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HYDROGEN PLASMA

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ABSTRACT: Low pressure weakly ionized hydrogen plasma is introduced. Different modes of plasma generation are presented and some advantages and disadvantages are emphasized. Characterization of plasma by Langmuir probes is briefly described and a recently developed catalytic probe for the measurement of atomic hydrogen density is described more detaily.

Vodikova plazma

KLJUČNE BESEDE: plazma vodikova, generiranje plazme, karakterizacija plazme, sonde enojne, sonde katalitične, pritisk nizek, plazma ionizirana, ionizacija šibka, tehnologije plazme, tipi plazme

POVZETEK: Prikazujemo nizkotlačno šibko ionizirano vodikovo plazmo. Opišemo različne načine generiranja plazme in poudarimo nekatere njihove prednosti in pomanjkljivosti. Na kratko opišemo karakterizacijo plazme z Langmuirjevimi sondami in podrobneje razložimo delovanje katalitičnih sond, s katerimi izmerimo gostoto atomarnega vodika.

1 Introduction

1.1 Some plasma technologies

The term *plasma* has become so frequently used that the old good question *Why should we use plasma?* has been replaced by the question *Is there any way to avoid using plasma?*. Really, plasma technologies have become so commonly used that the solutions of many problems arising in the processing of materials are often found by using some of plasma involved techniques. It was stated that if there was any field of science and technology that has been developing fast in the past decade, it would be the field of surface science and thin film processing. This could have been said also for the field of plasma technologies. Here is a short list of some most commonly used plasma technologies:

☐ Chemical and physical plasma cleaning
☐ Plasma etching, plasma ashing
☐ Sputtering and ion plating
☐ Plasma enhanced chemical and physical vapor deposition
☐ Plasma melting and smelting
☐ Plasma light sources.

1.2 Types of plasma

The term *plasma* was first introduced by I. Langmuir in 1926 /1/ when he studied the positive column of the glow discharge. Later, the term was used for the description of a certain state of gas. Since the original definition of Langmuir, many authors have tried to define the term more or less successfully. The most simple definition of plasma is that it is a partially ionized gas. Since all the gases are actually at least weakly ionized a requirement is stated at once, i. e. the density of charged particles should be rather high, or more physically, the Debye length should be much smaller than the typical dimension of the gas being studied. The Debye length is defined as

$$\lambda_D = \sqrt{\frac{\varepsilon_0 k T_e}{N e_0^2}} \qquad (1)$$

In equation (1), N is the density of charged particles, T_e the electron temperature and ε_0, e_0 and k are the influence constant, electron charge and Boltzmann constant, respectively. It is clear that a very rarefied gas can be described as plasma readily. On the other hand, dense gases can only be treated as plasma if the density of charged particles is very high. An overview of plasmas according to the density of charged particles and the average electron energy is given in Fig. 1.

Different types of plasmas have been divided into two major groups, i. e. thermal and non - thermal plasmas. Clearly, the main difference between the two groups is that thermal plasmas are in thermal equilibrium and non - thermal plasmas are not. More precisely, in thermal plasmas the temperatures of neutral gas, positive ions and electrons are fairly equal and the degree of dissociation is solely a function of the temperature. In non - thermal plasmas the electron temperature is usually more than 10000 *K*, while the gas temperature is 300 *K* or so. The positive ion temperature (i. e. the average

