

## Hydrocarbon Groups and Film Properties of SiOCH Dielectrics: Theoretical Investigations using Molecular Models

Nobuo Tajima,<sup>1</sup> Tomoyuki Hamada,<sup>2</sup> Takahisa Ohno,<sup>1</sup> Katsumi Yoneda,<sup>3</sup> Nobuyoshi Kobayashi,<sup>3</sup>  
Satoshi Hasaka<sup>4</sup> and Minoru Inoue<sup>4</sup>

<sup>1</sup>First Principles Simulation Group, Computational Materials Science Center, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Phone: +81-3-5452-6624, Fax: +81-3-5452-6625; E-mail: ntajima@fsis.iis.u-tokyo.ac.jp

<sup>2</sup>The FSIS Center for Collaborative Research, Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

<sup>3</sup>Research Dept.1, Semiconductor Leading Edge Technologies, Inc. (Selete), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

<sup>4</sup>Taiyo Nippon Sanso Corporation, Toyo Bldg., 1-3-26 Koyama, Shinagawa-ku, Tokyo 142-8558, Japan

### 1. Introduction

The PECVD SiOCH film has been introduced as a low- $k$  ( $k = 2.9$ ) dielectrics in the manufacturing of the 90 nm-node interconnects [1]. Moreover, so-called “porous” SiOCH film with less film density has been developed to reduce the  $k$ -value ( $k < 2.5$ ) for future technology node. However, porous materials suffer from degradation in mechanical strength which results in the CMP and packaging failures. Thus, we need some alternative strategies for reducing  $k$ -values without damaging mechanical strengths.

Theoretical calculations are indispensable for designing appropriate films at the molecular structure level. From this view point, we have recently worked on the molecular modeling of a PECVD SiOCH low- $k$  film as the first step [2]. In this paper, applying the molecular modeling method, we have tentatively investigated possibility for the film property improvement by substituting hydrocarbon groups in the SiOCH films.

### 2. Molecular Modeling of Film Structures

SiOCH films are amorphous siloxane polymers with substantial number of cross links (Fig.1), and the amorphous nature corresponds to random topologies of Si sites such as  $RR'SiO_2$ ,  $RSiO_3$ , and  $SiO_4$  where R or R' represents H or hydrocarbon groups. Since methods for molecular modeling of polymers with cross-links have never been proposed so far, we have developed a method originally [2].

The method is schematically visualized in Fig. 2 using a small example system. A periodic system with tens of atoms in a unit cell is used to represent a film structure. Film model structure is constructed by making Si...O bonds between  $R(R')SiO_n$  fragments. Types and numbers of the fragments are determined from chemical groups detected in actual film by spectroscopic measurements and experimentally observed atom composition of the film. We create  $\sim 500$  structures by preparing different fragment configurations before the bond creation, and pick up least distorted structures after constant pressure molecular dynamic simulations as possible structures in the actual film. Note that connections of fragments are not intended to simulate actual molecular reactions in PECVD reactor but

to generate possible connections of Si sites.

### 3. Results

We have employed an experimentally created PECVD SiOCH film (precursor: tetramethylcyclo-tetrasiloxane (TMCTS), density:  $1.38 \text{ g/cm}^3$ ,  $k$ : 2.9, Young's modulus: 17 GPa) as a reference film for the atom group substitutions. We have first generated its model structures, and compared their dielectric constants, Young's moduli, and IR spectrum with experimental results to know the performance of our calculations. To reproduce experimental atom compositions ( $Si:O:C:H = 1:1.54:0.67:2.14$ ), we have made our model to include seven  $CH_3SiO_3$ , three  $HSiO_3$ , and one  $SiO_4$  in a periodic box, which gives an atom composition  $Si:O:C:H = 1:1.55:0.64:2.18$ . See ref.2 for details of the calculations of the film properties. IR spectrum and dielectric constants have been calculated using the first-principles program PHASE [3].

Fig. 3 shows calculated IR spectrum of one of the generated structures with the experimentally observed one. The resemblance of the two spectra indicates that our modeling is quite successful.

Fig.4 shows the dielectric constants and Young's modulus for six modeled structures, including the structure for Fig. 3. The densities of calculated structures are scattered (ranging in  $1.32\text{--}1.57 \text{ g/cm}^3$ ), and accordingly their dielectric constants and Young's Modulus are various. Our modeling method can not reproduce experimental density since it just generates geometrically possible structures without reflecting experimental conditions of PECVD. We can however estimate  $k$  and Young's Modulus by finding values for the experimental film density in the density dependent data plot. The estimated values are  $k \sim 3.1$  and Young's Modulus  $\sim 13 \text{ GPa}$ , which are close to the corresponding experimental values, 2.9 and 17 GPa, respectively. Thus, our procedure will be appropriate for investigations of film properties of SiOCH dielectrics.

Applying our procedure, we have created model structures of hypothetical low- $k$  films to investigate hydrocarbon substitution effects on film properties: i) two of the methyl ( $-CH_3$ ) groups of the original film model above are substituted by vinyl groups ( $-CH=CH_2$ ), ii) one of the methyl

groups is substituted by an isopropyl group ( $-\text{CH}(\text{CH}_3)_2$ ). It is well established that the increase of hydrocarbon content in film results in both the decreases of  $k$  and Young's modulus, but the hydrocarbon content increase in i) and ii) is purely due to increase of hydrocarbon group size and do not lead to decrease of the number of network Si-O bonds.

