Formation of Carbon Films from C_2H_6–H_2 by ECR Plasma CVD by Application of a Negative DC Bias

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Synopsis. Hydrogenated amorphous carbon films were prepared from a C_2H_6–H_2 system by ECR plasma CVD. A negative DC bias ranging 0—−200 V applied to the ECR system induced an additional DC discharge to give an abrupt increase in the emission intensity of plasma beyond −110 V bias, where a soft (micro Vickers hardness of about 2 GPa) but flat surface with fine grains was formed.

Hydrogenated amorphous carbon films (a-C:H) attract much interest by their hardness and their chemical and electrical stabilities.[1—4] In the preparation of a-C:H films by various methods, ionic species impinging onto the substrates are known to play an important role in the growth mechanism of the films. Chemical vapor deposition by electron cyclotron resonance (ECR) has often been used for the synthesis of a-C:H films because of its high efficiency for the ionization of reactant gases.[5] Application of an additional negative DC bias to ECR plasma is reported to be effective for production of hard carbon films.[6,7] Our previous study on the diagnostics of the ECR plasma of CH_4–H_2 used for a-C:H deposition has shown that the emission intensity of the ECR plasma increases abruptly at about −100 V and flat a-C:H films with fine grains are formed.[8] This study has been carried over to the present work, where the relationship between the morphology of carbon films and the intensity of the emission spectra in ECR plasma CVD is examined for the C_2H_6–H_2 system.

Experimental

The reaction chamber of the apparatus used in this experiment was outlined previously.[8] A block diagram for the measurement of the emission spectra is shown in Fig. 1. A glass substrate was placed on a base plate, to which a negative DC bias was applied. The emission spectra of the plasma in the chamber were measured by an optical multichannel analyzer (Princeton Instruments Inc., detector: IRY-700 N/RB, spectrometer: HR-320, controller: ST-110).

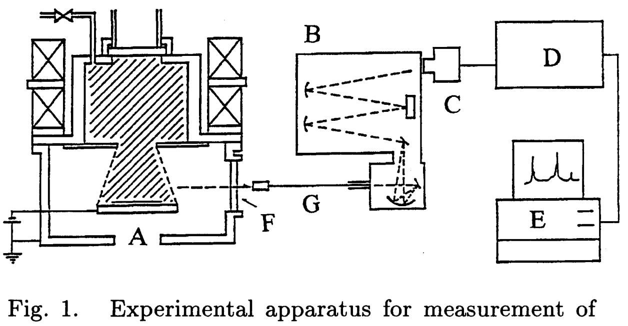

Fig. 1. Experimental apparatus for measurement of an emission spectrum. A: ECR plasma CVD apparatus, B: spectrometer, C: detector, D: controller, E: console, F: quartz glass window, G: glass fiber.

The experimental conditions were similar to those reported earlier:[8] flow rate of C_2H_6 gas, 10—20 cm^3 min^{-1}; flow rate of H_2 gas, 30 cm^3 min^{-1}; total pressure, 3×10^{-4} Torr (1 Torr=133.322 Pa); microwave power, 300 W; and bias voltage, 0—−200 V.

Results

The deposition rate of the carbon film was found to increase with the applied DC bias V_B, as shown in Fig. 2, but the micro Vickers hardness of the film did not increase (always below 3 GPa). This observation contrasts with our recent report[8] on the CH_4–H_2 system, where the application of a negative DC bias resulted in hard carbon films above 30 GPa.

As shown in Fig. 3, the surfaces of the films obtained with biases ranging between 0 and −110 V show coarse texture, but beyond this range they are flat with fine grains. Diagnostics of the C_2H_6–H_2 plasma revealed the relationship between the emission spectra and the morphology of the films. The emission spectrum of the plasma of the C_2H_6–H_2 system from 350 to 700 nm is shown in Fig. 4 together with that of the CH_4–H_2 system. They are composed of the line spectra of H_α,

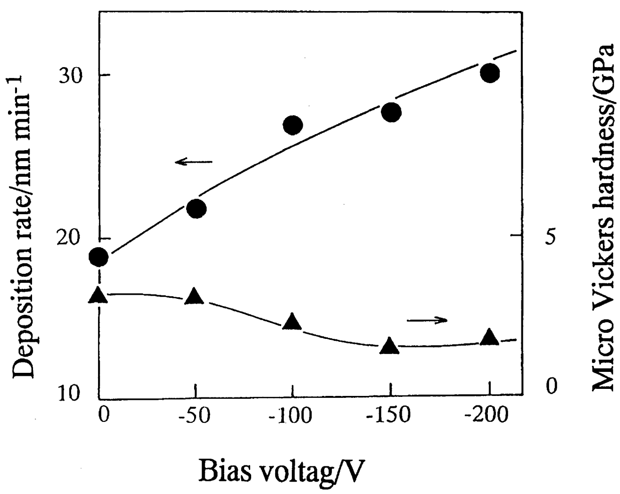

Fig. 2. Relationships between the additional negative DC bias (V_B), the deposition rate (●) and the micro Vickers hardness (▲) of the carbon films on glass substrates heated to 200°C. The flow rates of C_2H_6 and H_2 gases were 20 and 30 cm^3 min^{-1}, respectively.

