ESI: Modulation of band alignment with water redox potentials by biaxial strain on orthorhombic $NaTaO_3$ thin film

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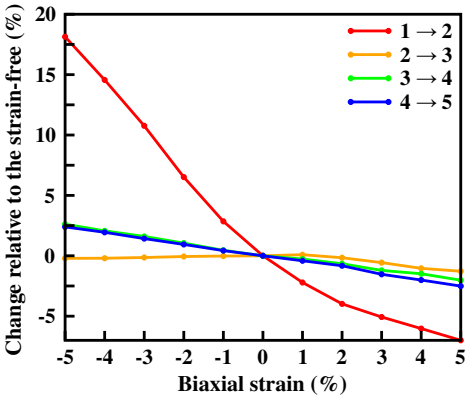
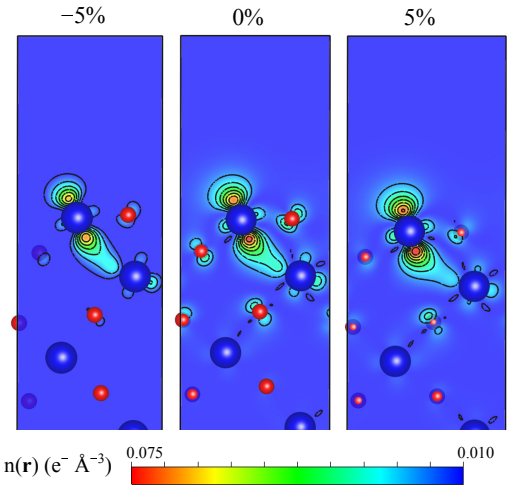
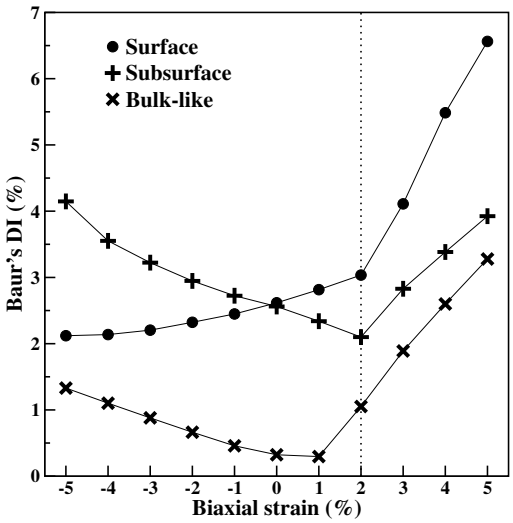


S. 1 The change on the interlayer distance with the biaxial strain emphasizing the sensitivity of the two outermost layers to strain. In legend, the distance $1 \rightarrow 2$ measures the distance between the surface and subsurface layers, $2 \rightarrow 3$ the one between the subsurface and the first bulk-like layer. Distances $3 \rightarrow 4$, $4 \rightarrow 5$ are measured between the layers inside the bulk-like region.



S. 2 The charge density $n(\mathbf{r})$ of the surface states evaluated at each strain state. The level curves clearly show the $5d_{3z^2-r^2} - 5d_{yz}$ overlap between surface and subsurface Ta $5d$ and their increase with tension.



S. 3 The change in the Baur's distortion index with biaxial strain emphasizing the inflection point at 2%. Further increases in tension lead to a more severe distortion of the overall thin film structure.

The compressive strain increases the energetic gaps, while the tensile strain initially decreases them. For biaxial strain values higher than 2%, both the bandgap and the defect gap increase with the tension. The change in the reduction trend at the 2% mark comes from the distortions of the TaO_6 octahedra (bulk-like and subsurface) and TaO_4 surface tetrahedra evaluated with the Baur's distortion index[1]:

$$DI = \frac{1}{N}\sum_{i=1}^{N}\frac{|l_i - \langle l\rangle|}{\langle l\rangle},$$

where l_i is the Ta-O bond distance, $\langle l\rangle$ the average bond distance, and $N = 4$ (6) for the surface (subsurface) polyhedra. Although the electrostatic repulsion on Ta $5d$ orbitals keeps decreasing with the tensile increase, the distortion of Ta polyhedra changes the steric interactions related to non-bonding $5d$ orbitals. Again from the crystal field picture, the energy levels of Ta $5d$ orbitals are minimal in the octahedral symmetry because there are no interactions between O $2p$ with Ta non-bonding $5d_{xy}$, $5d_{yz}$ and $5d_{xz}$ orbitals. As the ligands depart from the pristine octahedral configuration, the repulsive O$2p$-Ta$5d$ interactions increase, increasing the energy levels of the involved $5d$ states. The overall effect is the compensation of the Ta-O distance elongation on the energy levels.

Notes and references

1 W. H. Baur, *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry*, 1974, **30**, 1195–1215.

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