

### You may also like

# Photoactive Synthetic Polycrystalline Pyrite (FeS<sub>2</sub>)

To cite this article: A. Ennaoui et al 1985 J. Electrochem. Soc. 132 1579

View the article online for updates and enhancements.

#### - <u>Nano- FeS<sub>2</sub> for Commercial Li / FeS<sub>2</sub></u> <u>Primary Batteries</u> Yang Shao-Horn, Steve Osmialowski and

Quinn C. Horn

- Equilibrium Concentrations of FeS<sub>2</sub> and FeS in LiCl KCI Eutectic Melts Ram A. Sharma and Randall N. Seefurth

 Reinvestigation of Lithium Reaction Mechanisms in FeS<sub>2</sub> Pyrite at Ambient <u>Temperature</u> Yang Shao-Horn, Steve Osmialowski and Quinn C. Horn



## Photoactive Synthetic Polycrystalline Pyrite (FeS<sub>2</sub>)

A. Ennaoui, S. Fiechter, H. Goslowsky, and H. Tributsch

Hahn-Meitner-Institut für Kernforschung Berlin, Bereich Strahlenchemie, D-1000 Berlin 39, Germany

#### ABSTRACT

Polycrystalline layers of As-doped pyrite (FeS<sub>2</sub>) have been produced in bromine atmosphere with the aim of developing this sulfide material for solar energy applications. Its photoelectrochemical behavior in contact with an aqueous  $I_3$ -/ $I_2$  electrolyte was investigated. It operated as a photoelectrochemical solar cell and showed reasonably stable behavior under illumination. Optical measurements performed on FeS<sub>2</sub> show that visible light is absorbed in an extremely thin layer of 160Å in spite of the apparently indirect gap of this semiconductor ( $E_g = 0.95$  eV). This would make this photoesensitive material an interesting candidate for thin-layer solar cells. Scanning electron micrographs of the samples reveal well-developed crystallites of about 5-10  $\mu$ m with distinct boundaries. Scanning laser spot analysis over macroscopic areas (5 mm) showed homogeneous as well as inhomogeneous regions. The photoelectric properties of these first polycrystalline pyrite samples studied are poor, but there is presently no reason to assume that they cannot be developed.

Single crystals of  $FeS_2$  with pyrite structure have recently been considered in publications from our laboratory as a semiconducting material for photoelectrochemical and photovoltaic solar cells (1-3).  $FeS_2$  crystals in contact with an iodide/iodine containing electrolyte have exhibited large quantum efficiency and very high stability against photocorrosion (3). We are still far from understanding the solid-state chemistry of single-crystalline pyrite in all details. Nevertheless, it seems to be appropriate to start the development of polycrystalline pyrite at an early stage, owing to its potential advantage as a cheap material with promising photoelectrochemical properties.

As a material in photoelectrochemical cells,  $FeS_2$  has the advantage of being a d band semiconductor like  $MoS_2$ or  $WS_2$  with photoexcited holes reacting from quasinonbinding d states constituting the upper edge of the valence band (3).

#### **Pyrite Preparation and Properties**

Previous studies on pyrite synthesis.-Although large pyrite deposits have been found in the earth (4) and natural pyrite crystals of considerable size are well known, there has been no success in artificial growth of pyrite crystals in centimeter dimension. Synthesis of pyrite was first described by Wöhler (5) in the last century. Reacting sulfur and  $Fe_2O_3$  in an open system, he succeeded in the preparation of small brass-yellow octahedra. Bouchard (6) reported on the growth of pyrite crystals with 3 mm edge length by chemical vapor transport with chlorine. Transport from hot to cold occurred in a temperature gradient from 715° to 655°C. Our own experiments (3) show that transport with bromine at a gradient from 650° to 550°C yields crystals up to 6 mm edge length, while in the presence of iodine as transporting agent a transport rate two orders in magnitude smaller has been established. Wilke and co-workers (7) did not obtain larger crystals in growing pyrite from the solution with PbCl<sub>2</sub> as solvent.

Up to now, no attempts to prepare polycrystalline layers of photosensitive  $FeS_2$  have been reported. However,  $FeS_2$  formation has been observed during corrosion of carbon steel in the presence of a H<sub>2</sub>S gas/water mixture in nuclear power reactions, and the process, which is of electrochemical nature, has been studied (8).

