when their respective physical properties are very similar, through Fresnel imaging\textsuperscript{[6]}. The beams that pass through the different components of the superlattices interfere, leading to phase differences and contrast in the bright field image. However, a large amount of defocus (3÷6 $\mu$m) is required for good contrast (Fig. 1a) and the amount of information about the local electronic structure is limited. Energy Loss Spectroscopic Profiling (ELSP) is a route to obtaining spatially resolved energy loss
spectra (and therefore the spatially-resolved electronic structure) across linear features in transmission electron microscopes, under parallel illumination\cite{7}. This method utilizes the manner in which a Gatan Imaging Filter (GIF) forms images and energy loss spectra to collect two-dimensional data sets where one axis is the energy loss and the other orthogonal axis is the spatial dimension normal to the linear feature of interest (Fig. 1b).

Figure 1 a) Defocused (-5\,\mu m) energy-filtered image of the superlattice B120W40, with the barriers and wells indicated by the arrows. b) the corresponding ELSP image to Figure 1a, at the same defocus for visibility, showing the plasmon energy across the superlattice (the zero loss peak has been subtracted). The vertical dimension is identical to that in Fig 1a, to within a scaling factor. Subsequent experiments were performed at gaussian focus to eliminate elastic contributions to the plasmon peak energy.

Because the spatial dimension is acquired in parallel with the energy loss information, this method offers a very accurate positioning of each energy loss spectrum with respect to the linear feature of interest. A line at constant zero energy through Fig. 1b is identical,
to within a scaling factor, to an energy filtered image of the superlattice, integrated in the direction parallel to the linear feature.

The superlattices were deposited on (001) Si substrates using plasma enhanced chemical vapor deposition, with the bandgap modulated by alternating the dc self-bias between -190 and -265V, under computer control\cite{2,3}. The nominal dimensions of the sample are contained in its name, where B140W80 signifies that the barrier width is 140Å whilst the well width is 80Å respectively. Cross-sectional samples for TEM were prepared by mechanical thinning and polishing, followed by ion beam polishing. The as-deposited tunnel and barrier control films were removed from the Si substrate by using a HF:HNO$_3$ solution and floated onto Cu TEM grids.

For each of the superlattices and as-deposited tunnel and barrier samples, we have collected 40 images of the low energy loss spectra across the superlattices (the plasmon loss), 40 images of the beam in the absence of the specimen (the zero loss) and also 40 images of the zero loss beam with a preset voltage wobble applied to the drift tube for calibration of the energy scale. The typical energy dispersion was ~0.1eV/pixel whilst the typical dispersion of the spatial dimension was ~0.4nm. For each data set, the images were aligned in energy to within a pixel and the low loss set was also aligned, to within a pixel, onto a recognizable feature, such as the Si to superlattice interface or the superlattice-glue interface. The data for analysis was gathered with the sample near Gaussian focus, as opposed to Fig. 1b, where a large amount of defocus (~5 µm) was applied for visibility of layers.
The origin of the energy loss scale was defined as the centre of a Lorentzian curve fitted to the peak corresponding to electrons that have suffered no inelastic scattering (the zero-loss peak). Typically, at least 25 data points were fitted, which means the origin of the energy scale was defined to within 20meV whilst the energy dispersion was determined to within 5meV. A modified Lorentzian curve was used to fit the plasmon energy, over typically 100 data points (i.e. to within 10meV).

Figure 2 shows the variation of the plasmon energy across two of the superlattices, B140W80 and B120W40; we note that the energy difference of the plasmon peaks in the barrier and well decreases for the narrower well.

Figure 2. Comparison of the plasmon energy profiles across superlattices B140W80 and B120W40, showing a decrease in the barrier-well plasmon peak energy difference with decreasing well width, suggesting an increase in the well band gap.

The discussion of the spatial resolution of the information thus collected has two separate components: one relates to the instrument (dispersion, drift, chromatic aberration) and the other one relates to the delocalization of the physical event studied,
i.e. the energy lost by the incident electron through excitation of the collective oscillation mode (plasmon).

The short acquisition times used (0.5s) minimize the loss of spatial resolution due to drift (broadening~0.1 pixels) whilst the small energy range studied (0-25eV) means we can also neglect the effect of chromatic aberration. The most important contribution to the spatial resolution broadening is the ability to align the images to within a pixel. With care this can be achieved, in which case (for a normal distribution of alignments to within a pixel) the broadening is approximately 0.7nm (for a dispersion of ~0.45 nm/pixel).

