S7-3   Developments of organic-based low-k films deposited by plasma copolymerization

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This paper describes the properties of low-k materials produced by plasma copolymerization. Carefully chosen monomer precursors and suppression of excess dissociation enabled controlling film properties. For example, moduli of the copolymerized films were improved by enhancing bridging between the monomers. Dielectric constant of the film could be reduced by using low temperature deposition followed by annealing.

In order to satisfy the requirements for ULSIs, an interconnect structure with low dielectric constant (Low-k) films is one of possible solutions. We have proposed the strategic concept of "Low-k materials with scalability applicable to a few technology nodes" [1]. The major challenge to realize the scalable low-k material is to get solutions for controlling the dielectric constant and mechanical strength. Among several low-k film deposition methods, a plasma copolymerization technique has been developed for this purpose [2]. The concept of the technique is illustrated in Fig. 1. Basic film properties will be determined by the matrix monomer, and modified by copolymerization to achieve the lower dielectric constant and higher mechanical strength.

Figure 2 shows a schematic diagram of the experimental apparatus based on a plasma CVD system. DVS-BCB was chosen as a starting matrix skeleton monomer. The dielectric constant of the singly polymerized DVS-BCB film was 2.78 [2]. Typical deposition condition is shown in Table 1. Converged saddle point structures of DVS-BCB monomer by density functional method (B3LYP/6-31G*) were shown in Fig. 3 [3]. Table 2 shows the list of precursors for copolymerization. Three approaches from (a) to (c) were examined mainly to reduce dielectric constant. These precursors were chosen from the view point of possible copolymerization reactions with the matrix monomer, from calculated dielectric constant of the monomers, and from vapor pressure. The calculated dielectric constants for these monomers were shown in Fig. 4 [4,5]. DVS-BCB monomers show about the same value as the deposited film. Phenyl compounds show higher values than those of aliphatic compounds.

The QMS system could detect reaction products in the plasma through orifices at the chamber wall. Figure 5 shows the mass spectrum from 380 to 500 amu during discharge with DVS-BCB molecule in helium plasma [6]. As the mass number of DVS-BCB monomer is 390, the mass peaks observed here can be attributed to the polymerization reaction products in the plasma. Figure 6 shows electron density change against source power measured by a surface wave probe [7]. The low electron density suppresses excess dissociation of the monomers, and enables to inherit original characters of the monomers.

In method (a), phenyl compounds with unsaturated functional groups were introduced as modification monomers. They have smaller molecular volume than the DVS-BCB monomer and can polymerize with DVS-BCB. Therefore, the copolymerized films were expected to have lower dielectric constant by free volume being formed between the monomers, and higher mechanical strength by enhanced bridging between the monomers. The dielectric constant and modulus of the copolymerized film are shown in Fig. 7 as a function of the molar ratio of the modification monomers supplied to DVS-BCB. The modulus increases with the molar ratio. This was due to an increase in the copolymerization ratio [8]. However, the dielectric constant of the deposited polymers did not decrease. This indicates that free volume could not be formed in the film by copolymerization.

Low-k hydrocarbon compounds with unsaturated functional groups were used to introduce aliphatic component into the skeleton structure in method (b). Figure 8 shows the relationship between the dielectric constant and the modulus of the copolymers with DVS-BCB. Results for VNB and TVCH were plotted together with those for the phenyl compounds shown in Fig. 7. Notice that all the data points are distributed over the same range. This indicates that the deposited films had roughly the same characteristics. One possible reason for this result is the poor thermal stability of the aliphatic compounds. Aliphatic component deteriorated to thermally stable groups like naphthalene on a high-temperature wafer, and lost their low-k property.

