First-principles study of cobalt silicide nanosheet and nanotubes: Stability and electronic properties

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ABSTRACT

We perform first-principle calculations to study the geometric and electronic structures of cobalt silicide ($CoSi_2$) nanosheet and nanotubes. The structure of layered $CoSi_2$ is characterized by a $CoSi_2$ nanosheet, analogous to the (111) surface of $CoSi_2$ crystal. The strain energy involved in rolling up a $CoSi_2$ nanosheet to $CoSi_2$ nanotubes is very low. Both the $CoSi_2$ nanosheet and nanotubes are energetically stable. $CoSi_2$ nanotubes prefer to form bundles to further release strain energy. All $CoSi_2$ nanotubes exhibit uniformly metallicity and steady work functions, independent of tube chirality.

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1. Introduction

Since the discovery of carbon nanotubes (CNTs) [1], persistent studies of quasi-one-dimensional (Q1D) tubular materials have opened a new field in physics, chemistry, and materials science [2]. Besides conventional CNTs and BN nanotubes [3], metalliferous inorganic nanotubes, such as metal-disulphide nanotubes and metal-diboride nanotubes [4,5], have intriguing more and more attentions due to their unique geometric and electronic characteristics in last decades [2,4–6]. Exploring new type of nanotubes with varied morphologies and functionalities that are compatible with the well-established microelectronic and photonic technology is a goal of experimental works.

Due to the above stated reasons, silicon nanotubes (SiNTs) have aroused general interest both in experiment and theory [7–10]. Although, several groups have reported the fabrication of tubular silicon nanostructures that are composed of both sp^2 and sp^3 bonds with high ratio of sp^3 to sp^2 atoms [7–9], mass production of these SiNTs has not yet been achieved. Theoretical studies suggested that the single-walled SiNTs built analogously to CNTs are quite unstable, because Si atoms prefer to form sp^3 hybridization instead of sp^2 hybridization [10,11]. To stabilize single-walled SiNTs, great efforts have been paid on transition metal-doped SiNTs (TM-SiNTs) because TM atoms have inherent advantages on minimizing the strain in Si–Si bonds due to their active and functional 3d electrons [12,13]. The geometric and electronic properties of endohedral- and exohedral-doped TM-SiNTs were theoretically studied by several groups [14,15]. Among the TMs, Co is quite promising because cobalt silicide ($CoSi_2$) crystal has high-temperature stability and excellent conductivity [16–18]. More importantly, $CoSi_2$ materials have inherent advantages in coupling with the present silicon-based microelectronic technology, because of the small lattice mismatch between $CoSi_2$ and silicon crystals [16–18]. However, theoretical work concerning the energetic stability and related properties of $CoSi_2$ nanosheet and nanotubes formed by incorporating Co atoms into the network of silicon and SiNTs is still lack and thus becomes the goal of the present work.

In this contribution, we present a comprehensive study on the geometric and electronic properties of $CoSi_2$ nanostructures. A possible way to characterize the $CoSi_2NS$ and $CoSi_2NTs$ is also proposed based on the analysis of electron density of state (DOS). The work is expected to stimulate experimental and theoretical research on the SiNT-based nanomaterials and provide valuable information for exploiting nanoelectronic application of $CoSi_2NTs$.

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2. Methods and computational details

First-principle calculations were performed by utilizing the plane-wave basis Vienna *ab initio* simulation package known as VASP code [19], implementing the density functional theory (DFT) and ultrasoft pseudopotentials [20]. The electron–electron interaction was treated within generalized gradient approximation (GGA) with PW91 exchange-correlation functional [21]. The spin-polarization effects of Si or Co atoms were both considered. The structural optimization was performed employing conjugate gradient (CG) procedures to converge systems to their instantaneous ground states. The positions of all the atoms and the size of the super-cell were fully relaxed without any symmetric restrictions. The energy cutoffs used for plane-wave expansion of electron wave functions of both Si and Co atoms are 310 eV. The Brillouin zone was sampled on a grid of $4 \times 4 \times 1$ k points and $4 \times 4 \times 4$ k points for $CoSi_2$ layer and nanotubes, respectively. A sufficient vacuum space up to 30 Å was applied to exclude the image interaction. Forces were converged to 0.02 eV/Å and total energy was gained in 0.1 meV precision. The super-cells employed in the calculations of $CoSi_2NTs$ contain four layers of Si atoms with two layers of Co atoms along the tube axis for both armchair and zigzag tubes. We also calculated the $CoSi_2NTs$ with larger super-cells and did not find any geometric reconstruction or electronic structure modification.

3. Results and discussion

The energetic low-lying configuration of a $CoSi_2NS$ is firstly evolved by CG procedures and presented in Fig. 1(a)–(b). In $CoSi_2NS$, each Co atom bonds with six Si atoms and each Si atom is connected to three Co atoms, as shown in Fig. 1(a). The Si–Si distance in $CoSi_2NS$ is 2.54 Å, which is between that in bulk $CoSi_2$ (2.69 Å) and that in diamond Si (2.36 Å). The average Co–Si bond length is 2.27 Å, slightly shorter than that in bulk $CoSi_2$ (2.33 Å), implying the Co–Si interaction is strengthened in $CoSi_2NS$. The sheet thickness defined as the distance between two outmost Si layers is 1.33 Å, thinner by 0.22 Å than that of (1 1 1) trilayer of fluorite $CoSi_2$ crystal. This is related to the surface relaxation driven by the under-coordinated Co and Si atoms making the structure more compact. We calculated the formation energy (E_{form}), in terms of the energy difference per atom between $CoSi_2$ nanostructures and bulk $CoSi_2$ crystal, to verify their plausibility. The E_{form} of $CoSi_2NS$ is calculated to be 0.69 eV/atom. In view of the great successes of growing one or two layers of $CoSi_2NS$ on substrates [16–18], the synthesis of isolated $CoSi_2NS$ is highly expectable, even the E_{form} value is still a bit high. To probe the thermodynamic stability of $CoSi_2NS$, we heated the $CoSi_2NS$ in 1000 K for 2 ps by performing NVT dynamic simulations within Nosé thermostat. The $CoSi_2NS$ kept its well-order quasi-two-dimensional (Q2D) structure in this time scale, suggesting that the freestanding $CoSi_2NS$ is stable without support of substrate. Additionally, it has been addressed that two-dimensional atomic crystal, e.g., the BN, MoS_2, and graphite, can be efficiently fabricated using a so-call micromechanical cleavage procedure [22]. This may be a promising way to dissociate $CoSi_2NS$ from substrate.

