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Diamond-like carbon film deposition by super-wide electron-cyclotron resonance plasma source excited by traveling microwave

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An electron-cyclotron resonance (ECR) plasma source which generates 500 mm wide plasma has been developed. The plasma is generated by a 2.45 GHz traveling microwave which is supplied through a long slot antenna prepared in the waveguide in a divergent magnetic field generated by permanent magnets and a solenoid coil. Diamond-like carbon (DLC) films were deposited in a wide zone 320 mm in width. The breakdown field was ~8.4×10^6 V/cm and permittivity, 3.89. The prepared Al/DLC/Si metal/insulator/semiconductor (MIS) diode revealed fairly good field effect in its capacitance-voltage curve.

1. INTRODUCTION

Diamond-like carbon (DLC) films are metastable amorphous materials which typically have remarkable characteristics such as high mechanical hardness, low friction, high optical transparency over a wide spectral range, high electrical resistivity and chemical inertness. The high hardness and chemical inertness of the DLC films make them good candidates for a protective layer.

Recently, technology that utilizes DLC films as a protective layer for, for instance, mechanical tools and magnetic tapes is diffusing.1) To improve the productivity, a high-rate deposition technique which performs deposition uniformly for large-area materials at low temperature is needed. A number of deposition methods for DLC films have been studied so far,2) but it is not easy to produce DLC films of a large area uniformly by existing methods.

Microwave plasma sources utilizing electron-cyclotron resonance (ECR) discharge are very promising tools for chemical vapor deposition (CVD).3) ECR plasma apparatuses using solenoid coils to provide axial magnetic fields for exciting ECR plasmas are familiar tools for CVD. Plasmas generated by these apparatuses, however, suffer from radial distribution in their plasma density, which in turn causes nonuniform film deposition. Moreover, since cross sections of these plasmas are circular, they are ineffective and out of favor for use to rectangular or sheet-type substrate materials.

Generation of a wide plasma will serve as a key technology to ensure the high productivity of DLC deposition on large-area materials. Scrolling long and wide taped materials, if necessary, in the wide plasma will help, to large extent, in carrying out the process over their whole area.

We have been developing an ECR plasma source (a super-wide ECR plasma source) which can generate 500 mm wide plasma by the traveling microwave.4) This time, a success was obtained in improving the efficiency of large area deposition. With the improved equipment, a plasma whose cross section is divergent is generated successfully, and the deposition rate increased exceedingly.

We here demonstrate the preliminary experiments of the new super-wide ECR plasma source and application to DLC film formation on Si substrates in a 320 mm wide zone.

2. APPARATUS

A schematic diagram of the super-wide ECR plasma source and its cross section are shown in Figs. 1 and 2, respectively. To generate a wide plasma, a slot antenna whose width and length are 5 mm and 500 mm, respectively, is prepared in the side wall of a rectangular waveguide, and a microwave is supplied to the reaction chamber through the slot antenna. A 2.45 GHz microwave generated by a 1kW magnetron is introduced into the waveguide with the slot antenna via an isolator, a directional coupler, and a microprocessor-based automatic microwave stub tuner (AST) which can perform automatic microwave tuning and plasma impedance calculation simultaneously.[5)]

To provide a magnetic field, permanent magnets whose magnetism is 1.2 Tesla at room temperature are aligned in the middle of the propagation path between the slot antenna and the reaction chamber, as shown in Fig. 2. This alignment makes it possible to provide a divergent magnetic field. Permanent magnets are installed in an aluminum holder. The magnet holder and inside of the waveguides are air-cooled and, thus, magnets are not thermally affected.

Our finding obtained so far is that permanent magnets themselves are not capable of providing sufficiently a divergent magnetic field which facilitates the plasma reaching the substrate. To make it possible, a solenoid coil (a booster magnet) whose shape is oval is combined with permanent ones surrounding the slot antenna, as shown in Figs. 1 and 2. Using the permanent magnets and the booster magnet, a plasma whose cross section is divergent is generated, as shown in Fig. 2. The shape of the divergent magnetic fields and the plasma can be controlled by regulating the coil current. The ECR condition (875 G) is met at about 2 mm away from the quartz glass. Using only a solenoid coil, the divergent magnetic field mentioned above can be obtained, in principle. However, the apparatus will become huge because of the size of the solenoid coil necessary for satisfying the ECR condition. The size of the reaction chamber using permanent magnets and solenoid coil is so compact (700 × 200 × 230 mm in volume) that it could cut down the space for disposition of apparatuses.

