

# Lifetime of working mixtures of XeCl and KrCl excilamps

M.V. Erofeev, V.S. Skakun, E.A. Sosnin, V.F. Tarasenko, and E.B. Chernov

*Institute of High-Current Electronics,  
Siberian Branch of the Russian Academy of Sciences, Tomsk*

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XeCl ( $\lambda \sim 308$  nm) and KrCl ( $\lambda \sim 222$  nm) excilamps excited by the capacitive and a high-frequency glow discharge were studied in order to increase their service life. The reliability of the capacitive discharge excilamps is determined by the mechanism of the heterophase chemical reaction between atomic chlorine and a quartz wall with the formation of polymer chlorinesiloxane products. Sealed-off excilamps with the service life more than 1000 h were created.

## Introduction

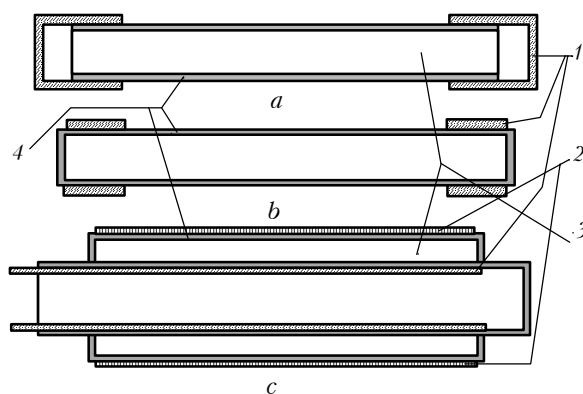
In recent years a significant progress has been achieved in creation of UV and VUV radiation sources<sup>1,3,4,6,7</sup> operating at electron transitions in an excimer and exciplex molecules (excilamps). However, practical use of such sources is limited by their short service life. In this paper we present the results of experimental studies of the stability of excilamps excited by glow, barrier, and capacitive discharges. The mechanisms of chlorine loss from the working volume of an electrodeless low-pressure quartz halogen-containing excilamps are discussed.

## 1. Experiment

In our experiments we used discharge tubes with the length of up to 55 cm and the inner diameter from 1.5 to 6 cm. The tubes were made from high-quality quartz with the transmittance better than 80% in the wavelength region from 200 to 300 nm.

In studying the characteristics of the glow discharge (Fig. 1a), electrodes and flanges for gas bleeding-in and evacuating were set at the tube ends. The electrodes in this case had a cylindrical shape, were 40 mm in diameter, and were made from a stainless steel or nickel. A positive potential from a dc voltage source was applied to the anode, while a zero potential to the cathode.

Excilamps of two different designs were used in the studies of the capacitive discharge characteristics. The classical capacitive discharge was obtained by using cylindrical tubes with ring electrodes on their walls. The electrode width can be varied from 0.5 to 10 cm (Fig. 1b). Another kind of the capacitive discharge, which is now widely used in excilamps,<sup>7</sup> – the so-called barrier discharge – was obtained with the use of a coaxial design (Fig. 1c). With the inner tube of 4 cm in diameter, the inner gap between the tubes was 7–8 mm, and the length of the working region enclosed by the solid (1) and perforated (2) electrodes did not exceed 15 cm. The electrode 2 had the transmittance of 82%.



**Fig. 1.** Design of excilamps of glow (a) and capacitive (b, c) discharges: solid electrode 1, perforated electrode 2, working volume 3, and shell 4.

It should be noted that the operating conditions of the barrier discharge and capacitive discharge excilamps differ significantly. A relatively high pressure of a working mixture characterizes the barrier discharge excilamps, and the discharge itself consists of a number of separate fragments. The discharge in a cylindrical capacitive discharge excilamps looks like a glow discharge and is characterized by a low working pressure. Let us also note that we are likely the first to use the cylindrical capacitive discharge excilamps.

The capacitive discharge excilamps were excited by a generator of sine-shaped voltage pulses. The generator was made as a push-pull circuit. It provided current pulses with the duration of  $\sim 1.2 \cdot 10^{-5}$  s at half maximum and the pulse repetition frequency of 22 kHz. The amplitude of voltage pulses did not exceed 6 kV.

Current and voltage were measured with an ohmic shunt and voltage divider, whose signals came to an S8-17 dual channel oscilloscope. The mean output power in a given wavelength range was determined with a FEK-22 SPU vacuum photodiode with the known spectral sensitivity in the visible and UV spectral regions. The signal from the photodiode came to a pulsed voltmeter or an S8-17 oscilloscope.

Emission spectra were recorded with a MUM monochromator with the inverse linear dispersion of 3.2 nm/mm.

Working mixtures were prepared directly in the lamp, which was filled in turn with a halogen ( $\text{Cl}_2$ ,  $\text{HCl}$ ), rare gas ( $\text{Xe}$ ,  $\text{Kr}$ ), and a buffer gas ( $\text{Ne}$ ,  $\text{He}$ ).

