WEAKLY IONIZED OXYGEN PLASMA

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Abstract: Weakly ionized oxygen plasma is electromagnetically induced plasma of low-pressure oxygen with a negligible density of charged particles and a relatively high degree of dissociation. The high density of atomic oygen makes it chemically very reactive. This characteristic is used in various surface engineering applications. Neutral atoms recombine into molecules upon contact with solid surfaces. The exothermic characteristic of this reaction is utilised for determining the density of the atom gas.

Šibko ionizirana kisikova plazma

Kjučne besede: šibko ionizirana plazma, radiofrekvenča plazma, rekombinacija, FCOP

Izvleček: Šibko ionizirana kisikova plazma je elektromagnetno inducirana plazma kisika pri nizkem tlaku z zanemarljivo gostoto nabitih delcev in razmeroma visoko stopnjo disociacije. Zaradi velike gostote atomarnega kisika je kemično zelo reaktivna. Ta lastnost je izkoriščena pri obdelavi površin. Ob stiku s površino atomi rekombinirajo v molekule. Eksotermen značaj te reakcije je v rabi pri določanju gostote atomarnega kisika.

1. Introduction

Plasma is often referred to as the fourth state of matter. It is also called ionized matter or ionized gas, which is more descriptive. Plasma indeed is a gas of charged particles, which are a product of ionization of the original gas, of course. It is a naturally occurring state and can be found in stars and interstellar space. Such plasma is a thermally equilibric state since the ionization is a product of very high temperature ($10^4 K$ and above). Thermal plasma can also be produced on Earth but because no material can stand the high temperature, it must be contained in magnetic fields (tokamaks). /1/

However, it is possible to create plasma at considerably lower temperatures by delivering the energy for the ionization by means of electromagnetic field. This kind of plasma (electromagnetic plasma) is not in thermal equilibrium with its surroundings, moreover, it isn't even in thermal equilibrium with itself. It is a mixture of at least two different gasses (electrons and positive ions) with different temperatures. Since this isn't a thermally equilibric state, the usual parameters used to describe a state of matter (temperature and pressure) aren't of much use and we have to turn to new ones in order to characterise the plasma. Most commonly used parameters are electron temperature (which is closely linked to the average electron kinetic energy), electron density, ion temperature and ion density.

Another important parameter of a plasma is the degree of ionization. That is the ratio of the number of the gas particles that have been ionized to the total number of the original gas particles. In the weakly ionized plasma, which is the topic of this seminar, that fraction is much smaller than unity which means that the density of charged particles is, if not negligible, at least considerably smaller than the densities of other species.

2. Electromagnetic plasma

EM plasma is created by putting low pressure gas in an electromagnetic field, either DC or AC. The principle of operation of the DC plasma, or DC discharges is that an electron source emits electrons which are accelerated by the stationary electrical field. On their way to the positive electrode, the accelerated electrons collide with other gas particles, producing new electrons.

2.1 Radiofrequency Plasma

The major disadvantage of DC systems is that an electron source is needed. This requirement is omitted by using a high frequency (above 1*MHz*) EM field. The field accelerates the few free electrons in the gas which in turn produce new electrons. The intensity of the field is

$$E = E_0 \cos \omega t \qquad (2.1)$$

And the force a charged particle feels is

$$m \frac{d^2 x}{dt^2} = eE \cos \omega t \qquad (2.2)$$

From this we obtain the expression for its velocity:

$$\frac{dx}{dt} = \frac{eE}{m\omega} \sin \omega t \qquad (2.3)$$

And finally the oscillation of the particle:

$$x = -\frac{eE}{m\omega^2} \cos \omega t \qquad (2.4)$$

E[V/m]	Oscillatory amplitude [m]	Maximum velocity [m/s]	Maximum kinetic energy [eV]
10	6.110 $^{-5}$	10^4	3.010 $^{-4}$
100	6.110 $^{-4}$	10^5	3.010 $^{-2}$
1000	6.110 $^{-3}$	10^6	3.0
10000	6.110 $^{-2}$	10^7	3.010 ^{2}

Table 1 - behaviour of electrons in a 27.12MHz electric field /1/

We can see that even in very strong field ($10^3\ V/m$) the maximum oscillatory amplitude of the electrons is relatively small, smaller than the diameter of a typical plasma vessel. Since the actual intensities in use are considerably lower (typically around $10^2\ V/m$), we can safely assume than an electron isn't forced by the field to collide with the walls of the vessel.

