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Novel silicon allotropes: Stability, mechanical, and electronic properties

Qingyang Fan,¹ Changchun Chai,¹ Qun Wei,^{2,a)} Haiyan Yan,³ Yingbo Zhao,¹ Yintang Yang,¹ Xinhai Yu,¹ Yang Liu,¹ Mengjiang Xing,⁴ Junqin Zhang,¹ and Ronghui Yao² ¹Key Laboratory of Ministry of Education for Wide Band-Gap Semiconductor Materials and Devices, School of Microelectronics, Xidian University, Xi' an 710071, People's Republic of China ²School of Physics and Optoelectronic Engineering, Xidian University, Xi' an 710071, People's Republic of China ³College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721013, People's Republic of China

⁴Faculty of Information Engineering and Automation, Kunming University of Science and Technology, Kunming 650051, People's Republic of China

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One quasi-direct gap phase (*Amm2*) and three indirect gap phases (*C2/m*-16, *C2/m*-20, and *I*-4) of silicon allotropes are proposed. The detailed theoretical study on the structure, density of states, elastic properties, sound velocities, and Debye temperature of these four phases is carried out by using first principles calculations. The elastic constants of these four phases are calculated by strain-stress method. The elastic constants and the phonon calculations manifest all novel silicon allotropes in this paper are mechanically and dynamically stable at ambient condition. The *B/G* values indicate that these four phases of silicon are brittle materials at ambient pressure. The anisotropy properties show that *C2/m*-20 phase exhibits a larger anisotropy in its elastic modulus, shear elastic anisotropic factors, and several anisotropic indices than others. We have found that the Debye temperature of the four novel silicon allotropes gradually reduces in the order of *C2/m*-20 > *Amm2* > *C2/m*-16 > *I*-4 at ambient pressure. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4935549]

I. INTRODUCTION

The scaffolding of life is carbon in the nature, and then mankind chose silicon as the building block of many hightech things. Obviously, silicon has several advantages, it deserves the title of "block" as silicon is the second most abundant element in the Earth's crust, its processing is well controlled at the industrial level, and its electronic properties and defect physics are theoretically well known. As an elemental substance, it is an intrinsic semiconductor that can readily be p- and n-doped with lots of different elements. This makes silicon the material of choice for many applications in electronics. Silicon is also the leading player in the important field of photovoltaic energy production, especially in solar cells industry. Diamond silicon (space group: Fd-3m) is the leading material in the current solar cell market. However, diamond Si is an indirect band gap semiconductor with a large energy difference (2.3 eV) between the direct gap and the indirect gap, which makes it an inefficient absorber of light. It is well known that, under extreme conditions, a crystalline material may undergo a structural transition to a phase which remains effectively stable upon returning to standard thermodynamic conditions. The great demand of society for new clean energy and the shortcomings of the current silicon solar cells are calling for new materials that can make full use of the solar power. Silicon is known to exist in a variety of allotropes, including the most stable cubic diamond silicon (Si-I) and several metastable silicon allotropes. Metastable BC8-structured Si-III¹ and R8-structured Si-XII² could be guenched to ambient pressure by decompressing the high-pressure phase, β -Sn structured Si-II. The high pressure phases of Si and Ge have been investigated,^{3,4} and it has been determined that both undergo a series of structural phase transitions from cubic $\rightarrow \beta$ -Sn \rightarrow simple hexagonal \rightarrow orthorhombic phase \rightarrow hexagonal close packed \rightarrow face centered cubic phase.^{3,4} Recently, Amrit De and Craig E Pryor⁵ calculated the electronic band structures and the dielectric functions for Si in the lonsdaleite phase. Silicon in the lonsdaleite phase has an indirect band gap of 0.95 eV.^{5,6} Xiang et al.⁷ developed a novel inverse band structure design approach, and utilizing their new method, they predict a cubic Si₂₀ phase with quasidirect gaps of 1.55 eV, which is a promising candidate for making thinfilm solar cells. Six metastable allotropes of silicon with direct or quasidirect band gaps of 0.39-1.25 eV are predicted utilizing ab initio calculations at ambient pressure by Wang et al.⁸ Five of them possess band gaps within the optimal range for high converting efficiency from solar energy to electric power and also have better optical properties than the Fd-3m phase. Recently, Botti et al.⁹ presented a number of low-energy silicon allotropes with quasidirect band gaps between 1.0 and 1.5 eV. These phases are predicted to exhibit better optical properties than *Fd-3m* phase of Si.

