Novel Two-Dimensional Silicon Dioxide with in-plane Negative Poisson’s Ratio

Zhibin Gao,† Xiao Dong,*†,‡ Nianbei Li,† and Jie Ren*,†

†Center for Phononics and Thermal Energy Science and School of Physics Science and Engineering, Tongji University, 200092 Shanghai, People’s Republic of China
‡Center for High Pressure Science and Technology Advanced Research, Beijing 100193, China

E-mail: xiao.dong@hpstar.ac.cn; Xonics@tongji.edu.cn

Abstract

Silicon dioxide or silica, normally existing in various bulk crystalline and amorphous forms, is recently found to possess a two-dimensional structure. In this work, we use ab initio calculation and evolutionary algorithm to unveil three new 2D silica structures whose thermal, dynamical and mechanical stabilities are compared with many typical bulk silica. In particular, we find that all these three 2D silica have large in-plane negative Poisson’s ratios with the largest one being double of penta-graphene and three times of borophenes. The negative Poisson’s ratio originates from the interplay of lattice symmetry and Si-O tetrahedron symmetry. Slab silica is also an insulating 2D material, with the highest electronic band gap (> 7 eV) among reported 2D structures. These exotic 2D silica with in-plane negative Poisson’s ratios and widest band gaps are expected to have great potential applications in nanomechanics and nanoelectronics.
Keywords

Two-dimensional material, silicon dioxide, in-plane Negative Poisson’s Ratio, 2D material with widest band gap, crystal structure searching

Introduction

Silicon dioxide with the chemical formula SiO$_2$ is the fundamental component of glass, sand and most minerals, which is also known as one of the building units of earth crust and mantle. There are a large number of isomers with the formula of SiO$_2$ in crystalline and amorphous forms, such as quartz, cristobalite and glassy SiO$_2$. In all of the known SiO$_2$ compounds, Si has $sp^3$ hybridization with 4-fold tetrahedron configuration. O is coordinated with 2 Si atoms, but sometimes with angle type like O in H$_2$O, sometimes with linear type like C in CO$_2$. The variety of SiO$_2$ phases mainly originates from the space stacking form of Si-O tetrahedron. Normally, bulk silicon dioxides are hard (α-quartz with theoretical Vickers hardness 30.2 GPa$^1$), high-quality electrical insulators and favorable dielectric materials. Due to the outstanding mechanic and electronic performances, SiO$_2$ films and slabs have significant applications in mechanics, optics and electronics.

Two-dimensional (2D) materials are substances with a monolayer or few atomic layers thickness.$^{2,3}$ Because of quantum confinement effect, electrons in these materials only have freedom in 2D plane, which could give rise to new physics. But so far, the 2D materials are quite rare and most of them are semimetals (e.g., graphene) or semiconductors (e.g., black phosphorus, sulfide and selenide), with few being insulators, e.g., h-BN, the reported insulating 2D structure with the widest band gap (4.7 eV theoretically$^{4,5}$ and 6.4 eV experimentally$^7$). It is well known that 3D silicon dioxide is a good insulator with wide band gap. Therefore, it is interesting to explore whether the corresponding 2D counterpart may also be stable as a monolayer and exhibit novel properties. If confirmative, it is likely to make contributions to transistors of nanomaterials and multifunctional van der Waals (vdW)
heterostructures.\textsuperscript{8,9}

Thin silica film has firstly been grown on metal Mo(112) substrate.\textsuperscript{10–13} Then slab crystalline silica sheet is grown on another metal Ru(0001).\textsuperscript{14,15} Furthermore, this hexagonal quasi-2D silica can even be supported by graphene.\textsuperscript{16} In this letter, we focus on the intrinsic mechanical properties and use theoretical structure prediction to explore 2D crystalline freestanding silicon dioxide. We identify three novel stable 2D-silica phases, besides the reported 2D-silica.\textsuperscript{14} They all display in-plane negative Poisson’s ratio (NPR), large band gaps, superhard mechanical properties compared to 3D $\alpha$-quartz.