Bulk collective modes of oscillation extend (normal to the beam direction) typically over 5-10nm\cite{8}. However, an interface between two media leads to the establishment of a surface mode of oscillation which acts to screen out the bulk plasmons from each other. This is known as the ‘begrenzungs’ effect\cite{8,9} and is expressed, as one approaches the interface from medium of dielectric function \(\varepsilon_A\), as the replacement (and not the superposition) of the bulk plasmon of medium A with the interface plasmon between A and B. In order to evaluate the increase in plasmon energy in the middle of the well that might be caused by the contributions from the interface plasmon and the barriers either side, we simulate the dielectric response in a theoretical structure consisting of a one-dimensional well of variable width, confined by infinitely long barriers. We use the classical dielectric approach\cite{10} to calculate the excitation probability and the energy loss of the relativistic electron, as a function of its position with respect to the well center. In solving Maxwell’s equations and applying the proper boundary conditions, formulae are obtained for a sandwich interface\cite{11}. Dielectric functions derived from the low energy
loss spectra of the well and barrier test layers deposited under the same conditions as in the superlattices studied were input in a dedicated program[12].

Before comparing with the experimental results, the calculated positions of the plasmon energies across a well are convoluted with our estimated spatial resolution (~0.7nm).

Figure 3a compares the plasmon energies across a 8 nm well and a 3 nm well, showing that there is a minute increase in the plasmon energy at the centre of the well.

Therefore, whilst the bulk plasmons are delocalized events, which can extend over several nanometers, the presence of interface excitations and their effective screening confines bulk plasmons within the interfaces, allowing for their measurement within areas narrower than their extinction distances. Only when the well width becomes small enough for the surface plasmons to couple (<1nm) there is a more significant contribution to the plasmon energy in the well from the surface and barrier plasmons (Fig. 3b). Even for well widths down to 0.5nm, it is possible to interpret the bulk plasmon energy by modeling the changes and applying a suitable correction.

Figure 3. a) Theoretical variation in the plasmon peak energy, calculated for well widths of 3 and 8nm respectively, using the relativistic dielectric theory on a sandwich model
layer, showing that there is very little contribution to the plasmon energy at the middle of the well from the adjacent barrier bulk plasmons and interface plasmons. The model used the measured dielectric functions of the test barrier and well layers deposited under identical conditions to the layers of the superlattices. b) Comparison of the barrier-well plasmon peak difference calculated with the effective mass as a parameter (half-filled triangles m* = 0.87m_e and open circles m* = 0.067m_e). The experimental results (filled squares) fit the lower effective mass. Also shown is the calculated contribution from the adjacent bulk plasmons and interface plasmons (open triangles), which is negligible for the ‘sandwiched’ layer thickness down to 1nm and accountable for layer widths down to 0.5nm.

Figure 3b also compares the experimental difference between the barrier and well plasmon energies, as a function of well width, with two theoretical calculations of this energy difference. The change in plasmon energy $E_p$ can be modeled using the nearly-free-electron model, with each electron bound by the gap energy $E_g$:

$$ E_p^2 = \hbar^2 \frac{\rho_e e^2}{\varepsilon_0 m} + E_g^2 $$

where $\rho_e$ and $m$ are the density of valence electrons and their mass, $e$ is the electron charge, $\hbar$ is the reduced Planck constant and $\varepsilon_0$ is the permittivity of vacuum. $E_g$ is the Penn gap, a parameter introduced to adjust the free electron model at small values of the wave vector $k$, for Bragg reflections and Umklapp processes (non-dipole transitions). The Penn gap is defined through the relationship:

$$ n^2 = 1 + \left( \frac{E_p}{E_g} \right)^2 $$

$$\varepsilon$$
Using the measured refractive indices $n_{\text{barrier}}=2.1$ and $n_{\text{well}}=2.2$ and the plasmon energies measured on the test barrier and well layers ($E_{p\text{barrier}}=24.400\text{eV}$ and $E_{p\text{well}}=24.225\text{eV}$), we calculate the Penn gap energies to be $E_{g\text{barrier}}=13.210\text{eV}$ and $E_{g\text{well}}=12.36\text{eV}$. These values are then used to model the changes in the ground state of an electron wavefunction trapped in the resulting well of depth $0.425\text{eV}$ (half the difference between the bandgaps), as a function of a well thickness. These “particle in-a-box” calculations are performed considering firstly the effective mass that has been associated with the plasmon energy of amorphous carbons\cite{15,16} ($m^*=0.87m_e$) and then the effective mass found by Silva et al\cite{2,3} to model the change in the optical properties of the superlattices, as a function of well width ($m^*=0.067m_e$)

Assuming that the free-electron component in equation 2 does not change with changing well width, we obtain the difference between the bulk and the well plasmon energies as a function of well width, for the two effective mass hypotheses (Fig. 3b, half triangles, open circles). From Fig. 3b, it is clear that $m^*=0.067m_e$ is a good fit for our measured changes in the plasmon energies between a well and its surrounding barriers, taken as an average over all the wells sampled. This confirms the results of Silva et al.\cite{2,3}, who determined the optical band gaps (as opposed to the Penn gaps) of these superlattices and found agreement with the particle-in-a-box model for $m^*=0.067m_e$. Because of the symmetry of the ground state, an inflexion point in the energy diagram is expected at the well boundary, explaining the low value of the effective mass. Therefore, this effective mass is the tunneling effective mass, whilst the value $m^*=0.87m_e$ relates to dipole transitions as selected by the small collector aperture used in acquiring energy loss spectra in an electron microscope (typically a few tens of mrad). Using EELS in an
electron microscope, we can determine the effective mass both at the bottom of the conduction band, as well as at the well boundaries for superlattice structures.