In this paper, four silicon phases with indirect band gaps ranging from 0.525 to 1.276 eV are investigated. Furthermore, the detailed physical properties (such as structural properties, elastic properties, and anisotropic and electronic properties) of novel silicon allotropes are studied.

^{a)}Author to whom correspondence should be addressed. Electronic mail: weiaqun@163.com.

TABLE I. The lattice parameters of the novel silicon allotropes.

Space group	a (Å)	b (Å)	c (Å)	β(°)	$V(\text{\AA}^3)$	Relative enthalpy (eV/atom)
<i>C2/m</i> -16 ^a	7.192	7.677	10.930	146.103	336.538	0.1274
C2/m-20 ^a	13.679	3.863	13.238	143.181	419.190	0.0956
I-4 ^a	8.496		8.411	90.000	607.048	0.0991
Amm2 ^a	3.864	8.450	13.098	90.000	427.683	0.1094
Fd-3m ^a	5.480			90.000	164.555	0.0000
Fd-3m ^b	5.431				160.191	

^aThis work.

^bReferences 25–27.

II. THEORETICAL METHOD

All calculations are performed by utilizing the local density approximation (LDA)^{10,11} augmented with generalized gradient approximation (GGA) functional in the Perdew, Burke, and Ernzerhof (PBE) functional¹² form in Cambridge sequential total energy package (CASTEP) package.¹³ The core-valence interactions were described as Ultra-soft pseudopotentials. The valence electrons configurations of Si $3s^23p^2$ are considered. The k-points in the first irreducible Brillouin zone were $8 \times 4 \times 5$, $5 \times 10 \times 5$, $6 \times 6 \times 6$, and $6 \times 6 \times 11$ for C2/m-16, C2/m-20, I-4, and Amm2, respectively. For four new Si phases, the ultrasoft pseudopotential was used with the cutoff energy of 340 eV. The Broyden-Fletcher-Goldfarb-Shanno (BFGS)¹⁴ minimization scheme was used in geometry optimization. The selfconsistent convergence of the total energy is $5 \times 10^{-6} \text{eV}/$ atom; the maximum force on the atom is 0.01 eV/Å, the maximum ionic displacement with in 5×10^{-4} Å, and the maximum stress within 0.02 GPa.

III. RESULTS AND DISCUSSION

There are four new phases of Si at ambient pressure which have not been reported yet. To investigate the possible phase transition sequence at ambient pressure, we first calculated the enthalpies of C2/m-16, C2/m-20, Amm2, and I-4 phases relative to Fd-3m phase. The relative enthalpies are calculated by this formula: $\Delta H = H_{novel phase}/n_1$ - $H_{diamond}/n_2$, n_1 and n_2 are the number of atoms in unit cell of five silicon phases. The calculated results are listed in Table I. From Table I, Fd-3m phase is the most stable phase at ambient pressure. The energy sequence of the four proposed Si phases from low to high is C2/m-20, I-4, Amm2, and C2/m-16. Among them, the most unfavorable C2/m-16 phase is



FIG. 1. Unit cell crystal structures of the novel silicon allotropes.

higher in energy than Fd-3m phase by 0.1274 eV/atom at ambient pressure, while the most stable C2/m-20 phase is 0.0956 eV/atom higher than Fd-3m phase.

