Electronic structures of air-exposed few-layer black phosphorus by optical spectroscopy

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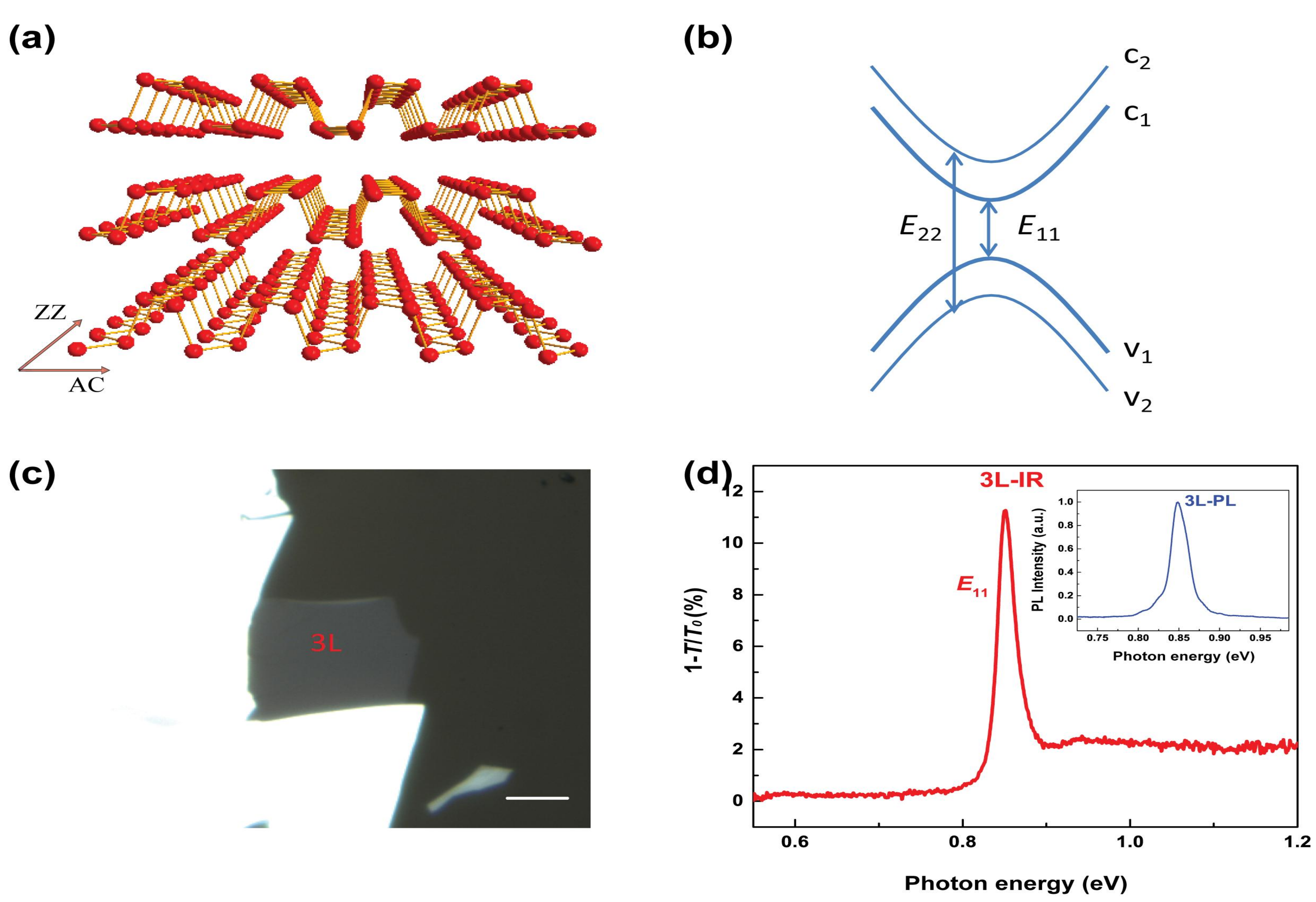
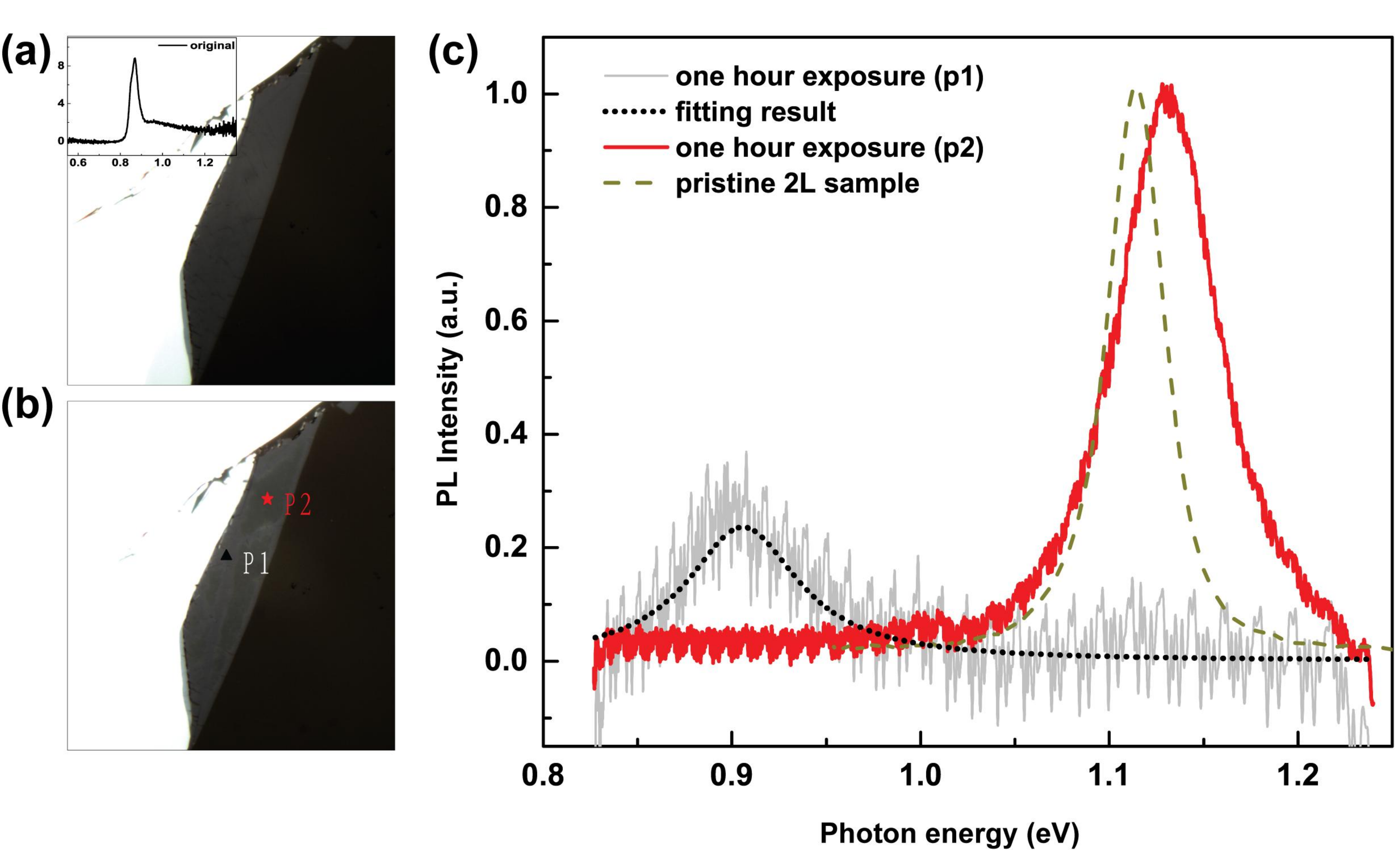
Introduction

