

Ultra Low-k Non-Porous SiOCH Film ($k < 2.2$) Formed by Ultra Precise Molecular Control in Polymerization Synthesis by Using Large-Radius Neutral-Beam-Enhanced CVD

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Abstract

By using hydrogen mixed with Ar neutral beam for polymerization of DMOTMDS as a precursor to form a low-k SiOCH film, an ultra-low k-value of 2.2 could be obtained with an extremely non-porous film. This film had a specific sharp peak of 1108 cm^{-1} by FTIR and was classified as dimethylsilicone ($-(\text{CH}_3)_2\text{SiO})_n-$) like a spin-on polymer. A long dimethylsilicone molecular chain is considered to have minimum oriental polarization. Surprisingly it was considered that DMOTMDS was polymerized by silane coupling, which is a well-known synthetic chemistry method, and the dimethylsilicone molecular chain was grown in film.

1. Introduction

In accordance with the shrinking of ultra-large-scale integrated devices, ultra-low-k (ULK) interlayer dielectric (ILD) material, which is a porous carbon-doped silicon oxide (SiOCH) dielectric, has been developed and used recently. However, in applying the ILD, there are a lot of problems in the integration process due to the insufficient modulus of the SiOCH film with high density pores [1]. To reduce the pores while keeping a low k-value of less than 2.4, orientation polarization of SiOCH has to be minimized by controlling the molecular structure precisely. However, this is impossible when using conventional plasma enhanced chemical vapor deposition (PECVD) because of excess disassociated precursor during deposition. Yasuhara et al. had reported that neutral beam enhanced CVD (NBECVD) was the best way to control film structure and obtained ULK SiOCH film by eliminating plasma damage [2]. However, there was not sufficient discussion about the pores in SiOCH and molecular structure. In this study, to control molecular structure in film for eliminating pores keeping low-k value by controlling the neutral beam energy and design of the chemical reaction, we developed a large-radius (370mm) neutral beam source.

2. Experimental procedure and concept

For a practical NBECVD system, a large-radius neutral beam source has been developed. It consists of a large-diameter microwave plasma (MWP) source and a

CVD process chamber to form SiOCH as shown in Fig. 1. The Ar neutral beam is generated with a MWP through the carbon plate, which has many apertures. Then, UV and electrons from the plasma is cut off completely by the aperture plate. The Ar neutral beam is irradiated to Si wafer surface while directly injecting the precursor to the Si wafer surface in the CVD process chamber. Dimethoxy tetramethyl disiloxane (DMOTMDS) was used as a precursor has four Si-CH₃ and two Si-O-CH₃ bonds (Fig. 2 (a)). When Ar neutral beam was set to 10 eV for polymerizing DMOTMDS to synthesize dimethylsilicone (DMS, $-(\text{CH}_3)_2\text{SiO})_n-$) in film, which cuts only the O-CH₃ bond (bond energy: 8 eV) keeping Si-CH₃ bond (14 eV) as shown in Fig. 2 (b) [3]. All of the SiOCH bonds are formed on 8 inch Si wafer. In comparison with NBECVD film, commercial PECVD porous SiOCH film was purchased to be used in general ILD material.

3. Results and discussion

Fig. 3 shows the results of investigating the correlation between neutral beam energy and k-value. The k-value of NBECVD SiOCH was decreased by increasing RF power and it minimized at 150 W. When high RF power was applied, the k-value was increased because the Ar neutral beam energy became too strong and destroyed the film structure. It is indicated that appropriate Ar neutral beam can enhance polymerization of DMOTMDS. However, higher leakage current was observed compared with PECVD SiOCH because it is considered that partial the Ar neutral beam energy was increased to more than 14 eV and then the dangling bond was introduced into the film. Furthermore, each O/Si and C/Si ratio was measured to verify our desired polymerization for NBECVD SiOCH with RF of 150 W, which were 1.48 and 4.45, respectively. Our SiOCH film included a higher carbon ratio, and it is suggested that the degree of polymerization in NBECVD SiOCH was not enough, and a large amount of O-CH₃ terminations remained. It means a long DMS chain was not fully grown. To terminate the dangling bond and enhance the synthesis of DMS, each hydrogen and oxygen addition in the Ar neutral beam was evaluated as shown in Fig. 4. Hydrogen addition could improve the k-value and leakage current at the same time, dramatically. Additionally, each

