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# OPTICAL EMISSION SPECTROSCOPY OF $Ch_4/Ar/H_2$ GAS DISCHARGES IN RF PLASMA CVD OF HYDROGENATED AMORPHOUS CARBON FILMS

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## ABSTRACT

Hydrogenated amorphous carbon (a-C:H) films are prepared by rf plasma CVD in a $CH_4$ source gas system diluted with Ar of $H_2$. The spectra of emissive and reactive species in the plasma are detected using in stiu optical emission spectroscopy. Inaddition, the relationship between the film properties which can be varied by the deposition parameters and the Raman spectra is studied. In the $CH_4/H_2$ gas system, the emission intensities of CH and $H\gamma$ decrease and those of $H\alpha$, $H\beta$, $C_2$ and Ar increase with increasing $H_2$ concentration. The formation of $C_2$ and CH in the $CH_4/Ar/H_2$ gas system is greatly suppressed by hydrogen addition and the excess of hydrogen addition is found to form graphite structure. The $C_2$ formation in the gas phase enhances a-C:H film formation.

## INTRODUCTION

Hydrogenated amorphous carbon (a-c:H) films are of interest inseveral applications, owing to their superior chemical, electrical, optical and mechanical properties. In these films different kinds of carbon bonds, tetrahedral $sp^3$, triagonal $sp^2$ and polymeric $sp^1$ hybridizations, exist and the ratio of $sp^3$ bonding to $sp^2$ bonding and the H content are the major factors influencing the a-C:H microsstructure and properties. It is reported that for the films fabricated by the sputtering or rf plasma chemical vapor deposition(CVD) methods, hydrogen exists in the films by the rate of 10-50at.%[1,2]. For varying the concentration of hydrocarbon feed gas, additives such as hydrogen and inert gases have been used in an attempt to modify the structure of these films. In a parallel-plate rf discharge reactor, the decomposition of $CH_4$ was more enhanced by using Ar as a dilution gas than using $H_2$[3]. Higher Ar fractions(>50%)lead to $C_2$ emission in the $CH_4/Ar/H_2$ plasma[4]. a-C:H films have been prepared by rf plasma CVD using the $CH_4$ source gas system diluted with Ar of $H_2$[5]. Both Arand $H_2$ gases tend to exclude the $sp_2$ structure from the film and enhance the diamond-like behavior of the film. In this study, we have carried out the in situ optical emission spectroscopic diagnosis of rf discharges in the $CH_4/Ar/H_2$ gas system. We opserve a strong correlation between $C_2$*, H* and Ar* emissions, and the growth rate and property of films, which supports the hypothesis that $C_2$* and Ar* are in fact active species in $CH_4/Ar/H_2$ mixtures. In addition, the relationship among the film properties, deposition parameters and the Raman spectra has been studied.

## EXPERIMENTAL PROCEDURE

The experimental apparatus for the film preparation is shown in Fig.1. Films were deposited with a parallel-plate capacitively-coupled rf plasma CVD system. The distance between the substrate holder electrode and the lower counter electrode was 25㎜. a-C:H films were prepared on silicon wafer substrates. The films were deposited at the rf power of 250 W and the total flow rate of 50 sccm. The At and $H_2$ gas flow rates were varied. The deposition conditions are listed in Table 1. The film thickness were measured with a stylus profilometer (Mitsutoyo SV-600). The electrical and optical properties were also investigated by van der Pauw method and UV-VIS-NIR spectrophotometer

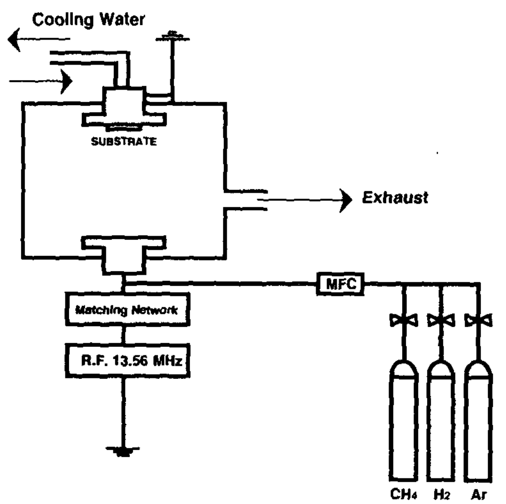


Fig. 1 Schemaic diagram of the rf plasma CVD system

(Shimadzu, UV3101PC). The chemical bonding in the film was analyzed by micro-Roman spectroscopy (Jasco, Model NR-1800). The Micro-Raman scattering was indrced at room temperature by using Ar laser (514.5nm) as an excitation source of the power 100 mW. An optical multichannel analyzing system (Princeton Instrument Inc.) with CCD and optical fiber was used to monitor the spectrum of reactive species in the plasma. The emission from the plasma was collected with a quartz optical fiber viewing a region of 15㎜ above the substrate and the emission spectra in the range of 360-840 nm were measured. The microhardness of the film was measured with a dynamic ultra micro hardness tester (Shamadzu DUH-200). The surface image of the film was examined using an atomic force microscope (AFM, SPM-9500).

