Species kinetics in Ar-S2 plasma of the pulsed periodic discharge

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Abstract. The kinetic (0D) model a longitudinal pulsed-periodic discharge in mixtures of sulfur vapor with argon based on solution of the balance equations for plasma species and an equation of the electron energy balance was developed and evolution of species densities was calculated in the discharge at pressure ~ 40 Torr. Radiation spectrum of the discharge is similar to solar spectrum in the wavelength range of 280–600 nm. The discharge plasma is electronegative; a discharge with electropositive plasma is non-stable and can exist during short time in a pulsed mode. As simulation shown densities of all charged and excited species fast increase during 1–1.5 \( \mu \)s after voltage pulse beginning, reach maximal values and then decrease because of diminishing el ectrons mean energy and density in decreasing field. It is found that density of \( S_2^* (B^3 \Sigma) \) molecules fast rises during voltage pulse and exceeds densities of other excited species; however when a pulse voltage decreases the density of \( S_2^* (B^3 \Sigma) \) molecules fast falls while density of resonance excited argon atoms decreases slower. This is the reason for appearance of strong Ar lines together with \( S_2 \) bands in spectra of the longitudinal pulsed-periodic discharge in argon/sulfur vapor mixtures.

1. Introduction
Light is very important for life. The quality of life, health and urban safety associated with traffic and crime prevention depend on the light and its quality. At the moment there is no light source that would fully satisfy all the requirements for light sources. All known light sources, such as incandescent, fluorescent, halogen, mercury, sodium, metal halide, xenon, sulfuric lamps and LED lamps have, along with advantages, significant disadvantages [1].

Plasma lamps based on sulfur vapour radiation are promising sources to create lighting devices with high luminous efficiency and high-quality spectrum that, in addition, do not require special recycling measures [1–3]. Discharges in mixtures of noble gases with sulfur vapors allow to obtain a radiation spectrum, close to the solar spectrum; such spectrum is caused by radiation of \( S_2 \) dimers \( B^3 \Sigma \rightarrow X^3 \Sigma \) – transition).

Microwave sulfur lamps were invented in 1990 [4] and serial production of the lamps was started in 2010. The characteristics of sulfur mw discharges were experimentally investigated since the 70s [5–7]. Along with the experimental work, theoretical studies of microwave sulfur lamps were carried out in order to understand the discharge properties [8, 9].

However, microwave sulfur lamps have disadvantages such as the complexity of the design, high cost of the lamp module, high temperature of vapor in the bulb, using microwave radiation, inertia and
large diameter of the luminous body. So, the search for types of discharges convenient for creating efficient sulfur lamps continues. Numerical modeling of discharge properties allows estimating the possibilities and prospects of sulfur lamps.

Here kinetics of charged and neutral species in Ar-S₂ plasma of the pulsed periodic discharge is studied. Evolution of species densities during voltage pulses was calculated using a 0D model of the pulsed-periodic discharge in argon – sulfur vapors mixtures. The kinetic (0D) model is based on solution of the kinetic equations for plasma species and an equation of the electron energy balance. The simulations were performed for experimental conditions of a longitudinal pulsed periodic discharge in mixtures of argon and sulfur vapors, studied in [10].

2. A kinetic model

The kinetic (0-dimensional) model based on solution of the balance equations for plasma species and an equation of the electron energy balance [11] was used to calculate time dependencies of densities of argon-sulfur vapour plasma species in the longitudinal pulsed-periodic discharge. Calculation of the densities even within the limits of a simple model what the kinetic model is, allows to receive the valuable information on plasma composition depending on the electric field and time that is difficult for measurement.

The kinetic scheme includes 30 reactions for 14 species: Ar, S₂, S, Ar*, Ar**, S₂*(B³Σ_u⁻), S*, S₂+, S+, Ar+, S₂-, S- and electrons. Electron excited reactions are presented in table 1.