Synthesis of  $FeS_2$  powder.—Stoichiometric amounts of high purity, H<sub>2</sub>-reduced iron powder and high purity sulfur lumps were heated up to 650°C in evacuated (10<sup>-5</sup> mbar) and sealed quartz ampuls of 20 mm diam and 200 mm length. In the presence of a small amount of iodine (0.5 mg/cm<sup>3</sup>), the reaction was terminated within 100h.

Preparation of polycrystalline FeS<sub>2</sub> layers.—2g of yellowish-white shining FeS<sub>2</sub> powder and 5 mg As as dopant were filled in quartz ampuls ( $\phi \approx 22 \text{ mm}$ , l = 300 mm) and evacuated to  $10^{-5}$  mbar. After admittance of 0.5 mg/cm<sup>3</sup> bromine, the tubes were sealed. FeS<sub>2</sub> powder was placed in one end of the ampul and, in order to clean the growth chamber from persisting powder particles, the free end was heated up to  $800^{\circ}$ C for 6h. Afterward, the temperature was reversed. The FeS<sub>2</sub> powder was heated to  $800^{\circ}$ C, and the powder-free end was kept at  $550^{\circ}$ C (Fig. 1, stage I) for 10 days. On account of the high dissociation pressure of FeS<sub>2</sub> at  $800^{\circ}$ C [p = 1 atm (16)], a thermal decomposition of FeS<sub>2</sub> according to the simplified equation

$$\operatorname{FeS}_2(s) \to \operatorname{FeS}(s) + 1/2 \operatorname{S}_2(g)$$
 [1]

was observed. Sulfur distilled into the cool end of the quartz ampul. The decomposition was accompanied with a strong coalescence (Ostwald ripening) of the produced FeS to large hexagonal phyrrhotite crystals (Fig. 1, stage II) up to 10 mm edge length and 2 mm thickness. By reversing the temperature gradient for 10 days, realized by the opposite position of the growth ampul in the furnace (Fig. 1, stage III), the pyrrhotite crystals were transformed into pyrite under preservation of their hexagonal shape (pseudomorphism). Investigations of the hexagonal surfaces with scanning electron microscopy revealed that the pseudomorphous crystals consisted of small pyrite crystals (5-10  $\mu$ m edge length) that were grown together forming a reasonably homogeneous surface (Fig. 2). In some areas, larger pyrite crystals (0.5 mm edge length) appeared on the polycrystalline substrate.

Polycrystalline layers were also prepared by transport in a gradient from 650° to 600°C in evacuated and closed quartz ampuls (l = 110,  $\phi = 22$  mm). The concentration of transporting agent NH<sub>14</sub>Br amounted to 0.5 mg/cm<sup>3</sup>. 0.35 mg As was added to 1.15g FeS<sub>2</sub> feed material. The intergrown pyrite crystals of the layer had dimensions of 10-100  $\mu$ m,

#### Solid-State Studies

Concerning the band structure of pyrite  $\text{FeS}_2$  (9), two details are particularly interesting because they permit a



Fig. 1. Position of growth tubes in the temperature gradient of the furnace and growth region of polycrystalline layers.

1580



Fig. 2. Scanning electron micrographs of polycrystalline FeS2. a(left): Front view of polycrystalline platelet. b(right): Edge side of platelet

better interpretation of the electric, magnetic, and optical properties.

First, the clear separation of a  $t_{2g}$  and a  $e_g$  energy band in relation with a low-spin  $t_{2g}^6$  system which results in a 0.95 eV  $t_{2g}/e_g$  bandgap.

Second, a relatively broad  $e_g$  band has been predicted (9) and XPS data confirm a single strong 3d peak of 0.9 eV width arising from a d energy band at the top of the FeS<sub>2</sub> valence band (10). These XPS data have been confirmed and extended in our laboratory (3).

The reported high electron mobility of  $230 \text{ cm}^2\text{-V}^{-1}\text{-s}^{-1}$ in synthetic crystals (11) confirms that the electronic structure of the material is sufficiently favorable for charge transport.

The electrical resistivity of our samples was measured using a four-probe technique. The measurements covered the temperature range from 76 to 500 K, and an exponential temperature dependence between 400 and 500 K according to the relation  $l = l_0 \exp \Delta E/KT$  was found. The activation energy  $\Delta E = 0.23$  eV of our samples is smaller than  $\Delta E = 0.46$  eV, previously reported for n-type single crystals of FeS<sub>2</sub> (9). At room temperature, the resistivity of our polycrystalline FeS<sub>2</sub> was 6  $\Omega$ -cm: Hall effect measurements gave a carrier concentration of  $3 \times 10^{17}$  cm<sup>-3</sup>. The Hall mobility in our samples was quite low:  $3 \text{ cm}^2 \text{-V}^{-1}\text{-s}^{-1}$ . The pyrite layers studied showed n-type behavior in photoelectrochemical measurements.

