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Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp846-847

DMOTMDS/MTMOS Multi-Stacked SiOCH films for Super-Low-k and Sufficient Modulus Formed by Damage-free Neutral Beam Enhanced CVD

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1. Introduction

The use of materials with lower k-values is urgently required for continuous shrinking of ultra-large-scale integrated (ULSI) circuit. [1]. A commonly used low-k thin film is SiOCH film formed by plasma-enhanced chemical vapor deposition (PECVD). In SiOCH film, the ratio between Si-O and Si-$(CH_3)_x$, and the proportions of linear, network, and cage Si-O structures are important to determine the k-value and modulus. However, the k-value of SiOCH film deposited by PECVD is between 2.6 and 3.0 [2] because of the high dissociation process in the gas phase and the irradiation damage resulting from UV photons and charged particles. As a result, it is very difficult for the PECVD to precisely control the molecular structure of SiOCH film for the k-value and film modulus. To obtain a lower k-value and a sufficient film modulus at the same time, we have already proposed a neutral-beam-enhanced CVD (NBECVD) [3]. NBECVD has several advantages such as enabling structure-designable and damage-free deposition of SiOCH low-k film. By changing the precursors, we could precisely control the k-value and modulus of low-k film.[4].

In this paper, based on these advantages of NBECVD, a multi-stacked SiOCH film consisting of dimethoxy-tetramethyl-disiloxane (DMOTMDS, k=1.9, 4GPa) and methyl-trimethoxy-silane (MTMOS, k=2.8, 10GPa) layers were demonstrated to satisfy a super low-k value and a sufficient modulus simultaneously. By controlling layer thickness ratio, super k-value (k<2.0) and sufficient modulus (>7GPa) were achieved.

2. NBECVD and experimental set-up

NBECVD consists of an inductively coupled plasma (ICP) source and process chamber connected through a carbon aperture (Fig.1). In NBECVD, precursors are injected directly into the process chamber and adsorbed to Si substrate. Accelerated positive Ar ions in the plasma were efficiently neutralized by passing through the carbon aperture while maintaining their motion energy. Then, high density neutral beam was bombarded to the surface without any charged particles and UV photons [3]. The beam energy can be controlled by supplying RF bias (600 kHz) to the carbon aperture. Two types of precursor, DMOTMDS and MTMOS, were alternately injected into the process chamber to form the multi-stacked SiOCH film at the substrate temperature of -20 ^oC. The single-layer low-k film formed by a DMOTMDS precursor has a k-value of 1.9 and a modulus of 4 GPa [4]. This film was used as a lower k-value layer in multi-stacked structure. Conversely, the single-layer low-k film formed by MTMOS has a modulus of 10 GPa and a k-value of 2.8 [3]. This film was used as a higher modulus layer. These two different thin layers were alternately stacked. The overall film composition in the muti-stacked film was measured by Fourier transform infrared spectroscopy (FT-IR). The film thickness was measured by ellipsometry, and the k value was determined by mercury probe. The modulus was also obtained using a nano-indenter.

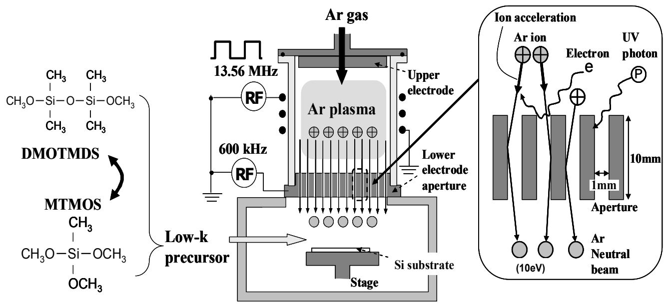

Fig. 1 Neutral Beam Enhanced CVD (NBECVD) apparatus.

3. Results and discussions

A. Basic Properties of multi-stacked SiOCH films

Two types of five-layer stacked SiOCH films with thickness ratios of the DMOTMDS/MTMOS layers of 43% (each layer thickness:10nm) / 57% (20nm) and 65% (20nm)/ 35% (25nm) were demonstrated, as shown in Fig.3. Figure3 also shows the TEM-EELS image of the five-layer stacked SiOCH films. We found that the five-layer film structures were successfully formed as we had designed them. In addition, interfaces between each layer were very clear because there was no plasma irradiation damage. These film properties and the compositions of Si-O and Si-$(CH_3)_x$ structures are listed in Table 1. By increasing the DMOTMDS layer thickness, linear type Si-O and Si-$(CH_3)_2$ structures increased. Conversely, by increasing the MTMOS layer thickness, network Si-O and Si-$(CH_3)_1$ structure increased in the stacked film. Under these conditions, we measured actual k-values and film modulus of the stacked films. When the thickness ratios of the DMOTMDS and MTMOS layers were 43% and 57%, respectively, the stacked film had a k-value of 2.5 and modulus of 10GPa. On the contrary, when thickness ratio of the DMOTMDS and MTMOS layers was 65% and 35%, respectively, the k-value was reduced to 2.1 and film modulus value was 7GPa. We found that the k-value and modulus of multi-stacked SiOCH films can be controlled by changing the thickness ratio of the DMOTMDS/MTMOS layers.

