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Suppression of Fluorine Diffusion into Low-k Material (Methyl-BCN) Using Low Temperature Etching

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1. Introduction

In order to achieve high performance interconnection with small RC delay, the integration of a low dielectric constant (low-k) interlayer and Cu interconnection is necessary for 32nm-node devices and beyond. Recently, porous low-k films have been investigated for their use as a film with low dielectric constant (k value). However, most porous low-k materials face serious issues such as low hardness and incorporation water, and residual fluorine in the porous material. We have investigated boron carbon nitride (BCN) film [1] and BCN film containing methyl group (Methyl-BCN) using tris(dimethylamino)boron (TMAB) gas, as an attractive new low-k material. We have already reported formation of the Methyl-BCN film with dielectric constant (k-value) of 1.8 and Young's modulus > 26 GPa [2, 3]. The Methyl-BCN film can easily keep a low-k value, due to nano space formed by methyl bonds in the film.

Figure 1 shows a schematic of a low-k film etched using metal hard mask. During dry etching process with fluorine based gases, fluorine component diffuses into the low-k film, especially, porous low-k film. There is concern that the residual fluorine induces low-k voiding and Cu corrosion [4]. In this study, we report the suppression of fluorine diffusion into Methyl-BCN using low temperature etching.

2. Experimental

Methyl-BCN film was deposited on the Si wafer by remote plasma-assisted chemical vapor deposition (PACVD) using TMAB gas at 350°C. The properties of Methyl-BCN film and molecular structure of TMAB gas are shown in Fig. 2. The films with the thickness of nearly 200-300 nm were deposited on the Si substrate. The Methyl-BCN films were etched with CF_4 gas using induced coupling plasma (ICP) etching equipment. In this paper, we investigated the dependence of etching characteristics on the substrate temperature of low-k materials (Methyl-BCN). RF bias was 100 W and 0 W with ICP power of 300 W during dry etching. The gas pressure and flow rate were 4 Pa and 10 sccm, respectively. The etching was performed at room temperature, 0°C, and -25°C. The substrate temperature was controlled by Frorinate circulation.

The film etching rate was estimated from the film thicknesses measured before and after dry etching. In this study, X-ray photoelectron spectroscopy (XPS) was carried out to examine the composition ratio of the constituent atoms of the Methyl-BCN films after dry etching. Current-voltage (*I-V*) and capacitance-voltage (*C-V*) characteristics were measured using a metal-insulator-semiconductor (MIS) structure of Cu/Methyl-BCN/Si at room temperature. The dielectric constant was estimated from the capacitance in the accumulation region of the *C-V* characteristics and the film thickness.

3. Results and discussion

The Methyl-BCN films can be etched by CF_4 gas. Figure 3 shows the temperature dependence of the etching rate of the Methyl-BCN film. The etching rate of Methyl-BCN film decreases with decreasing the substrate temperature. The etching rate, which is 200 nm/min at -25°C, is sufficient for LSI devices manufacturing. In addition, the etching rate by non-RF power (0 W) is drastically lower than that of RF power (100 W). This indicates that the Methyl-BCN film is mainly etched by fluorine ions.

Figure 4 shows the depth profiles of residual fluorine in the Methyl-BCN films after dry etching with CF_4 gas at the various substrate temperatures (room temperature, 0°C, and -25°C). Fluorine concentration in Methyl-BCN film after dry etching at low temperature is lower than room temperature. Low temperature etching process is effective in suppressing of fluorine diffusion into Methyl-BCN film.

Figure 5 shows the XPS spectra (F1s) of the surface on the Methyl-BCN film after dry etching at room temperature and low temperature (-25°C). The XPS peak at around 689 eV, which shows the fluorocarbon polymer (CF_x), is clearly observed at room temperature. On the other hand, this peak is not observed at low temperature. As there is little fluorocarbon residue on the Methyl-BCN film after low temperature etching, the fluorocarbon residue can be easily removed after treatment.

Figure 6 shows the *I-V* characteristics of Methyl-BCN film before and after dry etching at low temperature (-25°C). The leakage currents of the film after dry etching hardly increased. In addition, there is little change in dielectric constant of Methyl-BCN film before and after dry etching. Therefore, the properties of the Methyl-BCN film are hardly influenced on low temperature etching.

The fabrication of the Methyl-BCN film can be anisotropic etched by fluorine ion. Fluorine radical, which has the behavior of isotropic diffusion into the low-k material, can be suppressed by low temperature.

4. Conclusions

We have achieved an effective suppression of fluorine diffusion into Methyl-BCN film using low temperature etching process. This technology can be applicable to not only the Methyl-BCN but also porous SiOC film for next generation devices.