Table 1. Film preparation conditions

| | |
|---|---|
| Substrate | Si |
| rf power(W) | 250 |
| Total flow rate(sccm) | 50~100 |
| $CH_4$ flow rate(sccm) | 5~70 |
| Ar flow rate(sccm) | 50~95 |
| $H_2$ flow rate(sccm) | 5~50 |
| Deposition time(h) | 1 |

## RESULTS AND DISCUSSION

The optical emission bands observed in the plasmas are identified as CH*(430nm system: $A^2\Delta$-$X^2\Pi$), $C_2$(Swan system: $A^3\Pi g$-$X^3\Pi u$), the strong H* atomic lines ($H\alpha$:656.3, $H\beta$: 486.1, $H\gamma$:434.4nm, $H_\delta$:410.17nm)[6]. $H_2$ molecules and Ar atoms are also detected. Figure 2 shows the optical emission intensities in the plasma as a function of $H_2$ concentration in

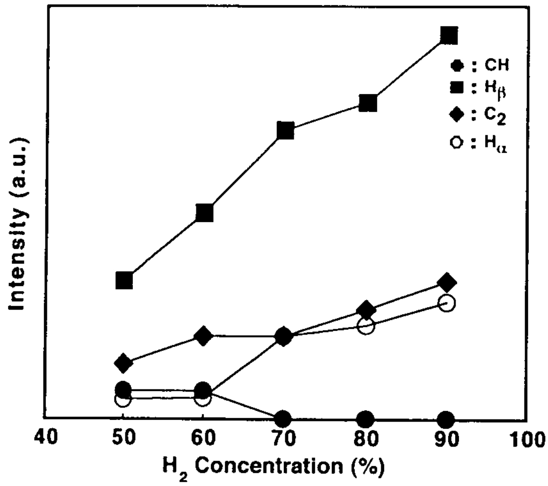


Fig. 2 Emission intensities from(●)CH, (■)Hβ, (◆)$C_2$, and (○) Hα as a function of $H_2$ concentration in the $CH_4/H_2$ gas system.

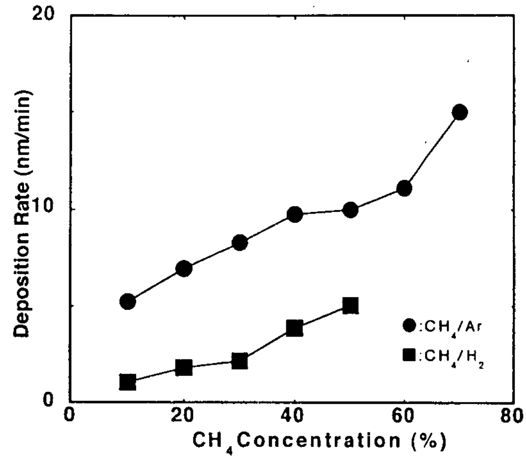


Fig. 3 Relationship between the deposition rate and $CH_4$ concentration for the $CH_4/Ar$ and $CH_4/H_2$ gas systems at the total flow rate of 50 sccm

the $CH_4/H_2$ gas system. Inthe $CH_4$ plasma diluted with $H_2$, the emissions of Hα, Hβ, Hγ, CH and $C_2$ are confirmed. The intensity of Hγ emission was very weak. However, the emission of H*($H_\delta$:410.17nm)was not detected. As the $H_2$ concentration increases, the emission intensities of CH and Hγ decrease, but those of Hα, Hβ and $C_2$ increase in the $CH_4/H_2$ gas system. Figure 3 shows the deposition rate of the film on Si substrate as a function of the $CH_4$ concentration in the $CH_4/Ar$ and $CH_4/H_2$ has systems. As the $CH_4$ concentration increases, the deposition rate increases almost linearly. A-C:H films were deposited at the rate of 5-15 nm/min in the $CH_4/Ar$ gas system. This deposition rate was about twice as large as the rate obtained in the $CH_4/H_2$ gas system.

