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Substrate temperature dependence of deposition profile of plasma CVD carbon films in trenches

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To control deposition profile of carbon films in trenches, we have studied substrate temperature and aspect ratio dependence of deposition rate of carbon films, deposited by CVD plasma of toluene diluted H_2, in trenches. The deposition rates increases with decreasing the aspect ratio, because the incident radical flux per surface area in a trench increases with decreasing the aspect ratio. The deposition rate increases with decreasing the substrate temperature, because of the lower etching rate by H atoms at the lower temperature.

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

1. Introduction

Diamond-like carbon (DLC) films first reported in the 1970s were deposited by ion beam deposition. [1, 2], and hydrogenated amorphous carbon (a-C:H) films introduced in the beginning of 1980s were deposited by rf plasma chemical vapor deposition (CVD) [3]. Since then a-C:H films deposited by rf plasma CVD have been studied intensively by several authors [4]. Moreover, the most widely used technique for DLC films deposition is rf plasma CVD. DLC is a term used to describe a variety of carbon based materials with attractive properties, such as a high mechanical hardness, chemical inertness, optical transparency and wide band gap [5-8]. DLC films have widespread applications as protective coatings in several areas such as car parts, biomedical coatings and micro-electromechanical systems (MEMS). Deposition profile of the DLC and a-C:H films in trenches is one of the concerns to realize coatings on patterned substrates.

We have studied deposition profile of plasma CVD Cu films in trenches for nano-fabrications [9-16]. We have succeeded in controlling deposition profile of Cu in trenches, and have realized sub-conformal, conformal and anisotropic deposition, for which Cu is filled preferentially from the bottom of trenches without being deposited on the sidewall of trenches, using a H-assisted plasma CVD method [9-16].

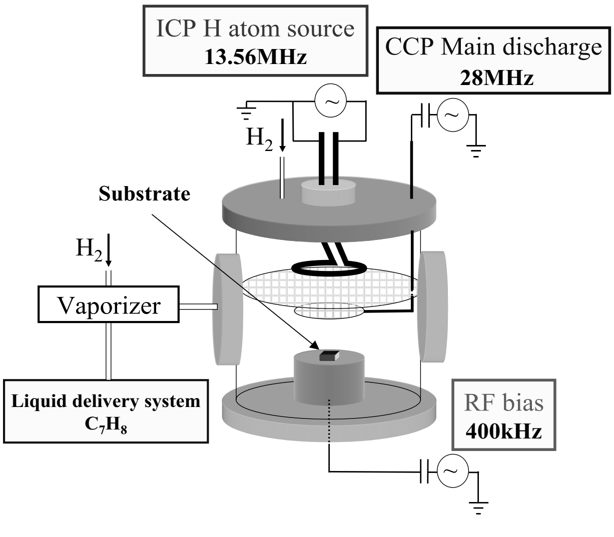

Fig. 1. Experimental setup.

We are applying the deposition profile control method to carbon films in trenches. Here, we report dependence of deposition rate of plasma CVD carbon films in trenches on substrate temperature and on aspect ratio.

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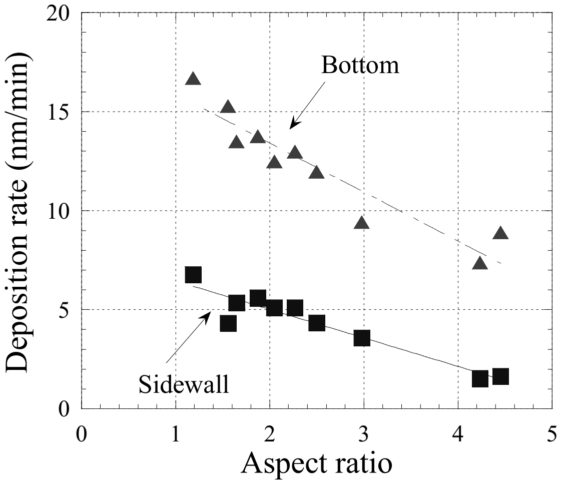

$$\text{Aspect ratio} = \frac{\text{trench depth}}{\text{trench width}}$$

Fig. 2. Dependence of deposition rate on aspect ratio. Substrate temperature 220 °C, P_m 45W, bias voltage -100 V, C_7H_8 4.5sccm. Trench width 2.0-2.2 μm.