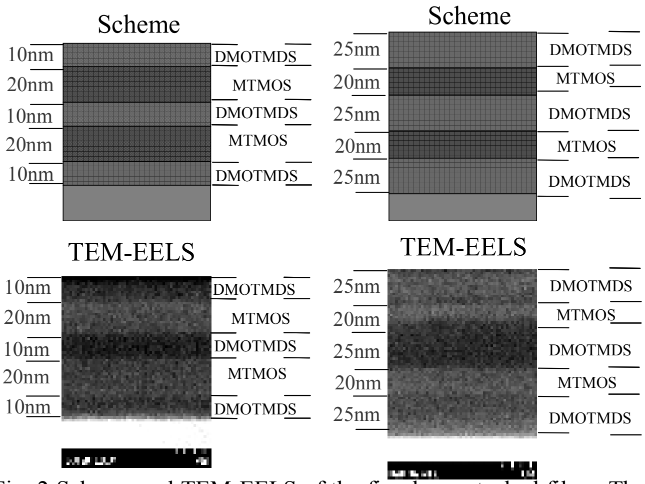

Fig. 2 Scheme and TEM-EELS of the five-layer stacked films. The five-layer film structures were successfully formed and the interfaces between each layer were very clear because there was no plasma irradiation damage.

			DMOTMDS/MTMOS[%]			
			100/0	65/35	43/57	0/100
FTIR	SiO structure	Linear[%]	51	48	45	43
		Network[%]	31	32	40	33
		Cage[%]	18	21	16	24
	Methyl	$Si\text{-}CH_3/Si\text{-}O$	7	6	3	2
		$Si\text{-}(CH_3)_2/Si\text{-}CH_3$	86	85	75	37
Relative SiO density			1.0	1.0	0.8	1.2
k-value			1.9	2.1	2.5	2.8
Modulus value [GPa]			4	7	10	10

Table 1 Film properties and compositions of five-layer stacked low-k film. By changing the thickness ratio, the film structure can be controlled.

B. Dependence of layer number

Deposition of multi-stacked film has possibilities to make super low-k film. However, it may be considered that multi-layer film has lower electrical stability. This is because there is difference in dielectric constant between each layer in the multi-staked film. This difference may affect RC delay. Therefore, we evaluated electrical stability of multi-stacked film by Electro-magnetic Field Simulation. This simulation was performed by Finite Element Method. We investigated the dependence of layer number on capacitance value of multi-staked film. We found that capacitance value decreased by increasing layer number, as shown in Fig.4. By increasing layer number, the capacitance along vertical and horizontal direction of stacked film decrease. This result indicates that increasing layer number is very effective to decrease *k* value for multi-staked film. On the basis of this result, we demonstrated multi-stacked film with more layers. We deposited nine-layer stacked film which consisted of 5 lower k-value layers and 4 higher modulus layers. Each layer thickness was approximately 10nm.We found that a super low k-value of 1.8 and a sufficient modulus of more than 7GPa was achieved at the same time (Fig. 5). We considered that film structure, including Si-O and $Si(CH_3)_x$, of multi-stacked film may be different from that of single layer when layer thickness decreases, which results in better film property than individual one.

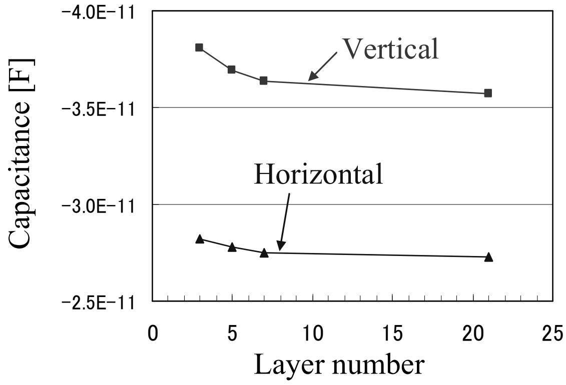

Fig.4 Layer number dependence of capacitances along vertical and horizontal directioss of multi-stacked film.

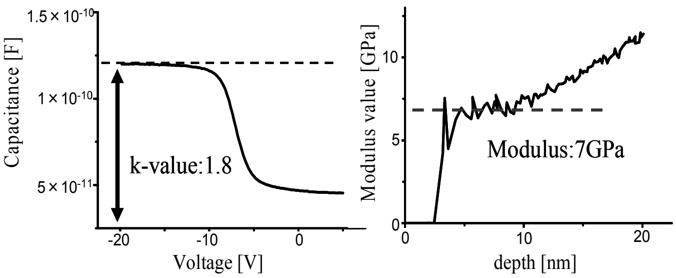

Fig.5 k-value of 1.8 and modules of 7GPa of nine-layer stacked low-k film.

4. Conclusions

We successfully fabricated a multi-layer stacked low-k film of DMOTMDS thin film (k=1.9, 4GPa) and MTMOS thin film (k=2.8, 10GPa) using damage-free neutral beam enhanced CVD. By changing the layer thickness ratio and the number of layers, the properties of low-k film were precisely controlled. Then, a super low-k SiOCH film with a k-value of 1.8 and a sufficient modulus of 7GPa was simultaneously realized by the nine-layer stacked structure composed of 10nm-thick-DMOTMDS (k=1.9, 4GPa) and 10nm-thick-MTMOS (k=2.8, 10GPa) layers .

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