Plasma Diagnostics in Reactive High-Power Impulse Magnetron Sputtering System Working in Ar + H₂S Gas Mixture

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Abstract: A reactive high-power impulse magnetron sputtering system (HiPIMS) working in Ar + H₂S gas mixture was investigated as a source for the deposition of iron sulfide thin films. As a sputtering material, a pure Fe target was used. Plasma parameters in this system were investigated by a time-resolved Langmuir probe, radio-frequency (RF) ion flux probe, quartz crystal monitor modified for measurement of the ionized fraction of depositing particles, and by optical emission spectroscopy. A wide range of mass flow rates of reactive gas H₂S was used for the investigation of the deposition process. It was found that the deposition rate of iron sulfide thin films is not influenced by the flow rate of H₂S reactive gas fed into the magnetron discharge although the target is covered by iron sulfide compound. The ionized fraction of depositing particles decreases from \( r \approx 40\% \) to \( r \approx 20\% \) as the flow rate of H₂S, \( Q_{H₂S} \), changes from 0 to 19 sccm at the gas pressure around \( p \approx 1 \) Pa in the reactor chamber. The electron concentration \( n_e \) measured by the Langmuir probe at the position of the substrate decreases over this change of \( Q_{H₂S} \) from \( 10^{18} \) down to \( 10^{17} \) m⁻³.

Keywords: HiPIMS; Langmuir probe; optical emission spectrometry; time-resolved probe measurements; H₂S, electron density; electron temperature; ionization fraction; SEM, XRD

1. Introduction

Reactive sputtering of sulfide thin films is still not a fully explored field. A lot of effort was devoted to the research of direct-current (DC) or radio frequency (RF) sputtering methods of various sulfides [1–3]. These can be semiconductor materials for example iron disulfide FeS₂ in the pyrite phase reported as a p-type semiconductor [1,2,4] or an n-type semiconductor suitable as a photoanode in solar water splitting cells when the pyrite phase was mixed with a small fraction of marcasite [5]. FeS₂ was investigated for various applications such as absorbing material in solar cells, material for photocatalysis or electrocatalysis [6]. The high absorption coefficient, \( \alpha = 6.10^6 \text{ cm}^{-1} \) for \( \lambda = 633 \) nm [7], which is several orders of magnitude larger than that of crystalline silicon, and the composition of abundant, cheap, and non-toxic elements makes pyrite an interesting material for solar cells and further photonic applications [1,8–13]. FeS₂ thin films with promising semiconductor properties were also prepared by reactive magnetron sputtering of an Fe target in Ar + H₂S gas mixture [1,2,4].

Iron mono sulfide FeS is an interesting material that exhibits transition from metal to semiconductor at a certain temperature close to 147 °C [14,15]. Below this temperature, FeS is a semiconductor and above this temperature it behaves as a metal. Based on this material, devices
triggered by heat can be realized. Furthermore, FeS films were found to be excellent low-friction materials working like solid state lubricants in tribological applications [16].

High-power impulse magnetron sputtering system (HiPIMS) is a relatively novel approach for the deposition of thin films [17–20]. This method utilizes very high discharge current densities during the pulse $j_{D} > 1 \text{ A cm}^{-2}$, but, simultaneously, average power applied in the HiPIMS discharge is similar to DC magnetron sputtering. These conditions result in a high degree of ionization of sputtered particles. Thus, the deposited films have higher density, better adhesion, and 3D objects such as trenches, etc. and can be more uniformly coated as well [21–23]. Recently, reactive HiPIMS in various gas mixtures has been used for the deposition of oxides, nitrides, and other materials [24–31].

In this paper, we will present the first study of plasma parameters in the reactive HiPIMS in Ar + H$_2$S gas mixture whose results could be further used for the optimization of deposition of iron sulfide thin films or other types of sulfides.

2. Experimental

The experimental setup of the reactive HiPIMS in Ar + H$_2$S gas mixture can be seen in Figure 1. The system is equipped with a pure iron Fe target with an outer diameter of 50 mm and a thickness of 0.8 mm. The stainless-steel reactor vacuum chamber is continuously pumped by a combination of turbomolecular (pumping speed $S_t = 250 \text{ L s}^{-1}$) and rotary vane pumps (pumping speed $S_r = 25 \text{ m}^3 \text{ h}^{-1}$). The gas flow rates of Ar (99.9999%) and pure H$_2$S (99.5%) are independently controlled by two mass flow controllers. It is useful to note that H$_2$S is an inflammable and highly toxic gas. Consequently, the use of H$_2$S in a laboratory is subject to approval by a respective official body. The pressure in the reactor chamber can be controlled by a gate valve placed between the reactor chamber and the turbomolecular pump. The magnetron cathode is connected with the HiPIMS power supply, which has a maximum current pulse of 200 A and maximum voltage of 1000 V at the output. The time-resolved Langmuir probe, the quartz crystal monitor (QCM) modified with an electron filter and biased collecting electrode, and the RF ion flux probe are placed at position of the substrate. The distance, $l_s$, between the target and the substrate is 70 mm for all presented experiments.