#### **Optical Experiments**

Optical transmission measurements for FeS<sub>2</sub> have up to now only been performed in the infrared toward the bandedge region. Schlegel and Wachter determined the absorption constant of  $\text{FeS}_2$  up to a photon energy of  $h\nu =$ 1.1 eV, where it was found to be approximately  $\alpha = 8 \times$ 10<sup>3</sup> cm<sup>-1</sup> (12). A crystal of natural pyrite (from Elba) with a cross section of  $10 \times 5 \text{ mm}^2$  was polished down to a thickness of  $\alpha = 8 \pm 0.5 \ \mu m$  while fixed to a glass support. This sample had holes on a surface area much smaller than 1%, so that a background was obtained in transmission. This gave rise to an apparent decrease of the absorption constant in the region of very high absorption coefficients. Since the small fraction of light passing through these holes does not depend on the wavelength, a calibration measurement is needed to adjust the absorption curve to the real values. This was done with the help of a null ellipsometer. In order to get the bulk properties, the surface of FeS<sub>2</sub> was etched using HF/CH<sub>3</sub>COOH/HNO<sub>3</sub> (1:1:2), which, according to ESCA studies, yields a  $FeS_2$ surface free of any covering layer (3). During the measurement, the FeS<sub>2</sub> was flushed with dry nitrogen. The complex refractive index determined at n = 632.8 nm was n =4.032 - 3.245i

The real reflective index was checked using the transmission interferences occurring in the range between 1800 and 2500 nm. The result was  $\operatorname{Re}(n) = 3.96 \pm 0.25$ .

A cross check was made using published data on the reflection properties of pyrite in combination with a calculation based on the Kramers-Kronig relation (12, 9). The values obtained were n = 3.6 - 3.03i [from Ref. (12)] and n = 3.5 - 3.8i [from Ref. (9)]. They only differ by less than 30%, which might be due to surface layers, which were not controlled in these measurements. Such deviations are to be expected according to variations of interface properties (13). Therefore, our measurements have to be considered reliable. The absorption coefficient determined from our data can be calculated to be  $\alpha = 6.4 \times 10^5$  cm<sup>-1</sup> at 632.8 nm.

The relative absorption coefficient in the visible spectral region measurement with a Perkin-Elmer Model 330 would thus be calibrated as shown in Fig. 3. Beyond 1050 nm, a normal absolute measurement was possible.

It can therefore be concluded that  $FeS_2$  is absorbing visible light within a narrow surface layer of approximately 160Å. Pyrite is thus absorbing at least one order of magnitude better than GaAs, which has a direct energy gap.

#### Photoelectrochemical Experiments

The FeS<sub>2</sub> samples were treated with an In-Ga alloy followed by Ag epoxy, making contact to a copper rod, which was then encapsulated with insulating resin (Scotchcast 3MXR 5241). A conventional three-electrode potentiostatic arrangement was applied. For photocurrent measurements, a 250W tungsten iodine lamp, a xenon lamp, or a helium neon laser were used.



Fig. 3. Adsorption coefficient of FeS<sub>2</sub> measured in transmission using a platelet 8  $\mu$ m thick (exposed area: 50 mm<sup>2</sup>). The value of 6.4  $\times$  10<sup>5</sup> cm<sup>-1</sup> at 632.8 nm was calibrated using ellipsometry. The insert shows the interference patterns of transmission.

