

Surface structure of sphalerite studied by medium energy ion scattering and XPS

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Abstract

The reactivity of high-Fe containing sphalerite ($\text{Zn}_{1-x}\text{Fe}_x\text{S}$), the major source of Zn, is of great interest for industrial applications. Since the initial reactivity depends on the physical and chemical properties of the surface, it is important to understand the structure of cleaved and fractured surfaces. $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ zincblende (110) oriented samples cleaved in air and in vacuum were studied with medium energy ion scattering (MEIS) in order to study surface relaxation and reconstruction associated with the possible formation of S dimers. The experimental results are presented together with ion scattering Monte Carlo simulations that have been performed using the different models of the surface structure. The MEIS blocking patterns are different for the air- and vacuum-cleaved specimens. Models for the air-cleaved samples found S atoms in the first layer that are relaxed outwards by 0.08 Å and Zn(Fe) atoms relaxed inwards by 0.51 Å, with some lateral translation of both species. Results for the vacuum-cleaved sample indicate S atoms have been displaced laterally by 0.5 Å at the surface. X-ray photoelectron spectroscopic (XPS) measurements provide evidence for a high binding energy species indicative of S–S bonds in the near-surface region that are consistent with the ion scattering structural data for both cleaving protocols.

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1. Introduction

Naturally occurring Fe-containing sphalerite $\text{Zn}_x\text{Fe}_{1-x}\text{S}$ is the world's primary source of Zn. A knowledge of the surface composition and structure for a number of metal

sulfides is of critical importance in the control of mineral surface reactivity, for mineral separation by flotation and in sulfide mineral leaching for metal recovery or control of environmental pollution [1,2]. The mineral industry generally crushes sulfide ores during processing, so that the surfaces of all ores separated by flotation represent varied fracture surfaces. Pure ZnS is a large bandgap ($E_g = 3.7$ eV) II–VI semiconductor – a material for which doping with Fe causes a decrease in the band gap with increasing Fe content [3].

Both sphalerite (β -ZnS), with the zincblende crystal structure (lattice constant = 5.4093 Å), and wurtzite (α -ZnS) forms of ZnS undergo considerable relaxation of surface atoms. Sphalerite has been examined using low energy

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electron diffraction (LEED), particularly the $\{110\}$ perfect cleavage surface [4–7]. We note that, in general, investigations of these insulating materials using an electron beam (or *any* charged particle) have proved challenging due to charging phenomena. These studies have revealed a perpendicular movement of the first layer Zn atoms (cations) *toward* the bulk by 0.51 \AA , with first layer S atoms (anions) moving *outward* by 0.08 \AA , resulting in the so-called ‘puckering’ of the upper layer of S atoms above the corresponding Zn atom layer. There is evidence of some lateral surface layer reconstruction. Theoretical density functional calculations [8] have successfully modeled this structure. Additionally, Vaughan et al. [2] have noted that Zn atoms in the second layer move inwards by 0.14 \AA . Note that the early LEED studies were performed on atomically clean surfaces that were prepared via sputtering and long time ($\sim 4 \text{ h}$) annealing at $650 \text{ }^\circ\text{C}$ in ultra-high vacuum (UHV) – a situation that is quite different both from the present studies and from those relevant for the mineral recovery process. It is possible for a lengthy annealing process to induce surface structural modifications.

Numerous questions remain concerning differences between the ‘clean’ surface of a mineral sulfide (in vacuum or in an inert environment) and the bulk. The surface reactivity in air or aqueous solution is also unresolved. The composition and structure of the sphalerite surface have been investigated previously via Rutherford backscattering spectrometry (RBS) [9,10] (but without monolayer resolution), XPS [1,9,11–13], secondary ion mass spectrometry (ToF-SIMS) [1,12,13] and, as mentioned previously, LEED [4–7]. The formation of sulfur polymers is known to increase the hydrophobicity of the surface layers and it is known that the reactivity of $\text{Zn}_x\text{Fe}_{1-x}\text{S}$ increases with increasing Fe content [1].

