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Quantification of electronic band gap and surface states on $FeS_2(100)$

F.W. Herbert [a,b], A. Krishnamoorthy [a,b], K.J. Van Vliet [a], B. Yildiz [b,c,]*

[a] *Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*
[b] *Laboratory for Electrochemical Interfaces, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*
[c] *Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

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The interfacial electronic properties and charge transfer characteristics of pyrite, FeS_2, are greatly influenced by the presence of electronic states at the crystal free surface. We investigate the surface electronic structure of FeS_2 (100) using scanning tunneling spectroscopy (STS) and interpret the results using tunneling current simulations informed by density functional theory. Intrinsic, dangling bond surface states located at the band edges reduce the fundamental band gap E_g from 0.95 eV in bulk FeS_2 to 0.4 ± 0.1 eV at the surface. Extrinsic surface states from sulfur and iron defects contribute to Fermi level pinning but, due to their relatively low density of states, no detectable tunneling current was measured at energies within the intrinsic surface E_g. These findings help elucidate the nature of energy alignment for electron transfer processes at pyrite surfaces, which are relevant to evaluation of electrochemical processes including corrosion and solar energy conversion.

1. Introduction

Pyrite or FeS_2 is a semiconducting mineral for which the electronic structure has been intensively studied in relation to reactivity in geochemical [1–4] and bio-catalytic [5–7] processes, as well as for photovoltaic (PV) and photoelectrochemical properties [8–12]. Heterostructures of FeS_2 and perovskite oxides such as $LaAlO_3$ have recently been proposed as promising devices for spintronics applications [13]. FeS_2 is also known to form in anoxic, H_2S-containing environments such as those encountered by the oil and gas industry, where it is typically incorporated into passive corrosion films on steel structures [14]. In the following, we review the literature and discuss the surface electronic structure of pyrite and its characterization by scanning tunneling microscopy and density functional theory calculations.

1.1. Surface electronic structure of pyrite

Despite this wide ranging scientific interest in pyrite, important questions remain regarding the fundamental electronic properties of its free surface, which is critical towards understanding how energy levels align during interfacial charge exchange with reduction–oxidation (redox) species in the surrounding environment. For example, the reactivity of semiconducting materials can be significantly altered by surface states that are either intrinsic to the crystal termination or have arisen from the presence of crystalline defects at the surface, such as steps, kinks, dislocations, impurities or vacancies [15,16]. Moreover, in the context of PV, low open circuit voltages (VOC) of <200 mV (or ~21% of the widely accepted bulk band gap of 0.95 eV) have been attributed to poor interfacial electronic properties of synthetic FeS_2 systems [12]. We have recently reported density functional theory (DFT) calculations on the electronic structure of pristine and defective $FeS_2(100)$ surfaces [17]. The aim of the present article is to combine rigorous first-principles calculations with experimental results obtained using scanning tunneling spectroscopy (STS) to provide a complete description of how interfacial electronic states affect the band gap and electronic properties of the pyrite surface. The crystal structure of FeS_2 (space group $Pa3$) comprises two interpenetrating cation (Fe^{2+}) and anion (S_2^{2-}) face centered cubic (fcc) sublattices, the latter of which is made up of S_2 persulfide dimers aligned along the cube diagonal direction <111>. Pyrite is a compound, d-band semiconductor with an electronic structure that can be qualitatively understood with the aid of a simple ligand field model [18]. Each Fe^{2+} ion in the bulk is octahedrally coordinated by S_2^{2-} ions (symmetry group O_h), creating a strong ligand field that splits the metal d states into non-bonding, triply degenerate Fe $3d\ t_{2g}$ states (d_{xy}, d_{yz} and $d_{x^2-y^2}$) at the top of the valence band (VB). The conduction band (CB) minimum consists of doubly degenerate Fe $3d\ e_g$ states (d_{z^2} and $d_{x^2-y^2}$) hybridized with S $pp\sigma^*$ orbitals. An indirect band gap E_g of 0.83–1.01 eV has been measured in synthetic, bulk FeS_2 using various optical [19,20], photoconductivity [21,22] and X-ray absorption/emission spectroscopy studies [23]. At the unreconstructed (100) surface termination of pyrite, the predominant growth and cleavage face, the symmetry of the Fe^{2+} site is reduced from O_h to square pyramidal C_{4v}, leading to a loss of degeneracy among the Fe $3d\ t_{2g}$ and E_g states. These further split into two discrete, intrinsic surface states associated with the Fe dangling bond. Recent density functional theory (DFT) calculations are consistent in identifying these two pronounced

