Control of Deposition Profile and Properties of Plasma CVD Carbon Films

Kazunori Koga[1], Tatsuya Urakawa[1], Giichiro Uchida[1],
Kunihiro Kamataki[2], Yenwoon Seo[1], Naho Itagaki[1,5], Masaharu Shiratani[1,6],
Yuuichi Setsuhara[3,6], Makoto Sekine[4,6], and Masaru Hori[4,6]

[1]*Graduate School of Information Science and Electrical Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan,*

[2]*Faculty of Arts and Science, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan*

[3]*Joining and Welding Research Institute, Osaka University, Osaka, Japan,*

[4]*Dept. of Electrical Engineering and Computer Science, Nagoya University, Nagoya, Japan,*

[5]*PRESTO, Japan Science and Technology Agency, Tokyo 102-0075, Japan*

[6]*CREST, Japan Science and Technology Agency, Tokyo 102-0075, Japan*

We have succeeded to deposit anisotropic and top surface deposition profile on substrates with trenches using H-assisted plasma CVD of Ar + H_2 + C_7H_8 at a low substrate temperature of 100 ^oC. For the anisotropic deposition profile, carbon is deposited without being deposited on side-wall of trenches. For the top surface deposition profile, carbon is deposited at only top surface. The optical emission measurements and evaluation of deposition rate have revealed that a high flux of H atmos is the key to the deposition profile control. The mass density of the films and their Raman spectrum have shown that their structure is a-C:H.

Keywords: carbon film, deposition profile, plasma CVD, trench

1. Introduction

Wide interest in carbon films such as diamond-like carbon (DLC) and hydrogenated amorphous carbon (a-C:H) stems from their attractive properties such as biocompatibility, chemical inertness, high mechanical hardness, optical transparency and wide band gap [1-6] and hence have widespread applications as protective coatings in several areas such as car parts, micro-electromechanical systems (MEMS) and as magnetic storage disks [5]. DLC films first reported in the 70s were deposited by ion beam deposition [7, 8], and a-C:H films introduced in the beginning of 80s were deposited by rf plasma CVD [9]. Since then a-C:H films deposited by rf plasma CVD have been studied intensively by many researchers [10]. In addition, the most widely used technique for DLC films deposition is rf plasma CVD. The plasma CVD has the advantage of being possible to deposit at a low substrate temperature compared with thermal CVD methods. The advantages allow us to make protective coatings on polymer such as PMMA (poly(methyl methacrylate)) employed for photoresist films.

Deposition profile control of carbon films on fine structures is one of the concerns for MEMS and ultra large scale integration (ULSI) applications. So far, we have succeeded in controlling deposition profile of Cu films on trench, and have realized sub-conformal, conformal and anisotropic deposition, for which Cu is filled without being deposited on side-wall of trenches, using a H-assisted plasma CVD method [11-16]. We have applied the method to carbon film deposition on trenched substrates in order to control deposition profile [17-21]. In this paper, we have examined effects of Ar gas addition to H_2+Toluene (C_7H_8) plasma on deposition profile

control at a low substrate temperature of 100°C using the H-assisted plasma CVD method.

2. Experimental

Experiments were performed using the H-assisted plasma CVD reactor, in which a capacitively-coupled main discharge and an inductive-coupled discharge for an H atom source were sustained as shown in Fig. 1. For the main discharge, a mesh powered electrode of 85 mm in diameter and a plane substrate electrode of 85 mm in diameter were placed at a distance of 33 mm. The main discharge is mainly used for producing carbon containing radicals as precursors for carbon deposition. The excitation frequency of the main discharge was 28 MHz and the supplied power P_m was below 45W. The discharge of the H atom source was sustained with an rf induction coil of 100 mm in diameter placed at 65 mm above the substrate electrode of the main discharge. The H atom source can generate a high flux of H atoms toward the substrate. The excitation frequency is 13.56 MHz and the supplied power P_H = 500 W. C_7H_8 was used for ingredient molecules for carbon film deposition. It vaporized at 150°C, and supplied with H_2. The C_7H_8 flow rate was 0.63 sccm. Ar diluted H_2 gas was introduced from the top of the reactor. The total flow rate of H_2 and Ar was 90 sccm. The total pressure was 13 Pa. The trench substrate set on a substrate electrode. The trenches were fabricated with SiO_2 on crystalline silicon wafers and were covered by WN layer. The aspect ratio which is defined as a ratio of the depth of the trenches and their width was between 0.7 and 5. An rf bias voltage of 400 kHz was applied to the substrate for controlling kinetic energy of ions incident on it. The bias voltage was -7 V. Since the plasma potential which was measured by Langmuir prove was 25 V, the ion energy E_i was 32 eV.

