

# Features of High Current Nanosecond Discharge in Mixture of High Pressure CuInSe<sub>2</sub> Chalkopyrite Vapor and Argon

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**Abstract:** The features of an over-voltage high-current nanosecond discharge in argon of high pressure (p=202 kPa) ignited between the electrodes of CuInSe<sub>2</sub> compound are presented. In the sputtering of massive chalcopyrite electrodes, the CuInSe<sub>2</sub> pair gets into the discharge plasma. Main products of dissociation of chalcopyrite molecules in the over-voltage nanosecond discharge are established. They were in excited and ionized states and in the spectra of plasma radiation they were predominantly represented by atoms and single charged ions of copper and indium. It is proposed to use the spectral lines of copper and indium to control the process of thin films of chalcopyrite deposition in a real time. Using gas-discharge method thin films of chalcopyrite are synthesized on quartz substrates. These films effectively absorb the radiation falling on their surface in the spectral range of 200-800 nm. This property opens the prospects for their application in photovoltaic devices

**Keywords:** Chalcopyrite Electrodes, Over-voltage High-Current Discharge, Excited and Ionized States, Thin Films

## 1. Introduction

At present, chalcopyrites of CuInSe<sub>2</sub> type are promising materials for use in solar panels. This is due to high coefficients of an solar radiation absorption by these materials and their high light stability. In papers [1, 2] results of investigations of characteristics and parameters of the laser erosion plasma formed from the corresponding polycrystal target (CuInSe<sub>2</sub>) in a vacuum are reported. Laser spraying allows to receive high-quality thin chalcopyrite films of the stoichiometric composition. However, in this case the output of materials for solar energy is low, and the process of synthesis of such films is too costly. Therefore, at present, the development of other physical methods for the synthesis of thin chalcopyrite films suitable for using in photovoltaic converters, remains relevant.

It may also be promising to use over-voltage nanosecond discharges in gases to sputtering of massive chalcopyrite and metal electrodes [3, 4]. At work in air of atmospheric pressure the necessity of application of cost vacuum and laser

equipment is eliminated. Due to the generation under some conditions in these discharges of beams of "escaping electrons" and associated X-rays, they are sufficiently homogeneous and suitable for deposition of thin nanostructured films on various substrates.

Currently the most studied are subnanosecond high-voltage discharges in air and nitrogen, which are ignited between metal electrodes at a distance between them in the range of 1-15 cm [5, 6]. Discharges of nanosecond duration between polycrystalline semiconductors at inter-electrode distances in the range of 1-5 mm are less studied.

This paper presents the results of a research of features of the over-voltage nanosecond discharge in high pressure Ar-CuInSe<sub>2</sub> vapor-gas mixtures with injection of chalcopyrite-based electrode vapors into gas medium due to their sputtering during the formation of ectons.

## 2. Experiment Conditions

The nanosecond discharge between chalcopyrite electrodes (CuInSe<sub>2</sub>) was ignited in the sealed discharge chamber

(Figure 1). The distance between the cylindrical electrodes of chalcopyrite with a diameter of 5 mm was 1 mm. The radius of curvature of the working end surface of chalcopyrite electrodes was the same and was of 3 mm.

The discharge chamber with the electrode system was evacuated by the low-vacuum pump to the residual air pressure of 5-10 Pa. The working pressure of high purity argon in the chamber was of 202 kPa.

The ignition of discharge was performed using the high-voltage modulator of bipolar voltage pulses with a total duration of 50-150 ns. The amplitudes of the positive and negative components of the high-voltage pulse were in the range of 10-40 kV. The repetition frequency of the pulse voltage in the experiments was of 100 Hz. Oscillograms of voltage pulses at the discharge gap and current waveforms of pulses were registered using the wide-band capacitor divider, the Rogowski coil, and the wide-wave oscilloscope 6-LOR-04. The temporal resolution of the measurement of electrical pulse characteristics was of 2-3 ns. To record plasma emission spectra it was used the MDR-2 monochromator and the photomultiplier FEU-106. The signal from the photomultiplier was fed to the amplifier and was recorded using the amplitude-to-digital converter in the automated spectrum measurement system with the personal computer display. The discharge radiation was analyzed in the spectral range of 200-650 nm. The experimental technique is given in [6] more detailed.

