論　文

INFRARED SPECTRA AND THERMAL DESORPTION SPECTRA OF ISOTOPICALLY MIXED AMORPHOUS HYDROGENATED CARBON FILMS PREPARED FROM MIXTURE OF CD_4 AND H_2 OR CH_4 AND D_2

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Isotopically mixed amorphous hydrogenated carbon films were prepared from 1:1 mixture of CH_4 and D_2 (a-CH:D). The atomoc ratio of H:D incorporated in the films were 0.83:0.17 for soft films and 0.80:0.20 for hard films. Compared the infrared spectra of these films with another spectra of the films prepared from 1:1 mixture of CD_4 and H_2 (a-CD:H), it was concluded that deuterium originating from D_2 in the plasma is considerede to be incorporated as an isolated aliphatic C-D bonds exclusively. Thermal desorption spectroscopy of hard a-CH:D films suports this idea because the films release H_2 and HD but very low D_2 by heat-treatment under vacuum.

Key Words : *amorphous, carbon film, IR spectra, TD spectra*

1. INTRODUCTION

One of the common preparation methods of amorphous hydrogenated carbon films (a-C:H) is the deposition in a hydrocarbon radio frequency glow discharge system onto negatively self biased substrates. It is well known that the application of negative bias onto substrates leads to the formation of hard a-C:H films[1]. The addition of hydrogen or nobel gases into the source gas also leads to the formation of hard a-C:H films[1]. Hard a-C:H films are considered to be formed by chemical etching or physical sputtering reactions by radicals and positive ions in the plasma. Chemical etching reactions subtract hydrogens from carbon atoms to give unsaturated carbons in the film which provides a bonding site for radicals in the plasma and in the film. The former leads to the film growth and the latter leads to carbon-carbon cross-linking bonds. Soft areas on the surface of deposited films are removed by physical sputtering. The net growth rate of a-C:H films is a result of the deposition of carbon materials and the erosion by radicals and ions in the plasma. Küpper et al reported the evidence for the hydrogen abstraction reaction that the impact of D atoms produced thermaly at surfaces of ultrathin a-C:H films bring about the formation of sp^3C-D from sp^3C-H through H-D substitution reaction[2] and also D-sp^3C-H from sp^2C-H by addition reaction of D[3]. The present paper gives some information about the etching process of a-C:H films; D atoms originated from D_2 are incorporated as an isolated aliphatic C-D bond in the films during RF plasma deposition.

2. EXPERIMENTAL

The amorphous carbon films were prepared using a radio frequency plasma (13.56 MHz) apparatus mentioned in the previous report[4]. After annealing Si substrates at 550K for overnight under

10^{-5} Pa , then they were treated with H_2 plasma (4 Pa, -300V bias) for 1 hour in order to reduce superficial oxide layer. Deposition conditions for amorphous carbon films are summarized in **Table 1**. The film thickness was monitored by He-Ne

laser interference signal *in situ*. Silicon substrate temperatures were ambient during deposition. The films made from CH_4-D_2 and CD_4-H_2 are assigned in this paper as a-CH:D films and a-CD-H films, respectively.

Table 1 Deposition conditions for the preparation of carbon films.

	Source Material	Pressure	Bias voltage (Power)	Deposition time
soft a-CH:D	CH_4(30sccm) D_2(30sccm)	6Pa	-40V(8W)	8 h 45 min
hard a-CH:D	CH_4(10sccm) D_2(10sccm)	4Pa	-300V(63W)	53 min
soft a-CD:H	CD_4(30sccm) H_2 (30sccm)	6Pa	-40V(8W)	11 h 54 min

The absolute concentrations of H and D were determined by elastic recoil detection (ERD) analysis using a beam of He^+ ions (E=2.6 MeV) from an accelerator and a scattering angle of 30°. The absolute concentrations of C and O were determined by proton enhanced cross section scattering (PES) analysis using a beam of H^+ ions (E=1.5 MeV) with a scattering angle of 165°. The reaction cross sections used for the determination of the components were taken from references[5-7]. Infrared spectra were measured using Perkin-Elmer Specrometer 1760X. The film thicknesses were measured mechanically by profilemeter TENCOR alpha-step 200.

