

XeCl excilamps with reduced ozonization level

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

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

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It is shown, for the first time, that modification of the quartz surface of UV-radiation source of an arbitrary geometry by hafnium dioxide HfO_2 reduces the generation of ozone at the quartz–wall boundary. A six-fold decrease in ozone concentration has been demonstrated by an example of the XeCl excilamp of a barrier discharge type with a modified bulb wall.

Introduction

At present, various sources of spontaneous UV radiation^{1,2} are widely used in photochemistry and photomedicine. All of these sources differ structurally, but their operation yields, due to UV radiation effect, generation of ozone exerting a harmful effect on human beings.

Known measures to reduce the ozonization consist in that the envelope of the lamp electrode system is placed inside a quartz flask of larger diameter and the space between the two is filled either with sulfur vapor³ or with a mixture of nitrogen and oxygen.⁴ The spacing between two vessels affects the extinction of the UV radiation. A disadvantage of the solution from Ref. 3 is that sulfur vapor filter out the radiation with wavelengths below 400 nm that makes the gas discharge device unfit for producing UV radiation. A common disadvantage of both solutions^{3,4} is that manufacturing of radiation sources becomes too complicated that increases its costs. Besides, it should be noted that modern UV-radiation sources,^{2,5} for example, excilamps of a barrier discharge have a high flexibility in choosing the envelope geometry (coaxial, planar, etc.). Engineering solutions proposed in Refs. 3 and 4 for cylindrical construction are inapplicable in above cases.

Another way to reduce ozonization by UV lamps is in using fused silica doped with Titanium ions, for example, that of the types M-235, M-235 plus, HQL-235, and HQL-250 from the Heraeus company.⁶ Such quartz becomes opaque for radiation at the wavelengths causing ozone formation in the air. However, doping the quartz with Titanium ions is complicated that is a disadvantage of this technology. Besides, there are certain restrictions on using such quartz, since its spectral transmission boundaries for radiation are steep, but the assortment of the so-called ozoneless types produced is quite limited. For example, M-235 plus quartz is used only for production of medium-pressure mercury lamps. However, the problem of ozone formation on the surface of quartz envelopes remains unsolved in all cases. In this paper we present a new method for

reducing ozonization produced by UV-radiation sources by an example of the barrier XeCl excilamp. This method is based on the quartz surface modification that conserves the radiation spectral characteristics.

1. Ozone generation at the quartz–air boundary

It is known that ozone is generated under certain natural conditions, during thunderstorms, at atmospheric electric discharges, in the upper layers of the atmosphere under the action of solar UV radiation (earth's ozonosphere). Modern theory of ozonizers describes the ozone generation mechanism in a barrier discharge^{7,8} in detail. Here we shall present only key features giving an idea of the ozone generation in air. The main requirement to ozone molecule formation is the atomic oxygen:



if the reaction proceeds in the open air, nitrogen plays the role of an intermediate M.

The electron impact in the electric discharge in the air (for example, in an ozonizer) can yield dissociation of O_2 molecule in two possible ways, i.e., through the excitation of the $A^3\Sigma_u^+$ state with the energy threshold about 6 eV and through excitation of the $B^3\Sigma_u^-$ state by electrons with the energy starting from 8.4 eV.⁷

At UV irradiation, the photons with $\lambda < 200$ nm have enough energy⁹ (6 eV and more) for the O_2 photodissociation. However, even if quartz opaque for $\lambda < 200$ nm is used, the UVC (200–280 nm)- and UVB (280–320 nm)-radiation sources produce ozone, which, in our opinion is generated at the quartz–wall–air boundary. We assume that formation of O_3 molecules at the radiator surface, under the action of ultraviolet radiation, is caused by the ability of quartz to adsorb molecular oxygen. Here two mechanisms can work simultaneously.

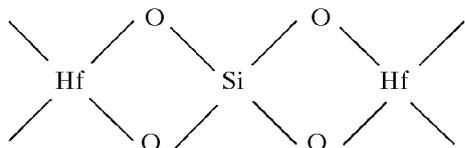
1. The first can be the interaction between oxygen molecule and the surface Si atoms, capable of deforming the orbitals of the O_2 molecule due to

formation of a bond following the donor–acceptor mechanism. This mechanism is realizable through the vacancy in the *d*-sublevel (orbital) of Si in the quartz structure. This weakens the atomic bond in O₂ molecule that can be broken under the action of UV radiation, then ozone is produced following the reaction (1).