The quartz substrate was installed at a distance of 3 cm from the center of the discharge gap (Figure 1). The discharge burning time was set of about 3 hours. Then, the gray film deposition was observed on the substrate. This film consisted of sputtering products of electrodes based on the CuInSe<sub>2</sub> compound. Method of investigation of the absorption spectra of films is presented in [10].

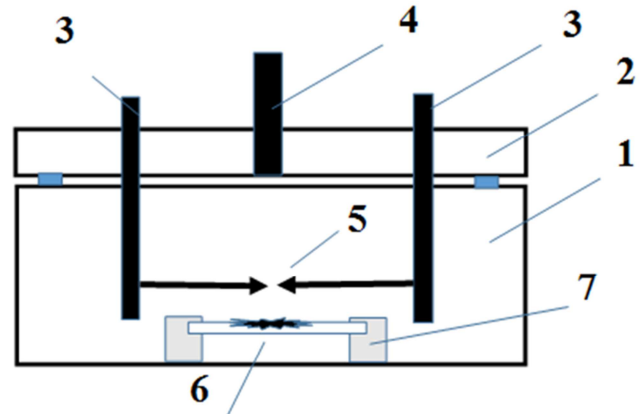
### 3. Characteristics of Discharge

In the system of chalcopyrite electrodes at the gas pressure  $p(\text{N}_2)$  and  $p(\text{Ar})=200$  kPa and at the distance between the electrodes  $d=1$  mm the spatially homogeneous discharge in the form of a sphere was ignited. This discharge was formed without an use of the separate system of pre-ionization of the interelectrode gap. The role of the pre-ionization system here can be played by an beam of "runaway" electrons or x-ray of electrons [8].

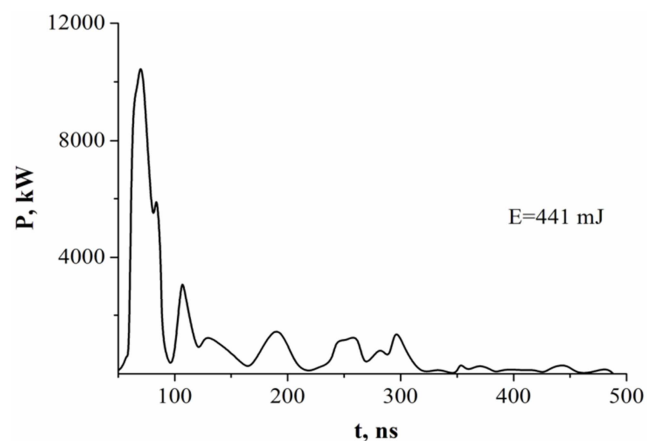
At the low gas pressure  $p=1-10$  kPa in the plasma a threshold of transfer of a large part of electrons to the continuous acceleration mode can be reached [9]. But at the atmospheric pressure of gases the efficiency of electron escape decreases sharply, so the main is the pre-ionization by X-ray radiation.

Typical dependences of the electric pulse power of the nanosecond discharge in argon are presented in Figure 2. The pulse power was obtained by graphically multiplying the oscillogram voltage across the gap and the discharge current. In the experiment, oscillations of the voltage at the discharge gap with a half-period close to 10 ns were

recorded. These oscillations are caused by a non-compliance of the output impedance of the high voltage pulse modulator with the load resistance. Current pulses of the over-voltage nanosecond discharge had the appearance of damping oscillations with amplitudes up to 150 A.



**Figure 1.** Scheme of the discharge device for the synthesis of thin chalcopyrite films on the glass surface: 1 - gas-discharge chamber of plexiglas, 2 - upper flange, 3 - sealed metal inputs, 4 - fitting for connection to the vacuum gas-mixing system, 5 - chalcopyrite electrodes, 6 - quartz film substrate based on scattered chalcopyrite electrodes, 7 - the plate mounting system.



**Figure 2.** Pulse power of over-voltage nanosecond discharge at  $p(\text{Ar})=202$  kPa.

The main part of the electrical pulse power was introduced into the plasma of the over-voltage nanosecond discharge in the first 100-150 ns. Maximal electric pulse discharge power in both vapor-gas mixtures was achieved at  $p(\text{Ar})=202$  kPa and was of 10.5 MW. When the pressure of gas environment was reduced to 1 kPa the pulse power was reduced to 7 MW.

