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Chemical Structural Control of Plasma-Polymerized, Divinylsiloxane Benzocyclobutene Films for sub 100nm-node ULSI devices

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1. Introduction

Increase in ULSI device operation speed requires introduction of low dielectric constant (low-k) materials into Cu interconnects. Recently, we have been developing a new plasma polymerization method, in which the organic monomer molecules are vaporized to carry into RF-plasma as shown in Fig. 1 [1-3]. By using liquid divinylsiloxane benzocyclobutene (DVS-BCB) monomers, low-k, plasma-polymerized BCB films (p-BCB) has been obtained with high thermal stability (>400°C).

In this paper, we investigate the effects of the deposition condition on the p-BCB film properties such as the dielectric constant, the chemical composition and the mechanical strength.

2. Experimental

The DVS-BCB monomers were vaporized at 210°C with He carrier gas, and were carried into a vacuum chamber with a wafer heated at 425°C. The RF-power was changed from 50W to 500W. The dielectric constant of p-BCB film was measured by Hg-probe method. The chemical compositions were characterized by the two factors followed;

- (1) [Average atomic mass]
= $(1.01n_H + 12.01n_C + 16.00n_O + 28.09n_{Si}) / (n_H + n_C + n_O + n_{Si})$
- (2) [H concentration] = $n_H / (n_H + n_C + n_O + n_{Si}) \times 100$

where n_H is a relative number of H-atoms, n_C of C-atoms, n_O of O-atoms, and n_{Si} of Si-atoms, which were estimated by Hydrogen Forward Scattering (HFS) and Rutherford Back Scattering (RBS) methods. The film density was investigated by Grazing Incidence of X-ray Refraction (GIXR). The mechanical strength of 1 μ m-thick films was investigated by nanoindentation method.

3. Results

3-1. Deposition Rates

Fig.2 shows the deposition rate as a function of the RF-power with the monomer flow rates (MFR) from 0.08g/min to 0.125g/min. The deposition pressure and He-carrier gas flow rate were fixed at 4.0 Torr and 500sccm, respectively. The deposition rates were increased linearly with increasing the RF-power, and then were saturated over 300W. Levels of the deposition rate saturated were increased with the increment of monomer flow rate.

3-2. Dielectric Constants

Fig. 3 shows the relation between the dielectric constants and the deposition rates in the case of MFR=0.08g/min at 4.0 Torr. The dielectric constant of p-BCB film was decreased linearly with decreasing the deposition rate, or essentially lowering the RF-power. The dielectric constant did not have clear relation with the film density (Fig. 4), but was proportional to the average atomic mass, which was determined by the H concentration in the p-BCB film (Fig. 5). When the H concentration in p-BCB was greater than that

in spin-on BCB (s-BCB) film, the dielectric constants were smaller than that of s-BCB ($k=2.7$).

3-3. Mechanical Strength

The modulus of p-BCB decreased when the dielectric constant was smaller than $k=2.6$, but all moduli were much larger than that of s-BCB of 2.90GPa (Fig. 6). The hardness slightly decreased with decreasing the dielectric constant of p-BCB. The low-k, p-BCB film is applicable to replacing high-k, SiCN films of etch-stopper and hard masks for brittle porous low-k films needed in 65nm-node ULSIs [4] (Fig. 7).

4. Discussion

Fig. 8 shows FTIR spectra of the p-BCB films with $k=2.53$, 2.60, and 2.80 and that of s-BCB as a reference. Comparing the p-BCB film with s-BCB, the peaks of tetrahydronaphthalene (THN) rings (1498cm^{-1}) and Si-CH₃ bonds (1256cm^{-1} , 795cm^{-1}) were decreased, while the peak of Si-H appeared. In the He-plasma, the THN ring opening and the H-atom termination occur (reaction-I), and Si-CH₃ bonds are replaced by Si-H bond with releasing $\cdot\text{CH}_2$ radicals (reaction-II). By the reaction-I, the H concentration in the p-BCB increases and the average atomic mass decreases, while the H concentration decreases by the reaction-II.

