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Dependence of ozone generation on the surface condition of dielectrics

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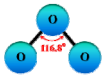
Introduction

- **Ozone**
  - **High reactivity**
    - ➢Oxidize, bleach, deodorize, sterilize
  - **Environment-friendly**
    - ➢No harmful by-products
  - Present usage (with low density ozone)
    - ➢Treatment of drinking water, agriculture



←----------→ with high density ozone

Application to new fields

- ■Environmental field (removal of dioxin, cleaning of substrate)
  - -Because of more quick processing of harmful materials
- ■Medical field (sterilization of medical equipment)
  - - As powerful sterilant for the conventional toxic substance

High density ozone is needed to apply ozone to **new fields!**

High density oxygen Atmospheric pressure O_2

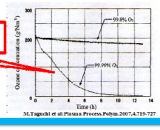
- **Ozone generation from O_2 using Dielectric Barrier discharge**
  - **Dielectric Barrier discharge (DBD)**
    - ➢Proposed by Siemens (1857)
    - ➢Presence of a dielectric layer between the discharge gap and at least one of the electrodes.
  - **Advantage**
    - ➢Efficient generation of ozone
      - •Efficient generating energetic electron to make radicals
      - •Not transiting to the arc discharge
    - ➢ A device of simple structure
  - **Disadvantage**
    - ➢Not uniform discharge

To generate high density ozone efficiently, Ozone generation from Atmospheric O_2 using DBD had been done!

But・・・

"Ozone-zero phenomena" occurs

The phenomenon which ozone concentration decreases with time and finally the concentration becomes almost zero!



M.Tagashi et al Plasma Process.Polym.2007,4,719-727

- **Ozone zero phenomena**
  - **Cause**
    - ➢ Destruction of ozone by rise of gas temperature?
    - ➢ Destruction of ozone in dielectric surfaces?
  - **Solution of this phenomenon**
    - ➢ Adding a small amount of impurities to oxygen

But these mechanism is not explained clearly yet !

Objective

To clear the mechanism of this phenomena

Dependence of ozone generation on **secondary electron emission coefficient** is examined.

Governing equations

Continuity equation (e , O , O_2 ,O_3 , O^+, O_2^+)

$$\frac{\partial n_k}{\partial t}+\nabla.\Gamma_k=S_k$$

$$\nabla.\Gamma_k=-\mu_k n_k \nabla.\phi-D_k\nabla n_k$$

Electron energy conservation

$$\frac{\partial(n_e\varepsilon)}{\partial t}+\nabla.[\frac{5}{3}\varepsilon\Gamma_e+Q_e]-e\Gamma_e.\nabla\phi+\sum_j\Delta\varepsilon_j=0$$

$$Q_e=\frac{2}{3}\kappa\nabla\varepsilon,\ \kappa=\frac{5}{2}n_e D_e$$

Poisson equation

$$\nabla^2\phi=\frac{-\rho}{\varepsilon_0}$$

$$\rho=n_{O^+}+n_{O_2^+}-n_O-n_{O_2^-}-n_{O_3^-}-n_e$$

$$E=-grad\,\phi$$

Gas equation

$$\frac{2}{5}kN[\frac{\partial T_g}{\partial t}+\nabla(v_g T_g)]=\nabla\Gamma_g+n_j e\mu_j E^2$$

$$\nabla.\Gamma_k=-\mu_k n_k\nabla.\phi-D_k\nabla n_k$$

Modeling

Initial Conditions

Gas & pressure: O_2(100%), 760Torr
Dielectric barrier thickness: 0.05cm
ε_r: 4.7
Gap length : 0.2cm
Applied voltage: V_a=7.5kV
Frequency: 200kHz
Initial gas temperature: 300 K
Secondary Electron Emission Coefficient (S.E.E.C.):
γ_{i0} =0.1, γ_{p0}= 0.01
$\gamma_i=\gamma_r\times\gamma_{i0}$, $\gamma_p=\gamma_r\times\gamma_{p0}$
γ_r= 0.1, 0.5, 1, 2, 3

Boundary condition

On dielectric surface

$$n_{e0}W=\Upsilon_i\Gamma_i+\Upsilon_p\Gamma_p$$

$$\Gamma_i=\frac{n_e W}{\tau_i}$$

$$\Gamma_p=\frac{n_e W}{\tau_p}$$

$$n_{e0}=\frac{\Upsilon_p n_e W}{W}$$

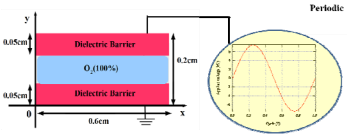
$$n_{e0}=\frac{\sum\tau_p}{4\pi r^2 W}\int_p N^0\exp(-\mu^2/t)\frac{\varepsilon\,d\varepsilon}{t^2}$$

