Oxidation Dynamics and Structural Evolution of ZrTe$_2$: A Pathway to Advanced Applications

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Abstract

Transition Metal Dichalcogenides(TMDs) exhibit great potential for nanoscale applications due to their unique properties. However, their susceptibility to oxidation under ambient conditions presents challenges for practical use. Interestingly, upon oxidation, Zr-based compounds form ZrO$_2$ which is known for its high dielectric properties, making it valuable for MOSFET design. Motivated by these facts we have investigated the oxidation kinetics and mechanisms of ZrTe$_2$ using AFM, HRTEM, Raman spectroscopy, and XPS to track the degradation process over time. The results show that ZrTe$_2$ undergoes rapid oxidation at its edges and surfaces, resulting in the formation of amorphous ZrO$_2$. This oxidation process significantly alters the material's electronic properties, with important implications for its potential use in low-cost oxygen sensors and electronic devices. Understanding the oxidation kinetics and mechanisms in ZrTe$_2$ could advance the development of stable, high-performance TMD-based devices.
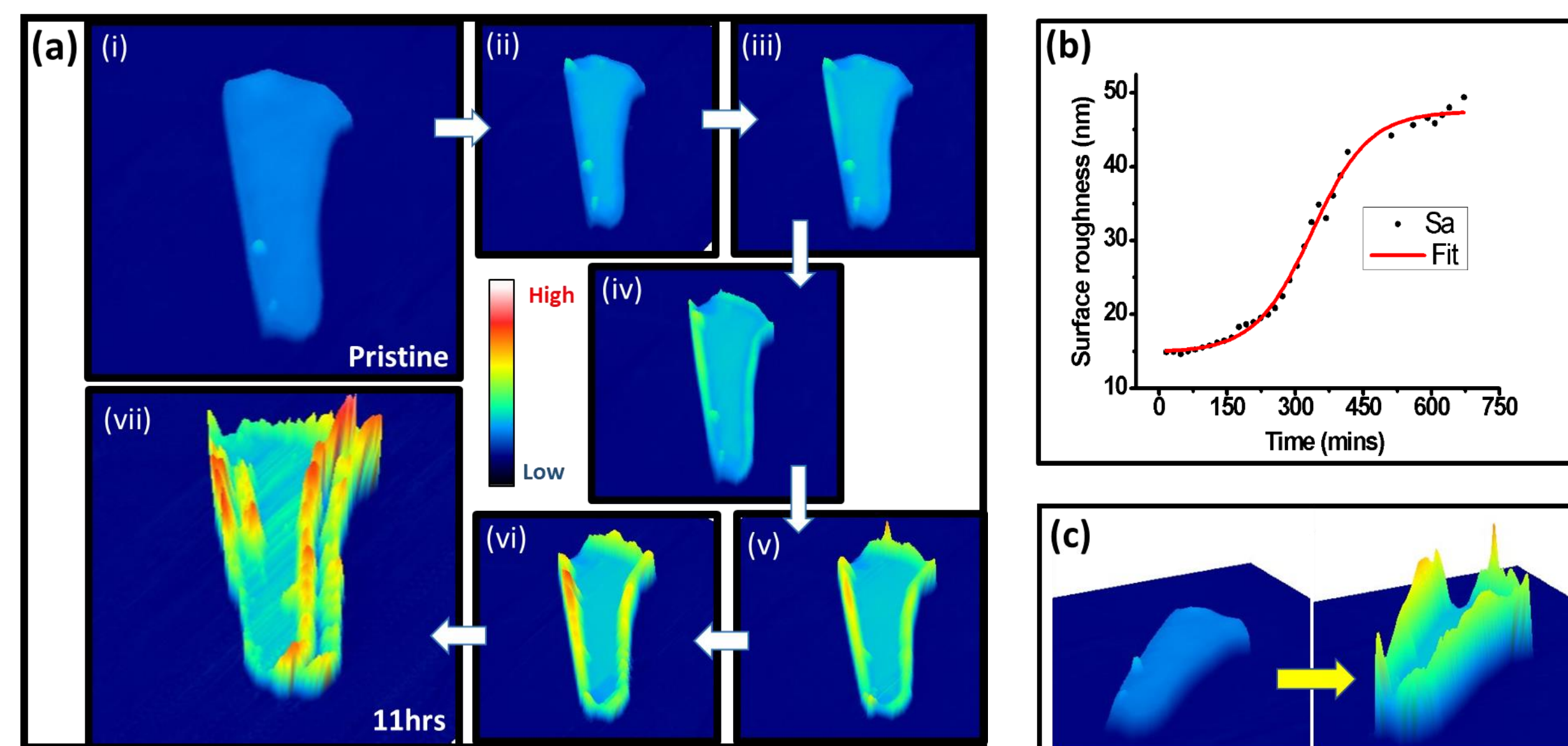
Motivation

