Plasma diagnostics in plasma processing for nanotechnology and nanolevel chemistry

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Abstract

The author reviews the role of various plasma diagnostics in plasma processing for nanotechnology, and points out some essential methods of spectroscopic methods to diagnose plasmas for nanoprocessing. Two experimental examples are discussed between the characteristics of nanomaterials and plasma parameters. One is measurement of rotation temperature in processing of carbon nanotube. The other is that of vibrational temperature in surface nitriding of titanium by nitrogen plasma processing. We summarize what to measure and how to measure them from the technical viewpoint of plasma diagnostics.

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1. Introduction

Generally, nanoparticles as well as materials with nanosize structures are frequently prepared by plasma processing, and consequently, the precise measurement of the plasmas for processing is a crucial issue to control the characteristics of the objective materials. For example, historically, one method of earliest preparation of C₆₀ was contact arc discharge [1]. Nowadays, the arc discharge is already established as an industrial standard method to generate fullerenes. In addition, recently special interest in the plasma processing for nanotechnology has been aroused for the processing of carbon nanotubes (CNTs) by plasma CVD processing [2]. It should also be added that the nanometer-level surface modification by plasma technology has also been eagerly studied concerning super hardening or innovative functionalization of material surfaces [3]. In such industrial applications of plasma technology, control of characteristics of prepared materials is a crucial issue, which is accomplished not only by characterization of prepared materials but also by precise measurement of the processing plasma. The characteristics of prepared materials strongly depend upon the plasma parameters during the processing. Therefore, the diagnostics of the processing plasma is quite an important technology in the material processing, particularly in nanotechnology and in nanolevel chemistry.

In the present review, we introduce how essential the plasma diagnostics is in the control of prepared nanomaterials by the plasma processing. Desirable conditions of plasmas are discussed for each processing, such as preparation for CNTs [4], and surface modifications of various substrates to nanometer depths [5]. Recently, the importance of the vibrational populations of molecular species in the plasma is frequently discussed in addition to the rotational temperature that is generally considered to be an approximate value of gas temperature. Experimental examples are discussed between the characteristics of nanomaterials and plasma parameters.

2. Preparation of CNTs and relationship with plasma parameters

Nozaki et al. [4] reported CNT preparation by atmospheric pressure glow discharge (APG) process. They utilized quartz plate coated with nickel thin film of 20 nm as a substrate. On the course of their experiment, they found...
that two different discharge modes. One mode is what they
call an APG, a special discharge mode of dielectric barrier
discharge (DBD). The other is a typical DBD where
streamers are predominant in the discharge. According
to their definition, the APG is spatially uniform, and in this
respect, it is different from the typical, i.e. streamer-like
DBD that is a group of streamers of micrometer order [6].
In order to obtain APG instead of the typical DBD, it is
already found that Penning ionization or cumulative ioniza-
tion of ions should be the essential process for ionization.
Nozaki et al. [4] chose helium, whose metastable levels are
energetic enough to ionize hydrocarbons or hydrogen by
Penning mechanism, as buffer gas media to generate APG,
and discuss appropriate conditions for preparation of CNTs.
The SEM photograph as well as Raman analysis revealed
that the APG successfully prepared CNTs (Fig. 1(a)),
whereas the streamer-like DBD (Fig. 1(b)) did not. The
diameter of the CNTs prepared by APG ranges 40–50 nm
and their density $10^9–10^{10} \text{ cm}^{-2}$. Meanwhile, Fig. 1(b)
shows that DBD discharge did not form CNTs, but particle-
like carbon with random structure covered the substrate.

They studied the difference in the plasma parameters of
both discharge modes, particularly in the average gas
temperature. In order to elucidate the difference in the gas
temperature distribution between the electrodes, they
carried out optical emission spectroscopy (OES) measure-
ment for the electronic transition ($A^2\Delta-X^2\Pi, v'=v''=0$) of
CH radical, and evaluated the rotational temperature, which
gives an approximate value of the gas temperature of the
plasma due to the short relaxation time of rotational and
translational motion [6]. They discussed the precise value of
average increase in the gas temperature of the plasma [7].

Fig. 2 shows the evaluated temperature increase in the
plasma reactor [8]. They found the remarkable difference in
the gas temperature distribution between the APG
(Fig. 2(a)) and the DBD (Fig. 2(b)). When the discharge
power was increased in the APG discharge, even streamers

![Image](image_url)

Fig. 1. SEM photographs of materials on the substrate prepared by
discharge: (a) CNTs by APG and (b) carbon clusters with random structure
dy DBD.