$$Q=e\int(-\Gamma_e+\Gamma_+)\,dt$$

・・・accumulated charge

At X=0.0,0.6cm

Periodic boundary condition

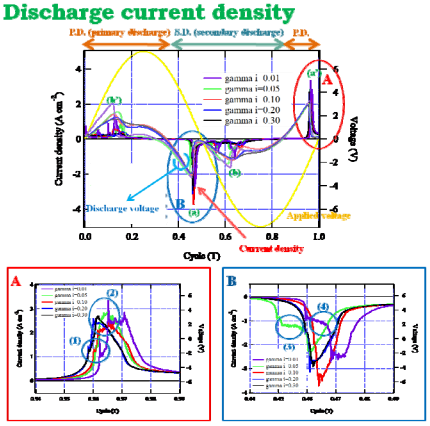


Reaction equations

Reaction	Rate coefficient (cm^3/s, cm^6/s $^{-1}$)
$O_2+e\rightarrow O_2(a^1\Delta_g)+e$	ra1(ev)
$O_2+e\rightarrow O_2(b^1\Sigma_g^+)+e$	rb1(ev)
$O_2+e\rightarrow O(^3P)+O(^3P)+e$	ra6(ev)
$O_2+e\rightarrow O(^3P)+O(^1D)+e$	rb2(ev)
$O_2+e\rightarrow 2O(^3P)+e$	r10(ev)
$O_3+e\rightarrow O_2^-+2e$	r16a(ev)
$O_2^++e\rightarrow O^++O$	r6a(ev)
$O(^3P)+e\rightarrow O(^1D)+e$	rea(ev)
$O_2(a^1\Delta_g)+e\rightarrow O+O(^3P)$	r6aa(ev)
$O_2(a^1\Delta_g)+e\rightarrow 2O(^3P)+e$	r6ab(ev)
$O_2(a^1\Delta_g)+e\rightarrow O_2^++e$	ra6(ev)
$O+e\rightarrow O(^3P)+2e$	r6ba(ev)
$O+O_2(a^1\Delta_g)\rightarrow O_3+e$	$3.01\times10^{-18}(T_g/300)^{0.5}$
$O_3^-+e\rightarrow 2O(^3P)$	2.28×10^{-7}
$O(^1D)+e\rightarrow O(^3P)+e$	8.00×10^{-10}
$O_2+e\rightarrow O(^3P)+O_2+e$	5.00×10^{-8}
$O_2^++O_2+e\rightarrow O_2^-+O_2$	4.68×10^{-20}
$e+O_3\rightarrow O+O_2^-$	1.00×10^{-9}
$2O(^3P)+O_2\rightarrow 2O_2$	8.00×10^{-33}
$O_2+O_2^-\rightarrow O_2+O_2^-$	4.00×10^{-10}

Reaction	Rate coefficient (cm^3s^{-1}/ cm^6s^{-1})
$O+O_2+O_2\rightarrow O_3+O_2$	$6.4\times10^{-34}\exp(663/T_g)$
$O_2(b^1\Sigma_g^+)+O_2\rightarrow O_2+O_2$	$7.23\times10^{-11}(T_g/300)^{0.5}$
$O_2+O_2^-\rightarrow O_2+O_2$	$2.0\times10^{-7}(T_g/300)^{0.5}$
$O_3+O_2^-\rightarrow 2O(^3P)+O_2$	1.00×10^{-7}
$O_3+O_2^-\rightarrow O_2+O_2+e$	2.30×10^{-10}
$O+O_2\rightarrow O_3+e$	5.00×10^{-16}
$O+O_2\rightarrow O_2+O(^3P)$	5.50×10^{-18}
$O_2+O(^1D)\rightarrow 2O_2$	8.42×10^{-11}
$O_2+O_3\rightarrow O_2+O_2$	$4.00\times10^{-21}(300/T_g)^{2.5}$
$O_2(b^1\Sigma_g^+)+O_3\rightarrow O_2+O_3$	$7.33\times10^{-11}(T_g/300)^{0.5}$
$O+O+O\rightarrow O_2+O$	$6.2\times10^{-34}\exp(-750/T_g)$
$O+O_2(a^1\Delta_g)\rightarrow O_2+O$	1.00×10^{-20}
$O(^1D)+O_2\rightarrow 2O_2$	1.21×10^{-10}
$O(^1D)+O_3\rightarrow O_2+2O$	1.21×10^{-10}

Discharge current density



➢In all cases of γ_i , the form of the current waveform is almost equal basically.

➢The current density wave consists of (a) large current peaks of the early period of discharge and (b) small peaks following them.

➢Two sharp peaks shown in (1)and(2) and flat parts are seen in (a) .

➢Two sharp peaks appear when primary streamers reached to the cathode.

➢Flat parts appear when surface discharges are generated.

In figure A and B

➢P. D.

➢As γ_i increases , current density wave initiates earlier and earlier.

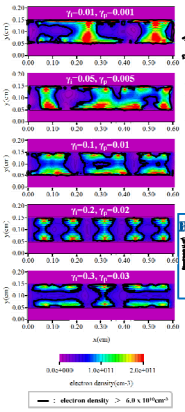
➢S. D.

