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A first-principles study of the mechanical properties of g-GeC

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ABSTRACT

We investigate the mechanical properties of graphene-like hexagonal germanium carbide monolayers (*g*-GeC) using first-principles calculations based on density-functional theory. Compared to graphene, *g*-GeC is much softer, with 41% in-plane stiffness, 44%, 42% and 37% ultimate strengths in *armchair*, *zigzag*, and *biaxial* strains respectively, as well as smaller ultimate strains. However, *g*-GeC has a larger Poisson's ratio, 0.28, about 1.5 times that of graphene. We obtained the second, third, fourth, and fifth order elastic constants for a rigorous continuum description of the elastic response of *g*-GeC. The second order elastic constants, including in-plane stiffness, are predicted to monotonically increase with pressure while the Poisson's ratio monotonically decreases with increasing pressure. The sound velocity of a compressional wave has a minima at an in-plane pressure of −7 GPa while that of a shear wave monotonically with pressure.

1. Introduction

Hexagonal germanium carbide monolayer (*g*-GeC) is a graphene-like 2D material which has attracted considerable interest due to its promising applications in optoelectronics and energy engineering (Şahin et al., 2009; Chigo Anota and Murrieta Hernandez, 2011; Lu et al., 2012). With a predicted wide band gap (> 3 eV), *g*-GeC is a good candidate for fabrication of blue and ultraviolet light emitting diodes, as well as photovoltaic applications (Shim et al., 1998; Sari et al., 2003; Ueno et al., 2006; Brazier and Ruiz, 2011; Mahmood and Sansores, 2005; Ganguly et al., 1991). It is also applicable for design and preparation of multilayer anti-reflection and protection coatings of infrared (IR) windows. Very recently, it was predicted that the indirect-direct band gap transition of *g*-GeC can be tuned by strain engineering (Lu et al., 2012). However, it is unclear that *g*-GeC can sustain such engineering since large strains were blindly applied without considering its mechanical instabilities. Without knowledge of the mechanical properties, this engineered strain might not be physical. Thus a systematic study of the mechanical properties including nonlinear elastic behaviors at large strains are highly desired. In spite of its importance, the mechanical properties are not studied to our best knowledge.

Several previous studies have shown that 2D monolayers present a large nonlinear elastic deformation during the tensile strain up to the ultimate strength of the material, followed by a strain softening until fracture (Lee et al., 2008; Liu et al., 2007; Xiao et al., 2004; Khare et al., 2007; Lu and Huang, 2009; Peng et al., 2012a; Peng et al., 2012b; Peng et al., 2012c). We expect that the *g*-GeC behaves in a similar manner. Under large deformation, the strain energy density needs to be expanded as a function of strain in a Taylor series to include quadratic and higher order terms (Hiki, 1981; Cadelano et al., 2009). The higher order terms account for both nonlinearity and strain softening of the elastic deformation. They can also express other anharmonic properties of 2D nanostructures including phenomena such as thermal expansion, phonon–phonon interaction, etc. (Lee et al., 2008).

The goal of this paper is to study the mechanical behaviors of *g*-GeC at large strains and find an accurate continuum description of the elastic properties from *ab initio* density functional theory calculations. The total energies of the system, forces on each atoms, and stresses on the

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simulation boxes are directly obtained from DFT calculations. The response of *g*-GeC under the nonlinear deformation and fracture are studied, including ultimate strength and ultimate strain. The high order elastic constants are obtained by fitting the stress–strain curves to analytical stress–strain relationships that belong to the continuum formulation (Peng et al., 2012a; Wei et al., 2009). We compared this proposed new material with the well known 2D materials such as graphene (Wei et al., 2009), graphyne (Peng et al., 2012c) and *g*-BN (graphene-like hexagonal boron nitride monolayer) (Peng and De, 2012; Peng et al., 2012b, 2013a). Based on our result of the high order elastic constants, the pressure dependence properties, such as sound velocities and the second order elastic constants, including the in-plane stiffness, are predicted. Our results for the continuum formulation could also be useful in finite element modeling of the multiscale calculations for mechanical properties of *g*-GeC at the continuum level. The remainder of the paper is organized as follows. Section 2 presents the computational method, including the computational details of DFT calculations and the basic nonlinear elastic theory applied to 2D hexagonal structures. The results and analysis are in Section 3, followed by conclusions in Section 4.