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* Corresponding author at: Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.
E-mail address: byildiz@mit.edu (B. Yildiz).

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surface states to be located around the VB maximum (Fe-d_{x^2} character) and at the CB minimum (Fe-$d_{x^2-y^2}$). The magnitude of the surface states decays almost entirely to zero beyond approximately three atomic layers into the bulk [24]. As a result it is theoretically estimated that E_g at the FeS_2 free surface is reduced by up to 0.3–0.4 eV, as compared to the bulk value (Table 1). In addition to the intrinsic surface states on $FeS_2(100)$, computational studies have identified a series of further surface states that appear within the fundamental surface E_g local to interfacial point defects [7,17,24]. We refer to such states as "defect" or "extrinsic" states to differentiate them from intrinsic surface states. Significant concentrations of neutral sulfur monomer vacancies V_S have been measured by X-ray photoelectron spectroscopy (XPS) on fractured $FeS_2(100)$ [25–28] as well as in situ ion-bombarded [29] and annealed [30] growth faces. Indeed, the formation energy ΔH_f for V_S is estimated to be as low as 0.1 eV experimentally [30] and 0.4–0.42 eV computationally [24,31], suggesting that up to 20% of surface sulfur sites on $FeS_2(100)$ may be vacant at ambient temperatures of 298 K, and therefore V_S electronic states are prevalent. Moreover, neutral Fe vacancies V_{Fe} on the surface have been imaged at the atomic scale by scanning tunneling microscopy (STM) and shown to comprise a comparably high fraction of the surface [32]. Via DFT, Zhang et al. predicted a maximum surface E_g of 0.72 eV for stoichiometric ($Fe:S = 1/2$) $FeS_2(100)$, but only 0.56–0.71 eV and 0–0.3 eV for sulfur-deficient and sulfur-rich surfaces, respectively. Other authors have theoretically calculated that V_S at the surface can reduce the surface E_g by more than this, even making the surface metallic [24]. Such arguments have been used, for example, to explain the low resistivity ($O(10^{-1})\ \Omega\cdot\text{cm}$) of manufactured pyrite thin films for PV applications [33]. Despite this recognition that $FeS_2(100)$ interfaces are non-stoichiometric, there remains a need to demonstrate experimentally the effect of defects on the electronic structure.

In this work, we define *surface* E_g as the energy difference between the extrema of the intrinsic surface bands that extend into the band gap of the bulk material. Discrete defect states lying within the fundamental E_g are therefore not included in the quantification of surface E_g.