In this work, a first attempt to study the (110) sphalerite surface has been made using the MEIS technique with an aim to verify high resolution XPS results that infer surface sulphur dimerization. MEIS is a high resolution variant of RBS wherein elastically scattered projectiles (*i.e.* H and He ions) are energy and angle analyzed by a toroidal electrostatic analyzer (TEA), instead of using a Si charged particle detector as used in conventional RBS. In general, the method lends itself to surface science applications for single crystal specimens (mono-elemental or binary alloys) and requires the use of channeling conditions for the incident ions. In such a configuration, the target is oriented such that incident charged particles are parallel to a major (*i.e.* low index) crystallographic direction. The TEA is positioned such that the central angle corresponds to a blocking geometry for the outward scattered ions, *i.e.* those ions emerge parallel to another major crystallographic direction. Thus, the geometrical technique is often described as a ‘double alignment’ method. Scattered yields are measured over a wide angular range, typically 30° , with a relative energy resolution $\Delta E/E \approx 0.2\%$ in favourable cases. Target species identification and depth distributions are given by the known scattering kinematics, as with con-

ventional RBS. The shadowing and blocking capabilities of MEIS provide a unique means to determine surface structure coupled with layer-by-layer depth profile information. Several reports are available describing the principles of the technique [14–20]. Extensive Monte Carlo computer simulations are required to extract atomic positions from measured yields. Such data are complementary to XPS investigations in that the MEIS measurements are insensitive to chemical bonding and can, in favourable situations, determine atomic positions and *absolute* areal densities directly, including surface relaxations and reconstructions.

2. Experiments

The sphalerite specimens chosen for the present investigations originated in Nacia, Mexico and were of high-Fe content type, *i.e.* $\text{Zn}_{1-x}\text{Fe}_x\text{S}$, where $x \approx 0.25$. The $\{110\}$ surfaces are known to be easily cleaved for this material [21]. The surface treatment chosen for the various studies depended on the type of information that was being sought: for the electron probe microanalysis (EPMA), Rutherford backscattering (RBS) and particle-induced X-ray emission (PIXE) measurements where bulk properties are examined, samples were cleaved in air and subsequently loaded into the analysis chamber, thereby precluding any determination of surface structure or composition on an atomic scale. For all the ion beam studies, no deleterious effects caused by sample charging were observed.

In order to ascertain the bulk stoichiometry of the present $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ sphalerite targets, a conventional RBS spectrum corresponding to incident $2.0 \text{ MeV } ^4\text{He}^+$ ions accelerated by a 1.7 MV Tandemron facility was recorded with a Si charged particle detector positioned at a scattering angle of 170° . The sample was continuously rotated around the azimuth with a tilt angle of 2.5° during the data acquisition in order to avoid channeling effects: such a spectrum then corresponds to a ‘random’ alignment. Additionally, quantitative electron microprobe analysis (EPMA) was performed by wavelength dispersive spectrometry using a JEOL 8900 electron microprobe operated at 20 kV and 20 nA .

For the PIXE measurements, the $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ sample was bombarded with normally incident $1 \text{ MeV } ^4\text{He}^+$ ions produced by the UWO 2.5 Van de Graaff accelerator, with a beam (on target) footprint size of $\sim 0.5 \times 0.5 \text{ mm}^2$. The S, Fe and Zn K X-ray yields were measured as a function of target tilt angle around the $\langle 110 \rangle$ axial channeling direction in order to determine the position of Fe atoms with regard to Zn atoms in the bulk. Additional K and L X-ray peaks arising from Mn and Cd, respectively, were also recorded. The RBS spectra were acquired simultaneously with a Si charged particle detector positioned at 150° . The PIXE spectra were acquired with a cooled HPGe detector (resolution 135 eV at 5.9 keV) having a 5 mm diameter Be entrance window of thickness $13 \text{ }\mu\text{m}$, positioned at an observation angle of 135° relative to the incident beam direction to minimize the bremsstrahlung X-ray

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