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Displacement cross sections of electron irradiated graphene and carbon nanotubes

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ABSTRACT

We calculate the displacement cross-sections (DCS) of low dimensional carbon systems under electron irradiation and present an analytical formula being able to evaluate displacement creations under various conditions. The calculations consider Mott scattering, charge screening effects and thermal vibrations of target atoms. DCS values of graphene and single-walled carbon nanotubes (SWNTs) as a function of electron beam energies, substrate temperatures, and tube diameters are calculated through combination with carbon threshold displacement energies obtained from molecular dynamics simulations. For SWNTs, the smaller the tube diameters the higher the DCS values. Such diameter dependence is the most pronounced for low energy electron beams. Furthermore, DCS values are most sensitive to temperatures when electron beam energy is low. However, the temperature sensitivity disappears at higher electron energy, specifically at 200 keV and beyond.

1. Introduction

Defect engineering of low dimensional carbon systems such as graphene and carbon nanotubes (CNTs) are important for various device applications [1–4]. Unique doping and structural modification have been reported under electron and ion bombardments [5–8]. Understanding of displacement creation and damage cascade evolution under particle irradiation are important for further tuning material properties. However, damage calculations in carbon materials have been largely influenced by uncertainty and scattered data from both modeling and experimental studies, as well as the complexity caused by geometry differences among different carbon nanostructures. For example, the threshold displacement energy (E_d) default value is 28 eV in the Monte Carlo simulation code SRIM for carbon materials [9], but experimental studies suggest E_d should be about 15–20 eV for CNTs [10] and 18–20 eV for graphene [11]. For modeling studies on graphene, Banhart et al. reported 22 eV using a dynamic model and 15 eV using a static model [12]. One suggested average is 22.2 ± 0.2 eV [13]. Molecular dynamics (MD) simulations on CNTs of different tube diameters suggest that E_d decreases from 22 eV for large diameter CNTs to 15 eV for the smallest CNT tubes [10,14]. On the other hand, the observation of CNT structural changes under bombardments of a 200 keV electron analysis beam in a transmission electron microscopy (TEM) chamber suggest that the true displacement energy could be even lower [14]. Recent modeling shows that carbon displacement is facilitated when electron momentum transfer direction is aligned with carbon thermal vibration direction, thus the threshold electron beam energy for displacement creation is further reduced [8,15].

Both fundamental studies and technological developments require high accuracy in calculating displacement creation in graphene and CNTs under electron irradiations, particularly in the energy region of 100 keV to 1 MeV since they are typical beam energies used by TEM. Irradiation effects need to be minimized as unwanted disturbance to original structures in many TEM characterization experiments. But in other experiments beam-induced effects are intentionally introduced for in situ electron irradiation and TEM characterization, in order to study radiation responses and subsequent dynamic structural evolutions of irradiated TEM specimens [5]. In both cases, calculations of carbon displacement numbers are needed. The calculations, however, are complicated and need to consider electron screening effects, relativistic energy transfer and thermal vibration of target atoms. Ideally, an analytic formula should be developed with flexibility for describing various electron irradiation conditions.

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2. Modeling procedure

The present study aims to calculate displacement cross-sections (DCS) by considering the complexity mentioned above. First, we calculate the screened Mott differential cross-sections, which give differential cross-sections under specific scattering configurations. Next, the energy transfer from electrons to carbon target atoms, including the influences from thermal vibration, are calculated under specific energy and scattering angle. Then, the total displacement cross-section is calculated through integration of the cross-sections corresponding to energy transfer larger than threshold displacement energies E_d. The integration additionally considers thermal vibration probability distributions from Debye model.

2.1. Screened Mott differential cross section

The first theoretical description of differential scattering cross-sections between a nucleus and a relativistic electron was given by Mott [16]. Unfortunately, the final expression is an infinite series Legendre expansion. Towards more realistic usage, many numerical approximations have been proposed [17–21]. One common approach is to modify Rutherford cross-sections obtained from binary collisions. Furthermore, the screening effect of atomic electrons must be considered [22–27]. The general expression of differential scattering cross section, is given by

$$\frac{d\sigma_{mott}}{d\Omega} = R_{mott} \times \frac{d\sigma_{Ruth}}{d\Omega} \times [1 - F_e(q)]^2, \tag{1}$$

where the term $[1 - F_e(q)]^2$ is the screening factor, R_{mott} is the ratio between Mott differential cross sections and Rutherford differential cross sections. The latter is expressed by Idoeta and Legarda as [20]:

$$\frac{d\sigma_{Ruth}}{d\Omega} = (Z \times r_e)^2 \times \left(\frac{1-\beta^2}{\beta^4}\right) \times \frac{1}{(1-\cos\theta)^2} \tag{2}$$

where θ is the scattering angle of electrons, β is normalized electron velocity v/c (v is the velocity of electrons, and c is the speed of light in vacuum), Z is the atomic number of target atom, and r_e is the classic radius of an electron ($r_e = 2.817938 \times 10^{-13}$ cm). The expression for R_{mott} is much more complicated. One widely used analytical expression was given by Mckinley and Feshbach, but it is valid only for low Z materials ($Z \leqslant 29$). For high Z materials, tabulated data is needed to calculate R_{mott} [21,28,29]. Boschinia et al. proposed the following format to cover a wider electron energy range (1 keV to 900 MeV) and more general target elements ($1 \leqslant Z \leqslant 118$) with 30 coefficients provided for each element [29],

$$\begin{aligned} R_{mott} &= \sum_{j=0}^{4} \alpha_j(Z,\beta)(1-\cos\theta)^{j/2} \\ \alpha_j(Z,\beta) &= \sum_{k=1}^{6} b_{k,j}(Z)(\beta-\overline{\beta})^{k-1} \end{aligned} \tag{3}$$