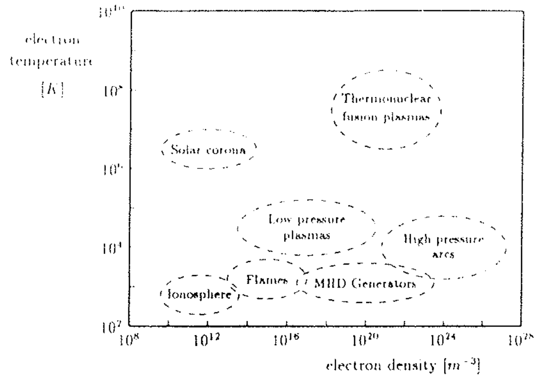

Fig. 1 *Classification of plasmas*

process	onset energy [eV]	max. cross section [$\cdot 10^{-16}$ cm^2]
$H_2 + e \dashrightarrow H_2^+ + 2e$	15.4	1.1
$H_2 + e \dashrightarrow H^+ + H + 2e$	18.0	0.005
$H_2 + e \dashrightarrow H^+ + H^+ + 3e$	46	0.005
$H_2^+ + e \dashrightarrow H^+ + H + e$	12.4	3-16
$H_2 + e \dashrightarrow H + H + e$	8.5	0.6
$H_2^+ + e \dashrightarrow H + H$	0	100
$H + e \dashrightarrow H^+ + 2e$	13.5	0.65
$H + e \dashrightarrow H^{\cdot}(2P) + e$	10.2	0.7
$H^{\cdot} + e \dashrightarrow H^+ + 2e$	3.3	15
$H_2 + e \dashrightarrow H_2^{\cdot} + e$	10.3	0.2

Table 1: *Some reactions in hydrogen plasma*

random velocity) is often close to the neutral gas temperature. Non - thermal plasmas are frequently used in advanced technologies.

1.3 Low pressure plasmas

Nonthermal plasmas are generated in vacuum systems. The neutral pressure may vary from 10^{-5} *mbar* to 10^1 *mbar*, according to special requirements. The density of charged particles vary from 10^{13} m^{-3} to 10^{20} m^{-3}. The electron temperature is between 104 *K* (≈ 1 *eV*) and 10^6 K (≈ 100 *eV*). The temperature of positive ions is rarely higher than a few thousand Kelvin. The neutral gas temperature is generally close to the room temperature. The fact that the positive ion temperature is only about 1000 *K* does not mean the ions impacting surfaces are fairly thermal. They may be accelerated in a high potential fall near the surfaces, reaching the (drift) velocity of several 100000 *m/s* (kinetic energy of several *keV*). High energy ions are used in many plasma technologies, such as sputtering, etching, ion plating, etc.

2. Low pressure hydrogen plasma

In the previous section we have stated some characteristics of low pressure non - thermal plasmas. Now we shall pay our attention to hydrogen plasma. Reactions that take place at inelastic collisions between fast electrons and heavy particles (neutral and ionized molecules and atoms) are summarized in table 1.

An important fact is that the onset energy for dissociation is much smaller than the onset energy for the ionization of a hydrogen molecule. Taking into account that the high energy tail of the electron distribution function is exponential (assuming the Maxwell distribution function), one can expect that the density of atoms in hydrogen plasma exceeds the density of charged particles for several orders of magnitude. This is true for most low pressure hydrogen plasmas. The only exception is plasma in tokamaks, where the ECR (Electron Cyclotrone Resonance) generation leads to very high ionization rates.

2.1 Plasma generation

Low pressure hydrogen plasma may be generated in many ways. Here is a list of some.

- ☐ Glow discharge. A glass tube with two metal electrodes is filled with gas at the appropriate pressure. A rather high voltage (of the order of several 1000 *V*) is applied between the electrodes. This method of plasma generation is nowadays rarely used since there are quite a few disadvantages, such as intensive sputtering of the cathode, low density of charged particles, low degree of dissociation, poor stability of the discharge, positive ion oscillations (known as striations), and the requirement of the high potential needed for the ignition of the discharge.
- ☐ Hot cathode discharge is nice for experimental study of hydrogen plasma, but of little practical importance. The cathode is a hot filament made of thoriated tungsten. The potential between the cathode and the anode is usually less than 100 *V*. The main disadvantage is the requirement of low pressure conditions. The typical pressure is of the order of 10^{-3} *mbar* or less. At higher pressure the ignition and the sustaining of the discharge is difficult.
- ☐ RF discharges are most commonly used in plasma technologies and industrial applications. Plasma is generated in a wide range of neutral pressures between 10^{-5} *mbar* and 10^2 *mbar*. At low pressure the ignition of the discharge is limited by the diffusion and the recombination of charged particles on the walls of the discharge vessel. Thus, large vessels are required for the sustaining of the discharge. The high pressure limit is determined by the output power of the RF generator. By the use of powerful generators this type of plasma generation has been extended to

