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***Corresponding author**

Alexander Shuaibov, DVNZ, Uzhgorod National University, Narodna pl. 3, Uzhgorod, Ukraine

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Mini Review

Simulation of Parameters of Overstressed Pulsed Discharge Plasma in Mixtures of Aluminum and Chalcopyrite Vapors ($CuInSe_2$)

Alexander Shuaibov* and Antonina Malinina

DVNZ, Uzhgorod National University, Ukraine

Abstract

By the method of numerical simulation of plasma parameters of an overstressed nanosecond discharge based on aluminum and chalcopyrite vapors, by solving the Boltzmann kinetic equation for the electron energy distribution function, the temperature and density of electrons in the discharge, specific discharge power losses for the main electronic processes and rate constants of electronic processes are calculated as a function of the value of the parameter E/N.

Introduction

Overstressed nanosecond discharges in atmospheric pressure gases between electrodes made of transition metals (Cu, Zn, Fe ....) have found application in point UV lamps and the synthesis of nanostructured films based on transition metal oxides [1]. The results of studying the characteristics of an overstressed nanosecond discharge between two aluminum electrodes and two electrodes made of ternary chalcopyrite ($CuInSe_2$) in atmospheric pressure gases were taken from [2,3].When an overstressed nanosecond discharge is ignited between an aluminum electrode and a triple chalcopyrite electrode, due to microexplosions on the electrode surfaces, vapors of aluminum and triple chalcopyrite are introduced into the plasma. This creates the prerequisites for the synthesis in such a discharge of thin films of quaternary chalcopyrite - $CuIn_{1-x}Al_xSe_2$, which has a number of advantages over ternary chalcopyrite when used in solar cells. Thus, in [4], the results of a study of thin-film solar cells $CuIn_{1-x}Al_xSe_2$ (CIASe), where polycrystalline CIAS thin films with a chalcopyrite structure were synthesized, are presented. Solar cells based on them had an efficiency of 6.5%, with a relative content of aluminum Al/(In+Al) equal to 0.2. Comparison of these values with similar data for a device without aluminum showed a significant increase in their efficiency due to an increase in the energy gap of the absorber in quaternary compounds of the $CuIn_{1-x}Al_xSe_2$ type and better matching of the solar radiation spectrum in the infrared wavelength range with the absorption spectrum of the quaternary chalcopyrite.

Therefore, a gas-discharge technology for the synthesis of such coatings may be of considerable practical interest. The experimental characteristics of an overstressed nanosecond discharge between an aluminum electrode and a ternary chalcopyrite electrode in air, nitrogen, and argon at atmospheric pressure are given in [5].This article presents the results of modeling the plasma parameters of a gas-discharge plasma-chemical reactor designed for the synthesis of thin nanostructured films based on quaternary chalcopyrite ($CuIn_{1-x}Al_xSe_2$), which is promising for use in solar batteries and other photovoltaic devices. The calculations were performed by decoupling the Boltzmann kinetic equation for the electron energy distribution function for the case of a plasma in which both aluminum vapor and chalcopyrite vapor are simultaneously present for various buffer gases of atmospheric pressure.