#### Results

When an electrode, prepared of a polycrystalline  $FeS_2$ layer, is placed in contact with an aqueous electrolyte containing 0.5M H<sub>2</sub>SO<sub>4</sub> and polarized in an electrochemical cell with three electrodes, a much more complicated current voltage behavior is observed than is with single crystals (3). A photocurrent of the order of 10 mA-cm<sup>-2</sup> is measured in concentrated xenon light (~ 1 W-cm<sup>-2</sup>). It is superposed by a dark current, which is rapidly growing as the magnitude of the applied voltage is increased. The shape of the current voltage curve is complicated due to oxide formation, and corrosion to  $Fe^{3+}$  and  $SO_4^2$  is clearly visible at elevated potentials. No oxygen evolution is observed. In the presence of redox systems such as  $I^-/I_3$  ( $E_o$ = 0.53 V),  $V^{2+}/V^{3+}$  ( $E_o = -0.7$  V), or  $S^{2-}/S_n$  ( $E_o = -0.51$  V), a FeS<sub>2</sub>/redox electrolyte/carbon configuration operates as solar cell (Fig. 4). Instead of largely different redox potentials, the open-circuit photopotentials are comparable and equally small (0.024-0.08V). Both the poor limiting current behavior of the semiconducting  $FeS_2$  layer and the constancy of the photovoltage indicate high concentrations of surface states and a situation of pinning of energy bands. Similar to single-crystalline  $FeS_2$  (3), etching treatment improves the photoelectrochemical behavior. Since the electrochemistry of  $FeS_2$  has been described using single crystals (3), we will limit ourselves to characterizing the photoeffect which has not yet been described with polycrystalline FeS<sub>2</sub>. Figure 5 shows the spectral dependence of photocurrent efficiency  $(\eta)$  of polycrystalline FeS<sub>2</sub>. Plots of  $(\eta h\nu)^{n/2}$  with n = 1 and n = 4 are given in Fig. 6.

The plot  $(\eta h\nu)^{1/2} vs. h\nu$  gives a straight line, suggesting that the optical transition in FeS<sub>2</sub> is indirect and yields a bandgap of 0.95 eV consistent with theory (14). This is in good agreement with reflection measurements, which indicated an optical bandgap of  $0.9 \pm 0.1$  eV (9), and with our optical results (Fig. 3). Laser spot measurements were made to test the homogeneity of the FeS<sub>2</sub> films produced. A sample of  $0.7 \times 0.5$  cm was scanned over a distance of 0.5 cm in three distinct positions. Figure 7 shows that homogeneous and heterogeneous regions are present. It is possible that creeklike structures in the polycrystalline film which can be seen in the optical microscope are responsible for some of the variations.

#### Discussion

Pyrite (FeS<sub>2</sub>), an abundant natural product which consists of cheap elements, has recently been proposed as a semiconductor material for solar cells (1-3). First experi-



Fig. 4. Power output characteristic of a synthetic polycrystalline  $FeS_2$  liquid junction solar cell. Electrolyte: (a, left curve) 3M KI,  $10^{-3}M$  I<sub>2</sub> (pH 2). Layer preparation I (b, right curve) 1M Cal<sub>2</sub>, 0.05M. Layer preparation II.



Fig. 5. Relative spectral response of  $\mbox{FeS}_{\rm z}$  solar cell under short-circuit condition.



Fig. 6. Plot of  $h\nu$  vs.  $(\eta h\nu)^{n/2}$ , where n = 1 and n = 4 (FeS<sub>2</sub> in 3M KI,  $10^{-2}$ M I<sub>2</sub>, aqueous electrolyte).

ments with synthetic single crystals yielded photovoltages of 200 mV and quantum efficiencies for photocurrent generation exceeding 90%, although neither doping nor interfacial properties has been optimized. The lack of knowledge of many solid-state properties makes it, at present, difficult to judge the development possibilities of this material with high reliability. However, information on certain parameters which are decisive for solar energy materials are becoming more transparent.

Our first experiments to produce polycrystalline layers of photosensitive FeS2 were successful. These layers could even be operated in low efficient solar cells. The choice of As as doping agent was probably not favorable, especially since this additive reduces the mobility (11). The control of doping remains an important task which has to be accomplished for  $FeS_2$ , and we feel that the very low photopotential of our polycrystalline samples is due to a Fermi level, which is situated too distant from the conduction band. As shown by the improvement obtained between the sample of curve a and that of curve b in Fig. 4, some systematic progress has already been obtained. We hope to have shown that polycrystalline  $FeS_2$ is an interesting solar material for long-term development, especially since ambient temperature and low temperature processes for FeS<sub>2</sub> synthesis in geological environments have also become known (17).

