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Surface defects and self-diffusion on pyrite {100}: An ultra-high vacuum scanning tunneling microscopy and theoretical modeling study

KEVIN M. ROSSO,[1,*] UDO BECKER,[2] AND MICHAEL F. HOCHELLA JR.[3]

[1]W.R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, MSIN K8-96, Richland, Washington 99352, U.S.A.
[2]Universität Münster, Institut für Mineralogie, Corrensstrasse 24, D-48149 Münster, Germany
[3]Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.

ABSTRACT

Various defects on {100} cleavage surfaces of pyrite (FeS_2) are observed directly using ultra high vacuum scanning tunneling microscopy. Step edges are aligned along $\langle 10 \rangle$ and $\langle 11 \rangle$ surface directions. Atomic scale images indicate that the atomic structure, with respect to the Fe lattice, and local density of occupied states is unchanged at a step edge, including kink and corner sites. The inferred presence of monosulfides at step edges, based on X-ray photoelectron spectra on similar surfaces elsewhere, does not lead to occupied states higher in energy than d_{z2} dangling bond states at Fe sites.

A sequence of consecutive images at the atomic scale captured evidence of dynamic structural changes at defects on this surface at room temperature. Step edges appear generally stable over the course of the STM observations, whereas vacancies, their surrounding sites, and corner step edge sites are not. Theoretical maps of the attachment energy for an Fe adatom over a {100} surface cell indicate the presence of low energy diffusion channels along the topology of the closest S atoms in the uppermost atomic S monolayer. Calculation of the activation energy barriers for the self-diffusion of an Fe adatom over a {100} terrace predict low 0.10 eV diffusion barriers along channels and 0.24 eV across channels. Subsequently, calculated Fe adatom mobilities over the time scale of the STM observations are very high, ranging from 10^5–10^6 Å over the course of one minute, calculated for room temperature and depending on the diffusion direction. The structural changes documented in the STM images are attributed to the natural process of surface self-diffusion.