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Analysis and characterization of Kr/Cl_2 based 222 nm far UV-C excimer source

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Dedicated to Prof B N Basu

A direct approach to limit airborne pathogens is to inactivate them within a short period of their production. Far-UV-C light (222 nm) through mercury free Krypton/Chlorine (Kr/Cl_2) excimer source has been found to efficiently kill the pathogens without causing any harm to human skin. In the present work, experimental and computational analysis of dielectric barrier discharge (DBD) in Kr/Cl_2 mixture excited by unipolar pulse of negative polarity has been carried out. The aim of the study is to identify the dominant charged species and various other operational parameters leading to the production of higher $KrCl^*$(B state) in Kr/Cl_2 excilamp. The creation and destruction mechanisms of various charged species in the gas-gap and the effect of chlorine percentage on the excimer density on the 222 nm radiation intensity have been analyzed. The characteristic emission spectra of the Kr/Cl_2 based excimer source is mainly centered on 222 nm and a weak band obtained at 258 nm of Cl_2 molecule. The 222 nm peak wavelength is the strongest line observed in the emission spectra that confirms the efficient generation of $KrCl^*$ excimer at this operating condition.

Keywords: Dielectric barrier discharge, Excilamp, Fluid equation, Excimer.

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1 Introduction

Excilamps are the efficient sources for the production of mercury-free vacuum ultraviolet (VUV)/ ultraviolet (UV) radiation, which are based on non-equilibrium emission of excimer and exciplex molecules [1]. The excimer or exciplex of different gases/ gaseous mixtures are generally used for the emission of radiations of their characteristic wavelengths [2-5]. They are based on the gas discharge mechanism in which the high pressure working medium is excited by radio frequency, sinusoidal (~10's of kHz), sub-microsecond and nanosecond high voltage pulses which produce the excimer of working gases such as Argon excimer (Ar_2^*(126 nm)), Krypton excimer (Kr_2^*(142 nm)), Xenon excimer (Xe_2^*(172 nm)), Chlorine excimer (Cl_2^*(259 nm)), and Bromine excimer (Br_2^*(289 nm)). The rare gas halogen exciplex such as Krypton Chloride ($KrCl^*$(222 nm)), Xenon Chloride ($XeCl^*$(308 nm)), Krypton Bromide ($KrBr^*$(207 nm)), Xenon Bromide ($XeBr^*$(282 nm)) and Xenon Iodide (XeI^*(253 nm)) are also found to be useful (here superscript * represents excited atom/ molecule or compound formed, when the rare gas is mixed with the halogen in some fixed definite proportion) [6-10]. The rare gas halogen exciplex (RgH) can be formed by the ionic recombination of positive rare gas ion and negative halogen ion by the interaction of excited rare gas atom with an electronegative molecule during the discharge. Mainly, the transition through B to X is the dominant transition of these exciplexes [7]. To generate the excimer radiations of higher power, different discharge

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mechanisms have been employed. The dielectric barrier discharge (DBD) based excimer lamps have been developed for the variety of applications such as in semiconductors, modification of material properties, medical area and water sterilization, and other various purposes [1].

In this paper, investigation has been carried out on the discharge dynamics of the co-axial DBD based Kr/Cl_2 excimer lamp excited by unipolar pulse of negative polarity for the generation of $KrCl^*$ excimer. The discharge dynamics has been analyzed by performing the experiment based on the computational investigation, which is carried out by using the 1-dimensional model developed in the COMSOL Multiphysics Software [11]. In addition, the effect of Cl_2 concentration on the 222 nm radiation intensity has also been analyzed. The model describes the temporal evolution of the density of $KrCl^*$ on the application of high voltage unipolar pulse at total pressure of 100 mbar at different Cl_2 concentrations. This study is useful in understanding the basic kinetic process occurring in an excilamp during the discharge and the factors responsible for the efficient generation of 222 nm radiation. The experimental characterization includes the diagnosis of the voltage-current waveform and the emission spectra to determine the different spectral lines of the excited Kr/Cl_2 excilamp.

2 Experimental Setup

The excimer lamp has a co-axial structure in which two quartz tubes placed co-axially making the gap of 5 mm. In the gap, Kr and Cl_2 mixture is filled at different proportions and at some fixed total pressure. Thin metallic Al foil is used as inner electrode which is covered by the inner dielectric tube. A 1.5 mm wide metallic tape wrapped over the outer tube acts as the ground electrode and is placed in such a way that sufficient gap exists between the consecutive circular rounds of the tape for radiation transmission. The excilamp was driven by a pulse voltage of amplitude 4 kV and pulse repetition rate of 50 kHz. A Tektronix voltage probe and a Pearson current transformer were used for measuring the voltage and current signals, respectively, which were further recorded in a Tektronix Oscilloscope. The generated emission spectra were recorded by the Ocean optics HR4000 Spectrometer having measuring range of 200-1000 nm.