Technique and Conditions for Numerical Simulation of Plasma Parameters

To numerically simulate the parameters of air and argon plasma for a pressure of 101 kPa and with admixtures of aluminum and copper vapors at pressures of 1000 Pa and 200 Pa, we chose a standard program for solving the stationary kinetic Boltzmann equation in a two-term approximation for the Electron Energy Distribution Function (EEDF). The parameters of the discharge plasma in mixtures of air, argon with aluminum and copper vapors were calculated numerically as total integrals of the EEDF. EEDF were found by solving the kinetic Boltzmann equation in a two-term approximation. The EEDF calculations were carried out using the program [6], where the effective cross section database also includes the effective cross sections for the interaction of electrons with argon and copper atoms. The effective cross sections for the interaction of electrons with aluminum atoms were used in the article [7]. For air, four components were selected: argon, nitrogen, carbon dioxide and oxygen; the effective cross sections of the processes for these components were taken from the program database [6]. Based on the calculated EEDF, the main parameters of the plasma were determined depending on the magnitude of the reduced electric field (that is, the ratio of the electric field strength (E) to the total air concentration of impurities of aluminum and copper vapors (N), as well as in the total concentration of argon i of impurities vapors of aluminum and copper (N). The range of variation of the parameter for a mixture of air with admixtures of aluminum and copper vapors was in the range E/N=1-300 Td ($1\ 10^{-17}$-$3{\cdot}10^{-15}$ Vcm^2) included and values of the parameter E/N, which were realized in the experiment. The range of variation of the parameter for a mixture of agon with admixtures of aluminum and copper was in the range E/N=1-1300 Td ($1{\cdot}10^{-17}$-$13{\cdot}10^{-15}$ Vcm^2) included and values of the parameter E/N, which were realized in the experiment. In the integral of collisions of electrons with molecules and atoms, the following processes were taken into account: elastic scattering of electrons by atoms of argon, nitrogen, carbon dioxide, oxygen, aluminum and copper, excitation of energy levels of argon atoms (threshold energy 11.50 eV), ionization of argon atoms (threshold energy, 15.80 eV) excitation of the rotational level of nitrogen molecules - threshold energy 0.020 eV, vibrational (threshold energies: 0.290 eV, 0.291 eV, 0.590 eV, 0.880 1.170, 1.470, 1.760, 2.060, 2.350; electronic: 6.170 eV, 7.000, 7.350, 7.360, 7.800, 8.160, 8.400, 8.550, 8.890, 11.03, 11.87, 12.25, 13.00, ionization (threshold energy - 15.60 eV) excitation of energy levels of oxygen molecules: vibrational (threshold energies: 0.190 eV, 0.380 eV, 0.570 eV, 0.750 eV), electronic (threshold energies: 0.977 eV, 1.627 eV, 4.500 eV, 6.000 eV, 8.400 eV, 9.970 eV, dissociative electron attachment (threshold energy - 4.40 eV), ionization (threshold energy - 12.06 eV) ,excitation of energy levels carbon dioxide molecules gas: vibrational (threshold energies: 0.083 eV, 0.167 eV, 0.252eV, 0.291eV, 0.339 eV, 0.422 eV, 0.505eV, 2.5eV), electronic (threshold energies 7.0 eV, 10.5eV), dissociative electron attachment (threshold energy 3.85eV), ionization (threshold energy 13.30 eV), excitation of energy levels of aluminum atoms (threshold energies: 3.1707 eV, 2.9032 eV, 4.1463 eV, 4.2339 eV, 4.1296 eV, 5.1220 eV), ionization of aluminum atoms (threshold energy 6.0000 eV), excitation of energy levels of copper atoms (threshold energies: 1.500 eV, 3.800 eV, 5.100 eV), ionization of copper atoms (threshold energy - 7.724 eV).