- High reactivity under ambient conditions poses a challenge.
- This reactivity also offers opportunities for developing low-cost oxygen sensors.
- Native high-dielectric ZrO2 serves as an ideal platform for low dimensional Next generation MOSFET.

Structure
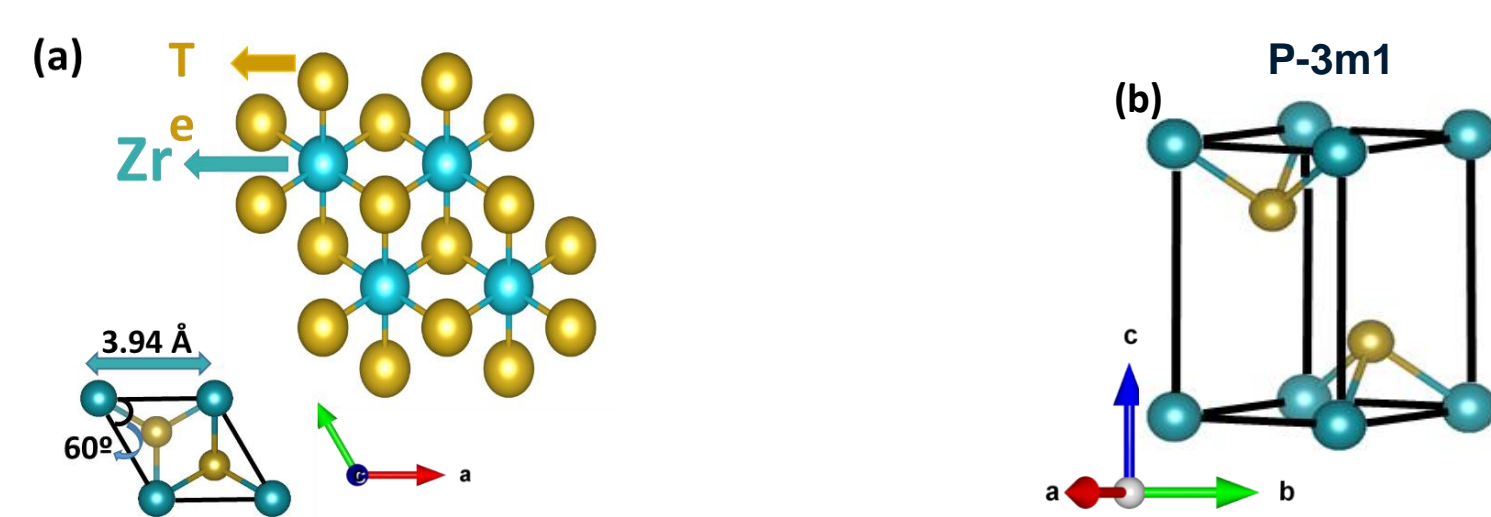
AFM

(a) (i–iv) AFM 3D morphology images (top view) depicting the surface roughness evolution of a ZrTe$_2$ bulk single crystal flake under ambient conditions. Color contrast reveals thickness variations, highlighting rapid edge oxidation from freshly exfoliated flakes to 12 hours. (b) Plot of average surface roughness over time, showing a fivefold increase.

