Extended Abstracts of the 2009 International Conference on Solid State Devices and Materials, Sendai, 2009, pp360-361

Impact of film structures on damage to low-k SiOCH film during plasma exposure

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1. Introduction

As the feature size of ultra-large-scale integration (ULSI) devices has become smaller, the RC delay of the inter connects has restricted circuit performance. To reduce crosstalk, SiOCH low-k interlayer dielectrics have been successively introduced from 90-nm nodes. Plasma enhanced CVD (PECVD) is generally used to form SiOC low-k film. However, it is difficult to reduce the k-value further using current PECVD methods such as PoroGen. We propose a newly developed neutral-beam-enhanced CVD method to control SiO structure in SiOCH film. This method could control dissociation of precursor and generate appropriate SiO structure with hydrocarbons as original precursor structures. As a result, we have obtained a k-value of 2.2 and sufficient modulus [1].

On the other hand, the effects of the plasma irradiation process on SiOCH low-k film is an important factor because the k-value is drastically increased during etching and ashing processes.

We focus on the effects of the plasma irradiation process on SiOCH low-k film structures, which consist of different SiO structures formed using NBECVD and PECVD. Finally, the relationship between SiO structure and magnitude of plasma-irradiation damage in low-k film was clarified.

2.Experimental

We investigated the relationship between the molecular-level structure of a low-k film and its resistance properties against plasma irradiation using low-k films with different SiO structure compositions.

We used two types of NBECVD films, which were prepared using Dimethyldimethoxysilane (NBECVD DMDMOS film), Methyltrimethoxysilane (NBECVD MTMOS film) and conventional PECVD low-k film formed by (Dimethoxytetramethyldisiloxane) DMOTMDS. Two NBECVD low-k film depositions were performed at 1500 W for the inductively coupled plasma (ICP) source (13.56 MHz: neutral beam density) and 30 W for the lower electrode bias (600 kHz: neutral beam energy). The pressure in the process chamber was kept at 100 mTorr, and the substrate temperature was −20°C. The film properties before plasma irradiation are listed in Table 1.

We used a transfer-coupled plasma (TCP) etching chamber shown in Fig. 1. The pressure, gas flow, source power, and bias power were 20 mTorr, 30 sccm, 500 w, and 50 W, respectively. We used O_2, Ar, and Ar/H_2, which are gases commonly used in low-k etching/ashing processes.

The film compositions were evaluated using Fourier transformed infrared spectroscopy (FTIR). Its deconvoluted absorption peak is shown in Fig. 2. The 950-1250-cm-1 absorption peak of the Si-O-Si asymmetric stretching band resolved into three peaks centered at 1023, 1063, and 1135 cm^{-1} as the linear, network, and cage structure [2, 3], respectively. To compare the $Si\text{-}CH_3/SiO_2$ ratio, we selected the 1273-cm^{-1} absorption peak as $Si\text{-}CH_3$ because there was no overlap with the other peaks. In addition, we measured the film thickness using ellipsometry, and measured the dielectric constant using the C-V method after depositing an Al electrode.

Table 1 Initial properties of NBECVD-DMDMOS, NBECVD-MTMOS, and PECVD-DMOTMDS films

			NBECVD		PECVD
			DMDMOS	MTMOS	DMOTMDS
FTIR	SiO	Linear	53%	43%	37%
		Network	25%	33%	53%
		Cage	21%	24%	10%
	$Si\text{-}CH_3/SiO_2$		3%	2%	3%
	$Si\text{-}(CH_3)_1/Si\text{-}(CH_3)_2$		38/62	63/37	58/42
Dielectric constant			2.2	2.8	2.6

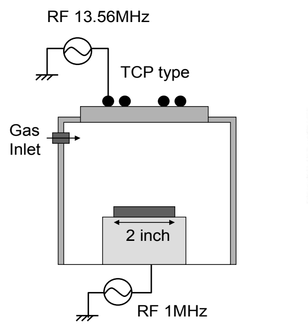

Fig.1. Schematic diagram of transfer-coupled-plasma (TCP) apparatus

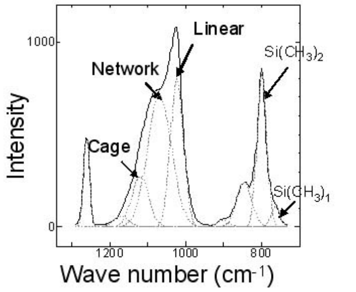

Fig.2. Example of FTIR spectrum of SiOCH low-k film

3. Result and discussion

3-1. Etching rate and change of dielectric constant

We measured the etching rate to find the film density as listed in Table 2. Despite the different film compositions, there was no difference in their etching rates. This shows that they have almost the same Si density and are affected to the same degree of plasma irradiation damage. Table 3 lists the dielectric constants before and after plasma irradiation. NBECVD DMDMOS low-k film remained at a k-value of less than 4 after plasma irradiation; however, the k-value of the PECVD DMOTMDS film exceeded SiO_2's k-value of 4 and increased to 7.9.

