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Relation of the polymeric ion species in plasma to the hardness of a-C:H film made by PSII&D

Noriaki Ikenaga [a],*, Kouhei Miyamoto [b], Shintaro Hayashi [b], Yoichi Kishi [a], Zenjiro Yajima [a], Noriyuki Sakudo [a]

[a] Research Laboratory for Integrated Technological Systems, Kanazawa Institute of Technology, 3–1 Yatsukaho, Hakusan, Ishikawa 924-0838, Japan
[b] Advanced Materials Science Research and Development Center, Kanazawa Institute of Technology, 3–1 Yatsukaho, Hakusan, Ishikawa 924-0838, Japan

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ABSTRACT

The amorphous carbon (a-C:H) films formed by plasma source ion implantation and deposition (PSII&D) have expanded the tribological properties. Especially, the hardness can be widely changed by adequately selecting RF power, pulse bias voltage, gas species and gas pressure. Previously, we reported that a-C:H film hardness depended on the electron temperature in C_2H_2 plasma which was ignited with pulsed RF power, and that the hardness was in inverse proportion to the electron temperature in the range of less than 2.5 eV. We have discovered that the film hardness is, in some cases, changing even if the electron temperature is constant. This suggests that there are some new factors to determine the film hardness besides the electron temperature in the plasma. In this study, we employ a quadrupole mass spectrometer to measure the intensity of each polymeric ion in C_2H_2. The film hardness is determined by the synergy of the polymeric ion abundances and ion irradiation.

1. Introduction

The amorphous carbon (a-C:H) films made by plasma source ion implantation and deposition (PSII&D) have many useful tribological properties. The films have been used for industrial applications to sliding parts and dies, since their friction coefficients are very low. And the films also have a high degree of hardness that can be realized by adequately changing RF power, pulse bias voltage, gas species and gas pressure for PSII&D.

Previously, we developed a new RF electrode for PSII&D plasma, i.e. a kind of hollow cathode which was capacitively coupled to a power source. The electron temperature and the density of the plasma could be independently controlled [1]. This new electrode showed availability to generate spatially uniform plasma throughout the process chamber. This plasma source was very useful for studying the effect of plasma parameters on film characteristics. Moreover, we found that the pulse-modulation of RF power was effective for changing each parameter freely. Thus, the electron temperature and the plasma density were independently controlled by adequately combining pulse repetition frequency with pulse duty. From the results of the experiment using this new electrode, we reported that hardness of a-C:H films deposited with C_2H_2 plasma was inversely proportional to the electron temperature in the range of less than 2.5 eV under the condition of constant plasma density [2]. However, it was quite unlikely to consider that the electrons colliding with the film had directly influenced the film hardness, since the value of the electron temperature was so low. So we suggest that there may be some other factors that influence the film hardness besides the electron temperature of C_2H_2 plasma. In this paper, we employ a quadrupole mass spectrometer to measure the ion spectra under various plasma conditions except the electron temperature being kept constant. We also discuss the correlation between the electron temperature and some specific ion-species abundance in plasma. Thus, the mechanism how the electron temperature of plasma affects the film hardness is speculated.

2. Experimental

2.1. Apparatus

The experimental apparatus for a-C:H film deposition as shown in Fig. 1 consists of a cylindrical vacuum chamber 500 mm in diameter and 800 mm in length, an RF power supply (13.56 MHz, 750 W), a negative high-voltage pulse power supply (−10 kV, 1 kHz, duty 10%) for sample bias, a double probe measurement system (JE Plasma Consult GMbH, L2P) for plasma diagnostics and a quadrupole mass spectrometer (ULVAC, MSQ400) for obtaining ion spectra of C_2H_2 plasma. The edge of the double probe or the orifice of the quadrupole is positioned very close to the substrate holder or in the place of the holder, as shown in Fig. 2 (b) or (c), respectively. The new electrode

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* Corresponding author. Tel.: +81 76 274 8272; fax: +81 76 274 8273.
E-mail address: n-ikenaga@neptune.kanazawa-it.ac.jp (N. Ikenaga).

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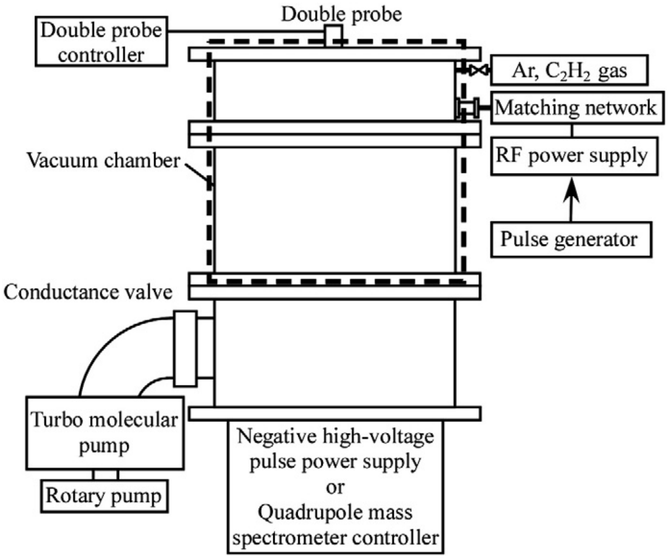

Fig. 1. Schematic drawing of the experimental apparatus for a-C:H film deposition.

for plasma generation is installed between the gas feed port and the substrate holder. The a-C:H films are formed with the setting in Fig. 2 (a) on Si substrate (001) at the pressure of 1 Pa, which is adjusted by controlling the conductance valve so as to keep the C_2H_2 gas flow at 80 sccm. The ionization chamber which a standard quadrupole mass spectrometer is equipped with is eliminated for this experiment in order to measure only the ion species originally existing in C_2H_2 plasma. The RF power is pulse-modulated in order to determine the electron temperature and the plasma density independently. The repetition frequency for the pulse can be changed from 0.1 to 100 kHz and the pulse duty from 20 to 80%. The relative values to the negative high-voltage pulse bias are fixed at −2 kV of peak voltage, 1 kHz of repetition frequency and 10% of pulse duty.