Results of Modeling

In (Figure 1) the dependences of the mean energy of electrons in the discharge plasma in mixtures of air and argon for a pressure of 101 kPa with admixtures of aluminum and copper vapors at pressures of 1000 Pa and 200 Pa on the reduced electric field strength are presented. The mean energy of discharge electrons for a mixture Air-Al- Cu= 101000: 1000: 200 Pa increases linearly from: 0.1350 eV to 6.717 eV with an increase in the reduced electric field strength from 1 Td to 300 Td (Figure 1, [1]), for a mixture Ar-Al-Cu=101000: 1000: 200 Pa increases linearly from: 1.020 eV to 17.99 eV with an increase in the reduced electric field strength from 1 Td to 1300 Td (Figure 1) [2]. In this case, the regularity of an increase in the rate of its change in the range of the reduced electric field strength of 1-100 Td for a mixture with air was observed, and for a mixture with argon, an increase in the rate was observed in the range of changes in the reduced electric field strength from 100 Td to 300 Td (Figure 1) [1,2]. [Table 1] shows the results of calculating the transport characteristics of electrons: mean energies (ε), temperature (T^0K), drift velocity (V_{dr}.) And electron concentration for two mixtures of air, argon and vapors of aluminum and copper mean energy of discharge electrons for a vapor-gas mixture air-aluminum-copper =1010000: 10000 200 Pa at the time moment 30 ns from the beginning of the pulse (E=6 10^6 V/m, E/N=243 Td) reached 5.811 eV, and at the time instant 220 ns from the beginning of the pulse (E=2 10^6 V/m, E/N=81 Td) the mean energy of the discharge electrons was 2.055 eV, and for the vapor-gas mixture Ar - Al - Cu=1010000: 10000 200 Pa at the time instant 30 ns from the beginning of the pulse (E=3 10^7 V/m, E/N=1215 Td) reached a value of 16.99 eV, and at the time instant 220 ns from the beginning of the pulse (E=1 10^7 V/m, E/N=405 Td) the mean energy of the discharge electrons was 9.137 eV. For a mixture of air-aluminum-copper, the mean electron energies, drift velocities, electron temperatures and electron concentrations decrease within: 5.811-2.055 eV, 67407.6-23838 K, $2.38\cdot10^5$ -$1.05\cdot10^5$ m/s and $1.87\cdot10^{20}$-$1.52\cdot10^{20}$ m^{-3} and for a mixture of argon - aluminum - copper, they decrease, and the concentration of electrons increases in the range: 16.99-9.137 eV, 197084-105989 0K, $6.9\cdot10^5$ m/s - $2.7\cdot10^5$, $4.6\cdot10^{19}$ -7, $0\cdot10^{19}$-$1.52\cdot10^{20}$ m^{-3}. (Figures 2 & 3) present the dependence of the specific power of discharge losses for elastic and inelastic processes of collisions of electrons with components of mixtures in a gas-discharge plasma on the reduced electric field strength. There is a regularity in the increase in the power of losses in the form of elastic and inelastic processes of collisions of electrons with the components of mixtures in a gas-discharge plasma with an increase in the reduced electric field strength for both mixtures and the loss of inelastic processes is higher than that of elastic ones. For a mixture of air with aluminum and copper impurities, a steep increase is observed first for elastic and inelastic processes of discharge losses in the range of 1-30 Td within one order of magnitude for elastic and several orders for inelastic (Figure 2), and in the range of 30-300 Td smooth growth within the same order. A similar pattern is observed for a mixture of argon with impurities of aluminum and copper in the ranges of 1-100 Td and 100-1300 Td. The power loss for inelastic and elastic processes of collisions of electrons with the components of the mixture for a vapor of a gas mixture of aluminum and copper with air is less than for a vapor of a gas mixture of aluminum and copper with argon [Table 2], which is explained by the lower values of the mean energy of electrons and the rate constants of excitation of spectral lines of atoms of aluminum and copper in several gas mixtures with air [Tables 1 & 3].

Table 1: Transport characteristics of electrons in the discharge in a mixture of air, argon with aluminum and copper vapors at a ratio of 101000: 1000: 200 Pa, for the time: 30 ns and 220 ns from the beginning of the discharge ignition.

		Mixture: Air - Al -Cu = 101000 : 1000 : 200 Pa			
τ, ns	**E/N, Td**	ε, eV	**T^0, K**	V_{dr}., m/s	N_e, m^{-3}
30	243	5.811	67407,6	$2,38\cdot10^5$	$1,87\cdot10^{20}$
220	81	2.055	23838	$1,05\cdot10^5$	$1,52\cdot10^{20}$
		Mixture: Ar - Al – Cu = 101000 : 1000 : 200 Pa			
τ, ns	**E/N, Td**	ε, eV	T^0, K	V_{dr}., m/s	N_e, m^{-3}
30	1215	16.99	197084	$6,9\cdot10^5$	$4,6\cdot10^{19}$
220	405	9.137	105989	$2.7\cdot10^5$	$7.0\cdot10^{19}$

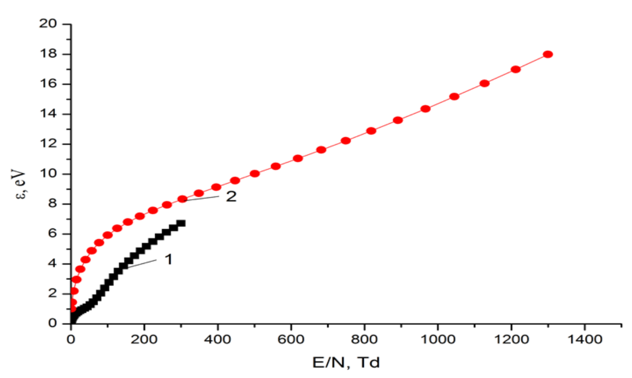

Figure 1: Dependence of the average energy of electrons in the plasma of vapor-gas mixtures on the reduced electric field strength: 1-Air-Al-Cu=101000: 1000: 200 at a total pressure of 102200 PA, 2-Ar-Al-Cu=101000: 1000: 200 at a total pressure of 102200 Pas.

