Nitrogen doped fluorinated amorphous carbon thin films grown by plasma enhanced chemical vapor deposition

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Nitrogen doped fluorinated amorphous carbon thin films for low dielectric constant interlayer dielectrics have been investigated. The films were deposited with a parallel-plate plasma enhanced chemical vapor deposition. Source gases were 100% CH<sub>4</sub>, CF<sub>4</sub>, and N<sub>2</sub>. The thermal stability of the films was increased as the increase in N<sub>2</sub> flow rate. X-ray photoelectron spectroscopy (XPS) measurement revealed that the C-N bonds were formed in the films with the addition of N<sub>2</sub>. The dielectric constant of the film was slightly increased to 2.5 with the addition of N<sub>2</sub>.

1. INTRODUCTION

With the increasing importance of multilevel interconnections for a ultra-large-scale integration (ULSI), reducing the interconnection delay caused by parasitic capacitance has been getting more attention. Low dielectric constant interlayer dielectrics are required to reduce this capacitance and to improve the switching performance of ULSI circuits. Fluoropolymers, such as polytetrafluoroethylene (PTFE), are known as low dielectric constant materials (for example, the dielectric constant of PTFE is 2.0). However, their low adhesive force and low thermal stability have hindered their use in microelectronics. On the other hand, hydrogenated amorphous carbon (a-C:H) films fabricated by plasma deposition with hydrocarbon gases have high electric resistivity and good thermal stability due to their highly crosslinked structures.

We have previously proposed fluorinated amorphous carbon (a-C:F) thin films which have not only similar composition to PTFE but also crosslinking structure like a-C:H, as low dielectric constant interlayer dielectrics for ULSI multilevel interconnections. The a-C:F films were deposited with a plasma enhanced CVD using 100% CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and CH<sub>4</sub>. We have deposited the thin films with a dielectric constant of 2.1. However, the films shrunk with 300°C annealing in a vacuum because of the desorption of the components of the films. The dielectric constant of the films increased to 2.7 with 300°C annealing. This suggested that the films did not have highly crosslinking structure.

2. EXPERIMENTAL

To improve the thermal stability, we noticed carbon-to-nitrogen bond, which enhance the crosslinking like imide rings. In this paper, we deposited nitrogen doped a-C:F films with a plasma enhanced chemical vapor deposition using CH<sub>4</sub>, CF<sub>4</sub>, and N<sub>2</sub>.

The nitrogen doped a-C:F films were produced in a conventional parallel-plate rf (frequency 13.56 MHz) reactor. The parallel-plate reactor was pumped with a turbo molecular pump and a mechanical booster pump to less than 10<sup>-5</sup> Torr. 100% CH<sub>4</sub>, CF<sub>4</sub>, and N<sub>2</sub> were introduced into the chamber as source gases through electrically controlled mass flow controllers. The deposition pressure ranged from 100 to 200 mTorr. The parallel electrodes housed in the vacuum camber were 20.3 cm in diameter, and were separated by 3.0 cm. 4-inch SiO<sub>2</sub>/Si(100) and p'Si(100) wafers were used as substrates. The temperature of the substrates during deposition was typically kept at around 50°C. The substrates were mounted on the powered (upper) electrode. The powered electrode is subjected to a negative dc self-bias voltage due to the large difference between ion and electron mobilities.

The film thickness was measured with a scanning electron microscope (SEM) and a step profilometer. The dielectric constant of the films was measured by determining the capacitance-voltage (C-V) characteristics (KEITHLEY Model 590) of a Al/a-C:F/p'Si diode at 1 MHz. Film structure and composition were determined by X-
ray photoelectron spectroscopy (XPS). The XPS spectra were collected with an ESCA/AES spectrometer using a Mg Kα X-ray anode operating at 300 W and 15 keV.

At the previous experiment with parallel plate reactor, a-C:F films were not deposited without adding hydrogen sources such as CH₄ to CF₄ gases. It was because of the etching reaction of F atom enhanced by the ion bombardment due to self bias voltage. Therefore, in this study, CH₄ were also added to CF₄ to scavenge etchant F atoms.

The total flow rate and CF₄/CH₄ flow ratio was fixed at 50sccm and 16 respectively, and N₂ flow rate was changed. Because, in the previous experiment, the a-C:F films with the dielectric constant of 2.1 were deposited at the same condition.

When the films were deposited with CH₄, CF₄, and N₂ mixtures directly on the Si substrate, the films peeled off from the substrate. However, we found that the peeling was suppressed by inserting the thin hydrogenated amorphous carbon buffer layer using only CH₄ between the substrate and the film. The thickness of the buffer layer is about 30nm and the capacitance component from the buffer layer was removed by the calculation when we determined the dielectric constant of a-C:F films.

3. RESULT AND DISCUSSION

Figure 1 shows the deposition rate of a-C:F films as a function of N₂ content in the feed gases.

The deposition rate decreased as the increase in N₂ content. This is because of the decrease in the flow rate of CH₄+CF₄ mixtures which were dissolved to the building blocks for the film formation.

Figure 2 shows the thickness of the films after 300 °C annealing in a vacuum for 1 hour normalized by their as-deposited thickness, and the nitrogen concentration of the films, as a function of N₂ content in the feed gases. The nitrogen concentration was determined by the total integrated XPS intensities of C1s, F1s and N1s peaks. The thickness of the films at 0% N₂ content decreased to 64% of their as deposited thickness. As the increase in N₂ content in the feed gases, the concentration of the nitrogen in the films increased and the thickness reduction was suppressed. Therefore, the nitrogen addition was found to be effective to improve thermal stability of the a-C:F films.

With a small content of N₂ addition, the nitrogen concentration of the films increased as the increases in N₂ content. However, it is found that the nitrogen concentration of the films was saturated at 13%. This saturated concentration is almost the same at any source power.

The fluorine concentration in the films measured by XPS was decreased from 35% to 40% with 40% N₂ content in the feed gases.

Figure 3 shows C1s XPS spectra of the films. This figure indicated that C-N groups at 287 eV were formed by the addition of N₂ in the feed gases. Thus, by the addition of N₂ in the source gases, the nitrogen was introduced into the a-C:F films by
forming C-N bonds. Fig. 4 shows N1s spectra of the films. As the peak was regarded as a single peak, there is almost only C-N bond and no N-F bond was formed in the films.

The binding energy of C-C bond and C-N bond were reported as 607 kJ/mol and 754.3 kJ/mol. Therefore, the improvement of the thermal stability with the addition of N₂ is attributed to the formation of the hard C-N bonds and enhancement of the crosslinking with the reduction of the F atom concentration, which terminates C-C bond and suppresses crosslinking.

Table 1 compares the dielectric constant of the nitrogen doped films at 10 % nitrogen content in the feed gases with previous a-C:F films which were formed without N₂. The dielectric constant of the films was slightly increased with the nitrogen addition because of the reduction of F atom concentration. The dielectric constant of the films without nitrogen was increased to 2.7 with 300°C annealing. However, the increase in dielectric constant could be suppressed by the nitrogen addition.

4. SUMMARY

We have deposited the nitrogen doped a-C:F films with the plasma enhanced chemical vapor deposition. The thermal stability of the a-C:F films could be improved with the N₂ addition. It was found that the C-N bonds were formed in the a-C:F films. The dielectric constant of the nitrogen doped a-C:F films was slightly increased to 2.5 with 10% N₂ addition in the feed gases.

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