3. RESULTS AND DISCUSSION

3.1 Elemental analyses of a-CH:D and a-CD:H films

Table 2 shows the elemental densities of a-CH:D and a-CD:H films determined by PES and ERD analyses together with the refractive indices of the films. Refractive indices of these films were

calculated by using optical film thicknesses estimated by He-Ne laser interference patteren and thicknesses measured mechanically by profilometry. Both soft a-CH:D and a-CD:H films were prepared under same conditions from 1:1 mixture of methane and hydrogen as shown in **Table 1**, however, the amount of incorporated hydrogen from additive D_2 or H_2 was different from each other, namely, the atomic ratio of H:D in the soft a-CH:D and hard a-CH:D films are 0.83:0.17 and 0.80:0.20, respectively. The ratio of H:D in the soft a-CD:H film is 0.23:0.77 as shown in **Table 2**. In this paper, the meanings of soft and hard are defined as whether the film could be scratched by a metal driver or not. The hard a-CH:D film prepared under -300V bias has a higher density of carbon atoms than soft films. The atomic ratio of (D+H)/C in hard films is much lower than soft films. This suggests that the concentrations of cross-linking C-C bonds in hard films is higher than that in soft films.

Table 2 Refractive indecis and densities of elements of carbon films obtained.

|	Optical thickness at 632 nm (nd)	Thickness by profilemeter (d)	Refractive index (n)	Elemental analyses C O D H (10^{22} cm^{-3})	Atomic ratio in H:D	Atomic ratio in (H+D)/C
soft a-CH:D	474nm	281nm	1.69	5.3 0.0 1.1 5.2	0.83:0.17	1.19
hard a-CH:D	790nm	370nm	2.14	8.3 0.0 1.0 4.0	0.80:0.20	0.60
soft a-CD:H	474nm	291nm	1.63	4.9 0.2 4.6 1.4	0.23:0.77	1.22

3.2 Infrared spectra

Figures 1(a), 1(b) and **1(c)** show infrared spectra of soft a-CH:D, hard a-CH:D and soft a-CD:H films, respectively. These spectra are presented here as the function of the extinction coefficient, k. These k spectra mean the extinction coefficient of the films including multiple coherent reflections in

the films themselves and taking into account the Kramers-Kronig-relation between the real and imaginary part of the refractive index. The method of making k spectra was similar to that reported previously[8].

As can be seen in **Figs. 1(a) , 1(b)** and **1(c)**, these carbon films show strong C-H stretching bands

around 2950 cm^{-1} and C-D stretching bands around 2150 cm^{-1}. There is a clear absorption edge at the region over 3000 cm^{-1} in **Fig.1(a)** while no absorption of the a-CD:H film can be seen in this region in **Fig. 1(c)**. The aborption over 3000 cm^{-1} is characteristic for sp^2C-H stretching band[9]. Therefore, it can be concluded that there is very few sp^2C-H bond formed in a-CD:H films. In other words, H originating from additional H_2 in the plasma is exclusively incorporated as sp^3C-H bond.
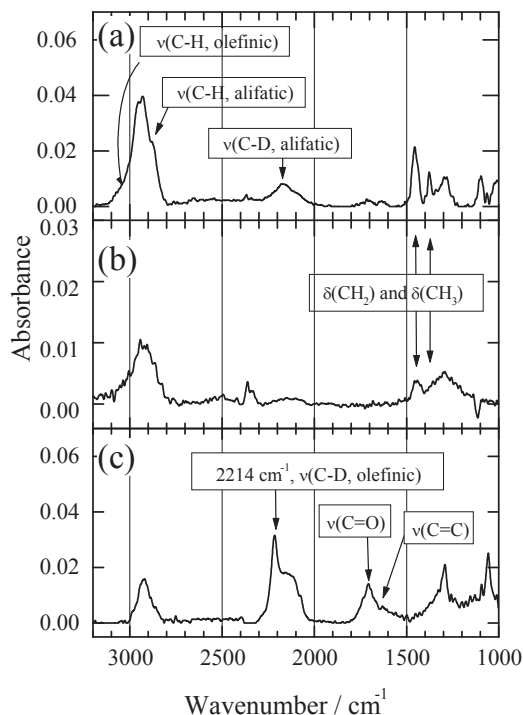
Fig. 1 Infrared spectra of amorphous hydrogenated films. (a) Soft a-CH:D film (prepared from mixture of CD_4 and H_2). (b) Hard a-CH:D film (prepared from mixture of CD_4 and H_2). (c) Soft a-CD:H film (prepared from mixture of CH_4 and D_2). These spectra are presented as the function of the extinction coefficient, k, see text.