$$R(t) = R_o + (R_{max} - R_o)/(1 + e^{-k_2 . t})$$

Raman Spectroscopy
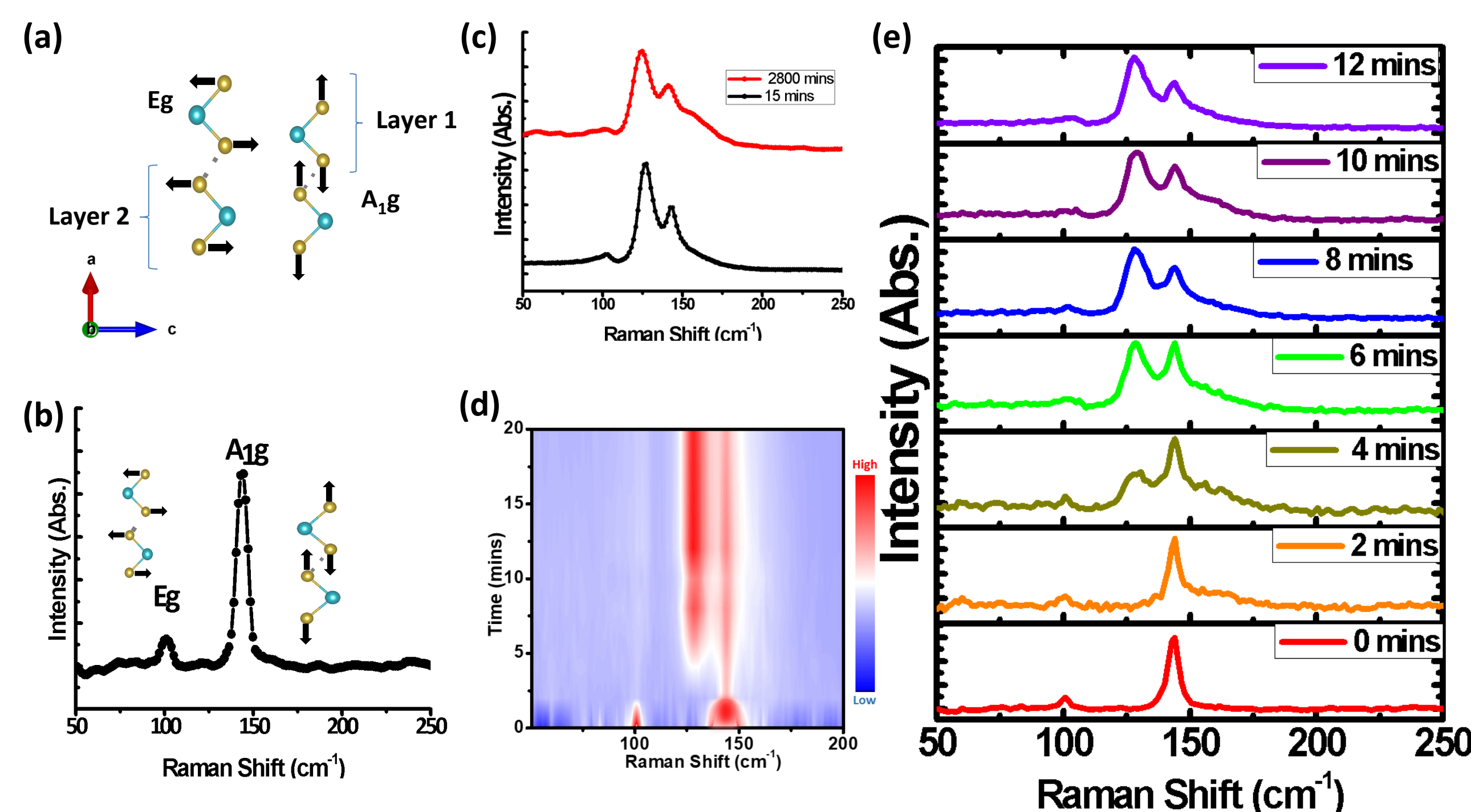
Raman spectral evolution of ZrTe$_2$ during oxidation. (b) Pristine ZrTe$_2$ (t = 0) shows the Eg mode at 103.5 cm^{-1} and A1g mode at 145 cm^{-1}. (c) Fully oxidized ZrTe$_2$ (t = 48 hours) exhibits the Eg mode at 124.8 cm^{-1} and A1g mode at 141 cm^{-1}. (e) Time-stacked spectra reveal the disappearance of the Eg mode at 103 cm^{-1}, broadening of the 145 cm^{-1} peak, and the emergence of a new peak at 127.5 cm^{-1}, shifting to 124.8 cm^{-1} as oxidation progresses.

