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Band Gap Engineering of Wurtzite Silicon by Uniaxial Pressure

Ziwei Cui

Abstract— **Electronic properties of wurtzite silicon (WZ-Si) are investigated by first-principle calculation. It is found that WZ-Si is an indirect band-gap semiconductor at ambient condition. A uniaxial strain along the c-direction can reduce the direct energy gap at Γ significantly. Calculated pressure needed to compress WZ-Si is not too high, which shows strained WZ-Si would be potential in practical use. The effective mass of electron is found strongly dependent on strain which could be used to tailor the transport properties.**

Keywords— **Electronic properties, Wurtzite silicon (WZ-Si), Uniaxial pressure**

I. INTRODUCTION

Silicon in cubic phase (c-Si) has been intensively studied due to its importance in electronic industry. However, c-Si is an indirect semiconductor and has low mobility, which dramatically limits its application in high-speed devices. Even though high mobility materials, such as GaN and AlN, have been synthesized, their incompatibility with the present Si industry largely limits their applications. Some strategies have been proposed to improve the performance of silicon. For example, strained silicon has been used in CMOS industry to increase the carrier mobility[1,2,3,4,5]. Another strategy is to search for new materials that are compatible with current Si technology but have better performance compared to c-Si. In this respect, silicon polymorphs, such as tetragonal, hexagonal, orthorhombic structures, and their strained structures, are attractive candidates. Existence of silicon polymorphs have been confirmed by high pressure experiments. Some of them could even be quenched to ambient condition. Therefore, there is considerable interest to study the electronic properties of various silicon polymorphs.

Among the many silicon polymorphs, wurtzite-structured silicon (WZ-Si) is the most interesting one. It can be easily synthesized at high pressure and even at normal condition. Experimentally, WZ-Si phase was first discovered as a byproduct in the process of synthesizing Si_3N_4 at high temperature[6]. Later, Dahmen *et al.*[7] synthesized WZ-Si by heating c-Si at 200 °C or in the presence of shear stresses at twin intersection under non-hydrostatic stress of 8 GPa in indentation experiment.[8] WZ-Si phase has also been prepared by laser ablation[9] and cluster-beam evaporation[10].

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Ziwei Cui, Space Star Technology CO., LTD., Beijing, China, e-mail: zwcui129@gmail.com.

Recently, silicon nanowires, prepared by the vapor-liquid-solid (VLS) method, were characterized to be in WZ-Si structure too[11]. Furthermore, 2H and other higher-order polytypes were found in poly-Si layers fabrication [12]. Theoretical studies have shown that Si and other group-IV elements, together with their compounds such as SiC, Si_xGe_{1-x} in wurtzite structure could have similar band-structure[8], *i.e.*, a minimum indirect band-gap at Γ→M and first direct band-gap at Γ→Γ. Apart from being an indirect band-gap semiconductor, their band-structure topology is similar to those of II-VI and III-V semiconductors, *e.g.*, wurtzite-structured ZnO and GaN (direct band-gap semiconductors)[14,15]. Then, an interesting question can be asked. Can one design a direct band-gap WZ-Si, or at least, minimize the difference between the direct band-gap and indirect band-gap? To address this question, in this work we study the electronic properties of WZ-Si under a uniaxial pressure using first-principle method. We focus on the effect of cell parameters on the direct (Γ→Γ) and indirect (Γ→M) band gaps. It is found that the direct energy gap can be engineered by a uniaxial compression along the *c*-axis and the difference between the direct and the indirect band gap can be reduced significantly.

II. AB-INITIO CALCULATION DETAIL

First-principle calculations were performed in the density-function theory framework. Generalized gradient approximation (GGA) is used to describe the exchange correlation functional. Our calculations are performed using the frozen-core all-electron projector augmented wave method implanted in the VASP code[16,17,18,19,20]. The electron wave function is expanded using plane waves with a cutoff energy of 400 eV. The Brillouin zone is sampled using a 11x11x11 k-point mesh based on the Monkhorst-Pack scheme[21]. The electrons effective masses are evaluated from the second derivative of eigenvalues *E* with respect to the wave vector *k*.

III. RESULTS AND DISCUSSION

A. Balanced Structure of Wuzite-Si

The atomic positions and cell parameters of strain-free WZ-Si were first fully relaxed. Figure 1 shows the atomic structure of the relaxed WZ-Si and the corresponding band-structure. The cell parameters and band gap properties of WZ-Si obtained from the present work are listed in Table I, together with data reported in the

literature[12,22,23,24]. The relaxed WZ-Si is an indirect band-gap semiconductor with a calculated band gap of 0.47 eV between the valence-band maximum (VBM) and the conduction-band minimum (CBM) at M, and a direct band gap of 1.02 eV at Γ, respectively. The *c/a* ratio of the fully relaxed structure is 1.654, which is slightly larger than that in the "ideal" WZ structure (√8/3 or 1.633). This deviation causes a slight distortion of the Si-tetrahedron and results in each silicon