![Figure 1](image-url)  
**Figure 1.** Experimental setup of reactive high-power impulse magnetron sputtering system (HiPIMS) deposition system in Ar + H$_2$S gas mixture.

Emission spectroscopy of HiPIMS plasma was carried out by a TRIAX JY spectrometer with focal length 0.5 m and grating 1200 gr/mm. The CCD detector provided time-averaged spectra over several seconds in the spectral range 200–1000 nm. The entrance slit and integration time of the CCD detector
was kept constant for a particular spectral range in order to be able to perform approximate quantitative comparison of particular conditions.

The HiPIMS magnetron discharge was always operated with the constant length of the active pulse, $T_{\text{ON}} = 100 \, \mu\text{s}$, and pulsing frequency, $f_p = 100 \, \text{Hz}$. The average power, $P_{\text{av}}$, applied in the discharge was slightly changed in different cases and was unambiguously related with presented pulse power, $P_p$, according to the formula:

$$P_{\text{av}} = P_p \cdot T_{\text{ON}} \cdot f_p.$$  \hspace{1cm} (1)

The current and voltage waveforms of HIPIMS discharge can be seen in Figure 3 and will be discussed later.

2.1. Langmuir Probe Measurement

The plasma parameters such as plasma density, $n_e$, and electron effective temperature, $T_{\text{eff}}$, were measured by the Langmuir probe. The Langmuir probe consists of fine tungsten wire (diameter 50 µm and length 2.2 mm) mounted on an ultra high vacuum (UHV)-compatible probe hardware from Scientific Systems, Inc. The probe was placed 70 mm axially from the target and radially above the target racetrack. An in-house developed electronic acquisition unit was capable of setting the probe voltage from −50 to 50 V with a step of 0.1 V and measuring the probe current with time resolution better than 5 µs [32]. The grounded chamber’s walls served as a reference electrode for the probe’s electrical circuit. The effect of the magnetic field on the probe measurement was negligible because the balanced magnetic field strength was less than 1 mT resulting in much larger Larmor radius of electrons in comparison with the radius of the probe.

Measured probe characteristics were evaluated under collisionless space charge sheath conditions because high-density HiPIMS plasma implies Debye length in the order of tens of µm whilst the mean free path of neutral-charged particle collision is in order of tens of mm [33]. The measured I–V characteristics were evaluated by using an in-house developed Langmuir probe software [34,35]. The software calculates the second derivative of the Langmuir probe characteristics numerically using the ‘sliding polynomial approximation’ method. This represents approximation of the selected odd number $M = 2m + 1 \, (m = 1, 2, \ldots)$ of adjacent data points (equidistantly spaced by $h$) around selected $x_i$ by a second order polynomial $p(x) = a_0 + a_1x + a_2x^2$ (for $x_i - m.h \leq x \leq x_i + m.h$). The second derivative at $x_i$ is hence $y''(x_i) = 2a_2$. Since the coefficient $a_2$ represents a weighted sum of the ordinates $y_l$ (for $l - m \leq l \leq l + m$) this method may be regarded as a digital filtering. As a result, by selecting a proper $n$, the noise on the computed second derivative could be reduced down to an acceptable level. The fact that we cannot calculate the second derivative at $m$ points at the start and the end of the characteristic can be compensated by collecting an adequate number of measured data points.

The electron energy distribution functions (EEDFs) in HiPIMS systems cannot be, in most cases, characterized by Maxwellian distributions [36]. Consequently, we had to calculate the basic plasma parameters, namely the electron density, $n_e$, and the electron mean energy, $\langle \varepsilon \rangle$, directly from the measured EEDF. The EEDF, $F(E)$, is related to the measured second derivative by the known Druyvesteyn relation [37,38], the formulae applicable in practice are given in [39]. Often the electron energy probability function, $f(E)$, is introduced (EEPF) as

$$f(E) = F(E)E^{-1/2}$$

where $E$ denotes the energy [40].

