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# Fluorinated amorphous carbon thin films grown by plasma enhanced chemical vapor deposition with $C_4F_8$ and $Si_2H_6$/He for low dielectric constant intermetallic layer dielectrics

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**Abstract**

Fluorinated amorphous carbon thin films (a-C:F) for the use of low dielectric constant intermetallic layer dielectrics are deposited by plasma enhanced chemical vapor deposition with $C_4F_8$ and $Si_2H_6$/He gas mixture as precursors. To characterize and improve film properties, we changed various conditions such as deposition temperature, and RF power, and we measured the thickness and refractive indexes and FT-IR spectrum before and after annealing. At low temperatures the film properties were very poor although the growth rate was very high. On the other hand, the growth rate was low at high temperature. The growth rate increased in accordance with the deposition pressure. The dielectric constants of samples were in the range of 1.5~5.

**Keywords** : a-C:F, PECVD, $C_4F_8$, $Si_2H_6$

## 1. Introduction

The importance of multilevel interconnections for ultra large-scale integration (ULSI) has led researchers to focus on the reduction of interconnection delays which was caused by parasitic capacitance from interlayer dielectrics and resistance from metal connection (RC time delay).[1] To reduce it, we must first reduce the parasitic capacitance of interlayer dielectrics, resistance of metal connections, or both. The reduction of the resistance of metal connection is a relatively narrow research area because only a few metals are available whose resistivity is lower than that of aluminum. However, there are many candidates for low dielectric constant materials such as fluorinated $SiO_2$, fluorinated carbon, diamond like carbon, and even air gap. Each candidate has some drawbacks. Those low dielectric constant materials can reduce not only the line-to-line capacitance, but also power consumption.

For many years fluoropolymers such as polytetrafluoroethylene (PTFE) have shown the lowest dielectric constant (dielectric constant=2.0). However their low thermal stability has made it difficult to use them in ULSI circuits. On the other hand, hydrogenated amorphous carbon (a-C:H) films fabricated by plasma deposition with hydrocarbon gases show high electric resistivity and good thermal stability. These characteristics have been considered the result of their highly cross-linked structures.[1] Thus, we could obtain a material that is thermally stable and that has a low dielectric constant if only we could make the films similar to PTFE in composition and to hydrogenated amorphous carbon in structure.

A number of studies have shown that fluorinated

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amorphous carbon deposited by plasma enhanced chemical vapor deposition (PECVD) has a dielectric constant of 2.0~2.4[2-4]. Mostly $CF_4$ or $C_2F_6$ was used as a carbon and fluorine source and $H_2$ or $CH_4$ as carriers for depositing fluorinate amorphous carbon thin films with PECVD. There was a report that showed promising results with disilane ($Si_2H_6$) and helium (He) mixture gas for carrier gas. [6] During the growth of amorphous fluorinated carbon films, the carrier gas is not only just carrying the precursor to the silicon wafer, but also capturing the excessive fluorine ions from carbon fluorine source. Because the excessive fluorine ions that came from the decomposed source gas by heat or plasma energy are very reactive, they can easily attack the films; therefore, choosing the carrier gas is as important as choosing the precursor itself. Therefore, it is recommended that one chooses a source that produces only small amount of excessive fluorine ions and a carrier gas that captures the excessive fluorine ions well ; for example, $H_2$ that combines with fluorine ion and turns into HF gas.

Normally in the semiconductor process the main fluorine ion provider is $CF_4$. However, since the C : F ratio of $CF_4$ is 1 : 4, $CF_4$ produces more fluorine ions than are required. The C : F ratio of fluorinated amorphous carbon (a-C:F) is 1 : 1, although the ratio can be somewhat improved if we use $C_2F_6$ (ratio is 1 : 3). Recent research has shown a trend of using the lower ratio fluorine source such as $C_4F_8$ (ratio is 1 : 2), and add another gas to the plasma such as $H_2$ and $CH_4$, which are known to create fluorine-deficient environment. [7] In this paper we deposited fluorinate amorphous carbon by PECVD using $C_4F_8$ and disilane/helium as precursors. $C_4F_8$ was the source for carbon and fluorine, disilane was for scavenging the excessive fluorine ions, and helium was the carrier gas. We measured growth rate, FT-IR, and thickness change after annealing.