**Computational details**

Crystal structure searching were performed via the \textit{ab initio} evolutionary algorithm in USPEX\textsuperscript{17–19} which has been successfully applied to a wide range of searching problems.\textsuperscript{20–22} Furthermore, we have reconfirmed the global four minimum free energy of our structures based particle-swarm optimization as implemented in CALYPSO code.\textsuperscript{23} We sequentially used 1-6 times of chemical formula SiO$_2$ (up to 18 atoms) per unit cell for searches. According to the experimental results,\textsuperscript{10,14} the thickness of hexagonal 2D-silica is 4.34 Å. Therefore, in order to cover some extraordinary 2D-silica, the original thickness was set up to 5 Å and permitted to relax during the evolution. The self-consistent energy calculations and structure optimization were employed using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional\textsuperscript{24} along with the projector-augmented wave (PAW) potentials\textsuperscript{25,26} as implemented in the Vienna \textit{Ab-initio} Simulation Package (VASP).\textsuperscript{27,28} The kinetic energy cut-off was 800 eV and tetrahedron method with Blöchl correction\textsuperscript{29} was used to integrate the Brillouin-zone. Energy convergence value in self-consistent field (scf) loop was selected as $10^{-8}$ eV and a maximum Hellmann-Feynman forces is less than 0.1 meV/Å. Such a high criteria is found to be required to achieve convergence for phonon calculations and all the elastic-constant components. All the results in this paper is also checked with the local den-
sity approximation (LDA) functional. Additionally, since both LDA and PBE approaches usually underestimate the band gap of semiconductor and insulator, we adopt the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06) for a more accurate calculation. Phonon dispersion curves were obtained using the Phonopy package.

Results and discussion

Structures

A number of low-energy structures had been searched and only the most stable four 2D structures obtained in our computations are discussed here, with space groups of $P6/mmm$, $Pbcm$, $P-4m2$ and $P-4m2$. For simplicity, we define them as $\alpha$, $\beta$, $\gamma$- and $\delta$-2D-silica, respectively. The optimized four silica structures were shown in Figure 1. $\alpha$-2D-silica is hexagonal and has been experimentally grown on Mo(112) and Ru(0001) surfaces, while we obtain it intrinsically in a freestanding form. This known structure has been discovered in our crystal structure prediction, which does validate the correctness of our computational method in high-throughout computing. Other three are our new discovered structures during the explorations. $\alpha$-2D-silica has a perfect $sp^3$ bonding network which means all O atoms are connected to Si atoms with same solid angles $109^\circ 28'$, i.e., Si is in a perfect O tetrahedron. The lattice constant in our computation of $\alpha$-2D-silica is 5.31 Å which is in good agreement with the experimental data 5.2-5.5 Å. This confirms the accuracy of our structure prediction and relaxation.

The optimized structural parameters of four structures are summarized in Table 1. In all of 2D silica, each silicon is connected with four oxygens, constituting a tetrahedron like bulk SiO$_2$. Therefore, silicon atoms share fourfold coordinations and oxygen two, which means all atoms have no redundant valence electrons. In the top view, $\alpha$-2D-silica, like graphene, indeed has a hexagonal crystal structure, while other three have rectangular crystal configurations. Specifically, $\beta$-2D-silica is an anisotropic structure in orthorhombic lattice
while $\gamma$-2D-silica and $\delta$-2D-silica are isotropic in tetragonal lattice. In the side view, $\alpha$-2D-silica with mirror symmetry to $z=0$ plane consists of a ‘double’ layers $\text{Si}_2\text{O}_3$ substructures connected by intermediate Si-O-Si bonds oriented perpendicular to the surfaces. However, other three structures have large inherent bucklings in their interlaminations and lost mirror symmetry relative to x-y plane at $z=0$. $\alpha$-2D-silica and $\delta$-2D-silica each have only one uniform length of Si-O bond, while $\beta$-2D-silica and $\gamma$-2D-silica have three different Si-O bond lengths. In top view, the Si-O bonds are like crossroads in $\beta$-2D-silica, $\gamma$-2D-silica and $\delta$-2D-silica crystal structures.

Figure 1: (color online). Equilibrium 2D monolayer silicon dioxide of (a) $P6/mmm \text{Si}_4\text{O}_8$ ($\alpha$-2D-silica), (b) $Pbcn \text{Si}_4\text{O}_8$ ($\beta$-2D-silica), (c) $P-4m2 \text{Si}_4\text{O}_8$ ($\gamma$-2D-silica) and (d) $P-4m2 \text{SiO}_2$ ($\delta$-2D-silica) in both top and side views. Large blue and small red balls in the (a), (b), (c), (d) represent silicon and oxygen atoms, respectively. The Wigner-Seitz cells are shown by the dotted black regions. The green solid arrows show the lattice vectors.

The four phases of 2D silica have different arrangement of Si-O tetrahedrons. By geometry (directions of Si-O bonds consistent with lattice vectors, lattice types and whether have mirror symmetry relative to $z=0$ plane), the above four structures can be divided into two classes, one is $\alpha$-2D-silica, the other are $\beta$-, $\gamma$- and $\delta$-2D-silica. The latter class has special crossed orientation of chemical bonds which is seldom found in silicon dioxide crystalline forms.

