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Analysis of dissociative excitation reaction of hexamethyldisilane in the microwave discharge flow of Ar

Arのマイクロ波放電フロー中でのヘキサメチルジシランの解離励起反応解析

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The hydrogenated amorphous silicon carbide films were formed by using the decomposition reaction of hexamethyldisilane ($Si_2(CH_3)_6$, HMD) with the microwave discharge flow of Ar. Mechanically hard films were formed by applying radio-frequency bias voltages ($-V_{RF}$) to the substrate. In addition, the process of the dissociative excitation of HMD was investigated based on a high-resolution emission spectroscopy. Atomic lines of the Si(4s-3p) transition and the molecular emission spectra of the SiH($A^2\Delta$-$X^2\Pi$), CH($A^2\Delta$-$X^2\Pi$), CH($B^2\Sigma^-$-$X^2\Pi$), and C_2($d^3\Pi_g$-$a^3\Pi_u$) transitions were observed. These intensities were dependent on $-V_{RF}$.

1. Introduction

A hydrogenated amorphous silicon carbide (a-SiC_x:H) films are formed from plasma decomposition reactions of organic materials containing Si atoms such as tetramethylsilane ($Si(CH_3)_4$, TMS). In our previous studies, TMS has been decomposed by the microwave (MW) discharge flow [1,2] and electron-cyclotron resonance (ECR) plasma [3,4] of Ar. Mechanically-hard films have been obtained by applying radio-frequency bias voltages ($-V_{RF}$) to the substrate [1,3]. In addition, the plasma decomposition processes occurring in the MW and ECR plasmas have been discussed on the basis of the high-resolution optical emission spectroscopy [2,4]. In this study, a-SiC_x:H films were formed by using hexamethyldisilane ($Si_2(CH_3)_6$, HMD). This study will put particular emphasis on the analysis of the plasma-decomposition reaction of HMD based on a high-resolution optical emission spectroscopy.

2. Experimental

Fig. 1 shows the experimental apparatus. The chamber was evacuated to <0.04 Pa. Then, Ar gas of 13 Pa was introduced into the chamber by passing through the desiccant (P_2O_5) and the discharge tube, and excited by a MW discharge (2.45 GHz, 100 W). HMD was also desiccated by passing through P_2O_5, and was introduced into the discharge flow through a nozzle. A radio-frequency (13.56 MHz) voltage was applied to the substrate stage with $-V_{RF}$ in the range of 0-100V. The optical emission produced by the dissociative excitation reaction of HMD was introduced into a double-pass monochromator of f= 1500 mm (Jovin Yvon THR1500) through a quartz window and two plano-convex lenses. Emission was detected by using a photomultiplier tube. The signals were processed by a photon counter (Stanford SR400). Film hardness was measured using Vickers indenter with the maximum load of 1 mN (Fischer HM500).

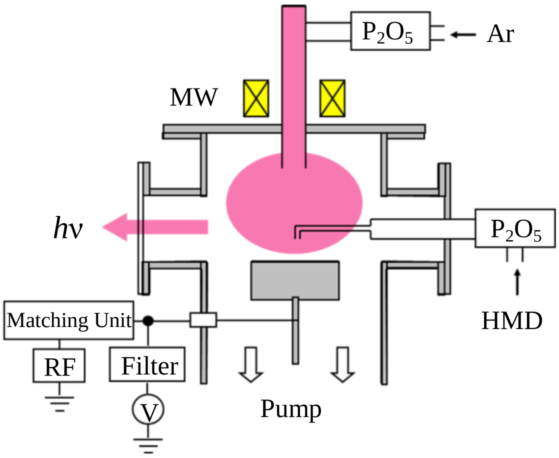

Fig. 1 MWCVD apparatus.

3. Results and discussion

Fig. 2 shows the mechanical hardness of films. Films were rather soft (0.6 GPa) under the condition of $-V_{RF}$=0 V, and increased the hardness

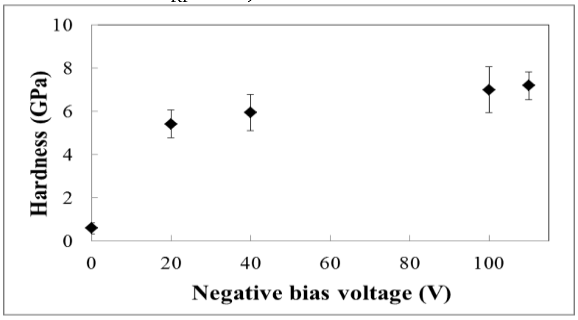

Fig. 2 Mechanical hardness of a-SiC_x:H films

steeply into ≈6 GPa when $-V_{RF}$ increased to 20 V.

Atomic lines of the Si(4s-3p) transition and molecular emission spectra of the SiH($A^2\Delta$-$X^2\Pi$), CH($A^2\Delta$-$X^2\Pi$), CH($B^2\Sigma^-$-$X^2\Pi$), and C_2($d^3\Pi_g$-$a^3\Pi_u$) transitions were observed in this study.

Fig. 3 shows the emission spectrum of the SiH(A-X), 0-0 band observed in the region of 410-416 nm.