The graphic integration of the pulse power over time allowed to calculate the energy of one discharge pulse introduced into the plasma. So, the energy contribution to the plasma for argon-based vapor mixtures at  $p(\text{Ar})=202$  kPa reached 440 mJ [10].

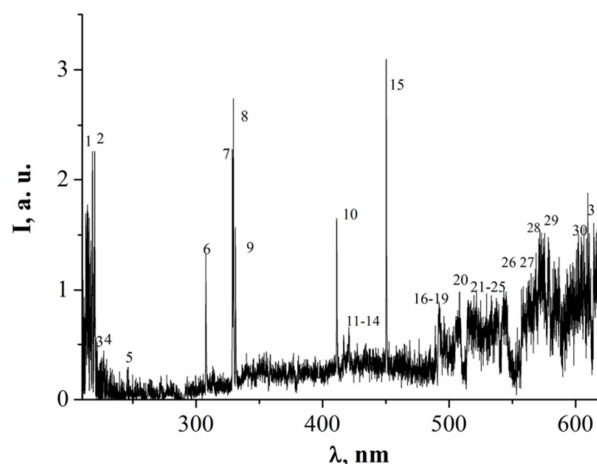
The linear part of the radiation spectrum was observed against the background of continuous radiation (continuum) of plasma. This may be due to the thermal radiation of the plasma or its recombination radiation. As it is shown in [11],

copper and indium atoms are the least bound in the chalcopyrite molecule, which is a constituent of massive electrodes. Therefore, the linear part of the plasma emission spectrum is predominantly due to separate spectral lines of atoms and singly charged copper and indium ions. This was observed both for the laser plasma formed on the surface of the compound target under vacuum conditions [12, 13] and for the gas-discharge plasma [14].

Figure 3 presents the spectrum of radiation of the over-voltage nanosecond discharge between chalcopyrite electrodes at the argon pressure of 202 kPa. Table 1 shows the results of decoding the most intense spectral lines and molecular bands and their relative radiation intensities, which correspond to Figure 3. The discharge radiation spectrum consisted of the group of intense spectral lines of the copper atom and the single charged indium ion in the spectral range of 200-230 nm. A similar phenomenon was observed in the plasma of the over-voltage nanosecond discharge at the atmospheric pressure and the distance between copper electrodes  $d=2$  mm [15, 16] (in the part of atoms and single charged copper ions). As the argon pressure increased from 101 to 202 kPa, the intensity of the spectral lines of 218.17 and 219.95 nm of the copper atom decreased. This is probably due to an increase of UV radiation absorption and an increase in the concentration of chalcopyrite vapor or its

decay products in the discharge plasma, since the pulse energy contribution to the plasma increases.

The intensities of the ion spectral lines of indium increased with increasing argon pressure from 101 to 202 kPa and, accordingly, with increasing energy contribution to the discharge. Also, intensities of copper ion lines for the over-voltage nanosecond discharge in air of the atmospheric pressure between copper electrodes were increased.



**Figure 3.** Radiation spectrum of over-voltage nanosecond discharge between chalcopyrite electrodes at argon pressure of 202 kPa.

**Table 1.** Results of identification of the most intensive spectral lines and bands of decay products of chalcopyrite molecule in over-voltage nanosecond discharge at  $p(\text{Ar})=202$  kPa.