Table 1. Reactions in Ar-S₂ plasma initiated by electrons (T_e = \bar{E}/1.5).

| No. | Reaction | Rate constant (m³n/s; n = 0,1,2) | Ref. |
|-----|----------|----------------------------------|------|
| 1   | e+Ar→e+Ar | k₅(\varepsilon) | [12] |
| 2   | e+Ar→Ar⁺+e | 1.0×10⁻¹⁷T_e⁻⁰.⁷⁵ | [13] |
| 3   | e+Ar→e+Ar** | 5.0×10⁻¹⁸T_e⁻⁰.⁵ | [13] |
| 4   | e+Ar⁺→e+Ar⁺ | k₆(\varepsilon) | [12] |
| 5   | e+Ar→2e+Ar⁺ | k₇(\varepsilon) | [12] |
| 6   | 2e+Ar⁺→e+Ar⁺ | 5.4×10⁻³⁹/T_e⁻⁴.⁵ | [15] |
| 7   | e+Ar⁺+Ar→Ar⁺+Ar⁺ | 2.3×10⁻³⁴/T_e⁻².⁵ | [16] |
| 8   | e+S₂→e+S₂ | k₈(\varepsilon) | [17] |
| 9   | e+S₂→e+S₂*(B³Σ_u⁻) | k₉(\varepsilon) | [18] |
| 10  | e+S₂→2e+S₂⁺ | k₁₀(\varepsilon) | [19] |
| 11  | e+S₂→S⁺ | k₁₁(\varepsilon) | [20] |
| 12  | e+S₂→S⁺ + S⁺ | k₁₂(\varepsilon) | [20] |
| 13  | 2e+S₂⁺→e+S₂⁺ | The detailed equilibrium principle | [21] |
| 14  | e+S₂⁺→S⁺ | 3.0×10⁻¹⁴T_e⁻⁰.⁵ | [21] |
| 15  | e⁺+S→e⁺+S⁺ | k₁₅(\varepsilon) | [22] |
| 16  | e+S→e⁺+S⁺ | k₁₆(\varepsilon) | [21] |

The rate constants of reactions 1, 5, 8–12 and 15, 16 in the table 1 were calculated by averaging cross sections of corresponding reactions on the electron energy distribution function (EEDF). The EEDF was calculated using program BOLSIG+ [25], cross sections of electron collisions with sulfur molecules and atoms were taken from [17–20, 22, 26], cross sections of electron collisions with argon atoms were taken from [12, 27]. A rate constant of three-body recombination S₂⁺ ions was calculated by principle of detailed equilibrium.

Heavy species reactions are presented in table 2. Rate constants of mutual neutralization of positive and negative ions were estimated by Coulomb interaction model [21] and rate constant of charge transfer from Ar⁺ ions to S atoms estimated as k = πe(α/\mu)¹/², where α is atom polarizability, \mu is reduced mass of colliding species and e is electron charge [21].
Table 2. Heavy species reactions in Ar-S\textsubscript{2} plasma.

| No. | Reaction                                | Rate constant (m\textsuperscript{3}\textbullet s\textsuperscript{-1}) | No. | Reaction                                | Rate constant (m\textsuperscript{3}\textbullet n\textsuperscript{-1}; n = 0,1,2) | Ref. |
|-----|----------------------------------------|-----------------------------------------------------------------|-----|----------------------------------------|--------------------------------------------------------------------------------|------|
| 1   | S\textsubscript{2}^-+S\textsubscript{2}^+\rightarrow S\textsubscript{2}^*-+S\textsubscript{2} | 2.92\times10\textsuperscript{-14}                                  | 8   | S\textsuperscript{2}^-+Ar\rightarrow S\textsubscript{2}^*+Ar       | 3.22\times10\textsuperscript{-43}                                              | [21] |
| 2   | S\textsuperscript{2}^-+S\textsubscript{2}^*-+S | 3.21\times10\textsuperscript{-14}                                  | 9   | Ar**+Ar\rightarrow Arm+Ar          | 1.0\times10\textsuperscript{-16}                                              | [13] |
| 3   | S\textsubscript{2}^-+Ar\rightarrow S\textsubscript{2}^*-+Ar** | 3.33\times10\textsuperscript{-14}                                  | 10  | Ar**+Ar\rightarrow Ar^*+Ar        | 1.0\times10\textsuperscript{-16}                                              | [13] |
| 4   | S\textsuperscript{2}^-+Ar\rightarrow S\textsuperscript{2}^*+Ar** | 3.51\times10\textsuperscript{-14}                                  | 11  | Ar^*\rightarrow Ar+hv             | 2.0\times10\textsuperscript{6}                                                 | [13] |
| 5   | S\textsuperscript{2}^-+S\textsuperscript{2}^*+S | 3.78\times10\textsuperscript{-14}                                  | 12  | Ar**\rightarrow Ar+hv            | 3.0\times10\textsuperscript{7}                                                 | [13] |
| 6   | S\textsubscript{2}^-+S\textsuperscript{2}^*-+S | 3.58\times10\textsuperscript{-14}                                  | 13  | S\textsubscript{2}^*-\rightarrow S\textsubscript{2}+hv          | 5.3\times10\textsuperscript{7}                                                 | [23] |
| 7   | Ar\textsuperscript{2}^*-+S\rightarrow Ar+S** | 4.72\times10\textsuperscript{-16}                                  | 14  | S\textsuperscript{2}^*\rightarrow S\textsubscript{2}+hv          | 1/\tau                                                                      | [24] |

The model equations represent a stiff system of the ordinary differential equations. The system was solved using the VODE software package [28].

