Research paper

Structural prediction for scandium carbide monolayer sheet

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ABSTRACT

A two-dimensional tetragonal scandium carbide monolayer sheet has been constructed and studied using density functional theory. The results show that the scandium carbide sheet is stable and exhibits a novel tetracoordinated quasiplanar structure, as favored by the hybridization between Sc-3d orbitals and C-2p orbitals. Calculations of the phonon dispersion as well as molecular dynamics simulations also demonstrate the structural stability of this scandium carbide monolayer sheet. Electronic properties show that the scandium carbide monolayer sheet is metallic and non-magnetic.

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1. Introduction

Due to its unique properties and potential applications in many fields, graphene has drawn a large amount of attention on two-dimensional (2D) nanomaterials [1–3]. With reduced dimensions and symmetry, 2D materials show many novel physical and chemical properties often in clear distinction to the corresponding bulk materials. These novel properties include high electron mobility, high thermal conductivity, the emergence of Dirac fermions and changes in the band structure [4,5]. Recently, researches into 2D materials have extended well beyond graphene. Using micromechanical cleavage techniques, researchers have successfully isolated individual crystal planes from a large variety of strongly layered materials including BN, several transition metal dichalcogenides (such as MoS_2 and NbS_2) and complex oxides (Ba_2Sr_2-$CaCu_2O_x$) [6]. Surprisingly, this work has shown that many of these atomically thin 2D materials are stable at room temperature and even retain high crystal quality and macroscopic continuity in air. These experimental achievements regarding two-dimensional semiconductors have been quite encouraging, and since then, notable results have been achieved in the synthesis of layered BN, MoS_2, WS_2 and other inorganic analogues of graphene [7–17]. It is noteworthy that hybridized $B_xC_yN_z$ with varying contents of B, C and N shows various hexagonal layered structures that are interesting analogues of graphene [18–21], and various 2D monolayer

sheets of GaSe [22], Bi_2Te_3 [23] and Cu_2Si [24] have also been reported to exhibit hexagonal, layered structures although, in detail, they have different properties.

In 1970, Hoffmann et al. [25] first proposed the possible existence of planar, tetracoordinated carbon (ptC) [26]. Subsequently, in 1976, Collins et al. [27] identified the first ptC molecules through systematic computations, and in 1977, Cotton and Millar synthesized the first ptC compound [28]. Since then, several molecules containing ptC structures have been reported, such as the planar tetracoordinated carbon motifs in 2D networks based on C_5^{2-} [29], B_xC_y [30], SiC_2 [31], and Al_xC [32]. Recently, Zhang et al. [33] reported a two-dimensional tetragonal titanium carbide (TiC) monolayer sheet with high kinetic stability and anisotropic mechanical properties. More recently, our group reported an exceptionally stable hollow cage containing 20 scandium atoms and 60 carbon atoms, which has a volleyball-like shape that we refer to below as "*Volleyballene*" [34]. In the present work, we propose a novel ScC monolayer, which is identified using first-principles density-functional theory (DFT). Its high stability has been verified through studies of the phonon dispersion and molecular dynamics (MD) simulation.

2. Computation method

The basic crystal structure of the ScC sheet was identified using the particle-swarm optimization (PSO) method as implemented in the CALYPSO code [35] which offers a fast and efficient way to obtain reliable structures with the input of only the chemical composition. In our PSO simulation, the primitive cell contained one C

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atom as well as one Sc atom, and the number of formula units per simulation cell was set to be either 1 or 2; that is, the unit cells contained a total of either 2 or 4 atoms. The population size was set to be 20 and the number of generations was set to be 30. The structural relaxations carried out during the PSO simulations were performed at the level of the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) [36] exchange correlation functional as implemented in VASP [24].

The structural relaxation and total-energy calculations for the ScC sheet performed using the CALYPSO code were further refined using DFT with higher accuracy as implemented in the Vienna *ab initio* simulation package (VASP) [37]. The projector-augmented wave (PAW) [38,39] method was used for the core region, and a kinetic energy cutoff of 500 eV was used in all calculations. The convergence threshold was set to be 10^{-5} eV/Å in energy and 10^{-4} eV/Å for forces. The vacuum space in the direction perpendicular to the sheet was set to be 15 Å in order to avoid interactions between adjacent layers. The Brillouin zone was sampled with a $16 \times 16 \times 1$ Γ-centered Monkhorst-Pack (MP) [40] K-points grid. The phonon dispersion was calculated using density-functional perturbation theory (DFPT) [41] with the phonopy package [42]. To further test the thermodynamic stability, Born-Oppenheimer Molecular dynamics simulations were conducted using NVE micro-canonical ensembles [36]. A double-numerical basis set including polarization (DNP) [43] and the PBE exchange correlation functional were used. The total simulation time was

set to be 2.0 *ps* with a step of 1.0 *fs* at four different initial temperatures of 2000 K, 3000 K, 3500 K and 4000 K.