In the case of low RF-power (<200W), the polymerization reaction among the four member rings and the C=C bonds as well as a part of the THN ring opening occur simultaneously, increasing the H concentration in the p-BCB films and decreasing the dielectric constant to $k=2.53$ (Fig. 10(a)). In the case of high RF-powers (>200W), the dissociation reaction-II is enhanced to replace steric hindrance -CH₃ bonds containing three H atoms with a small H atom, decreasing H concentration in the p-BCB film and pushing up the dielectric constant (Fig. 10(b)). Grazing Incidence of Small Angle X-ray Scattering (GISAXS) indicates that the p-BCB film with $k=2.80$ by high RF-power applied has 6nm ϕ nanopores, which might be clusters of skeletons of -CH₃ released.

5. Conclusion

In the plasma-polymerization method, H-content in the p-BCB film, or essentially the dielectric constant, is controlled by the RF-power applied. The low-k p-BCB film is applicable to the mechanical supporting layers such as the etch-stopper and the hard masks for brittle porous low-k films needed in 65nm-node ULSIs.

Acknowledgement

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References

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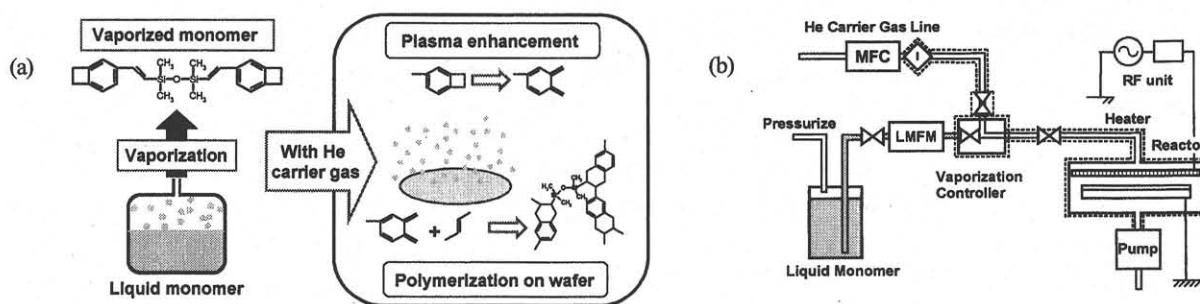


Fig.1 Schematic illustrations of (a) the plasma polymerization process, and (b) the deposition system, and the apparatus for the low-k organic deposition such as DVS-BCB.

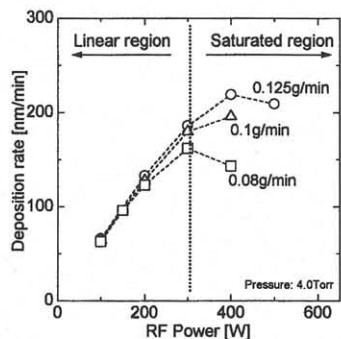


Fig.2 Deposition rate of p-BCB film as a function of RF-plasma power with different monomer supply rates.

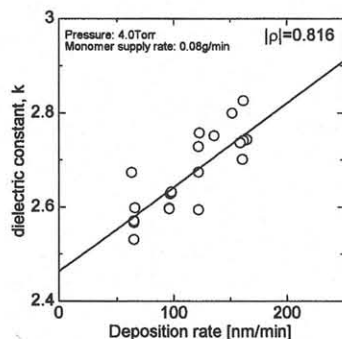


Fig.3 Relation between the dielectric constant of p-BCB and the deposition rate.

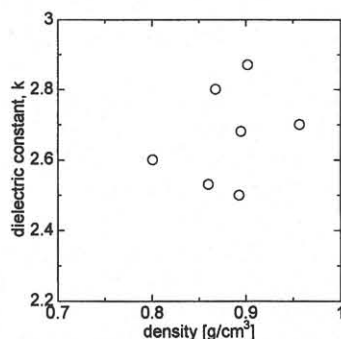


Fig.4 Relation between the dielectric constant of p-BCB and the film density.