Carrying over this consideration to the a-CH:D film, it is expected that the a-CH:D film has a similar structure. Namely, the a-CH:D film has almost no sp^2C-D bond. Küpper et al reported about the infrared spectra of a-C:H and a-C:D films and they assigned the peak around 2150 cm^{-1} to be the mixture of stretching sp^2C-D and sp^3C-D bonds. They estimated sp^2C-D absorption band to be 2274 cm^{-1} by a fitting process using spectra of a-C:H films and isotope factor (1/1.36)[3]. Using this isotope factor, aromatic C-H bond at 3057 cm^{-1} shifted to 2248 cm^{-1} and olefinic C-H bond at 3010 cm^{-1} similarly shift to 2214 cm^{-1}. As can be seen in

Fig. 1(c), the a-CD:H film has a strong absorption peak at 2214 cm^{-1} while the a-CH:D film has not as shown in **Fig. 1(a)**. The lack of sharp absoprtion at 2214 cm^{-1} for a-CH:D in **Fig. 1(a)** is referred to the lack of the absorption over 3000 cm^{-1} for the a-CD:H film in **Fig.1(c)**.

If the absorption centered at 2925 cm^{-1} in the infrared spectrum of the a-CD:H film in **Fig. 1(c)** contains H-sp^3C-H stretching, there should appear remarkable H-sp^3C-H deformation absorptions at around 1470 and 1380cm^{-1}, which is observed clearly in the infrared spectrum of the a-CH:D film in **Fig. 1(a)**. However there is no such absorptions in such region. Therefore, the absorption centered at 2925 cm^{-1} is considered to be isolated methyn type sp^3C-H stretching mode. In other wards, sp^3 carbon does not bond with more than one H. On the other, absorption band centered at 2175 cm^{-1} in **Fig. 1(a)** is considered to be isolated sp^3C-D stretching. These discussion is supported by TDS spectra mentioned later. The absorption intensity of C=C stretching around 1515 cm^{-1} in **Fig. 1** is rather low. However, the infrared spectrum of some di-substituted olefine, for example trans-C_3H_7-CH=CH-CH_3, often lacks C=C stretchng band around 1500 cm^{-1}.

Another characteristic difference between the two infrared spectra of two soft films in **Fig. 1** is that the a-CD:H film shows rather strong absorption around 1720 cm^{-1} (**Fig. 1(c)**) while the a-CH:D films does not. Since this band is assignable to C=O stretching (**Fig. 1(a)**), the a-CD:H films are likely to be oxidized easily while a-CH:D films are not. This result is confirmed by RBS analysis shown in **Table 2**. It is not clear from what this different property against oxidation originates. However, as can be seen in **Table 2**, the soft a-CH:D film has a little higher carbon density than the a-CD:H film. As mentioned previously, hard films with high carbon density over 8×10^{22} cm^{-3} show high resistivity against oxidation. It was suggested in the paper that the small pore size of hard films prevents the penetration of O_2 and H_2O into the film[10] which results in the high resistivity against erosion in air. The critical carbon density showing the resistivity against oxidation might lie in the region between that of these two soft films.

### 3.3 Heat treatment under vacuum (TD spectra)

As was reported previously, when soft a-C:D film are heated in air, its releasing rate of deuterium is much higher than that of carbon and after deuterium depletion the films show a resistivity against further erosion due to annealing in air[11]. It

is well known that amount of double bonds in a-C:H films increases during heat treatment. Craig et al reported that heat treatment under 1 mPa at 770K caused the increase in absorption of 1620 cm^{-1} [12]. In the present study this was confirmed by the increase in 1610 cm^{-1} absorption in infrared spectra when the film was heated in air. However there was no clear increase detected in this infrared reagion when the film was heated under vacuum below 10^{-7} Pa in the present study. Therefore less formation of C=C double bond during heat treatment under vacuum may responsible for sublimation of soft carbon films.