A deeper insight is that Si-O tetrahedron of symmetry group $T_d$ has two special orthogonal projections: one goes through a vertex and the center of its opposite face (3-fold axis);
the other goes through on opposite edges (2-fold axis). For most bulk SiO$_2$ phases and α-2D-silica, the lattice vector is along 3-fold axis, which means this direction is easy to build a spacial framework by Pauling’s third rule$^{33}$ (rule of sharing of polyhedron corners, edges and faces). The representative local structure is double tetrahedron structure of [Si$_2$O$_7$]$^{-6}$, which is the fundamental structure of α-2D-silica and quartz. Here when the structure is limited to two dimension, the expansion in three dimensional space become not very important, and the lattice vector can build the slab along 2-fold axis to get β-, γ- and δ-2D-silica. These coupling of lattice symmetry and Si-O tetrahedron symmetry also is the origin of NPR which will be discussed later.

As quasi-2D structures, the atomic thickness of α-, β-, γ- and δ-2D-silica are 4.34, 3.51, 3.84 and 1.71 in Å, respectively. If we add two van der Waals (vdW) radii of the outmost surface atoms,$^{34}$ we can get their effective thicknesses are 7.38, 6.55, 6.88 and 4.75 in Å, respectively. It is observed that δ-2D-silica is the thinnest structure, while the thickness increases by the sequence of δ, β, γ and α-2D-silica. β-, γ- and δ-2D-silica are thinner than α-2D-silica, which implies they are more like pure two-dimensional structures and have more low dimensional effects. Lower thickness makes these three phases to lose mirror symmetry and they have not enough spaces for double tetrahedron structure of [Si$_2$O$_7$]$^{-6}$, that is why they have different Si-O bond orientations. In this way, β-, γ- and δ-2D-silica can be seen as a metastable intermediate products when the atoms build silica from zero thickness to α-2D-silica.

**Stability and wide bandgap**

Now our first priority is to answer the question whether these new freestanding 2D silicon dioxide materials are stable. In normal condition, silica exists in many crystalline forms. Here we compare the free energies of our 2D silica structures and 3D counterparts in thermodynamics and the calculation are implemented in HSE06 method (Figure 2). Compared with α-quartz, who has the lowest energy to be the thermal-dynamically stable phase of SiO$_2$,
Table 1: Optimized structural properties of the four different 2D silicon dioxide crystal structures. $|\vec{a}_1|$, $|\vec{a}_2|$ and $|\vec{a}_3|$ are the lattice constants defined in Figure 1. Atomic positions are the group Wyckoff positions for each independent atoms in fractional coordinates. $E_c$ is the cohesive energy per atom in eV. $E_{G-HSE}$ is the band gap calculated by HSE06.

| Phase             | $\alpha$-2D-silica(Si$_4$O$_8$) | $\beta$-2D-silica(Si$_4$O$_8$) | $\gamma$-2D-silica(Si$_4$O$_8$) | $\delta$-2D-silica(SiO$_2$) |
|-------------------|--------------------------------|-------------------------------|-------------------------------|-----------------------------|
| space group       | $P6/mmm$                       | $Pbcm$                        | $P-4m2$                       | $P-4m2$                     |
| $|\vec{a}_1|$(Å)    | 5.31                           | 20.00                         | 5.64                          | 2.84                        |
| $|\vec{a}_2|$(Å)    | 5.31                           | 5.07                          | 5.64                          | 2.84                        |
| $|\vec{a}_3|$(Å)    | 20.00                          | 5.53                          | 20.00                         | 20.00                       |
| Atomic Positions  | Si 4h $(0.67,0.33,0.42)$       | Si 4d $(0.55,0.70,0.25)$      | Si 4k $(0.50,0.75,0.55)$      | Si 1d $(0.00,0.00,0.50)$    |
|                   | O 6i $(0.50,0.50,0.39)$        | O 4d $(0.52,0.39,0.25)$       | O 2f $(0.50,0.50,0.40)$       | O 2g $(0.50,0.00,0.46)$    |
|                   | O 2d $(0.33,0.67,0.50)$        | O 4c $(0.50,0.75,0.50)$       | O 2g $(0.50,0.00,0.59)$       | O 4i $(0.73,0.27,0.50)$    |
| $E_c$(eV/atom)    | 6.61                           | 6.54                          | 6.44                          | 6.37                        |
| $E_{G-HSE}$(eV)   | 7.31                           | 7.69                          | 7.40                          | 7.34                        |
| thickness(Å)      | 4.34                           | 3.51                          | 3.84                          | 1.71                        |