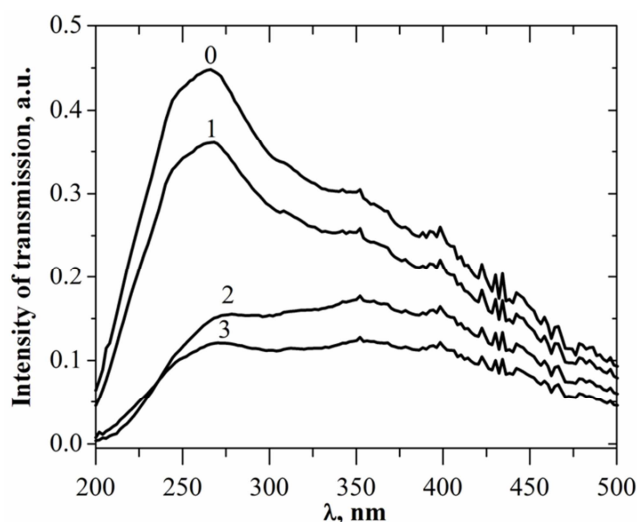
| №  | $\lambda$ , nm | I, a. u. (at $p(\text{Ar})=202$ kPa) | Object | $E_{\text{low}}$ , eV | $E_{\text{up}}$ , eV | Lower level   | Upper level       |
|----|----------------|--------------------------------------|--------|-----------------------|----------------------|---------------|-------------------|
| 1  | 218.17         | 0.33                                 | Cu I   | 0.00                  | 5.68                 | $4s^2S$       | $4p^1^2P^o$       |
| 2  | 219.95         | 0.37                                 | Cu I   | 1.39                  | 7.02                 | $4s^2^2D$     | $4p^1^2D^o$       |
| 3  | 225.57         | 1.66                                 | In II  | 12.68                 | 18.17                | $5s5d^3D_3$   | $5s4f^3F^o$       |
| 4  | 226.37         | 1.64                                 | Cu II  | 8.92                  | 14.39                | $4p^1^1F^o$   | $4d^3G$           |
| 5  | 246.02         | 0.41                                 | In II  | 12.68                 | 17.72                | $5s5d^3D$     | $5s7f^3F^o$       |
| 6  | 307.38         | 1.70                                 | Cu I   | 1.39                  | 5.42                 | $4s^2^2D$     | $4p^1^2F^o$       |
| 7  | 328.27         | 2.35                                 | Cu I   | 5.15                  | 8.93                 | $4p^1^4F^o$   | $4d^1^2G$         |
| 8  | 329.05         | 3.27                                 | Cu I   | 5.07                  | 8.84                 | $4p^1^4F^o$   | $4d^1^4F$         |
| 9  | 330.79         | 1.76                                 | Cu I   | 5.07                  | 8.82                 | $4p^1^4F^o$   | $4d^1^4G$         |
| 10 | 410.17         | 1.75                                 | In I   | -                     | 3.02                 | $5s^25p^2P^o$ | $5s^26s^2S_{1/2}$ |
| 11 | 417.83         | 0.73                                 | Ar II  | 16.64                 | 19.61                | $4s^4P$       | $4p^4D^o$         |
| 12 | 422.26         | 0.85                                 | Ar II  | 19.87                 | 22.80                | $4p^2P^o$     | $5s^2P$           |
| 13 | 427.75         | 0.7                                  | Ar II  | 18.45                 | 21.35                | $4s^1^2D$     | $4p^1^2P^o$       |
| 14 | 436.20         | 0.95                                 | Ar II  | 18.66                 | 21.50                | $3d^2D$       | $4p^1^2D^o$       |
| 15 | 451.13         | 3.27                                 | In I   | 0.27                  | 3.02                 | $5s^25p^2P^o$ | $5s^26s^2S_{1/2}$ |
| 16 | 487.98         | 1.12                                 | Ar II  | 17.14                 | 19.68                | $4s^2P$       | $4p^2D^o$         |
| 17 | 501.76         | 0.83                                 | Ar II  | 17.14                 | 19.64                | $4s^2P$       | $4p^4D^o$         |
| 18 | 502.82         | 0.75                                 | Cu II  | 14.43                 | 16.87                | $4d^3D$       | $4f^3F^o$         |
| 19 | 506.06         | 0.8                                  | Cu II  | 8.54                  | 10.99                | $4p^3P^o$     | $4s^2^3P$         |
| 20 | 507.22         | 0.63                                 | Cu II  | 14.42                 | 16.87                | $4d^3F$       | $4f^3F^o$         |
| 21 | 510.00         | 0.52                                 | Cu II  | 14.43                 | 16.86                | $4d^3D$       | $4f^3D^o$         |
| 22 | 515.32         | 0.7                                  | Cu I   | 3.79                  | 6.19                 | $4p^2P^o$     | $4d^2D$           |
| 23 | 520.09         | 0.76                                 | Cu I   | 5.42                  | 7.80                 | $4p^1^2F^o$   | $5s^4D$           |
| 24 | 521.82         | 0.87                                 | Cu I   | 3.82                  | 6.19                 | $4p^2P^o$     | $4d^2D$           |
| 25 | 522.00         | 0.85                                 | Cu I   | 3.82                  | 6.19                 | $4p^2P^o$     | $4d^2D$           |
| 26 | 556.69         | 1.21                                 | Se II  |                       |                      |               |                   |
| 27 | 557.69         | 0.90                                 | In II  | 15.81                 | 18.03                | $5s7p^1P^o$   | $5s10d^3D$        |
| 28 | 570.02         | 0.67                                 | Cu I   | 1.64                  | 3.82                 | $4s^2^3D$     | $4p^2P^o$         |
| 29 | 572.18         | 1.15                                 | In II  | 15.29                 | 17.46                | $5s7s^1S$     | $5s9p^1P^o$       |
| 30 | 594.92         | 1.10                                 | Ar I   | 13.28                 | 15.35                | $4p^1[1^1/2]$ | $6d[1^1/2]$       |
| 31 | 622.42         | 2.20                                 | In II  | 15.77                 | 17.76                | $5s7p^3P^o$   | $5s9d^3D$         |

