Effective band gap narrowing of anatase TiO$_2$ by strain along a soft crystal direction

Wan-Jian Yin,[1] Shiyou Chen,[1] Ji-Hui Yang,[1] Xin-Gao Gong,[1,a)] Yanfa Yan,[2] and Su-Huai Wei[2]

[1]*Department of Physics and Key Laboratory for Computational Physical Sciences (MOE), Fudan University, Shanghai 200433, People's Republic of China*
[2]*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*

Due to its large band gap (3.2 eV), TiO$_2$ cannot absorb sun light effectively. To reduce its band gap, various approaches have been attempted; most of them are using doping to modify its band structure. Using first-principles band structure calculations, we show that unlike the rutile phases, the band gap of TiO$_2$ in the anatase phase can be effectively reduced by applying stress along a soft direction. We propose that this approach of tuning the band gap by applying stress along soft direction of a layered semiconductor is general and should be applicable to other anisotropic materials. © 2010 American Institute of Physics. [doi:10.1063/1.3430005]

TiO$_2$ has drawn much attention of researchers over the past decades due to its excellent photocatalytic activity and long-term chemical stability, especially in photoelectro-chemical (PEC) hydrogen production through water splitting.[1–4] However, its large band gap of 3.2 eV has limited its use as an ideal photoelectrode because it is not efficient to absorb visible light (with photon energy ~1.7–3.1 eV). To improve its efficiency, great efforts have been made to reduce the band gap of TiO$_2$, most of those are through doping of foreign elements such as Cr, Fe, Co, Mo, N, and C (Refs. 5–9) or introducing oxygen vacancies in TiO$_2$.[10] However, these approaches introduce defect levels into the host, which could decrease the carrier mobility and become recombination centers. As a result, so far the PEC efficiencies of TiO$_2$ have not been improved significantly by doping, even if the band gap is reduced.

In this paper, we propose to narrow the band gap of TiO$_2$ by strain. The advantage for this approach is that applying stress with a reasonable magnitude can keep the material defect-free, thus, improve its carrier collection. Indeed, several recent experimental studies have shown that strain can be used to tune the band gap of TiO$_2$ and enhance its PEC efficiency.[11] For example, Shibata *et al.*[12] found that for the anatase TiO$_2$ film with tensile stress, the photoinduced hydrophilic conversion rate in water was five times greater than that without residual stress. Tavares *et al.*[13] deposited poly-crystalline TiO$_2$ thin films on polymer sheets and found that for strain less than 5% the photocatalytic activity is largely enhanced. Kamei *et al.*[14] also reported that anatase TiO$_2$ film under epitaxial strain could enhance the electron-hole charge separation. However, there are also reports showing that the PEC activity is reduced after strain is applied.[15,16] This indicates that a better theoretical understanding of strain-induced change in the optical properties of TiO$_2$ is needed.

The band gap of a conventional semiconductor is usually sensitive to external pressure or volume deformation.[17] For example, the valence band maximum (VBM) of GaAs has As p character and the conduction band minimum (CBM) of GaAs has mostly Ga s character. The hydrostatic band gap

pressure coefficient (BGPC) of GaAs is 10.8 meV/kbar, which means that the band gap of GaAs will increase by about 1 eV when 10 GPa hydrostatic pressure is applied. For most ionic oxides, the hydrostatic pressure coefficient is much smaller.[17] For TiO$_2$ with its CBM having large Ti 3d character, the pressure coefficient could be even negative. However, quantitative study of strain-induced changes on optical properties of TiO$_2$ is still lacking. In this paper, we will study the strain effect on the band gap of TiO$_2$ using first-principles method. We find that the pressure coefficients of TiO$_2$ is usually too small to have a meaningful change in the band gap by stress. However, for TiO$_2$ in the anatase phase, because it has a layered structure with soft direction perpendicular to the layer plane, its band gap can be tuned efficiently by applying stress along this direction. In contrast, TiO$_2$ in rutile phase has no such a soft crystal direction, thus its band gap is hard to change under various strain conditions.

Our first-principles calculations are based on density functional theory as implemented in the VASP code,[18] using the projector augmented wave method.[19] The PW91 generalized gradient approximation (GGA) (Ref. 20) is adopted for exchange-correlation potential. Dense Monkhorst–Pack k-point mesh of $(13 \times 13 \times 5)$ for conventional anatase cell and $(9 \times 9 \times 13)$ for rutile unit cell are used and the electronic wave functions are expanded in plane waves with energy cutoff of 500 eV for getting reliable Pulay stress. The calculated lattice parameters are listed in Table I. The calculated elastic properties are listed in Table II. All these results are in good agreement with experimental results and previous theoretical calculations.

TABLE I. The calculated structural parameters, a (Å), c (Å), u, Ti–O bond length d_{eq}(Å), d_{ap}(Å), and density (10^3 kg/m^3). a and c are lattice constants. After considering symmetry, the O coordinates in rutile and anatase are independently determined by (u,u,0) and (0,0,u), respectively.

	a	c	u	d_{eq}	d_{ap}	Density
Rutile	4.6558	2.9674	0.3046	1.96	2.01	4.13
Anatase	3.8188	9.6875	0.2069	1.95	2.00	3.76

a)Electronic mail: xggong@fudan.edu.cn.

