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Control of reactive plasmas: adventure to improve and to expand plasma processing

Ryohei ITATANI

Department of Electronics, Kyoto University, Yoshida-hommachi, Sakyo-ku 606, Kyoto, Japan

Abstract The concept on control of reactive plasmas is discussed and methods to change electron temperature and to separate reactions in different stages in plasmas are presented by introducing activities on control of reactive plasmas in Japan. Efforts to develop new plasma reactors are also mentioned.

1. INTRODUCTION

There is a long history that low pressure glow discharge plasmas have been used to manufacture solid state devices and many kinds of functional thin films. Now, plasma processing is one of key technology indispensable to material processing and device manufacturing. More suitable plasmas are still strongly required for ultra fine processing with no damage to ULSI manufacturing, and for highly uniform and reliable processing of large area to display device production.

Requirement to plasma process is not satisfied at present by using plasmas as they are, and people feel necessity to control plasmas as they wish. In order to realize more reliable, reproducible, precise and fine processing with plasmas, our task is to establish the systematic way to control reaction in a plasma. The subject to achieve this are: (a)to control electron energy distribution to improve the selectivity of reaction, (b)to control ion velocity falling to the solid surface to reduce damage and undercut, (c)to separate simultaneous reactions into simple ones to reduce complexity, (d)to reduce the degree of freedom by increasing number of method to control plasmas, (e)to reduce the influence of the wall, (f)to realize highly uniform processing in large areas, and (g)to establish scaling law for reactor design.

In order to respond to above scientific and social request, organized study on control of reactive plasmas has started in 1988 as three years project with the mission to get quantitative understanding and to establish control methods of reactive plasmas, with the support of Grant-in-Aid for Scientific Research in Priority Areas of Japanese Ministry of Education, Science and Culture.

Our study program is as follows: (1) study of elementary reaction in a plasma and on a surface and compilation of cross section data,
(2) development of diagnostic method for non-emissive species and for electric field distribution, (3)analysis of reactive plasmas and modeling, and (4)study on new control methods and new reactor concept.

Here, some results of topics(4) obtained through the study mentioned above are mainly introduced as well as those done in industries in Japan.

2. GENERAL DISCUSSION TO CONTROL REACTIVE PLASMAS

There are three categories of reactions in plasma reactors; the first stage of reaction is decomposition of stable molecules into radicals by inelastic collision of electrons, the second stage reaction is inelastic collision between radicals and particles of any kind, resulting in modification of the radicals generated by the first stage reaction, and the third one takes place in the boundary layer between the plasma and the surface on the substrate, where radicals and ions fall on the surface and desired reactions occur on it. These reactions take place simultaneously in plasma reactors, and this causes complexity of phenomena in plasmas.

For both to understand processing plasmas and to achieve well-controlled plasmas, it is necessary to find out the relation between control variables and plasma parameters, and to control contribution of each category of reaction mentioned above separately. We have to note that influence of wall to plasmas is quite strong because balance of particle and electric charge are mainly governed by wall conditions.

2.1 Characterization of plasmas by time constant and frequency

Plasma behaviors are described with a set of transport equations, consisting of two terms, one is a production term or a source term and the other is a decaying one and are in the form of $dA/dt=S-A/\tau_A$, where τ_A is time constant of quantity A.

The surface reactions are characterized with the sticking coefficient, defined as the ratio of numbers of particles attaching to hitting. The particles need some time to find out the sites where they settle on the surface or to form networks of a solid. Detail of reactions on the surfaces is quite different from those in plasmas. However, by introducing both the concept of effective surface and of time constant, unified treatment of controlling plasma becomes possible. Energy loss time of electron is very sensitive to concentration of impurity having lower potential of excitation.

As well known, behaviors of dynamical system are easily predicted by observing the time constants in each equation. In the dynamic state, plasma parameters can change freely from the steady state values discussed above. From the equation of continuity, when $dn/dt>0$, $W_e>W_edc$, and vise versa, where W_e is electron kinetic energy. Consider the current density in plasmas j is increased suddenly. As $j=en_eu$, and the time constant of u and W_e is much smaller than that of n_e, then u and W_e can increase faster than n_e, and higher W_e is observed during transient state of density increase[2)3)].

At the view point of chemical reaction, steady states hide the difference of the time constant and make it difficult to observe the phenomenon of interest of small time constant. On the contrary, in the case of transient state, the difference of time constant becomes clear and the reaction having small time constant can be observed separately from the one having large time constant.