As shown in Fig. 8, it is difficult to preserve aliphatic components in an organic skeleton structure at a deposition temperature of 400 °C. On the other hand, in silica-based low-k materials, these aliphatic compounds are often used as porogens to form pores in the film after curing the spin-coated film. Thus we conceived that it might be possible to form pores even in organic-based films obtained by low-temperature deposition with aliphatic compounds followed by annealing to vaporize some of the aliphatic components. This is method (c). A 2-dimethylvinylsiloxane-tricyclodecane (2DMVS-TCD) monomer having an aliphatic and siloxane molecular structure was used as a matrix skeleton monomer. This monomer has a lower dielectric constant than DVS-BCB as indicated in Figure 4 (c). Figure 9 shows the effect of deposition temperature and subsequent annealing on the dielectric constant. Acetylene (C_2H_2) was added to enhance the deposition rate. It can be seen that the low-temperature deposition led to a lower dielectric constant. Moreover, annealing at 400 °C after the deposition did not change the dielectric constant. A dielectric constant of 2.48 was obtained by deposition at 300 °C followed by annealing at 400 °C.

[1] T. Kikkawa, Ext. Abst. ADMETA 2003: Assian session, 1-2, (2003) 4, [2] J. Kawahara, et al., Technical Dig. IEDM 2003, 6-2, (2003) 143, [3] M. J. Frisch, et al., "Gaussian 03 Revision B.05", Gaussian, Inc., Pittsburgh PA, (2003), [4] T. Fukuda, et al., Jpn. J. Appl. Phys., 41, (2002) L307, [5] K. Kinoshita, et al., Proc. AMC2004, P.14 (2004), [6] K. Kinoshita, et al., Proc. DPS2003, 3-1, (2003) 61, [7] K. Nakamura, et al., Proc. DPS2004, P-29, (2004) 169, [8] N. Kunimi, et al., Proc. IITC 2004, 8.5, (2004) 134
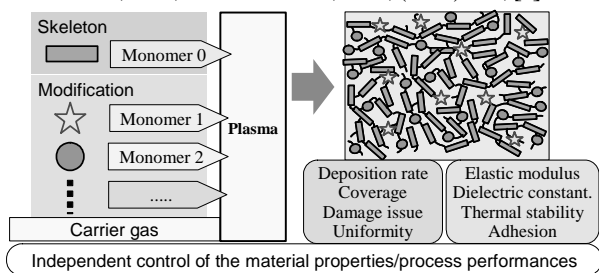
Fig. 1 Concept of a new plasma-enhanced co-polymerization [1].

Table 1 Typical deposition condition for the copolymerization.

RF power	250 W
DVS-BCB matrix monomer liquid flow	0.2 g/min (~ 11.5 sccm)
He carrier gas flow	700 sccm
Pressure	400 Pa
Substrate temperature	200-400 ℃

Table 2 Skeleton monomer and modification monomer to reduce dielectric constant by three different approaches [5]

Fig. 2 Schematic diagram of a plasma polymerization apparatus with diagnose system.
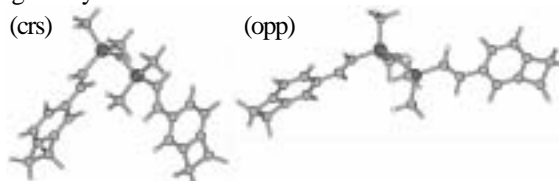
Fig. 3 Converged molecular structures of DVS-BCB monomer by density functional method (B3LYP/6-31G*).

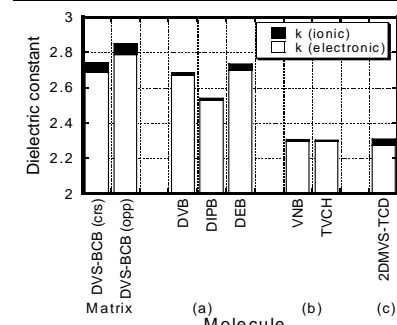|		Molecule	Abbreviation
Matrix	Skeleton	divinylsiloxane-bis-benzocyclobutene	DVS-BCB
(a)	Free volume formation	divinylbenzene, diisopropenylbenzene, diethynylbenzene, trimethylbenzene	DVB, DIPB, DEB, TMB
(b)	Introducing aliphatic	vinylnolbornene, trivinylcyclohexane	VNB, TVCH
(c)	Low temperature deposition	trivinylcyclohexane, 2-dimethylvinylsiloxane-tricyclodecane	TVCH, 2DMVS-TCD (as matrix)