The structure of the novel silicon allotropes C2/m-16, C2/m-20, *I*-4, and *Amm2* phases is shown in Fig. 1, and the atomic positions in the novel silicon allotropes are listed in Table II. There are 16, 20, 28, and 20 atoms in unit cell of C2/m-16, C2/m-20, *I*-4, and *Amm2* phase, respectively. The densities of our predicted novel silicon allotropes in increasing order are *I*-4 (2.1511 g/cm³), *Amm2* (2.1809 g/cm³), *C2/m*-16 (2.2172 g/cm³), and *C2/m*-20 (2.2251 g/cm³), but they are all slightly smaller than *Fd*-3*m* phase (2.2673 g/cm³). The calculated equilibrium lattice parameters of the novel silicon allotropes are listed in Table I. As can be seen, our calculated lattice parameters for *Fd*-3*m* phase are reasonable compared with previous study and experimental results. The

TABLE II. The structure parameters of the silicon allotropes.

Space grou	Wyckoff position
Amm2	Si1:2b (0.5000,0.0000,0.1896), Si2:4e (0.5000,-0.2307,0.7355), Si3:4e (0.5000,-0.1401,0.5611), Si4:4d (0.0000,-0.2638,0.4932), Si5:4e (0.00000,0.1428,0.8220), Si6:2a (0.0000,0.0000,0.0869)
C2/m-16	Si1:8j (0.4741,0.7402,0.8800), Si2:4i (0.2091,-0.0000,0.3337),Si3:4i (0.1440,-0.0000,0.6752)
C2/m-20	Si1:4i (0.0741,-0.0000,-0.5176), Si2:4i (-0.5122,0.0000,-0.3354), Si3:4i (0.7517,-0.0000,-0.0486), Si4:4i (-0.9866,0.0000,-0.9018), Si5:4 (-0.3646,0.0000,-0.7292)
I-4	Si1:8g (-0.1212,-0.2712,-0.6215), Si2:8g(0.4061,-0.1787,0.0506),Si3:8g (0.4816,0.2496,-0.3794), Si4:2a (0.5000,0.5000,0.5000),Si5:2d (0.0000,0.5000,0.7500)

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TABLE III. The bond length (in \AA) of the silicon allotropes.

Space group	Amm2	<i>C2/m</i> -16	C2/m-20	I-4	Fd-3m
Si-Si	2.354	2.318	2.416	2.348	2.373
	2.409	2.324	2.366	2.370	
	2.359	2.341	2.383	2.366	
	2.368	2.408	2.344	2.345	
	2.370	2.339	2.424	2.348	
	2.377	2.464	2.347	2.383	
	2.343	2.401	2.334	2.398	
	2.413		2.317	2.362	
			2.373		
Average	2.364	2.380	2.368	2.370	2.373

calculated bond lengths of the novel silicon allotropes are listed in Table III. C2/m-16 phase has seven different bond lengths; Amm2 phase has eight different bond lengths; C2/m-20 phase has nine different bond lengths; and *I*-4 phase has eight different bond lengths, the average bond lengths are 2.380 Å, 2.364 Å, 2.368 Å, and 2.370 Å, respectively. The bond lengths of the four proposed Si phases from short to long are Amm2, C2/m-20, *I*-4, and C2/m-16 phase. Among them, the most favorable C2/m-20 phase is higher in bond length than Amm2 phase at ambient pressure, but lower than that of *I*-4 and C2/m-16 phase, while lower than that of the most stable *Fd-3m* phase (2.373 Å).

The elastic (stiffness) constants are calculated by the strain-stress method as presented in Table IV. For a stable monoclinic structure (C2/m phase), its independent elastic constants should obey the following generalized Born's mechanical stability criteria:

$$C_{ii} > 0, i = 1 \sim 6,$$
 (1)

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \qquad (2)$$

$$(C_{33}C_{55} - C_{35}^2) > 0, (3)$$

$$(C_{44}C_{66} - C_{46}^2) > 0, (4)$$

$$(C_{22} + C_{33} - 2C_{23}) > 0, (5)$$

$$[C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{25}^2C_{33}] > 0,$$
(6)

$$2[C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{23}) + C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})] - [C_{15}^{2}(C_{22}C_{33} - C_{23}^{2}) + C_{25}^{2}(C_{11}C_{33} - C_{13}^{2}) + C_{35}^{2}(C_{11}C_{22} - C_{12}^{2})] + C_{55}g > 0,$$
(7)

$$g = C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23}.$$
(8)

