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Dynamics of point defect formation, clustering and pit initiation on the pyrite surface

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ABSTRACT

The collective behavior of point defects formed on the free surfaces of ionic crystals under redox conditions can lead to initiation of local breakdown by pitting. Here, we controllably generated sulfur vacancies on single crystal $FeS_2(100)$ through *in vacuo* annealing, and investigated the resulting evolution of surface chemistry using synchrotron x-ray photoelectron spectroscopy (XPS). By measuring the S 2*p* photoemission signal intensity arising from sulfur defects as a function of temperature, the enthalpy of formation of sulfur vacancies was found to be 0.1 ± 0.03 eV, significantly lower than the reduction enthalpy of bulk FeS_2. Above 200 °C, the created sulfur vacancies together with preexisting iron vacancies condensed into nm-scale defect clusters, or pits, at the surface, as evidenced by scanning tunneling microscopy (STM). We provide a mechanistic description for the initiation of pits that requires the concerted behavior of both the sulfur and iron vacancies, and validate this model with kinetic Monte Carlo (kMC) simulations. The model probes realistic length and time scales, providing good agreement with the experimental results from XPS and STM measurements. Our results mechanistically and quantitatively describe the atomic scale processes occurring at pyrite surfaces under chemically reducing environments, important in many natural and technological settings, ranging from its role as a passivating film in corrosion to its potential use as a photovoltaic absorber in solar energy conversion.

1. Introduction

Iron disulfide (FeS_2), or pyrite, is a stable Fe-S phase that has received considerable attention in a range of technological and geochemical processes. It is established that FeS_2 can form in sulfidic corrosion scales on iron alloy-based oilfield structures, where dissolved H_2S and oxidizers such as low-valent sulfur (polysulfide, sulfite, thiosulfate) are present [1]. In these anoxic environments at working temperatures up to 200 °C, surface interactions with molecular species such as H_2S, H_2O, H_2, and CH_3 (and their derivatives S^{2-}, HS^-, etc.) are important in the formation, growth and stability of pyrite as a passivating film component on steel [2]. Furthermore, the oxidation of pyrite by H_2O and O_2 is responsible for ground water acidification (i.e., "acid mine drainage"),[3] and FeS_2-H_2S interactions have been proposed as an energy source for primitive life [4]. Technologically, pyrite has been used as a cathode in Li-ion batteries [5–7] and its application as an earth-abundant photovoltaic (PV) absorber has also received renewed interest due to its promising optical properties [8]. Experimental reports of relatively low open circuit voltages (<200 mV) in pyrite devices–as compared with an optical band gap energy E_g of $\approx$ 0.95 eV [9–13]–have recently motivated a re-examination of the bulk [14] and surface [15] electronic properties of FeS_2.

Given this range of contexts motivated by pyrite defect composition and chemistry, this paper aims to elucidate two interconnected phenomena in which surface vacancies on pyrite play an important role. First is the chemical degradation of corrosion-passivating films, typically ionic compounds formed by reactions between metallic surfaces and molecular species in the environment. Anion and cation vacancy condensation is a key process postulated by the Point Defect Model (PDM) for the growth and breakdown of passive films on metallic surfaces in contact with aqueous corrosive solutions [16,17]. Both on metals and on ionic passive films, clustering of point defects (vacancies) is thought to be necessary for pit initiation, the rate-controlling step in overall pitting corrosion

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[18]. This process has been observed on pure metals [19–21] and alloys [22–24]. On the other hand, understanding the surface pitting mechanism on ionic passive films has been a challenge, experimentally limited to only few successfully studied systems such as Ni-O, Ni-OH and Cr_2O_3, [25–27] and without a concerted modeling and experimental demonstration at the atomic scale. Even in simpler systems such as pure metals and semiconductors, where surface pitting is relatively better understood, modeling of surface degradation is generally limited to the use of empirical kinetic parameters. Matching simulated time scales to experimental ones has remained challenging and has lacked experimental validation of model results [28–32]. Here we take pyrite as a model passive film system for investigating the surface pitting process at the atomic spatial scale and the experimental time scales. Vacancy formation and pitting are not induced electrochemically in this work, but rather via *in situ* annealing of $FeS_2(100)$ single crystals at different temperatures up to 330 °C under ultra-high vacuum (UHV) conditions. Recalling that our $FeS_2(100)$ single crystals were synthesized under sulfur-rich conditions, the experimental conditions which are sulfur-poor in UHV here form a strong driving force to create sulfur vacancies and pull iron vacancies from the bulk to the surface. We are careful to contrast this with typical aqueous corrosion environments, under which the primary driving force for cation vacancy formation is an applied electric field which induces cation dissolution at the material surface. In this work we rely on the large chemical potential gradient *in vacuo*, coupled with thermal activation to provide the energy for point defect formation and migration- more akin to 'dry corrosion' or 'scaling' that occurs at elevated temperatures in the absence of water. Despite this difference, the formation of cation and anion vacancies observed in pitting conditions could be induced either chemically or electrochemically as long as the effective chemical potentials are equivalent. Thus our approach permits a highly resolved observation of incipient pitting in ionic materials under carefully controlled and clean conditions.