A particular importance we emphasize here can be seen in the uniform excitation of the wide plasma by the traveling microwave only. If a standing wave exists in the waveguide, it will result in development of spatial nonuniformity in the plasma density. Therefore, in the present apparatus, a microwave passing the endpoint of the slot antenna (without plasma coupling) is completely absorbed by the dummy load.

The microwave power supplied through the slot antenna will decrease as the microwave propagates along the antenna in the present equipment. For leveling the microwave power fed to the reaction chamber through the slot antenna, the waveguide is equipped with a pair of inner metal plates, as shown in Fig. 1(b). This is called a power averaging system (PAS). These plates are kept in electrical contact with the inside of the waveguide. Their

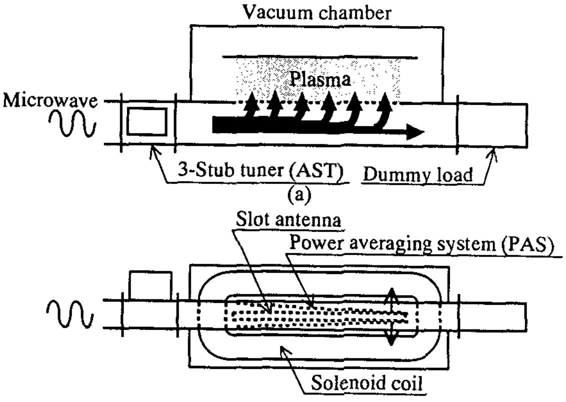

Fig. 1. Schematic diagram of the super-wide ECR plasma source: (a) top view and (b) side view.

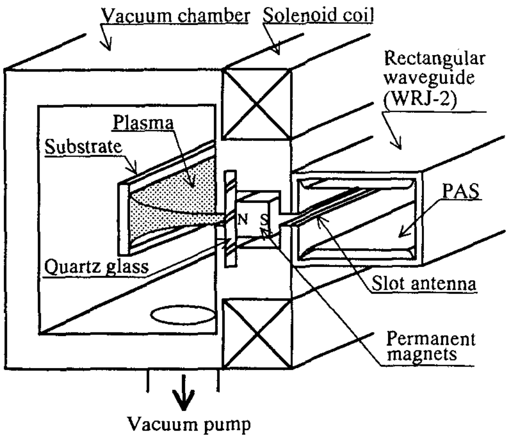

Fig. 2. Schematic diagram of the cross section of the super-wide ECR plasma source.

ends on the generator side are fixed and those on the dummy load side are movable. They can be tilted by moving the movable ends, and microwave power allotment supplied to the chamber can be manipulated by handling them. These plates move mainly on the dummy load side at present for tentative use. In this paper the PAS is not used when plates are not tilted but is used when both movable ends of metal plates meet at the end of the slot antenna, as shown in Fig. 1 (b).

3. EVALUATION OF APPARATUS AND PLASMA

Using the improved super-wide ECR plasma source, a wide plasma diffusing toward the substrate was successfully generated along the slot antenna.

The magnet field generated by the permanent magnets and the booster magnet was sufficiently uniform, though the data are not given here. Figure 3 shows the spatial distribution of plasma parameters measured by a single electrostatic probe placed in the chamber 18.5 mm away from the surface of the quartz glass. Apparent bowing can be seen in the electron density distribution, and especially at the generator side, the nonuniformity seems conspicuous. We should note here that the plasma density considerably increases when the PAS is used. The plasma density increases largely on the dummy load side. This is because the metal plates inside the waveguide move mainly on the dummy load side as mentioned before. Nevertheless, it definitely suggests that the PAS works effectively. Finding suitable PAS structure, it will contributes to the uniform microwave supply and therefore the uniform plasma generation.

The same characteristic features were obtained from the plasma emission in intensity measurement, though the data are not given here.

4. EVALUATION OF DLC FILMS

DLC films were deposited on p^--Si ($\sim 1 \times 10^{16}$/cm^3) substrates in CH_4 and Ar mixed-gas ambient. The IR absorption peaks relevant to the DLC structure were obtained by a Fourier transform infrared spectrometer (FTIR), though the data are not given here. The distribution of the film thickness and electrical characteristics such as permittivity and break down field were investigated. The spatial distribution of the film thickness deposited 57.5 mm away from the surface of the quartz glass is shown in Fig. 4. Gas pressure, microwave power, coil current and deposition time are 10 mTorr, 400 W, 200 A and 1 min., respectively. When the PAS is not used, the deposition rate is high over the region from the center of the chamber to the dummy load side, and this tendency is similar to that of the plasma density. But, though the plasma density of the highest place (80 mm) is three times as much as that of the lowest place (-160 mm), the deposition rate of 80 mm is twice that of -160 mm. This may be due to the smoothing effect owing to diffusion of the plasma species. Here, we should notice that when the PAS is used, the deposition rates increase, especially on the dummy load side, and the rate is high, that is, about