For a stable orthorhombic structure (*Amm2* phase), the criteria for the mechanical stability are given by

$$C_{ii} > 0, i = 1 \sim 6,$$
 (9)

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0,$$
(10)

$$(C_{11} + C_{22} - 2C_{12}) > 0, (11)$$

$$(C_{11} + C_{33} - 2C_{12}) > 0, (12)$$

$$(C_{22} + C_{33} - 2C_{23}) > 0.$$
⁽¹³⁾

The criteria for the mechanical stability of tetragonal structure (I-4 phase) are given by

$$C_{ii} > 0, i = 1, 3, 4, 6,$$
 (14)

$$(C_{11} - C_{12}) > 0, (15)$$

$$(C_{11} + C_{33} - 2C_{13}) > 0, (16)$$

$$[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0.$$
⁽¹⁷⁾

It can be found that the calculated elastic constants of the novel silicon allotropes are positive and satisfy the Born's mechanical stability criteria of monoclinic structure, orthorhombic structure, and tetragonal structure, indicating that all novel silicon allotropes are mechanically stable in this paper. To confirm the thermodynamic stability of the novel silicon allotropes, the phonon dispersion is calculated at ambient pressure. There are no imaginary frequency along the whole Brillouin zone of these phases (see Fig. 2), indicating these phases are thermodynamic stable. It is common to use the arithmetic average of Voigt and Reuss bounds for the evaluation of bulk modulus and shear modulus, which is called the Voigt-Reuss-Hill approximation.¹⁵ The polycrystalline bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio v, and B/G of the novel silicon allotropes are also shown in Table IV. The Young's modulus *E* and the Poisson's ratio *v* are taken as: E = 9BG/(3B+G), v = (3B-2G)/[2(3B+G)]. The bulk modulus and the shear modulus of the four novel

TABLE IV. The elastic constants (in GPa) and the elastic modulus (in GPa) of the silicon allotropes.

Space group	<i>C</i> ₁₁	<i>C</i> ₁₂	C ₁₃	C ₂₂	C ₂₃	C ₃₃	C_{44}	C ₅₅	C ₆₆	В	G	B/G	Ε	v
C2/m-16 ^a	146	51	47	146	43	164	48	53	53	82	51	1.60	127	0.24
C2/m-20 ^a	184	36	46	167	46	143	55	52	52	83	55	1.50	135	0.23
<i>I-4</i> ^a	142	48	50	142	50	145	47	47	55	80	48	1.68	120	0.25
Amm2 ^a	161	37	42	179	38	131	44	44	51	78	51	1.54	126	0.23
Fd-3m ^a	154	56					79			88	64	1.38	155	0.21
Fd-3m ^b	165	64					87							

^aThis work.

^bReference 28.



FIG. 2. Phonon spectra for Amm2 phase (a), C2/m-16 phase (b), C2/m-20 phase (c), and *I*-4 phase (d).

silicon allotropes are extremely close, so that the Young's modulus of the four novel silicon allotropes is extremely close, too. The bulk modulus *B*, the shear modulus *G*, and the Young's modulus *E* of the four novel silicon allotropes are all smaller than *Fd-3m* phase, but the Poisson's ratio *v* is slightly larger than *Fd-3m* phase. Pugh¹⁶ proposed the ratio of bulk to shear modulus (*B/G*) as an indication of ductile verses brittle characters. If *B/G* > 1.75, the material behaves in a ductile manner,¹⁷ otherwise, the material behaves in a brittle manner. The *B/G* of the four novel silicon allotropes is all less than 1.75, which suggests that the four novel silicon allotropes are prone to brittle.