Figure 2: (color online). Energy landscape versus band gap of 3D and 2D silica materials as performed in the HSE06 method. As $\alpha$-quartz is the most stable silica at low temperatures and is the most common form of crystalline silica, we set it as the benchmark reference in green dashed line to compare all silica structures.
all 2D silica are meta-stable phases. The structure of α-2D-silica with highest symmetry has the lowest energy (0.047 eV/f. u.) in 2D silica whose energy is comparable to α-quartz which is chosen as the reference point of zero energy. Compared with other 2D-silica, α-2D-silica is thicker and more like bulk silica. That is why it has a similar energy to bulk quartz. Si-O bond length in α-2D-silica is 1.63 Å with a quite similar to 1.61 Å of α-quartz, while the Si-O bonds are 1.64 Å, 1.65 Å, 1.66 Å for β-, γ- and δ-2D-silica, respectively, which means there is a positive correlation between energy of structure and Si-O bond length since shorter distance intensifies the strength of Si-O bonds. In a word, [SiO$_4$] tetrahedral unit in α-2D-silica is more similar to α-quartz than β-, γ- and δ-2D-silica.

Besides, according to Pauling’s fifth rule (parsimony rule), the number of essentially different kinds of constituents in a crystal tends to be small. The repeating units will tend to identical because each atom in the structure is most stable in a specific chemical environment. α-2D-silica and α-quartz have only one type of tetrahedral, while β-, γ- and δ-2D-silica have two or three distorted tetrahedral because of symmetry breaking. Therefore, the energy of α-2D-silica is close to bulk material with lower energy.

Though α-2D-silica has been grown experimentally, it is not useless to explore other interesting phases with a little higher energy in complicated but brand new 2D silica energy surface. As a matter of fact, metastable phases are common in condensed matter and the ubiquitous metastable phases do not produce a bad effect on their vast and tremendous applications in modern industrial societies and our daily life. The energies of β-2D-silica (0.253 eV/f. u.), γ-2D-silica (0.542 eV/f. u.) and δ-2D-silica (0.758 eV/f. u.) are comparable to stishovite and seifertite, much lower than energy of fibrous W-silica. Since stishovite and seifertite are observed by high pressure experiments and quenchable to ambient condition, and W-silica can be synthesized by chemical methods, it is reasonable to believe that our three novel 2D phases can exist as a metastable phases at normal condition. It is also worth highlighting that β-2D-silica has both the largest band gap (up to 7.69 eV) in our HSE06 calculations and a moderate low free energy.
The dynamical stability has been confirmed by calculating phonon dispersion relations shown in the Figure S1. All the structures of four 2D silica are free from imaginary frequencies, which means they are dynamically stable. Furthermore, the dynamical stability of these freestanding 2D silica is also validated by performing \textit{ab initio} molecular dynamics simulations using canonical ensemble at a series of elevated temperatures with lifetime longer than 10 ps (Figure S2). The result shows that all 2D-silica are still robust even at high temperature (1000 K). Particularly, $\beta$-2D-silica can live in the high temperature of 2500 K which is much higher than the melting point of quartz (1986 K). \textsuperscript{39}

For 2D elastic solid materials, mechanical stability is indispensable to the existence of materials. If a 2D material is mechanically stable, the corresponding elastic constants have to satisfy $C_{11}C_{22}-C_{12}^2>0$ and $C_{66}>0$. \textsuperscript{40} We have guaranteed that all the elastic constants (shown in the Table S1) of four 2D silica always meet this compulsory requirement. Therefore, we have verified that $\alpha$-, $\beta$-, $\gamma$- and $\delta$-2D-silica are metastable phases.

Band gap is the fundamental electronic property for semiconductor and insulator. Theoretically, we find that 2D-silica is of the largest band gap in all reported 2D crystal materials. As the electronic band structures are shown in the Figure S3, $\alpha$-, $\beta$-, $\gamma$-2D-silica are direct insulators while $\delta$-2D-silica is an indirect insulator. Compared with h-BN which is reported to have a large band gap of 4.7 eV theoretically\textsuperscript{46} (6.4 eV experimentally\textsuperscript{7}), silica put the upper limit of 2D band gap to 7.69 eV. This implies it is hard to change its electronic states in 2D-silica. Since the absorption of light is related to the band gap and the thickness, 2D-silica can be the most transparent materials in the world.

As good insulators, 2D-silica can be an outstanding candidate for dielectric materials. Dielectric constants of $\alpha$-, $\beta$-, $\gamma$-2D-silica and $\delta$-2D-silica are 3.18, 2.42, 2.24 and 2.49, respectively. Notably, based on the formula of in-plane parallel capacitor $c = \varepsilon S/4\pi kd$, capacitance of $\delta$-2D-silica is around 1.76 times larger than $\alpha$-quartz because it is 0.31 times thinner than $\alpha$-quartz. This means it is a favorable dielectric material for next nanomaterials transistors such as 2D transistors and 2D electronic devices\textsuperscript{41} and a supercapacitor candidate\textsuperscript{42}. 

