



# Photochemical deposition of FeS<sub>x</sub>O<sub>y</sub>

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## ABSTRACT

FeS<sub>x</sub>O<sub>y</sub> thin films were deposited on indium–tin–coated glass substrates using the photochemical deposition technique from an aqueous solution containing FeSO<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The experiments were performed at room temperature with and without Fe powder attached on the substrate. A very thin film with S-rich composition was obtained without Fe powder. With Fe powder adhered on the substrate, Fe- and O-rich black films with a thickness larger than 1 μm were obtained. From the photoelectrochemical measurement, the deposited FeS<sub>x</sub>O<sub>y</sub> film showed n-type conduction and photoconductivity.

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## 1. Introduction

The Fe–S system has a broad range of compositions occurring between FeS and FeS<sub>2</sub> [1], and shows interesting magnetic and electrical properties [2,3]. In addition, nanoparticles of the FeS<sub>x</sub> system receive interests because of their unique magnetic properties [4–6]. Iron pyrite (FeS<sub>2</sub>) has attracted considerable attention as a potential candidate for photovoltaic and photo-electrochemical applications [7]. Because of the very high light absorption coefficient ( $\alpha \geq 5 \times 10^5 \text{ cm}^{-1}$  for  $\lambda \leq 700 \text{ nm}$ ) and the band gap of about 0.95 eV, it will be suitable for solar cells. Several methods have been used for the preparation of thin pyrite films: low pressure chemical vapor deposition [8], metalorganic chemical vapor deposition [9], spray pyrolysis [10], sulfurization of electrodeposited iron films [11–14], sulfurization of sputtered [15] and vacuum evaporated iron films [16,17]. In most of the previous works, the conduction type was found to be p-type, but n-type conduction was also reported [14].

Photochemical deposition (PCD) technique has not been used to make Fe-related thin films, yet. PCD is a very simple and low cost technique for the deposition of thin films. PCD has been used to prepare several photovoltaic thin films such as CdS [18,19], ZnS [20] and Cu<sub>x</sub>S [21]. In the present work, we apply the PCD method to the Fe–S system.

## 2. Experimental

An aqueous solution of 50 ml containing FeSO<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was used. The solution pH was 4.7–4.9 for all the solutions given

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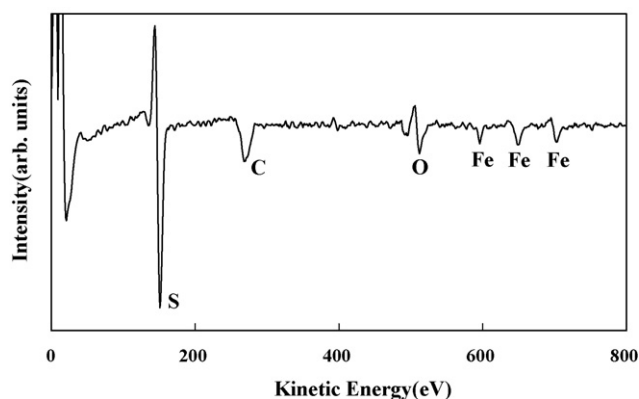
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in the next section. According to our observation, sulfur colloid is formed by decomposition of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions in pH range below 3, and the solution was clear in the pH range of 4.7–4.9. The indium–tin–oxide (ITO) coated glass substrate was washed in alkyl benzene in an ultrasonic bath, and then dried using nitrogen gas flow. The PCD apparatus consists of an ultra-high pressure mercury arc-lamp for UV light irradiation with the power density of the order of 100 mW/cm<sup>2</sup>. The substrate to solution surface distance was maintained about 3–5 mm. The deposition time is 1 h. The deposition temperature was room temperature, initially 20–25 °C, and increased by about 10 °C during the deposition. We once applied stirring and found that it caused the formation of precipitate under some conditions, and hence we decided not to stir the solution during the deposition process.

