

Atomically resolved electronic structure of pyrite {100} surfaces: An experimental and theoretical investigation with implications for reactivity

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ABSTRACT

Clean pyrite {100} surfaces, generated by cleaving in UHV, were investigated using scanning tunneling microscopy and spectroscopy for the purpose of understanding the electronic structure at the surface. Calculations of the surface atomic structure and LEED data support a {100} surface structure that undergoes very little relaxation and can be approximated by a simple termination of the bulk structure along a plane of cleaved Fe-S bonds. UPS spectra show a well defined peak at ~1 eV forming the top of the valence band for the near surface. Calculated densities of states for the bulk crystal suggest that this band is comprised primarily of non-bonding Fe 3d t_{2g} character and lesser S 3p and Fe 3d e_g character. Slab calculations predict that the loss of coordination at the surface results primarily in the displacement of Fe 3d $_z$ -like surface states into the bulk band gap. Evidence for this surface state is found in low bias STM imaging and normalized single-point tunneling spectra. Calculations of the LDOS at surface Fe and S sites indicate that the highest occupied state is primarily of 3d $_z$ -like character and the lowest unoccupied state is of mixed Fe 3d $_z$ -S 3p character. The results predict that due to the dangling bond surface states, Fe sites are energetically favored over S₂ sites for redox interaction with electron donors or acceptor species on this surface. Surface redox reactions are expected to involve the quenching of these high energy dangling bonds, leading to new bonds and surface species, changing the chemical makeup of the surface.