![Image](image_url)

Fig. 2. Measured gas temperature in the plasma reactor. (a) APG and
(b) DBD. The horizontal axis shows the distance from the dielectric plate
that covers the ground electrode. That is, the position $B=1 \text{ mm}$
corresponds to the substrate on which CNT is grown.
were also observed. Therefore, practically, the discharge power should be lower to keep APG. Since the negative glow was limited to the close position to the electrode in the APG, the hot spot was also restricted to its vicinity, and the average gas temperature of the plasma bulk is generally lower than that of DBD. The results of OES measurement showed that the bulk plasma region of the DBD had high gas temperature. Consequently, CNTs may be grown in the gas phase of the plasma, not on the surface of the substrate. Then, after they have grown up in the bulk plasma, the particles may accumulate on the substrate in the DBD plasma processing.

On the other hand, in the APG processing, the high gas temperature region was restricted near the substrate due to the negative glow. Consequently, the active species that can react with catalytic nickel nanoparticles are generated just near the surface due to the gas temperature distribution of the APG. The desirable process to the formation of CNTs is realized in the APG, which was confirmed by the gas temperature measurement by OES. This shows how essential the measurement of the gas temperature is in the plasma processing for nanotechnology.

3. Surface modification to several hundreds of nanometer depth by plasma processing and its diagnostics

Modern plasma technology is widely applied to material industry where substrates have microstructures, at least, several tens of nanometers order. For example, we always apply plasma etching of SiO₂ for fabrication of LSI. The width of the trench on the SiO₂ is reduced to less than 100 nm for the next generation, say in 2012, and as a result, the precise control of plasmas is essential in the microelectronics [9]. Another example is surface modification of various functional metal surfaces, where the reactions to several tens of nanometers from the surface are essential to improve the characteristics of the substrate materials. For instance, Gicquel et al. [10] studied the relationship between plasma and nitrides in nitriding of titanium. They showed that the discharge condition drastically changed the nitrogen concentration to the several hundreds of nanometer depth. We need plasma parameters to elucidate the mechanisms of surface modification. Although similar experimental studies have been reported for these ten years, we still need experimental study to understand the relationship between the characteristics of the modified surfaces of the substrate processed and those of the plasmas.

From above points of view, the present author has been studying plasma nitriding process of titanium. In this section, we will introduce some of our experimental study of plasma nitriding of titanium by two kinds of nitrogen plasma source [5]. One is a microwave discharge nitrogen plasma, and the other is an arc-heated magnetically trapped expanding plasma jet. The former has high vibrational temperature and is considered to have a considerable amount of vibrationally excited nitrogen molecule. The latter is considered to have a higher dissociation degree of nitrogen molecule.

Fig. 3 shows a relationship between the vibrational temperature and the intensity of the IR absorption, which is approximately considered as nitriding degree, of the irradiated titanium of the microwave discharge nitrogen plasma. A strong positive correlation was found between them, whilst the rotational temperature, the electron temperature and density had little correlation with the nitriding degree. It should be noted that the XRD pattern of the irradiated titanium remains that of Ti metal (α phase) [10]. That is, it consists of an interstitial solid solution of nitrogen in the closed-packed hexagonal lattice of titanium. It is also found that the target temperature increased due to energy transfer from the highly vibrationally excited nitrogen molecules to the target, and the high temperature of the target results in the higher degree of nitriding. From the microscopic point of view, nitrogen molecules must be dissociated into atoms, or at least, to form some kind of activated state with the Ti-substrate on the surface in order to form the solid solution, since the nitrogen should take the form of atoms, not molecules, in titanium. It is considered that not only the higher temperature of the Ti-substrate but also the higher vibrational temperature of the nitrogen molecules is effective to the formation of the activated state to form the solid solution of atomic nitrogen.

Concerning the irradiation of nitrogen arc-jet, the surface density of nitrogen atoms is less affected by the target temperature. The low correlation between them can be interpreted as follows. If the nitrogen plasma has a large dissociation degree of molecular nitrogen and contains...
a large number of atomic nitrogen radicals, the nitrogen atoms can diffuse into the Ti-substrate, without forming activated compound states or surface dissociation process. Consequently, it is considered that the dependence of the nitriding degree on the substrate temperature becomes less remarkable for the arc-jet processing than for the microwave plasma processing. Further experimental study is necessary on the diagnostics of number density of nitrogen atoms in the arc-jet plasma. In addition, theoretical study like molecular dynamic simulation may be necessary to elucidate the different mechanism by these two plasmas.