Figure 4 shows micro-Ramanspectra of the films deposited on Si substrates obtained at the same conditions in Fig. 2. The pair of bands at 1360 and 1580cm$^2$ is the most diagnostic feature and is designated as the D bandand G band, respectively[7]. The D band

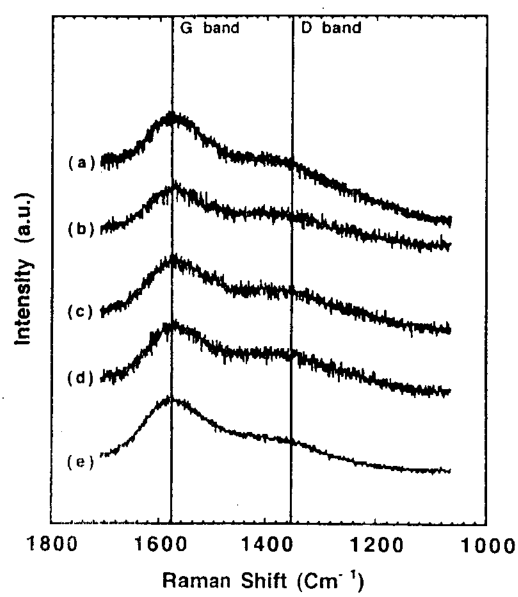


Fig. 4. Raman spectra of the films prepared at various $H_2$ concentrations in the $CH_4/H_2$ gas system; $H_2$ concentration(a):50%, (b):60 %, (c):70%, (d):80%, and (e):90%

intensity decreases with increasing $H_2$ concentration in the $CH_4/H_2$ gas system. for the films deposited at the $H_2$ concentrations of 50 and 60%, the increase in the D bband intensity is probably related to decrease in the emission intensities of Hα, Hβ, and $C_2$, because CmHn species are necessary for a-C:h film formation.

Figure 5 shows the intensities of the observed emission bands for plasma of the $CH_4/Ar/H_2$ gas system. The $CH_4$ and Ar flow rates were kept constant at 50 sccm (Ar 5 sccm) under the $H_2$ concentrations of 9-37% and the rf power of 250W. As $H_2$ concentration increases, the emission intensities of CH and Ar decreases, whereas of Hα, Hβ, and $C_2$ increase.

A weak intensity of emission of ho was detected. Compared with the deposition rate in the $CH_4/H_2$ gas system in Fig. 3, the deposition rate was higher at lower $H_2$ concentrations. Thus, the emission intensities of CH and Hr which are observed in the above deposition conditions, are stronger compared with those in the $CH_4/H_2$ gas system. the enhancement of these active species is due to a penning effect by Ar under metastable states in the plasma. Micro-Raman spectra of lthe films deposited on Si substrate under the same conditions as in Fig. 5 are shown in Fig. 6. The Dband intensity decreases with increasing $H_2$ concentra tion, but it is much stronger and sharper at the $H_2$ concentration of 37% the Raman D band is attributed to the scattering from a zone boundary phonon activated by the disorder associated with finite crystallite size[8]. The micro Raman spectra obtained here, agree with the results of low emission intensity of Hβ in Fig. 5, which suggests that the addition of Ar has a quenching effect on $C_2$ and CH emission. The formation of $C_2$ and CH in the $CH_4/Ar$ gas system is greatly suppressed by hydrogen addition and the excess of hydrogen addition is found to form graphite structure. It is considered that the properties and structure of a-C:H films are influenced predominately by behavior of Hβ and $C_2$.

The permanent depth hardness of the deposited films are shown in Fig. 7 as a function of the $H_2$ concentration. The hardness increases

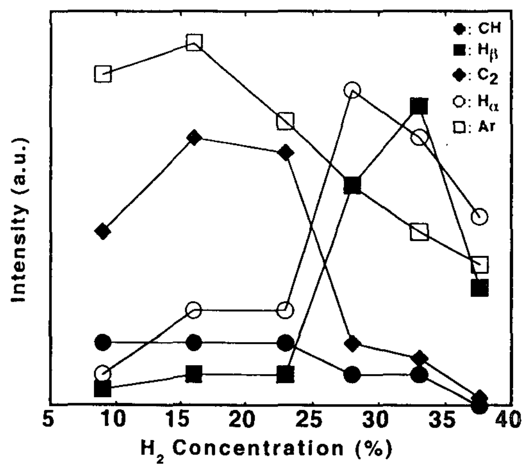


Fig. 5. Intensities of the observed emission bands as a function of the $H_2$ concentrations in the $CH_4/Ar/H_2$ gas system