## 2. Results and discussion

To obtain stable power parameters of excilamps, one should minimize the rate with which the working gas leaves the volume. This rate depends on the temperature of the working medium and of the device walls, on the material the bulb and electrodes are made from, possible contamination, and the lamp design.

The main mechanism that shortens the service life of the halogen-containing glow discharge excilamps is halogen interaction with the electrodes. The decrease of the  $[\text{Cl}_2]$  concentration in the mixtures with the total pressure optimal from the viewpoint of the efficiency leads to a significant decrease in both the efficiency and output power of the UV radiation of an excilamp.<sup>10</sup> Pure chlorine (and hydrogen in reaction with  $\text{HCl}$ ) possessing the highest reactivity under conditions of low pressure is accumulated via the harpoon reaction



It is well known that the rate of  $\text{HCl}$  reconstruction in the reaction  $\text{H} + \text{Cl} \rightarrow \text{HCl}$  far exceeds the rate of reaction of atomic chlorine with metal electrodes. Therefore, the excilamp service life could be increased, as in Ref. 2, by adding small amounts of hydrogen to the working volume during the lamp operation. Unfortunately, as was shown in Refs. 3 and 4, the use of  $\text{HCl}$  instead of  $\text{Cl}_2$  markedly decreases the mean output power.

The chlorine loss can be decreased in a different way by using chemically resistant electrodes, for example, nickel ones. Thus, in a  $\text{XeCl}^*$  excilamp with the binary mixture  $\text{Xe}/\text{Cl}_2 = 5/1$  at the total pressure of 4.5 mm Hg and energy deposition from 0.29 to 1.1  $\text{W}/\text{cm}^3$  the working mixture lifetime  $t_w$  did not exceed 1 h when using stainless steel electrodes. The replacement of these electrodes by nickel ones increased  $t_w$  by an order of magnitude. For example,  $t_w$  was 15 h with the specific energy deposition  $\sim 0.15 \text{ W}/\text{cm}^3$ . A seventy-hour pause in operation of this lamp did not lead to a decrease in the output, what indirectly indicates that the operation stability of a glow discharge excilamp is determined by the percentage of atomic chlorine produced in the reactions (1).

The capacitive and barrier discharge excilamps allow the problem of working medium contact with the electrode material to be resolved. However, this not always automatically provides for a significant increase in the working mixture lifetime as compared with the glow discharge excilamps.

Adsorption of working mixture atoms and molecules by the device walls can be one of the factors decreasing the output power of the capacitive discharge excilamps. In the case that the shell of the gas

discharge device is filled with a mixture of rare gases and the total pressure exceeds several tens mm Hg, adsorption of gases for a long time does not lead to a marked changes in the device operation. However, in low-pressure mercury lamps or hydrogen lamps the adsorption processes can significantly shorten the service life of a device, and the gas loss should be compensated for in this case.<sup>5</sup> This problem is also urgent in chlorine-containing electrodeless excilamps.

The service life of the cylindrical capacitive discharge excilamps (see Fig. 1b) directly depends on the technology of lamp preparation for operation. Let us consider, as an example, a  $\text{KrCl}$  excilamp (mixture  $\text{Kr}/\text{Cl}_2 = 6/1$ , pump power density  $P_d$  about 0.2  $\text{W}/\text{cm}^3$ ) with the inner diameter of 3.8 cm and the gap between the ring electrodes of 10 cm.

Before testing this lamp, we restricted ourselves to several cycles of bulb filling with  $\text{Kr}$  and evacuating. The level of the mean output power of the lamp after this dropped down to 10% of the initial level in 1 h (Fig. 2). If the filling/evacuating cycles were followed by bulb filling with 15 mm Hg  $\text{Cl}_2$  and then the system was passivated for two days, then its service life grew by an order of magnitude. Even higher growth of  $t_w$  can be obtained if active passivation by the discharge is used. The gases with which the lamp will then be filled should be used for its passivation. This method was used, for example, in creation of a small-size sealed-off  $\text{XeCl}^*$  excilamp with the inner diameter of 1.8 cm and a 1-cm gap between the ring electrodes. The specific pump power in this lamp achieved 0.35  $\text{W}/\text{cm}^3$  (that is, it was higher than that in the above examples). At the same time, the service life of the excilamp after the active passivation was increased by more than two orders of magnitude (Fig. 3).

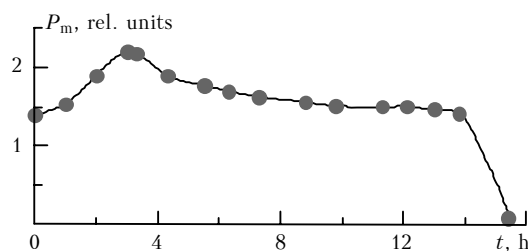


Fig. 2. Mean output power of glow discharge  $\text{XeCl}^*$  excilamp vs. operation time. Mixture  $\text{Xe}/\text{Cl}_2 = 5/1$ . Total pressure of 4.5 mm Hg, specific pump power  $\sim 0.15 \text{ W}/\text{cm}^3$ .