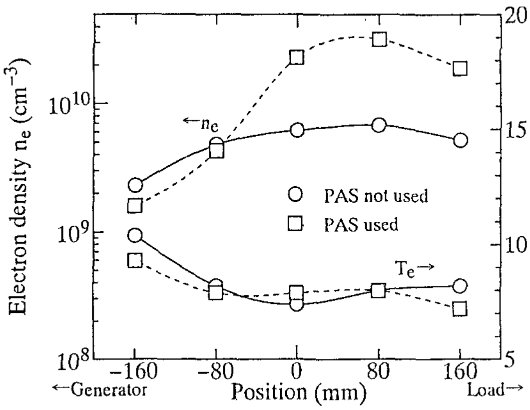

Fig. 3. Spatial distribution of electron density n_e and electron temperature T_e.

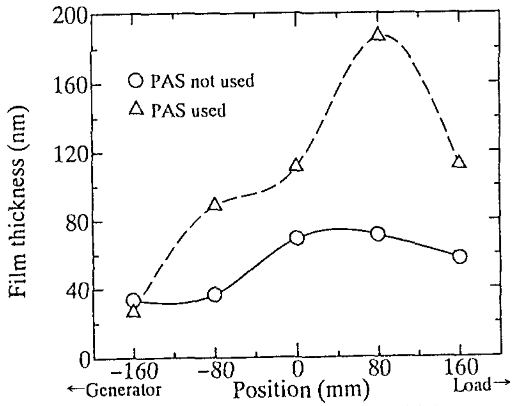

Fig. 4. Spatial distribution of DLC film thickness.

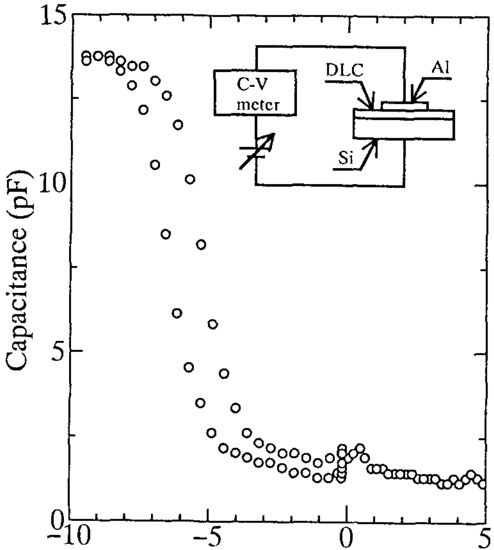

Fig. 5. C–V curve of MIS–diode.

190 nm per minute. It can be said that the structure of the PAS greatly effect on the deposition rate and the distribution of the film thickness. Optimization of the PAS structure makes high rate and uniform deposition possible, and the improvement is now in progress.

The Al/DLC/p$^-$–Si MIS–diodes were fabricated for electrical characteristic measurements. The samples were subjected to the CH_4 and Ar plasma ($Ar:CH_4 = 1:4$) for 60 seconds at room temperature. The microwave power was 400 W at 10 mTorr, coil current was 200 A and the PAS was not used. The depositions were also performed under the different conditions in which the microwave power, the location of the PAS and the volume fraction of argon and methane were changed. An example of the capacitance–voltage (C–V) curve of the MIS–diode whose DLC film thickness is 40.5 nm is drawn in Fig. 5. Static permittivity ε_r obtained by measuring the C–V curves were in 3~4 and it is worth noting that the Si–MIS diode made by such a high–rate deposition method can work just like the specimen prepared with the thermally oxidized gate oxide (SiO_2). Moreover, the break down field of the film reached 8.4×10^6 (V/cm), sufficiently high for practical use. Optimization of the deposition condition and improvement of the apparatus itself may promise to provide good characteristic of the DLC films.

5. CONCLUSION

We have developed an ECR plasma source which generates 500 mm wide plasma diffusing toward the substrates in the divergent magnetic field, using traveling microwave excitation, and deposited DLC films in a wide zone using this apparatus. Although the uniformity of the plasma distribution was not sufficient at present, the PAS prepared inside the wave guide had good effect on controlling the microwave power supplied to the chamber and is full of promise in uniforming the plasma. The DLC film deposited using this apparatus served as a good gate insulator for a Si–MIS diode: ε_r~3.89 and the break down field ~8.4×10^6 V/cm.

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