Another group of intense spectral lines (lines 6-15, Table) was observed against the background of the continuous radiation intensity. The continuum intensity increased slightly with the wavelength increasing (Figure 3). The intensities of these spectral lines of copper and indium atoms as well as single-charged argon ions increased with increasing argon pressure and pulsed energy contribution to the plasma. The radiation in the spectral range of 460-630 nm was in the form of molecular bands, on the background of which some low-intensity spectral lines of atoms and ions were observed.

An accurate identification of these lines requires the use of a higher spectral resolution spectrophotometer. Most likely, the emission spectrum of the discharge plasma in this case is related to the emission of selenium molecules, as well as atoms and ions of argon. The following intense spectral lines of copper and indium atoms in the spectral range of 300-460 nm can be used to diagnose the process of depositing chalcopyrite thin films on solid glass or quartz substrates: 307.38 CuI, 329.05 Cu I, 410.17 In I and 451.13 nm I.

#### 4. Transmission Spectra of Films

Typical transmission spectra of the deuterium lamp radiation in the spectral region of 200-500 nm of chalcopyrite film samples, which were synthesized in our experiments at various argon pressures, are shown in Figure 4. The transmission of chalcopyrite films compared to the transmission of the substrate decreased by 2-3 times and was minimal for argon-based mixtures at  $p(\text{Ar})=101$  kPa. Transmission spectra shapes of chalcopyrite films at argon pressures of 13.3 and 101 kPa were the same.



**Figure 4.** Transmission spectra of samples of chalcopyrite films deposited on quartz substrates depending on the pressure and type of gas environment: 0 - without sample; 1 - pure quartz glass; 2 - CuInSe<sub>2</sub> electrodes at  $p(\text{Ar})=13.3$  kPa; 3 - CuInSe<sub>2</sub> at  $p(\text{Ar})=101$  kPa.

The strong absorption of deuterium lamp radiation by chalcopyrite films in the spectral region of 200-500 nm is due

to the fact that when the chalcopyrite films are deposited with gas-discharge method, they repeat the stoichiometry of the electrode material.

#### 5. Conclusions

Thus, it was found that at the pressure of argon equal to 202 kPa between electrodes based on the CuInSe<sub>2</sub> compound and at 1 mm interelectrode distance, the homogeneous nanosecond discharge with the pulsed electrical power of 7-10.5 MW and the energy contribution to the plasma of 0.35-0.44 J is ignited. The investigation of spectral characteristics of the plasma based on Ar-CuInSe<sub>2</sub> vapor-gas mixtures showed that the most intensive are the spectral lines of the copper atom in the range of 200-250 nm and the spectral lines of the indium atom and the copper and indium ions in the longer-wavelength region of the spectrum.

The features of the plasma emission spectra allows to suggest the presence of selective mechanisms for the formation of excited atoms and ions of copper and indium in the plasma, which are determined by the transfer of energy from metastable atoms and argon molecules to chalcopyrite molecules. Based on the measured relative intensities of the spectral lines of copper and indium atoms and ions, it is possible to estimate the temperature and electron density of the studied plasma. The following separately positioned and most intensive lines in the spectral range of 300-460 nm can be used to diagnose the chalcopyrite film sputtering: 307.38 CuI, 329.05 Cu I, 410.17 In I, 451.13 nm In I.

Investigation of the transmission spectra of probing radiation in the spectral range of 200-800 nm by chalcopyrite films deposited by the pulsed gas discharge method showed that the smallest transmittance is characteristic of films that were synthesized at argon atmospheric pressure.

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