As follows from [39], the second derivative of the electron component of the probe current $I_e$ with respect to the probe voltage $U_p$, $d^2I_e/dU_p^2$, is related to $f(U_p)$ by the relation:

$$\frac{d^2I_e}{dU_p^2} = \frac{q_0^{3/2}}{2\sqrt{m_e}} \frac{1}{\sqrt{\pi} A_p} n_e A_p f(U_p),$$  \hspace{1cm} (2)

where $q_0$ and $m_e$ are the electron charge and mass respectively, $A_p$ is the probe surface area. The EEPF is normalized to one, i.e., $\int_0^\infty f(U_p)U_p^{3/2}dU_p = 1$. 


We start the probe data processing by computing the second derivative of the measured probe characteristic with respect to the probe voltage using the method described above. We assume that the second derivative of the positive ion component of the probe current can be neglected. Then we continue by estimating the electron density from the integral of the calculated second derivative:

$$n_e = \left(\frac{2}{q_0}\right)^{3/2} \frac{m_e^{1/2}}{a_p} \int_0^\infty U_p^{1/2} \frac{d^2f}{du_p^2} dU_p.$$  

(3)

The electron mean energy $<$ in electron-volts) is estimated from the normalized $f(U_p)$ by the relation:

$$\frac{<e>}{q_0} = \int_0^\infty U_p^{3/2} f(U_p) dU_p = \int_0^\infty U_p^{-1/2} \frac{d^2f}{du_p^2} dU_p.$$

(4)

The effective temperature $T_{ef}$ (in electron-volts) is then given by the relation: $T_{ef} = 2/3 <e>$.

2.2. Ion Flux Density Measurement by a Planar RF Ion Probe

Voltage at RF frequency, $f_M = 350$ kHz, and amplitude, $U_{RF} = 50$ V, was applied on the planar ion flux probe placed at the position of the substrate (see Figure 1). The RF signal was connected to the probe through a blocking capacitor, $C$, in order to measure only RF currents through the probe. The RF voltage and RF current waveforms were measured by a RF current transformer wound on a Teflon core and a capacitive voltage probe respectively. The signals from these probes were fed to the digital oscilloscope DSO7104B Agilent technologies (1 GHz, 4 GSa) Santa Clara, CA USA. The current transformer and capacitive probe were homemade and calibrated at frequencies in the region from 100 kHz up to 4 MHz. The calibration was done by the use of professional dummy load 50 Ω (1.5 kW VHF-UHF Dry dummy load 1-650 MHz Model MFJ-264, MFJ Enterprises, Inc. Starkville, MS USA). The complex correction function was created by this calibration procedure and the measured signal was corrected by this function after discreet Fourier transformation (DFT) done in the software OriginPro 2015, produced by OriginLab Corporation Northampton, MA USA. The accuracy of these measurements was tested on selected passive complex impedances with known real and imaginary part of impedance in the range 100 kHz–4 MHz. The accuracy of this measurement configuration was estimated to be below 5%. The probe was a planar disc with the area of approximately $S = 1$ cm². The RF substrate voltage and current waveforms, $U_{RF}$ and $I_{RF}$, were measured by RF current and voltage probes connected to the digital storage oscilloscope. The ion flux density of positive ions $j_S$ to the substrate was calculated from these waveforms by the method developed by Sobolewski [41,42]. The example of these RF waveforms on the planar ion flux probe during HiPIMS pulse can be seen in Figure 2. The current to the RF probe consists of three components, $I_p(t) = I_i(t) + I_e(t) + I_c(t)$. All those currents follow the probe voltage, $U_{RF}$. We assume that $I_i(t) = I_0$ is saturated, i.e., at sufficiently negative probe voltage, $I_i$ does not depend on $U_{RF}$. The probe ion current, $I_0$, can be determined from $I_{RF}$ at the time when the RF voltage $U_{RF}$ has a peak of negative value because here $dU_{RF}/dt = 0$ [41,42]. At this time, the capacitive current through the probe $I_c = 0$ and all electrons are repelled from the surface of the probe. It is necessary to remind here that this approach is valid only in case $f_M$ is well below ion plasma frequency $\omega_i >> f_M$ [41,42]. The ion flux density, $j_{SR}$, can be calculated from $I_0$ as $j_{SR} = I_0/S$ where $S$ is the area of the ion flux probe. We were able to get in this way the time evolution of the substrate ion flux density during the HiPIMS pulse. An advantage of the Sobolewski method for the ion flux calculation is the independence of this value on the resistivity of the deposited film on the probe since only AC values of $I_{RF}$ and $U_{RF}$ are used for the $j_{SR}$ calculation.
Figure 2. RF current and voltage waveforms on the RF ion flux probe.

