Low Dielectric Constant Insulator by Downstream Plasma CVD at Room Temperature Using Si(CH₃)₄/O₂

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We present an insulator with a dielectric constant lower than 3.0 and a good gap-filling characteristics by downstream plasma CVD at room temperature using Si(CH₃)₄/O₂ gases. This film is stable up to 450 °C and does not absorb water after annealing at 350 °C. The insulator is deposited through the gas phase reactions where formation and consumption of water are competing.

1. INTRODUCTION

A formation technology of interlayer dielectric films is essential for the fabrication of multilevel interconnections in ULSI devices[1]. Low dielectric constant, good gap-filling properties and stability under high temperature processing are required[2,3].

In this paper we propose an insulator with a dielectric constant lower than 3.0 and a good gap-filling characteristics. The room temperature deposition method which utilizes organic materials and excited oxygen as source gases has been investigated for this purpose. The film characterization and properties are described. The deposition mechanism is also discussed.

2. EXPERIMENTAL

The schematic diagram of the experimental apparatus is shown in Fig.1. The system consists of an injection nozzle connected to a discharge tube and a cylindrical quartz reaction chamber, which is pumped down by a mechanical rotary pump.

![Schematic diagram of experimental apparatus](image)

Figure 1: Schematic diagram of experimental apparatus.

A piece of silicon substrate (3×12 cm²) was placed in the reaction chamber at room temperature. We used two types of samples. One was a Si substrate with and without deep trenches, and the other was a sample with aluminum lines on thermally grown SiO₂. Source gases were tetra-methyl-silane (Si(CH₃)₄, TMS) and oxygen, which were mixed close to the silicon substrate. A 2.45 GHz microwave discharge system was used to produce oxygen atoms, which were introduced into the chamber through the injection nozzle. Infrared light can pass across the quartz tube through KBr windows to allow analysis of the gas phase reaction to be carried out in situ.

3. RESULTS AND DISCUSSION

Fig.2 shows a cross-sectional SEM micrograph of deep trenches filled with the insulator. Deposition parameters are 2 Torr total pressure, 0.1 Torr partial pressure of TMS, 100 Watt microwave power, 2 min deposition time, and 4 cm reaction distance (explained later). The insulator was deposited in and from the bottom of trenches[4], and showed the same good-filling properties for spaces between Al lines.

![Cross-sectional SEM micrograph of trenches filled with the insulator](image)

Figure 2: Cross-sectional SEM micrograph of trenches filled with the insulator.

To examine the film properties, we carried out FT-IR analysis and found the peaks of Si–CH₃ (1250 cm⁻¹), and Si–H (2200 cm⁻¹)in the spectrum in addition to the main Si–O–Si peak (1080 cm⁻¹). This result shows that the film contains carbon and hydrogen atoms as well as silicon and oxygen atoms.

We then estimated amounts of Si and C atoms using the molybdenum blue light absorption spectroscopy and the absorption spectroscopy with the high-frequency combustion method, respectively. The results are shown in Fig.3(a). The ratio of C to Si shows a strong dependence on the reaction distance (r_d), which is the distance between the mixing point of source gases and the substrate.
The C/Si ratio varies from 3.7 to 2.6 as \( rd \) increases. Surprisingly, the dielectric constant obtained from the C-V measurement at 1 MHz by means of the metal-insulator-semiconductor (MIS) structure indicates a similar \( rd \) dependence, as shown in Fig.3(a). It decreases monotonically from about 4 to 2 as \( rd \) increases.

As shown in Fig.3(b), the ratio of the integrated intensity of Si-CH\(_3\) FT-IR absorption to that of Si-O-Si peak also decreases as \( rd \) increases, while the ratio of Si-H absorption to Si-O-Si absorption monotonically increases with an increase of \( rd \). These \( rd \) dependences suggest that polymerization in the film proceeds as \( rd \) increases.

To clarify the origin of the \( rd \) dependence, we carried out an analysis of the deposition properties. Fig.4 shows the dependence of film thickness on \( rd \) for a deposition time of 2 min. The film thickness also shows a strong \( rd \) dependence. It rapidly increases as \( rd \) increases, and reaches the maximum value at about \( rd \) of 2 cm. It decreases drastically as \( rd \) increases over 2 cm.

