

Super-Low-k SiOCH Film ($k=1.9$) with High Water Resistance and High Thermal Stability Formed by Neutral-Beam-Enhanced-CVD

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1. Introduction

The continuous shrinking of ultra-large-scale integrated (ULSI) circuits requires the use of materials with lower k values [1]. The commonly used low- k film is plasma enhanced chemical vapor deposition (PECVD) SiOCH; however, the k -value is between 2.7 and 3.0 [2]. To decrease the dielectric constant, we must control the dissociation of precursor in the gas phase and understand the relationship between molecular-level structure and film characteristics. We have already proposed the structure-designable method for forming super low- k SiOCH film using neutral-beam-enhanced (NBE)CVD [3]. In the case of using dimethyl dimethoxy silane (DMDMOS), the film structure mainly consists of linear Si-O with a smaller amount of network and cage Si-O. Then, a k -value of 2.2 and reasonable modulus could be obtained at the same time because the linear-type Si-O structure has a larger amount of $-\text{CH}_3$ [3]. Based on these previous results, a larger molecular weight precursor, including longer linear Si-O, should be used to obtain further a lower k -value of less than 2.0.

We investigated Dimethoxy-tetramethyl-disiloxane (DMOTMDS) to form super-low- k film using low-temperature NBECVD. We found that NBECVD with DMOTMDS could provide super low- k SiOCH film with a k -value of 1.9, reasonable modulus, higher water resistance, and higher thermal stability.

2. NBECVD and experimental set-up

NBECVD consists of an inductively coupled plasma (ICP) source and process chamber connected through carbon apertures, as shown in Fig. 1. In NBECVD, precursors are injected directly into the process chamber and adsorb to the substrate surface. By accelerated positive Ar ions passing through the carbon aperture, Ar neutral beams are formed by maintaining their motion energy through the neutralization process and bombarding the surface without charged particles and UV photons [4]. The beam energy can be precisely controlled from a few eV (RF=0W) to a few tens eV (RF=10W) by supplying RF bias (600 kHz) to the carbon aperture. The pressure of the process chamber is fixed at 30 mTorr, and the substrate temperature is -20°C to efficiently absorb the precursor on the substrate surface. Then, the random dissociation of these precursors in the gas phase can thus be nearly eliminated, and low- k films with

structures corresponding to those of the precursors are deposited. Consequently, the k -value and film modulus can be precisely controlled by changing the ratio between Si-O and $\text{Si}-(\text{CH}_3)_x$ and the proportions of linear, network, and cage Si-O structures in the film by changing the precursor structure and neutral beam energy. We used DMOTMDS as a precursor, has four $\text{Si}-\text{CH}_3$ and two $\text{Si}-\text{OCH}_3$ bonds. Basically, it is speculated that NBECVD-DMOTMDS will produce a larger amount of linear Si-O structures, compared with NBECVD-DMDMOS, even at the same beam energy. Furthermore, by changing the neutral beam energy, the formation balance of linear, network and cage Si-O structures will be precisely controlled. The film composition was measured using Fourier transform infrared spectroscopy (FTIR), the film thickness was measured using ellipsometry, and the k -value was measured using a Hg probe. The modulus was obtained using a nano-indenter. As a comparison, we also evaluated a conventional PECVD SiOCH film.

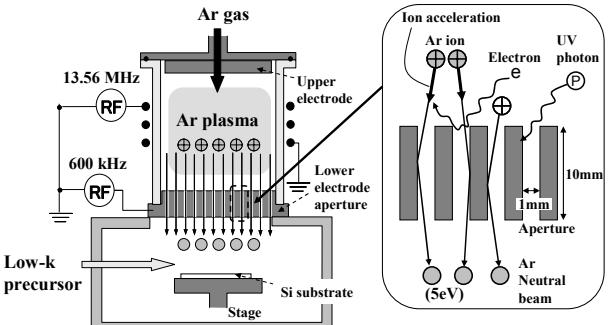


Fig. 1 Neutral Beam Enhanced CVD (NBECVD) apparatus.

3. Film characteristics of NBECVD-DMOTMDS SiOCH low- k film

Film Property

By using DMOTMDS as a precursor, the deposition rate was about twice as much as that of DMDMOS even at the same bias power (RF=10 W). This means a higher molecular weight precursor has higher absorption coefficient on the Si surface.

Figure 2 shows the FTIR spectrum of NBECVD-DMOTMDS, NBECVD-DMDMOS, and PECVD-DMOTMDS low- k films. The Si-O absorption peak was resolved into components based on linear, network, and cage structures, and the $\text{Si}-(\text{CH}_3)$ absorption

