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Supporting Information

Iron pyrite thin films deposited via non-vacuum direct coating of iron-salts/ethanol based precursor solutions

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S1. Estimation of partial pressure of sulfur during sulfurization[1]

When the reaction chamber is filled with nitrogen and sealed, n_N moles of nitrogen are contained in the total volume V_T. Before evaporation of S, the number of moles of gas molecules, n_B, inside the container of volume V_B is given by:

$$n_B = n_N \frac{V_B}{V_T}$$

The number of moles of gas molecules outside the container, n_C, is given by:

$$n_C = n_N \frac{V_C}{V_T}$$

where V_C is the volume of the reaction chamber. Note that we conserve the total volume and number of gas molecules:

$$V_C + V_B = V_T$$
$$n_C + n_B = n_T$$

After the S has completely vaporised, the concentration of gas molecules inside the container has risen by an amount n_s:

$$n'_B = n_N \frac{V_B}{V_T} + n_s$$

The internal pressure is now greater than the external pressure. This causes a fraction F of the gas molecules inside the container to move out, after which the pressures are equal. Then we have:

$$n_{B,eq} = (1 - F)\left(n_N \frac{V_B}{V_T} + n_s \right)$$

and:

$$n_{C,eq} = n_N \frac{V_C}{V_T} + F\,(n_N \frac{V_B}{V_T} + n_s)$$

Now writing the internal and external pressures after equilibration explicitly, and making them equal, we have

$$P_B = RT\,(1 - F)\left(\frac{n_N}{V_T} + \frac{n_S}{V_B}\right) = P_c = RT\left(\frac{n_N}{V_T} + F\left(\frac{n_N V_B}{V_T V_c} + \frac{n_s}{V_c}\right)\right)$$

where R is the gas constant (8.314 $\mathrm{JmolK^{-1}}$) and T the sulfurization temperature. Rearranging for F and making the following substitutions:

$$P_{S,B} = n_S \frac{RT}{V_B}$$

the partial pressure of S inside the container if all the S had remained inside it, and

$$P_N = n_N \frac{RT}{V_T} = P_{N,\ RT} \frac{T}{303}$$

Where P_N is the background pressure of nitrogen and $P_{N,RT}$ is P_N at room temperature, we obtain:

$$F = \frac{P_{S,B}}{\left(\frac{V_B}{V_C} + 1\right)(P_{S,B} + P_N)}$$

We can now calculate the partial pressure of S inside the container after equilibration, $P_{S,\,eq}$:

$$\frac{P_{S,eq}}{P_{S,B}} = (1 - F) = \frac{P_N + \frac{P_{S,B} V_B}{V_T}}{P_N + P_{S,B}}$$

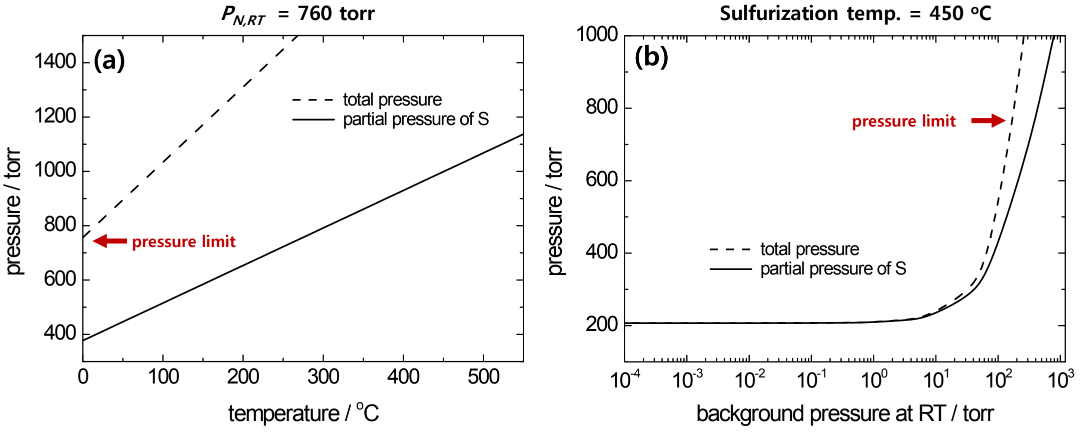


Fig. S1 calculated $P_{S,\,eq}$ and P_{total} as functions of (a) temperature and (b) background pressure at room temperature ($P_{N,RT}$)