The frequency of the power source also gives a plasma appreciable effects through change of ω/ν[4)]. In addition, plasmas have some resonance frequencies at which electron or ion receive energy selectively. ECR is suitable to make high electron energy low pressure plasma with cold ions, because the magnetic field provides cyclotron motion of electron and enhances ionization and wave field energy transfers resonantly to electrons only.

2.2 Effect of condition of vessel and electrode to plasmas

As mentioned above, dimension or size of a plasma reactor is one of the key parameters to govern reactivity of the plasma. This is expressed as the surface to volume ratio of the plasma S/V (=1/Λ). There, S and V are corresponding, respectively, to the ability of a plasma reactor for loss and production of particles of interest.

Condition of the wall determines the boundary condition of the plasma, that is, charge and particle balance at the wall[5)]. This means, as example, that the surface emitting electron has smaller effective area than the real one and that even a little change of S for impurity may induce drastic change of We.

The control of incident energy of ions to surfaces is achieved easily by changing bias voltage applied to the substrate or to the second plasma generated independently of the first plasma. Ion flux from a plasma is a function of electron energy. Thus, control of electron energy is most important to control reaction in the reactive plasma for both flux of radical and ion.

3. EXAMPLES ON CONTROL OF REACTIVE PLASMAS

Electron temperature Te is the most important parameter in reactive plasmas and normally fixed by fixing gas pressure in a steady state plasma because it is the function of gas pressure and of the dimension of the plasma vessel. Reaction rates in plasmas are a function of electron density, electron temperature and gas pressure. To change Te arbitrarily in fixed gas pressure is one of challenging topics.

3.1 Control of electron temperature

It was demonstrated that Te can be continuously controlled between the lower value of 0.4 eV and the normal value of 4 eV by changing cathode conditions[6)]. This means that change of boundary conditions of a plasma produces inhomogeneity of the plasma and results in change of Te as shown in Fig.1. It was also demonstrated to produce localized higher Te by the use of ECR zone in the pressure range of 0.1 Pa[7)], and also better performance for etching in that condition[8)]. Modulation of the electric power is the most powerful method to control Te and this is demonstrated with DC[9)] and microwave[10)]. Figure 2 shows the change of W_e as the change of luminous color of Ne-Hg discharge.

3.2 Control of reactions through difference of relaxation time

In reactive plasmas, there are many physical processes and chemical reactions, and each has each time constant or each relaxation time which means the characteristic speed of the process or reaction. Modulation of electric power enhances differences in time constants and may lead to new methods to control processes.

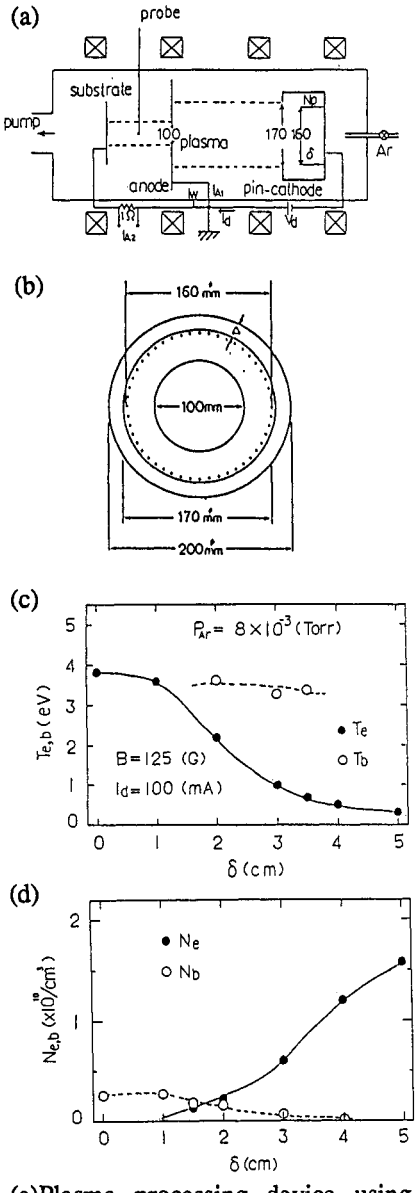


Fig.1 (a)Plasma processing device using pin-hollow cathode. (b)Pin-hollow cathode. (c)Dependence of bulk electron temperature T_e and beam electron temperature T_b on the pin length δ. (d)bulk electron density n_e and beam electron density n_b.