3. Results and discussion

Figure 1a shows the mean electron energy in discharges in Ar-S\textsubscript{2} mixtures as function of reduced electric field at concentration of S\textsubscript{2} vapors in the mixture of 0.5–10 %. One can see, that increasing the S\textsubscript{2} molecule concentration in Ar-S\textsubscript{2} mixtures promotes decreasing the mean electron energy, that results in rising rate constants of the electron attachment to sulfur molecules and atoms and diminishing the ionization and excitation rate constants of S\textsubscript{2} molecules and Ar atoms.

![Figure 1a](image1.png)

**Figure 1.** a) Dependencies of the mean electron energy on reduced electric field (E/n) at different S\textsubscript{2} fraction in Ar-S\textsubscript{2} mixtures; b) Ionization and attachment rate constants as functions of reduced electric field in 98% Ar-2% S\textsubscript{2} vapour mixture.

Increase in the reduced electric field E/n leads to raise in mean electron energy that results into growth of the ionization and excitation rate constants of both S\textsubscript{2} molecules and Ar atoms as well as into diminution of rate constants of the electron attachment to molecules and atoms of sulfur (figure 1b).

Figure 2 shows the critical electric field, at which total ionization rate equals total attachment rate, as a function of S\textsubscript{2} vapors fraction in the mixtures. One can see, that the breaking field E*/n, at which a transition from electronegative to electropositive plasma takes place, increases with sulfur vapour fraction in Ar-S\textsubscript{2} mixture.

The calculations of species kinetics were carried out for experimental conditions similar to [10], where a luminescence of the longitudinal pulsed-periodic discharge plasma containing sulfur vapour was studied. The radiation source represents a gas discharge tube with inner diameter of 12 mm and
gap length between electrodes of 25 cm disposed on opposite ends of the tube. Sulfur powder was scattered over inner bottom side of the tube. Argon pressure was 40 Torr and pressure of sulfur saturated vapors was determined by temperature of gas discharge tube wall varied due self-heating from the room temperature up to 160°C. The pulsed-periodic discharge was excited with a thyratron oscillator ensured the pulse repetition rate of 10 kHz at charging voltages up to 10 kV [10].

Figure 2. Dependency the breaking electric field $E^*/n$ as a function of $S_2$ fraction in Ar-$S_2$ mixtures.

Figure 3 shows changing reduced electric field ($E/n$) and mean electron energy during the voltage pulse in form $2U_0/(\exp(t/\tau_p)+\exp(-t/\tau_p))$, used in simulations, where $U_0 = 7$ kV, $\tau_p \sim 10$ μs, and $P_{Ar} = 40$ Torr, $P_{S_2} = 0.8$ Torr.

Figure 3. Variation of reduced electric field ($E/n$) and mean electron energy ($\varepsilon$) during the voltage pulse; $U_0 = 7$ kV, $\tau_p \sim 10$ μs, $P_{Ar} = 40$ Torr, 2% $S_2$ in Ar-$S_2$ vapour mixture.

Figure 4 shows evolution of charged species densities in 0.98 Ar-0.02 $S_2$ mixture during two consecutive voltage pulse: first and second. Evolution of charged species densities during the third pulse is similar to that during the second pulse. Initial densities of electrons and $Ar^+$ ions were set to $10^9$–$10^{11}$ cm$^{-3}$, initial densities of other ions were set to zero. One can see during both cycles all charged species densities begin increase when the pulse is applied and reach their maximums at about 2 μs when electric field decreases on ~10% of maximal value and mean electron energy decreases on about 3–4% of maximal value. After reaching the maximum values densities begin to decrease. Most rapidly decreases density of electrons. At high field the principal positive ion is $S_2^+$ and densities of $S_2^-$ and $S^-$ negative ions are close. During whole cycle plasma is electronegative: electron density is lower than densities of $S_2^-$ and $S^-$; the electronegativity increases when reduced electric field and the mean electron energy decrease. $S_2^+$ and $S^-$ decreases with $E/n$ diminishing faster compared other ions.
densities so after about 10–15 μs the picture changes, the abundant positive ions became Ar$^+$ and S$^+$ and abundant negative ions became S$_2^-$.

