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Effects of Precursor Gas Molecules on the Deposition Properties of Hydrogenated Amorphous Carbon Films by Plasma Chemical Vapor Deposition

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Hydrogenated amorphous carbon (a-C:H) films serve as hard masks in high aspect ratio (HAR) etching for semiconductor manufacturing. Enhancing their properties requires high density, low compressive stress, and high deposition rates. In this study, cumene (C_9H_{12}) was used as the precursor gas, expecting to achieve both high-density films due to its low hydrogen-to-carbon ratio [1] and high deposition rates from its high carbon atom content [2]. Additionally, cumene is cost-effective (56 USD/L) [3]. To evaluate the effectiveness of cumene plasma CVD, we studied (1) deposition characteristics using methane, acetylene, and cumene, and (2) effect of incident ion energy on mass density.

A capacitively coupled plasma CVD device was used to deposit a-C:H films. Two parallel electrodes were placed at the center of the chamber. The distance of the electrode was set 115 mm. A 1 cm² Si substrate was placed on the lower electrode, and Ar diluted precursor gas was introduced. Plasma was generated by applying 13.56 MHz or 400 kHz high-frequency voltage to the lower electrode. For the 400 kHz discharge, the precursor gas was introduced at a total flow rate of 100 sccm with a precursor concentration of 5%, the total gas pressure was 0.02 Torr, and the discharge voltage was Vpp = 1600 - 2400 V. For the 13.56 MHz, the flow rate was 100 sccm, the concentration 5 – 50%, pressure 0.02 – 0.3 Torr, and Vpp = 100 or 250 V.

First, at 13.56 MHz, as shown in Figure 1(a), films deposited using acetylene and cumene exhibited higher deposition rate than those deposited using methane. Additionally, as shown in Fig. 1(b), at 400 kHz, films deposited using cumene exhibited high density of 2 g/cm³ and low stress of 1.0 GPa. Furthermore, the deposition rate for cumene was higher than that of acetylene. In addition, the film has low stress at around 1.0 GPa, independent of mass density.

Second, the correlation between ion energy and mass density was examined. As shown in Fig. 1(c), by defining the ion energy index as |Vdc| / pressure / Nc, where |Vdc| and Nc is the bias voltage and the number of carbon atoms per molecule, respectively, it was suggested that mass density is determined independently of precursor gas and discharge frequency. Moreover, as shown in Fig. 1(d), the hydrogen content estimated from Raman spectroscopy exhibited a negative correlation with mass density, regardless of precursor gas or discharge frequency. On the other hand, as shown in Fig. 1(e), the intensity ratio of D peak and G peak in Raman spectra, an indicator of the sp²/sp³ ratio, correlated with mass density in region where the total ion energy (|Vdc| / pressure) was low.

References

[1] J. Robertson, Mater. Sci. Eng. R37 (2002), 129.
[2] P. Koidl et al., Mater. Sci. Forum, 52 (1990), 41.
[3] https://www.chemicalbook.com/ChemicalProductProperty_EN_CB2191522.htm

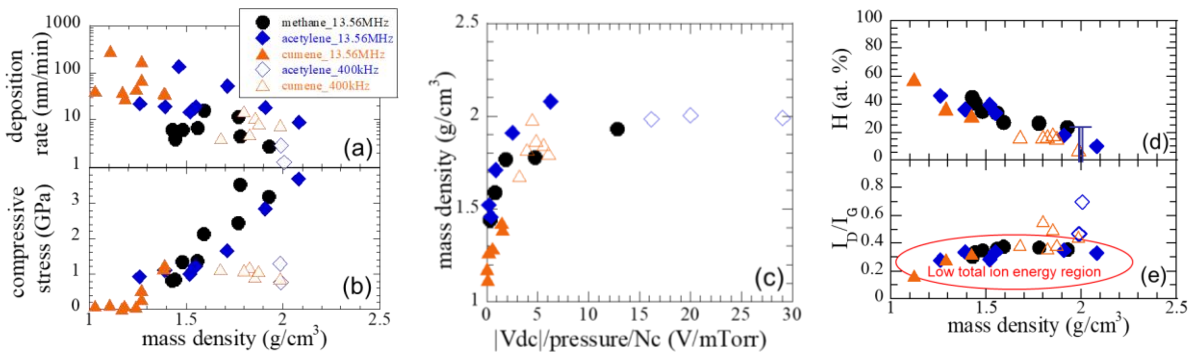

Figure 1. Mass density dependence of (a)deposition rate and (b)compressive stress, (c) correlation between mass density and ion energy index, and mass density dependence of (d) hydrogen content and (e) intensity ratio of D-peak and G-peak in Raman spectra.