2. Since quartz surface is microscopically inhomogeneous and porous, it is possible that O₂ molecule penetrate into the quartz structure. There the O₂ molecule undergoes the action of electrostatic fields, which may appear due to localized clustering of the electric charges at microinhomogeneities. The action of electrostatic forces deforms the bond between the atoms of the O₂ molecule making it weak enough to cause the O₂ photodissociation thus yielding atomic oxygen.

It should be noted here that interaction between the oxygen molecule and quartz surface makes the probability of the deformed atomic bonding to break higher the shorter the radiation wavelength is.

In order to reduce or completely exclude initiation of the O₃ formation by the quartz surface, its modifying has been proposed. To achieve this, the external radiator surface was coated in a special way¹⁰ with a film from hafnium dioxide (HfO₂). Thus formed compound of HfO₂ with quartz surface is known as the hafnon, HfSiO₄:



The film disables both of the above-mentioned adsorption mechanisms. On the one hand, HfSiO₄ is a chemically inert material and, consequently, it does not interact with O₂, on the other hand, the film from HfO₂ is the coating that smoothens the microscopic inhomogeneities of the quartz surface. Besides, HfO₂ provides a sufficiently good optical transmission in the UV region¹¹ (starting from $\lambda > 213$ nm).

2. Experimental setup and results

In our experiments, we have made two XeCl excilamps of a barrier discharge, the surface of excilamp 2 was coated with HfO₂ film, and another lamp (excilamp 1) was left uncoated. The excilamps had identical sizes; diameters of the external and internal tubes were 43 and 20 mm, respectively, the length was 15 cm. The vessels were filled with gas mixture of Xe and Cl₂ of 200/1 ratio at the total pressure of 120 Torr. The external electrode in the form of a metal mesh was placed on the surface of the external tube, and the solid one, made from foil, was placed on the inner surface of the internal tube. Pulse unipolar voltage was applied to the electrodes from the power source, and the barrier discharge was initiated in the gap (Fig. 1).

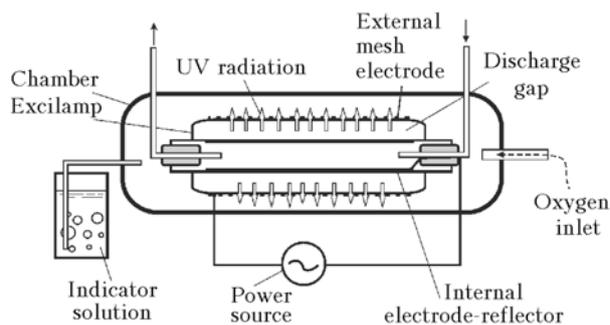


Fig. 1. Experimental setup for ozone indication.

The specific density of radiation power for both excilamps was measured by means of a HAMAMATSU H8025-222 photodetector on the radiator surface and was about 8 mW/cm² in all experiments. Radiation spectrum was recorded with a StellarNet EPP2000-C25 spectrometer. Radiation spectrum of the excilamps (Fig. 2) has not changed after coating the surface of a lamp with HfO₂ film.

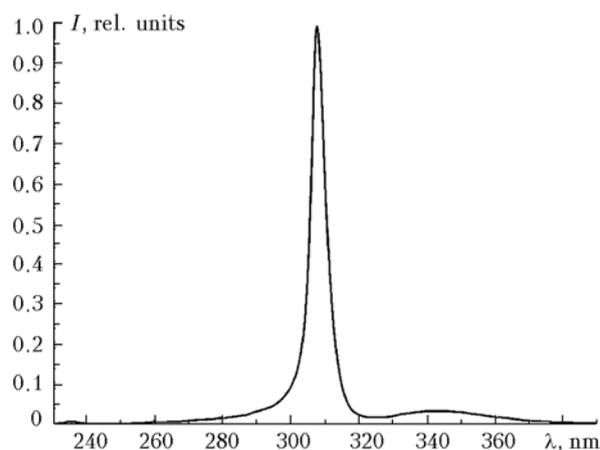
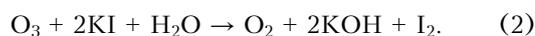


Fig. 2. Spectrum of the XeCl excilamps of a barrier discharge.