The projections of Poisson's ratio, shear modulus, and Young's modulus at different crystal planes are demonstrated in Figs. 3, 4(a)-4(c), and 4(d)-4(f), respectively. It is very apparent that the anisotropy of the Poisson's ratio for different silicon allotropes has large change. Moreover, the differences among the anisotropy of shear modulus and Young's modulus are very clear. The three-dimensional (3D) surface construction is a valid method to describe the elastic anisotropic behavior of a solid perfectly. The 3D figures of the directional dependences of reciprocals of the Young's modulus for the four novel silicon allotropes are different due to their various crystal structures.¹⁸ The 3D figure appears as a spherical shape for an isotropic material, while the deviation from the spherical shape exhibits the content of anisotropy.¹⁹ As for the orthorhombic structure Amm^2 phase (Fig. 5(a)), the 3D surface of the Young's modulus along x-axis, y-axis, and zaxis deviates from the spherical shape largely, which means Amm2 phase is highly anisotropic in Young's modulus. From Figs. 5(b) and 5(c), it can be seen that the 3D figure of the Young's modulus for the monoclinic structure C2/m-20 phase has a deviation from the sphere, indicating that the Young's modulus for C2/m-20 phase shows larger anisotropic than that of C2/m-16 phase. Fig. 5(c) shows that the Young's modulus for C2/m-20 phase, the x-axis is more anisotropic than the zaxis because of the values of C_{33} larger than C_{11} . For the tetragonal structure *I*-4 phase, the 3D figures of the Young's modulus are characterized by more anisotropic along the x axis than that along the z axis. The maximum value (minimum value) of Amm2, C2/m-20, *I*-4, and C2/m-16 phases is 164 GPa (111 GPa), 166 GPa (109 GPa), 135 GPa (108 GPa), and 149 GPa (104 GPa), respectively. The $E_{max}/E_{min(Amm2)}$ = 1.477, $E_{max}/E_{min(C2/m-20)}$ = 1.523, $E_{max}/E_{min(I-4)}$ = 1.250, and $E_{max}/E_{min(C2/m-16)}$ = 1.433 show that C2/m-20 phase has the largest anisotropy in these four novel silicon allotropes.

The elastic anisotropy of a crystal can be depicted by many different ways. In this work, we calculate several anisotropic indices, such as the percentage of anisotropy ($A_{\rm B}$ and $A_{\rm G}$) and the universal anisotropic index ($A^{\rm U}$). The calculated results of B_V , B_R , G_V , and G_R of the four novel silicon allotropes are presented in Table V, together with the A^{U} , A_{B} , and $A_{\rm G}$ are also listed in Table V. The equations used can be expressed as: $A_{\rm B} = (B_{\rm V} - B_{\rm R})/(B_{\rm V} + B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm V} - G_{\rm R})/(B_{\rm R})/(B_{\rm R})/(B_{\rm R})/(B_{\rm R})/(B_{\rm R})/(B_{\rm R}), A_{\rm G} = (G_{\rm R})/(B_{\rm R})/(B_{\rm R})/($ $(G_{\rm V}+G_{\rm R})$, and $A^{\rm U}=5G_{\rm V}/G_{\rm R}+B_{\rm V}/B_{\rm R}-6$, there $A^{\rm U}$ must be more than or equal to zero. The A^{U} fluctuate from zero indicate the high anisotropic mechanical properties. For A^{U} , C2/m-20 phase also shows larger anisotropic than others. The universal anisotropic index A^{U} is a better indicator than other indices, which provides the unique and consistent results for the mechanical anisotropic properties of these materials.²⁰ The larger the values of A^{U} is, the stronger the anisotropic of materials. Thus, the elastic anisotropic sequence of these materials forms the following order: C2/m-20 > C2/m-16 > Amm2 > I-4, and I-4 phase is very close to Fd-3m phase. Amm2 phase has the largest value of $A_{\rm B}$, which means that Amm2 phase shows the greatest anisotropic in bulk modulus among these silicon allotropes. The calculated $A_{\rm B}$ for *Fd-3m* phase is zero, because the





Voigt and Reuss methods predict the same values for the bulk modulus. From Table V, it is found that C2/m-20 phase and *I*-4 phase have the greatest and smallest $A_{\rm G}$.

