# Valence band structure of defective pyrite (100) surface: experimental and *ab initio* study

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Surface reactivity of pyrite is significant in a wide range of geochemistry, environmental science, photoelectricity, metallogeny, and mineral processing. The surface reactivity is strongly controlled by its surface structure. The reaction occurs on pyrite surfaces depends on the electron structure of pyrite, especially the valence band structure. How different surface sites contribute to the valence band is the main question to understand the reactive nature of pyrite surfaces. In this study, Valence band structure of defective pyrite (100) surface has been studied by experimental X-ray photoelectron spectroscopy (XPS) valence band spectra and density-functional theory (DFT). Series of defective pyrite (100) surfaces were prepared by $Ar^+$-ion bombarding. Sulfur 2*p*, iron 2*p*, and valence band spectra of the defective pyrite (100) surfaces were collected with a conventional XPS equipment. Charge distribution and density of state of defective pyrite (100) surfaces were calculated by DFT+U method. The results show that the intensity of XPS valence band spectra of pyrite surface is relative to the surface defects. The intensity ratio of peak at 0.8eV to peak at 4.0 eV is in direct proportion to the surface defect density. Surface defective mono S atoms ($S_M$) undergo charge transfer from their dimer brothers: $S_2^{2-} \rightarrow S^{2-}$ ($S_M$) + $S^0$ while no distinct charge transfer occurs among surface defective iron atoms formed from surface sulfur vacancies. The outer side of the valence band top is experimentally confirmed to be contributions from Iron 3*d* (non-bonding) surface contributions, which was proposed as a hypothesis by H. W. Nesbitt in 2004. Surface defective Fe atoms contribute more to the top of the valence band than pristine surface Fe atoms. S monomers contribute more to the top of the valence band than other surface S atoms, indicating the high reactivity of the defective pyrite surfaces arises from surface S vacancies. Based on the theoretical model, simulated XPS valence band spectra which consider the experimental cross-section at the used photon energy (1487 eV) agree the experimental spectra well. These results provide additional XPS and DFT information to interpret the reactivity of pyrite surfaces.