The ions on the other hand, are too massive to follow the oscillations of the electrical field and therefore can't receive any energy from it. That's why in radiofrequency plasma the ions remain at the temperature of the original gas.

2.2 Microwave discharge

With heightening of the frequency, even electrons aren't capable of following the oscillations of the field anymore and thus accumulating enough energy to cause further ionization. The only way for an electron to obtain enough energy is when its direction changes in such way that it follows the changing of the direction of the field. For that reason, the best results are achieved when the electron's oscillatory amplitude is approximately the same as its mean free path. At the frequency of 1 GHz the amplitude is 0.1 mm which corresponds with the mean free path at $10^3\ Pa$.

3. Collision processes

As mentioned, the EM field accelerates the electrons which collide with other gas particles. Through these collisions other plasma species are produced. The most important collision process which sustains the glow discharge is ionization. The accelerated electron transfers enough of its energy to the target atom or molecule that the atom or molecule emits another electron.

$$e^- + O_2 \rightarrow 2e^- + O_2^+ \qquad (3.1)$$

This type of collision process must be frequent enough that the production of new electrons accommodates the loss of electrons through entrapping on the walls of the plasma containing vessel.

When the accelerated electron fails to transfer enough of its energy to ionize the target atom or molecule it can still excite it.

$$e^- + O_2 \rightarrow e^- + O_2^* \qquad (3.2)$$

The particle relaxes back to its ground state by emitting a photon if that is allowed by the selection rules. This is why plasma glows.

Another important process, especially for the weakly ionized plasma, is dissociation. This happens in non-noble gases, when a colliding electron brings a molecule enough energy to overcome its binding potential and break it apart.

$$e^- + O_2 \rightarrow e^- + O + O \qquad (3.3.)$$

The dissociated molecules or, plainly put, atoms, are the most important species of weakly ionized plasma. At this point it makes sense to define another plasma parameter - the degree of dissociation. This is the fraction of the original molecules that have been dissociated.

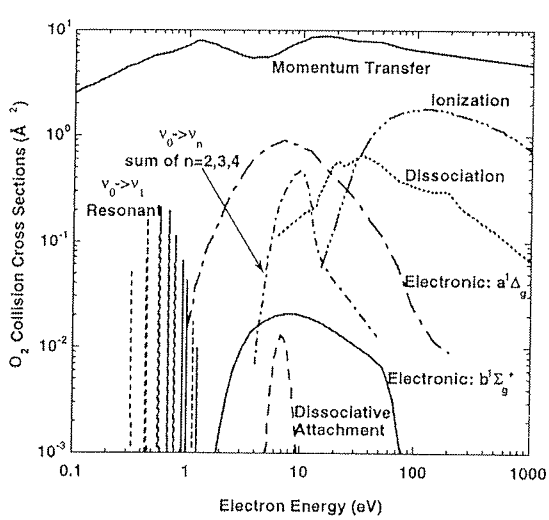

Figure 1: electron collision cross-sections in oxygen. /2/

4. Atom gas

The ionization and dissociation processes happen very roughly at the same rate (depending on the electron energy), so the production of charged particles and neutral atoms is approximately of the same value. However, the density of neutral atoms is in the range of 10% (or higher) of the original molecules while the density of charged particles is several orders of magnitude lower. This is because charged particles 'do not survive' contact with a solid surface, namely the walls of the vessel that contains the plasma. When an electron reaches a solid surface, it binds to it. Ions are more likely to receive than electron (and thus become neutral) than to bind, but in terms of the degree of ionization, the sonsequences are the same. Effectively speaking, charged particles disappear from the plasma upon contact with solid surfaces.

That is not the case with atoms - they see the wall as a field of potential holes, each deep several electron volts, so that once an atom is caught in such a hole, it can not get out by itself. However, there is only a limited amount of such holes and once they're all occupied (the surface is saturated), the next incoming atoms will not be caught in the holes and will bounce off the wall with great probability.

However, upon contact with solid surface atoms do recombine into molecules, but with the right choice of material for the walls, it is possible to reduce this recombination to a negligible level. Recombination inside the vessel is highly improbable because due to the conservation of momentum, this requires a simultaneous collision of at least three particles which is a very rare event in gas of low pressure.

As mentioned, the neutral atoms are the most important species of the weakly ionized plasma. Their most obvious characteristic is that they are not electrically charged and thus the EM field has no effect on them, neither do they interact with other particles over distances larger than their diameter.

From this point of view, the behaviour of the atom gas is very similar to the behaviour of the original, molecular gas. There are two main differences, however.