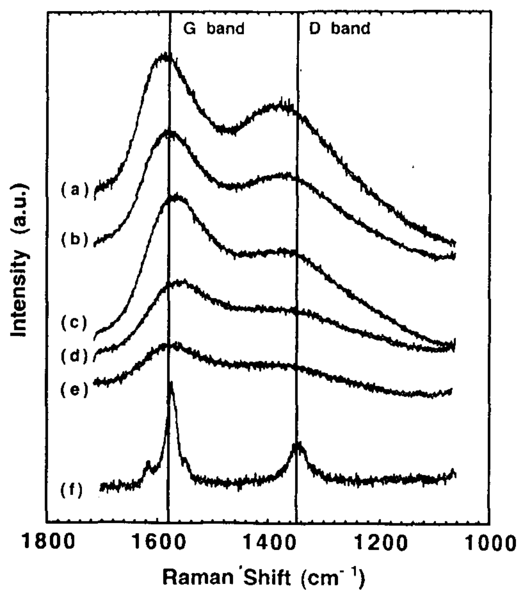


Fig. 6. Raman spectra of the films prepared at various $H_2$ concentrations in the $CH_4/Ar/H_2$ gas system : $H_2$ concentration (a):9%, (b):16 %, (c):23%, (d):28%, (e):33%, and (f): 37%

as $H_2$ concentration. However, it decreases abruptly at the $H_2$ concentration above 37%. The electrical resistivity($\rho$) measured at room temperature was $3.4 \times 10^{-1}$cm for the film obtained at the $H_2$ concentration of 37%. This is due to the graphite structure of the deposited film, because the micro-Raman spectrum of this film is similar to that of glassy carbon. The AFM image of the film is shown in Fig. 8, where the surface with finite grains evenly distributed is seen over the whole surface of the Si substrate. The average grain size is 4-5nm.

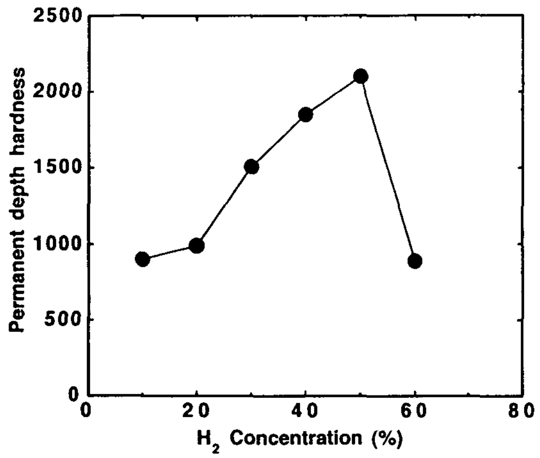


Fig. 7 Relationship between Dynamic Ultra Micro Hardness and $H_2$ concentration in $CH_4/Ar/H_2$ gas system

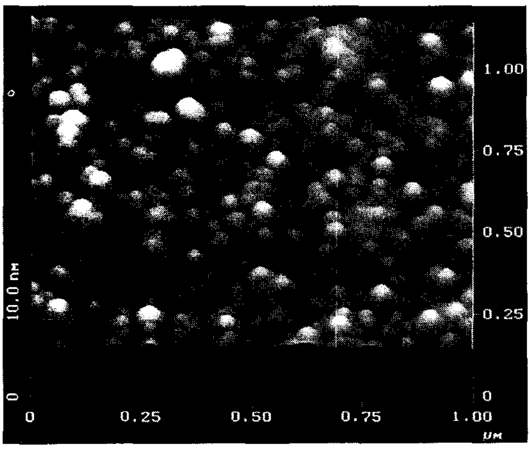


Fig. 8. AFM image of the film prepared at $H_2$ concentration of 37% in the $CH_4/Ar/H_2$ gas system

## CONCLUSIONS

The reactions related to $C_2$, CH and H radical are considered to play important roles in a-C:H synthesis. a-C:H film was formed with the intensity of $C_2$ emission simultaneously increased, which enhanced the a-C:H formation. From the Raman spectra analysis, a glassy cabon film formed at higher $H_2$ concentrations in the $CH_4/Ar/H_2$ gas system. In the case of $CH_2/Ar/H_2$ gas system, the enhancement of active species occurs due to the penning effect by Ar in metastable states in the plasma. The emissions of $C_2$ and CH were less detected at hydrogen concentration of 37 % and the excess hydrogen addition formed graphite structure in the $CH_4/Ar/H_2$ gas system. The $C_2$ formation in the gas phase enhances the a-C:H film formation.

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