3 Simulation Model

In the present work, plasma simulation has been carried out in the COMSOL Multiphysics Software [11]. The simulation model comprises of fluid equations that describe the spatial and temporal behavior of the electrons, ions, and other neutral species. The evolution of the electron density n_e and energy density n_ε during the discharge dynamics have been estimated by Eqs (1) and (2), respectively in which $\boldsymbol{\Gamma_e}$ and $\boldsymbol{\Gamma}_\varepsilon$ are the electron flux and electron energy flux.

$$\frac{\partial n_e}{\partial t} + \nabla.\boldsymbol{\Gamma_e} = R_e \tag{1}$$

$$\frac{\partial n_e}{\partial t} + \nabla.\boldsymbol{\Gamma}_\varepsilon + \mathbf{E}.\boldsymbol{\Gamma}_e = \mathrm{S}_{en} - (\mathbf{u}.\nabla)\, n_\varepsilon \tag{2}$$

$$\boldsymbol{\Gamma_i} = -(\boldsymbol{\mu_i}.\mathbf{E})\boldsymbol{i} - \mathbf{D_i}.\nabla)\, n_i \tag{3}$$

Here, R_e is the rate of gain and loss of electrons, S_{en} is the rate of gain or loss of energy in inelastic collision of electrons with the heavy species such as neutral, excited and ionic species, $\mathbf{u}$ is the velocity of gaseous atoms/ molecules and $\mathbf{E}$ is the electric field. Other parameters: $\boldsymbol{\mu}_i$ represents the mobility and $\mathbf{D_i}$ represents the diffusivity of electron e and electron energy ε (with i in the subscript assumes e or, ε, respectively).

The electric field is calculated using Poisson's equation (4) and (5) as given below in which ε_0 is the permittivity of air, ε_r is the permittivity of dielectric material, n_p is positive ion density and V is the scalar potential, corresponding to the ambipolar plasma electric field coupling together with the transport of electrons and ions.

$$\nabla.(\varepsilon_0\, \varepsilon_r\, \mathbf{E}) = -\, e\, (n_e - n_p) \tag{4}$$

$$\mathbf{E} = -\nabla\, V \tag{5}$$

The density of heavy species which is the mixture of neutral atoms/molecules, excited atoms/molecules and ions is obtained by solving the diffusion equation (6) . In which, w_k is the mass fraction of species k, $\mathbf{J_k}$ is the diffusive flux vector, R_k is the rate of production-destruction of species k, ρ is the density of the mixture and q is the number of heavy species in the mixture.

$$\frac{\partial w_k}{\partial t} + \rho\, (\mathbf{u}.\nabla) w_k = (\nabla.\, \mathbf{J_k}) + R_k\, ;\, k = 1, 2, ...(q-1) \tag{6}$$

The source term of the equation depends on the plasma chemistry which are shown in Table 1. The rate coefficient and the transport properties as a function of mean electron energy are obtained by considering the Maxwellian electron energy distribution function computed using the Boltzmann Two Term Approximation Interface in COMSOL [11]. The reaction included in the model to define the plasma chemistry is shown below:

