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The Formation of Excited Molecules Chloride Argon, Chlorine and Hydroxyl Radicals in the Nanosecond Barrier Discharge

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Abstract: The results of an experimental study of radiation characteristics of a barrier discharge in a mixture $ArCCl_4$ were presented in this paper. Formation of molecules ArCl(B) and Cl_2(D') in the barrier discharge plasma depends strongly on the partial pressure of freon vapor is shown. The intensity of the radiation band Cl_2(D'-A') on the value of the pulse repetition rate current at a charging voltage U_d = 13 kV were close to the line that indicates the possibility of increasing the average power of the VUV-UV discharge at frequencies f > 1 kHz.

Key words: Nanosecond barrier discharge, argon chloride, carbon tetrachloride, emission.

1. Introduction

Excited argon chloride molecule—ArCl(B), chlorine—Cl_2(D') and hydroxyl radicals, OH are approved from environmentally friendly sources of mercury-free high-power UV-VUV radiation pumped by different forms of electric discharge [1-3]. Such lamps, in most cases, operate in the wavelength range of 200-350 nm. The conditions for the intense VUV radiation at the band 175 nm ArCl(B→X) received much less attention. This is due to the known difficulties of working in the vacuum ultraviolet. Studies of molecular formation ArCl(B) in the emitter pumped by a transverse volume discharge in our laboratory conducted. The optimization of the output intensity of the VUV radiation is made of argon chloride [4, 5]. The absolute intensity investigation of such lamps based on the band 175 nm ArCl(B→X) has shown that it is possible to obtain energy in a pulse of ~ 0.6 mJ and the peak power density of ~ 0.4 kW/cm^2 [6]. A common drawback of these studies is the use of exposed metal electrodes, which react chemically with chlorine carriers—HCl, Cl_2, CF_2Cl_2. This leads to a significant reduction in service life of the gas-static excilamps rare gas chlorides.

Development ArCl-lamp-based on barrier discharge with short pulse duration, where the electrodes are placed outside the plasma environment is important. But these developments are hampered by the absence of data on the conditions and the mechanism of ArCl(B) molecules formation in the nanosecond barrier discharge.

ArCl(B) molecules formation in a pulsed electrical discharge plasma is accompanied by the formation of excited molecules chlorine-Cl_2(D'), which decay with the emission band 258 nm. This band is close to the wavelength of the spectral lines of the mercury atom (253 nm HgI), which is widely used today in many optical technologies. Therefore band 258 nm Cl_2(D'-A') may be one of the candidates that can replace the working environment of low pressure mercury lamps. Furthermore, the band is closest to the

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absorption maximum of DNA ($\lambda \approx 260$ nm) [1] that may lead to increased efficiency in the corresponding bactericidal lamp.

Since it is known that metastable argon atoms efficiently transfer their energy to the molecules of water, which leads to the formation of OH radicals (A), which decompose to form a band $\lambda \approx 309$ nm [7, 8], this opens the possibility of developing universal broadband UV-VUV emitter on the basis of the bands 175 nm, 258 nm and 309 nm pumped working mixture by nanosecond barrier discharge.

Results of the study of excited molecules of argon chloride, chlorine and hydroxyl radicals in the repetitively pulsed nanosecond barrier discharge, which is held on the intensity of bands 175 nm ArCl(B→X), 258 nm Cl_2(D'-A') and 308 nm OH(A→X) depending on the pressure of working mixture and the conditions of discharge ignition in this article are presented.

2. Experimental Setup

Nanosecond discharge with a total duration of current pulses 50-100 ns and two dielectric barriers ignited in a cylindrical quartz bulb KU-1. Working length of the emitter bulb was 20 cm and the diameter of the inner quartz tube—14 mm. The distance between electrodes in the discharge was approximately 4.5 mm. Inner electrode was prepared as a solid aluminum cylinder and installed in the inner quartz tube. External electrode was a nickel wire coil, transparency of 80%.

The barrier discharge ignited with a source of high voltage pulses with a resonant charge storage capacitor of 1.54 nF and the switch—hydrogen thyratron TGI-I-1000/25. The amplitude of the voltage pulses at the output of the modulator increased using the pulse transformer cable is approximately three times and reached 40-55 kV with single ejection duration of 20 ns. The amplitude of the main peak of the current pulse reaches 50 A for the pulse duration 20-30 ns.

Radiation from the plasma was analyzed in the spectral range 140-310 nm using vacuum monochromator and a photomultiplier FEU-142 with a window of lithium fluoride. The registration system was calibrated radiation on the relative spectral sensitivity.

The barrier discharge ignited in a diffuse mode, and its filaments stage was not shown.

