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Fluorine Doped SiO_2 for Low Dielectric Constant Films in Sub-Half Micron ULSI Multilevel Interconnection

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Plasma CVD of fluorine doped SiO_2 (SiOF) for interlayer dielectrics in ULSI multilevel interconnection was investigated. Resistance to water absorption of SiOF was found to depend on CVD method. And low dielectric constant of 3.3 without water absorption was obtained by using high density plasma CVD. Then it was confirmed that the key factor to form high quality films was energy of ions impinging on wafer surface. Moreover, it was concluded that the reason the water absorption of SiOF with high F content was formation of Si-F_2 in the films by FT-IR measurement.

1. INTRODUCTION

Multilevel interconnection is becoming increasingly important for fabricating high performance sub-half micron devices. Regarding multilevel interconnection of sub-half micron devices, a strong demand for interlayer dielectric films is a low dielectric constant as well as high film quality such as high resistance to water absorption. We have been developing F-doped SiO_2 (SiOF) as a promising material for interlayer dielectrics with low dielectric constant(1)(2)(3)(4). However, it was found that water absorption increased with increasing F content in exposing atmosphere. This is a serious problem because it causes device degradations(5).

In this paper, we describe the relationship between plasma CVD methods and water absorption property of SiOF, and the result of investigations for CVD mechanisms and water absorption mechanism.

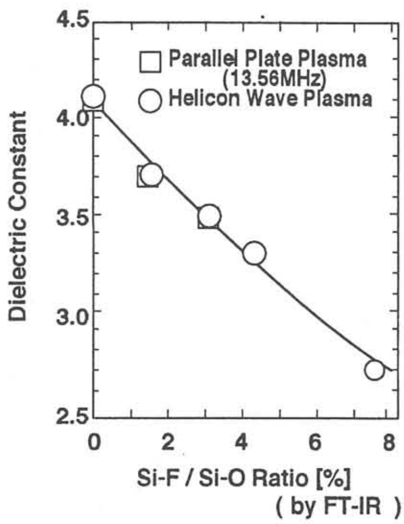


Figure 1: Dielectric constant of as-deposited F-doped SiO_2 as a function of F content in films

2. EXPERIMENT

We used two types of plasma enhanced CVD reactors. One of them was an anode-couple type parallel plate electrode reactor (13.56 MHz), and another reactor was a high density plasma CVD reactor with helicon wave excited plasma source. These reactors have already been described in previous publication in detail(2). Tetramethylsilane(TEOS) and O_2 were used as CVD source gases and CF_4 was used to add F into SiO_2 during CVD process. F content in SiO_2 was controlled to change adding CF_4 flow rate.

3. RESULTS AND DISCUSSION

3.1 DIELECTRIC CONSTANT

Figure 1 shows the dielectric constant of CVD films produced by different CVD methods as a function of F content in SiO_2. In our experiment, F content of the films are given as integrated intensity ratio of Si-F(bond stretching)/Si-O(bond stretching) by FT-IR measurement.

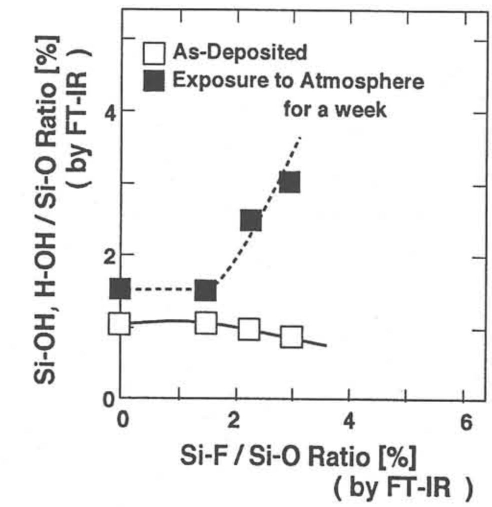
Dielectric constant uniquely depended on F contents and did not depend on the CVD methods as shown in Fig.1. We could obtain the dielectric constant of 2.7 to use high density plasma for as deposited film.