Figures 2, 3 and 4 show thermal desorption spectrometry (TDS) spectra for soft a-CH:D, hard a-CH:D and soft a-CD:H films with mass spectra, respectively. Herein, some of the signals of quadrupole mass analyzer (QMS) are plotted as a function of the substrate temperature. As was reported in the previous paper, most strong signal besides mass number 18 amu for TDS spectrum for softa-C:D films are mass number 28[11]. In the present study for soft a-CH:D and a-CD:H films, the signals for mass number 28 also shows strong peak as shown in Figs. 2(b) and 4(b). The respossible molecules for mass number 28 are CO, C_2H_4 and C_2D_2. If C_2H_4 is exclusively responnsible
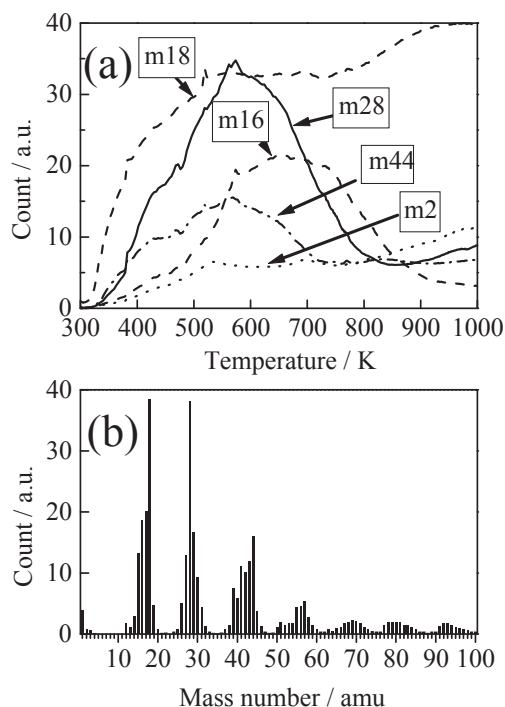
Fig.2 (a)Thermal desorption (TD) spectra of the soft a-CH:D film monitored at mass numbers of 2(indicated as m2 in the figure), 16, 28 and 40 amu. (b)Mass spectrum of the soft a-CH:D film obtained at 540K.
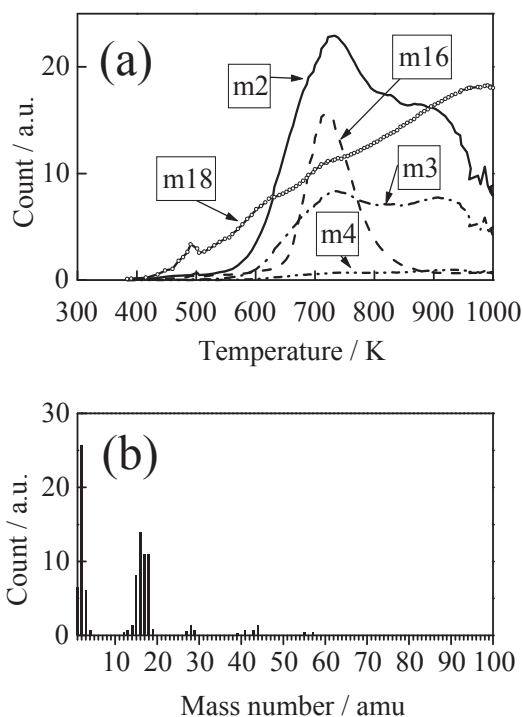
Fig.3 (a)Thermal desorption (TD) spectra of the hard a-CH:D film monitored at mass numbers of 2(indicated as m2 in the figure), 3 and 4 amu. (b)Mass spectrum of the soft a-CH:D film obtained at 760K.
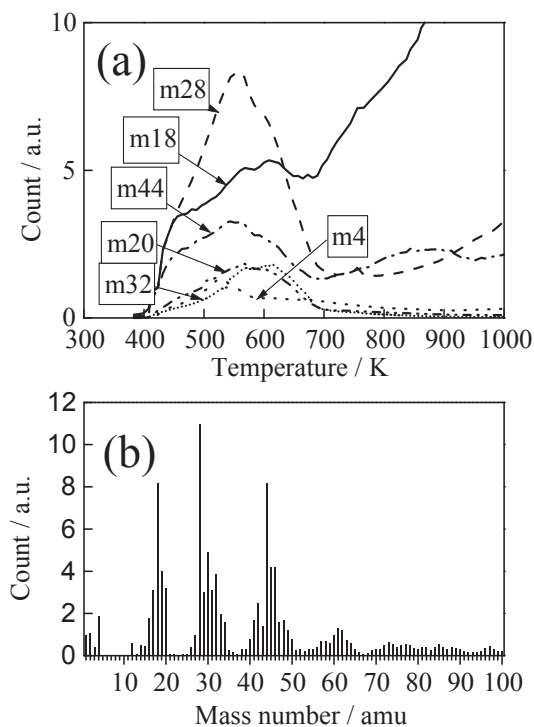
Fig.4 (a)Thermal desorption (TD) spectra of the soft a-CD:H film monitored at mass numbers of 4(indicated as m4 in the figure), 18, 20, 28, 32 and 44 amu. (b)Mass spectrum of the soft a-CH:D film obtained at 570K.