2. Density functional theory calculations

We consider a conventional unit cell containing 6 atoms (3 carbon atoms and 3 germanium atoms) with periodic boundary conditions (Fig. 1). The 6-atom conventional unit cell is chosen because there is a soft mode leading to mechanical instability, and this key factor in limiting the strength of monolayer materials can only be captured in unit cells with hexagonal rings (Marianetti and Yevick, 2010).

The total energies of the system, forces on each atoms, stresses, and stress–strain relationships of *g*-GeC under the desired deformation configurations are characterized via first-principles calculations with density-functional theory (DFT). DFT calculations were carried out with the Vienna Ab-initio simulation package (VASP) (Kresse and Hafner, 1993, 1994; Kresse and Furthuller, 1996a; Kresse and Furthuller, 1996b) which is based on the Kohn–Sham density functional theory (KS-DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) with the generalized gradient approximations as parameterized by Perdew, Burke and Ernzerhof (PBE) for exchange–correlation functions (Perdew et al., 1996). The electrons explicitly included in the calculations are the ($2s^2 2p^2$) electrons. The core electrons ($1s^2$) are replaced by the projector augmented wave (PAW) and pseudo-potential approach (Blöchl, 1994; Jones and Gunnarsson, 1989). A plane-wave cutoff of 600 eV is used in all the calculations. The calculations are performed at zero temperature.

The criterion to stop the relaxation of the electronic degrees of freedom is set by total energy change to be smaller than 0.000001 eV. The optimized atomic geometry was achieved through minimizing Hellmann–Feynman forces acting on each atom until the maximum forces on the ions were smaller than 0.001 eV/Å.

The atomic structures of all the deformed and undeformed configurations are obtained by fully relaxing a 6-atom-unit cell where all atoms were placed in one plane. The simulation invokes periodic boundary conditions for the two in-plane directions while the displacement to out-of-plane direction is forbidden.

The irreducible Brillouin zone was sampled with a gamma-centered $17 \times 17 \times 1$ *k*-mesh. Such a large *k*-mesh was used to reduce the numerical errors caused by the strain of the systems. The initial charge densities were taken as a superposition of atomic charge densities. There was a 15 Å thick vacuum region to reduce the inter-layer interaction to model the single layer system. To eliminate the artificial effect of the out-of-plane thickness of the simulation box on the stress, we used the second Piola–Kirchhoff (P-K) stress (Peng et al., 2012a) to express the 2D forces per length with units of N/m.

For a general deformation state, the number of independent components of the second, third, fourth, and fifth order elastic tensors are 21, 56, 126, and 252 respectively (Hiki, 1981). However, there are only fourteen independent elastic constants need to be explicitly considered due to the symmetries of the atomic lattice point group D_{6h} which consists of a sixfold rotational axis and six mirror planes (Wei et al., 2009).

The fourteen independent elastic constants of *g*-GeC are determined by a least-squares fit to the stress–strain results from DFT based first-principles studies in two steps, detailed in our previous work (Peng et al., 2012a), which had been well used to explore the mechanical properties of 2D materials (Peng et al., 2012d; Peng et al., 2013b; Peng et al., 2013c; Peng et al., 2013d; Peng et al., 2013e). A brief introduction is that, in the first step, we use a least-squares fit to five stress–strain responses. Five relationships

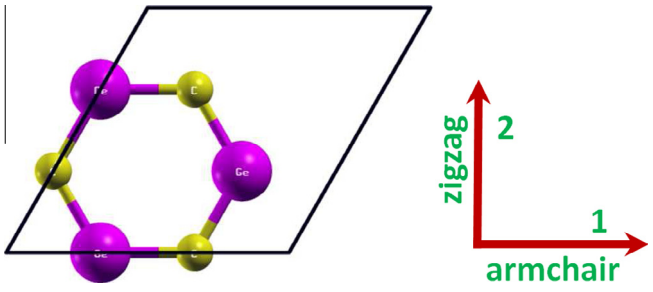

Fig. 1. Atomic structure of *g*-GeC in the conventional unit cell (6 atoms) in the undeformed reference configuration.