8th Asia-Pacific Conference on Plasma Physics, 3-8 Nov, 2024 at Malacca

Structural change in a-C:H films deposited using cumene PECVD by ion irradiation

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Hydrogenated amorphous carbon (a-C:H) films are widely employed as protective coatings for semiconductor etching owing to their excellent physical properties and chemical inertness [1]. For improving etch selectivity and productivity, it is necessary to establish a high-rate deposition process that realize the high film density and low film stress. The mechanical properties of a-C:H films are determined by the composition of sp^2 bonds, sp^3 bonds, and hydrogen atoms. For a-C:H film deposition process, ion energy impinging to the film surface is an important factor to determine the film structure. Cumene (C_9H_{12}) has a high number of carbon atoms and a low number of hydrogen atoms per molecule, thus deposition using C_9H_{12} is expected to achieve a high deposition rate and high mass density. Here, we studied the effect of ion irradiation by controlling the substrate bias voltage to understand the cumene plasma chemical vapor deposition (CVD).

The a-C:H film were deposited by a parallel-plate capacitively coupled plasma CVD [2]. A Si (100) substrate was put on the lower electrode. Cumene and Ar was introduced with the gas flow rates of 5 and 45 sccm, respectively. The total gas pressure P was 10 and 50 mTorr. To generate plasma, an RF voltage (28 MHz, 300 Vpp) was applied to the upper electrode. To control the substrate bias voltage |Vdc|, a 400 kHz RF voltage was applied to the substrate holder, then the |Vdc| was from 680 to 1120 V.

We measured a dependence of deposition rate, film density and compressive stress on the |Vdc|. The deposition rate slightly increases with increasing |Vdc| at P = 10 mTorr, while, at P = 50 mTorr, the deposition rate significantly increases with |Vdc|. In addition, the same trend is observed in plasma emission intensity at 431 nm, originated from CH, measured by optical emission spectroscopy. These results suggest that the rate of precursor dissociation increases with |Vdc| increasing. Considering that the discharge voltage at the top electrode is constant, the increase of DR and CH emission intensity are caused by the effect of secondary electrons from the biased electrode. The increase secondary electron flux by increasing |Vdc| leads to increase the electron impact dissociation of cumene.

For the P= 10 and 50 mTorr, the film density is independent of |Vdc| and the compressive stress decreases with increasing |Vdc|. The conventional a-C:H has a positive correlation between mass density and compressive stress. However, in the case of deposition using cumene, the compressive stress decreases while retaining the film density constantly with increasing |Vdc|. To elucidate the cause of the stress relaxation, we estimated the film structure by raman spectroscopy.

The raman spectra of the films deposited at P = 10 mTorr are shown in Fig. 1. The photoluminescence background is too low to presume the content of hydrogen atoms [3]. Hence, the H content of the films seems lower than the detection limit of 20 at%. The G peak position is shifted to higher wavenumber from 1545 cm^{-1} at |Vdc| = 770 V to 1553 cm^{-1} at |Vdc| = 1120 V. The peak shift suggests the sp^2/sp^3 ratio in the films is increased [4]. The FWHM of G peak decreases from 176 cm^{-1} at |Vdc| = 770 V to 162 cm^{-1} at |Vdc| = 1120 V. The decreasing FWHM of G peak suggests the crystallinity of the sp^2 bonds in the films is increased [4]. According to these results, it is thought that the graphitic structure in the films grows by thermal impact of energetic ions impinging to the film surface, resulting in reducing the compressive stress.

References

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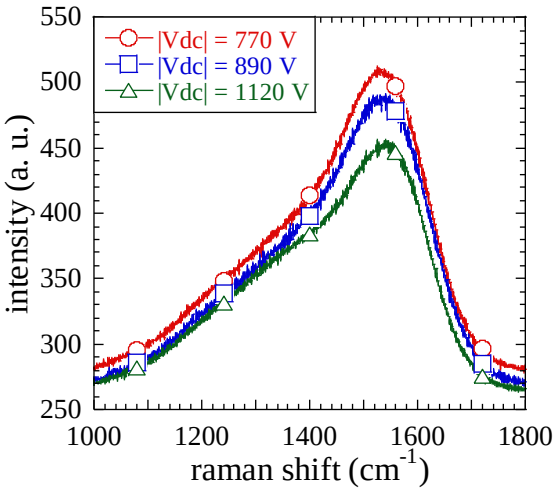

Figure 1. Raman spectra of the a-C:H films as a parameter of |Vdc| for P= 10 mTorr.