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Current Status and Future Prospects of Low Dielectric Constant Materials for ULSI Applications

Kazuhiko Endo
Silicon Systems Research Laboratories, NEC Corporation
1120 Shimokuzawa, Sagamihara, Kanagawa 229-1198, Japan
e-mail: k-endo@cb.jp.nec.com

The shrinking design rule of ULSI circuits has recently led to an increase in the interconnection delay caused by parasitic capacitance so much that it has become more of a problem than the gate delay in transistors. Low-dielectric-constant (low-k) materials have been studied intensively as a possible way of reducing it. This paper discusses recent developments and the future prospects of low-k dielectrics.

1. Introduction

Multilevel interconnection technology is a key technology for the production of high-performance ultra-large-scale-integration (ULSI) circuits. The shrinking design rule of ULSI circuits has recently increased the interconnection delay caused by parasitic capacitance so much that this delay has become more of a problem than the gate delay of transistors, as Fig. 1 shows.[1,2] We must reduce the dielectric constant of the inter-metal dielectrics (IMD) as well as the resistance of the wiring metals to reduce this delay. For this reason, a great deal of effort has been exerted developing low-dielectric-constant (low-k) materials and Cu interconnects.[3] This paper discusses recent developments and future prospects of low-k dielectrics.

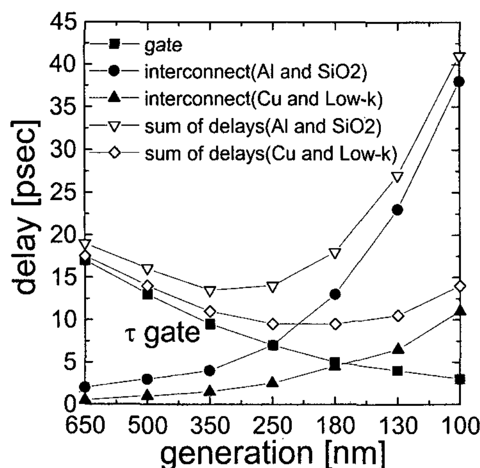

Fig. 1. Delay time of ULSI devices as function of technology generation, assuming SiO_2 (k = 4.0) and low-k (k = 2.0).

2. Low-k films

Silicon dioxide (SiO_2) films formed below 450°C have been used for the IMDs,[4] and the relative dielectric constant of the SiO_2 film deposited by a plasma enhanced chemical vapor deposition (PE-CVD) technique with tetraethoxysilane (TEOS) and O_2 gas system is more than 4.3.[5] Since the early 90's, a great amount of effort has been focused on the development of low-k dielectrics to reduce the dielectric constant of IMDs below 4. Most low-k dielectrics are categorized into several groups. The modification of conventional SiO_2 by introducing low-k components is one of the major challenges we currently have. Fluorine, hydrogen, and organic polymer are incorporated into the film, and fluorine-doped silica (FSG) and methyl silsesquioxiane (MSQ) films are among the promising candidates. On the other hand, polymers typically have a lower dielectric constant than inorganic materials and thus thermally stable polymer is the other group of low-k films.

2.2 FSG Films

Fluorine-doped silicon oxide, or fluorosilicate glass (FSG), were developed in the early 90's for low dielectric constant IMDs. Several reports indicate that the dielectric constant of silicon oxide films can be reduced by increasing the amount of fluorine. The lowest dielectric constant is around 3.0, with fluorine concentrations ranging from 2 to 14 at. %.[6-12]. Plasma enhanced chemical vapor deposition (PE-CVD) and atmospheric chemical vapor deposition (AP-CVD) processes have been extensively investigated.[13-16]

Due to the similarities in deposition process with SiO_2, FSG films can be easily integrated into ULSI production without significant changes in manufacturing. Though a higher fluorine concentration in FSG film can reduce the dielectric constant, the films with fluorine concentrations above 15 at.% are out of scope as they absorb significant amounts of water. Moisture absorption causes not only the degradation of devices and reduces reliability,[17] but also results in higher dielectric constants because of the presence of highly polarizable absorbed water.