Under Dirac-Hartree-Fock-Slater screening model, the $F_e(q)$ term in Eq. (1) can be expressed as [27]:

$$F_e(q) = \sum_{i=1}^{3} A_i \frac{[ha_i/(2\pi)]^2}{[ha_i/(2\pi)]^2 + q^2} \tag{4}$$

where h is the Plank constant, and q is the momentum transfer depending on scattering angle and electron kinetic energy. Detail expression of q and tabulated parameters of A_i and α_i are provided in [27].

2.2. Energy transfer from electrons to target atoms and displacement cross section

For collisions with a static target atom without considering thermal vibration, the energy transfer from relativistic electron, E_t, is calculated by

$$E_t = \frac{\left[(E_k + m_e c^2)\sin^2\theta + Mc^2(1-\cos\theta)\right]E_k(E_k + 2m_e c^2)}{\left(E_k + Mc^2\right)^2 - E_k(E_k + 2m_e c^2)\cos^2\theta} \tag{5}$$

where θ is electron scattering direction, E_k is the kinetic energy of electrons, M is the mass of target atom, and m_e is electron mass. If thermal vibration is considered, the final expression of E_t for relativistic electrons is very complicated. In the framework of special relativity, the 4-vector momentum is defined as $P^\mu = [E, P_x c, P_y c, P_z c]$, where E, P, and c, are energy, momentum, and speed of light, respectively. Based on the momentum conservation, $\vec{P}_a + \vec{P}_b = \vec{P}_c + \vec{P}_d$, where $\vec{P}_a$, $\vec{P}_b$, $\vec{P}_c$, and $\vec{P}_d$ are momentum of the electron and the target atom before and after scattering, we obtain the following equation,

$$\begin{aligned} &\left(mc^2 + Mc^2 + E_k + E_{thermal}\right)E_t + m^2c^4 - \left(mc^2 + E_k\right)^2 \\ &- \sqrt{E_k(E_k + 2mc^2)E_{thermal}\left(E_{thermal} + 2Mc^2\right)}\cos\alpha \\ &+ \left[\sqrt{E_k(E_k + 2mc^2)}\cos\theta + \sqrt{E_{thermal}\left(E_{thermal} + 2Mc^2\right)}\right. \\ &\left.\times(\cos\alpha\times\cos\theta + \sin\alpha\times\sin\theta)\right]\sqrt{(E_k - E_t)(E_k - E_t + 2mc^2)} = 0 \end{aligned} \tag{6}$$

where α is target atom's original trajectory before collision, $E_{thermal} = 0.5Mv^2$ is thermal vibrational energy of a target atom and v is vibrational speed of atoms. The Eq. (6) is based on the condition that the target atom's thermal vibration direction is aligned with the electron momentum direction, and the likelihood is determined by the probability distribution under Debye mode. It is worth noting that Meyer et al. provided a simplified analytic expression for E_t, the detailed of derivation of which was not given [15]. The solutions in the present study are obtained by numerically solving Eq. (6), and the results are compared to Meyer et al. [15]. The total displacement cross-section in both methods is calculated by

$$\sigma = \int_{-\infty}^{\infty} p(v)\sigma_d(v)\Theta(v)dv \tag{7}$$

where v is vibrational speed of atoms, $p(v)$ is the probability distribution of speeds and dependent on the Debye temperature of the target atom [15], and $\sigma_d(v)$ is total cross-sections to scatter target atoms with energies larger than E_d. Atomistic vibrations play a role in the recoiled energy E_t, as reflected by the dependence of E_t on $E_{thermal}$ in Eq. (6). $\Theta(v)$ is a function to ensure $E_t > E_d$, and equals 1 when $E_t > E_d$, and 0 when $E_t < E_d$. Eq. (7) is based on the Debye model and is valid in the temperature region of $T \geqslant 150$ K. At $T < 150$ K, the resonance and isomer shifting invalidate both the Debye model and Einstein model [15,29].

3. Results and discussions

Fig. 1 shows the comparison of differential cross-sections of electron-carbon scattering, obtained from the present study by using Eq. (1), and from the code ELSEPA [30], and NIST database [31]. Both ELSEPA and NIST data use the partial wave approximation. Good agreement among the three sets of data suggests that our calculation based on tabulated data is accurate when compared with widely accepted data. It is worth noting that ELSEPA