\textsuperscript{9}
Superhard mechanical properties with NPR

When a material is stretched in one direction, it usually contracts in the other two directions perpendicular to the applied stretching direction, so-called positive Poisson’s ratio (PPR). Most materials have a PPRs ranging from 0 to 0.5. From the classical theory of elasticity, for 3D isotropic materials, the Poisson’s ratio cannot be less than -1.0 or greater than 0.5.43 Materials with NPR have the property that when stretched, they become auxetic perpendicular to the applied force. These materials are also called auxetics by its auxetic property with external strain. This interesting phenomenon was firstly presented in foam structure in 1987.44 And then materials with NPR attract a lot of scientific interest by its wide applications, such as single-layer graphene and graphene ribbons,45,46 single-layer black phosphorus,47,48 h-­‐silica,50 penta-graphene,40 borophenes,20 and semi-metallic Be3C2,51 and can be used in vanes for aircraft,52 packing materials,53 body armor and national defense.54 Furthermore, we find that in-plane NPR is rare and novel in 2D materials based on the collected data from the available published papers with our utmost endeavor shown in the Figure S4.

Poission’s ratio $\nu$ and Young’s modulus $E$ in the xy plane can be expressed as following equations:

$$
\nu_{xy} = -\frac{d\varepsilon_y}{d\varepsilon_x}, \quad \nu_{yx} = -\frac{d\varepsilon_x}{d\varepsilon_y},
$$

$$
E_x = \frac{\sigma(\varepsilon_x)}{\varepsilon_x}, \quad E_y = \frac{\sigma(\varepsilon_y)}{\varepsilon_y},
$$

(1)

Where $\nu_{xy}$ is the Poisson’s ratio of the x direction which is induced by a strain in the x axis. $E_x$ is the Young’s modulus of the x direction which is the slope in the stress-strain curve. Similarly, $\nu_{yx}$ and $E_y$ are the Poisson’s ratio and Young’s modulus in the y direction. $\sigma$ is the stress as a function of strain $\varepsilon$. We quantitatively calculated the Poisson’s ratio $\nu$ and Young’s modulus $E$ for our four 2D silicon dioxides according to the Eq. (1) for uniaxial strain. The results of Poisson’s ratio are shown in Figure3. We also calculated the mechanical property by the elastic solid theory (the detailed description of this method is discussed in
Figure 3: (color online). The Poisson’s ratio (short dashed lines denote the linear response counterpart) as a function of uniaxial tensile strain of $\alpha$-2D-silica, $\beta$-2D-silica, $\gamma$-2D-silica and $\delta$-2D-silica in the (a) x-direction ($\nu_{xy} = 0.522, -0.048, -0.022$ and $-0.112$) and (b) y-direction ($\nu_{yx} = 0.522, -0.123, -0.022$, $-0.112$). The horizontal black dashed lines are set to zero for comparison.

the Supporting Information). The results of elastic solid theory and strain method are quite similar (Table S2). Therefore, both methods confirm that our three 2D silica phases have NPR mechanical property. In order to check the correctness of our computational method and results, we select graphene and black phosphorus as references. Our results shown in the Table S2 are in good agreement with the published results. As we have mentioned above, $\alpha$-2D-silica, $\gamma$-2D-silica and $\delta$-2D-silica are isotropic materials, while $\beta$-2D-silica is an anisotropic material. Therefore, except $\beta$-2D-silica, all other three materials have the mechanical properties $E_x = E_y$ and $\nu_x = \nu_y$.

Figure 3(a) displays the strain response in the y direction when applying stretch in the x direction. Similarly, the Poisson’s ratio of the y direction is shown in Figure 3(b). Obviously, there are two kinds of mechanical response when four 2D silica are stretched. $\alpha$-2D-silica is contracted perpendicular to the applied force, while $\beta$-2D-silica, $\gamma$-2D-silica and $\delta$-2D-silica are auxetic during the uniaxial strain in 2D plane. Remarkably, $\beta$-2D-silica in the y-direction
and δ-2D-silica in both x and y directions have large NPR values -0.123 and -0.112. These absolute values of NPR are quite high, which equal to double of penta-graphene (\(\nu=-0.068\)), three times of borophenes (\(\nu_x=-0.04, \nu_y=-0.02\)) and are different from single-layer black phosphorus whose NPR occurs in the yz plane.