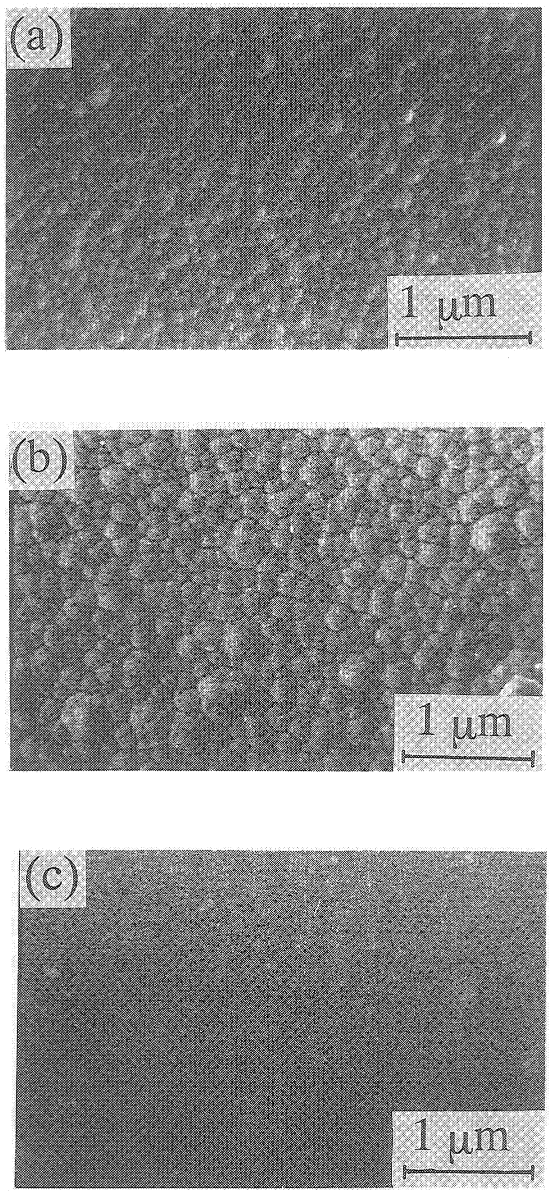

Fig. 3. SEM photographs of the carbon films on glass substrates heated to 200°C. The flow rates of C_2H_6 and H_2 gases were 10 and 30 cm^3 min^{-1}, respectively. The bias voltages (V_B) were (a) V_B=0 V, (b) V_B=−100 V, and (c) V_B=−150 V.

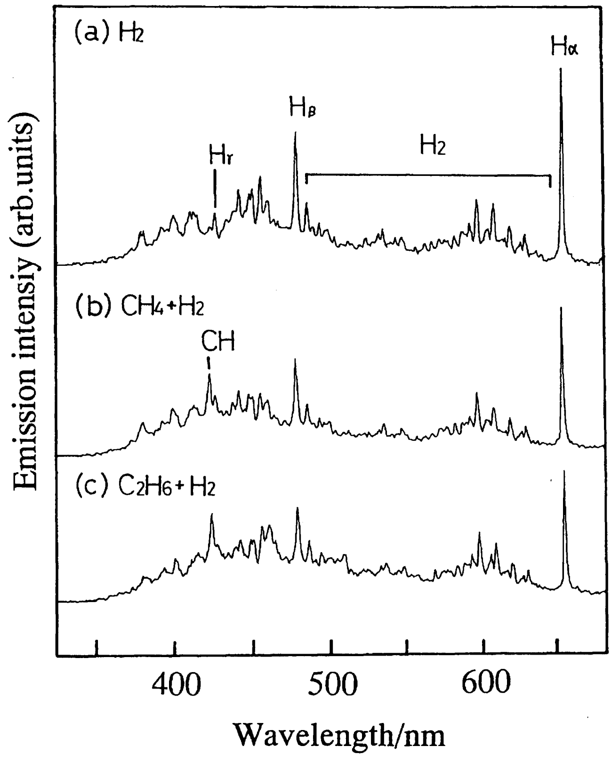

Fig. 4. Observed emission spectra of the plasma in ECR plasma CVD. The flow rates of CH_4, C_2H_6, and H_2 gases were 10, 10, and 30 cm^3 min^{-1}, respectively. The bias voltage (V_B) was −100 V.