1.2. Quantitative analysis from scanning tunneling spectroscopy

The STM operating in ultra high vacuum (UHV) provides a controllable metal-vacuum-semiconductor tunnel junction to probe these electronic states at the surface. A limited number of STS studies on natural [34,35] and synthetic [36,37] FeS_2 single crystals have produced inconsistent results, with apparent band gaps ranging from ~0 eV to the accepted bulk value of 0.95 eV (Table 2), and a lack of detailed insight into the nature of the pyrite surface states. Here our aim is to determine the role of surface states in determining the surface E_g through quantitative analysis of tunneling spectroscopy (STS) measurements. We adopt the approaches developed in modeling STS data from semiconductor surfaces that was advanced from the late 1980s by R.M. Feenstra and others. Early work began with the traditional cubic tetrahedrally bonded [38] and III–V [39] semiconductors, on which band edges and surface-related features could be determined to within an accuracy of ±0.03 eV. The concurrent development of tunneling spectrum models based on computations of potential distributions and tunneling current has helped identify the role of other physical phenomena in experimental STS spectra, such as tip-induced band bending (TIBB) [40] and surface states [41]. TIBB greatly affects the STS measurement of unpinned semiconductor surfaces, in which changes in the tip-induced electric field lead to an unrestricted accumulation or depletion of charge carriers at the surface which act to screen the tip potential. In this case, the electron chemical potential μ_e in the sample shifts freely with applied bias, distorting the CB and VB near the surface. However, if surface states are present on the sample, charges from the bulk bands can fall into them and E_F becomes pinned at the level to which the surface states are occupied. STS spectra of E_F-pinned surfaces typically yield more consistent band onsets and are less affected by localized quantum effects such as inversion or accumulation currents arising from TIBB. These phenomena are discussed in more detail in Section 3.1, in the context of our experimental results.

Table 1
Calculated bulk band gap E_g, and surface E_g, both for pristine and defective $FeS_2(100)$. Defective surface here refers to the presence of a single sulfur vacancy V_S in a single 1 × 1 unit surface supercell.

Bulk E_g(eV)	Pristine surface E_g(eV)	Defective surface E_g(eV)	Ref.
0.87	0.40	0.27	[7]
1.02	0.56–0.71	N/A	[31]
0.86	0.55	0–0.2	[17]
0.90	0.60	0.0	[24]

Table 2
Experimental surface Eg measurements by scanning tunneling spectroscopy (STS).

Sample/surface type	Surface E_g measurement (eV)	Ref.
Natural, fractured in UHV	0.04	[34]
Natural, fractured in air	0.20	[35]
Synthetic, as-grown surface	0.95	[36]
Synthetic, fractured in air	0.00	[37]

1.3. First-principles modeling of surface states

In this paper, we report systematic STS measurements obtained on high-purity $FeS_2(100)$ single crystals. In parallel, DFT-computed DOS was used to theoretically predict the existence of both intrinsic and defect-related surface states on this material. Using the DOS derived from DFT, we modeled the effect of intrinsic surface states on FeS_2 tunneling spectra, and compared the model results to our experimental data. When the intrinsic surface states were considered to be surface-localized acceptor/donor states that pin the Fermi level, as has been suggested by Rosso [4], we found that no realistic range of input parameters was able to replicate the experimental spectra. However, a reasonable fit was obtained when it was assumed that the intrinsic surface states overlap continuously with the FeS_2 bulk CB and VB, and therefore contribute to tunneling within the fundamental bulk E_g without pinning E_F. From this modeling-enabled interpretation of our experimental measurements, we estimate the effective surface E_g to be 0.4 ± 0.1 eV. Further, our modeling suggests that neutral surface point defects V_S and V_{Fe} can contribute extrinsic surface states that appear discretely within E_g, additionally pinning the surface Fermi level due to charge redistribution over significant fractions of the surface. We do not observe any detectable tunneling current from these extrinsic states due to their low areal and state density, coupled with a low perpendicular tunneling probability. These results demonstrate the effectiveness of applying first-principle calculations to infer meaningful data from experimental tunneling spectra — especially those in which clear features cannot be distinguished in the raw tunneling current-bias response. In doing so, we reconcile the theoretical surface electronic structure of $FeS_2(100)$ with the computational and theoretical calculations performed by the present authors as well as others, with implications toward understanding interfacial charge transfer in both natural and synthetic pyrite-based systems. As well as being informative for surface reactivity, the results may help explain the low open circuit voltage of synthetic FeS_2 PV devices, which could be related to a reduced surface E_g and Shockley–Read–Hall recombination at mid-gap defect states.

2. Methods

2.1. Experimental

High purity single crystals of FeS_2 were synthesized by chemical vapor transport (CVT) in closed quartz ampoules, based on techniques

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