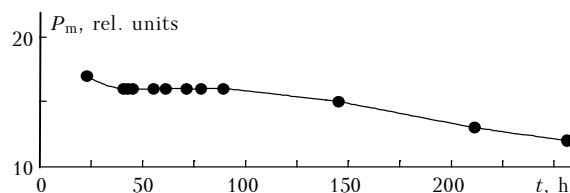


Fig. 3. Mean output power of capacitive discharge  $\text{XeCl}^*$  excilamp vs. operation time. Mixture  $\text{Xe}/\text{Cl}_2 = 8/1$ . Total pressure of 3.3 mm Hg, specific pump power  $\sim 0.35 \text{ W}/\text{cm}^3$ .

In Ref. 6 we optimized the pump conditions and working mixtures for the barrier discharge excilamps. This optimization allowed the efficiency of the XeCl and KrCl excilamps up to 10% to be obtained.<sup>6</sup> However, the service life of excilamps in our experiments usually did not exceed 100 h.

As in the case of the glow discharge, the output power of UV radiation in the barrier discharge depends on the concentration of Cl<sub>2</sub> in the mixture.<sup>7</sup> The natural loss of chlorine on the walls decreases its content in the discharge zone and causes a decrease in the output power.

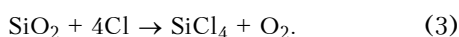
Let us consider the mechanisms of chlorine losses in the barrier discharge excilamps.

(1) Adsorption and absorption of Cl<sub>2</sub> molecules in the period when quartz micropores do not yet contain significant amounts of the gas.

(2) Adsorption, absorption, and chemical interaction of atomic chlorine produced at discharge initiation in the process of dissociative adhesion of electrons:

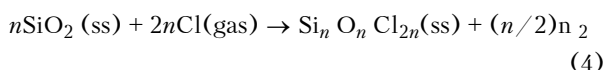


(3) Mechanism associated with the oxygen separation from the quartz walls of the lamp:



The reaction (3) is energy-profitable, but the probability of simultaneous local action of four chlorine atoms on the quartz lattice is very low because of the low Cl concentration in the volume.

(4) Heterophase chemical reaction of atomic chlorine with the quartz wall.<sup>9</sup> The reaction proceeds with formation of polymer chlorinesiloxane products (Si<sub>n</sub>O<sub>n</sub>Cl<sub>2n</sub>)<sub>x</sub>, (n = 3–5), for example,



(ss means solid state).

Thermodynamic calculations show that this reaction is more energy-profitable than the reaction (3). The standard enthalpy of formation of SiO<sub>2</sub> (quartz) and SiO<sub>4</sub> (liquid phase) is, respectively, 910.7 and 662.2 kJ/mol (Ref. 10). The standard enthalpy of formation of Si<sub>n</sub>O<sub>n</sub>Cl<sub>2n</sub>(ss) ranges between the above values, since this product is intermediate between SiO<sub>2</sub> (quartz) and SiO<sub>4</sub> (liquid phase). In Ref. 9 it was shown that most probable mechanism of this reaction is the anti-Yander mechanism.

We can assume that the role of the fourth mechanism in the barrier discharge is higher than in the classical glow and capacitive discharges initiated in cylindrical tubes. This is connected with the radiator design (see Fig. 1c), in which the gap between the walls of the inner and outer quartz tubes usually does not exceed 1 cm. Under these conditions such characteristics as the mean free path of chlorine ions and the high strength of the field across the discharge gap favor formation of a chlorinesiloxane film. From

this it follows that to increase the service life of the barrier discharge excilamps with chlorides, the active passivation of the working medium should take longer time than in the case of the classical capacitive discharge. We checked this point using a coaxial lamp identical to that described above and containing Xe and Cl<sub>2</sub> in the ratio 8/1 at the total pressure of about 2 mm Hg. In this case the total service life of the excilamp exceeded 1000 h (Fig. 4).

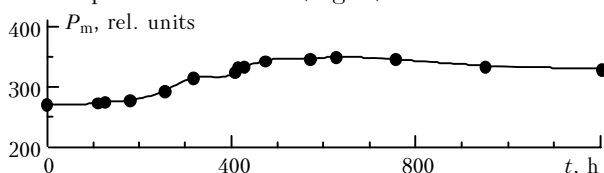


Fig. 4. Mean output power of a barrier discharge XeCl\* excilamp vs. operation time. Mixture Xe/Cl<sub>2</sub> = 8/1; total pressure of 2 mm Hg.

## Conclusion

Thus, our studies have shown that along with the high output power and efficiency, the XeCl and KrCl sealed-off excilamps can possess the service life longer than 1000 h. The long service life can be most readily achieved in electrodeless excilamps excited by the capacitive discharge of different types (barrier and classical capacitive discharge). The reliability of the capacitive discharge excilamps is determined by the mechanism of the heterophase chemical reaction of interaction between atomic chlorine and the quartz walls with formation of polymer chlorinesiloxane products.

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