In Fig.S1(a), it is clear that the $P_{S,\,eq}$ and P_{total} linearly increases with temperature. However, it should be noted that these calculated values are not achievable due to the pressure limit. Because the background pressure itself was 760 Torr, P_{total} in all temperature range is definitely be higher than 760 Torr. Thus, part of the mixture gas ($N_2 + S_2$) will be exhausted through the pressure relief valve and the actual S partial pressure and total pressure will be lower than those shown in Fig. S1(a). In this case, we can calculate the actual S partial pressure considering the ratio between $P_{S,\,eq}$ and P_{total} as follow;

$$P_{S,\,eq,actual} = P_{total,actual}\,(760\text{ torr}) \times \frac{P_{S,\,eq}}{P_{total}}$$

$P_{S,\,eq,actual}$ at selected temperatures are summarized in Table. 1. Due to the pressure limit, it is noticeable that $P_{S,\,eq,actual}$ at all temperatures same as 378.5 Torr. Thus, we can say in this case the phase evolution behavior is indeed temperature dependent under the same partial pressure of S.

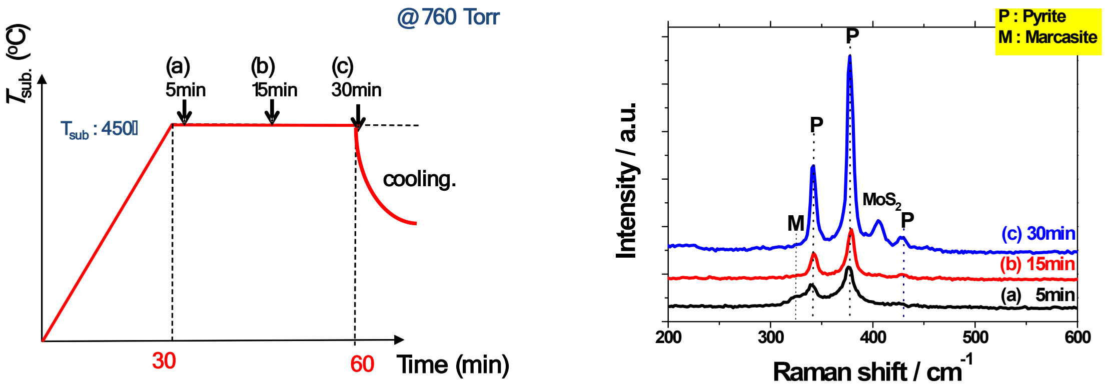
$P_{S,\,eq,\,actual}$ under different $P_{N,RT}$ at a same sulfurization temperature of 450 °C were calculated in a similar way. Fig. S1(b) is the calculated $P_{S,\,eq}$ and P_{total} as a function of $P_{N,RT}$, and actual pressures under selected $P_{N,RT}$ conditions considering the pressure limit are presented in Table 1. In this case, it is noticeable that P_{total} under $P_{N,RT}$ of 10^{-3} Torr is lower than the pressure limit. Therefore, $P_{S,\,eq}$ is equal to $P_{S,\,eq,actual} =$ 206.9 Torr.