the high pressure regime. The development of the high pressure, inductively coupled plasma torches has been reported /2/. The frequency of the RF generator is usually 13.56 *MHz* or a close harmonious. Plasma is coupled either capacitively or inductively. In the case of capacitively coupled discharge, the RF potential is applied between planar electrodes, while inductively coupled discharges are generated by using a coil. Capacitively coupled plasmas are generated in cases high drift velocity of ions at the electrode is needed, while inductively coupled plasmas are applied in the cases plasma is only a source of chemically active (thermal) particles. The RF discharges are applied in several modes including the popular magnetron discharges.

☐ MW discharges. A nice way of avoiding the high pressure troubles of RF discharges is the use of microwave discharges. Plasma is generated in a resonant cavity. The wavelength of microwaves is of the order of a **cm**, and that is the typical dimension of the resonant cavity. The MW plasmas are used, for instance, in the production of diamond films.

☐ Other discharges. They include the ECR (Electron Cyclotrone Resonance) and laser discharges. Their application is limited by the high cost of the equipment.

☐ Combination of discharges. In all the cases of plasma generation mentioned above plasma parameters depend on the power of the source and cannot be varied independently. However, in practical application it is often required that one of plasma parameters is changed while the others remain constant. In these cases it is advisable to combine two or more different means of plasma generation. The RF discharges are, for instance, often combined with the glow discharge. The RF field causes a rather high ionization rate of gas, while the energy of positive ions impacting the cathode is rather well controlled by the DC potential of the glow discharge. The combination of the hot filament and the glow discharge is efficient in some applications as well /3/.

3. Plasma characterization

3.1 Plasma parameters

Starting at the definition that plasma is a mixture of three types of ideal gases, i. e. the neutral gas, the positive ion gas and the electron gas, the state of plasma is well described, if the densities and the temperatures of the three gases are known. Usually, the density of neutral gas is much higher than the density of charged particles, so it can be easily determined by a vacuummeter. The temperature of neutral gas is also easily determined by a thermometer. The temperature of positive ions is often close to the neutral gas temperature, and since its density is equal to the electron gas density, one often describes the state of plasma by knowing only two plasma parameters, i. e. the density and the temperature of electrons. These parameters may be determined by the use of different electrical probes.

3.2 Single electrical probes

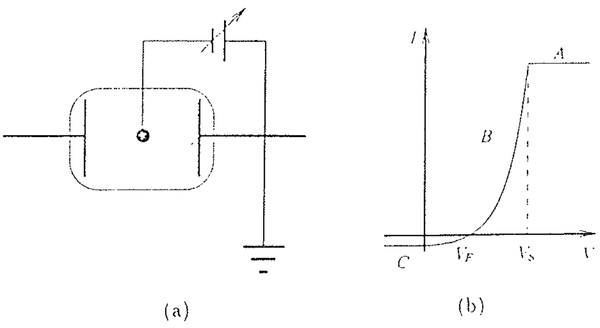

Fig. 2: Electrical circuit of a single probe (a) and its characteristic (b)

A single electrical probe is a small metal electrode immersed into plasma and connected to a variable voltage source, as shown in Fig. 2(a). The density and the temperature of electrons can be calculated from the probe characteristics, which is shown in Fig. 2(b).

When the probe is at the plasma potential, the net current on the probe is the sum of the electron random current and the positive ion random current. Since the positive ion current is much lower than the electron current it can be neglected. Speaking in terms of equations

$$I(V = V_S) = \frac{1}{4} N \overline{c_e} e_0 A_p \qquad (2)$$

Here, N is the electron density in plasma, $\overline{c_e}$ the mean random velocity in plasma and A_p the probe area. In the case electron distribution function is maxwellian, the current on the probe at the plasma potential is

$$I(V = V_S) = N e_0 A_p \sqrt{\frac{k T_e}{2 \pi m_e}} \qquad (3)$$

where T_e is the electron temperature and m_e its mass. The equation (3) gives the relation between the density and temperature of electrons. If we want to evaluate each of them, one must be determined separately. This may be done as follows. In section B on the characteristics (see fig. 2(b)) the electron current rises steeply with increasing potential. If the electron distribution function is maxwellian, this part of characteristics is exponential and we obtain

$$I(V_F < V < V_S) = I_0 \exp\left(\frac{e_0 (V_S - V)}{k T_e}\right) \qquad (4)$$

A plot of $\ln(I)$ *vs* V is linear with the slope of $-e_0/kT_e$, so we can calculate the electron temperature. Once T_e is known the density of electrons is calculated using the equation (3).