HRTEM
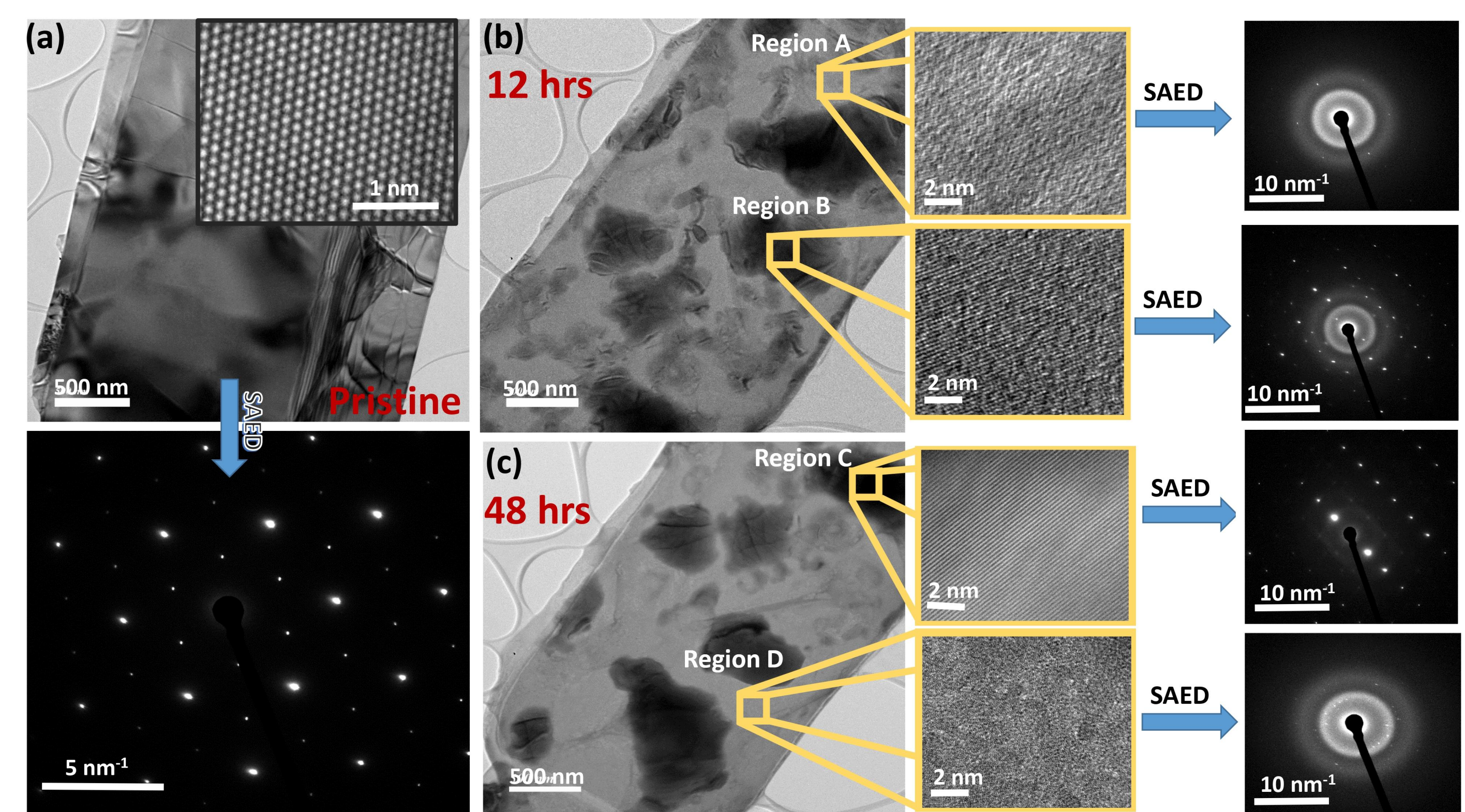
(a) Pristine ZrTe$_2$ (t = 0) shows atomic resolution and hexagonal SAED pattern. (b) After 12 hours, regions lose crystallinity; Region A becomes amorphous, while Region B retains partial crystallinity.