➢In the cases of γ_i =0.1, 0.5 , flat parts shown in (3)and (4) appear earlier than two sharp peaks.

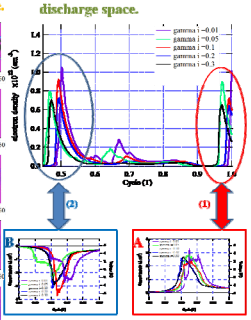
➢ In the cases of γ_i =1, 2 ,3 , as γ_i increases , current density wave initiates earlier and earlier.

Electron density

Spatial distributions of electron density averaged by one cycle.



Averaged electron density in discharge space.



➢As shown in (1)and(2) , electron density waveforms don't synchronize with current density ones.

➢High electron densities are seen in the vicinity of dielectric surfaces.

➢Surface discharges are generated there.

◆**In high S.E.E.C. case(γ_i=2 ,3).**

➢Symmetric distribution is obtained between electrodes and in x direction.

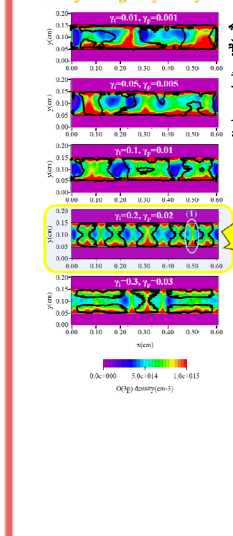
◆**In low S.E.E.C. case(γ_i=0.1 ,0.5, 1).**

➢Asymmetric distribution is obtained between electrodes and in x direction.

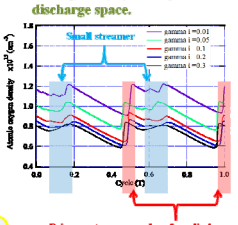
➢Low densities are obtained on ground electrode side.

O(³P) density

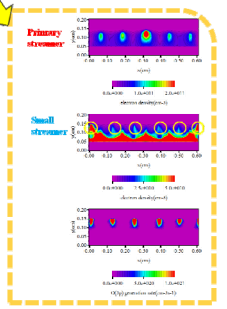
Spatial distributions of O(³P) density averaged by one cycle.



Averaged O(³P) density in discharge space.



Primary streamer and surface discharge



➢Atomic oxygen are generated by dissociation reaction.

➢High atomic oxygen densities region is corresponding to the region where electron densities are high.

➢As shown in (1) , high atomic oxygen densities region is corresponding to the region where electron densities are not high, too.

➢Small streamers are generated there.

➢High densities are obtained on ground electrode side.

➢As γ_i increases , higher and higher densities are obtained.

◆**In high S.E.E.C. case(γ_i=2 ,3).**

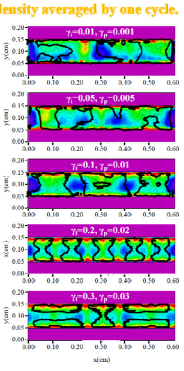
➢Symmetric is obtained in x direction.

◆**In low S.E.E.C. case(γ_i=0.1 ,0.5, 1).**

➢Asymmetric distribution is obtained in x direction.

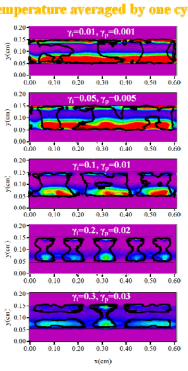
Ozone density

Spatial distributions of ozone density averaged by one cycle.



Gas Temperature

Spatial distributions of gas temperature averaged by one cycle.



➢Ozone is made mainly from atomic oxygen.

➢High ozone densities region is corresponding to the region where atomic oxygen densities are high.

➢High ozone densities are seen in the vicinity of dielectric surfaces.

➢More ozone are generated by surface discharges than streamer discharges.

➢High gas temperatures are obtained on ground electrode side.

➢As γ_i increases , higher and higher gas temperatures are obtained.

◆**In high S.E.E.C. case(γ_i=2 ,3).**

➢Symmetric ozone density distribution is obtained between electrodes and in x direction.

➢Symmetric gas temperature distribution is obtained in x direction.

◆**In low S.E.E.C. case(γ_i=0.1 ,0.5, 1).**

➢Symmetric distribution is obtained in x direction.

➢Asymmetric gas temperature distribution is obtained between electrodes and in x direction .

Conclusion

➢To examine the dependence of ozone generation on S.E.E.E. the modeling of AC atmospheric DBD in oxygen has been done.

➢The current density wave consists of large current peaks of the early period of discharge and small peaks following them.

➢Electron density waveforms don't synchronize with current density ones.

➢High atomic oxygen densities region is corresponding to the region where electron densities are not high, too, and small streamer discharges are generated there.

➢More ozone are generated by surface discharges than streamer discharges.

➢As γ_i increases , higher and higher atomic oxygen densities and gas temperatures are obtained.

➢High atomic oxygen density is advantage for the ozone generation

➢High gas temperature is disadvantage for the ozone generation