Figure 4: (color online). The explanation of Poisson’s ratio for our new 2D silicon dioxide structures. Each silicon atom is surrounded by four oxygen atoms, due to its shape, the SiO\(_4\) groups is called SiO\(_4\) tetrahedron. (a) when the tensile strain (in green arrows) is applied to the direction of the median line of bottom of the tetrahedron (vertical to 3-fold axis), because the angular variation, the distance of two oxygen atoms decreases (in black arrows), leading a positive Poisson's ratio (\(\nu>0\)). On the contrary, (b) when the tensile strain is applied to the edge to the tetrahedron (vertical to 2-fold axis), similarly, because the angular variation, the distance of two oxygen atoms increases, leading a NPR phenomenon (\(\nu<0\)).

NPR of our novel three 2D silica structures originates from the low dimensional effect. As discussed in structure section, [SiO\(_4\)] tetrahedron is the basic units in both slab and bulk SiO\(_2\). Normally in 3D system, by the request of sharing of polyhedron corners (Pauling’s third rule), the lattice is along 3-fold axis of Si-O tetrahedron. The tensile strain (in green arrows) on the direction of the median line of bottom of the tetrahedron makes the distance of two oxygen atoms decrease (in black arrows), which implies a positive Poisson’s ratio (\(\nu>0\)) shown in Figure 4(a). However, for 2D materials, there is spatial constrains and the lattice can be along in 2-fold axis. When the tensile strain is applied to the edge to the tetrahedron, the distance of two oxygen atoms increases, leading to a NPR phenomenon (\(\nu<0\)) shown in Fig. 4(b). Therefore, we believe the distinction between these two situations
stems from the coupling of lattice symmetry and Si-O tetrahedron symmetry, which is a low dimensional effect.

In a word, our three new structures are thinner than $\alpha$-2D-silica with stronger low dimensional effect in geometry. This low dimensional effect further leads to a different type of matching between lattice symmetry and Si-O tetrahedron symmetry, which finally leads to this interesting NPR phenomenon.  

We have also revealed the Young’s modulus of these 2D silica materials and prove they are superhard 2D materials. As we have explained above, we use the effective thickness of 2D materials, including two vdW radii. The calculated Young’s modulus are exhibited in the Table S2. Generally, Young’s modulus can be obtained by dividing the tensile stress by the extensional strain in the elastic region of the stress-strain graph. A material whose Young’s modulus is high can be regarded as rigid. According to the experimental and theoretical values, the Young’s modulus of 3D $\alpha$-quartz is around 100 GPa without extra external pressure. It is to be disclosed that all four 2D silica are much harder than $\alpha$-quartz. Young’s modulus of $\delta$-2D-silica (346 GPa) is more than triple of that of $\alpha$-quartz (100 GPa) and is comparable to that of single-layer Boron Nitride (BN) (366 GPa). Interestingly, the Young’s modulus of $\beta$-2D-silica in the y direction (247 GPa) is more than double of that in the x direction (97 GPa) which due to the strong anisotropy of its special crystal structures. The hardness of these 2D silica can be explained by tetrahedral silica structure in Figure 4 and phonon dispersion realations in the Figure S1. The slope of phonon dispersions denotes the group velocity of each phonon. The bigger group velocity, the more rigid of the material. Therefore, $\delta$-2D-silica and $\beta$-2D-silica have a superhard and strong anisotropic mechanical properties.
Conclusion

In conclusion, we have performed a systematic structure searching and computationally-guided material discovery for 2D silicon dioxide and found $\beta$, $\gamma$- and $\delta$-2D-silica. The thermal, dynamical and mechanical stability checking guarantees that these 2D-silica can exist as metastable phases at atmosphere condition. In particular, in-plane NPR has been identified in these three structures, whose values are so large that they are double that of penta-graphene, three times of borophenes ($\nu_x=-0.04, \nu_y=-0.02$) and are different from single-layer black phosphorus’s NPR in the yz plane. The NPR originates from the coupling of lattice symmetry and Si-O tetrahedron symmetry which is a low dimensional effect. We have also proved these three 2D silica to be superhard materials, which indicate superior thermal conductivities compared to bulk silica materials. Furthermore, with its largest electronic band gaps in reported 2D crystal materials, we believe these novel 2D-silica can be used as the most transparent insulators and good dielectric materials, which is expected to have great applications in many fields.

The authors declare no competing financial interest.

Supporting Information Available: Novel Two-Dimensional Silicon Dioxide with in-plane Negative Poisson’s Ratio. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgments

The numerical calculations were carried out at Shanghai Supercomputer Center. This work is supported by the National Youth 1000 Talents Program in China, and the 985 startup grant (No. 205020516074) at Tongji University, (Z.G. and J.R.), and by the NSF China with grant No. 11334007(N.L.). X.D. also acknowledges the support of NSAF with grant No. U1530402.
References

(1) Chen, X.-Q.; Niu, H.; Li, D.; Li, Y. Intermetallics 2011, 19, 1275 – 1281.