**Figure 4.** Evolution of charged species densities during the voltage pulse: a) 1$^{\text{st}}$ period, $U_{\text{max}} = 7$ kV; b) 2$^{\text{nd}}$ period, $U_0 = 6.4$ kV, $\tau_P \sim 10 \mu$s, $P_{Ar} = 40$ Torr, 2% S$_2$ in Ar-S$_2$ vapour mixture.

Figure 5 shows evolution of neutral species densities in 0.98Ar-0.02S$_2$ mixture during two consecutive voltage pulse: first and second. Evolution of neutral species densities during the third pulse is similar to that during the second pulse. Initial densities of Ar atoms and S$_2$ molecules were calculated as $n = P/kT$; initial densities of other neutral species were set to zero. Evolution of S atoms differs from evolution of excited species as well as evolution of Ar$_m$ metastable atoms differs from evolution of other excited species. One can see evolution of excited species densities excepting Ar$_m$ is similar to evolution of ions densities. When the voltage pulse is applied the densities increases, reach their maximums at about 2 μs and then decrease. Density of S atoms after about 2 μs reach $\sim 10^2$ m$^{-3}$ and then saturate remaining almost unchanged during the subsequent time. Density of Ar$_m$ metastable atoms unlike evolution of other excited species, which densities fast decrease after reaching its maximum, slowly diminishes, being decreased by less than an order of magnitude from the maximum value toward the beginning of the next pulse. It worth noting, that density of S$_2^*$ fast increases at the pulse beginning and reach value greater than other excited species, so strong radiation of S$_2(B^3\Sigma \rightarrow X^3\Sigma –$ transition) exists for the time interval of 1–2 μs, after then S$_2^*$ density fast decreases, even faster than densities of other excited species.

**Figure 5.** Evolution of neutral species densities during the voltage pulse: a) 1$^{\text{st}}$ period, $U_0 = 7$ kV; b) 2$^{\text{nd}}$ period, $U_0 = 6.4$ kV, $\tau_P \sim 10 \mu$s, $P_{Ar} = 40$ Torr, 2% S$_2$ in Ar-S$_2$ vapour mixture.
The discharge with electropositive plasma is non-stable and can exist during short time in pulsed mode. Under $E/N<E^*/N$, when plasma is a bit electronegative, the primary positive ions in Ar-S$_2$ plasma are S$^+$ ions and under $E/N<<E^*/N$ when plasma becomes very electronegative the primary positive ions are S$^+$ and Ar$^+$. In both cases the negative ions S$^-$ and S$^-$ are in commensurable amounts in the plasma.

4. Conclusion

The 0D model of a discharge in Ar-S$_2$ mixtures was developed and applied to study species kinetics of Ar-S$_2$ plasma existing during short voltage pulse at moderate pressure and small S$_2$ fraction in the mixture; these parameters close to conditions of the longitudinal pulsed-periodic discharge. The argon/sulfur vapor discharges is an effective source of radiation spectrum, close to the solar spectrum in the wavelength range of 280–600 nm. It was shown that Ar-S$_2$ plasma is electronegative, density of electrons is less than density of ions during whole pulse duration. Discharge with electropositive plasma is non-stable and can exist during short time in a pulsed mode. Densities of all charged and excited species except argon metastable atoms fast change during voltage pulse, reaching maximum at about 1–2 $\mu$s after pulse beginning. Density of S$_2^*(B^3\Sigma)$ molecules fast rises and exceeds densities of other excited species; however when pulse voltage decreases and as a consequence energy of electrons diminishes excited sulfur molecule density fast falls while density of resonance excited argon atoms decreases very slowly. This is a reason for appearance of strong Ar lines together with S$_2$ bands in spectra of the longitudinal pulsed-periodic discharge in argon/sulfur vapor mixtures. Reactions of ion mutual neutralization introduce the great deposit into S$_2^*$ generation along with excitation of S$_2$ molecules by direct electron impact, their contribution into S$_2^*$ generation increases when electric field decreases.

Acknowledgements

The author is very grateful to Dr. A. Heneral for discussions and information on properties of discharges in mixtures of argon and sulfur vapors and his help in finding cross-sections of electron collisions with sulfur molecules.

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