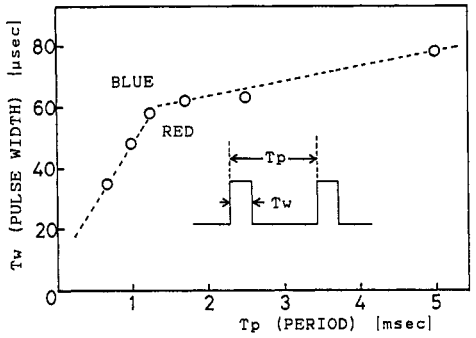


Fig.2 Change of the luminous color of Ne-Hg discharge by pulse modulated microwave.

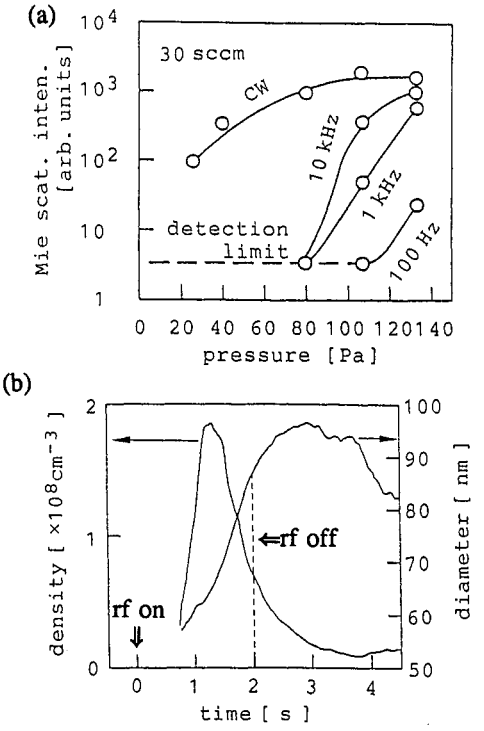
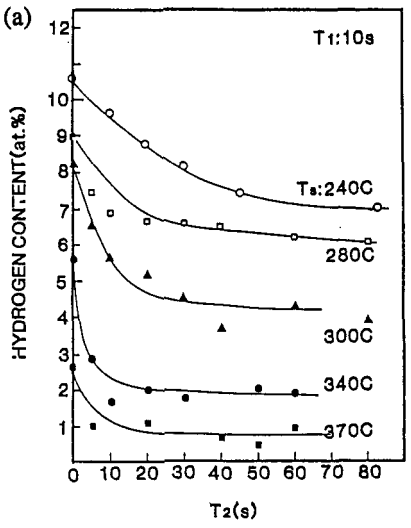


Fig.3 (a)Pressure dependence of Mie scattering intensity. (b)Temporal evolutions of particle size and density. (f_M=1kHz D=40% 10%SiH_4 30ccm 53Pa rf power 40W)

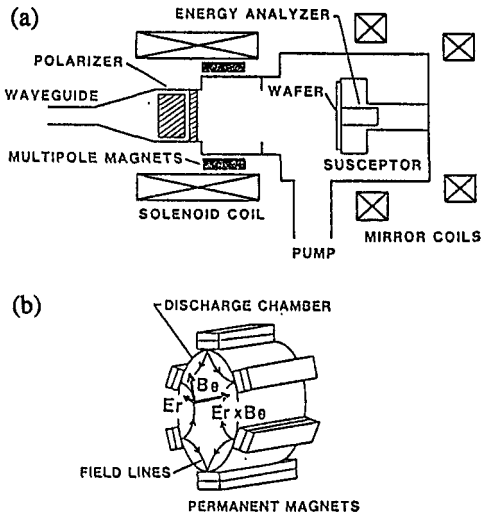
Low frequency discharge plasmas up to 100kHz have higher Te than rf discharge plasmas, because intermittent discharge takes place at lower frequency and it changes to CW discharge at rf[11]. The modulation is effective to microwave plasmas[10]. Powder formation is almost perfectly suppressed in the SiH_4 plasma produced by pulse modulated rf discharge in spite of high speed deposition[12]. Observation by Mie scattering are shown in Fig.3. The same method is applied successfully to SiC deposition[13]. In film formation on a substrate, a characteristic time exists[14] as shown in Fig.4. Systematizing above leads to a new process of high flexibility by using differences of time constants[15].

3.3 Control by hybrid technique

For the process to produce multi-component materials such as SiC and High Tc super conducting material, it is impossible with only one plasma to change composition of the compound arbitrary, even if the composition of raw material is carefully adjusted. However, it is easily achieved to produce $Si_{1-x}C_x$ of arbitrary x by using rf for silane and microwave for ethyrane respectively[16].