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. This reactor provided independent control of generation rates of deposition radicals and H atoms. 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 discharge of 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. Deposition was carried out without employing the H atom source. The excitation frequency of the main discharge was 28 MHz and the supplied power P_m was below 45 W. An rf bias voltage of 400 kHz was applied to the substrate for controlling kinetic energy of ions incident on it. The supplied power P_{bias} was 0-5 W. Toluene (C_7H_8) was vaporized at 150 °C, and supplied with H_2. The flow rate of toluene and that of H_2 were 4.5 sccm and 90 sccm. The total pressure was 13 Pa and the partial pressure of toluene was 0.62 Pa. Si substrates with trenches covered with WN were treated by ultrasonic cleaning using trichloroethylene, acetone, and ultra pure water, then they were dried before deposition experiments.

Thickness and deposition profile of carbon films in trenches were obtained with a scanning electron micro scope (SEM:JEOL, JSM-6320FZ). Chemical compositions were analyzed with an energy dispersive X-ray spectrometer (EDS:OXFORD, ISIS-L200). Information on structure of carbon films was obtained with a laser Raman spectrometer (JASCO, NRS-3100).

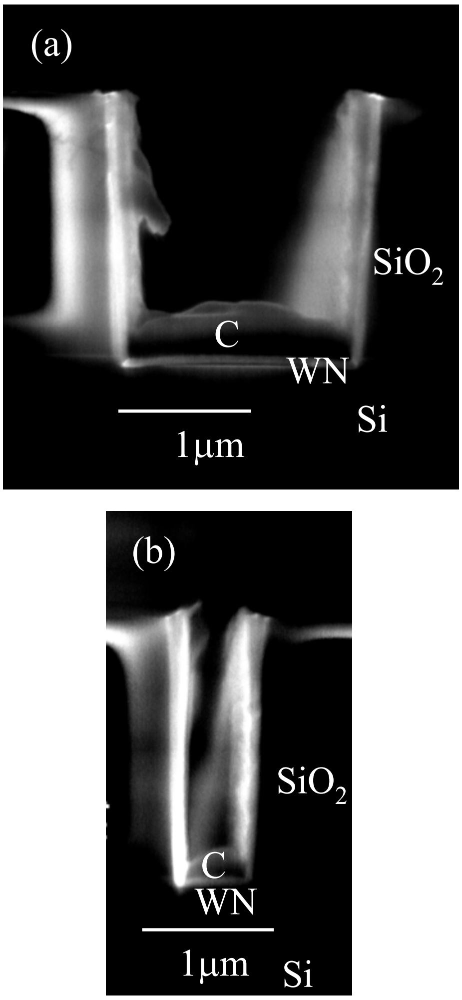

Fig. 3. Cross section SEM images of carbon films deposited in a trench. P_m 45W, bias voltage -100 V, C_7H_8 4.5sccm. Substrate temperature 220 °C.
(a) Aspect ratio =1.18, and (b)aspect ratio = 4.46.

3. Results and Discussion

First, we have studied aspect ratio dependence of deposition rates at the bottom and sidewall of trenches. Figures 2 and 3 show the results. The deposition rate at the bottom increases from 7.39 nm/min to 16.7 nm/min and at the sidewall increases from 1.53 nm/min to 6.78 nm/min with decreasing the aspect ratio from 4.23 to 1.18. The maximum deposition rate of 16.7 nm/min at the bottom and 6.78 nm/min at the sidewall are obtained for the aspect ratio of 1.18. The deposition rates at the bottom and sidewall increases with decreasing the aspect ratio. We speculate that the incident radical flux per surface area in a trench increases with decreasing the aspect ratio and hence the aspect ratio dependence in Fig.2 is realized.

Next, we have studied dependence of the deposition rates at the bottom, sidewall and top of trenches on the substrate temperature. Figures 4 and 5 show the results.