Miyajima et al. have pointed out that ion bombardment is one of the key factors for obtaining high resistance to moisture absorption.[18] They used a $TEOS/O_2/CF_4$ gas system for FSG film deposition using PE-CVD, or helicon wave type high-density plasma (HDP) CVD without RF biasing. They suggest that HDP produces ions such as O^+ and O_2^+ with higher ion energy than PE-CVD and that these ions densify the Si-O network, removing carbon and hydrogen from precursors.

Takeishi et al. have reported an N_2O-plasma annealing to stabilize FSG films deposited by using a $TEOS/O_2/C_2F_6$ gas system.[19] They found that N_2O-plasma

annealing at 400°C is effective at blocking moisture absorption. The dielectric constant rarely changes after plasma annealing. Swope et al. have reported the same results for N_2O-plasma annealing.[20] In addition to blocking moisture absorption, they improve the adhesion of highly doped FSG film with subsequent depositions of foreign passivation films such as silicon nitride or silicon oxynitride.

2.3 Organic Silicate

2.3.1 Silsequioxiane

Silsesquioxiane with an empirical formula of ($RSiO_{2/3}$), where R is hydrogen or an organic group, was studied for low-k spin on dielectrics, as shown in fig. 2.[21] The dielectric constant of methylsilsesquioxiane (MSQ) is 2.7 and aggressive reduction of the dielectric constant is demonstrated. However, some critical problems exist for MSQ integration. Void formation has been reported in MSQ film between the wiring after Cu metallization annealing due to the absorbed fluorine in the MSQ during the etching process.[22] Therefore, the etching process should be improved to overcome this void formation. As MSQ contains many CH_3 groups to reduce the dielectric constant, adhesion to SiO_2 hardmask and SiC (N) dielectric for etch-stop and Cu passivation layer gets worse. Due to mechanical and thermal stress during integration, low adhesion generates many defects during the chemical mechanical polishing process and causes degradation in the yield. Therefore, it is necessary to develop an improved MSQ with high adhesion as well as to optimize the process.

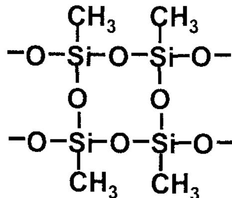

Fig. 2. Schematic formula of MSQ films.

2.3.2 CVD SiOC

Organic incorporated silica is deposited by using PECVD.[23] Organosilane, such as tetramethylsilane (3MS), is typically used as a precursor. Figure 3 shows schematically that the film consists of Si-O and Si-CH_3 bonds, as in the MSQ film. Therefore, the same adhesion problem occurs due to the presence of CH_3 group at the interface. However, plasma grown SiOC is advantageous because plasma decomposes some CH_3 components during deposition to form adhesive components with a chemical bonding. Also, plasma post treatment can decompose CH_3 groups at the surface of the film and improve adhesion.

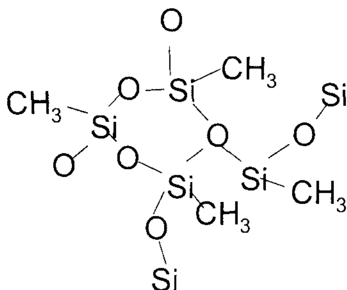
Fig. 3. Schematic formula of CVD SiOC films.

2.4 Polymers

Polymers generally have lower dielectric constants than inorganic materials. However, to apply organic polymers to multilevel interconnects, thermal stability needs to be sufficient at the highest process temperature.

Polytetrafluoroethylene (PTFE) is known to have the lowest dielectric constant, around 1.9. However, PTFE does not have enough thermal stability because of its uncrosslinked C-C structure. Also, as polymer chains are saturated with fluorine atoms, there is little chemical interaction between adjacent chains. Therefore, to improve thermal stability in the organic polymers, it is necessary to make a stiff chemical bond and crosslink the polymer chains with a three-dimensional network.