XPS
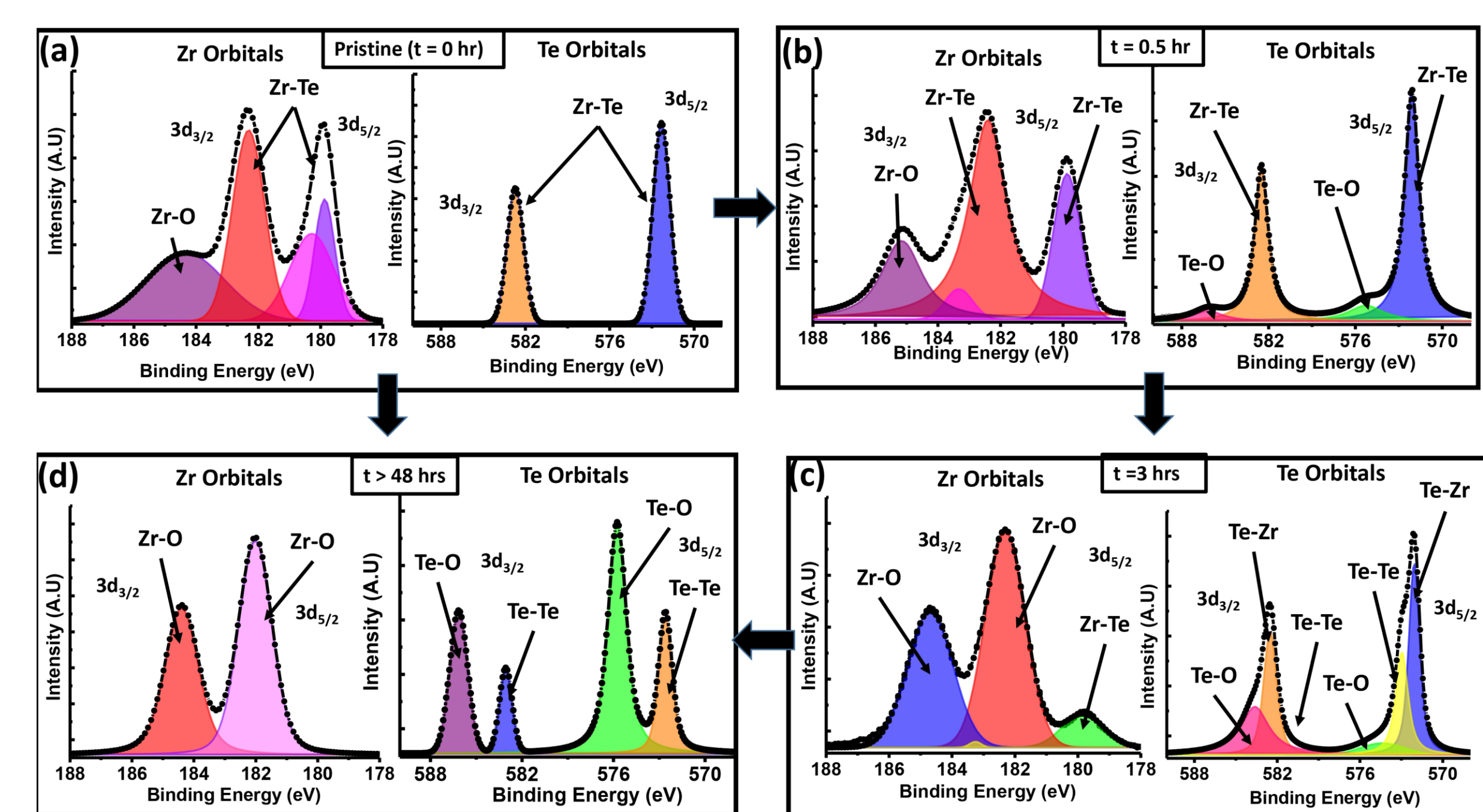
(a) At t = 0, pristine ZrTe$_2$ shows Zr-O, Zr-Te, and Zr^0 species, with Te Bonded only to Zr-Te. (b) At t = 0.5 hours, Zr^0 vanishes, indicating oxygen bonding, increased Zr-O, degraded Zr-Te, and formation of Te-O. (c) At t = 3 hours, Zr-O intensifies, Te-Te bonds appear, and distinctive pink and yellow peaks emerge in 3d$_{3/2}$ and 3d$_{5/2}$.

Summary

- Oxidation starts with O$_2$ physisorption and chemisorption on basal and edge planes.
- Rapid dissociation of O$_2$ forms O-Zr-Te bonds on a nanosecond timescale.
- Edge planes drive O$_2$ diffusion into the bulk due to more negative adsorption energy.
- Zr atoms are pushed into van der Waals gaps, forming new Zr-O and interlayer Zr-Te bonds.
- These structural changes disrupt and break down the layered crystal structure.