The anisotropic mechanical properties of materials play a significant role in the technological applications. Consequently, we continue to investigate the anisotropic of the shear modulus. The shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes. The shear elastic anisotropic factors A_1 (for the {100} shear planes between the $\langle 011 \rangle$ and $\langle 010 \rangle$ directions) can be defined as

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}}.$$
 (18)

The shear elastic anisotropic factors A_2 (for the {010} shear planes between $\langle 101 \rangle$ and $\langle 001 \rangle$ directions) can be defined as

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}}.$$
 (19)

The shear elastic anisotropic factors A_2 (for the {001} shear planes between $\langle 110 \rangle$ and $\langle 010 \rangle$ directions) can be defined as

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}}.$$
(20)

Furthermore, the factors A_1 , A_2 , and A_3 must be 1.0 for isotropic crystals. On condition that any value of the three factors is smaller or larger than 1.0, we could confirm that

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FIG. 4. 2D representation of shear modulus in the *xy* plane (a), *xz* plane (b), and *yz* plane (c) for the novel silicon allotropes. 2D representation of Young's modulus in the *xy* plane (d), *xz* plane (e), and *yz* plane (f) for the novel silicon allotropes. The solid line represents the maximum and dashed line represents the minimum. The black, red, blue, and magenta line represents the *Amm2*, *C2/m*-16, *C2/m*-20, and *I*-4 phases.

the crystal has elastic anisotropy.²¹ The calculated A_1 , A_2 , and A_3 of the four novel silicon allotropes are illustrated in Fig. 6, all of the novel silicon allotropes have shown varying degrees of anisotropy. The A_1 and A_2 of *I*-4 phase are 1.055, which are suggestive of their weaker anisotropy at {001} shear planes. Moreover, since the shear anisotropic factors A_1 and A_2 of *Fd*-3*m* phase are equal to their corresponding factor A_3 , it is easy to know that their {100}, {010}, and {001} shear planes have the same anisotropy. And it is the same as {100} and {010} shear planes of *I*-4 phase.

The sound velocity and the Debye temperature are two fundamental parameters for evaluating the chemical bonding characteristics and the thermal properties of materials in materials science. The average sound velocity v_m and the Debye temperature Θ_D can be approximately calculated by the following relations:^{22,23}

$$\Theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m, \tag{21}$$

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_s^3} + \frac{1}{v_p^3}\right)\right]^{-\frac{1}{3}},$$
(22)

where *h* is the Planck's constant, k_B is the Boltzmann's constant, N_A is the Avogadro's number, *n* is the number of atoms in the molecule, *M* is the molecular weight, and ρ is the density. v_p and v_s are the compressional and shear sound velocities, respectively, which can be obtained from Navier's equation²⁴

$$v_p = \sqrt{\left(B + \frac{4}{3}G\right)\frac{1}{\rho}}, \quad v_s = \sqrt{\frac{G}{\rho}}.$$
 (23)

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The values of sound velocity and Debye temperature of the novel silicon allotropes are listed in Table VI. As a matter of fact, crystal with small density and large bulk modulus and shear modulus may have large Debye temperature as well. As can be seen from Table VI, Fd-3m phase has the largest $\Theta_{\rm D}$ value and the $\Theta_{\rm D}$ value of *I*-4 phase is the smallest. Besides, the calculated average sound velocities of these novel silicon allotropes are relatively large which are over 5200 m/s, less than that of Fd-3m phase (5859 m/s). It is worth to mention that there is a reasonable fact for the phenomenon above, that these novel silicon allotropes have low density and high bulk modulus and shear modulus.

TABLE V. The calculated anisotropic indices of the novel silicon allotropes $(B_{\rm V}, B_{\rm R}, G_{\rm V}, \text{ and } G_{\rm R}$ are in unit of GPa, $A_{\rm B}$ and $A_{\rm G}$ are in unit of percentage).