**4. What to measure and how to measure them in plasma processing for nanotechnology and nanolevel chemistry**

In this section, we summarize what to measure and how to measure them as plasma parameters in the plasma processing for nanotechnology. As two examples described so far showed concretely, in order to understand plasma-chemical reactions and mechanisms of nanomaterial formation in the plasma, we should understand the characteristics of the plasmas for processing in nanotechnology and nanolevel chemistry. In particular, we should understand the interactions between plasma-gas phase and the substrate. Consequently, we naturally need gas temperature distribution in the plasma to control the quality of CNTs by APG discharge, in particular, by avoiding transition to DBD. We also understand the vibrational temperature to understand the mechanism of surface nitriding by nitrogen plasma processing.

In addition, we need to know density of radicals in the plasma to control quality of nanomaterials by the processing. From the more fundamental viewpoint, we should understand how the reactive species are generated in the plasma to determine their densities. Therefore, more fundamental plasma parameters, such as electron temperature and density, and the electron energy distribution function (EEDF), should also be measured for precise control of quality of nanomaterials prepared.

When we measure the plasma temperatures, we must realize that the processing plasmas are generally in a state of non-equilibrium. We can define many kinds of temperatures according to kinetics of particles as well as to population distribution of excited states.

As fundamental plasma parameters, we should measure electron temperature \( T_e \) and electron density \( n_e \) in the plasmas. For this purpose, Langmuir probe is useful and convenient. There are many theories and textbooks where practical usage of the probes is explained \[11\]. We can also measure EEDF of the plasma by the second derivative of the \( V-I \) characteristics of the single probe \[11\]. Generally, the EEDF of process plasmas are not Maxwellian. Many plasmas are categorized into two temperature plasmas with high electron energy tail, which is quite essential for plasma chemistry since it can generate reactive radicals more.

However, we should be careful for the usage of probe diagnostics for plasma chemistry since the processing is often carried out at atmospheric pressure or subatmospheric pressure, where the theory of Langmuir probe is not valid. At this time, we should choose other methods to measure \( T_e \) or \( n_e \), to say nothing of EEDF. The author makes an attempt to measure them by OES together with the interpretation of the excited states populations by collisional radiative model, which describes the number densities of excited states as functions of \( T_e \) and \( n_e \) \[12\]. Of course, laser assisted measurement is also a powerful tool to obtain \( T_e, n_e \) and even EEDF \[13\].

Next important parameters for the plasma processing are vibrational temperature \( T_v \) and rotational temperature \( T_r \). Fig. 4 shows an example of the 2nd positive system of \( \text{N}_2 \) molecule, which is often applied to the analysis of \( T_e \) and \( T_r \) \[14\]. They are easily measured by OES if the Franck–Condon factors and HönL–London factors are known, respectively, when we treat plasmas of molecular species. Rotational temperature is obtained by OES even when the spectroscopic devices do not have sufficient resolution to separate each line corresponding to a different transition. If we calculate the spectra as functions of \( T_r \) with the instrumental width of the spectroscopic equipment, we can determine \( T_r \) by comparison of the calculated spectra with experimentally measured ones \[15\].

Mass spectrometer is useful for the detection and identification of reactive radicals, although it leaves a little to be desired since the component may be affected during

![Fig. 4. An example of second positive band spectra calculated as functions of rotational temperature with vibrational temperature 0.8 eV. Even when the spectral resolution is not sufficient enough to separate each line, we can estimate the rotational temperature by comparison of experimentally observed spectra with calculated ones.](image)
the sampling to the mass analysis chamber [16]. In order to avoid these perturbation, optical absorption spectroscopy, particularly in VUV range, or laser induced fluorescence spectroscopy is useful. Technical details should be referred to in Ref. [14] due to page limitation. When it becomes difficult to apply lasers or VUV absorption spectroscopy, a simple OES by actinometry is convenient, since it requires just passive spectroscopic equipment [14].

5. Conclusion

In the present review paper, the author reviewed the role of some plasma diagnostics in plasma processing for nanotechnology, and pointed out essentiality of spectroscopic measurement of plasmas. Gas temperature or vibrational temperature, which are measured by OES, often plays an important role in various plasma processing of nanotechnology. When we discuss the mechanisms of nanotechnology or nanolevel chemistry by plasma processing, the diagnostics of the plasma and the interpretation of them are quite essential to understand the mechanism and to control the nanoprocessing optimum, since various nanoparticles are produced through the non-equilibrium reactions in plasma phase or at the interfaces between plasmas and substrates.

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