TABLE II. The calculated bulk modulus (B), Young's modulus along a(Y_a) and c(Y_c) axis, and elastic constants of rutile and anatase phases compared with experimental results and some other theoretical calculations. All values are in GPa.

	B	Y_a	Y_c	$c_{11}+c_{12}$	c_{13}	c_{33}
Rutile						
Our results	215	343	365	451	161	480
Issak *et al.*[a]	209	354	386	443	147	484
Manghnani[b]	216	356	383	449	150	484
Anatase						
Our results	177	266	100	501	148	187
Igua[c]	174	255	103	471	143	190
Dubrovinsky *et al.*[d]	178 ± 1					
Arlt *et al.*[e]	179 ± 2					

[a]Reference 21.
[b]Reference 22
[c]Reference 24.
[d]References 25 and 26.
[e]Reference 23.

Both anatase and rutile have tetragonal crystal structures, in which the slightly distorted TiO_6 octahedra [Figs. 1(c) and 1(d)] could be considered as the building blocks. Both octahedra have four equivalent equatorial Ti–O bonds (Ti–O_3, Ti–O_4, Ti–O_5, and Ti–O_6) with bond length d_{eq} and two longer equivalent apical Ti–O bonds (Ti–O_1 and Ti–O_2) with length d_{ap}. As d_{ap} is larger than d_{eq} (Table I), the apical axes are softer than equatorial ones in TiO_6 octahedra. As shown in Fig. 2, the TiO_2 crystals could be considered as the packing of these TiO_6 octahedra. In rutile phase, a half of soft axis lies along the [110] direction and the other half lies along the [1$\bar{1}$0] direction. Whereas in anatase, all of the soft axes lie along the [001] direction, making [001] the soft direction in the anatase phase. Consequently, anatase phase can be considered as a layered structure with more *empty* room
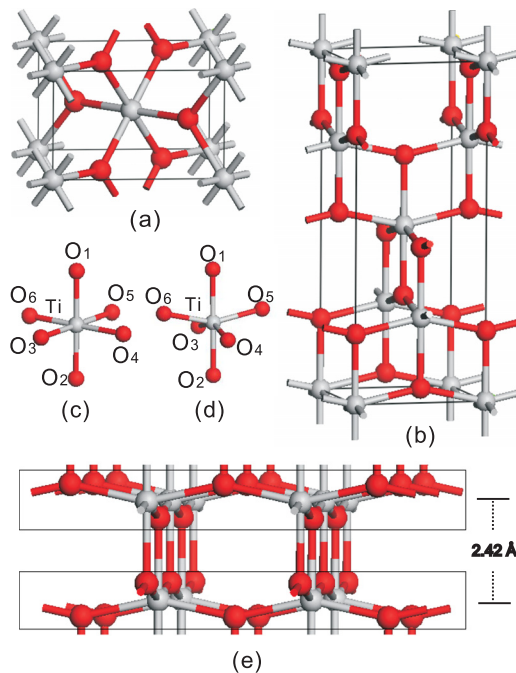

FIG. 1. (Color online) The tetragonal crystal cells of rutile (a) and anatase (b). The atomic structures of TiO_6 octahedron in rutile (c) and anatase (d). (e) The schematic layered structure of anatase.
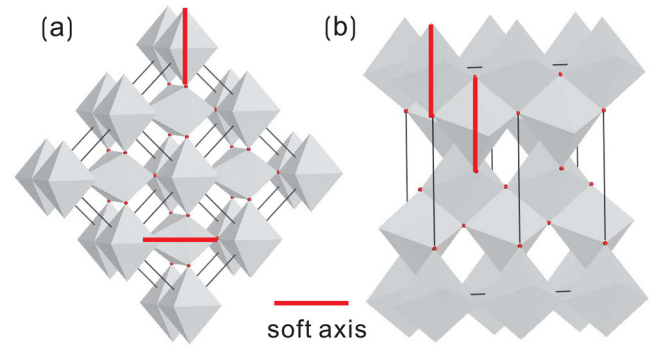

FIG. 2. (Color online) The octahedra-packing style of rutile (a) and anatase (b) TiO_2. The apical (soft) axis of representative octahedra is labeled as a thick line. The layered structure of anatase phase is obvious with all the soft axis directing along one direction.

outside TiO_6 octahedra and the layers are linked with each other by soft apical Ti–O bonds [Fig. 1(e)], thus making its *c* direction have good compressibility. The calculated elastic properties are listed in Table II. Our results are in good agreement with experimental results[21–23] and some previous theoretical calculations.[24–26] We find that the $c_{11}+c_{12}$ and c_{13} parameters of anatase phase are close to those of rutile phase whereas the c_{33} coefficient is much smaller than that of rutile. As a result, the Young's modulus of anatase phase along *c* axis is significantly smaller than rutile phase.