## 2. Experimental Procedures

Fluorinate amorphous carbon films were deposited by the PECVD system that has a parallel electrode with 2.54 cm spacing and 15.24 cm radius. The volume ratio of disilane and helium was 1 : 19 (5% disilane, 95% helium). We fixed the flow ratio of C4F8 to disilane/helium mixed gas as 1 : 1 - i.e. the ratio of C4F8 to disilane is 20 : 1. We changed various deposition conditions by varying the temperature from room temperature to 200℃ with 25℃ step and the working pressure from 100mTorr to 800mTorr with a 100 mTorr step. RF plasma power was limited to 300W, and the deposition time was 10 minutes.

After film growth, we measured thickness, the refractive index, the energy gap, and FT-IR. Then we annealed the sample at 400℃, $N_2$ ambient, 500 mTorr for 30 min. After annealing, we again measured the thickness, refractive index and FT-IR. We used an N & K Analyzer 1280 that can measure thickness, refractive index, and energy gap at the same time. Finally we measured the C-V characteristics of all samples with a HP 4280 to calculate the dielectric constant of deposited samples. The voltage sweep range was from -30 V to 30 V. The electrode material was aluminum, and the radius of the upper electrode dot was made as large as 1mm to reduce errors.

## 3. Results and Discussion

### 3.1 Growth rate and thickness change

In spite of a high growth rate at room temperature and at 50℃, the film properties were very unstable (not uniform growth). They showed very poor adhesion to the substrate, and the shrinkage rate was too large. It was also very difficult to maintain such low temperature under plasma and that made the results unreliable. Therefore, we disregarded the results from conditions of room temperature and 50℃.

Fig. 1 shows thickness as a function of temperature and pressure when the deposition time was 10 minutes. At low temperatures the growth rate was relatively high; it started to decrease as temperature was increased.

On the contrary, the growth rate increased as working pressure increased. At 200℃ the growth rates were very small and it was difficult to measure the thickness precisely at higher temperatures. Therefore we doubted the reliability of measurement about the sample grown at 200℃, so we decided not to advance the experiment to over 200℃. The slopes of each graph are relatively linear, implying that the film growth rate was directly affected by pressure and deposition temperature change. Even though the pressure was high, if the temperature was around 200℃, the film growth rate was very low, so we deduced that the temperature was more critical than working pressure. It was confirmed with the overall tendency of each slope that shows a diminishing growth rate difference through temperature increase, since the graph showed larger slope at higher pressure.

Fig. 2 shows the shrinkage rate of deposited films as a function of temperature and pressure after 400℃ annealing. Samples grown at 200℃ had a very small original (before annealing) thickness; thus, the shrinkage rates of 200℃ samples can be ignored. At low pressure deposition the shrinkage rate increased in accordance with increasing temperature (except 200℃). However, at high pressure results do not show any apparent relationship with temperature change. Most samples

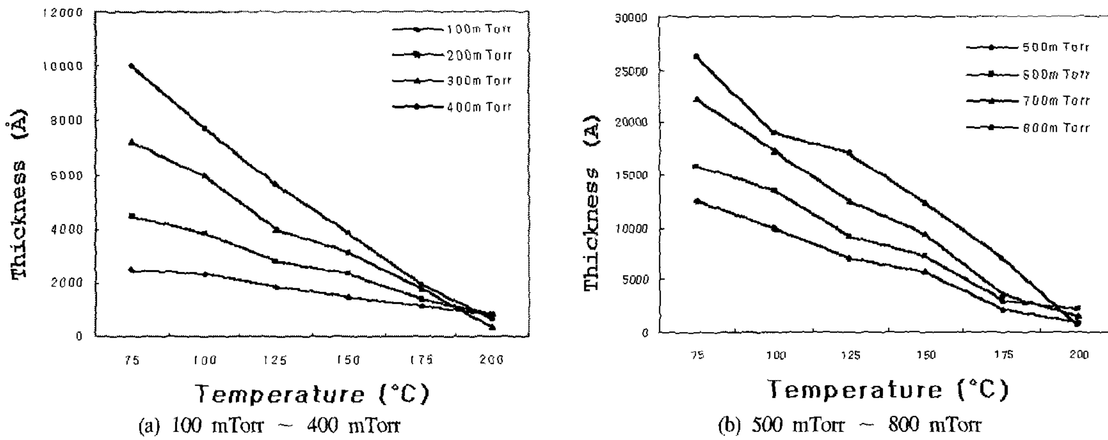



Fig. 1. The thickness as a function of deposition temperature and pressure.