The results are shown in Fig.5. Provided that these two film structure modifications affect the film density only little, the  $k$  values should decrease for both the substitutions, and the Young's modulus should increase for the isopropyl substitution. For the vinyl group substitution, we can not mention about the Young's modulus because of the widely scattered data points. The decrease of  $k$ -value is quite understandable in terms of increase of hydrocarbon amount, while the increase of Young's modulus for isopropyl substitution is noteworthy. Probably, the bulky isopropyl group makes the Si-O bond network rigid by the steric hindrance effect.

Further analyses are needed, but it is implied that film properties may be improved by chemical modifications like i) and ii) if they are possible experimentally.

#### 4. Conclusions

By performing first principles calculations for molecular models of SiOCH films, we have investigated the possibility of film property modifications by the hydrocarbon group substitutions. The calculated results suggest that  $k$ -values can be decreased without decreasing mechanical strengths.

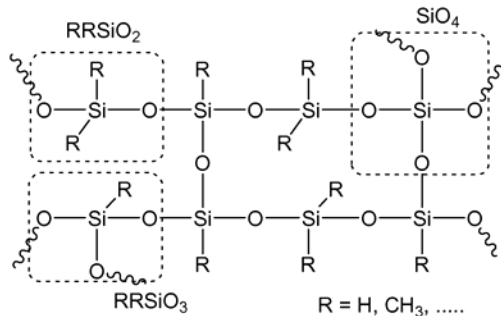


Fig. 1 Chemical structure of SiOCH films.

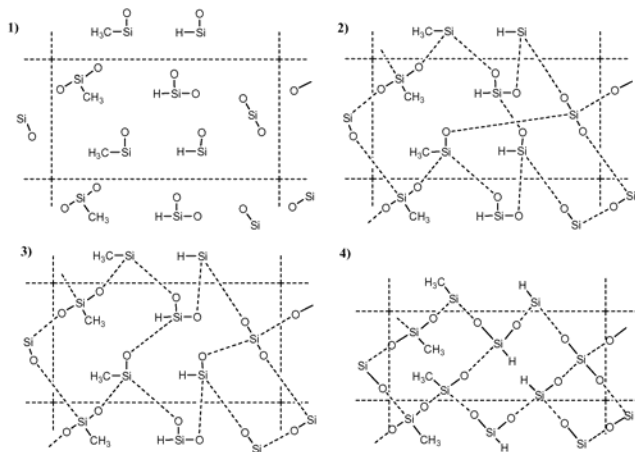


Fig. 2 Method to create molecular models of SiOCH films.

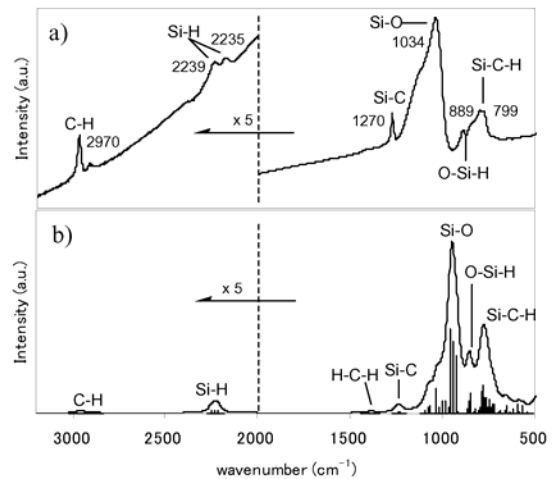


Fig. 3 a) Experimentally observed FTIR spectrum and b) calculated IR curve for a model structure. Vertical lines under IR curve in b) represent IR intensities of individual normal modes.

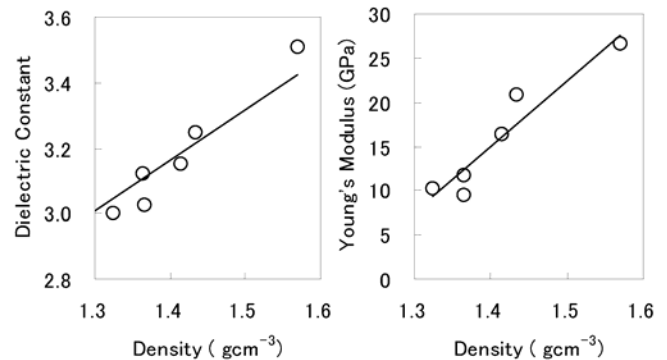


Fig. 4. Dielectric constants and Young's moduli of the model structures for the PECVD SiOCH film of TMCTS.

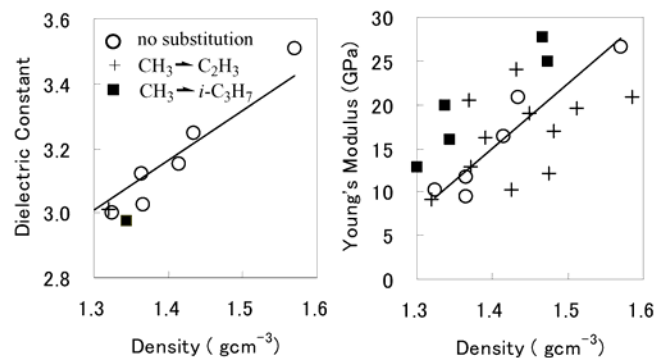


Fig. 5. Dielectric constants and Young's moduli of the model structures with hydrocarbon substitutions to the TMCTS film model.

#### References

- [1] C. -H. Jan *et al.*, *Proc. IEEE IITC*, (2004) 205.
- [2] N. Tajima, T. Hamada, T. Ohno, K. Yoneda, N. Kobayashi, S. Hasaka and M. Inoue, *Proc. IEEE IITC*, (2005).
- [3] *PHASE*: Institute of Industrial Science, University of Tokyo, Tokyo, 2004.