The first one is that the atom gas is chemically much active than the original one. The chemical reactions that take place are still the same as those of the original gas, but they happen much more easily since the potential barrier is considerably lower. For example:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (4.1)$$

For this reaction to take place, certain energy barriers must be overcome. In the case of oxygen, the molecule must be first dissociated before the reaction can happen, which means that we must bring in enough energy to overcome the E_{dis} (*5.12 eV* for oxygen), the dissociation potential, usually in the form of heightening the temperature. In the atom gas, that potential barrier has already been overcome and such reactions can take place at room temperature.

4.1 Recombination

Another important characteristic of the atoms is, as mentioned, that they recombine into molecules upon contact with solid surfaces.

Because of the law of conservation of momentum, in gas the reaction

$$O + O \rightarrow O_2 \qquad (4.2)$$

is not possible. Because the molecule has, by definition, lower potential energy than both the atoms combined, another particle is needed to take on the surplus energy, usually in the form of kinetic energy, for example:

$$O + O + O_2 \rightarrow O_2 + O_2 \qquad (4.3)$$

where the second oxygen molecule is the one to take the surplus energy. Such processes are very unlikely at the pressures in use in weakly ionized plasma technologies (*1Pa-10Pa*), so the only significant recombination is the recombination that takes place on solid surfaces, namely the walls of the plasma containing vessel. There are three different ways that atoms can recombine on solid surfaces /1/:

1. Two atoms simultaneously strike upon a small area of the surface. They join into a molecule; the atoms of the surface absorb some of the surplus energy. Since there isn't enough time for accommodation, the molecule leaves the surface in a high vibrational state.
2. Atoms are bound to the surface. The atom that hits upon the surface forms a molecule with a bound atom. The bound atom is accommodated on the surface and so the resulting molecule leaves the surface in ground state or a low vibrational state.
3. Two atoms that are bound to the surface form a molecule that leaves the surface. Because both atoms are accommodated, the molecule leaves the surface in ground state or a low vibrational state.

The probability of the first kind of recombination process can be approximated as the probability that two atoms hit the same small area in a limited time range. Let's assume the area to be the size of a basic crystal cell, which is of the order of $10^{-19} m^2$. Furthermore, we can estimate the time range as the time it takes an atom to travel a distance that corresponds with a typical dimension of such a cell. The average velocity of the atoms is

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \qquad (4.4)$$

which is around 700 m/s at room temperature. That means that the time range, t, is of the order of $10^{-12} s$. The flux of the atoms to the surface is $\phi = \frac{1}{4} n\bar{v}$ and the density of atoms, n, is of the order of $10^{21}/m^3$, so the flux is of the order of $10^{23}/m^2s$. The average number of atoms that land on that small area in that limited time range is therefore

$$\bar{N} = \Phi S \tau = 10^{23}/m^2 s * 10^{-19} m^2 * 10^{-12} s = 10^{-8} \qquad (4.5)$$

The possibility that at least two atoms hit that part of surface in that time frame equals one minus the possibilities that either one or no atoms do so.

$$P(N \geq 2) = 1 - P(N=0) - P(N=1) \qquad (4.6)$$

We calculate separate possibilities using the Poisson possibility distribution:

$$P(N) = \frac{\bar{N}^N}{N!} e^{-\bar{N}} \qquad (4.7)$$

That gives us

$$P(N \geq 2) = 1 - e^{-10^{-8}} - 10^{-8} e^{-10^{-8}} \qquad (4.8)$$

which is very close to zero. We have thus established that the first process is negligible, at least at the pressures in use (*1Pa-100Pa*) so the recombination must happen through the second two processes. We can sum up their effect in a quantity called the recombination coefficient. It is defined as the probability that an incoming atom recombines upon contact with surface.

Material	Recombination coefficient
Nickel	0.27
Silver	0.015 – 0.24
Stainless steel	0.0099 – 0.17
Aluminium	0.0018 – 0.01
Pyrex	$1.6*10^{-6}$ - $2.4*10^{-3}$
Quartz	$3.1*10^{-5}$ - $3.2*10^{-4}$
Teflon	$7.5*10^{-5}$

Table 2: recombination coefficients for oxygen

It should be noted that recombination coefficients aren't the same for every gas and that they strongly depend on the roughness of surface. While this dependency has not yet been properly studied, it is believed to be the cause of large discrepancies in reported values of recombination coefficients for certain materials (up to orders of magnitude).