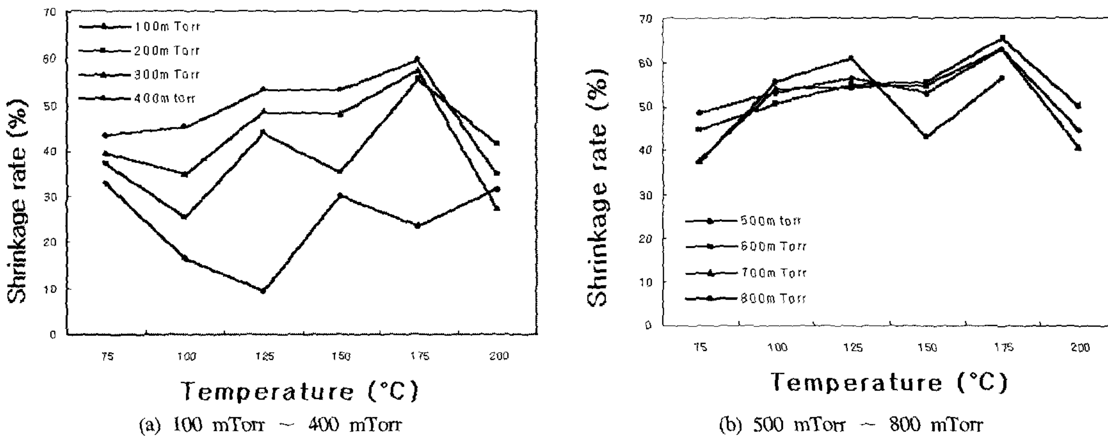



Fig. 2. The shrinkage rate as a function of deposition temperature and pressure.

have about 40~60% shrinkage rate, and mostly higher-growth rate samples have a higher shrinkage rate. The shrinkage rate of 40~60% means very large shrinking through annealing and it is nearly impossible to actually use the film as in intermetallic dielectrics. However, compared to other samples, the sample grown at 100 mTorr and 125℃ had an apparently good result, which is under 10% shrinkage rate (actually 9.4%). There seems to be some relation between temperature and shrinkage rate at low pressure ambient (100 mTorr ~400mTorr). The shrinkage rates of 200 mTorr, 300 mTorr and 400 mTorr have a similar tendency. If we shift the shrinkage rates of 100 mTorr condition to a lower temperature, the curvature of the shrinkage rate is similar to the above conditions. This suggests that there is a relationship between temperature and pressure for deposition condition even if temperature seems critical.

There are no shrinkage data for 200℃ and the 800 mTorr condition because the sample was too thin to measure shrinkage rate. The samples were getting non-uniform on the silicon surface as temperature was increased. We suggest that separated zone growth on substrate due to the very small growth rate caused the non-uniform film.

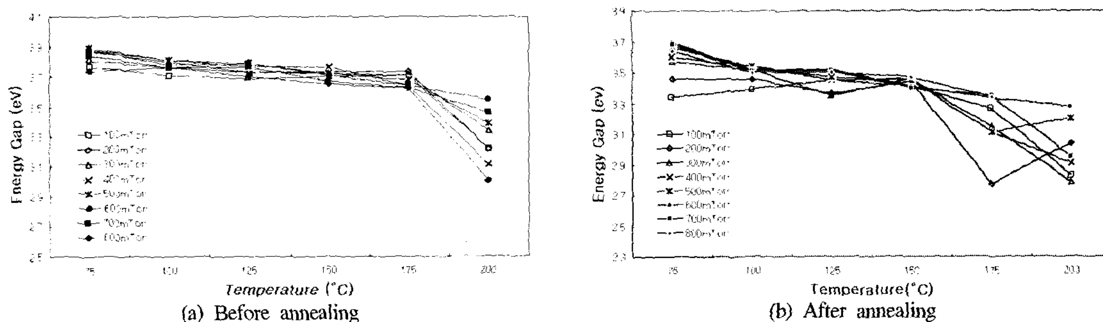
Fig. 3 shows the energy gap dependence on temperature and pressure. The energy gap was not much changed, compared with the change in thickness. All samples grown at 200℃ showed relatively low energy gap while the other samples showed few differences. With this result and growth rate we can conclude that a high temperature process makes a films' bonding weak; i.e., it prevents a films' cross-linking.