References

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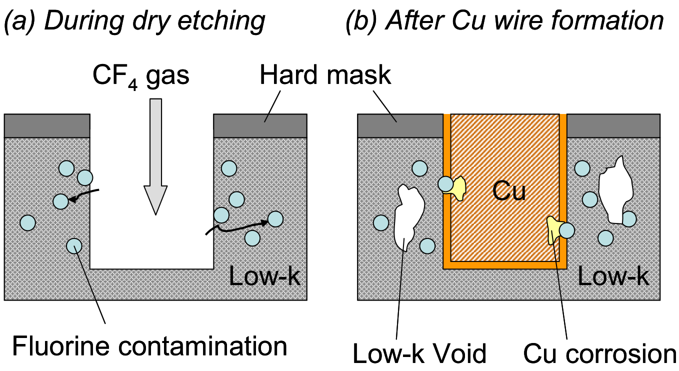

Fig.1 Trench structure formation of a damascene interconnection by dry etching.

Properties of Methyl-BCN film (deposition at 10W RF power)	
Composition ration (H isn't included)	B: 36% N: 34% C: 30%
Dielectric constant (k value)	1.8 ～
Young modulus (GPa)	>26
Resistivity (Ωcm)	6×10^{12}

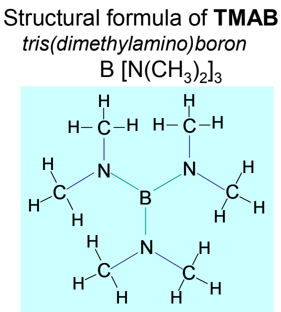

Fig.2 The properties of Methyl-BCN film and chemical structure of TMAB gas.

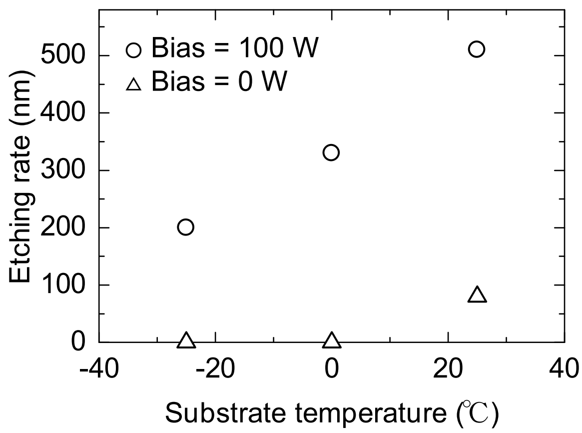

Fig.3 Etching rate of Methyl-BCN film with CF_4 gas at various substrate temperature (room temperature, 0 °C, and -25 °C).

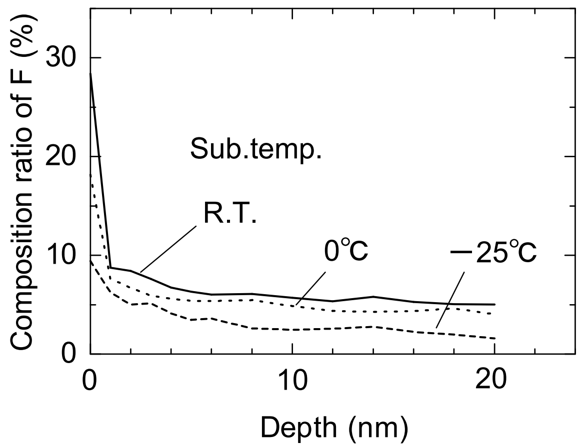

Fig.4 XPS depth profile of Fluorine component in Methyl-BCN film after dry etching.

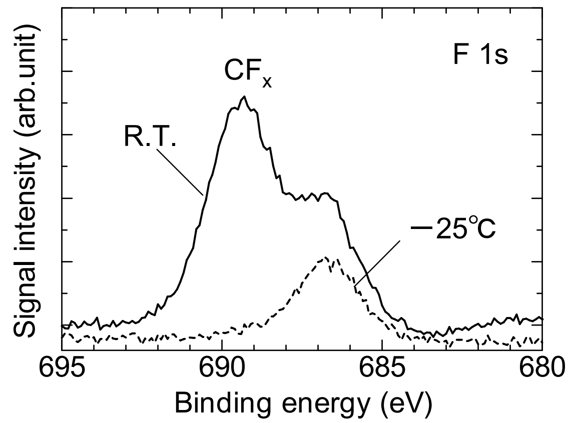

Fig.5 XPS spectra (F 1s) of the Methyl-BCN surface after dry etching. (Ar sputtering time = 0 s)

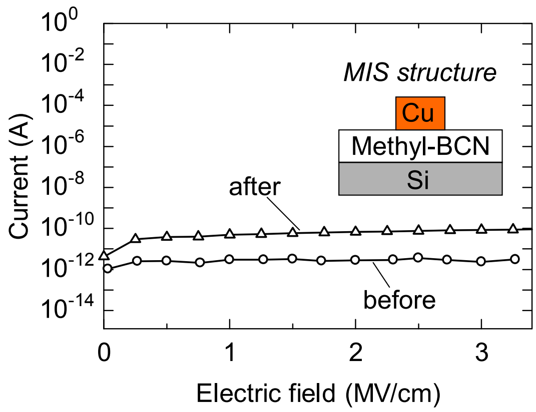

Fig.6 *I-V* characteristics of Methyl-BCN film before and after dry etching.