4.2 Lifetime of atoms in a plasma system

Once we agree that the only mechanism of loss of atoms is recombination on the walls of the plasma vessel, we can estimate the half-life of an atom.

The probability that an atom survives a collision with the wall is

$$P_1 = 1 - \gamma \quad (4.9)$$

For *N* collisions, that probability is

$$P(N) = (1-\gamma)^N \quad (4.10)$$

To calculate that probability as a function of time, we must first estimate how many times an atom hits upon the wall in unit time. Let us suppose that our plasma vessel is a cylindrical tube with the radius *r* and the length *L*. If the density of the atoms is *n*, then the total number of atoms in the vessel is

$$T = nV \quad (4.11)$$

where the volume of the vessel is $V = \pi r^2 L$. The flux of atoms to the surface is

$$\phi = \frac{1}{4}\bar{v}n \quad (4.12)$$

and the total number of atoms that hit the surface in unit time is

$$F = \phi S = \frac{1}{4}\bar{v}n(2\pi rL) \quad (4.13)$$

The ratio F/T is the average number of times an atom hits a surface in unit time:

$$\frac{dN}{dt} = \frac{F}{T} = \frac{\frac{1}{4}\bar{v}n2\pi rL}{n\pi r^2 L} = \frac{\bar{v}}{2r} \quad (4.14)$$

Now we can write down the probability that an atom hasn't recombined after the length of time *t*:

$$P(t) = (1-\gamma)^{\frac{\bar{v}t}{2r}} \quad (4.15)$$

At room temperature, the average speed for oxygen atoms is around $\bar{v} = 700\,m/s$. Let us take a look what happens in a glass tube ($\gamma = 10^{-4}$) with the radius $r = 5$ *cm*.

t[s]	P
1	0.993
10	0.932
100	0.497

Table 3: Probabilities of recombination in a glass tube $\gamma = 10^{-4}$

We can see that it is more likely for an atom to be pumped out of the plasma system than to recombine on the walls. However, if we make the vessel of a material that is a good catalyst ($\gamma = 0.1$), then we get drastically different results.

t[s]	P
1	0.000627
0.1	0.478
0.01	0.929

Table 4: Probabilities of recombination in tube of a catalytic material, $\gamma = 0.1$

The chance that an atom hasn't recombined after in a second's time is practically zero. We see that with by choice of material for the plasma containing vessel, we can assure either decent stability of the atom gas, or the completely opposite result.

5 Measuring atom density

As mentioned, various parameters are used to characterize plasma. In weakly ionized plasma the most important parameter is the degree of dissociation or more simply put, density of the atom gas.

There are various methods available for determining atom density in plasma /3/:

- *NO* titration
- mass spectrometry
- optical emission spectrometry
- optical absorption spectrometry
- catalytic probes

Among the mentioned methods, optical absorption spectrometry is the one that is the most accurate. It is however a very demanding method and as such isn't always availible. The catalytic probes aren't as accurate as optical absorption spectrometry, but they are a much more convenient technique. While the rest of the mentioned methods can only be used to determine the order of magnitude of the atom density, the catalytic probes can yield accuracy as good as 30%.

5.1 Catalytic probes

A catalytic probe is basically a small piece of metal submerged in the plasma /4/. It utilises the exothermic characteristic of the recombination reaction

$$O + O \rightarrow O_2 \tag{5.1}$$

The metal acts as a catalyst for recombination. The greater the rate of recombination is, the more the probe is heated. Atom density can be determined by observing the temperature of the probe. The choice of metal depends on the type of gas atoms we want to measure. A certain metal can act as an excellent catalyst for one gas but be completely inactive in another.For measuring the density of atoms in oxygen plasma, for example, the most widely used metal is nickel.

As mentioned, the probe is heated by atoms recombining on its surface, which can be expressed as

$$P_{heat} = \frac{1}{4} S n \bar{v} \gamma E_{dis} \tag{5.2}$$

where P_{heat} stands for the heating power, S for the surface of the probe, $\bar{v}$ for the average velocity of the atoms and n for the density of the atoms. The recombination coefficient of the metal is represented by γ, E_{dis} is the dissociation energy that is released with each two atoms that recombine into a molecule. This value is 5.12eV for oxygen, for example.