Table1. Estimation of $P_{S,\,eq,actual}$ and $P_{total,actual}$ at selected conditions

	Temperature effects $P_{N,RT}$ = 760 Torr				**Background Pressure ($P_{N,RT}$) effects** Temp. = 450 °C	
	250 °C	**350 °C**	**450 °C**	**500 °C**	**10^{-3}**	**760**
P_{total}	1449.0	1726.1	2003.1	2141.6	206.9	2003.1
$P_{S,\,eq}$	722.5	860.6	998.8	1067.8	206.9	998.8
$\frac{P_{S,\,eq}}{P_{total}}$	0.498	0.498	0.498	0.498	1	0.498
$P_{total,actual}$	760	760	760	760	206.9	760
$P_{S,\,eq,actual}$	**378.5**	**378.5**	**378.5**	**378.5**	**206.9**	**378.5**

unit of pressure : Torr

S2. The phase evolution observed during isothermal sulfurization



(a)

(b)

Fig. S2. (a) temperature profile of the isothermal sulfurization at 450 °C. When the sulfurization time reached (a) 5, (b) 15 and (c) 30 min, the samples were taken for Raman measurement. (b) Raman spectra of the samples taken at different sulfurization time. Initial chamber pressure was adjusted to be 760 Torr for all the cases.

S3. Potential-pH diagram for the iron-sulfur-water system[2]

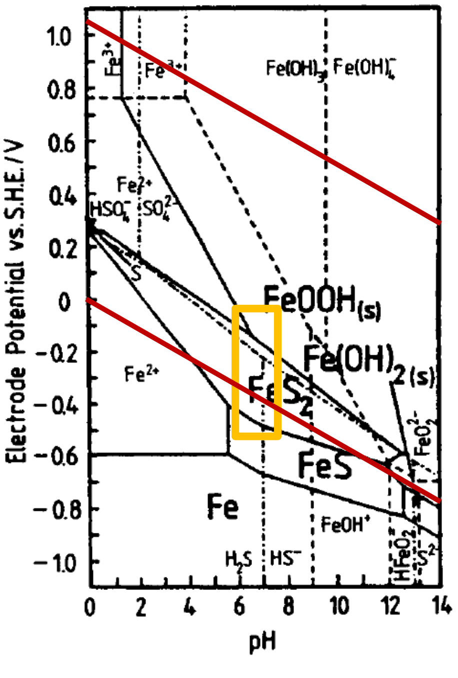
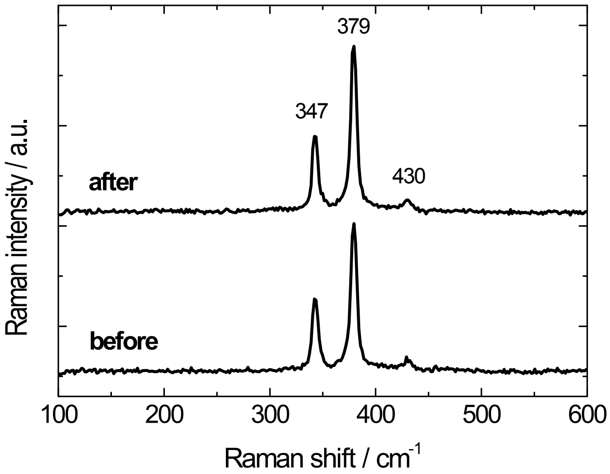


Fig. S3. (a) Potential-pH diagram for the iron-sulfur-water system at 25 °C.

S4. The Raman measurements



phase	Raman peak positions (cm^{-1})
pyrite	347, 379, 430
α-Fe_2O_3	225, 247, 299, 412, 498, 613
Fe_3O_4	300, 532, 661
α-FeOOH	299, 385, 479, 550
γ-FeOOH	245, 373, 522

Fig. S4. Raman spectra of the pyrite/Mo/SLG sample taken before and after the electrochemical measurement (left). Raman peak positions for various iron-oxide and –oxyhydroxide are presented for comparison (right).[3]

References

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3. D. L. A. de Faria, S. V. Silva, M. T. de Oliveira, *J. Raman Spectrosc.* **1997**, 28, 873.