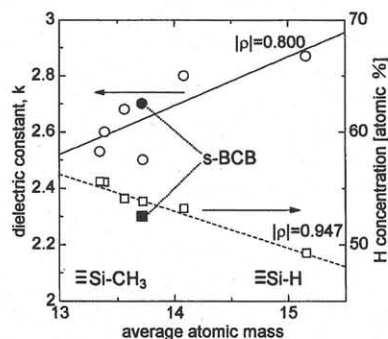


Fig.5 Dielectric constant and H concentration in the p-BCB as a function of the average atomic mass.

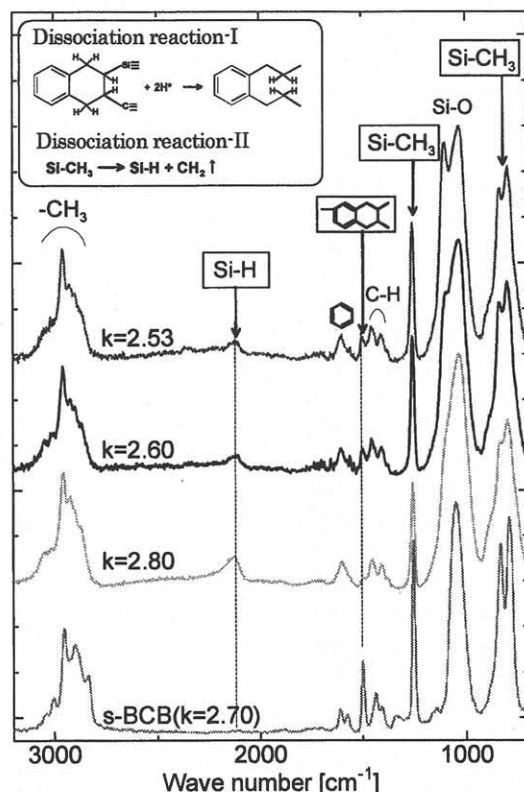


Fig. 8 FTIR spectra of the p-BCB films with k=2.53, 2.60, and 2.80 and of spin-on BCB (s-BCB) with k=2.70.

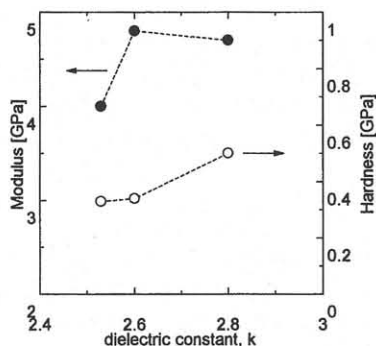


Fig. 6 The modulus and the hardness of p-BCB as a function of the dielectric constant.

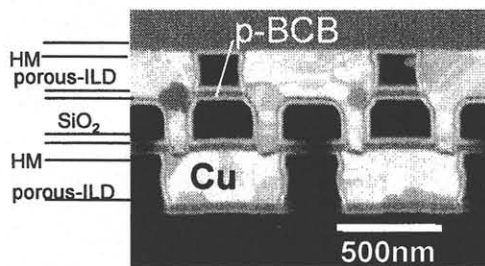


Fig. 7 Cu-DDIs in porous organosilica film with the etch-stop layer of p-BCB film replaced from high-k SiCN film [4].

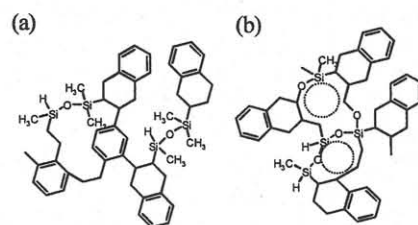


Fig. 9 Schematic structure model of the p-BCB films; (a) low RF power, and (b) high RF power.