2.3. Ionization Fraction of Depositing Particles Measurement by a Modified QCM with a Magnetic Electron Filter

A modified quartz crystal monitor with a magnetic electron filter (m-QCM) was already used in the HiPIMS system for the purpose of measuring the ionization fraction of depositing particles and was described in details elsewhere [43,44]. This system uses an auxiliary constant magnetic field placed at the working collecting electrode of the QCM in order to eliminate the major fraction of electron flux on this working electrode. The working electrode can be either biased by the positive voltage or connected to ground. In the case of applied positive bias on the working electrode, we can measure only the neutral flux, $i_n$, of depositing particles whilst the positive ions are repelled from the working electrode. When the bias on the working electrode of QCM is zero we can measure the total flux, $i_{tot}$ (neutral + ionized), of depositing particles. Thus, we can calculate the ratio $r$:

$$ r = \frac{i_{ion}}{i_{ion} + i_n} $$

(5)

where $i_{ion}$ is the flux of positively ionized depositing particles and $i_n$ is the flux of neutral particles. The flux of positive particles, $i_{ion}$, is not directly measured and is calculated according to the formula:

$$ i_{ion} = i_{tot} - i_n. $$

(6)

2.4. Iron Sulfide Thin Film Deposition

In order to show that iron sulfide thin films can be deposited by the reactive HiPIMS, the first deposition experiments of these thin films were done at selected conditions. Iron sulfide films were deposited on glass substrates. Chemical composition was measured by an electron microprobe Bruker XFlash 6 110 and the structure of deposited films was determined by an XRD in grazing incidence configuration (Figure 8).

SEM (TESCAN LYRA3 RISE) photographs of surfaces of the films S1–S4 are presented as well (Figure 9). The distance between the target and the substrate was 70 mm for all the deposition conditions. The substrate was heated during the deposition to 250 °C by external heater. The deposition conditions were similar to those used for plasma diagnostics and presented in Figure 3. The gas pressure in the reactor chamber was held at the constant value $p = 1$ Pa. The flow of argon was for all the samples $Q_{Ar} = 20$ sccm ($= 3.3 \times 10^{-2} \text{ Pa m}^3\text{s}^{-1}$). The changed parameters, such as the flow of H$_2$S, $Q_{H_2S}$, pulsed power during active HiPIMS discharge $P_p$, and the cathode voltage $U_c$ measured in the middle of active HiPIMS pulse, are mentioned in Table 1. Other HiPIMS discharge conditions
for all the samples were the same as in the plasma diagnostic experiments. Chemical composition of deposited films measured by electron microprobe can be seen in Table 2.

Table 1. Deposition conditions of deposited iron sulfide thin films (Q_{H2S} – H2S gass flow rate, P_p pulse discharge power, U_c cathode voltage).

| Sample no. | Q_{H2S} [sccm] | Q_{H2S} [m^3 \cdot s^{-1} \cdot Pa] | P_p [kW] | U_c [V] (middle of pulse) |
|------------|----------------|-------------------------------------|----------|---------------------------|
| S1         | 3.8            | 6.3 \times 10^{-3}                  | 32.1     | 556                       |
| S2         | 7.6            | 1.26 \times 10^{-2}                 | 34.1     | 567                       |
| S3         | 11.4           | 1.9 \times 10^{-2}                  | 37.3     | 575                       |
| S4         | 15.2           | 2.53 \times 10^{-2}                 | 39.8     | 510                       |
| S5         | 19             | 3.17 \times 10^{-2}                 | 36.0     | 600                       |
| S6         | 22.8           | 3.8 \times 10^{-2}                  | 37.3     | 575                       |

Table 2. Chemical composition measured by electron microprobe.

| Sample no. | Fe at.% | S at.% | O at.% |
|------------|---------|--------|--------|
| S1         | 40.7    | 54.8   | 4.5    |
| S2         | 40.1    | 54.7   | 5.2    |
| S3         | 39.4    | 56.8   | 3.8    |
| S4         | 41.0    | 56.0   | 3.0    |

3. Results and Discussion

The results of current and voltage waveforms measurement of reactive HiPIMS in Ar + H2S gas mixture can be seen in Figure 3 for different mass flow rates of H2S gas, Q_{H2S}, in the range from 0 up to 19 sccm and at the constant argon mass flow rate Q_{Ar} = 20 sccm. The total gas pressure in the reactor chamber was held at the constant value p = 1 Pa by the control gate valve. The pulse power applied to the HiPIMS discharge during the “ON” time was in the range P_p = 33–36 kW as marked at the particular graphs (see Figure 3).