The band gap of a semiconductor changes with the bond lengths and bond angles. It is well-known that the stress coefficient of the band gap is equal to the strain deformation potential divided by elastic constants.[17] For oxides such as TiO_2, because it has large elastic constants, the stress coefficients are usually small. To narrow the band gap of TiO_2 by stress effectively, it is clear that the most possible way is to apply stress along the weakest crystal direction because both of the bond lengths and bond angles changes more in this way at finite stress.

Rutile has a direct fundamental band gap located at Γ point. The fundamental band gap of anatase is indirect, with VBM located at near L point and CBM at Γ point in tetragonal Brillouin zone. The calculated band gap of rutile and anatase are 1.64 eV and 1.88 eV, smaller than experimental values 3.02 eV and 3.2 eV, respectively, due to the GGA band gap underestimation. However, the band gap deformation potential calculated from GGA is quite consistent with experimental results with an error usually less than 10%.[17]

The calculated results of band gap variations under various stress conditions are presented in Fig. 3. In deformation potential theory,[27,28] the band gap change under stress is given by

$$E_g(\sigma_a, \sigma_c) = E_g(0) + b_a\sigma_a + b_c\sigma_c, \quad (1)$$

where $E_g(0)$ is band gap of unstrained bulk crystal; b_a and b_c are BGPC of epitaxial and uniaxial stress, respectively. According to this theory, the hydrostatic BGPC is b_a+b_c, which is consistent with our calculated results. As expected, in Fig. 3, the band gap change is much more significant when stress is applied along weak direction of anatase. The b_a and b_c in the anatase phase could reach 35.3 and −39.8 meV/GPa. While in the rutile phase, the band gap change is less than 0.08 eV under stress up to 10 GPa. A recent theoretical calculation also show large b_a of 43.51 meV/GPa in GGA calculation.[29] Our results indicate that applying the pressure
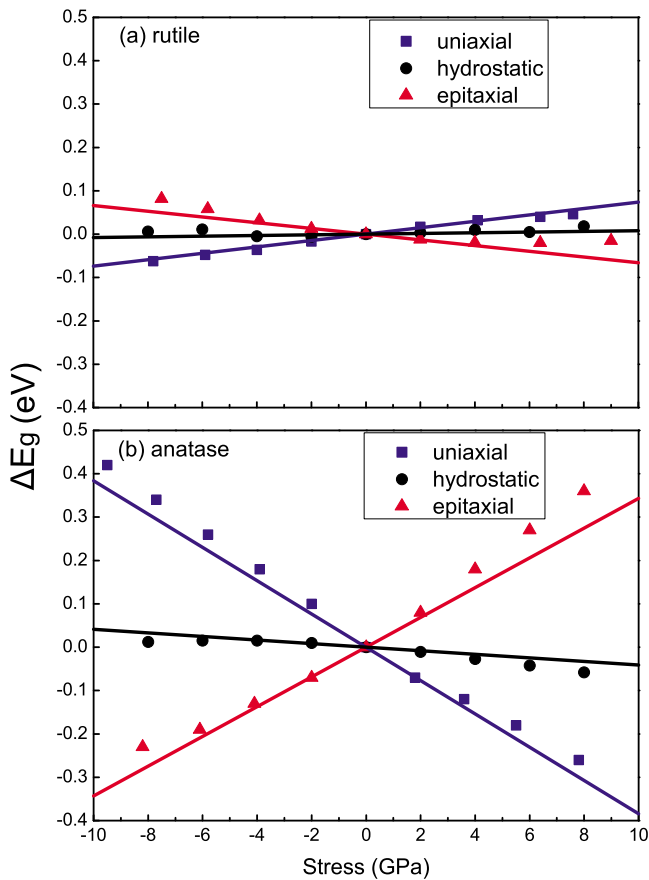
FIG. 3. (Color online) The band gap variation in rutile (a) and anatase (b) under hydrostatic, epitaxial, and uniaxial stress. The dots are the calculated results and the lines are their linear fittings across origin.

along *c* axis of anatase may be more effective for narrowing the band gap than inducing the epitaxial tensile stress in *xy* plane as $|b_c| > |b_a|$. Furthermore, the epitaxial strain is limited by the achievable critical thickness of the film and the availability of the substrates. On the other hand, the uniaxial pressure might be more easily applied and manipulated in mechanical way. Experimental tests for our results are called for.

In conclusion, we have investigated the crystal structures of anatase and rutile TiO$_2$ together with their elastic properties and find that anatase could be considered as a layered structure with a weak *c* crystal direction. The calculated elastic properties have verified this assumption. The band gaps have significant changes when stress is applied along this weak direction, therefore, it can be an effective way of narrowing the band gap of anatase and enhance its PEC activities. We suggest that tuning the band gap by applying stress along soft direction of a layered semiconductor is general

and should be applicable to other anisotropic materials.

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