Table 1: Calculated equilibrium structural parameters and band-gap properties of WZ-Si

	a(Å)	*c/a*	Γ-Γ(eV)	Γ-M(eV)	*Δcr*(eV/atom)
Present	3.85	1.654	0.765	0.217	0.035
cal. [a]	3.80	1.654	1.000	0.270	0.036
cal. [b]	3.80	1.650			
expt. [c]	3.84	1.635			
expt. [d]	3.84	1.609			

a. Ref. 7; b. Ref. 17; c. Ref. 18; d. Ref. 19

Table 2: Site-decomposed density of states (PDOS) for VBM at Γ and CBM at Γ and M

WZ-Si		Band-Index*	p_y	p_z	p_x
VBM	Γ	1	0.000	0.427	0.000
		2	0.361	0.000	0.093
		3	0.093	0.000	0.361
CBM	Γ	4	0.000	0.043	0.000
		5	0.207	0.000	0.069
		6	0.069	0.000	0.207
	M	4	0.026	0.046	0.009

* The band indices are the same shown in figure 1(c).

atom having three nearest neighbor atoms at 2.362 Å and another at 2.381 Å. The crystal field splits the valence band maximum into a twofold (p_x and p_y) Γ_{6v} band and a onefold (p_z) Γ_{1v} split-off band.[12, 14] This splitting also occurs in CNM at Γ_{6c}. Details of the band structure near the VBM are shown in figure 1(c). The site-decomposed density of states (PDOS) of VBM and CBM are listed in Table II, where the band indices are indicated in figure 1(c). It is found that p_z has the greatest contribution to CBM at both Γ and M points, while p_x and p_y contribute to VBM at Γ point.

B. Band-Structure Under Uniaxial Compression

As many WZ-semiconductors show a negative volume coefficient for the Γ→Γ direct gap and positive one for the Γ→M indirect band gap[25], study of band properties at non-hydrostatic condition would be of great interest. The calculated difference between the Γ→Γ direct gap and the

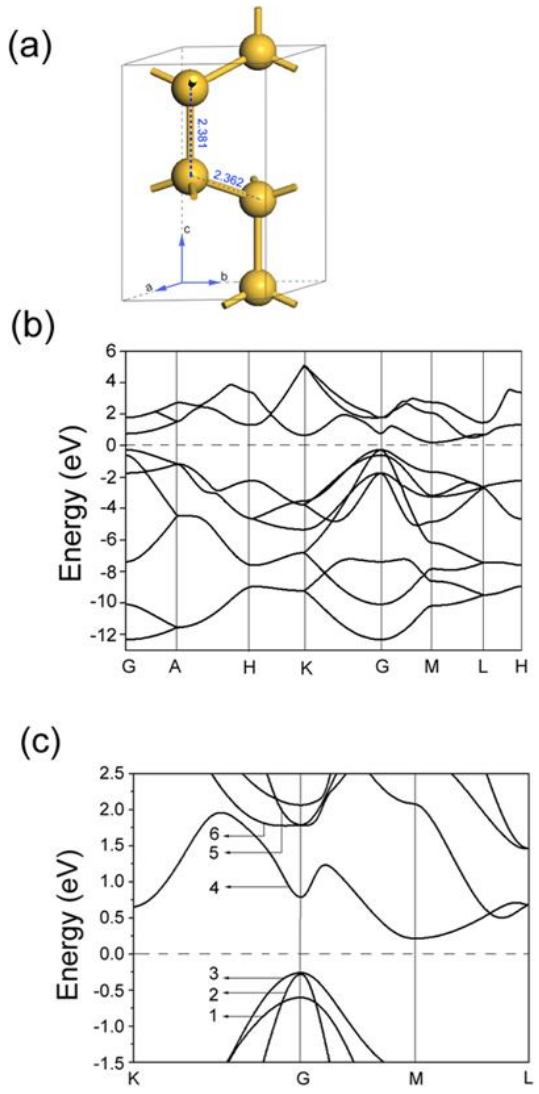

Fig 1: (color online) (a) Unit cell of optimized WZ-Si. (b) Calculated band structure of strain-free WZ-Si. (c) Detailed band structure of WZ-Si near the VBM and CBM

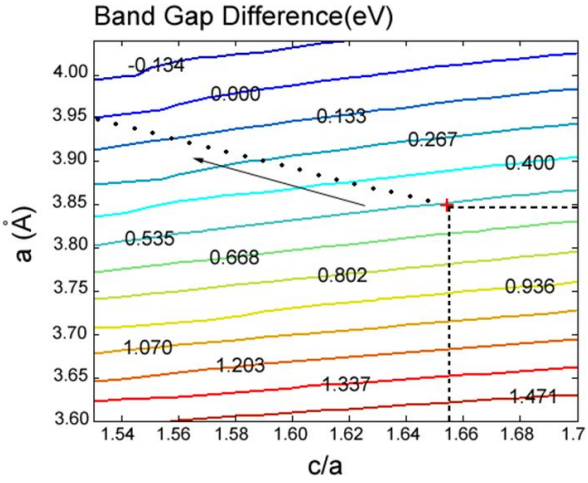

Fig 2: (color online) Difference between the direct energy gap at Γ and the indirect energy gap (Γ→M) as a function of cell parameters (a and c/a). The " + " indicates position

of strain-free WZ-Si. The dots and the arrow correspond to path of increasing uniaxial compression along the c-axis