3. Results and Discussion

Emission bands with a maximum at λ = 175 nm ArCl(B→X), 258 nm Cl_2(D'-A') and the band at λ = 309 nm OH(A→X) in emission spectra of the plasma barrier discharge in argon with vapor "liquid" freon (CCl_4) and a small admixture of water vapor ($p \sim$ 10-20 Pa) argon contained in a "technical" purity in the spectral range $\Delta\lambda$ = 150-312 nm were more intense. A weak emission band 169 nm ArCl(D→X) registered in the vacuum ultraviolet region, and in the longer wavelength spectral range, a weak band with a maximum at λ = 199 nm ArCl(C→A).

The emission bands of the hydroxyl radical OH(A→X) and exciplex molecules ArC(B→X) prevailed in the emission spectrum of the discharge at a partial pressure of argon in a mixture of Ar-CCl_4 equal to 24 kPa and low partial pressure of the vapor Freon (Fig. 1a). Main in the emission spectrum are $ArCl^*$(B→X) and Cl^*_2(D'-A') bands increased when the partial vapor pressure of CCl_4 to 160 Pa (Fig. 1b). The increase the partial pressure of the vapor freon to 200 Pa (Fig. 1c) lead to a strong suppression of the intensity of the emission band of 175 nm $ArCl^*$(B→X) and an increase intensity of the band with a maximum at λ = 258 nm Cl^*_2(D'-A') four times. The intensity of the emission bands $ArCl^*$(B→X) and OH(A→X) in a mixture with a further increase of the partial vapor pressure of CCl_4($p(CCl_4) > 200$ Pa) was reduced to near background levels.

Weak emission band, which can be identified with radiation dissociation products in a discharge freon, and 283 nm band OH(A→X, (1, 0)) were observed in

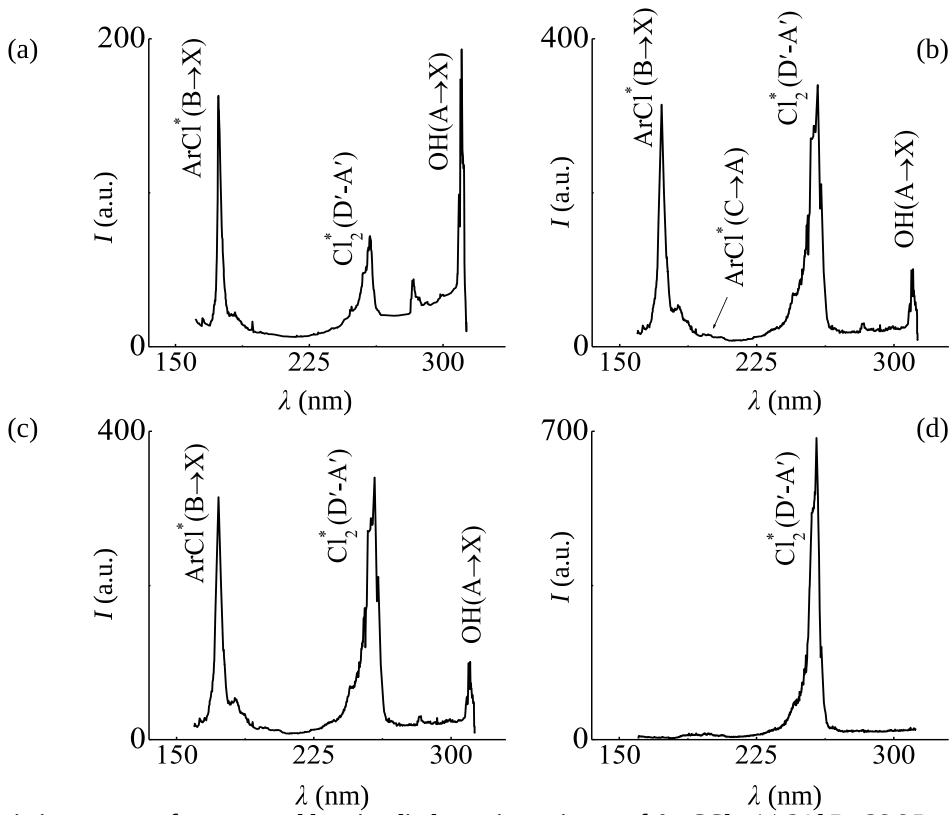

Fig. 1 The emission spectra of nanosecond barrier discharge in a mixture of Ar-CCl_4: (a) 24 kPa-26.6 Pa, (b) 24 kPa-160 Pa, (c) 24 kPa-266.6 Pa, (d) 24 kPa-293.3 Pa.

the spectral range $\Delta\lambda$ = 280-285 nm. The intensity of emission bands argon chloride, chlorine and the radical of the molecule of the hydroxyl value of CCl_4 vapor partial pressure at a constant pressure of argon shown in Fig. 2. They characterize the efficiency of the simultaneous formation of molecules ArCl(B), Cl_2(D') and OH(A) depending on the composition of the working fluid.