Fig. 4 Calculated dielectric constant by density functional method (B3LYP/6-31G*) [4,5]. Both electronic and ionic polarizations are displayed. (a) to (c) indicate monomers for different approaches.
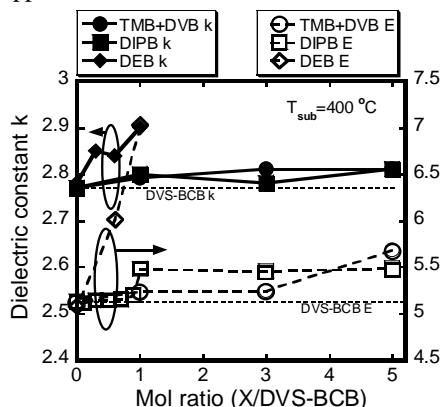

Fig. 5 Mass spectrum of the plasma polymerization reaction products, and their molecular structures [6].

Fig. 6 Electron density change against source power for helium plasma with DVS-BCB molecule measured by surface wave probe [7].

Fig. 7 Dielectric constant and modulus of copolymerized film of DVS-BCB with phenyl compounds as a function of supplied molar ratio to DVS-BCB [2,5].
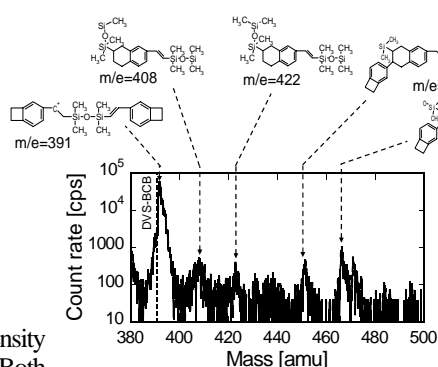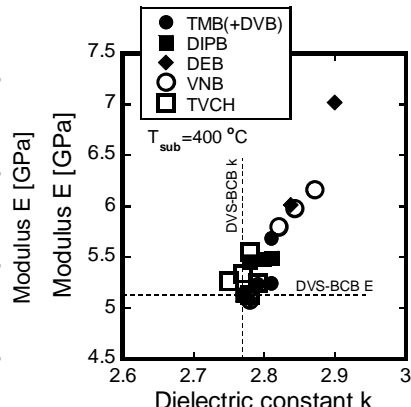

Fig. 8 Relation between dielectric constant k and modulus for copolymer of DVS-BCB with phenyl compounds (closed) and hydrocarbon compounds (open) [5].
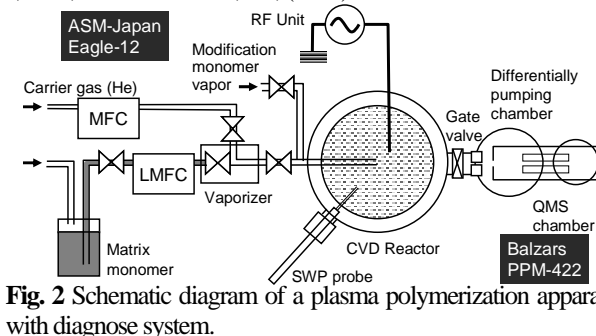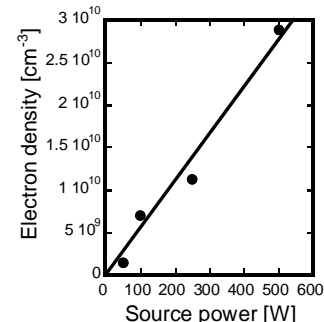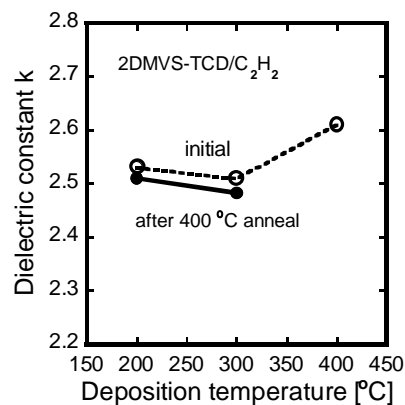

Fig. 9 Effect of deposition temperature on dielectric constant of 2DMVS-TCD/C_2H_2 copolymerized film. Low dielectric constant of 2.48 was achieved [5].