G-2-2

SiOCH Films with Hydrocarbon Network Bonds: First-Principles Investigation

Nobuo Tajima, [1] Tomoyuki Hamada, [2] Takahisa Ohno, [1]
Katsumi Yoneda, [3] Seiichi Kondo, [3] Nobuyoshi Kobayashi, [3]
Manabu Shinriki, [4] Kazuhiro Miyazawa, [4] Kaoru Sakota, [4] Satoshi Hasaka, [4] and Minoru Inoue[4]

[1]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: +81-3-5452-6624: E-mail: ntajima@fsis.iis.u-tokyo.ac.jp
[2]The FSIS Center for Collaborative Research, Institute of Industrial Science, University of Tokyo,
4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
[3]Semiconductor Leading Edge Technologies, Inc. (Selete), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
[4]Taiyo Nippon Sanso Corporation, Toyo Bldg., 1-3-26 Koyama, Shinagawa-ku, Tokyo 142-8558, Japan

1. Introduction

The SiOCH films have been studied extensively as the low-k materials of silicon devices. Nowadays, SiOCH films with extremely small k-value ($k < 2.5$) can be obtained, for example by using the sacrificial porogen approach. However, films of smaller k-value are less compatible to the integration processes since they have smaller mechanical strengths. Accordingly, the chemical structures of films that give large mechanical strength after the k-value reduction are a matter of concern. Several studies suggest importance of cross-links of hydrocarbon component (Fig.1) for creating high-modulus SiOCH films [1-3]. Hydrocarbon component goes to the network terminals usually, but their cross-links are experimentally creatable by using particular monomer precursors [1,2]. In this study, we have performed theoretical calculations to verify the significance of hydrocarbon cross-links for obtaining SiOCH films with the improved properties.

2. Method of Molecular Modeling of SiOCH Films

Atomistic model structures of SiOCH films with or without hydrocarbon cross-links have been created, and their mechanical and dielectric properties have been compared. Three dimensionally periodic molecular structures of tens of atoms in a unit cell have been used as models to represent the polymer networks of SiOCH films. The network structures have been made by connecting atom groups given for a target film into chemically possible geometries. The method to create molecular models of SiOCH films had been developed originally and the detail is described elsewhere [4-6].

The Young's moduli of model structures have been calculated via classical constant pressure molecular dynamics (MD) simulations [7] with the MM3 force field [8]. The electronic and ionic contributions of dielectric constants have been calculated separately using the time dependent perturbation theory [9] and the Berry phase polarization theory [10], respectively, based on the density functional theory [11]. The dielectric constants have been calculated using program *UVSOR* [12].

3. Results

3.1. Hydrocarbon Component at Network Terminal and in Polymer Network

Model structures consisting of seven CH_3-SiO_3(T-unit), three H-SiO_3(T-unit), and a SiO_4(Q-unit) in a unit cell have been created as reference structures. Model structures with hydrocarbon cross-links Si-(C_2H_4)-Si have been created by bonding a pair of Si-CH_3 in each reference structure (model A). The types and the numbers of the Si-units of the reference structures are those of model structures created previously for a PECVD-SiOCH film of TMCTS precursor [4,5].

The calculated properties of the modeled structures are listed in Table 1. Six different model structures have been created. The influence of the C-C bond creation is different from one structure to another, but the Young's modulus (E_Y) increases significantly as a whole. The average increase of Young's modulus is more than 5 GPa, although the number of cross-links, defined as the number of linkages between the Si-units, increases by only 6 % (from 17 to 18) through the C-C bond creation. It is confirmed that making hydrocarbon cross-links to remove network terminals is an effective way to obtain high modulus films actually.

In contrast to the Young's modulus, the k-values increase slightly on the average. The k-value increases because the model structure shrinks by the C-C bond creation, but the increase is limited by the relatively small structure shrinkage. There is another factor to limit the k-value increase: The polarizabilities of model structures decrease by the loss of electrons and ions upon the substitution 2Si-$CH_3 \rightarrow$ Si-(C_2H_4)-Si.

The calculated mechanical and dielectric properties are plotted in Fig. 2. The figure illustrates that the film properties change favorably for the low-k dielectrics by the C-C cross-link creation: Structures of model A have larger Young's moduli than the reference structures of about the same k value. It would be suggested that the hydrocarbon component in SiOCH films should be involved in the polymer network as much as possible to solve the trade-off problem of the low k-value and large mechanical strength.

3.2. Structures without Network Terminals

To verify the suggestion in the previous section, we have examined SiOCH structures where all the hydrocarbon components are involved in the polymer network. For this purpose, we have created model structures that consist only of Si-O-Si bonds and Si-X-Si bonds (X = CH_2, C_2H_4, and C_3H_6). The atom compositions of these structures are $Si_6O_6X_6$. Note again that these structures have hydrocarbon components only in the *polymer network*, while the model structures in the previous section have most of them at the *network terminal*.

The properties of the model structures for each film type are plotted in Fig. 3. (The data for the TMCTS film model structures is shown again as a reference in this figure.) The model structures $Si_6O_6X_6$ have smaller k-values and smaller Young's Moduli on going from X = CH_2 to X = C_3H_6. The smaller k-values result from the carbon richer nature, and the smaller Young's Modulus result from the longer network segment Si-X-Si.