The increase in the partial pressure of the vapor refrigerant led to an almost linear increase in the efficiency of formation of excited molecules of chlorine. The optimum partial pressure of freon for the formation of molecules ArCl(B) was 200-220 Pa, and for molecules Cl_2(D')—(140-160) Pa.

The optimum argon pressure to forming the excited molecules studied was 10-15 kPa. Increasing the partial pressure of argon in the discharge of 10-50 kPa, resulted in a decrease in the intensity of radiation at 175 nm band is three orders, and at 258 nm band only three times. The optimal value of the argon pressure for the formation of OH radicals was 5-10 kPa.

The results that characterize the efficiency of formation of molecules ArCl(B) and Cl_2(D') as a function of the pulse repetition frequency of the generator voltage pump are shown in Fig. 3.

In the frequency range 40-400 Hz depending nonlinear with increasing frequency up to 1,000 Hz they are scheduled without signs of saturation intensity.

Such a dependence possibly due to the contribution of the products of the dissociation of the molecules in the formation of molecules CCl_4 ArCl(B) and Cl_2(D').

Dependence of the efficiency of formation of molecules ArCl(B) and Cl_2(D') based on the number of discharge pulses in a mixture of $p(Ar)$-$p(CCl_4)$ = 13.33-0.1333 kPa is shown in Fig. 4. The efficiency of formation of molecules $ArCl^*$(B) (Fig. 4a) is increased with an increase in the number of discharge pulses with 2×10^5-2.5×10^5. The $ArCl^*$(B) molecules density after 2.5×10^5 pulses reach a steady level. For

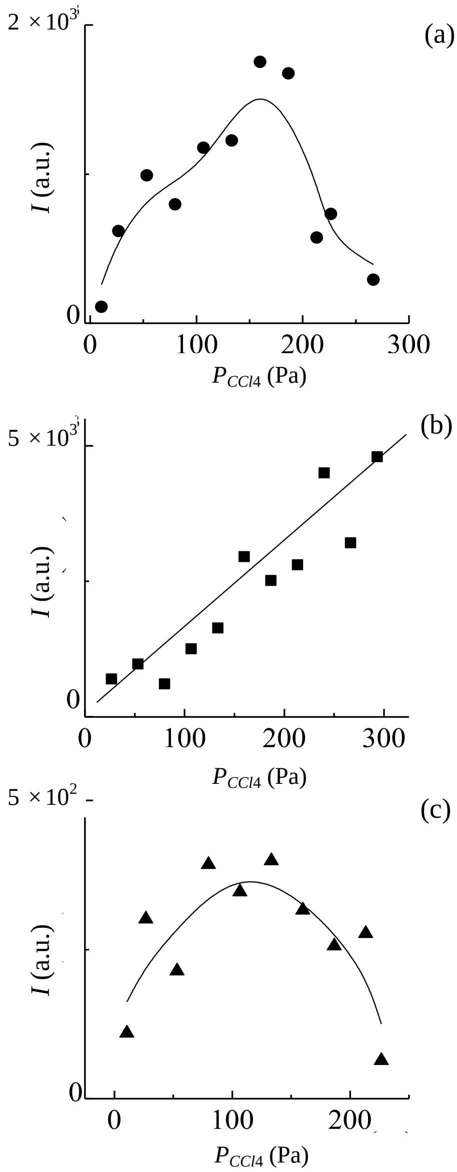

Fig. 2 The intensity of emission bands with maxima at (a) λ = 175 nm ArCl*(B→X), (b) λ = 258 nm Cl$^*_2$(D'-A'), (c) λ = 309 nm OH*(A→X) for $p(Ar)$ = 24 kPa.