The HiPIMS discharge current waveforms for different Q_{H2S} qualitatively differ as it can be seen in Figure 3a–d. The case of Q_{H2S} = 0 sccm (see Figure 3a) looks like a typical HiPIMS metallic iron sputtering with a gas rarefaction in the vicinity of the target causing the discharge current decreases during the pulse. The situation changes when H2S reactive gas is added into the discharge and the target is very probably covered by iron sulfide compound. The graph in Figure 3b shows that the current waveform character changes even for small Q_{H2S} = 3 sccm. In this case, the discharge current after initial fast growth shortly drops and after that slowly grows until the end of the active plasma pulse. A similar situation appears for higher Q_{H2S} (Figure 3b–d). It means the discharge current slightly decreases in the first part of the pulse and after that again increases until the end of pulse. In order to better explain this phenomenon we have to discuss at first the deposition rate measured by modified QCM and results of emission spectroscopy.
Figure 3. Discharge current and voltage waveforms for different values of mass flow rates of H\textsubscript{2}S, \(Q_{\text{H2S}}\), and time dependence of the pulse substrate ion flux density, \(j_{\text{SP}}\). a) gas flow of H\textsubscript{2}S \(Q_{\text{H2S}}=0\) sccm, b) gas flow of H\textsubscript{2}S \(Q_{\text{H2S}}=3\) sccm, c) gas flow of H\textsubscript{2}S \(Q_{\text{H2S}}=7.6\) sccm, d) gas flow of H\textsubscript{2}S \(Q_{\text{H2S}}=19\) sccm.

Figure 4 shows the ionization fraction, \(r\), of depositing particles for different \(Q_{\text{H2S}}\) as measured by modified QCM with the electron filter (left axis). We can also see the deposition rate on the right axis of the graph at Figure 4a. The maximum ionization fraction, \(r\), was found to be \(r = 43\%\) for pure Fe deposition without H\textsubscript{2}S. As \(Q_{\text{H2S}}\) grows, the ionization fraction, \(r\), gradually decreases to the value \(r = 20\%\). On the other hand, the deposition rate increases twice for even the smallest \(Q_{\text{H2S}} = 3\) sccm and remains constant up to high values of \(Q_{\text{H2S}} = 19\) sccm. On the contrary, we can see the substantial decrease of deposition rate for higher pressure (see Figure 4b) and decrease of ionization fraction for gas pressure, \(p = 4\) Pa.
Figure 4. (a) Dependence of ionization fraction of depositing particles $r = i_{\text{ion}}/(i_{\text{ion}} + i_{\text{a}})$ (left axis) and deposition rate (right axis) on the mass flow rate of H$_2$S $Q_{\text{H}_2\text{S}}$. (b) Dependence of ionization fraction of depositing particles $r = i_{\text{ion}}/(i_{\text{ion}} + i_{\text{a}})$ (left axis) and deposition rate (right axis) on the gas pressure in the reactor, $p$.

The results of optical emission spectroscopy can be seen in Figures 5 and 6. We can see spectra for different $Q_{\text{H}_2\text{S}}$ at constant pressure $p = 1$ Pa. Strong lines of Fe$^+$ and Fe at the spectrum for $Q_{\text{H}_2\text{S}} = 0$ sccm can be identified. The presence of strong Fe$^+$ and Fe lines was still observed with similar intensity for cases of high mass flow rate of H$_2$S up to $Q_{\text{H}_2\text{S}} = 19$ sccm. Furthermore, we can observe intensive sulfur lines in the optical emission spectra as shown in Figure 6 for different $Q_{\text{H}_2\text{S}}$. It can be seen that intensity of sulfur spectral lines and, thus, the sulfur atom concentration in the plasma grows for higher $Q_{\text{H}_2\text{S}}$ but the argon line intensity decreases with increasing $Q_{\text{H}_2\text{S}}$. These sulfur atoms are generated probably as a product of dissociation of H$_2$S gas in the plasma, and a certain fraction probably comes also from the target covered by iron sulfide. Intensities of measured lines Fe, Fe$^+$, Ar, and S for particular $Q_{\text{H}_2\text{S}}$ are in Table 3.
Time-resolved measurement with the Langmuir probe was carried out for different mass flow rates, \( Q_{H2S} \), and standardly at the pressure \( p = 1 \) Pa except the case of \( Q_{H2S} = 19 \) sccm when we also measured characteristics at \( p = 3 \) Pa. The obtained plasma parameters such as plasma density, \( n_e \), and electron effective temperature, \( T_{eff} \), are shown in Figure 7. Since the process of time-resolved measurements of the I–V probe characteristic is rather complicated, we assessed the general error of the plasma parameters estimated from the probe data as 20%. The \( H_2S \) mass flow rate varied between 0 and 19 sccm. As we can see in Figure 7a, the highest plasma density slightly above \( n_e \approx 10^{18} m^{-3} \) was reached for pure argon discharge during the second part of the plasma pulse. Adding a small amount of \( H_2S \) to the working gas resulted in a notable decrease of \( n_e \). Further \( H_2S \) mass flow rate increase led to slight decrease of the \( n_e \) whilst temporal evolution of \( n_e \) during the plasma active pulse and even during the plasma off-time was practically unchanged. The higher pressure resulted in lower \( n_e \). The most probable reason of electron concentration, \( n_e \), decrease for higher partial pressures of \( H_2S \) in the plasma can be attributed to the fact that \( H_2S \) is electronegative [45]. The electron attachment to \( H_2S \) is dissociative, producing negative ions \( HS^- \), \( H^- \), and \( S^- \) [45]. That causes loss of electrons from the tail of EEDF due to dissociation of \( H_2S \) molecules. Further, \( H_2S \) molecules can be dissociated by an electron impact and by interaction with other species (Ar) present in the plasma. Dissociation of
Figure 6. Emission spectra with S and Ar spectral lines of HiPIMS plasma for different mass flow rates of H2S gas $Q_{H2S}$ (a) for H2S gas flow $Q_{H2S} = 0$ sccm, (b) for H2S gas flow $Q_{H2S} = 7.8$ sccm, (c) for H2S gas flow $Q_{H2S} = 19$ sccm.

