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Monte Carlo simulations of measured electron energy-loss spectra of diamond and graphite: Role of dielectric-response models

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ABSTRACT

In this work we compare Monte Carlo (MC) simulations of electron-transport properties with reflection electron energy-loss measurements in diamond and graphite films. We assess the impact of different approximations of the dielectric response on the observables of interest for the characterization of carbon-based materials. We calculate the frequency-dependent dielectric response and energy-loss functions of these materials in two ways: a full ab initio approach, in which we carry out time-dependent density functional simulations in linear response for different momentum transfers, and a semi-classical model, based on the Drude–Lorentz extension to finite momenta of the optical dielectric function. Ab initio calculated dielectric functions lead to better agreement with measured energy-loss spectra compared to the widely used Drude–Lorentz model. This discrepancy is particularly evident for insulators and semiconductors beyond the optical limit ($\mathbf{q} \neq 0$), where single-particle excitations become relevant. Furthermore, we show that the behaviour of the energy-loss function obtained at different accuracy levels has a dramatic effect on other physical observables, such as the inelastic mean free path and the stopping power in the low energy (<100 eV) regime and thus on the accuracy of MC simulations.

1. Introduction

Electron beams are widely used in materials characterization for probing composition and structure as well as in the fabrication of electronic devices via plasma-based etching processes and lithography. In particular, the success of electron microscopy and spectroscopy in reaching high resolving power is due on the one hand to the much smaller electron beam wavelength in comparison to light; and on the other hand to the ease of handling electrons, which can be detected, counted and analyzed with respect to energy and angular distribution using electromagnetic fields. Therefore, the study of electron-transport inside materials is of paramount importance to understand and to control the interaction mechanisms and energy-transfer scattering processes that occur at different energy ranges in electronic devices [1–3].

Moreover, the synthesis of novel carbon allotropes, such as nanotubes and graphene, by chemical vapour deposition (CVD) on metals [4] or by mechanical exfoliation resulted in a renovated interest in carbon-based electronics [5–7]. Nevertheless, growth techniques, mainly focused on the enhanced catalytic activity of metallic substrates, are still largely debated [8], being of particular concern the graphene flake after-growth transfer to different semiconductor substrates and the high working temperature of heteroepitaxial synthesis approaches [9]. Unfortunately, difficulties encountered in growing high-quality graphene sheets currently hamper the theoretical potential of this 2D material. Furthermore,

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the use of graphene in micro-electronic applications forces the opening of a band gap [10,11].

However, other stable or naturally occurring allotropic forms of carbon, such as diamond, multi-layer graphene, and graphite, along with its intercalation compounds, could be used as viable candidates for an all-carbon electronics revolution. In particular, diamond was long considered an ideal candidate for enhancing the performances of electronic devices due to its high thermal conductivity and charge mobility, wide band gap, optical isotropic structure and robustness owing to its strong covalent sp^3-hybridized structure. On the other hand, graphite is the most stable carbon allotrope, arranged in the form of a layered solid, showing both strong two-dimensional sp^2-hybridized lattice bonds, similar in strength to those found in diamond, and weak interplanar bonds that make it soft and malleable as well as anisotropic to external perturbations. Furthermore, graphite shows optimal heat and electricity conductivity retaining the highest natural strength and stiffness even at temperatures in excess of 3000 °C.

In this respect, this work is aimed at modelling the electron-transport properties of diamond and graphite films by calculating a number of observables of paramount importance for designing novel optical and electronic devices, such as inelastic mean free path, stopping power, plasmons and secondary electron spectra. The specific goal of our analysis is to unravel the impact that different theoretical approaches for calculating the dielectric function, ranging from ab initio calculations to the use of a parametrized models, such as Drude–Lorentz (DL), may have on the assessment of the dielectric response of these two materials by comparing our simulations with experimental reflection electron energy-loss spectra (REELS). This study represents thus a fundamental step towards a better understanding of the basic properties characterizing both bulk and thin-film carbon materials as well as an important contribution towards the development of an all-carbon electronics.

We notice that all the observables considered in our analysis are based on the accurate assessment of the frequency-dependent dielectric function, which links microscopic properties, such as the band structure of solids, to macroscopic features that are the direct outcome of spectroscopic experiments, such as the absorption coefficient, the surface impedance or the electron energy-loss.