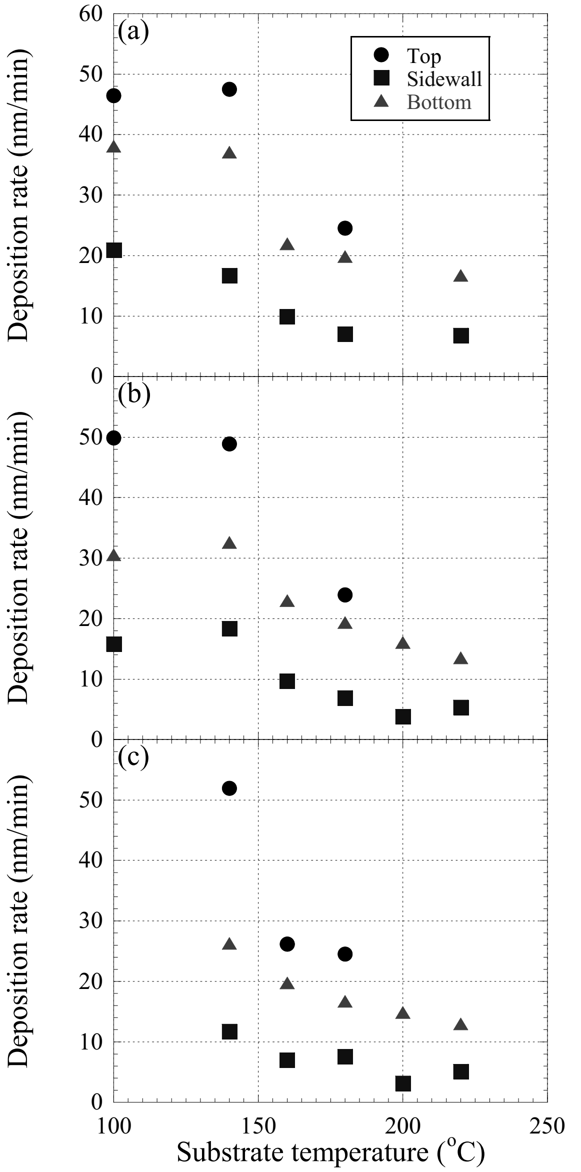

Fig. 4. Dependence of deposition rate on substrate temperature for aspect ratio of (a)1.18-1.42, (b)1.43-1.78, (c)2.29-2.49, P_m 45W, bias voltage -100 V, C_7H_8 4.5sccm. Trench width 2.0-2.2 μm.

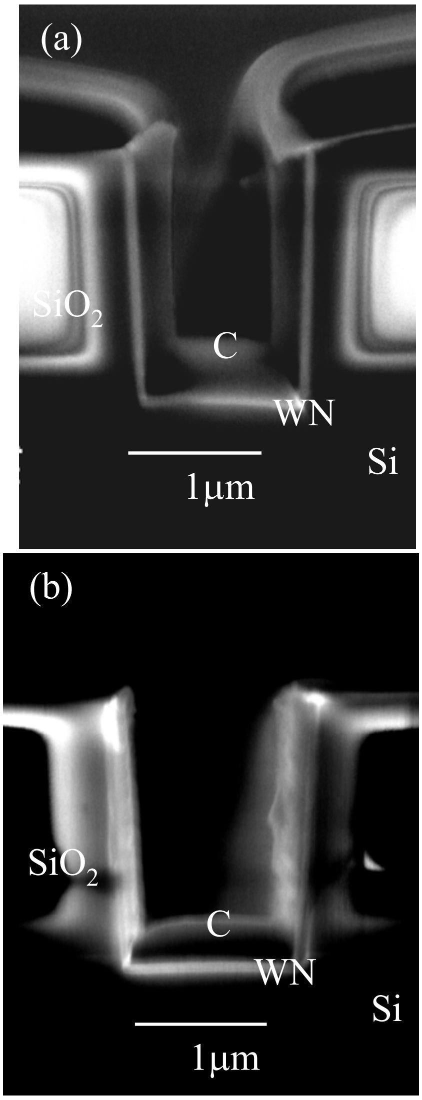

Fig. 5. Cross section SEM image of carbon films deposited in a trench. P_m 45W, bias voltage -100 V, C_7H_8 4.5sccm.

(a) nearby conformal profile at substrate temperature of 100°C, and (b) anisotropic profile at substrate temperature of 220°C.