Table 3. Emission spectra of observed elements Fe, Fe+, S, and Ar.

| Element | Line wavelength [nm] | Intensity, arb. units $Q_{H2S} = 0$ sccm | Intensity, arb. units $Q_{H2S} = 7.8$ sccm | Intensity, arb. units $Q_{H2S} = 19$ sccm |
|---------|---------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| Fe⁺     | 273.69              | 5862                                     | 3587                                     | 3304                                     |
| Fe⁺     | 273.95              | 6832                                     | 5559                                     | 4774                                     |
| Fe⁺     | 275.32              | 7497                                     | 6009                                     | 5143                                     |
| Fe      | 302.40              | 5059                                     | 6653                                     | 6665                                     |
| Ar      | 922.45              | 10,646                                   | 5809                                     | 4987                                     |
| S       | 921.28              | 0                                        | 7492                                     | 11,829                                   |
| S       | 922.80              | 0                                        | 5230                                     | 8071                                     |
| S       | 923.75              | 0                                        | 3164                                     | 4753                                     |

H2S in plasma was already described for example in [46,47]. The H2S molecule can be dissociated in plasma by a direct electron impact as follows from [46,48]:

$$e + H_2S \rightarrow HS + H + e.$$  

Further mechanism of H2S dissociation is a two-step process as follows, e.g., from [46,48]. First the H2S⁺ positive ion is formed by an electron impact, by a charge transfer with ionized argon or by a reaction with a metastable excited argon. In principle, in place of argon we can also imagine another specie present in plasma.

$$e + H_2S \rightarrow H_2S^+ + 2e, \text{ or } Ar^+ + H_2S \rightarrow H_2S^+ + Ar, \text{ or } Ar^+ + H_2S \rightarrow H_2S^+ + Ar + e$$

(7)

The $H_2S^+$ molecular ion, however, quickly recombines with electrons by dissociative recombination: $H_2S^+ + e \rightarrow HS + H$. 

H₂S⁺ ions can be dissociated also by reaction with metastable excited species present in the plasma, e.g., Ar⁺ + H₂S → HS + H + Ar (Ar⁺ metastable states have an energy around 11.5 eV [49,50], well above the ionization energy of H₂S, which lies around 10.3 eV [51]). The ion chemistry of H₂S⁺ is rather complex and has been studied, e.g., in [51]. Therefore, we were able to give here just the qualitative discussion.

Apart from the energy lost by dissociation, the total energy contained in the discharge can also be distributed among the excitation of rotational and vibrational states of the molecular species added and, at the end, the efficiency of ionization, i.e., the electron density, is reduced. The sputtered Fe atoms can also contribute to the electron cooling since they are ionized by electron impact. However, this effect is also present without introducing H₂S, and we do not have clear evidence that the addition of H₂S would increase the sputtering of the iron target.