2.2. Measurements of film properties and plasma parameters

The film hardness is measured with the nano indentation hardness tester (ELIONIX, ENT1040) using a load of 0.2 mN with a Berkovich indenter at a loading speed of 0.02 mN/s. The hardness value plotted in a figure is the average of 10 measured values and the error bar represents the difference between the maximum and the minimum. The film thickness is measured with a surface profilometry (Dektak3, ULVAC) from the step height at the edge of the masked substrate. The measurements of plasma parameters, i.e. plasma density and electron temperature, are carried out with a double probe measurement system (Fig. 2(b)). The ion species abundances in C_2H_2 plasma are measured with a quadrupole mass spectrometer (QMS) equipped with a secondary electron multiplier (SEM) (Fig. 2(c)). Mass number can be scanned from 1 to 80 atomic mass unit (AMU), and the mass resolution of half height width is 1 AMU with ion current of more than 10^{-11}A.

3. Conditions for film formation

The source gas used for a-C:H film deposition is C_2H_2. The film thickness for this study is unified into 250 nm, which is larger than the indentation depth for hardness measurement so as to avoid the influence of substrate material on the measured hardness [4]. Two kinds of RF power, the continuous and the pulse-modulated, are used for plasma generation, and the film properties deposited with the different RF powers are compared and investigated.

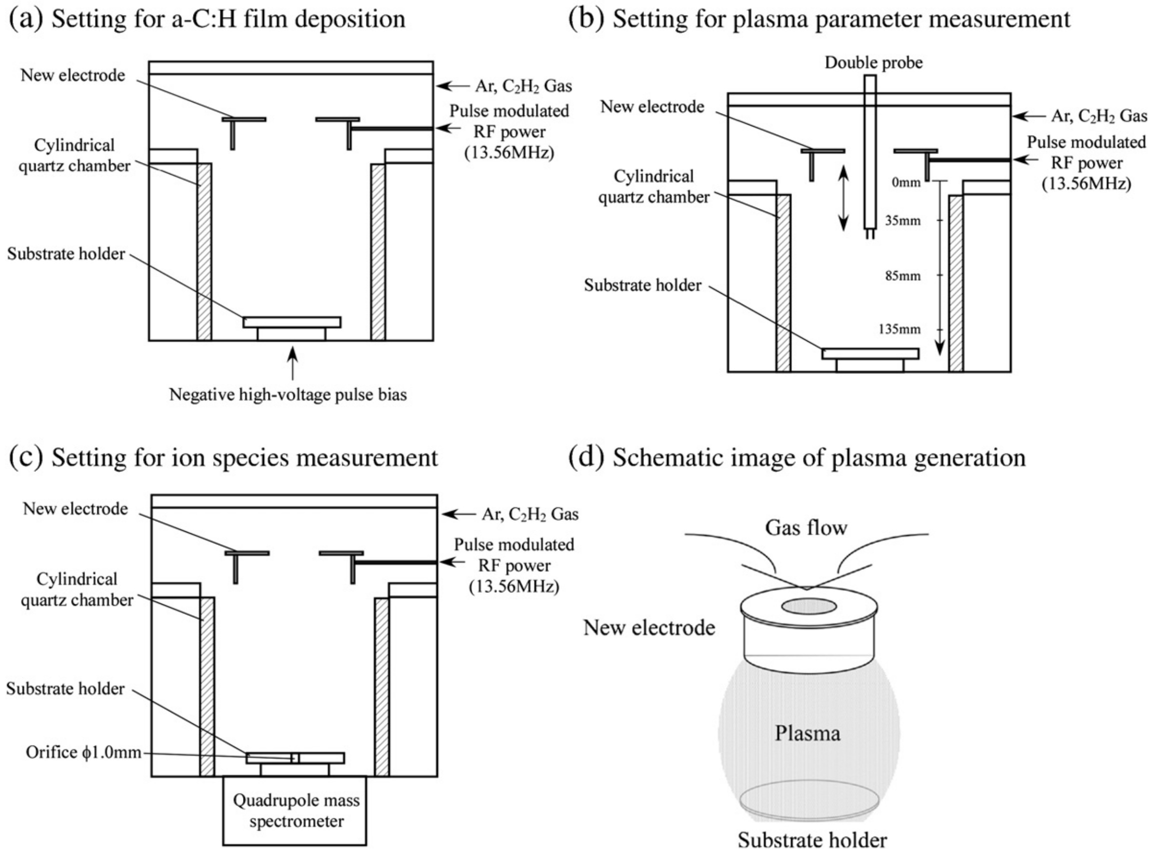

Fig. 2. Schematic drawings of various settings of inner parts of the experimental apparatus (a to c) and schematic image of plasma generation (d).