O/Si and C/Si ratio was improved to 1.50 and 1.92, respectively. The carbon ratio was decreased and was close to the ideal value. It indicates hydrogen effectively enhanced the synthesis of DMS and helps to grow a longer molecular chain, and also the dangling bond was terminated. Furthermore, the film properties and structure were investigated as shown in Table I and Fig. 5. NBECVD SiOCH had a higher modulus than PECVD SiOCH and no pores in the film measured by small angle X-ray scattering as expected. The film structure was changed drastically. In particular, the wave profile of siloxane frameworks (1000 to 1200 cm^{-1}) was shifted to a higher wave number in accordance with the decreasing k-value. Remarkably, the hydrogen additive sharpened and had a peak at 1108 cm^{-1} . The peak around 1108 cm^{-1} peak is caused by the known vibration of the 150° Si-O-Si angle in oxide film being incorporated in the methyl. As similar phenomena, a sharp peak was known to be observed in a spin-on-polymer such as a Methyl silsesquioxane. Therefore, the 1108 cm^{-1} peak in the NBECVD SiOCH film is considered to be vibration caused by a long DMS chain in the film to be polymerized DMOTMDS by hydrogen addition. This synthetic flow can be explained by silane coupling. First, Si-OCH₃ is hydroxylated to Si-OH by hydrogen and Ar neutral beam energy. Next, two Si-OH and Ar beam energy can enhance the silanole reaction and make Si-O-Si bond by anhydration. It is said that chemical synthetic was achieved in vacuum chamber by NBECVD method.

4. Conclusion

Using the NBECVD method and an appropriate chemical reaction with DMOTMDS and hydrogen, DMS was synthesized by silane coupling and a long molecular chain was grown in film. The non-porous ultra-low-k SiOCH of 2.2 was achieved with high film strength.

References

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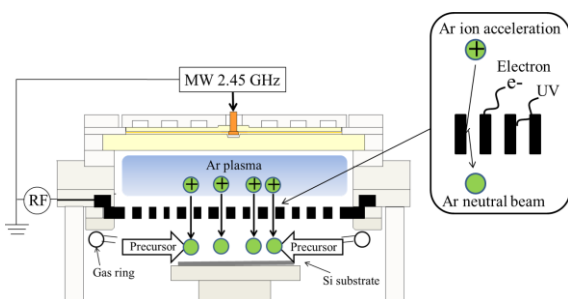


Fig. 1 Large-radius NBECVD system has many apertures with holes between MWP chamber and deposition chamber to convert ions in plasma to neutral particles that have only kinetic energy. The aperture is connected to RF generator and matching system to apply RF power to accelerate neutral beam.

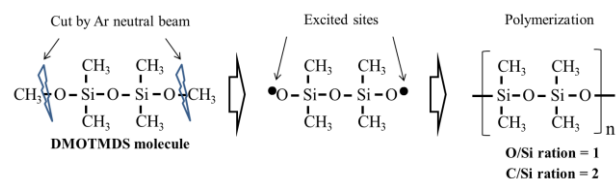


Fig. 2 DMOTMDS molecular structure and synthetic flow of dimethylsilanole using Ar neutral beam. When molecular structure is controlled precisely as dimethylsilanole, each ratio of O/Si and C/Si is 1 and 2 respectively.

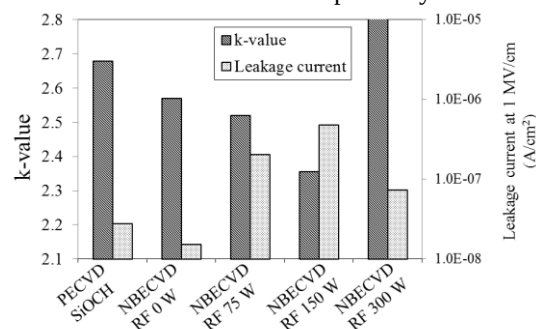


Fig. 3 k-value and leakage current of each PECVD and NBECVD SiOCH film.

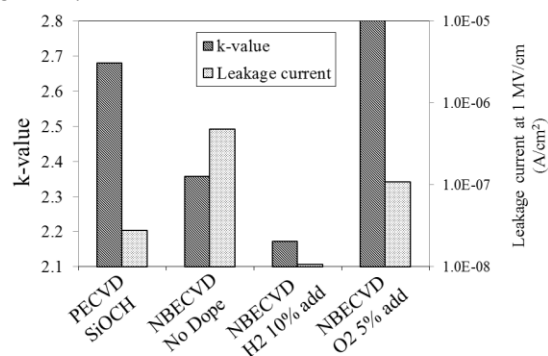


Fig. 4 Additive effect of doping for k-value and leakage current.

Table I Conditions and properties of Each SiOCH process

NBECVD process conditions		Film properties			
RF power	Beam gas	k-value	Leakage (A/cm ²)	Pore (nm)	Modulus (GPa)
(a) PECVD		2.68	2.8×10^{-8}	1.2	6
(b) 150W	Ar	2.36	4.8×10^{-7}	ND*	12
(c) 150W	Ar / H ₂	2.17	1.1×10^{-8}	ND*	12

*Not Detected

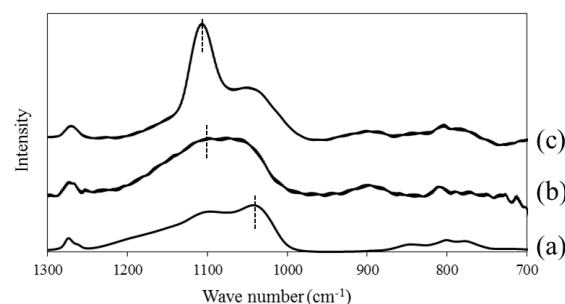


Fig. 5 Film structure change of siloxane for each SiOCH film