Figure 7b clearly demonstrates significant impact of \( Q_{H2S} \) on the mean energy of plasma electrons. The decrease of the \( T_{ef} \) during the first 40 µs is consistent with other observations in non-reactive and reactive HiPIMS systems. Plasma pulse onset is accompanied by beam-like electrons with energy of roughly 100 eV at the probe position, which are reflected from the negative space charge sheath around the cathode [4]. The minimum of \( T_{ef} \) within the plasma pulse having magnitude between 1.0 eV and 1.2 eV (depending on the H₂S mass flow rate) is probably connected with massive ionization of sputtered particles that have much lower ionization potential than argon atoms (Fe ionization potential is around 7.9 eV). Nevertheless, after 40 µs from the pulse onset, we can observe increase in the \( T_{ef} \). This is probably connected with the fast recombination reactions of the (molecular) ions created after the pulse onset. It is a known fact that the rate of recombination is (almost) inversely proportionally dependent on the electron temperature, see e.g., Figure 9 in [52] showing the rate of recombination of SH⁺ with electrons on the electron energy. The process of recombination then depletes the lower-energetic part of EEDF resulting in a higher \( T_{ef} \). This increase of \( T_{ef} \) becomes less pronounced with increasing \( Q_{H2S} \). The electron effective temperature, \( T_{ef} \), shows gradual decrease during the plasma pulse for pressure \( p = 3 \) Pa, and, moreover, \( T_{ef} \) is significantly smaller in comparison with measurement at lower pressure. That fact is understandable as electrons have to undergo more elastic and inelastic collisions with particles of processing gas.

Very similar behavior of the time evolution of the electron density and electron temperature after discharge switch-on was observed in an argon HiPIMS with a titanium target in a recent work [53]. The authors explained the local minimum of the \( T_e \) by cooling of the EEDF due to increasing density of metallic species. Cooler electrons reduced the plasma generation rate and, consequently, the sputtering rate was reduced accompanied by the rise in \( T_e \). Moreover, the authors of [54] observed similar behavior of \( n_e \) and \( T_e \) in the switch-on phase of the HiPIMS discharge. Since we do not have clear evidence about the sputtering of our iron target, we cannot conclusively determine the reason of the temporal behavior of the \( T_{ef} \) in our experiment.
As we have discussed above, the current waveforms in the presence of H₂S in the plasma qualitatively differ from those in pure argon and the discharge current increases at the end of the pulse in the reactive mode. In any case, this phenomenon is probably connected with the covering of the target surface with an iron sulfide layer as usually happens in case of reactive sputtering (target poisoning). As we can see in Figure 4a, the deposition rate does not decrease for higher Q_{H₂S} but increases instead. Thus, the sputtering rate of the poisoned target with sulfide layer is still high and similar to pure iron target sputtering so the gas rarefaction should still exist in front of the target in the reactive case. This statement is also confirmed by results of emission spectroscopy (see Figure 5) where we can see intensive Fe and Fe⁺ emission lines also for high Q_{H₂S}. Higher ion–electron secondary emission from iron sulfide deposited on the target can be responsible for the discharge current growth during the second part of HiPIMS pulse in the reactive case. It is difficult to provide accurate evidence for this statement because we do not know the exact structure of the sulfide layer created on the target surface, but the work function of pyrite FeS₂ is around ≈4.3 eV as reported in [55] and the work function of pure iron is between 4.7 and 4.8 eV as reported in [56]. These facts can support our discussion of the character of the discharge current in the reactive case.

The time evolution of the ion flux density at the position of the substrate obtained by the RF (350 kHz) Sobolewski method can be seen in each graph in Figure 3 as well. We can see in Figure 3, the dependence of maximum substrate ion flux density in the HiPIMS pulse as a function of H₂S mass flow rate Q_{H₂S}. The pulse power, P_p, is again mentioned at each point in the graph. As can be seen in Figure 3a–d, the substrate ion flux density gradually grows during the HiPIMS pulse with a maximum value very close to the end of the pulse. The substrate ion flux density should be a function of ion concentration, n_i, near the substrate and electron temperature, T_e, approximately according formula:

\[
\text{\text{Formula here}}
\]
where $e$ is elementary charge, $k_B$ is Boltzmann’s constant, and $M_i$ is the mass of ions.

The time evolution of ion flux density, $j_{SP}$, during the HiPIMS pulse for different $Q_{H_2S}$ can be correlated with the time evolution of electron concentration, $n_e$, obtained from Langmuir probe data (see Figure 7). The substantial growth of $j_{SP}$ during the pulse is in agreement with the growth of $n_e$ (the plasma is quasineutral, $n_e = n_i$). Furthermore, we can see in Figure 3 that the maximum achieved $j_{SP}$ during the pulse decreases with increase of $Q_{H_2S}$ at constant pressure $p = 1$ Pa. The absolute values of $j_{SP}$ are quite high in HiPIMS pulse and certainly will influence the growth of films during the pulse.