Our measurement of an indirect energy gap of 0.95 eV in polycrystalline FeS<sub>2</sub> layers (Fig. 6) is in agreement with optical (12) and electrical (9) measurements. Such an energy gap, which is only slightly smaller than those of CuInSe<sub>2</sub> (1 eV) and Si (1.1 eV), still permits a theoretical solar energy conversion efficiency between 14 and 18%



Fig. 7. Scanning laser spot analysis of polycrystalline  $\mbox{FeS}_2$  in  $1\mbox{-}/l_2$ solution under short-circuit condition. (Three parallel scans on a 7 mm platelet in distinct regions. Scan velocity: 25  $\mu$ m steps in X-direction. Beam width: 20  $\mu$ m.)

and a photovoltage output of approximately 0.5V. This, however, will necessitate a careful optimization of bulk and surface properties of FeS<sub>2</sub>. An important parameter is the nature of the electronic transition of FeS<sub>2</sub>. Scientists dealing with solar energy materials usually associate with indirect energy gaps a deep penetration of light which can only be compensated by high diffusion lengths of charge carriers (as in crystallized Si). Such materials cannot be used for light collection as very thin layers. Experience with transition metal sulfides of d band character such as  $WS_2$  or  $MoS_2$ , however, shows that indirect bandgaps can be associated with high absorption constants (~  $1 \times 10^5$  cm<sup>-1</sup>) (14). This is also the case for FeS<sub>2</sub>.

With an absorption coefficient of approximately  $\alpha = 6.4$  $\times$  10<sup>5</sup> cm<sup>-1</sup> in the visible, the photogeneration of electronhole pairs occurs in a thin surface layer of approximately 160Å. The spectral dependence of photocurrents (Fig. 5)

Further research will be needed to understand how the state of the surface interacts with holes, generated with different photon energy in a comparable distance from the semiconductor of electrolyte interface. Interestingly  $RuS_2$ , which also has an extremely high absorption coefficient ( $\alpha = 3 \times 10^5$  cm<sup>-1</sup>), a similar crystal structure, comparable energy gap ( $E_g = 1.25 \text{ eV}$ ), and an analogous electronic structure, does not show a decay of photocurrents towards the UV region (15). This gives rise to the hope that it will be possible to develop solar cells which are only several hundred angstroms thick and extremely flexible and easy to handle.

#### Acknowledgments

The authors would like to thank Mr. W. Beran for his assistance in SEM measurements and Dr. Jaegermann for interesting discussions. The project was supported by BMFT Grant no. 03E-83 5-A.

Manuscript submitted June 18, 1984; revised manuscript received March 25, 1985.

Hahn-Meitner-Institut für Kernforschung Berlin assisted in meeting the publication costs of this article.

#### REFERENCES

- 1. W. Jaegermann and H. Tributsch, J. Appl. Electrochem., **13**, 743 (1983). .. Ennaoui and H. Tributsch, Solar Cells, **13**, 197
- $\mathbf{2}$ . Α. (1984).
- 3. A. Ennaoui, S. Fiechter, W. Jaegermann, and H. Tributsch, Submitted to This Journal.
- 4. J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, "Comprehensive Inorganic Chemistry," Vol. 2, p. 796, Pergamon Press, London (1973)

- W. Wöhler, Lieb. Ann., 17, 260 (1836).
  R. J. Bouchard, J. Cryst. Growth, 2, 40 (1968).
  K.-Th. Wilke, D. Schultze, and K. Töpfer, ibid., 1, 41 (1967)
- 8. D. W. Shoesmith, T. E. Rummery, M. G. Bailey, and
- D. G. Owen, This Journal, **126**, 911 (1979). . T. Bither, R. J. Bouchard, W. H. Cloud, P. C. Donohue, and W. J. Siemons, Inorg. Chem., 7, 2208 9. A. (1968).
- 10. H. Van der Heide, R. Hemmel, C. F. van Bruggen, and
- C. Haas, J. Solid State Chem., 33, 17 (1980). . T. Shuey, "Semiconducting Ore Minerals," R. T. 11. **R**. Shuey, Editor, pp. 304-318, Elsevier Scientific Publishing Co., Amsterdam (1975).
- 12. A. Schlegel and P. Wachter, Solid State Phys., 9, 3363 (1976).
- 13. D. E. Aspnes and A. A. Studna, Phys. Rev. B, 27, 985 (1983).
- 14. Ch. Sugiura, J. Chem. Phys., 80, 3 (1984).
- 15. H.-M. Kühne and H. Tributsch, J. Electroanal. Chem., To be published.
- 16. R. Juza and W. Biltz, Z. Anorg. Allg. Chem., 205, 273 (1932).
- 17. R. O. Halberg, N. Jahrbuch F. Mineralogie, Monatshefte, 481 (1972).