CH versus T_2 (Data from "SWE")



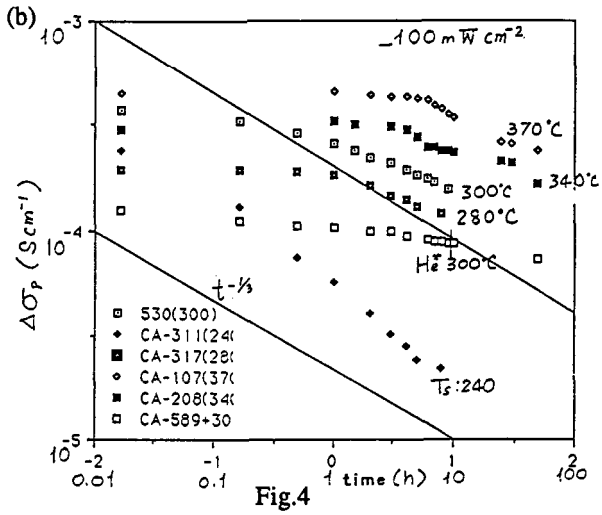


Fig.4

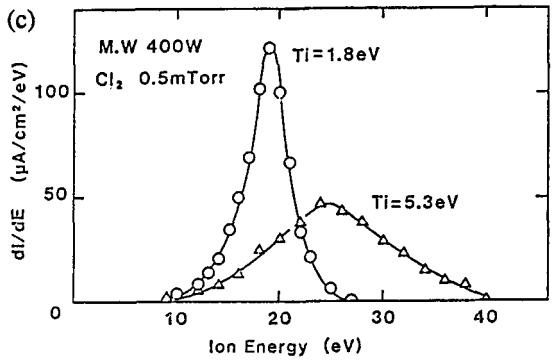


Fig.5

To reduce spread of ion velocity onto substrates in etching plasmas is great important to get fine etching and was achieved by superposition of multipole magnetic field to a mirror type plasma[17]. Fig.5 shows the remarkable reduction of ion energy spread.

The hybrid plasma using two rf power sources of different frequencies demonstrated for amorphous Si film deposition, the lower frequency rf power acting to modify ion impinging energy onto the film[18].

3.4 Large, high density and uniform plasma production with ECR

To generate the plasma of large diameter, the launching system was developed by modifying slotted antenna and the plasma of 40 cm in diameter was produced[20]. To generate the high density plasma, the electron cyclotron wave is effective, propagating from stronger magnetic field toward ECR zone parallel to magnetic lines of force, because of no cutoff in the plasma of any density according to the theory of plasma waves. Experimental evidences on wave propagation, and absorption are demonstrated in comparison with theory and density as large as 400 times cutoff density to 2.45GHz are achieved[21]. Figure 6 shows the change of W_e by changing W as the result of Landau damping. Two dimensional simulation for ECR plasma including wave propagation and ionization has started[22].

ECR plasmas using permanent magnets are developed and it was proved that the theory of plasma waves is valid qualitatively even in the field the characteristic length of variation of which is shorter than wave length as shown in Fig.7[20] and Fig.8[23].

The shape of a plasma can be change almost arbitrarily by changing the shape of magnetic field and of ECR zone and by adjusting a launching system[24]. With these techniques the plasma of large area spreading in perpendicular to the magnetic lines of force is generated.

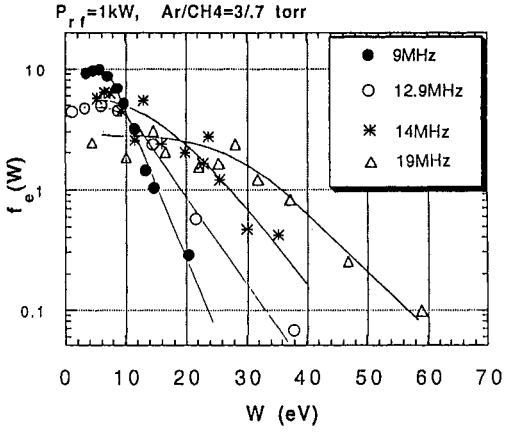
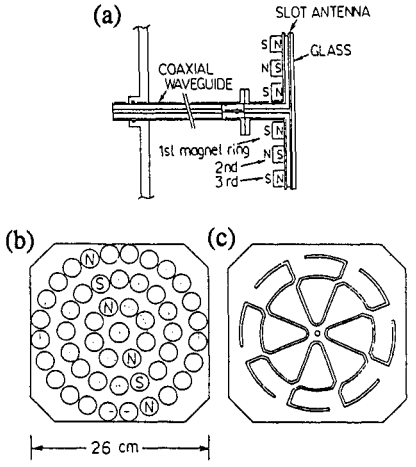