Finally, we can correlate the measured ionization fraction, $r$, of depositing particles with the results of Langmuir probe measurements (see Figure 7). It is obvious that an ionization cross section of an electron impact ionization collision that undergo the sputtered particles increases with higher electron kinetic energy in the interval just above the ionization potential of these atoms [57]. Thus, the total rate of ionization collisions of electrons with sputtered particles is proportional to $n_e$ and is also dependent on $T_e$ [33]. These facts clearly show that the increase in the measured plasma parameters ($n_e$, $T_e$) should simply increase the ionization fraction $r$. If we add H$_2$S gas into plasma $Q_{H_2S} = 3.8$ sccm the $n_e$ decreased more than three times. If we consider that the change of effective $T_e$ is not significant for this change of $Q_{H_2S}$, the decrease of ionization fraction from $r = 43\%$ to $r = 30\%$ is in qualitative agreement with the Langmuir probe data. Further decrease of $r$ for higher $Q_{H_2S}$ is again in agreement with the electron concentration, $n_e$, decrease for these H$_2$S flows.

The results of XRD of deposited iron sulfide can be seen in Figure 8 for samples S1–S6 with increasing amount of H$_2$S gas flow $Q_{H_2S} = 3.8–22.8$ sccm (Table 1). We can see that for lowest $Q_{H_2S}$ (S1) we could identify the mixture of FeS troilite phase with pure iron Fe. For increasing $Q_{H_2S}$ (S2,S3), we could identify a similar mixture but with gradually decreasing amount of pure iron phase Fe. For S4, only the FeS troilite phase was identified. The sample S5 for further increase of $Q_{H_2S}$ was a mixture of FeS$_2$ of pyrite and marcasite and FeS with troilite phase. The highest amount of pyrite FeS$_2$ was identified for sample S6 for the highest-used $Q_{H_2S} = 22.8$ sccm and this sample was a mixture of pyrite and marcasite.

![Figure 8. XRD diffraction patterns for the samples S1–S6 from Table 1.](image)

The results of analysis (electron microprobe) of composition of the deposited iron sulfide films (the samples S1–S4 in Table 2) show that these films contain Fe and S atoms with the atomic ratio...
slightly higher than unity. The analyzed films also contain a contamination of O with several at.%. Therefore, the film stoichiometry was close to FeS. The SEM photography of the typical part of the surface of the films (S1–S4) can be seen in Figure 9. We can identify a higher amount of macroparticles for the deposition conditions with lower $Q_{H_2S}$.

![Figure 9. SEM photography of the surface of samples S1–S4.](image)

4. Conclusion

A reactive HiPIMS system in Ar + H$_2$S gas mixture with a pure iron target was investigated at suitable conditions for iron sulfide thin film deposition. Plasma parameters such as electron density, $n_e$, and effective electron temperature, $T_{\text{eff}}$, were determined by the time-resolved Langmuir probe. The electron concentration reached the value $n_e \approx 10^{18}$ m$^{-3}$ after the middle of the HiPIMS pulse for the non-reactive case of $Q_{H_2S} = 0$ sccm. As the mass flow rate of H$_2$S gas gradually increased up to $Q_{H_2S} = 19$ sccm, the electron concentration gradually decreased down to the value $n_e \approx 10^{17}$ m$^{-3}$. The effective electron temperature, $T_{\text{eff}}$, was always in the range $T_{\text{eff}} = 1–1.6$ eV during the active part of HiPIMS pulse for all the values of used $Q_{H_2S}$ and gas pressure $p = 1$ Pa. These findings correspond to results obtained by the QCM with magnetic filter used for the ionization fraction of sputtered particles $r$ measurement. The value of $r = 40\%$ measured for pure Fe HiPIMS sputtering at $Q_{H_2S} = 0$ sccm, decreased to the value $r = 30\%$ for $Q_{H_2S} = 5$ sccm, and $r = 20\%$ was found for $Q_{H_2S} = 19$ sccm. The deposition rate increased in the reactive sputtering mode in comparison with pure iron sputtering and was nearly constant for all investigated H$_2$S gas flows up to $Q_{H_2S} = 19$ sccm at pressure $p = 1$ Pa. This is in agreement with the results of optical emission spectroscopy since we have found still intensive Fe$^+$ ion and Fe neutral lines in the plasma also for high $Q_{H_2S} = 19$ sccm. The study of current waveform character shows that although the deposition rate increases for higher $Q_{H_2S}$, the discharge current gradually increases in the second part of the active HiPIMS pulse for $Q_{H_2S} > 0$ sccm in comparison with the non-reactive case where we observed current decrease due to sputtering wind. Since the gas rarefaction near the target should probably still exist at these reactive conditions, this phenomenon could be explained by the higher yield of ion-induced electron secondary emission from the covered target by iron sulfide compounds. The iron sulfide thin films were deposited at conditions used for plasma diagnostics for different gas flow of H$_2$S. For lower $Q_{H_2S}$ we obtained rather FeS with the structure of trollite and for higher amount we obtained a mixture of pyrite and marcasite.

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