(2) Geim, A. K.; Grigorieva, I. V. Nature 2013, 499, 419–425.

(3) Miro, P.; Audiffred, M.; Heine, T. Chem. Soc. Rev. 2014, 43, 6537–6554.

(4) Peng, Q.; De, S. Physica E 2012, 44, 1662–1666.

(5) Churchill, H. O.; Jarillo-Herrero, P. Nat Nanotechnol. 2014, 9 (5), 330 – 331.

(6) Xu, Y.-N.; Ching, W. Y. Phys. Rev. B 1991, 44, 7787–7798.

(7) Zunger, A.; Katzir, A.; Halperin, A. Phys. Rev. B 1976, 13, 5560–5573.

(8) Liu, Y.; Weiss, N. O.; Duan, X.; Cheng, H.-C.; Huang, Y.; Duan, X. Nat. Rev. Mater. 2016, 1, 16042.

(9) Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. H. Science 2016, 353.

(10) Weissenrieder, J.; Kaya, S.; Lu, J.-L.; Gao, H.-J.; Shaikhutdinov, S.; Freund, H.-J.; Sierka, M.; Todorova, T. K.; Sauer, J. Phys. Rev. Lett. 2005, 95, 076103.

(11) Todorova, T. K.; Sierka, M.; Sauer, J.; Kaya, S.; Weissenrieder, J.; Lu, J.-L.; Gao, H.-J.; Shaikhutdinov, S.; Freund, H.-J. Phys. Rev. B 2006, 73, 165414.

(12) Schroeder, T.; Adelt, M.; Richter, B.; Naschitzki, M.; Bäumer, M.; Freund, H.-J. Surf. Rev. Lett. 2000, 7, 7–14.

(13) Seifert, J.; Blauth, D.; Winter, H. Phys. Rev. Lett. 2009, 103, 017601.

(14) Löffler, D.; Uhrlrich, J. J.; Baron, M.; Yang, B.; Yu, X.; Lichtenstein, L.; Heinke, L.; Büchner, C.; Heyde, M.; Shaikhutdinov, S.; Freund, H.-J.; Wlodarczyk, R.; Sierka, M.; Sauer, J. Phys. Rev. Lett. 2010, 105, 146104.
(15) Heyde, M.; Shaikhutdinov, S.; Freund, H.-J. *Chem. Phys. Lett.* **2012**, *550*, 1–7.

(16) Huang, P. Y.; Kurasch, S.; Srivastava, A.; Skakalova, V.; Kotakoski, J.; Krasheninnikov, A. V.; Hovden, R.; Mao, Q.; Meyer, J. C.; Smet, J.; Muller, D. A.; Kaiser, U. *Nano Lett.* **2012**, *12*, 1081–1086.

(17) Oganov, A. R.; Glass, C. W. *J. Chem. Phys.* **2006**, *124*, 244704.

(18) Oganov, A. R.; Lyakhov, A. O.; Valle, M. *Acc. Chem. Res.* **2011**, *44*, 227–237.

(19) Lyakhov, A. O.; Oganov, A. R.; Stokes, H. T.; Zhu, Q. *Comput. Phys. Commun.* **2013**, *184*, 1172–1182.

(20) Mannix, A. J.; Zhou, X.-F.; Kiraly, B.; Wood, J. D.; Alducin, D.; Myers, B. D.; Liu, X.; Fisher, B. L.; Santiago, U.; Guest, J. R.; Yacaman, M. J.; Ponce, A.; Oganov, A. R.; Hersam, M. C.; Guisinger, N. P. *Science* **2015**, *350*, 1513–1516.

(21) Niu, H.; Oganov, A. R.; Chen, X.-Q.; Li, D. *Sci. Rep.* **2015**, *5*, 18347.

(22) Dong, X.; Li, Y.-L.; Oganov, A. R.; Li, K.; Zheng, H.; Mao, H.-k. *arXiv preprint arXiv:1603.02880* 2016.

(23) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. *Physical Review B* **2010**, *82*, 094116.

(24) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(25) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953–17979.

(26) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758–1775.

(27) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(28) Kresse, G.; Furthmüller, J. *J. Comput. Mater. Sci.* **1996**, *6*, 15–50.

(29) Blöchl, P. E.; Jepsen, O.; Andersen, O. K. *Phys. Rev. B* **1994**, *49*, 16223–16233.
(30) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048–5079.

(31) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2003**, *118*, 8207–8215.

(32) Togo, A.; Oba, F.; Tanaka, I. *Phys. Rev. B* **2008**, *78*, 134106.

(33) Pauling, L. *The nature of the chemical bond, 3rd ed.*; Cornell University Press: Ithaca, NY, 1960.

(34) Xu, W.; Zhang, G.; Li, B. *J. Chem. Phys.* **2015**, *143*, 154703.