The second aspect of this investigation, which is complementary to the first, regards the unresolved non-stoichiometry of pyrite surfaces, which cannot be explained based on defect chemistry of the bulk material. Native point defect concentrations in bulk FeS_2 are generally low ($O(10^6)\ cm^{-3}$) at room temperature [33,34] and this is important for the performance of pyrite as a passivating thin film in corrosion as well as a PV absorber. On the other hand, anionic vacancies, specifically sulfur vacancies denoted as V_S, are expected to be far more prevalent at free surfaces, with calculated formation enthalpies as low as 0.4 eV [35,36]. This has led to difficulties in obtaining surfaces with low intrinsic defect concentrations in nanocrystalline pyrite precursors and films [10,13,37–41]. Sulfur deficiency is typically put forward as a source of non-ideal electronic and optical properties in synthetic FeS_2. However, there remains a need to experimentally quantify the formation energy of V_S on the surface to understand whether these defects are indeed a significant source of off-stoichiometry in pyrite surfaces.

The crystal structure of pyrite is NaCl-type cubic, with Fe^{2+} at the cation site and $S_2{}^{2-}$ dimers at the anion site, aligned along the cube diagonal <111>. The (100) surface of FeS_2 is unreconstructed and is the most stable surface, as shown by low energy electron diffraction (LEED) [42,43] and scanning tunneling microscopy (STM) [44,45]. The sulfur S 2*p* x-ray photoemission peak of pyrite, when accessed using soft x-ray synchrotron radiation, reveals highly detailed information about the different binding environments of sulfur in the near-surface region. In addition to the dimer $S_2{}^{2-}$ signal from the crystal bulk, pyrite's S 2*p* photoelectron spectrum distinguishes two additional, surface-localized and coordinately reduced sulfur environments at more negative binding energies [46–49]. Quantification of these surface-localized defect environments enables further understanding of the two open areas summarized above.

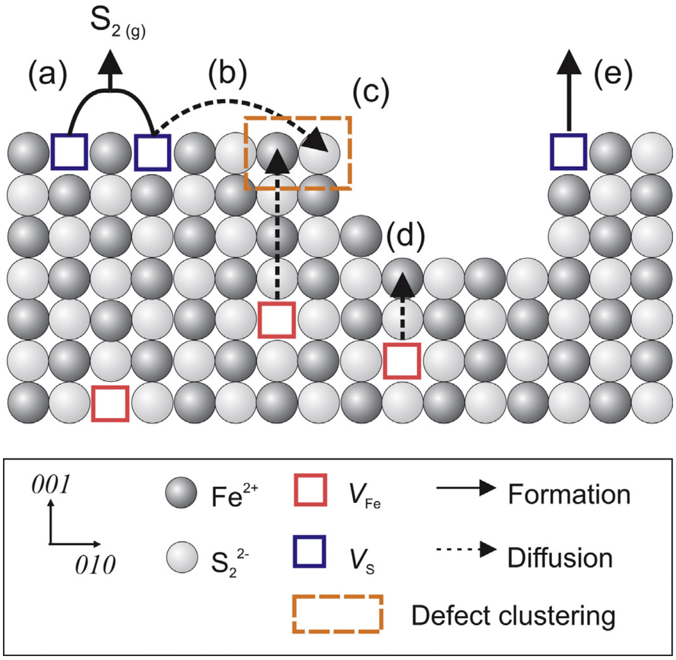

Fig. 1. Illustration of atomic processes involved in the proposed mechanism of pit formation and growth on pyrite (100). (a) Formation of surface sulfur monovacancies V_S through evaporation into vacuum. (b) Diffusion of V_S to a pit site. (c) Agglomeration of vacancies on the iron and sulfur sublattices by diffusion, leading to the initiation and growth of the pit. Presence of an initiated pit (as depicted in this figure) is not a necessary precursor to the process in (c). (d) Iron vacancies, denoted as V_{Fe}, that are already present in the bulk migrate to the surface during annealing. (e) V_S formation at under-coordinated sites surrounding pits has lower formation enthalpy as compared to isolated vacancy formation process in (a).

The concentration of defects at each stage was evaluated using the S 2*p* peak from synchrotron XPS and quantified by systematic peak fitting, allowing us to estimate the enthalpy of sulfur vacancy formation. In addition, we demonstrated using STM that upon reduction in UHV at temperatures in excess of 200 °C, surface defects aggregate to form clusters of up to 10 nm in width and exactly one-half or one lattice parameter in depth. We identified three basic atomistic processes–vacancy formation, vacancy annihilation and vacancy diffusion–which, in tandem, lead to the formation of the observed pits. The mechanism combining these unit processes, described in Fig. 1, was validated using a kinetic Monte Carlo (kMC) model of the FeS_2 (100) surface.

Our experiments and computational model demonstrate how point defects in both cation and anion sublattices in ionic solids can condense at elevated temperatures to form nanoscale surface pits. The defect formation and diffusion processes required for such a phenomenon are key assumptions in the point defect models for describing the passive film breakdown in extreme redox environments [50,51]. The low formation enthalpy for V_S supports the hypothesis that FeS_2 surfaces are off-stoichiometric and highly reducible, with detrimental implications for the performance of pyrite-containing passive films and synthetic pyrite-based devices.

2. Methods

2.1. Experimental Methods

Single crystal pyrite samples were synthesized by chemical vapour transport (CVT) in the presence of Br as a transport agent, as described in Ref. [15]. Growth faces were identified to be primarily (100) by electron back-scattered diffraction (EBSD; Zeiss Supra-55 scanning electron microscope). Phase purity of both