During the operation, the excilamp was placed into a sealed chamber (see Fig. 1). After the discharge was initiated in the excilamp, the air was slowly pumped through the chamber. In order to cool the lamp the internal cavity containing a solid electrode, was purged with air. Then, the air from the chamber was blown through a standard solution of starch and KI in the distilled water (bubbling solution), used for indication of strong oxidants.¹²

One can judge on the ozone concentration by the fractional conversion of KI. The coloring of solution and its intensity variation depend on the amount of dissolved ozone:



As follows from the equation, one O₃ molecule produces one molecule of I₂. Then, the deposited iodine reacts with starch that causes solution coloring:

$I_2 + \text{starch} \rightarrow \text{blue coloring.}$ (3)

The coloring intensity depends on the amount of I_2 released in the solution as well as, respectively, on the amount of the dissolved ozone. The degree of solution coloring was controlled by recording, with a spectrometer, the transmission spectra $T(\lambda)$ of solutions (Fig. 3) at bubbling with air ozonized by the excilamps 1 and 2, respectively.

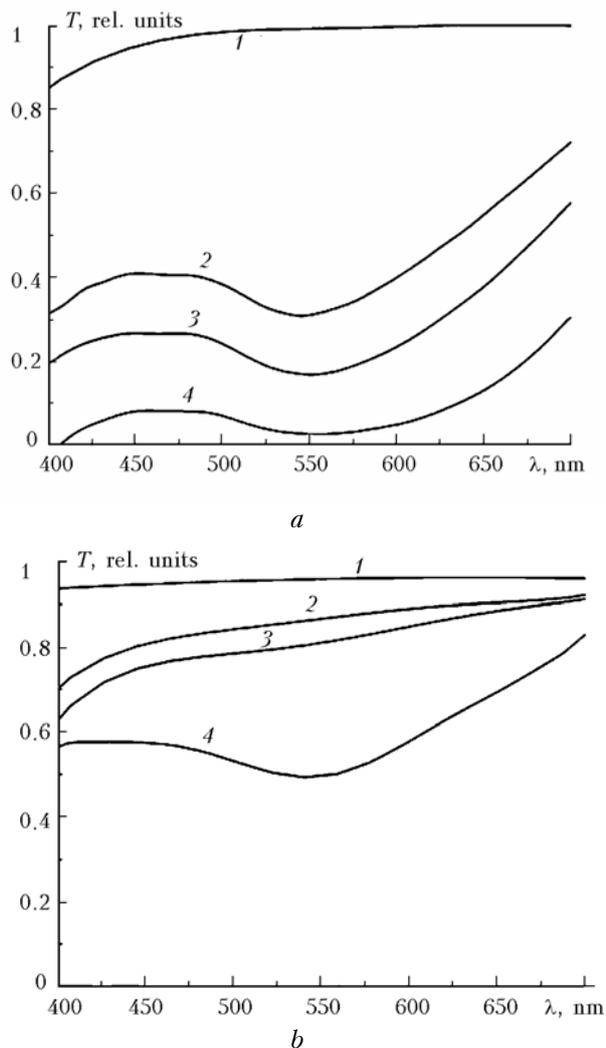


Fig. 3. Transmission spectra of solutions ozonized by the excilamp 1 (a) and 2 (b) for 6 min (1); 36 min (2); 48 min (3), and for 78 min (4).

As follows from Fig. 3, (for the same irradiation time) the transmission T reduces much faster at irradiation by the excilamp 1, rather than by excilamp 2. This evidences of more intense production of O_3 molecules and higher release of I_2 in solution at operation of the excilamp 1 and under other conditions being the same (radiation spectrum, specific and average radiation power) the lamp with modified surface has really reduced ozonization level. The solution coloring varied from the matt-white (not bubbled solution) to the bluish-violet (solution bubbling during 90 and 174 min for the excilamps 1

and 2, respectively). For a control test, the solution barbotage has been carried out with clean air (lamp switched off). In this case, the solution coloring has not change.

There are representative minima in the spectra near 550 nm (Fig. 3a, curves 2–4 and Fig. 3b curve 4). These transmission minima are characterized by their shift to longer wavelength at increase in I_2 amount that has been released and reacted with starch. Therefore, for the excilamp 2 at solution bubbling for 78 min, the transmission minimum is at $\lambda = 541$ nm (see Fig. 3b, curve 4). In the case with the excilamp 1 after the bubbling for 36 and 78 min, the transmission minimum in spectra falls at $\lambda = 544$ and 550 nm, respectively.

Another feature confirming the efficiency of surface coating with HfO_2 is the change of the integrated transmission spectrum S of the bubbled solution in time, recorded in using excilamps 1 and 2 (Fig. 4).