3.2 WATER ABSORPTION PROPERTIES

Water absorption property of SiOF depended on a CVD method. Figure 2 shows water absorption properties for the SiOF films produced by parallel plate plasma CVD and high density plasma CVD. Figure 2 (a) shows Si-OH+H-OH/Si-O band integrated intensity ratio measured by FT-IR as a function of F content in the films before and after exposing atmosphere for a week in the case of parallel plate plasma CVD. And Fig.2 (b) shows that in the case of high density plasma. In both cases, differences between before and after exposing atmosphere present quantity of water absorption during the atmosphere exposure.

In this results, at the F content lower than 2 %, water absorption took place for both cases of CVD methods. these slight water absorption could be considered to be due to the existence of OH bond in as deposited films. It was reported that OH bonds in SiO_2 have strong relationship with water absorption.(6) At F content higher than 2 %, water absorption increased remarkably with increasing F content for the parallel plate plasma CVD. On the other hand, water absorption was not observed at F content between 2 - 4 % in the case of high density plasma CVD. However, at F content higher than 4 %, water absorption increased drastically.

(a)



(b)

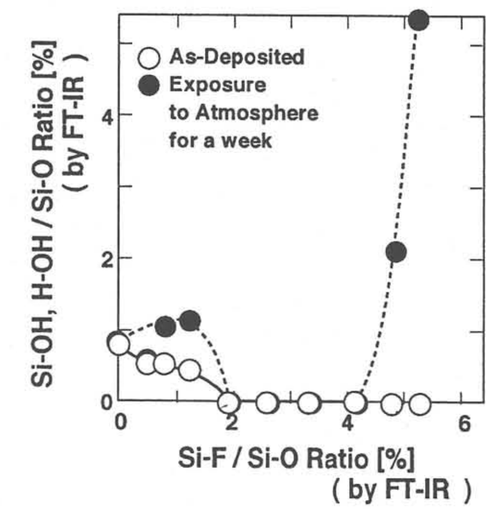


Figure 2(a): Fig. 2(a)shows Si-OH+H-OH/Si-O band integrated intensity ratio measured by FT-IR as a function of F content in the films before and after exposing atmosphere for a week in the case of parallel plate plasma CVD. Fig.2(b) shows that in the case of high density plasma.

Next we investigated the reason for the film qualities difference between CVD methods from the CVD mechanisms point of view.

3.3 CVD MECHANISM

We focused on gas dissociation efficiency and energy of ions impinging on the wafer surface to understand CVD mechanisms. Then we found that gas dissociation efficiency of high density plasma CVD was higher than that of parallel plate plasma CVD, as reported previously.(2)

Next, we investigated energy of ions impinging on the surface by Q-pole mass analysis for different CVD apparatus. Experimental procedure of this measurement was reported previously (3). Figure 3 shows the result of ion energy distribution measurements for the parallel plate plasma CVD and high density plasma CVD. In this experiment, we measured O_2^+ ions energy distributions using O_2 plasma to avoid the contamination due to deposition gas in the Q-pole analyzer, and discharge pressure and input power were the same as deposition conditions. From this result, it was clear that ion energy of high density plasma was higher than parallel plate plasma CVD. From these results, we concluded that gas dissociation efficiency and ion energy strongly related to film qualities. Namely, high gas dissociation efficiency caused to produce much F in the gas phase, which could be considered to scavenge impurities such as C and H from deposition precursors in the gas phase and surface. And incidence of higher energy ions could aiso be considered to remove carbon and hydrogen effectively from precursors sticking on the surface. Actually impurity inclusion in SiOF film produced by high density plasma CVD is lower than that of parallel plate

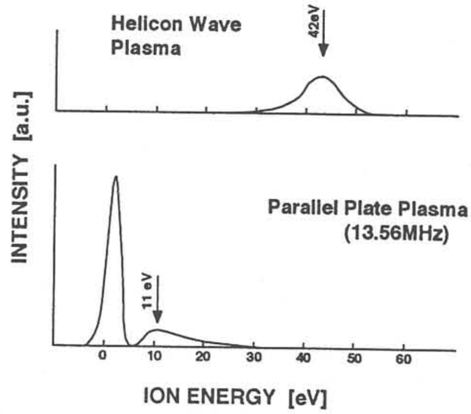


Figure 3: Ion energy distributions of O_2^+ in O_2 discharge

plasma CVD. Moreover, it could be considered that ion bombardment caused to densify Si-O network. However, relationship between ion energy and network structure have not been clarified in detail. These impurity inclusion and network structure could be considered to affect water absorption