When the temperature of the probe is constant, it means that the heating power and the cooling power are closely matched. The probe is cooled by various processes, of which thermal conductivity of the surrounding gas is the predominant. The cooling power is difficult to calculate because it depends of many parameters which aren't always very well known. However, by observing the decline of the temperature immediately after the plasma is switched off, it can be evaluated as:

$$P_{cool} = m c_p \frac{dT}{dt} \tag{5.3}$$

In this expression, m stands for the mass of the metal part of the probe, c_p is the thermal capacity of the metal and $\frac{dT}{dt}$ is the steepest part of the temperature curve after the plasma has been switched off. By switching plasma off we mean that the EM field is switched off and the atom density rapidly falls to zero.

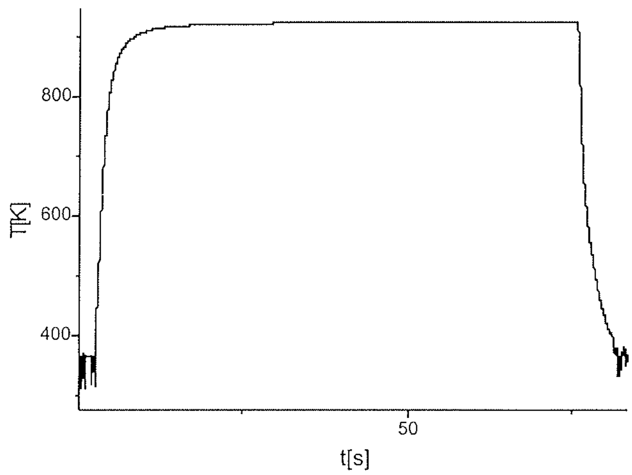

Figure 2: Determining atom density through observation of probe temperature. Temperature plot of a measurement of atom density.

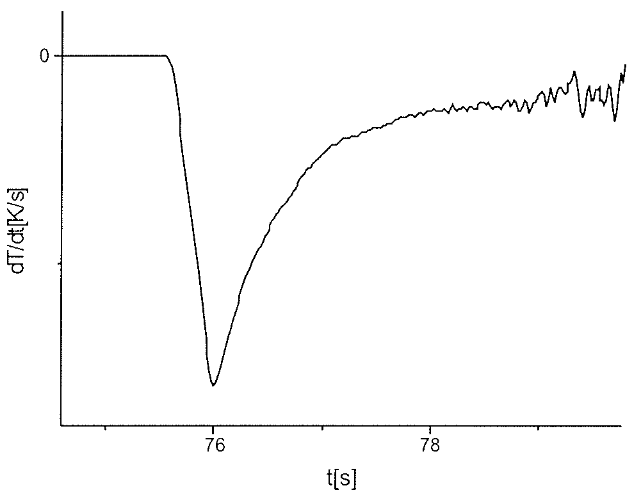

Figure 3: Time derivate of the temperature of the probe, the cooling part of the slope.

The early designs of the catalytic probe included a metal disk attached to thermocouple wires as its essential component. A more advanced design is the Fiber Optic Catalytic Probe. Here the metal disk is substituted by a small piece of metal foil closely wrapped around a small glass sphere (typical diameter is about 0.3 mm) which is attached to an optic fiber. As the foil heats, it emits radiation, which is transmitted through the fiber to an optoelectronic detector, where it is transformed to an electrical one. /5/

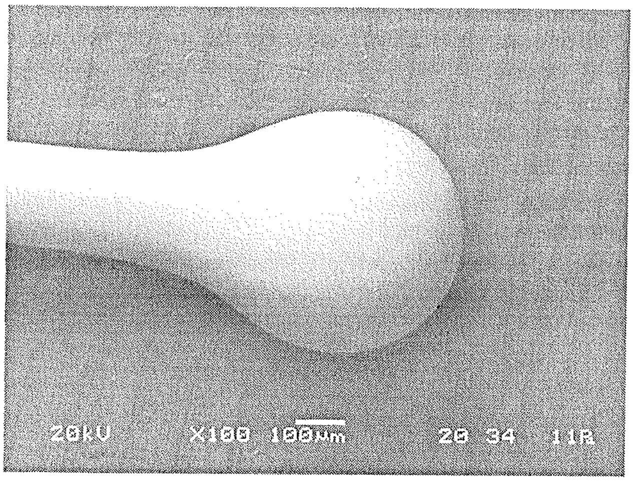

Figure 4: Tip of the FCOP

The advantage of this design to the thermocouple one is that the probe causes less of a disturbance in the surrounding atom gas density because the characteristic dimensions of the metal are much smaller. Furthermore, because the signal is an optical one, it is unaffected by electromagnetic interferences which are quite strong in a radiofrequency system. /6/

However, the catalytic probe has certain limitations, especially the FCOP design. Because the signal to noise ration worsens considerably at lower temperatures (around 400K), it is impossible to measure very low concentration. On the other hand, at high concentration of the atoms, the temperature is so high that the optical signal exceeds the operational range of the optoelectronic detector (signal overflow). Although this can be improved by replacing the detector for a one with a more suitable range of operation, the limitation still remains because extremely high temperatures (well above 1000K) can destroy the probe.