The maximum deposition rate of 38.1 nm/min at the bottom and 20.9 nm/min at sidewall are obtained for 100°C. The deposition rates at the bottom and sidewall increase with decreasing the temperature from 220°C to 100°C. The experimsntal deposition rate DR is expressed as, $DR=DR_{neutral} + DR_{ion} - ER$, where $DR_{neutral}$ and DR_{ion} are the deposition rate due to neutral radicals and ions, and ER is the chemical etching rate due to H atoms. The first two terms is the right hand side of the above equation have little temperature dependence [17]. The etching rate by H atoms increases with temperature, and hence the experimental deposition rate decreases with temperature as shown in Fig. 4. Moreover, we have deduced the apparent activation energy from the results above 140°C. Table 1 shows the activation energies of deposition rates at the sidewall and bottom for trenches of aspect ratio of 1.18-1.42, 1.43-1.78 and 2.29-2.49. All activation energies are minus, which corresponds to the lower deposition rates at the higher temperature.

Table I. Activation energy of deposition rate.

Aspect ratio	1.18-1.42	1.43-1.78	2.29-2.49
Sidewall	-0.17 [eV]	-0.20 [eV]	-0.22 [eV]
Bottom	-0.14 [eV]	-0.097 [eV]	-0.12 [eV]

We have analyzed chemical compositions of the films

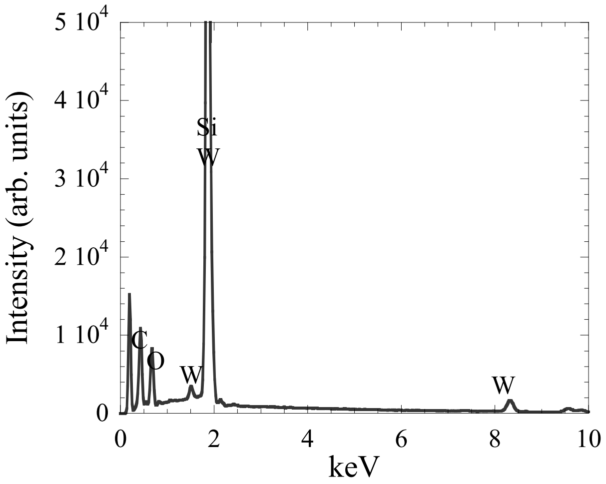

Fig. 6. Chemical compositions of cross section of a trench of film. P_m=45W, Substrate temperature 153°C, C_7H_8 4.5sccm, H_2 90sccm, total pressure 0.1 Torr.

with EDS. Figure 6 shows the chemical compositions of cross section of a trench with film. The main chemical composition of films is carbon.

Finally, we have measured Raman spectrum of carbon films. Figure 7 shows the result. There exist a small graphite-peak (1580cm^{-1}) and a disorder-peak (1380cm^{-1}) .

4. Conclusions

We have realized sub-conformal and conformal deposition of plasma CVD carbon films in trenches. We have studied substrate temperature and aspect ratio dependence of deposition rate of carbon films in trenches. The deposition rates increases with decreasing the aspect ratio, because the incident radical flux per surface area in a trench increases with decreasing the aspect ratio. The deposition rate increases with decreasing the substrate temperature, because of the lower etching rate by H atoms at the lower temperature.

Acknowledgement

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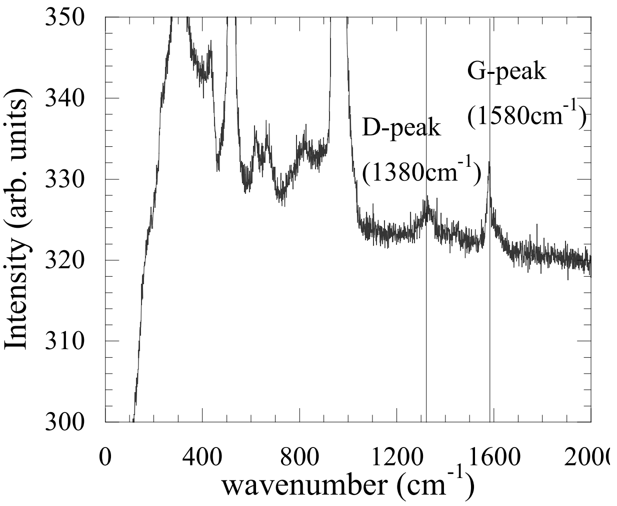

Fig. 7. Raman spectrum of carbon film. P_m=45W, Substrate temperature 153°C, C_7H_8 4.5sccm, H_2 90sccm, total pressure 0.1 Torr.

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