3.4 WATER ABSORPTION MECHANISM

Next we investigated water absorption mechanism at F content more than 4 % for high density plasma. In this region, water absorption could be strongly related to the Si-F bond produce in the SiO_2, because the as deposited film did not include OH and other impurities as mentioned previously. First of all, we measured Si-F bond structure in detail by FT-IR[(4)]. Fig.4 shows FT-IR spectrum of Si-F bond for the film with F content of 9 %. As shown in Fig.4(a) absorbance band of the Si-F bond was deconvoluted three Gaussian bands.The peak at around 940 cm^{-1} and 988 cm^{-1} were corresponded to the Si-F bond and the $Si\text{-}F_2$ bond , respectively. The peak at around 920 cm^{-1} could not be assigned clearly, however, it could be considered to be Si-F bond which was close by another Si-F bond. Fig.4(b) shows integrated intensity change of these 3 bands as a function of F content of the films. As shown in Fig.4(b), $Si\text{-}F_2$ band appeared at F content more than 4 % at which water absorption started to increase drastically. On the other hand, Si-F band (940 cm^{-1}) increase monotonously with increasing F content. This result suggest $Si\text{-}F_2$ strongly related to water absorption. Actually, we confirmed that the band at 988 cm^{-1} for SiO_2 with 9 % F disappeared after absorbing water in exposing to atmosphere. Namely, this result presented that $Si\text{-}F_2$ reacted easily with H_2O. We concluded that $Si\text{-}F_2$ formation in the film caused water absorption. However, the formation mechanism of $Si\text{-}F_2$ could not be clarified.

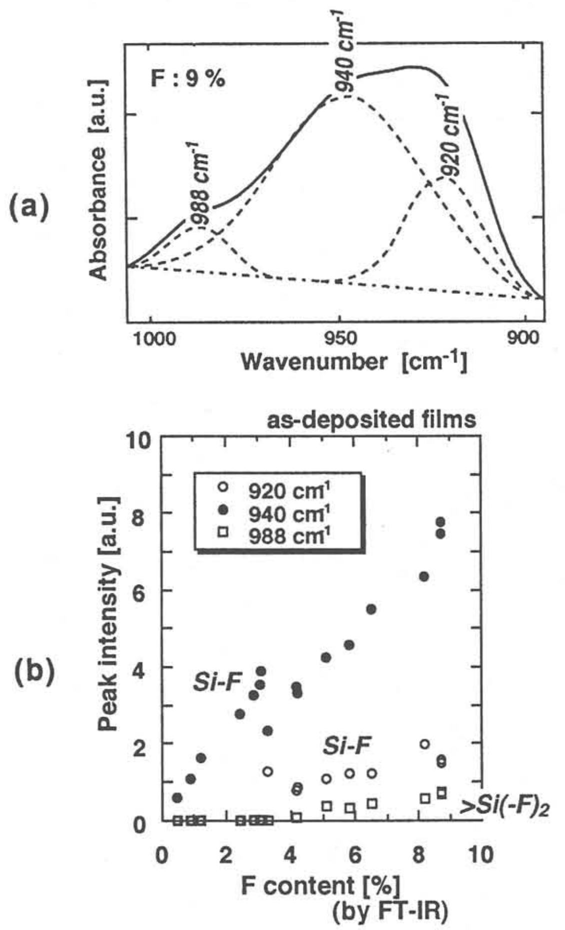


Figure 4: Fig. 4(a) shows FT-IR spectrum of Si-F bond for the film with F content of 9 % deconvoluted with 3 Gaussiuan bands. Fig 4(b) shows integrated intensity change of these 3 Gaussian bands as a function of F content in films.

4. CONCLUSIONS

Low dielectric constant SiO_2 could be formed by adding F using plasma CVD. Water absorption in SiOF increased with increasing F content. The resistance to water absorption in atmosphere was found to depend on CVD method. We obtained low dielectric constant of 3.3 without water absorption using high density plasma CVD. It was confirmed that ion bombardment was one of the key factors to produce high quality films. And $Si\text{-}F_2$ formation in the films could be considered to cause water absorption for high F content films.

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