Space group	Amm2	<i>C2/m</i> -16	C2/m-20	I-4	Fd-3m
B _V	78.5	81.7	83.2	80.4	98.0
$B_{\rm R}$	77.5	81.5	82.6	80.4	98.0
$G_{\rm V}$	51.3	51.6	56.3	48.2	72.2
$G_{\rm R}$	50.0	50.1	54.2	47.6	67.2
$B_{\rm V}/B_{\rm R}$	1.013	1.003	1.007	1.000	1.000
$G_{\rm V}/G_{\rm R}$	1.026	1.018	1.040	1.014	1.073
A^{U}	0.151	0.152	0.208	0.070	0.336
$A_{\rm B}$	0.641	0.128	0.347	0.014	0.000
$A_{\rm G}$	1.359	1.475	1.971	0.691	3.500



FIG. 6. The calculated shear anisotropic factors of the novel silicon allotropes.

TABLE VI. The calculated density (ρ in g/cm³), the longitudinal, transverse, and mean elastic wave velocity (v_s , v_p , and v_m in m/s), and the Debye temperature (Θ_D in K) for the novel silicon allotropes.

Space group	ρ	vs	vp	v _m	$\Theta_{\rm D}$
Amm2	2.1809	4836	8182	5357	575
C2/m-16	2.2172	4796	8225	5320	574
C2/m-20	2.2251	4972	8382	5506	595
I-4	2.1511	4724	8182	5244	560
Fd-3m	2.2673	5303	8727	5859	639

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FIG. 7. Electronic band structure for the Amm2 phase (a), C2/m-16 phase (b), C2/m-20 phase (c), and I-4 phase (d) at 0 GPa. The red dot and blue dot represent the CBM and VBM, respectively.

It is well known that the electronic structure determines the fundamental physical and chemical properties of materials. The calculated electronic band structure for these novel silicon allotropes is presented in Fig. 7. The electronic structure demonstrates all these novel silicon allotropes are indirect band gap semiconductors. For Amm2 phase, the conduction band minimum (CBM) is at (0.0 0.0 0.225) point along the $\Gamma - Z$ direction (see inset of Fig. 7(a)), while the valence band maximum (VBM) is located at U point. The direct gap at Γ point is 0.753 eV which is slightly larger than indirect gap of 0.742 eV. So Amm2 phase is a quasi-direct gap Si. For C2/m-16 phase, the VBM located at Z point and CBM at $(-0.5 \ 0.0$ 0.061) point along B-D direction. The top of the valence band and the bottom of the conduction band occur along the Γ -Z and Γ -M direction of C2/m-20 and I-4 phase, respectively. It is known that the calculated band gaps with density functional theory (DFT) are usually underestimated by 30%-50%, and the true band gap must be larger than the calculated results. The band gap of these novel silicon allotropes reduces in the sequence of I-4 > Amm2 > C2/m-16 > C2/m-20.

IV. CONCLUSIONS

In summary, we have predicted the four novel silicon allotropes with space group C2/m, Amm2, and I-4, which

they are all mechanically and dynamically stable at ambient condition. C2/m-16, C2/m-20, and I-4 phases are indirect band gap semiconductors materials with band gap of 0.561, 0.525, and 1.276 eV, respectively. Amm2 phase is a quasidirect gap phase with gap of 0.742 eV. The difference between the direct gap and the indirect gap is only 0.011 eV. 3D surface contour of the Young's modulus is plotted to verify the mechanical anisotropic of the novel silicon allotropes. Meanwhile, C2/m-20 phase exhibits the greater anisotropic among the four novel silicon allotropes in the shear elastic anisotropic factors and a slice of anisotropic indices. In addition, the Debye temperature of Amm2, C2/m-16, C2/m-20, I-4, and Fd-3m phases calculated by elastic modulus is 575 K, 574 K, 595 K, 560 K, and 639 K, respectively.

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