3.3 Catalytic probes

Single electrical probes are commonly used tools which give information on the plasma density and the electron temperature. However, they cannot determine other plasma parameters, the most important being the density of atomic hydrogen. This could have been determined only by the use of expensive detecting machines. Recently, however, we have developed a somehow changed probe, which gives straightforward data on the density of atomic hydrogen.

In order to make measurements of atomic hydrogen density, an electrical probe must be made as follows. The disc should be made of a metal with a high recombination coefficient for the reaction $H + H \rightarrow H_2$. Instead of the leading wire, a pair of thermocouple wires should be connected to the disc.

When a probe is immersed into the hydrogen plasma, the temperature of the disc rises substantially over the ambient temperature because of the energy dissipated on its surface due to the recombination of hydrogen atoms. At the recombination process, an amount of energy equal to the dissociation energy of a hydrogen molecule is released. The density of random flow of hydrogen atoms on the disc surface is

$$j = n\sqrt{\frac{kT}{2\pi m}} \tag{5}$$

where n is the density of atomic hydrogen in the vicinity of the probe, T is the temperature of the surrounding gas and m is the mass of a hydrogen atom. The energy dissipated on the disc in a unit time is

$$P = n\sqrt{\frac{kT}{8\pi m}}\,\gamma W_D A_p \tag{6}$$

Here, γ is the recombination coefficient /4/, W_D the dissociation energy of a hydrogen molecule and A_p the total area of the disc, i. e. $A_p = 2\pi r^2$.

Since the temperature of the surrounding gas is lower than the temperature of the probe, it is cooled through the processes of radiation and thermal conduction of the surrounding gas:

$$P_1 = (1 - a)\,\sigma\left(T_p^4 - T^4\right)A_p, \tag{7}$$

$$P_2 = \frac{3pk\,\alpha\left(T_p - T\right)A_p}{\sqrt{4\pi kTm}} \tag{8}$$

Here, a is the reflection coefficient, α the accommodation coefficient, T_p the temperature of the probe and p the total pressure. Cooling of the disc through the thermocouple wires has been neglected since the wires are very thin. In the thermal equilibrium the heating of the disc is equal to the cooling so we can write $P = P_1 + P_2$ or

$$n = \frac{(1-a)\,\sigma\left(T_p^4 - T^4\right)A_p}{\sqrt{\frac{kT}{8\pi m}}\,\gamma W_D A_p} + \frac{3pk\,\alpha\left(T_p - T\right)A_p}{\sqrt{4\pi kTm}\sqrt{\frac{kT}{8\pi m}}\,\gamma W_D A_p} \tag{9}$$

The density of atomic hydrogen in the vicinity of the probe can be calculated using the equation (9). However, the equation (9) includes not precisely determined constants, such as the reflection and accommodation coefficient, so it is better to determine the cooling experimentally. When the plasma is extinguished for a few seconds, the temperature of the disc decreases with time. The first derivation of the $T_p = T_p(t)$ curve is a measure of the disc cooling:

$$P_1 + P_2 = M c_p \frac{dT}{dt}. \tag{10}$$

Here, M is the mass of the disc and c_p its specific thermal capacity. The thermal equilibrium equation is simplified:

$$n = \frac{M c_p \frac{dT}{dt}}{\sqrt{\frac{kT}{8\pi m}}\,\gamma W_D A_p}. \tag{11}$$