Black phosphorus (BP) has unique physical properties, such as in-plane anisotropy , widely tunable direct bandgap from mid-infrared to visible frequency range and relatively high carrier mobility. Unfortunately, the unpaired electron on the surface makes it reactive to air, causing degradation in samples. Although the mechanism of degradation is still inconclusive, a growing consensus shows photo-oxidation, aided by moisture, is the main cause. Oxygen breaks the P-P bonds and irreversibly converts BP into P_xO_y compounds. Moisture accelerates the subsequent decomposition of P_xO_y. Though many efforts have been devoted to exploring the mechanisms and products of degradation, little is known regarding the band structure of air-exposed BP.

Optical characterization of pristine BP samples

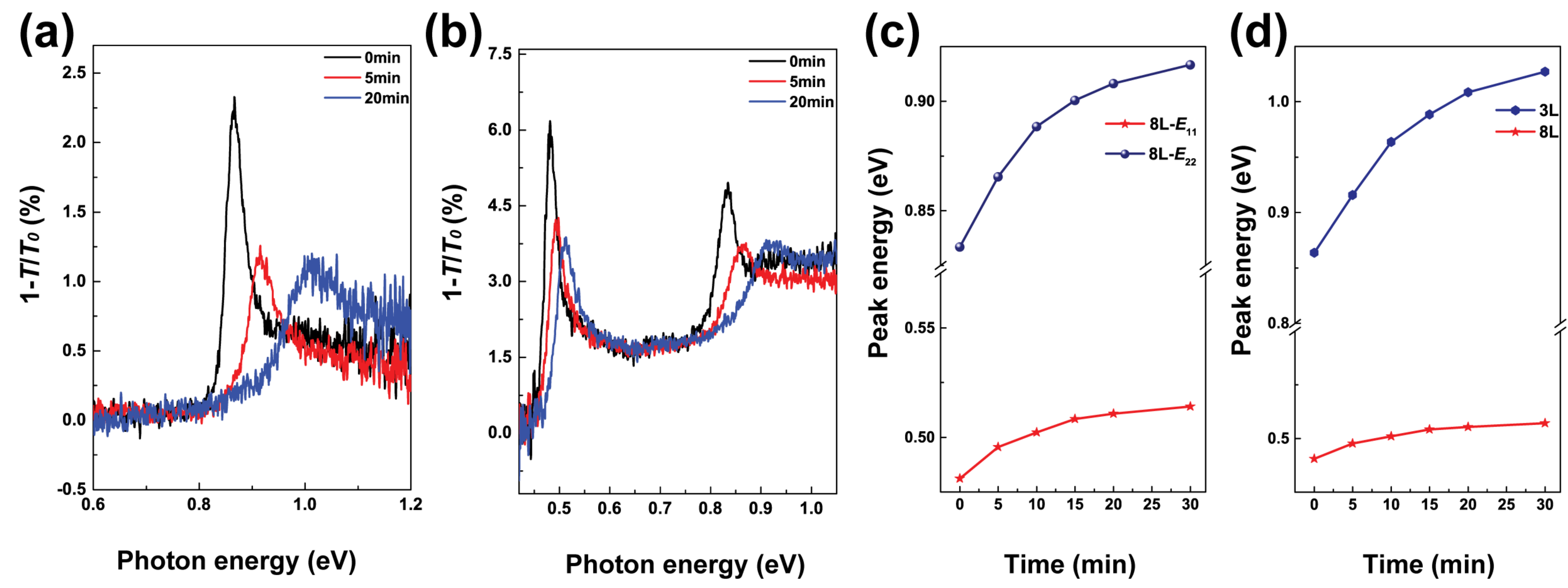


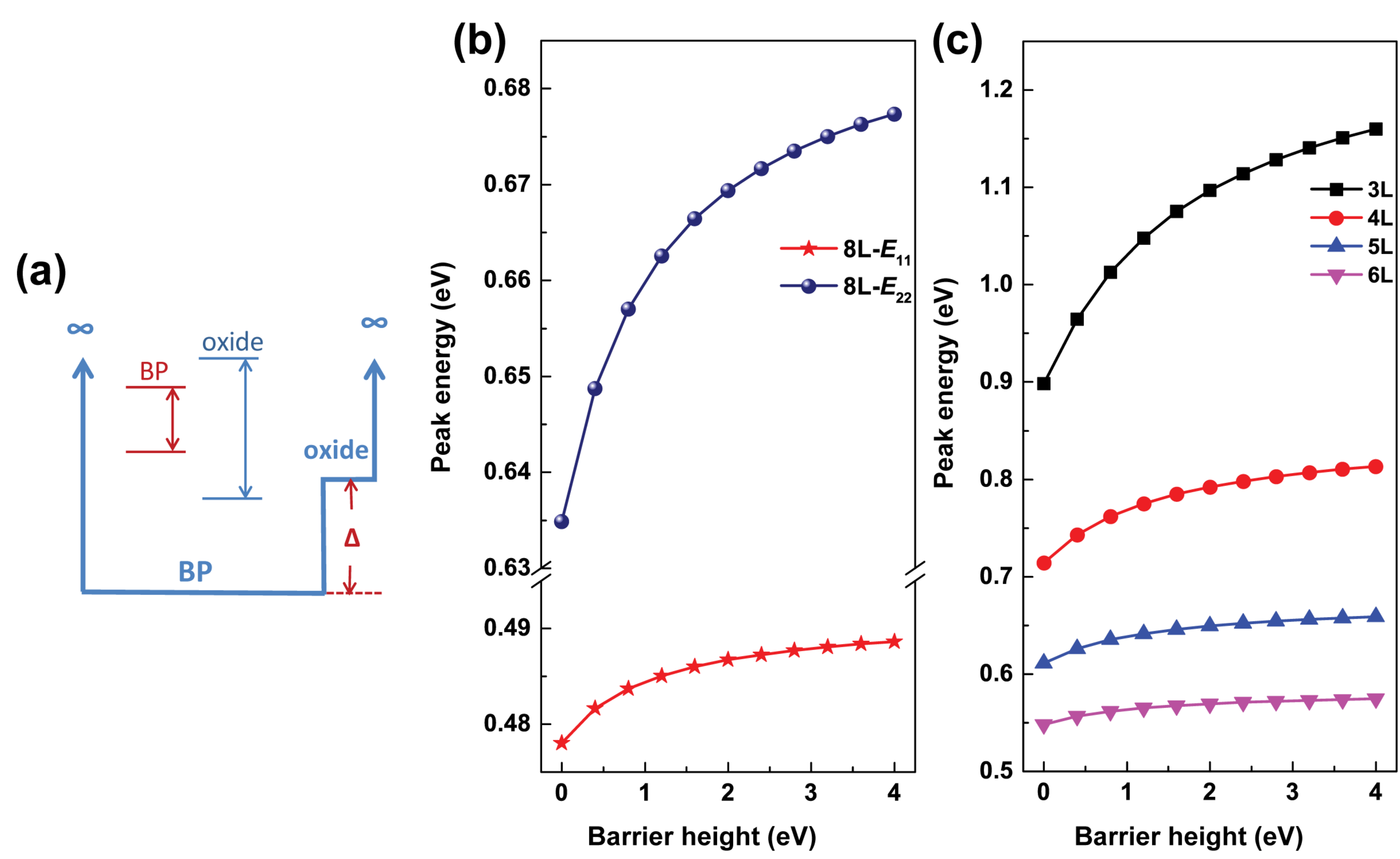
Inhomogeneous layer thinning

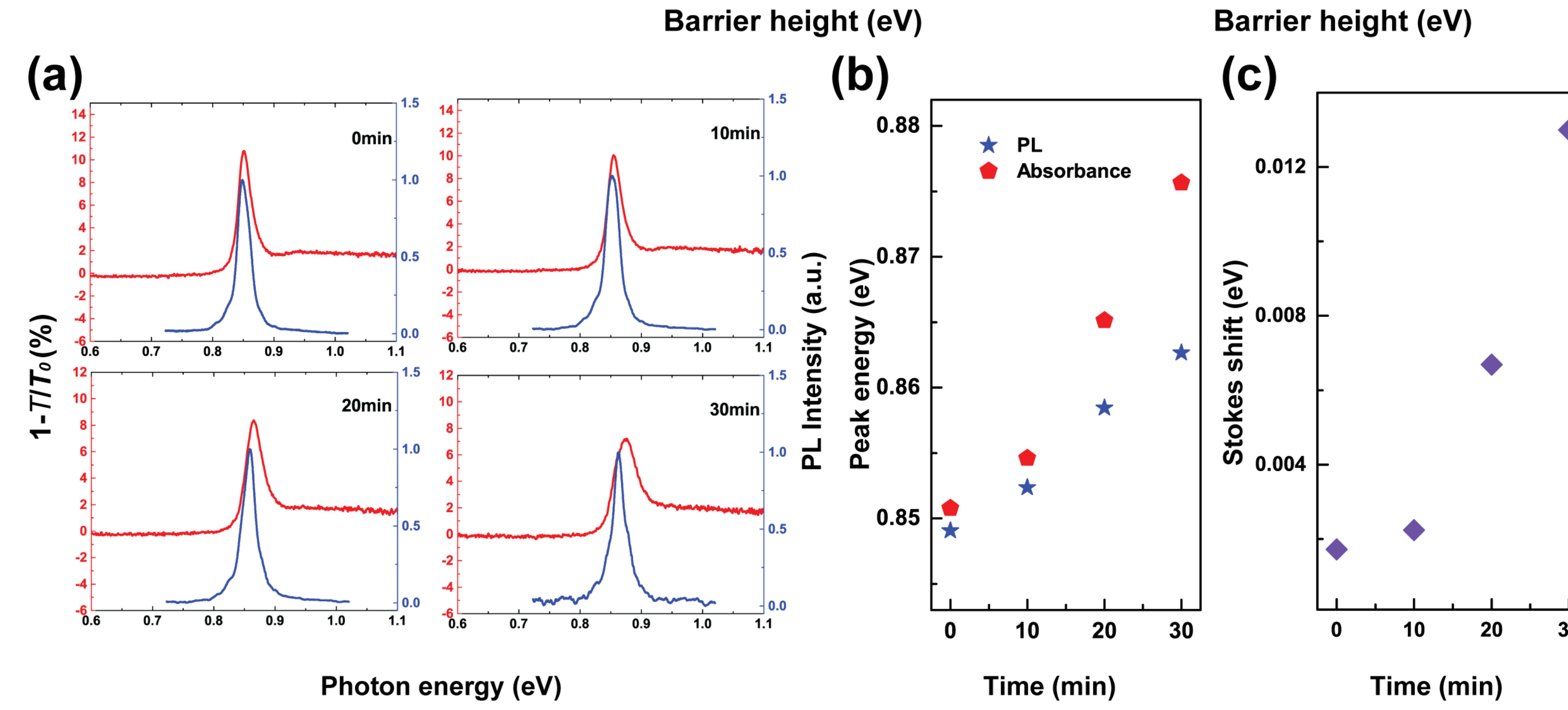


Evolution of optical bandgap

- **Subband– and layer dependent blueshift**
  1. higher order subband transition is more sensitive
  2. thinner sample is more sensitive
- **Enhanced Stokes shift**







Summary

We demonstrated that air-exposure has a strong effect on the electronic structure of BP. The band gap and higher order subband transitions shift to higher energies. A quantum well model can well account for our observations. The signatures of early-stage degradation include blueshift and broadening of resonance peaks, as well as Stokes shift in PL. Later stage degradation causes layer number reduction, typically inhomogeneously. Our study not only provides a sensitive means to characterize the quality of BP samples, but also paves a way for band structure tuning through controllable defect engineering.

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