Fig.6 Frequency dependence of electron energy distribution in Ar/CH_4 plasma. P(Ar)=0.4Pa, $P(CH_4)$=0.09, P_{rf}=1kW



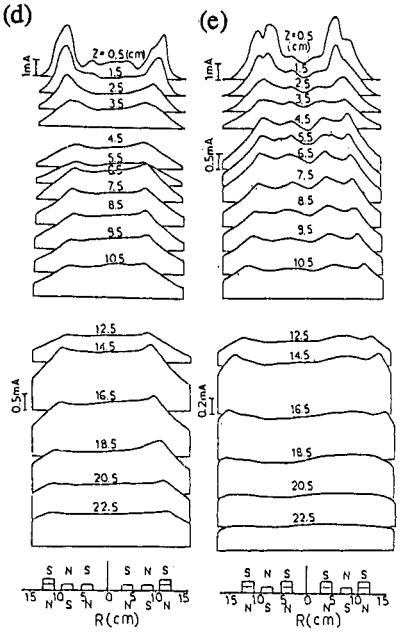


Fig.7 (a) structure of the flat ECR antenna (b) location of permanent magnets (c) configuration of slots (d) and (e) radial distributions of electron saturation currents and the location of magnets.

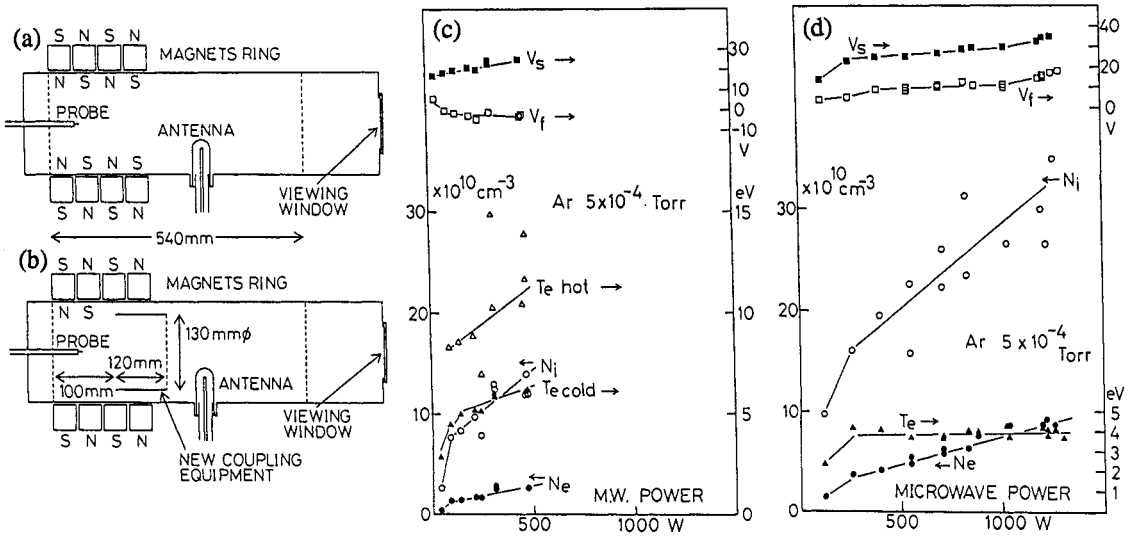


Fig.8 (a) Experimental setting and (b) structure of the new coupling equipment: (c) and (d) microwave power dependence of the plasma parameters produced with setting (a) and (b), respectively.

4. CONCLUDING REMARK

Studies on plasmas to expand possibilities of processes leading to highly refined process in future is on going in parallel with efforts to understand currently used plasmas. In this paper, a part on such efforts has been described. Since the system of equations to describe plasmas is definite, accumulation of basic data of elementary reaction and of knowledge on boundary condition at the interface will lead to the goal of controlling reactive plasmas in the next ten years.

However, as number of kind of material is infinite, effort to seek the most suitable process for each material will continue forever. Plasma processing is just a simulation of creation of the universe and we can have large pleasant dreams to create,to modify,to grow everything existing in the universe by plasma processing.

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