Table 1. Plasma Chemistry Reactions

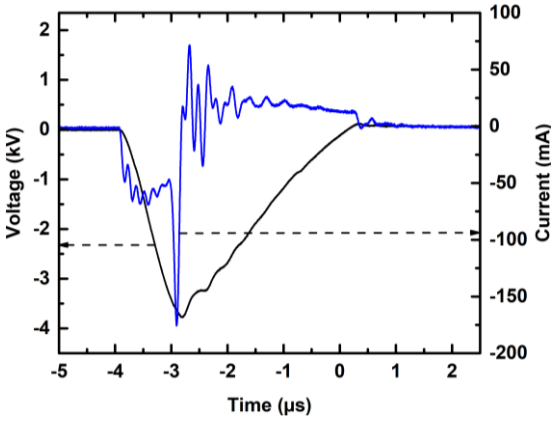
Elastic Collision	$e + Kr \rightarrow e + Kr$
	$e + Cl_2 \rightarrow e + Cl_2$
Electron Impact Excitation	$e + Kr \rightarrow e + Kr^*$
	$e + Kr \rightarrow e + Kr^{***}$
Electron Impact Ionization	$e + Kr \rightarrow 2e + Kr^+$
	$e + Cl_2 \rightarrow e + e + Cl_2^+$
	$e + Cl_2 \rightarrow e + Cl^- + Cl^+$
	$e + Cl_2 \rightarrow 2e + Cl + Cl^+$
Electron Attachment	$e + Cl_2 \rightarrow Cl^- + Cl$
Ion Conversion	$2Kr + Kr^+ \rightarrow Kr + Kr_2^+$
	$Cl^+ + Cl_2 \rightarrow Cl + Cl_2^+$
Recombination	$e + Cl_2^+ \rightarrow Cl + Cl$
	$Cl^+ + Cl^- \rightarrow Cl_2$
Penning Ionization	$Kr^* + Kr^* \rightarrow Kr + e + Kr^+$
Excimer Formation	$Kr^+ + Cl^- \rightarrow KrCl^*$
	(Harpoon reaction)
	$Kr^* + Cl_2 \rightarrow KrCl^* + Cl$
	$Cl^- + Kr_2^+ \rightarrow KrCl^* + Kr$
Radiative Decay of Excimer	$KrCl^* \rightarrow Kr + Cl$ (222 nm)
Excimer Loss	$KrCl^* + Kr \rightarrow 2Kr + Cl$
	$KrCl^* + Cl_2 \rightarrow Kr + Cl_2 + Cl$
	$KrCl^* + 2Kr \rightarrow Kr_2Cl + Kr$

For the present atudy, initial electron density of 10^{11} m^{-3} has been used in the simulation, whereas for maintaining the electron-neutrality the initial density of Cl_2^+, Kr_2^+, Cl^+, Cl^- ions and Kr^+ have been set to be 10^{10} m^{-3} and 8×10^{10} m^{-3}, respectively. The value of secondary electron emission coefficient in the

simulation model is 0.01 for Kr^+ and, 0.005 for Cl_2^+ and Kr_2^+ [12]. The impact of the electrons, ions, and neutral species on the surface of the dielectric barrier are considered by taking the appropriate boundary condition. Galerkin finite element method has been used to discretize the Eqs (1 - 6) which is inherent in the COMSOL and are solved using time dependent solver PARDISO by taking the initial time step of 1×10^{-13} s.

4 Results and discussion

Figure 1 presents the measured V-I characteristics and the discharge image of the developed co-axial excimer lamp. A negative unipolar pulse of amplitude 4 kV is applied to the inner electrode while the outer electrode is grounded. Initially, when the voltage pulse is applied, the current obtained is low which is also known as the displacement current. When the voltage reaches to the magnitude of ~3.5 kV during the rising phase, sharp increase in current is observed and reaches to its maximum value of ~175 mA. This is known as the total current i.e. sum of the displacement current and the conduction current. This increase in current is mainly due to the direct ionization of the Kr and Cl^{+2} via electron impact ionization process as shown in Table 1. During the falling phase multiple peaks are observed corresponding to the secondary discharge. At this operating condition discharge appears to be filamentary in nature which fills the entire volume of the lamp.



(a)

(b)

Fig 1. (a) Temporal evolution of current (blue line) with the applied voltage (black line), (b) The discharge image of developed 222 nm radiation source.

Figure 2 shows a typical emission spectrum of the developed excimer source in the range of 200-1000 nm. The different bands have been observed corresponding to the characteristic emission of Kr and Cl_2. The spectra show that the intense narrow-band radiation at 222 nm has been formed which is mainly due to the $B_{1/2}\rightarrow X_{1/2}$ transition of $KrCl^*$ excimer. This transition is the strongest and the full width half maximum (FWHM) of ~8 nm has been achieved within the pressure range used. Along with the peak at 222 nm, another weak peak is observed at around 235 nm due to the overlapping of $C_{2/2}\rightarrow A_{3/2}$ and $B_{1/2}\rightarrow A_{1/2}$ transitions. A broad, low intensity emission is also observed near 258 nm, due to the $D \rightarrow A$ transition of Cl_2^* excimer. This exciplex of $KrCl^*$(222 nm) and excimer of Cl_2^* (258 nm) are clearly observed during the discharge as shown

in Fig 2. This intensity curve is studied at different Cl_2 concentrations in order to identify the optimized value. The result illustrates that an increase in the Cl_2 concentration from 0.1 to 5% the intensity of 222 nm radiation gets enhanced as more steamers are produced during the discharge specially at higher pressure (<100 mbar).