Following the route of rolling up a graphene to a single-walled CNT, a $CoSi_2NT$ can be derived analogously from a $CoSi_2NS$. The structural parameters and E_{form} values of a series of armchair and zigzag $CoSi_2NTs$ are listed in Table 1. The equilibrium configurations of (6,6) and (10,0) $CoSi_2NTs$ are shown in Fig. 1(c)–(f). Obviously, the tube walls of $CoSi_2NTs$ have sandwich-like structures with Co interlayer lying between two Si layers. The wall thicknesses of $CoSi_2NTs$ are thinner than that of an unfolded
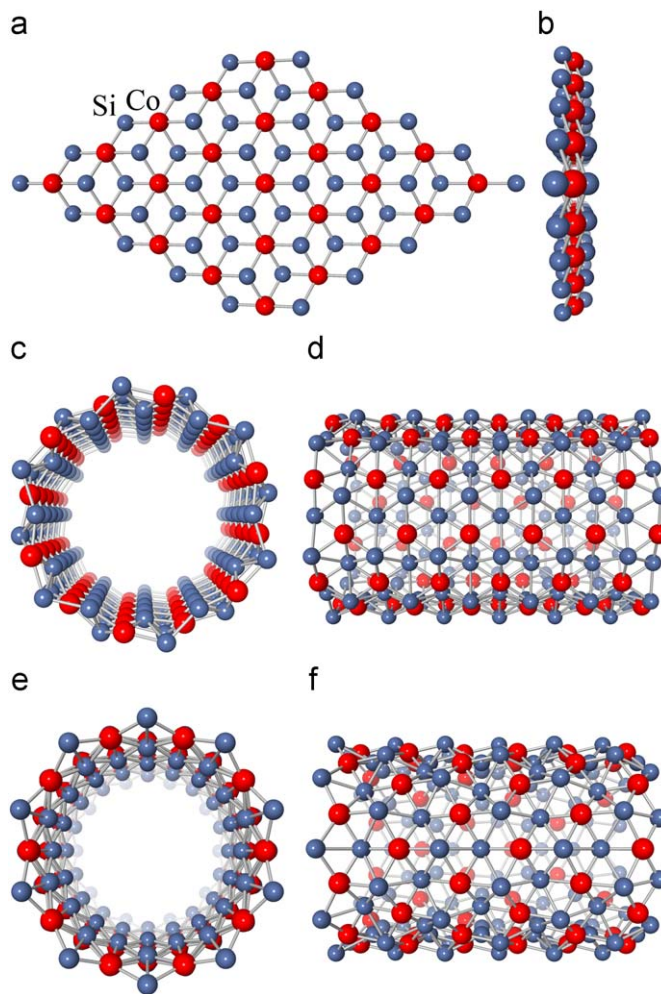

Fig. 1. (Color online) Top and side views of (a, b) $CoSi_2NS$, (c, d) (6,6) $CoSi_2NT$, and (e, f) (10,0) $CoSi_2NT$. Big red balls represent Co atoms while small blue balls are Si atoms.

Table 1
Average diameters (d), thicknesses (T), the nearest distances between Co and Si (Co–Si), Si and Si (Si–Si), Co–Si–Co bond angle (Co–Si–Co), formation energy (E_{form}), and work functions (WFs) of configurations (Conf.) of $CoSi_2NTs$ and $CoSi_2NS$.

Conf.	d (Å)	T (Å)	Co–Si (Å)	Si–Si (Å)	Co–Si–Co (deg.)	E_{form} (eV/atom)	WFs (eV)
(3,3)	6.65	1.08	2.30	2.47	112.8	0.76	4.82
(4,4)	8.71	1.04	2.31	2.47	114.1	0.74	4.88
(5,5)	10.68	1.16	2.28	2.48	113.3	0.72	5.03
(6,6)	12.82	1.17	2.28	2.49	113.4	0.71	5.00
(7,7)	14.80	1.19	2.28	2.49	113.2	0.71	4.94
(6,0)	7.55	0.99	2.30	2.44	114.3	0.77	4.77
(8,0)	9.93	1.16	2.28	2.48	113.3	0.73	5.00
(10,0)	12.07	1.15	2.28	2.48	113.6	0.72	5.11
(12,0)	14.57	1.22	2.28	2.51	112.9	0.71	5.06
(14,0)	17.00	1.27	2.27	2.52	112.3	0.71	5.04
$CoSi_2NS$	∞	1.33	2.27	2.54	111.7	0.69	4.99

$CoSi_2NS$ and increase with the increase of tube diameters as shown in Table 1. With increasing tube diameter, the nearest Si–Si distance increases while the Co–Si distance decreases. The Co–Si–Co bond angle is prone to increase with the decrease of tube diameter, endowing more sp^2 components to the surface Si atoms. The E_{form} values of (6,6) and (10,0) $CoSi_2NTs$ are 0.71 and 0.72 eV/atom, higher by 2.9% and 4.3% than that of $CoSi_2NS$,