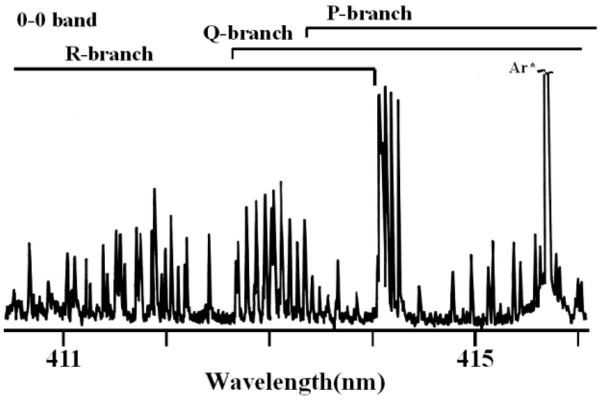

Fig. 3 Emission spectrum of the SiH(A-X) transition.

Fig. 4 shows the emission spectrum of the CH(A-X) transition. The 0-0 and 1-1 bands were observed. In Figs. 3 and 4, intense atomic lines of Ar were also observed. In addition to the A-X band, the 0-0 band of the CH(B-X) transition was also observed.

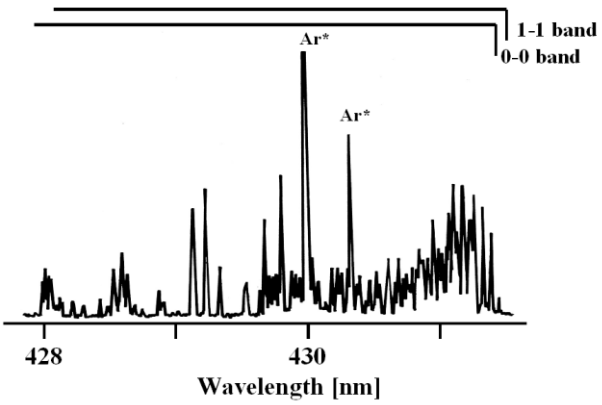

Fig. 4 Emission spectrum of the CH(A-X) transition.

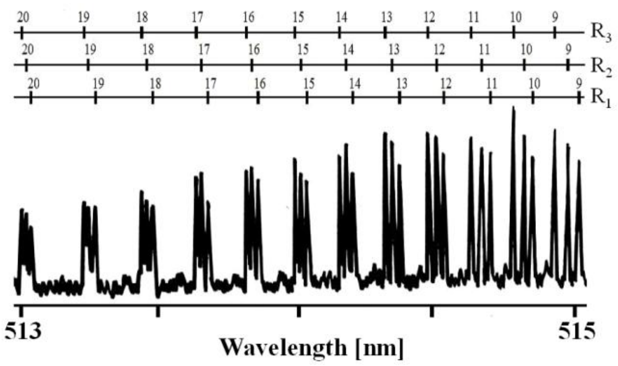

Fig. 5 emission spectrum of the C_2(d-a) transition.

Fig. 5 shows the part of the 0-0 band of the C_2(d-a) transition, The assignments of the rotational lines of the R branch were indicated.

Fig. 6 shows the dependences of the emission intensities of the SiH(A-X), CH(A-X), CH(B-X), C_2(d-a), and Si(4s-3p) transitions on $-V_{RF}$. The vertical axis is the relative emission intensity normalized to the intensity under the condition of $-V_{RF}$=0 V. The intensities of the SiH(A-X), CH(A-X), CH(B-X), and C_2(d-a) transitions are dependent on $-V_{RF}$, whereas the intensity of the Si(4s-3p) transition is almost independent of $-V_{RF}$. This observation may indicate the difference of the mechanism of the production of the relevant electronic-excited states.

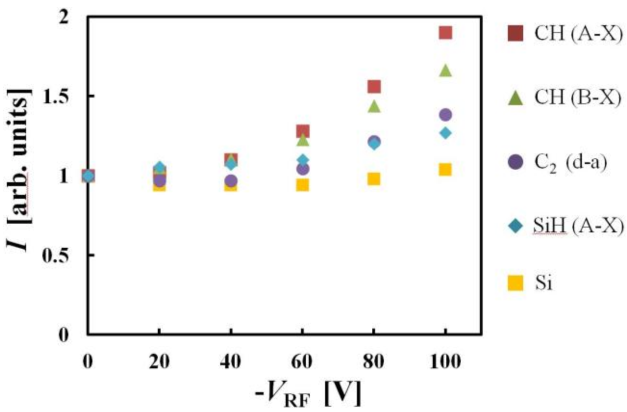

Fig. 6 Relative emission intensity vs. $-V_{RF}$.

4. Concluding remarks

The dissociation excitation reaction of HMD with the MW discharge flow of Ar was investigated by using high-resolution optical emission spectroscopy. The Si(4s-3p) atomic lines and the molecular emissions of SiH(A-X), CH(A-X), CH(B-X), and C_2(d-a) transitions were observed. The emission intensities of SiH(A-X), CH(A-X), CH(B-X), and C_2(d-a) showed positive dependence on $-V_{RF}$, whereas the intensity of Si(4s-3p) was almost independent. It was suggested that the mechanism of plasma decomposition is dependent on the application of RF-bias.

References

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