The structures for X = C_2H_4 and C_3H_6 have much improved E_Y-k relation over the reference model structures, as suggested in the previous section. The figure implies that the k-values of these films can be decreased further by about 0.5 than the ordinary SiOCH films keeping the minimum value requirement on the Young's Modulus. The SiOCH films of these types seem to have potential to be the low-k dielectrics of the future technology node.

As to structures for X = CH_2, their k values and Young's modulus are too large to be compared directly with the data for the TMCTS model. Nevertheless, the structures for X = CH_2 will not be so excellent since they have substantially larger dielectric constants than the structures for X = C_2H_4 and C_3H_6. These data imply that the film properties are improved sufficiently only when particular types of hydrocarbon components are included in the cross-link.

4. Conclusion

It has been suggested from theoretical calculations that making hydrocarbon cross-links is a way to obtain high-modulus and low-k SiOCH films.

References

[1] D. Geraud *et al.*, *Proc. IEEE IITC*, 226 (2005).
[2] S. Sugahara *et al.*, *J. Electrochem.Soc.*, **148**, F120 (2001).
[3] T. Furusawa *et al.*, *Proc. IEEE IITC*, 45 (2005).
[4] N. Tajima *et al.*, *Proc. IEEE IITC*, 67 (2005).
[5] N. Tajima *et al.*, *Extended Abstracts of SSDM*, 548 (2005).
[6] N. Tajima *et al.*, *Proc. IEEE IITC*, (2006).
[7] H. J. C. Berendsen, *et al.*, *J. Chem. Phys.*, **81**, 3684 (1984).
[8] N. L. Allinger, Y. H. Yuh, and J.-H. Lii, *J. Am. Chem. Soc.*, **111**, 8551 (1989)., **111**, 8566 (1989)., **111**, 8576 (1989).
[9] G. Harbeke "Optical Properties of Semiconductors", in *Optical Prop of Solids*, F. Abeles, Ed., Amsterdam, North–Holland, pp.21-92 (1972).
[10] R. D. King-Smith, D. Vanderbilt, *Phys. Rev.*, **B47**, 161 (1993).,R. Resta, *Rev. Mod. Phys.*, **66**, 899-915 (1994).
[11] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865 (1996)., J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, **78**, 1396 (1997).
[12] *UVSOR ver. 1.0*: University of Tokyo, Tokyo, 2005.

hydrocarbon groups in the polymer network (cross-link)

R = H, CH_3, ...
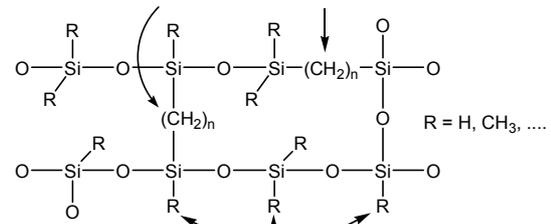
hydrocarbon groups (or H atoms) at the network terminal

Fig. 1. Chemical structure of SiOCH film with hydrocarbon cross-links.

Table 1. Calculated properties of the modeled structures[a]

	ρ/gcm^{-3}	k	E_Y/GPa	V/nm^3
1	1.31(1.34)	2.98(3.07)	7.6(8.2)	0.735(0.722)
2	1.41(1.26)	3.13(2.94)	9.2(5.8)	0.683(0.768)
3	1.45(1.47)	3.19(3.28)	17.0(10.5)	0.665(0.656)
4	1.57(1.57)	3.59(3.41)	31.9(16.8)	0.562(0.618)
5	1.58(1.55)	3.39(3.39)	15.9(13.2)	0.601(0.624)
6	1.70(1.71)	3.57(3.64)	35.0(28.5)	0.569(0.565)
Average	1.53(1.48)	3.31(3.29)	19.4(13.8)	0.637(0.659)

[a] Data in parentheses for the reference structures, data without parentheses for structures of model A. ρ: density, k: dielectric constant, E_Y: Young's Modulus, V: Volume per unit cell.
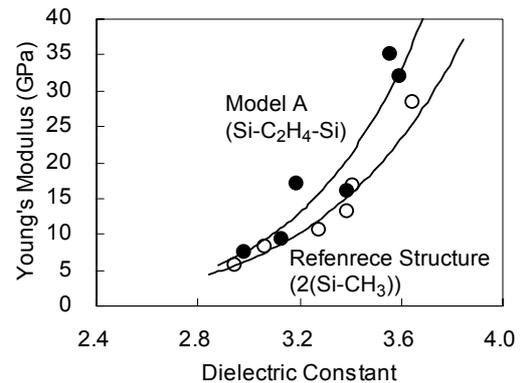

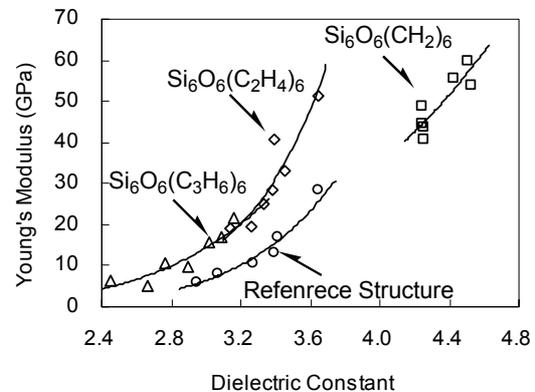**Fig. 2.** Young's moduli and dielectric constants of the structures of model A and the reference structures.

Fig. 3. Young's moduli and dielectric constants of the model structures $Si_6O_6X_6$ (X = CH_2, C_2H_4, and C_3H_6) and the reference structures.