In PCD of sulfides, S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions absorb UV light and release electrons. While Fe<sup>2+</sup> ions are released from FeSO<sub>4</sub>, S atoms are released from S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions. The released S atoms and solvated electrons react with iron ions in the presence of light. Dissolved oxygen can participate the reaction, to form an oxide. The presence of the ITO substrate inside the solution being illuminated provides the necessary nucleation sites. As described below, high purity Fe powder was pasted on the edges of the substrate, using double side adhesive tape. Fe powder was found to be a good catalyst and speed up the deposition reactions.

The films were characterized by X-ray diffraction (XRD) using Cu K $\alpha$  radiation, scanning electron microscope (SEM) with the acceleration voltage of 10 kV, Auger electron spectroscopy (AES), and optical transmission. For the determination of the conduction type and estimation of the photosensitivity, the photoelectrochemical (PEC) measurement was carried out using a three-electrode cell with saturated calomel electrode used as the reference electrode. 100 mM thiosulfate solution was used, and a Xe lamp (about 100 mW/cm<sup>2</sup>) was used as the light source. The incident light was



**Fig. 1.** AES spectrum of  $\text{FeS}_x$  films deposited from an aqueous solution containing 10 mM of  $\text{FeSO}_4$  and 100 mM  $\text{Na}_2\text{S}_2\text{O}_3$  without Fe powder.

turned off and on under a linearly increasing bias, and the current was measured.

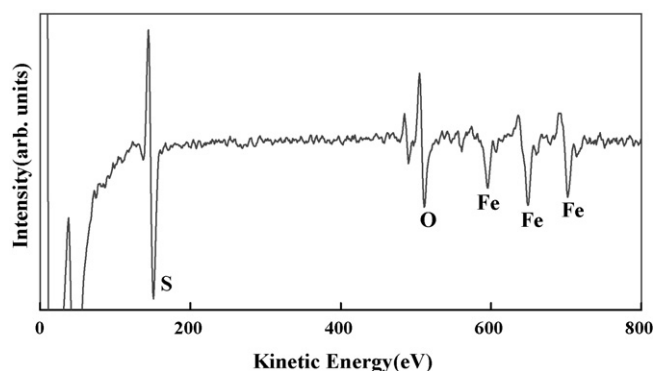
### 3. Results and discussion

Films were first deposited from an aqueous solution containing 5–300 mM of  $\text{FeSO}_4$  and 100–1000 mM of  $\text{Na}_2\text{S}_2\text{O}_3$  without Fe powder. No matter how much the  $\text{FeSO}_4$  concentration is, the film thickness is so small that we were not able to evaluate. Fig. 1 shows the Auger spectrum of the film deposited from a solution containing 10 mM  $\text{FeSO}_4$  and 100 mM  $\text{Na}_2\text{S}_2\text{O}_3$ . Since the film thickness was so small, the substrate signal appeared and complete removing the carbon contamination on the surface by sputtering was not possible. Fe/S ratio obtained from the spectrum is 0.41. A solution containing 275 mM  $\text{FeSO}_4$  and 100 mM  $\text{Na}_2\text{S}_2\text{O}_3$  led to the formation of a little thicker and yellow in color deposit but containing more oxygen. In several different deposition conditions, S-rich films were deposited but they were too thin for further studies such as XRD.

Next, deposition was carried out with Fe powder using aqueous solutions containing different values of  $\text{FeSO}_4$ , from 5 to 300 mM and 100 mM of  $\text{Na}_2\text{S}_2\text{O}_3$ . Fe powder was used either by adding to the solution, spreading over the solution surface or pasting on the edges of the substrate. The deposition results are summarized in Table 1. The optimum condition was found when the solution contained 50 mM of  $\text{FeSO}_4$  and 100 mM of  $\text{Na}_2\text{S}_2\text{O}_3$  with Fe powder adhered on the substrate edges near to the irradiated area. Fe powder showed very strong enhancement effects for the deposition, but when it was fixed far from the irradiated area of the substrate, the enhancement effect was negligible. We found that if only very small amount of Fe powder is on the deposition area, the substrate is covered with a uniform black film. The amount of Fe powder in that case is too small to be evaluated. It was observed that if the substrate with Fe powder adhered on its edges is immersed in the solution while not being illuminated, no deposition occurs. Fig. 2 shows the AES spectrum of the film (sample no.154) with Fe powder adhered on the edges of the substrate. The AES analysis indicated that the film consisted of the main elements Fe, S, and O, and the