Γ→M indirect gap is shown as a function of *a* and *c/a* in figure 2 using a contour plot. It is clearly seen that compressing *c/a* or increasing *a* both decrease the direct-indirect band gap difference, to the extent that the direct band gap is smaller than the indirect band gap when $a > 3.97$ Å, or a direct band gap WZ-Si. However, this situation may not be easily reached by a uniaxial compression along the *c*-axis. The dots and arrow in figure.2 indicate responses of lattice parameters to a uniaxial compression, obtained by relaxing the lattice parameter *a* and atomic positions for each fixed *c/a* ratio. When the *c/a* is compressed down to 1.53, the direct energy gap is still larger than the indirect gap. To further illustrate this trend, we show the band-structures for *c/a* = 1.65 and 1.56 in figure.3(a) and figure.3(b), respectively, and the variation of the energy gaps with the *c/a* ratio (*a* is relaxed) in figure.3(c). The direct band gap is found to decrease much faster than the indirect Γ→M band gap as *c/a* decreases, which is different from the behavior of a semiconductor under hydrostatic compression.[26] By further increasing the uniaxial compression or compressing *c/a*, the total energy of the system shows a discontinuity at c/a=1.53 which may be an indication of a structural instability.

The effective mass of electron at CBM at Γ point is found to decrease from $0.189m_e$ in strain-free WZ-Si to $0.172m_e$, where m_e is the mass of a free electron, as c/a is reduced from 1.65 to 1.53, as shown in figure.3(d). This is remarkably smaller than $1.03m_e$ in c-Si phase. The small effective mass in WZ-Si makes it possible for higher electron mobility and faster switch speed in electronic circuits. Pressure needed to compress WZ-Si in c-axis direction is not too high, for example, to reduce the *c/a* value to less than 1.58, a pressure of about 1 GPa is required, as seen in figure.3(d) which is practically possible.

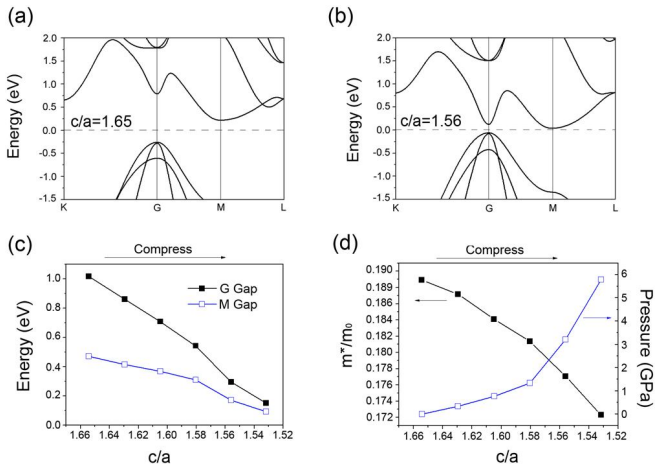

Fig 3: Band structure of WZ-Si for c/a = 1.65 (a) and c/a = 1.56 (b), a is relaxed in both cases, and variations of the direct and indirect energy gaps (c) and electron effective mass (d) with c/a

Actually, unlike hydrostatic compression, uniaxial strain could in addition breaks the crystal symmetry, and further alters band structure properties, like diminishing degeneration of bands and modifying the morphology of energy-isosurface in near VBM region, which would have dramatically influence on photon absorption behavior in semiconductor. Considering the spin-orbital coupling, previous studies[27] reported that uniaxial compression can split the original four-fold $p_{3/2}$ state into two doubly degenerated Kramers states at VBM. This degeneracy makes the photon absorption be related to its polarization relative to applied stain direction[28], which is interesting both in fundamental and practical research for strained WZ-Si in further study.

IV. CONCLUSION

In summary, electronic properties of WZ-Si have been investigated by first-principle calculation. It is found that WZ-Si is an indirect band-gap semiconductor at ambient condition. But the electronic properties can be significantly altered by cell deformation. By compressing *c/a* or expanding *a*, which can be realized by applying uniaxial compression along the c-axis, the direct energy gap of WZ-Si can be reduced significantly. Effective mass of electron at Γ point is dramatic smaller than c-Si, which is strongly dependent on the strain. The calculated external pressure needed to compress WZ-Si is reasonable in practical use. This study will shed light to the fabrication of a direct band-gap Si semiconductor.

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Ziwei Cui is a mechanism and structure designer in the Space Star Technology CO., LTD. He has more than 6 years' experience in the field of mechanical system design. Besides that, he also has more than 2 years' experience in the field of system engineering.

He has a Bachelor degree in automobile engineering,and a Master degree in mechanical engineering.