After annealing, the energy gap of all films became smaller. This result was expected from the thickness change through annealing, which was actually too large to consider as attributable to just shrinkage, except for a few samples. We assumed that there was some film loss during annealing process and that the loss was caused by heat that decomposed fluorinate carbon. We deduced that during the annealing process the heat of 400℃ weakened the carbon-fluorine bonding or carbon-carbon bonding or both, and that as a result the band gap of the film was lowered.

## 3.2 FT-IR and C-V measurements

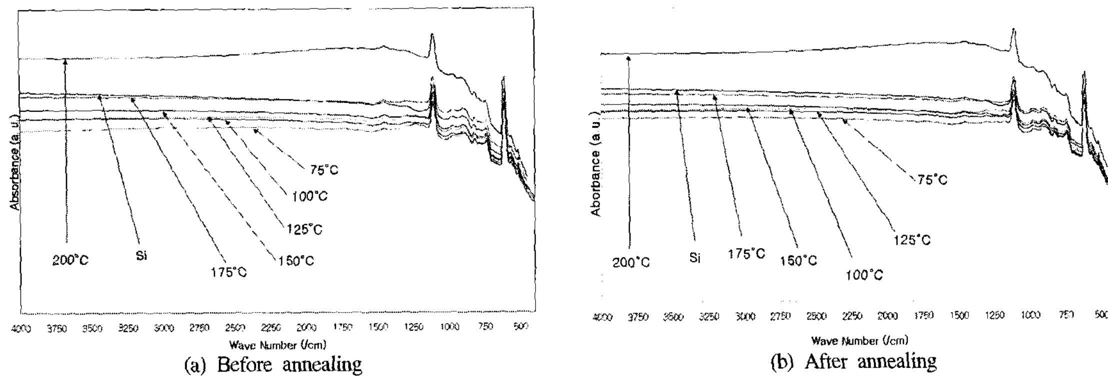
In order to examine the chemical bonding structure change of films such as C-F bonding through the annealing process, we measured the Fourier transform infrared (FT-IR) absorption spectra.

Fig. 4 shows the spectra from a bare silicon wafer to the sample grown at 200℃. Other conditions were fixed such that ambient pressure was 100mTorr and RF power was 300W. The basic shapes of each spectrum are not much different from each other except for the sample grown at 200℃ that shows quite different absorption curvature. In fact it was an expected result; we had guessed that there would be some difference between 200℃ samples and others because the results from other measurement had shown much different



(a) Before annealing
(b) After annealing

Fig. 3. Energy gap change as a function of deposition condition.




(a) Before annealing (b) After annealing

Fig. 4. The FT-IR result as a function of growing temperature. The working pressure was 100 mTorr.

characteristics. However, we also expected a gradually different curvature from different conditions because the growth rate of each temperature was quite different, gradually decreasing as increasing temperature, but there was no apparent difference between them. It seems that the annealing process has little affect on the bonding structure, because there was no big difference between as-deposited samples and annealed samples. The broad absorption around 1100 $cm^{-1}$ is assigned as the overlap of CF(1000-1110 $cm^{-1}$), $CF_2$ (1050~1250 $cm^{-1}$) and the absorption around 700 is assigned $CF_3$ in -$CFCF_3$ or -$CF_2CF_3$.[8]

We measured the capacitance of samples with a voltage sweep range of -30 V to 30 V. The resultant dielectric constants of samples were between 1.6~5. The sample grown at 125℃ and 100mTorr showed the lowest shrinkage rate of 9.4% and had a relatively low dielectric constant of 2.18. As we mentioned at the band gap dependency, the film's bonding strength in the high temperature process was weaker than the low temperature sample's, and it made the film more polarized. As a result, the dielectric constant of high temperature process sample became higher.

## 4. Conclusions

We deposited and investigated fluorinate amorphous carbon films using PECVD with disilane/helium mixture and $C_4F_8$ as precursor gases. At deposition temperatures below 100℃ the growth rate was very high, but the film properties were very poor. At deposition temperatures above 150℃ the growth rate was too small to measure the growth rate properly and non-uniform growth was occurred. A relatively good result was obtained from the sample grown at 125℃ temperature and 100 mTorr. It had under 10% shrinkage rate compared with other sample's 40~60% shrinkage rate and had a relatively low dielectric constant of 2.18. The growth rate was affected by temperature and working pressure directly and linearly, while temperature played more significant role in film deposition and characteristics. The energy gap changes showed no apparent dependence on temperature change. The entire sample's energy gap was lowered after annealing. The FT-IR result shows that there was no large difference among various temperature samples, except for the sample grown at 200℃.

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