**Table 1**  
Composition and characteristics of  $\text{FeS}_x\text{O}_y$  PCD films with Fe powder.

Sample no.	$\text{FeSO}_4:\text{Na}_2\text{S}_2\text{O}_3$	Color of the films	S/Fe ratio	O/Fe ratio	Thickness ( $\mu\text{m}$ )
139	0.300:0.100	Deep yellow	0.76	0.72	Very rough
150	0.005:0.100	Black	0.40	0.73	2
153	0.030:0.100	Black	0.50	0.79	0.75
154	0.050:0.100	Black	0.63	0.53	1.5



**Fig. 2.** AES spectrum for the sample no. 154, deposited from a solution containing 50 mM of  $\text{FeSO}_4$  and 100 mM  $\text{Na}_2\text{S}_2\text{O}_3$  with Fe powder fixed near the edge of the substrate.

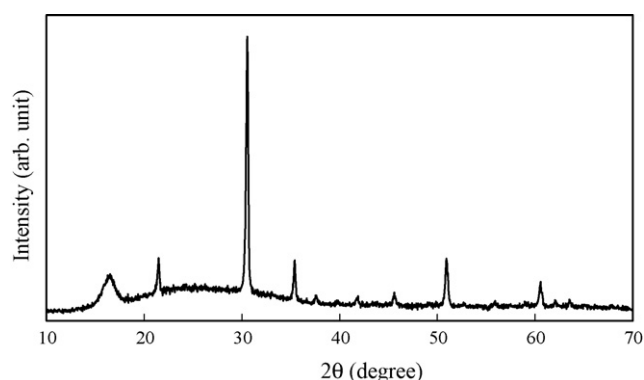
composition ratio is  $\text{FeS}_{0.63}\text{O}_{0.53}$ . It is understood that not all the iron is in the bonded form with sulfur but with oxygen also. As shown in Table 1, the film prepared from a bath more concentrated in  $\text{FeSO}_4$  has larger S/Fe ratio. The reason for that is not understood.

The enhancement effects on the reactions due to the Fe powder have never been reported, and their detailed mechanism is not known. It seems that the Fe catalytic effect enhances the reaction rate of  $\text{Fe}^{2+} + 2e^- = \text{Fe}$ . If the Fe powder is directly put in the deposition area, the enhancement effect is excessive. Then Fe/S ratio was large, and the excess Fe was oxidized after the deposition. Hence the deposit color was orange, or was initially black but shortly changed to orange (color of  $\text{FeO}_x$ ).

Fig. 3 gives the XRD pattern of the film (sample no. 154) with Fe powder adhered on the edges of the substrate. A relatively broad peak is observed at  $2\theta = 16.36^\circ$ . We could not identify this peak. All the peaks in a range from  $20^\circ$  to the end of the spectrum are due to the ITO substrate. In Ref. [3], a peak due to a superstructure (long range ordering) was observed near  $15^\circ$ . However, in the present case, since the related fundamental peak is not observed, it is not probable that the peak at  $2\theta = 16.36^\circ$  is due to the superstructure. The absence of peaks related to Fe–S or Fe–O compounds indicates that the deposited film is of amorphous nature.

The SEM photograph of the sample no. 154 is shown in Fig. 4. The substrate surface is fully covered with a uniform film with particles on it. The particles seem to have similar composition to the uniform background since we did not find significant variation in composition between different focus positions in the AES measurement.

Fig. 5 shows the optical transmission spectrum measured for a 0.4  $\mu\text{m}$ -thick film deposited under the same condition as no. 154. The spectrum showed no clear absorption edge. This indicates that



**Fig. 3.** XRD pattern of the sample no. 154.

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