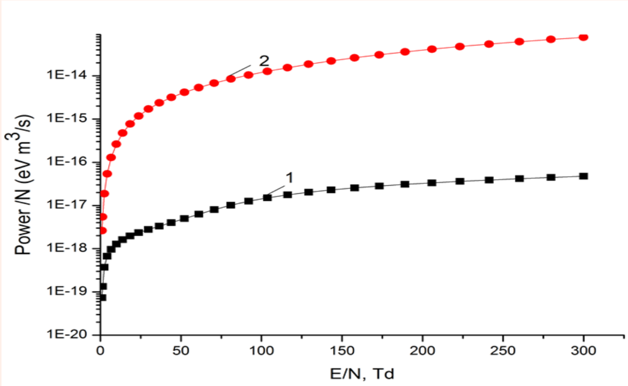

Figure 2: Dependence of specific power of discharge losses on elastic (1) and non-elastic (2) processes of collisions of electrons with air, aluminum and copper atoms on the reduced electric field strength in plasma of steam-gas mixtures Air-Al-Cu=101000: 1000: 200 Pa at total pressure 102200 Pa.

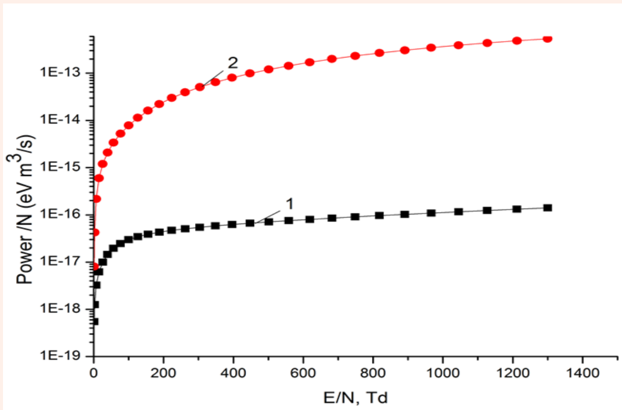

Figure 3: Dependence of the specific power of discharge losses on elastic (1) and non-elastic (2) processes of electron collisions with argon, aluminum and copper atoms on the reduced electric field strength in the plasma of gas-gas mixtures Ar-Al-Cu=101000: 1000: 200 Pa at total pressure 102200 Pa.

Table 2: Specific power of discharge losses for elastic and non-elastic processes for mixtures: Air-Al- Cu=101000: 1000: 200 PA and Ar-Al-Cu=101000: 1000: 200 PA.

Mixture: Air-Al-Cu = 1010000 : 1000 :200 Pa		
E/N,Td	Elastic, power/N (eV m^3/s)	Inelastic, power/N (eV m^3/s)
243	0.3882E-16	0.5432E-13
81	0.1017E-16	0.8436E-14
Mixture: Ar-Al-Cu = 101000 : 1000 :200 Pa		
E/N,Td	Elastic, power/N (eV m^3/s)	Inelastic, power/N (eV m^3/s)
1215	0.1323E-15	0.4854E-1**2**
405	0.6254E-16	0.8020E-13

Table 3: Constants of the excitation rate of the spectral lines of aluminum and copper atoms for the values of the reduced electric field strength in the plasma on a pair of gas mixtures of argon with aluminum at a time of 30 ns and 220 ns from the start of the ignition discharge. E_{thr}. - energy of the excitation threshold of the spectral lines of aluminum and copper atoms.

E/N, Td	Mixture: Ar-Al-Cu = 101000 : 1000 : 200 Pa					
1215	Al	E_{thr}., eV	4.13	4.23	2.90	3.17
		k, m^3/s	0.1616E-14	0.1958E-14	0.2337E-14	0.4216E-14
	Cu	E_{thr}., eV	1.5	1.5	3.8	5.1
		k, m^3/s	0.2860E-13	0.2265E-13	0.8774E-12	0.2336E-15
405	Al	E_{thr}., eV	4.13	4.23	2.90	3.17
		k, m^3/s	0.1456E-14	0.1928E-14	0.1901E-14	0.3607E-14
	Cu	E_{thr}., eV	1.5 eB	1.5 eB	3.8eB	5.1 eB
		k, m^3/s	0.2900E-13	0.2235E-13	0.5937E-12	0.1554E-15