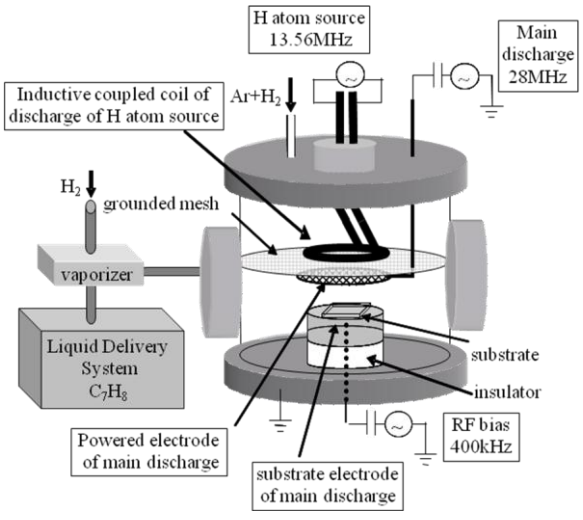

Fig. 1. H-assisted plasma CVD method.

3. Results and Discussion

The flux of H atoms towards the substrate is an important factor for the carbon film deposition. The deposition rate is reduced by etching by H atoms. To study effects of Ar dilution on the H atom generation, we have measured optical emission intensity of H_α at 20 mm above the center of the substrate electrode. Figure 2 shows dependence of the H_α intensity on a flow rate ratio R= $[H_2]/([H_2]+[Ar])$. The intensity has a maximum value around R= 22 %. It indicates that generation of the H atoms is enhanced by Ar dilution. To evaluate the deposition profile control, we have evaluated a ratio of the deposition rate ratio at side wall of the trenches and that at top $DR_{sidewall}/DR_{top}$ ant a ratio of the deposition rate at bottom and that at top DR_{bottom}/DR_{top}. Figure 3(a) and 3(b) shows dependence of $DR_{sidewall}/DR_{top}$ and DR_{bottom}/DR_{top} on an aspect ratio of the trenches as a parameter of R, respectively. The deposition rate at the top is constant irrespective of the aspect ratio, whereas the deposition rates at the sidewall and bottom tend to decrease with increasing the aspect ratio.

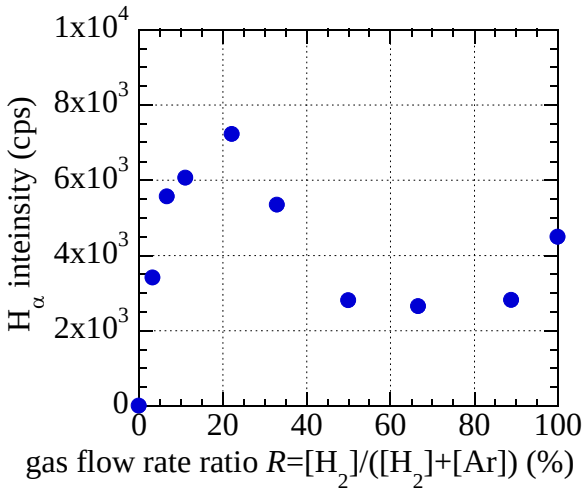

Fig. 2. Dependence of H_α intensity on gas flow rate ratio R.

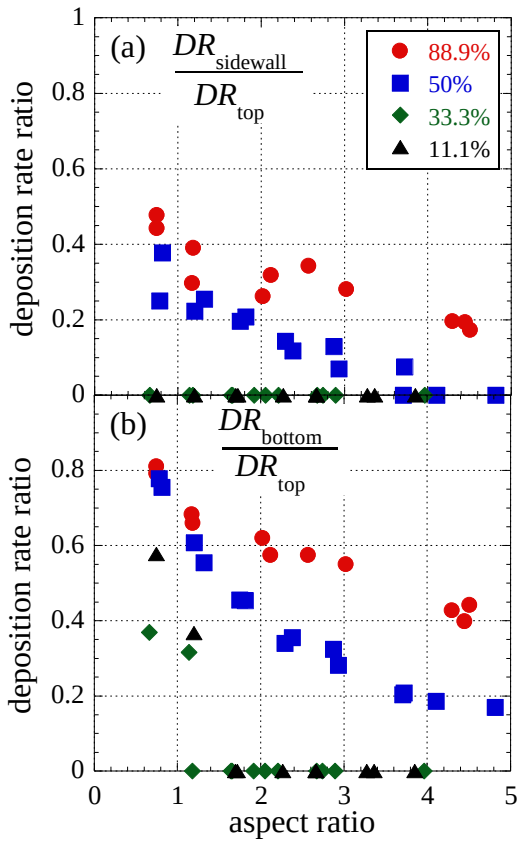

Fig. 3. Dependence of deposition rate ratio on aspect ratio of trenches as a parameter of R.