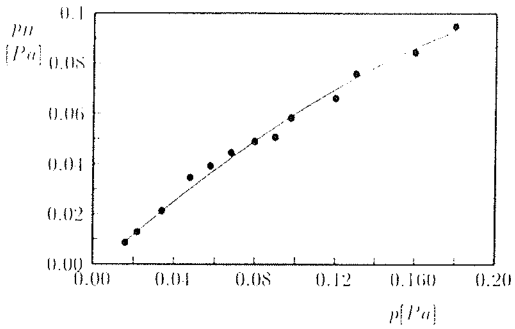

Fig. 3: *Partial pressure of atomic hydrogen vs total pressure.*

The density of atomic hydrogen is thus determined as follows: When a probe is immersed into the hydrogen plasma, the temperature rises until it reaches the constant value at the thermal equilibrium. This takes between one and several hundreds of seconds, depending on the density of atomic hydrogen and the mass of the disc. When the thermal equilibrium is reached, the plasma is extinguished for a few seconds and the measurement of the $T_p = T_p(t)$ curve is performed. The density of atomic hydrogen is then calculated using the equation (11).

The probes have been used to determine the density of hydrogen atoms in the reaction tube of a high vacuum system which we use for studies on the reduction of metal oxide thin layers at low temperature /5/. The reaction tube was connected to an atomic hydrogen source, which is low pressure inductively coupled RF hydrogen plasma. The probe was a nickel disc with the radius of 1*mm* connected to thermocouple wires chromel - alumel with the radius of 0.012 *mm*. The density of atomic hydrogen was measured at different total pressures between 0.02 *Pa* and 0.2 *Pa*. The result is shown in Fig. 1. It is evident that the degree of dissociation of hydrogen remains constant in this pressure range having the value of about 60%.

4. Application of hydrogen plasma

Besides the use of hydrogen plasma for studies in controlled fusion, its most important application is in discharge cleaning of oxidized metal surfaces. Atomic hydrogen, which is produced in plasma, readily reacts with impurities chemically bonded in surfaces. By these reactions impurities such as oxides, chlorides, sulphides can be completely removed from the surface layer of samples treated by plasma. A very nice example of the efficiency of hydrogen plasma treatment is the discharge cleaning of old silver coins. Fig. 4 represents the composition of the surface layer of a coin before (a) and after (b) the treatment.

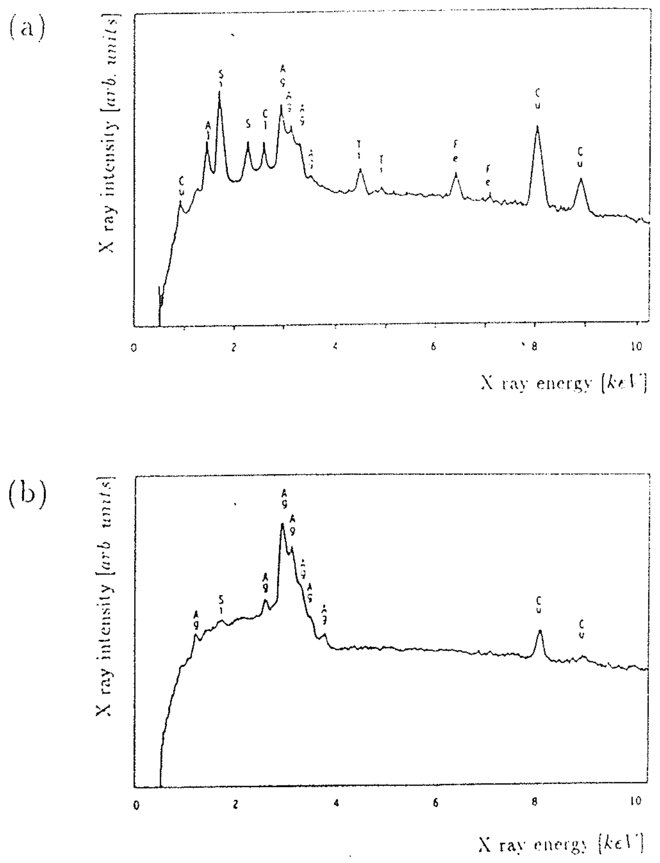

Fig. 4: Composition of the surface layer of a silver coin before (a) and after (b) hydrogen plasma treatment.

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