These limitations could be overcome if the probe was retracted along a dead end tube, which should be closed with a metal part with a very high recombination coefficient. That would mean that the density of atoms at the end of the tube would be zero while the density at the beginning of the tube would be the same as in the main plasma vessel. By knowing the density distribution along the tube, it would be possible to determine the density of atoms in the main vessel by measuring a much lower density inside the dead end tube and thus to expand the working range of the probe.

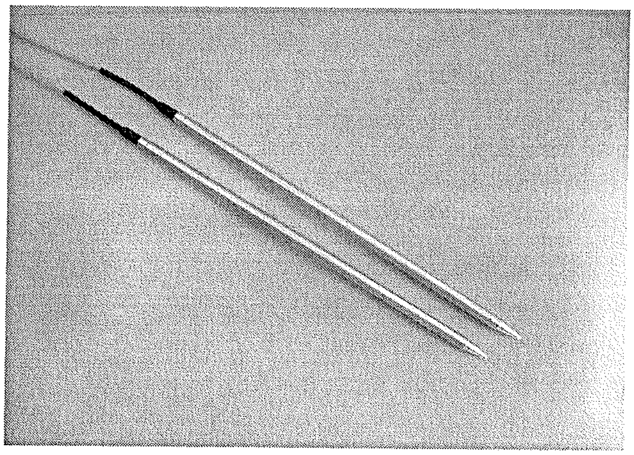

Figure 5: A pair of Fiber Optical Catalytic Probes

6 An example of a simple RF plasma system

This is a simple plasma system located in the plasma lab of the F4 department of IJS. The plasma containing vessel is an around half a meter long glass tube with the diameter of 4 cm. The system is pumped with a two-stage rotary pump which is capable of creating maximum flux of $28m^3/h$. Plasma is produced by means of a 700W radiofrequency generator which is inductively coupled with the plasma. The tube itself is replaceable which allows various variations of system setup. This usually means the choice between a tube that is uniform in diameter or one that has a short (around 5 cm) narrow (diameter of 1 cm) part in the middle. This part separates the 'glow' vessel and the 'post-glow' vessel. The coil of the generator is wound around the glow vessel - here the plasma is created. The narrow part ensures that no charged particles come to the post-glow vessel. That is because the charged particles bind to the walls upon contact and by forcing the plasma to pass through the narrow part, the chance of charged particles reaching the wall of the vessel improves dramatically. The tube also forks out into smaller side tubes through which probes or specimens to be processed are installed.

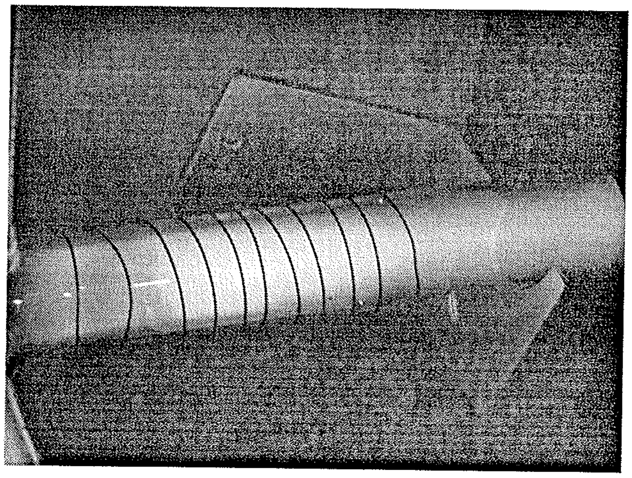

Figure 6: Photograph of a RF glow discharge.

Because this system is relatively small it is primarily intended for research of plasma behaviour rather than mass specimen treatment.

7 Conclusion

We have characterized weakly ionized oxygen plasma as a mixture of molecular and atom oxygen gasses. The relatively high share of atoms in the mixture makes such plasma chemically very reactive and thus suitable for surface engineering. Atoms recombine into molecules upon contact with solid surface. The recombination coefficient is different for each material, which has to be taken into account when constructing the plasma containing vessel. We have also shown a very successful method for measuring the density of the oxygen atoms.

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