3. Results and discussion

Using the CALYPSO code, we first generated 600 initial 2D ScC sheet structures using a primitive cell with only two atoms as well as 600 initial double supercell 2D ScC sheet structures with 4 atoms in the supercell. The results showed that in both the most nearly stable primitive cell or the most nearly stable double supercell of the 2D ScC sheet, the Sc and C atoms lay in a single plane with all atoms being tetracoordinated. Each C atom is bonded to four neighboring Sc atoms, and each Sc atom is bonded to four neighboring C atoms. The lattice parameters are $a = b = 3.169$ Å, $\gamma = 90.0°$, and the ScC sheet has $P4/mmm$ symmetry. However, there is an imaginary frequency in the phonon dispersion spectrum, indicating that this structure is not stable.

Further, we adjusted the 2D ScC sheet according to the vibration mode corresponding to the imaginary frequency. After successfully eliminating the imaginary frequency, we obtained a stable quasi-planar ScC structure with $C2/m$ symmetry as shown in Fig. 1a. All the C atoms are in the same plane while the Sc atoms are located on either side of this plane. Compared to the structure predicted by CALYPSO code, the two opposite Sc atoms adjacent to the C atom moved upward and the other two Sc atoms moved down-
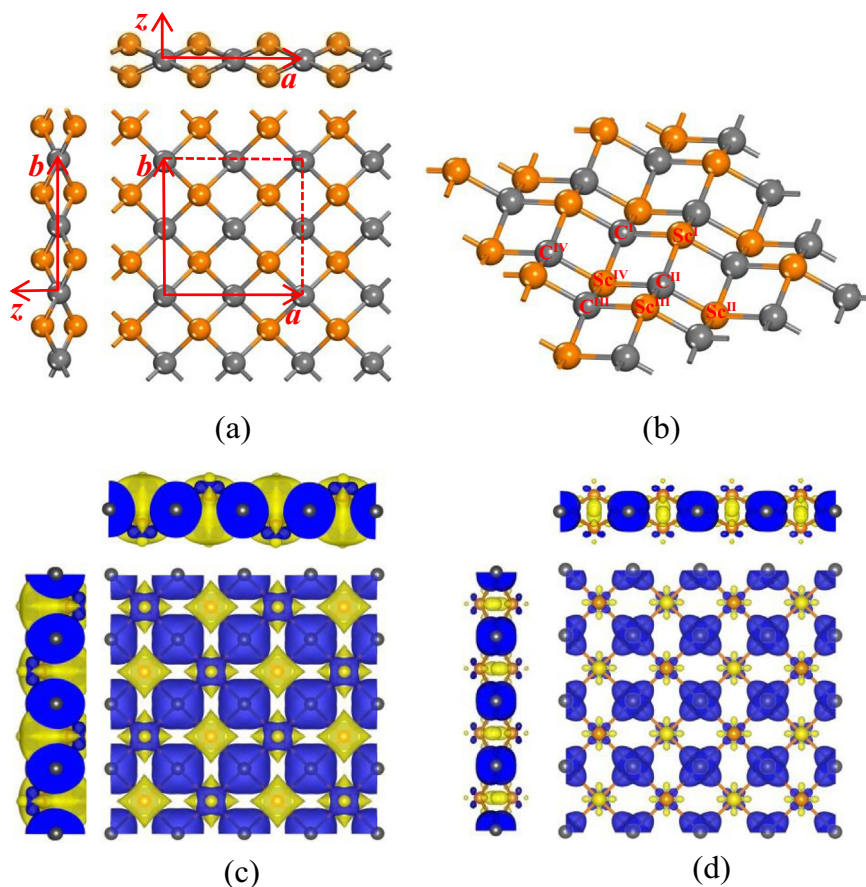

Fig. 1. (a) Top and side views of the ScC monolayer sheet with a 2×2 supercell. (b) Top view of the ScC monolayer sheet after rotation along *z*-axis direction. (c) Deformation electron density of the ScC sheet. Charge accumulation and depletion regions are in blue and yellow, respectively, with the isosurface set at 0.003 e/Bohr³. (d) Deformation electron density for the ScC sheet, with the isosurface set at 0.008 e/Bohr³. Here Sc and C atoms are in orange and gray, respectively. The atoms of two structural fragments were labeled, and the angles were measured: $\angle C^I$-Sc^{IV}-$C^{III} = 142.4°$; $\angle C^{II}$-Sc^{IV}-$C^{IV} = 142.8°$; $\angle Sc^I$-C^{II}-$Sc^{III} = 142.4°$; $\angle Sc^{II}$-C^{II}-$Sc^{IV} = 142.8°$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)