Table 2 Etching rates of SiOCH low-k films by plasma exposure

	O_2 plasma	Ar plasma	Ar+H_2 plasma
NBECVD-DMDMOS	26.9	5.2	11.0
NBECVD-MTMOS	25.2	7.7	10.8
PECVD-DMOTMDS	24.3	7.7	11.1

Table 3 Variation of dielectric constant due to plasma exposure

	Initial	O_2 plasma	Ar plasma	Ar+H_2 plasma
NBECVD-DMDMOS	2.2	3.9	3.7	3.7
NBECVD-MTMOS	2.8	4.6	4.1	5.7
PECVD-DMOTMDS	2.6	6.5	5.4	7.9

3-2. Dependence of plasma-irradiation damage on SiOCH film characteristics

The composition ratio changes in each film structure after each plasma irradiation are shown in Fig. 3. NBECVD DMDMOS film shows that the composition ratio remained almost unchanged. Conversely, PECVD DMOTMDS film's composition ratio drastically changed. From these results, the SiO linear structure is more durable than the SiO network structure against plasma irradiation. This trend corresponds to the increase in the k-value.

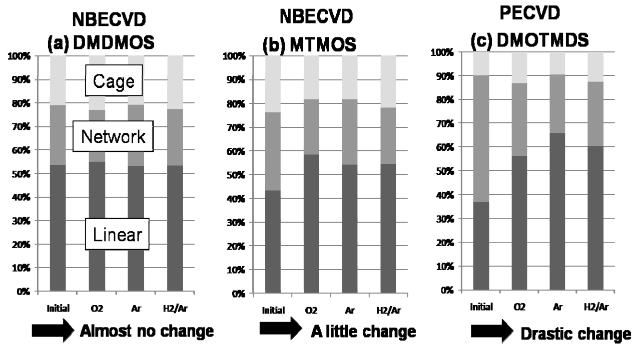

Fig.3 SiOCH low-k film structures before and after plasma exposure

Figure 4 shows the percentage of remaining methyl bonded with Si in SiOC low-k film after plasma irradiation. The NBECVD DMDMOS film retained more than 40% of original quantity. On the other hand, the PECVD DMOTMDS film lost almost all the methyl functional groups from original quantity. This difference also corresponds to the increase in the k-value of low-k film. We then investigated the film depth profile after plasma irradiation using XPS (Fig. 5). In the PECVD DMOTMDS film, which has more cage and network SiO structures, the carbon concentration drastically decreased, even at deeper depths. On the contrary, only the surface carbon concentration in the NBECVD DMDMOS film decreased and the film bulk maintained a higher carbon concentration. These results suggest that the higher carbon concentration in SiOCH low-k film causes drastic absorption of UV and VUV because the carbon efficiently absorbed UV and VUV photons. Consequently, the SiO linear structure including a higher carbon concentration exhibits a higher UV absorption coefficient than cage and network structures [4]. As a result, the NBECVD DMDMOD film exhibits higher resistance to plasma irradiation, compared with conventional PECVD film.

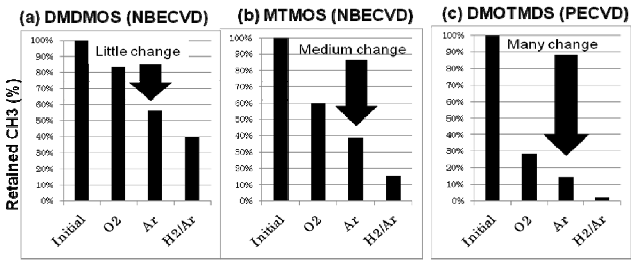

Fig.4 Percentage of remaining methyl groups bonded with Si in low-k films after 1 unit time plasma irradiation

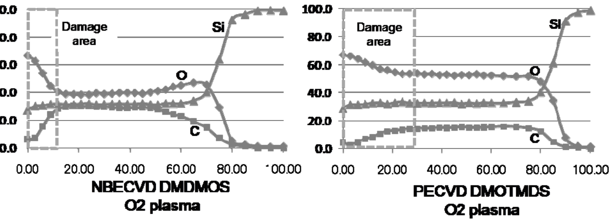

Fig.5 XPS depth profile of low-k films etched with O2 gas

4. Conclusion.

We investigated the relationship between SiO structure and plasma irradiation damage. SiO linear structure with a large amount of carbon concentration is durable against plasma irradiation due to higher absorption of UV photons at the surface of SiOCH low-k film.

Acknowledgements

We would like to thank Mr. T. Ozaki of Tohoku Univesity for his technical help.

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