Thus, the deposition rate ratio decreases with increasing the aspect ratio. This is because the incident deposition radical flux per surface area in a trench decreases with increasing the aspect ratio. The deposition rate ratio tends to decrease with decreasing the *R*. The $DR_{sidewall}/DR_{top}$ is smaller than DR_{bottom}/DR_{top}. The decrease in the deposition rate ratio for the side wall is larger than that for the bottom. No deposition takes place at the sidewall of trenches of all aspect ratio in Fig. 3(a) for the gas flow ratio *R* = 33.3 % 11.1 %. In other words, we have succeeded in deposition carbon films on trenched substrates in an anisotropic way. Figure 4(a) shows a cross-section SEM image of the anisotropic deposition profile. For *R*= 33.3 % and 11.1 %, the carbon films does not deposit at both of the sidewall and bottom for the aspect ratio > 1.6. We have realized top surface deposition. Figure 4(b) shows a SEM image of top surface deposition profile.

Experimental deposition profiles are determined by the balance between deposition of carbon containing radicals and etching by H atoms. When the etching rate surpasses the deposition rate of carbon containing radicals, no deposition takes place there. Irradiation of ions induces structural modification at the film surface [22]. The etching rate for the modified hard films is significantly lower than that for the unmodified films. Therefore etching rates at the top and bottom is lower than that at sidewall, because ion fluxes on the top and bottom are higher than that on the sidewall. Moreover, incident deposition radical flux per surface area at the sidewall and bottom is lower than that at the top. Because of the lower incident deposition radical flux per surface area and the higher etching rate, the deposition rate at the sidewall is the lowest. The etching rate at the top is lower than that at bottom, because ion fluxes on the top is higher than that on the bottom. Thus, the deposition rate at the bottom is lower than that at the top. We can realize anisotropic and top surface deposition with increasing H atom flux to suppress sidewall and bottom deposition. Therefore, a high H atom flux is the key to anisotropic and top surface deposition.

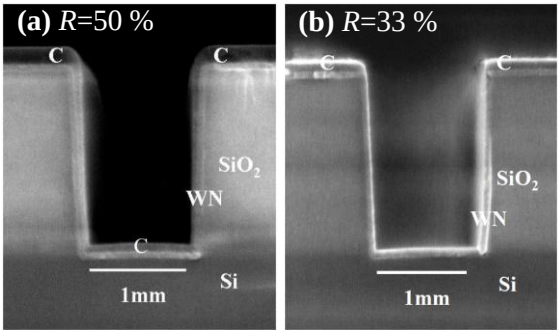

Fig. 4. Cross-section SEM images of (a) anisotropic deposition profile for *R*= 50 % and (b) top surface deposition profile for *R*= 33.3 %.

The hardness of the carbon films is important to employ this deposition profile control to fabricate protection layer in fine structures. We have evaluated properties of the films deposited for *R*= 33%. Table 1 shows the film density, peak intensity ratio of G band and D band in Raman spectrum and etch selectivity of the films for SiLK films which is used as low-k materials for dielectric layer in ULSI. The films density of 1.54 g/cm^3 and the Raman peak ratio of 1.93 show that the deposited film is a-C:H films. The films have a moderate value of the etch

Table 1. Film properties of the carbon films deposited for R= 33.3 %.

Film properties for *R*= 33 %	
Mass density (g/cm^3)	1.54
Raman peak ratio of G band and D band	1.93
Etch selectivity for SiLK^{TM}	0.88

selectivity of 0.88. To improve the hardness of the films, we have found that the E_i is an important parameter [20, 21]. For E_i= 100 eV, the film density and the etch selectivity have maximum values. The film density and the etch selectivity for E_i= 100 eV is 2.27 g/cm^3 and 4.4, respectively [20, 21]. The results indicate our deposition profile control method is useful for depositing protection layer in fine structures.

4.Conclusions

We have studied the aspect ratio dependence of deposition rate ratio as a parameter of *R*. The following conclusions are obtained in this study.

1) Optical emission intensity of H_α in the main discharge region has a maximum value for *R*= 22 %. The generation of H atoms is enhanced by Ar dilution. A high H atom flux is the key to anisotropic and top surface deposition.

2) We have succeeded to deposit anisotropic and top surface deposition profile on substrates with submicron wide trenches using H-assisted plasma CVD of Ar + H_2 + C_7H_8 at a low substrate temperature of 100 ^oC.

3) The films deposited for R= 33.3 % are a-C:H films and has a moderate etching selectivity for SiLK films of 0.88. To improve the film hardness, the ion energy is important. For E_i=100eV, the etch selectivity increases to 4.4.

Acknowledgements

This work was partly supported by JST, CREST and MEXT.

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