peak was resolved into components based on Si-(CH₃)₁ and Si-(CH₃)₂. The NBECVD low-k films contained a higher amount of linear SiO structure and Si-(CH₃)₂ compared with the PECVD low-k film. Table 1 lists the film properties of NBECVD-DMOTMDS, NBECVD-DMDMOS and PECVD-DMOTMDS film. The NBECVD-DMOTMDS films had larger amounts of Si-(CH₃)₂ bonds, which is a symbolic functional group of linear Si-O structures, than that in the NBECVD-DMDMOS films, whereas the conventional PECVD films consisted mainly of network structures. The two Si-(CH₃)₂ and two Si-OCH₃ bonds in DMOTMDS could generate a linear Si-O-Si structure through chemical reactions such as gelification by hydrolysis. On the other hand, PECVD caused a high amount of network structure due to higher dissociation of precursors. In addition, we found that the film property of NBECVD-DMOTMDS could be precisely controlled by bias power of the aperture. By decreasing the bias power, the percentage of linear structures increases, which causes a lower k-value. At a bias of 0 W, we could obtain a super-low k-value of 1.9. The modulus of NBECVD-DMOTMDS was lower than that in PECVD-DMOTMDS; however, this modulus value of 4 GPa is enough for Cu/low-k interconnect integration. Additionally, enough adhesion force (more than 5.5 N/cm) between low-k and underlying SiCN was also observed by peeling and scratch tests.

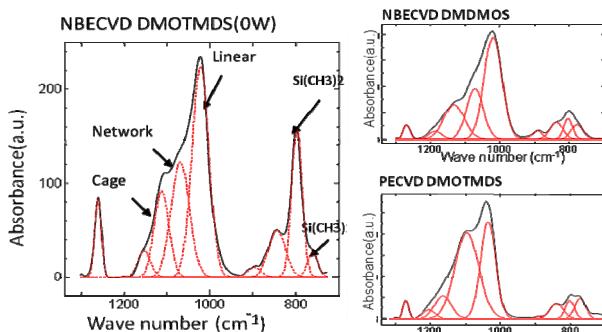


Fig. 2 FTIR spectra of NBECVD-DMOTMDS, NBECVD-DMDMOS, and PECVD-DMOTMDS low-k film.

Table 1 Film properties of NBECVD-DMOTMDS

			PECVD	NBECVD			
			DMO	DMOTMDS			
			TMDS	30W	0W	5W	10W
F T I R	SiO	Linear(%)	37	53	51	46	42
	Struc ture	Network(%)	53	25	31	38	41
		Cage(%)	10	21	18	16	17
	Met hyl	Si-CH ₃ /Si-O	3	3	7	8	8
		Si-(CH ₃) ₂ / Si-(CH ₃) ₁	42/28	62/38	86/14	80/20	81/19
		k-value	2.6	2.2	1.9	2.3	2.4
			Modulus	6	6	4	5

Water Resistance and Thermal Stability

Because water absorption increases the k-value of low-k film, we have to evaluate water-absorption efficiency in

low-k film. Figure 3 shows the wide range of FTIR spectrum of NBECVD- and PECVD- DMOTMDS low-k film. If the low-k films contain water, we would see a peak around 3500-4000 cm⁻¹. We did not observe any water peak in both low-k films. The NBECVD-DMOTMDS low-k film deposited at -20°C has similar water resistance to the conventional PECVD low-k film deposited at 400°C. It is suggested that NBECVD can efficiently polymerize SiOCH film by bombarding of neutral beams even at low temperature.

As there are many thermal processes, such as annealing, for fabricating Cu/low-k interconnects, we investigated thermal stability. Table 2 lists the results of FTIR analysis of NBECVD low-k films before and after 400°C annealing in vacuum for 2 hours. We could not observe any change of NBECVD low-k film structure, as shown in table 2. Additionally, the NBECVD low-k film properties (thickness, k value and modulus) were not changed even after 400°C thermal annealing. It is believed that the carbon-rich NBECVD low-k film has higher water resistance and thermal stability because of efficient polymerization of SiOCH due to neutral beam bombardment.

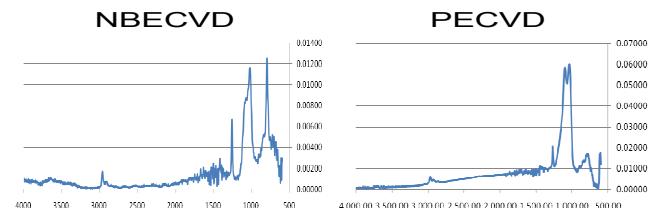


Fig. 3 Wade-range FTIR spectrum of NBECVD-DMOTMDS and PECVD low-k film.

	PECVD		NBECVD 0W		NBECVD 5W		NBECVD 10W	
	B	A	B	A	B	A	B	A
Linear(%)	37	49	51	51	46	48	42	43
Network(%)	53	42	31	37	38	34	41	39
Cage(%)	10	9	18	12	16	19	17	18
Si-CH ₃ /Si-O	3	2	7	7	8	7	8	6
Si-(CH ₃) ₂	42	47	86	82	82	79	81	77
Si-(CH ₃) ₁	58	53	14	18	18	21	19	23

Table 2 Thermal stability of NBECVD-DMOTMDS low-k film
B:Before annealing, A:After annealing

4. Conclusions

We found that NBECVD with DMOTMDS provides low dielectric, highly water-resistant, and highly thermal stability SiOCH low-k film. We also showed that this is because the NBECVD-DMOTMDS film has a large amount of liner SiO structures and methyl groups.

References

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