E/N, Td	Mixture: Air-Al-Cu = 101000 : 1000 : 200 Pa					
243	Al	E_{thr}., eV	4.13	4.23	2.90	3.17
		k, m^3/s	0.9425E-15	0.1372E-14	0.1363E-14	0.2707E-14
	Cu	E_{thr}., eV	1.5	1.5	3.8	5.1
		k, m^3/s	0.1914E-13	0.1442E-13	0.3127E-12	0.8365E-16
81	Al	E_{thr}., eV	4.13	4.23	2.90	3.17
		k, m^3/s	0.1424E-15	0.2446E-15	0.3191E-15	0.6704E-15
	Cu	E_{thr}., eV	1.5	1.5	3.8	5.1
		k, m^3/s	0.3260E-14	0.2354E-14	0.3593E-12	0.9981E-17

[Table 3] shows the values of the rate constants for the excitation of individual spectral lines of aluminum and copper atoms by the discharge electrons in the investigated vapor-gas mixtures for the values of the reduced electric field strength, which were at the time of 30 ns and 220 ns from the beginning of the discharge ignition for both mixtures and having the excitation threshold energies (E_{thr}.) 4.13, 4.23, 2.90, 3.17 eV for aluminum atoms and 1.5, 1.5, 3.8, 5.1 eV for copper atoms. They vary in the range $0.9981 \cdot 10^{-17}$-$0.3127 \cdot 10^{-12}$ m^3/s for the characteristic values of the reduced electric field strength. Moreover, their value for copper atoms is higher than the values for aluminum atoms in all the mixtures under study. Increased values of the rate constants of excitation of the spectral lines of both aluminum and copper atoms at the time instant from the onset of discharge ignition (30 ns) are also characteristic, as compared to the time instant 220 ns. This pattern is explained by different values of the reduced electric field strength for the time instant of 30 ns and 220 ns and, accordingly, different values of the mean electron energy (Table 1 & Figure 1), which leads to different values of the absolute value of the effective cross sections inelastic collisions of electrons with atoms of aluminum and copper. The effective cross sections of inelastic collisions of electrons for copper atoms are larger than for atoms of aluminum [6] and therefore the rate constants of excitation of spectral lines for copper atoms are also higher in value.

Conclusion

Thus, the simulation of the parameters of the overstressed nanosecond discharge showed that between the aluminum and chalcopyrite electrodes in vapor-gas mixtures based on buffer gases of atmospheric pressure Ar, N_2, or air showed the following. The study of the transport characteristics of electrons, the power of the discharge loss for elastic and inelastic processes of collisions of electrons with the vapor components of gas mixtures of air, argon with atoms of aluminum and copper and an increase in the mean energy and temperature of electrons in a mixture with argon, electric field strengths, which were at the moment of time 30 ns from the beginning of the ignition of the discharge in comparison with the moment of time 220 ns have been established. The maximum values of the mean energy and temperature of electrons were 16.99 eV and 197084 °K, respectively, for the vapor of the gas mixture Ar-Al-Cu=10100: 1000: 200 Pa. The power loss of the discharge for elastic and inelastic processes of collisions of electrons with the components of the vapor of gas mixtures have a similar pattern. They are larger in values for the reduced electric field strength, which were at the beginning of the ignition of the discharge and have large values for non-elastic processes of collisions of electrons with the components of the vapor of the gas mixture with argon. The maximum value (0.4854E-12 eV m^3/s) is also observed for the Ar-Al-Cu mixture=10100: 1000: 200 Pa. Also characteristic are the increased values of the excitation rate constants of the spectral lines of both aluminum and copper atoms at the time instant from the onset of discharge ignition (30 ns) as compared to the time instant 220 ns for both vapors of gas mixtures. Their value is in the range of $0.9981 \cdot 10^{-17}$- $0.3127 \cdot 10^{-12}$ m^3/s. Due to the fact that in the Ar-Al-Cu=101000: 1000: 200 Pa mixture, large values of the rate constants of excitation of spectral lines of both aluminum atoms and copper atoms are observed, provides their high intensity in the discharge, it is mainly used for diagnostics and deposition of corresponding films.

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