for the intensity at mass number 28 in **Fig. 2(b)** for a-CH:D, C_2D_4 (mass number 32) for a-CD:H in **Fig. 4(b)** should samely show strong intensity. However, **Fig. 4(b)** does not show strong intensity for mass number 32 but 28. In addition, the profile of mass number 28 makes large peaks which indicates that this signal does not come from back ground CO as shown in **Fig. 2(a)**. Besides the onset temperatures for mass number 18, 28 and 44 amu are almost the same. Then a part of H_2O(m18), CO (m28) and CO_2 (m44) are assumed to be evolved by sample itself.

As was mentioned previously, soft a-C:H films release hydrocarbon species exclusively during annearing under vacuum, while hard a-C:H films release predominantly H_2 molecules to give semi-hard a-C:H films with very low hydrogen concentration[10]. We assumed in relation to the infrared spectra that sp^3 carbon does not bond with more than one D in the a-CH:D films. TDS spectrum of hard a-CH:D film in **Fig.3** supports this idea. Namely, it releaes H_2, HD with about a half signal intensity of H_2, and very low D_2. In addition, the intensity of mass number 16 show peak which indicates that CH_4 must be evolved from the bulk of the hard films. However, it is not clear at present whether CH_4 was produced by the thermal degradation of the film itself or by the simple diffusion of free gaseous CH_4 incorporated in the films.

As mentioned above, H originating from H_2 is exclusively incorporated as aliphatic C-H bonds in a-CD:H films. As can be seen in **Table 2**, the ratio of incorporated H isotope is estimated as an atomic ratio of H/D of 0.23/0.77. Taking into the consideration that there is little sp^2C-H bond in the a-CD:H films, this atomic ratio seems to be rather high. Küpper et al reported that D generated by thermal dissociation of D_2 reacts with sp^3C-H to give sp^3C-D through H-D substitution reaction[2] and also reacts with sp^2C-H to give D-sp^3C-H by addition reaction of D[3]. If the addition reaction of H radicals and/or H^+ ions to C=C double bonds formed in the film is the exclusive main reaction to form C-H bonds, it is clear that there is no sp^2C-H bond in the film, because the addition reacion of H convert sp^2C to sp^3C spontaneously. In order to estimate this addition reaction, a soft a-C:D film without C-H bond prepared from CD_4 was treated in a H_2 plasma with self bias of -40, -80, and -120V. However there is no increase in the absorption region of sp^3C-H around 2950 cm^{-1} nor decrease of sp^2C-D at 2214 cm^{-1} in infrared spectra. Only erosion with the decrease of film thickness could be observed. So this experiment is failed to show the direct evidence of addition reaction or substitution reaction of H on the film surfaces. Therefore it is not clear at present why there is so little sp^2C-H bond in the a-CD:H films.

4. CONCLUSIONS

(1) Compared the infrared spectra of a-CH:D and a-CD:H films, it was concluded that the strong absorption peak at 2214 cm^{-1} was assigned to olefinic C-D stretching band.
(2) In the soft a-CD:H film, H originating from H_2 in the plasma was incorporated as an isolated aliphatic C-H bond exclusively. Because -CH_2- and -CH_3 deformation absorptions at 1470 and 1380 cm^{-1} were missed in the infrared spectrum of the a-CD:H film.
(3) Thermal desorption spectroscopy of hard a-CH:D films suports above conclusion because the films release H_2 and HD but very low D_2 by heat-treatment under vacuum.

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