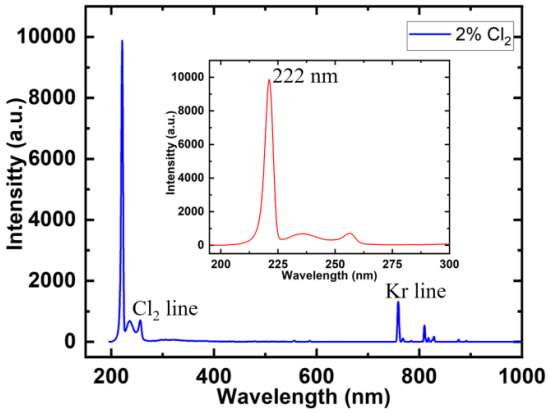


Fig 2. Emission spectra of Kr/Cl_2 excilamp for 4 kV, 50 kHz and a total pressure of 200 mbar with the 2% Cl_2.

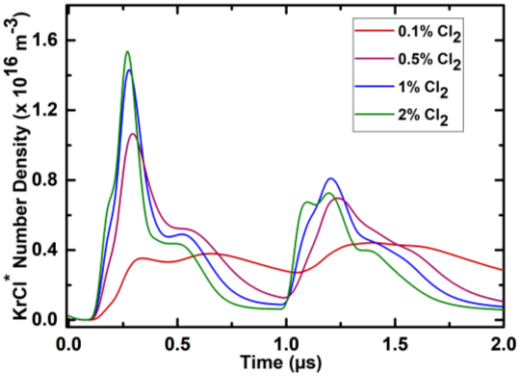


Fig 3. Temporal evolution of KrCl* excimer density at different Cl_2 percentage for a total pressure of 100 mbar.

Figure 3 presents computational analysis of the temporal evolution of number density of $KrCl^*$excimer with the different Cl_2 concentrations using COMSOL Multiphysics software. In this figure, two peaks are observed corresponding to the application of voltage pulse and its rising and falling phase. The main source of $KrCl^*$ is through harpoon reaction shown in Table 1 and also by reaction $K^* + Cl_2 \rightarrow KrCl^* + Cl$. It is clearly observed that at 500 ns the density of $KrCl^*$decreases because of dominancy of the electron attachment process. This further leads to destruction of Cl_2 molecule and, therefore, decreases the electron density. The decrease in the electron density results in low ionization rate due to which Kr^+ ion is less populated and results in the less production of the excimer density. Further, Kr^* is mainly produced by electron impact excitation reaction which is efficiently quenched by Cl_2 to produce the $KrCl^*$. However, as the electron density decreases with time, the number density of $KrCl^*$ also decreases. In fact, the destruction of $KrCl^*$ is through radiative de-excitation and also reaction with Kr to form Kr_2Cl as shown in the Table 1. Figure 3 clearly illustrates that as the Cl_2 percentage increases from 0.1 to 2%, the number density of $KrCl^*$ also increases which somehow reflects the enhancement in the intensity of 222 nm radiation. The effect of Cl_2 concentration on the intensity of 222 nm radiation is also observed experimentally as shown in Fig 4.

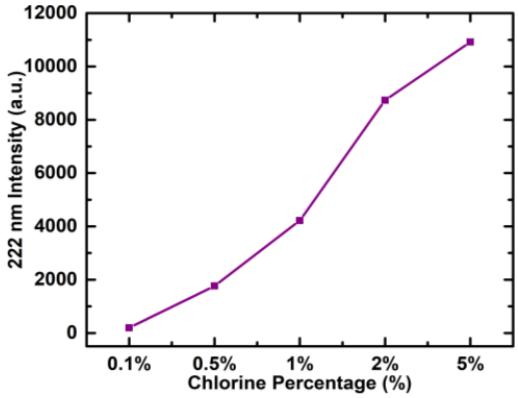


Fig 4. Peak value of 222 nm radiation intensity versus different Cl_2 percentages for a total pressure of 100 mbar.

5 Conclusion

The experimental and simulation study of the developed excimer source has been carried out to investigate the formation of KrCl* excimer and corresponding emission spectra. The measured emission spectra confirm the generation of 222 nm radiation from the developed Kr/Cl_2 excimer source which increases as the Cl_2 concentration increases and also shows filamentary discharge at higher pressure. The plasma simulation result clearly shows the effect of the Cl_2 percentage on the KrCl* excimer density. The simulation has been done to analyze the kinetic processes which describe the temporal and spatial evolution of number density of different species responsible to produce KrCl*. The model describes the transient behavior of the KrCl* excimer density at different proportions of Kr and Cl_2 during the rising and falling phase of the voltage pulse, respectively.

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