At the same time, the capability of gap-filling also shows a strong dependence on \( rd \). In the region of \( rd \) longer than 2 cm, this filling capability is excellent, as shown in Fig.2. In the region of \( rd \) below 2 cm, however, the filling capability is inferior, and the insulator obtained at 1 cm \( rd \) shows significantly poorer step coverage, as shown in Fig.5.

To obtain further understanding of the strong dependence of several properties on \( rd \), we analyzed the gas phase precursor in situ with FT-IR as shown in Fig.6.

A broad weak peak at 1080 cm\(^{-1}\) is attributed to the Si-O-Si stretching mode, and indicates the formation of a precursor with the Si-O-Si bond.

There are three types of absorption peaks of H-OH at around 1400-1700 cm\(^{-1}\) (I), 3400 cm\(^{-1}\) (II), and 3600-3900 cm\(^{-1}\) (III). The absorption peaks in the region of 1400-1700 and 3600-3900 cm\(^{-1}\), (I) and (III), have fine structures owing to the interaction between vibration and rotation of H\(_2\)O, and are attributed to the bending mode for (I) and asymmetric stretching mode for (III) of gas phase H\(_2\)O, respectively. The peak at about 3400 cm\(^{-1}\), that is (II), arises from a vibrational mode of liquid phase H\(_2\)O.

The intensity of the H\(_2\)O absorption peaks increases at \( rd = 2 \) cm (Fig.6(A)), indicating that water is released during the reaction in the gas phase. At the distance larger than 3 cm (Fig.6(B)), the intensity of H\(_2\)O peaks decreases, indicating that the water-consuming reaction becomes dominant.

From the above results, we propose the following reaction mechanism; at small \( rd \) Si-(CH\(_3\)) bonds react on discharged oxygen in gas phase and form Si-OH bonds. In contrast, at larger \( rd \) values Si-(CH\(_3\)) bonds react on H\(_2\)O directly, forming Si-OH bonds. Two precursors with Si-OH bonds react, producing Si-O-Si bonds and H\(_2\)O in both cases, but the first reaction path results in the release of extra water to the gas phase while the second reaction path consumes water in the gas phase.

In the case of deposition on Si substrate, the intensity of the gas phase H-OH peaks increases considerably, indicating that the process responsible for releasing extra water to the gas phase is enhanced by surface reactions.

The strong dependence of deposition characteristics on \( rd \) suggests that both excited oxygen gas and H\(_2\)O contents...
Figure 6: FT-IR spectra of gas phase in situ analysis of Si(CH$_3$)$_4$ + O* reaction in the case of rd = 2 cm (A) and 3 cm (B). (a)–(d) showed right after deposition, 1, 2, and 3 minutes for deposition time, respectively.

play important roles in the hydroxylation mechanism of the formation of this insulator film.

To examine the potential of the film as an insulator for multilayer interconnection, the water absorption properties were studied by means of thermal desorption spectroscopy and FT-IR spectroscopy. There were two peaks of H$_2$O$^+$ (M/e=18) desorption in the temperature range of 35-650 °C, as shown in Fig.7. The desorption peak at about 250 °C is attributed to the water included in the film during the deposition, and the desorption peak at about 580 °C resulted from the water produced by polymerization through the dehydration reaction between –OH bonds, which formed syloxane bonds (Si–O–Si).

Figure 7: H$_2$O$^+$(m/e = 18) TDS spectra of as-deposited insulator film.

Furthermore, we kept the film in air for one week after annealing at up to 350 °C and found that no additional absorption band of water was detected as shown in Fig.8. This result indicates that the film does not absorb water after annealing at 350 °C.

In order to improve the quality of this unique insulator, it is necessary to identify the effective precursors and to study the concentration profile of excited oxygen along the reaction path.

4. CONCLUSION

We present an insulator with a dielectric constant lower than 3.0, which was deposited by downstream plasma CVD using Si(CH$_3$)$_4$ and oxygen. The film has good gap-filling capability and thermal stability below 450 °C, and showed no water absorption after annealing at 350 °C. The film properties, such as C/Si ratio, film thickness and dielectric constant, have strong dependence on the reaction distances. The in situ analysis with FT-IR shows that the amount of water vapor also depends on reaction distance, which suggests the hydroxylation of TMS and its reaction intermediates may change along the reaction distance.

REFERENCES