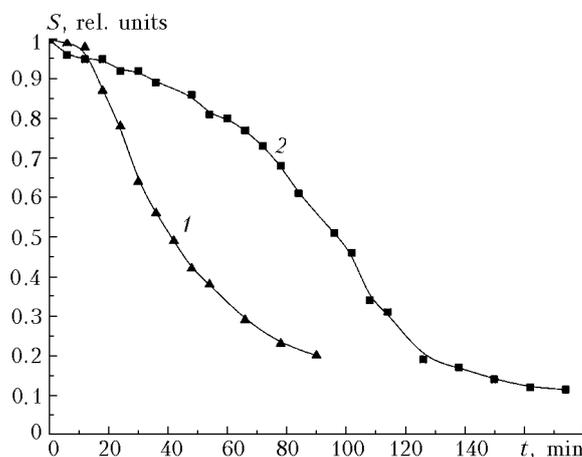


Fig. 4. Change of the integrated solution transmission spectrum at ozonization by the excilamps 1 (curve 1) and 2 (2), respectively.

It is seen that, on the whole, the reaction of I_2 substitution with the O_3 molecule in the starch solution with KI proceeds nonlinearly. However, one can isolate time intervals within which, according to the reaction (2), variation of the coloring intensity of the bubbled solution is proportional to the amount of dissolved ozone and released I_2 . At this stage, these reactions can be modeled by the linear dependence. For this, the linear regression equation is written using experimental points

$$d = kt + c. \quad (4)$$

Here d is the optical density, k is the reaction rate; t is the reaction time; c is the initial condition constant. In our case, k is the qualitative quantity characterizing the rate of I_2 release in the solution (dimensionality of a quantity $\times \text{min}^{-1}$) that, in turn, is the indicator of the amount of ozone generated. Therefore, comparison of k_1 (excilamp 1) and k_2 (excilamp 2) will allow estimating how much the air

ozonization by the excilamp 1 is stronger than that by the excilamp 2 (Fig. 5).

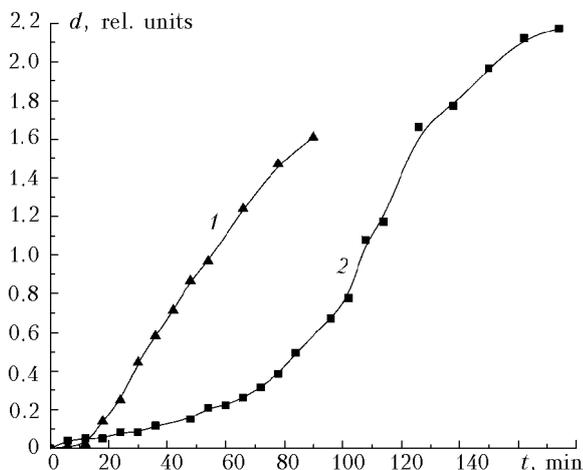


Fig. 5. Change in optical density for solutions ozonized by the excilamps 1 (curve 1) and 2 (curve 2), respectively.

Let us isolate in the d dependences obtained the portions where d changes linearly with time. For both excilamps, t varies from 18 up to 48 min. For the selected points of d dependence, the linear regression is formed and k_1 and k_2 are calculated by Eq. (4). In our case, $k_1 = 1.92 \cdot 10^{-2} \text{ min}^{-1}$ and $k_2 = 3.2 \cdot 10^{-3} \text{ min}^{-1}$, $R_1 = 0.99$ and $R_2 = 0.98$ (correlation coefficients of linear regression), $k_1/k_2 = 6$.

The ratio k_1/k_2 obtained shows that the ozone production rate is 6 times higher for the excilamp 1, as compared with the excilamp that was modified with HfO_2 film.

Conclusion

It has been shown experimentally that quartz surface modification with hafnium dioxide, HfO_2 , for the XeCl excilamp of a barrier discharge, enables one to reduce the ozonization level compared with the same excilamp that was not subjected to the surface treatment, power and spectral characteristics of both excilamps being identical. The qualitative estimation for ozone generation rate has shown that ozone

concentration produced by the excilamp 2 is 6 times lower than in the case of excilamp 1.

Let us note that the advantages of the approach proposed are the simplicity of engineering implementation and possibility of its application to the UV-source bulbs of any geometry. Probably, our quartz surface modification method with HfO_2 can completely exclude ozone generation at the quartz–air boundary. This might be dependent on the quality of the radiator surface coating with HfO_2 film that requires additional research. We assume that in addition to HfO_2 the nonozone coating for UV sources could be made from zirconium dioxide, ZrO_2 . Zirconium, being the metal of d -subgroup, is very close to the hafnium by its chemical properties and has a relatively broad transmission spectrum (starting from $\lambda > 229 \text{ nm}$)¹¹ in the UV region.

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