H_β, H_γ, and CH. The measured emission intensity of the plasma as a function of the applied DC bias is shown in Fig. 5. The curve increases abruptly at −110 V. This increase in the emission intensity correlates with the drastic change observed in the morphology of the films (Fig. 3).

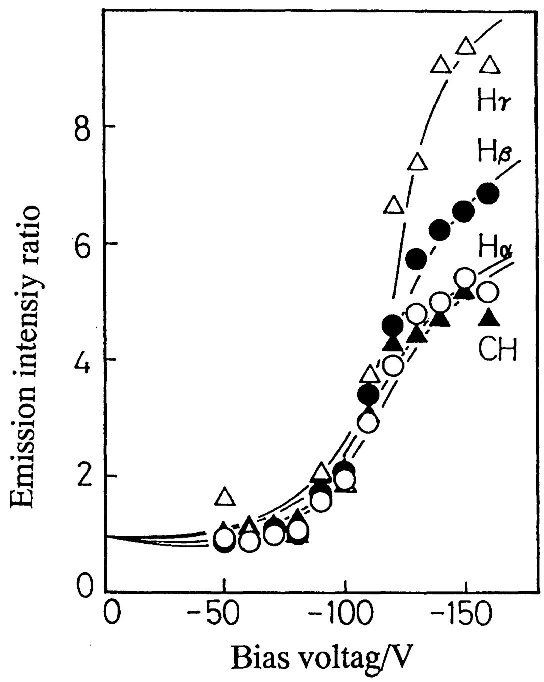

Fig. 5. Relationships between the negative DC bias and the emission intensities of H_α (○), H_β (●), H_γ (△), and CH (▲) in the emission spectra of the C_2H_6–H_2 system, where the intensities of H_α, H_β, H_γ, and CH at V_B=0 are normalized.

Discussion

Application of a negative DC bias to the C_2H_6–H_2 system caused an abrupt increase in the emission intensity of plasma at about −110 V. The increase in the emission intensity of the plasma in this case accompanied the increase in the total pressure in the reaction chamber, which means that the decomposition of C_2H_6 to various fragments is enhanced by the application of the negative DC bias. The emission spectra of hydrogen in the Balmer series are found to depend strongly on the type of the plasmas.[9] The DC plasma of methane shows the strongest H_β peak in the Balmer series, while the H_α peak is the strongest in the RF and MW plasmas. In the present study the H_β peak increases faster than the H_α peak, as shown in Fig. 5. This suggests that the applied DC bias induces a DC discharge at about -110 V bias to cause an abrupt increase in the emission intensity.

According to a mass spectrometric observation of Vandentop et al.,[10] the methyl radicals appeared to be the dominant intermediates in the growth of a soft carbon film, and the deposition rate decreased remarkably by the introduction of NO, a radical scavenger. In this case, a negative self-bias caused an increase in the deposition rate and the hardness. In the present study for the C_2H_6–H_2 system, however, application of a DC negative bias is not effective to form a hard carbon film in contrast to the CH_4–H_2 system, where a DC negative bias caused a significant increase in the deposition rate and the hardness.[8] Previous investigations[11,12] confirmed that a transition from ordinary amorphous carbon to diamond-like material takes place when a film is subjected to bombardment by energetic ions during its growth. According to Savvides,[13] a hard carbon film is formed when the arrival rate of the ions to condensing atoms, Ar^+/C in this case, is high and the impinging ions have high energies. The concentration of the ions in the plasma in the present study can be estimated by the magnitude of the direct current through the bias circuit. The direct current through the bias circuit in the C_2H_6–H_2 system (0.28 A) is lower than that in the CH_4–H_2 system (0.40 A) at -150 V bias. The observed emission spectra of the plasmas of the CH_4–H_2 and C_2H_6–H_2 systems from 350 to 700 nm are essentially identical. In addition, the emission intensities of the plasmas, deposition pressures and gas feeding rates in these systems are nearly equal. Thus the arrival rates of the ions to condensing radicals in this C_2H_6–H_2 system may not be sufficient to obtain hard carbon films. In the CH_4–H_2 system, this current decreased after a long deposition time and resulted in a soft carbon film.[14] This decrease in the current may be caused by the formation of insulating substances on the substrate, which causes charging and reduces the accelerating potential difference and the arrival rates of the ions. The present observations show that bombardment of energetic ions on the substrate surface and/or the high arrival rates of the ions to condensing radicals are necessary to obtain a hard carbon film.

The reason why the observed drastic increase in the emission intensity does not lead to that in the deposition rate remains uncertain. However, the observation of a surface with fine grains formed by an additional DC discharge is an indication of the impact of high-speed ions, molecules and electrons in the plasma on the surface, which prevent aggregation of primary particles into larger secondary particles.

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