To compute the dielectric function dependence on the transferred momentum we proceed along three different routes: i) first, we use a semi-classical approach, whereby one assumes the knowledge of the long-wavelength or optical limit of the dielectric function ($q \to 0$ limit); this information is usually provided by experimental measurements of optical absorption [12], transmission electron energy-loss experiments [13,14] or ab initio simulations [15]. To go beyond the optical limit, we extend the dielectric response to finite momenta by using a DL model. In this approach, the dielectric function is approximated by a number of damped harmonic oscillators with frequencies equal to the plasmon frequencies obtained by fitting experimental data [16,17] and a friction-type force to simulate general dissipative processes; ii) second approach uses ab initio simulations to calculate the dielectric response for vanishing momentum transfer, eventually extended to finite momenta by a DL model; iii) third, we find the dispersion law of the dielectric function at finite momentum q by using a full ab initio (AI) approach, based on time-dependent density functional simulations [18] in the linear response (LR-TDDFT) [19].

The combination of ab initio calculations with electron-gas models for calculating physical observables such as the inelastic mean free path, has been previously studied also by Nguyen-Truong [20], Chantler et al. [21] and Sorini et al. [22]. In particular, the extension of the dielectric response at finite momenta with the Drude–Lorentz approach turned out to be the most accurate semi-empirical model available, as reported by Garcia-Molina et. al [23].

The so-derived dielectric functions are used as input for a Monte Carlo description of the inelastic scattering probability to calculate the energy loss of electrons along their path within the solid. The comparison between our simulated and recorded REELS allows us to assess the impact that external tuneable parameters and semi-classical assumptions might have on the accuracy of simulated spectral lineshapes.

2. Experimental details

A polycrystalline diamond film was deposited on a silicon substrate in a microwave tubular reactor using a CH_4-H_2 gas mixture. After exposure to atmospheric pressure, the film was inserted into an Ultra High Vacuum (UHV) system equipped with both a sample preparation and an analysis chamber. Highly Oriented Pyrolytic Graphite (HOPG) was cleaved ex-situ before inserting into the UHV system. The two samples were cleaned by annealing at 600 °C for 10 min in UHV. REEL spectra were acquired in a PHI 545 system operating at a base pressure of $\approx 2 \times 10^{-10}$ mbar. The instrument is equipped with a double-pass cylindrical mirror analyzer (CMA), a coaxial electron gun, a non-monochromatic MgKα ($h\nu = 1253.6$ eV) X-ray source and a He discharge lamp. In CMA, incoming electrons cross the surface at a fixed angle with respect to the sample normal, while outgoing electrons cross the surface at a variable angle dependent on the angle between the surface normal and the CMA axis (30°), the entrance angle to the analyser (42 ± 6°) and the azimuth angle in a plane normal to the CMA axis. Spectra are taken at a constant energy resolution of 0.6 eV, as measured on a Pd Fermi edge. The measured FWHM of the zero-loss peak (ZLP) is 0.9 eV. The energy of incident electrons ranges from $T = 250$ eV to $T = 2000$ eV. Once acquired, REEL spectra are corrected for the energy dependence ($E^{-0.9}$) of the analyser transmission function.

3. Computational details

3.1. Computed observables for charge transport simulations

The physical quantity relating the microscopic and macroscopic description of the electron-beam interaction with matter is given by the dielectric response function. It is important to distinguish between microscopic and macroscopic quantities, where the latter are defined as averages over the unit cell of the former. In fact, the total electric field induced by an external perturbing field can exhibit rapid oscillations at the atomic level, while at larger scale the response function is homogeneous. For periodic crystals (as we model diamond and graphite films periodic in the in-plane direction), one can exploit the translational symmetry and the microscopic dielectric function can be conveniently written in reciprocal space, i.e. $\varepsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, W) = \varepsilon(\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G}', W)$, where $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal lattice vectors, $\mathbf{q}$ is the transferred momentum contained in the first Brillouin zone (IBZ) and W is the transferred energy. Using this notation $\varepsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, W)$ is also often called dielectric matrix. It can be shown [19] that the relation between the experimentally measurable macroscopic dielectric function and the microscopic one is [24,25]:

$$\varepsilon(\mathbf{q}, W) = \left[\varepsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q}, W)\right]^{-1} \quad (1)$$

In particular, electron transport observables, such as the energy loss per unit path or the inelastic scattering cross section, are