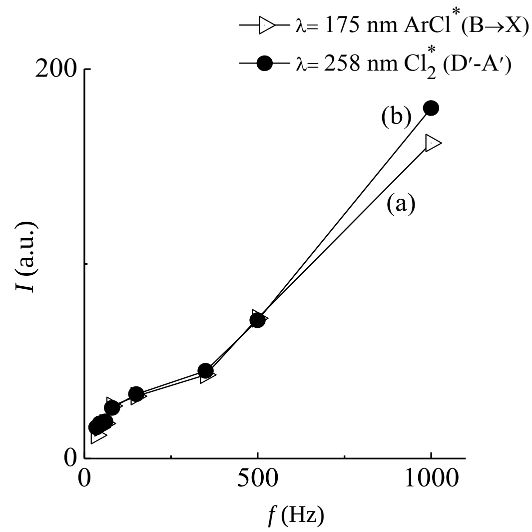

Fig. 3 The intensity of the bands ArCl*(B→X) and Cl$^*_2$(D'→A') of the pulse repetition rate current at a charging voltage U = 13 kV for a mixture of $p(Ar)$-$p(CCl_4)$ = 13.33-0.1333 kPa.

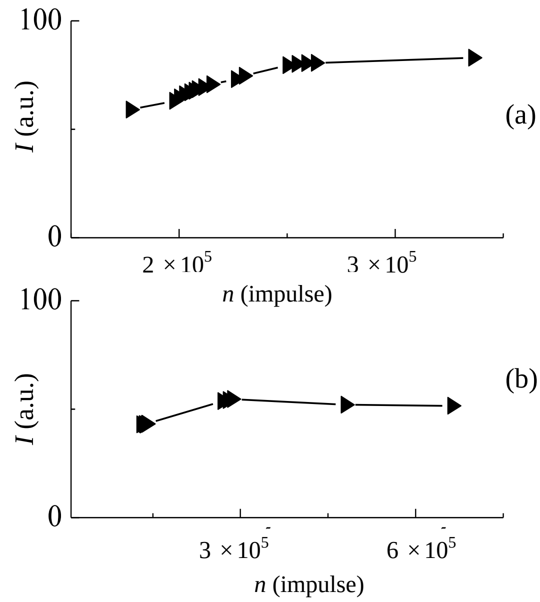

Fig. 4 The intensity of the radiation band (a)—ArCl*(B→X) and band (b)—Cl$^*_2$(D'-A') the number of discharge pulses barrier discharge for a mixture of $p(Ar)$-$p(CCl_4)$ = 13.33-0.1333 kPa and U = 13 kV.

molecules of chlorine produced approximately the same results, indicating that the operating time with the time of the chlorine atoms or radicals, which are involved in the formation of molecules ArCl(B) and Cl_2(D'). More pronounced these effects were in the exciplex lasers and lamps pumped by transverse discharge lamps or appropriate. The rate constant for the forward reaction formation ArCl(B→X; C→A) during the collision of atoms Ar ($3p^2$) c molecule CCl_4—1.6×10^{-11} cm^3 s^{-1} is shown in Ref. [9]. This is a rather small value, so the more efficiently the molecules ArCl (B; C) of the secondary reactions of "harpoon" reaction atoms Ar($3p^2$) with chlorine molecules and ion-ion recombination of Ar^+ ions with ions of Cl^-.

The mechanism of formation of excited molecules in such a complex environment as a barrier discharge in a mixture of argon, freon and water vapor will require a complex kinetic model of physical-chemical processes and numerical simulation of the plasma parameters. This will establish specific mechanisms for the formation of the most important components including taking into account the dissociation processes of freon.

4. Conclusions

Thus for the first time establishes the conditions for common formation of excited molecules of argon chloride, chlorine and hydroxyl radicals, which can be used as working for a lamp with an inexpensive and non-toxic work environment Ar-CCl_4-H_2O and the operating wavelength λ = 175 nm $ArCl^*$(B→X); 258 nm Cl^*_2(D'-A'); 309 nm OH(A→X), the optimal partial vapor pressure of CCl_4, in which the maximal intensity of the radiation plane $ArCl^*$(B→X), is in the range of 100-200 Pa, a band for OH(A→X)-p(CCl_4) = 75-100 Pa; optimum argon pressure did not exceed 10 kPa.

Formation exciplex molecules ArCl(B) and exciplex similar chlorine molecules—Cl_2(D') in the plasma of a barrier discharge is most strongly dependent on the partial pressure of the freon vapor, which allows to control the emission spectrum of UV-VUV light by varying the vapor content of CCl_4 in the working mixture.

The optimal conditions for the emission band 258 nm Cl_2(D'-A'), which can be considered as one of the possible candidates to replace environmentally harmful mercury low pressure lamps, realized at $p(CCl_4) > 200$ Pa.

Nature of the dependence of the radiation intensity of the excited chlorine molecules from the pump pulse repetition indicates their participation in the formation of products of dissociation of CCl_4.

High resource characteristics: $n > (2.5\text{-}5) \times 10^5$ pulses can hope for a UV-VUV lamp with long lifetime of work in the gas-static operation at frequencies $f > 1$ kHz.

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