Using spatially resolved low energy loss spectra acquired in a TEM, under parallel illumination, we have characterized the electronic structure of amorphous carbon superlattices. We have shown that the changes in plasmon energy measured for wells, as a function of decreasing well width, are due to quantum confinement and can be modeled using the ‘particle-in-a-box’ theory. By modeling the contribution of the interface plasmon excitations, we show that the delocalized bulk collective excitations measured in the wells and barriers are good measures of the electronic properties of the wells and barriers respectively down to well thicknesses of ~0.5nm, due to the effective screening provided by the interfaces. We find that the tunneling effective mass is $m^*=0.067m_e$; coupled with the high coherence length of carriers, it makes possible high frequency (>10GHz) large area electronics.
References


Dear Sir/ Madam

Re: Sub-nanometer resolved measurement of the tunnelling effective mass using bulk plasmons
Authors: V. Stolojan, P. Moreau, M. J. Goringe and S. R. P. Silva

Please find enclosed the above named manuscript for your consideration for publication in Advanced Materials as a Communication.

This paper describes the measurement of the tunnelling effective mass from sub-nanometre-resolved bulk plasmons of the layers of hydrogenated amorphous carbon superlattices, using energy loss spectroscopy in an electron microscope. This is done in a configuration that allows the simultaneous acquisition of one spatial dimension and the energy dimension, without the need for a focused electron probe. We first show that bulk plasmons can be confined in sandwiched layers to sub-nanometre regions, well within their extinction distances (5-10nm). We then measure directly quantum sized effects in the amorphous carbon superlattices, allowing us to determine their tunnelling effective mass; we find this mass low enough to warrant their application in high-speed carbon-based electronics.

The ability to define and measure this collective mode of oscillation has been previously thought to be in excess of several nanometers, due to the long extinction distances of the bulk plasmons. However, we demonstrate that, in a ‘sandwich’ structure such as a superlattice, bulk collective excitations can be measured in layers with thicknesses as low as 5Å, due to the effective screening of the interface oscillations between the layers component of the ‘sandwich’ structure. The ability to interpret the most easily and readily available signal in an electron energy loss spectrum on the sub-nanometre scale, in layered structures, opens the way to extract chemical, energy, bond hybridisation and structural information on a scale previously unimaginable with bulk plasmons. This also reduces drastically the confines imposed on the stability of the equipment, as the acquisition times are an order of magnitude less than in the case of core-loss excitations. Furthermore, our results show that the interpretation of resonance energies can be pushed to levels of accuracy of 10-20 meV, conceivable only with synchrotron high radiation sources.

Here, we measure the bulk plasmon energy for a range of superlattice well layer widths in order to extract the tunnelling effective mass, which we find to be 0.067m_e, the same order of magnitude as in GaAs heterojunction devices currently used in the electronics industry for high-frequency applications. We also show that such applications can be modelled using classical quantum mechanical theories, such as the ‘particle-in-a-box’ model. The very low tunnelling mass measured could also point the way to a carbon-based electronic material that can be processed inexpensively over large areas, at room temperatures.
Furthermore, the homogenous nature of carbon superlattices (they are essentially the same material) offers a great advantage over crystal structure-based superlattices as it improves the mechanical stability of such devices. Indeed, during our research, we compared the electronic properties and the morphologies of recently grown superlattices with superlattices grown, under identical conditions, more than 10 years ago and have observed very little variation.

This proves that carbon electronics is feasible, and coupled with the efficient, inexpensive and reliable method for depositing amorphous carbon films, it offers a direct and immediate route to the research and development of carbon devices.

We look forward to your response.

Best Regards,
S. Ravi P. Silva
Director, Advanced Technology Institute
Professor of Solid State Electronics
University of Surrey
Guildford, GU2 7XH
UK
Email: S.Silva@surrey.ac.uk

Suggested referees include:

Prof. A. Howie, Cavendish Laboratory, University of Cambridge, UK

Prof. J. Hutchison, Department of Materials, University of Oxford, UK

Prof Y. Ando, Meijo University, Japan

Prof. G. A. J. Amaratunga, Department of Engineering, University of Cambridge, UK

Prof. D. McKenzie, School of Physics, University of Melbourne, Australia.