(35) Smyth, J. R.; Swope, R. J.; Pawley, A. R. *Am. Mineral.* **1995**, *80*, 454–456.

(36) Glsplnrr, T. *Am. Mineral.* **1990**, *75*, 739–747.

(37) Dera, P.; Prewitt, C. T.; Boctor, N. Z.; Hemley, R. J. *Am. Mineral.* **2002**, *87*, 1018–1023.

(38) Weiss, A.; Weiss, A. *Z. anorg. allg. Chem.* **1954**, *276*, 95–112.

(39) Deer, W. A.; Howie, R. A.; Zussman, J. *An Introduction to the Rock-forming Minerals, 2nd ed.*; Longman Scientific and Technical: Essex, 1992; pp 1–696.

(40) Zhang, S.; Zhou, J.; Wang, Q.; Chen, X.; Kawazoe, Y.; Jena, P. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 2372–2377.

(41) Franklin, A. D. *Science* **2015**, *349*, aab2750.

(42) Bonaccorso, F.; Colombo, L.; Yu, G.; Stoller, M.; Tozzini, V.; Ferrari, A. C.; Ruoff, R. S.; Pellegrini, V. *Science* **2015**, *347*, 1246501.

(43) Landau, L. D.; Lifshitz, E. M. *Theory of Elasticity*; Pergamon: Oxford, 1995.

(44) Lakes, R. *Science* **1987**, *235*, 1038–1040.

(45) Jiang, J.-W.; Chang, T.; Guo, X.; Park, H. S. *Nano Lett.* **2016**, *16*, 5286–5290.
(46) Jiang, J.-W.; Park, H. S. *Nano Lett.* **2016**, *16*, 2657–2662.

(47) Jiang, J.-W.; Park, H. S. *Nat. Commun.* **2014**, *5*, 4727.

(48) Du, Y.; Maassen, J.; Wu, W.; Luo, Z.; Xu, X.; Ye, P. D. *Nano Lett.* **2016**, *16*, 6701–6708.

(49) Jiang, J.-W.; Kim, S. Y.; Park, H. S. *Appl. Phys. Rev.* **2016**, *3*, 041101.

(50) Özçelik, V. O.; Cahangirov, S.; Ciraci, S. *Phys. Rev. Lett.* **2014**, *112*, 246803.

(51) Wang, Y.; Li, F.; Li, Y.; Chen, Z. *Nat. Commun.* **2016**, *7*.

(52) Baughman, R. H.; Shacklette, J. M.; Zakhidov, A. A.; Stafström, S. *Nature* **1998**, *392*, 362–365.

(53) Grima, J. N.; Evans, K. E. *J Mater Sci* **2006**, *41*, 3193–3196.

(54) Liu, Q. *Literature review: materials with negative Poisson’s ratios and potential applications to aerospace and defence*; (DSTO, Defence Science and Technology Organisation, 2006).

(55) Wei, X.; Fragneaud, B.; Marianetti, C. A.; Kysar, J. W. *Phys. Rev. B* **2009**, *80*, 205407.

(56) Sánchez-Portal, D.; Artacho, E.; Soler, J. M.; Rubio, A.; Ordejón, P. *Phys. Rev. B* **1999**, *59*, 12678–12688.

(57) Wei, Q.; Peng, X. *Appl. Phys. Lett.* **2014**, *104*, 251915.

(58) Qiao, J.; Kong, X.; Hu, Z.-X.; Yang, F.; Ji, W. *Nat. Commun.* **2014**, *5*, 4475.

(59) Keskar, N. R.; Chelikowsky, J. R. *Nature* **1992**, *358*, 222 – 224.

(60) Wu, X.; Varshney, V.; Lee, J.; Zhang, T.; Wohlwend, J. L.; Roy, A. K.; Luo, T. *Nano Lett.* **2016**, *16*, 3925–3935.
(61) Wu, X.; Varshney, V.; Lee, J.; Pang, Y.; Roy, A. K.; Luo, T. arXiv preprint \textit{arXiv:1607.06542} 2016,

(62) Zubov, V.; Firsova, M. Soviet. Phys. Cryst. \textbf{1962}, \textit{7}, 374–376.

(63) Ohno, I. \textit{J. Phys. Earth} \textbf{1995}, \textit{43}, 157–169.

(64) Kimizuka, H.; Ogata, S.; Li, J.; Shibutani, Y. \textit{Phys. Rev. B} \textbf{2007}, \textit{75}, 054109.

(65) Andrew, R. C.; Mapasha, R. E.; Ukpong, A. M.; Chetty, N. \textit{Phys. Rev. B} \textbf{2012}, \textit{85}, 125428.