Aromatic polyimides are one of the polymers that have a rigid crosslinked structure, as shown in fig. 4. However, the dielectric constant of aromatic polyimide is much higher than PTFE, showing around 3.2, due to the crosslinked structure.[24] Therefore, to use as low-k IMDs it is necessary to balance the rigid structure and low dielectric constant. Fluorinated polyimide is one of the candidates for decreasing the dielectric constant of polyimide.[25] Furthermore, plasma enhanced CVD in amorphous carbon film to make crosslinked fluorinated polymer is being intensively investigated with dielectric constants ranging from 2.1 to 2.7.[26] As fluorine terminates the crosslinked structure, it is important to balance fluorine concentration to make low-k fluorinated carbon films. Polyarylether (PAE), as shown in fig. 5, also offers a balance of dielectric constant and thermal stability due to having less rigid ether bonding than in polyimide.[27]

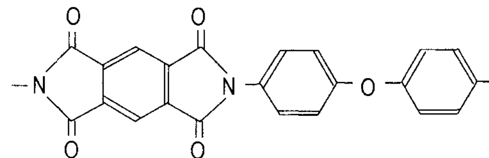
Fig. 4. Structural formula of polyimide.

Organic polymer has advantages in the integration of dual damascene structure with Cu. A dual damascene structure was formed without resist poisoning by using a two-layer hard mask. Consequently, a good via yield was obtained.[28] However, due to the higher thermal expansion coefficient, voids were formed at the bottom of the via after the cyclic thermal process for multi-layer wiring formation at 400°C.[29] As a result, an increase in via resistance and degradation of the via chain yield were observed as the number of thermal cycles increased. Therefore, adjustment of the thermal expansion coefficient is the next major challenge for polymer IMDs.

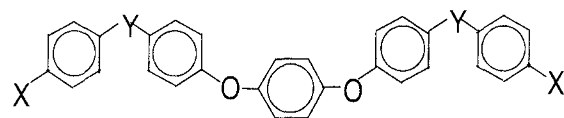
Fig. 5. Structural formula of arylether.

2.5 Porous material

Lowering the dielectric constant of IMDs by decreasing the density of the dielectric can be achieved by introducing pores in the dielectric. It is believed that a porous material is necessary to achieve an ultra low-k dielectric (k<2.0). Efforts in developing porous dielectrics have focused on sol-gel based spin on silica,[30] porous polymers,[31] and porous silsesquioxiane films.[32] The effect of porosity on the dielectric constant can be estimated using Bruggeman's effective medium approximation with the results indicating that the dielectric constant scales linearly with porosity.[33] However, other properties, such as mechanical properties, also scale with porosity, as indicated in fig. 6.[34] This provides further challenges in the integration of porous materials. These materials also pose other problems. The pore size must be much smaller than both the film thickness and minimum device feature size. It is also desirable that porosity should be in the form of closed pores in order to prevent absorption and diffusion of contaminants.

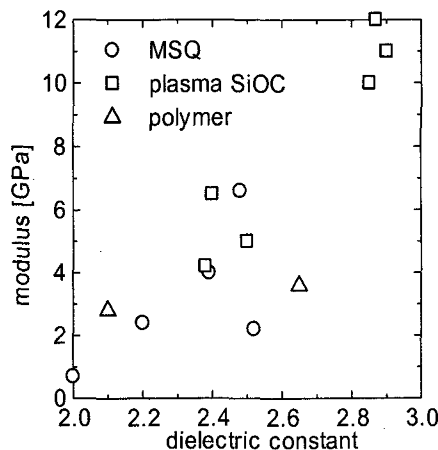

Fig. 6. Mechanical properties of typical low-k dielectrics as a function of the dielectric constant.

3 Theoretical understanding of dielectric constant

Dielectric constant is a function of polarization raised in the dielectric when an electric field is applied. Therefore, the mechanism for reduced dielectric constant can be considered as a change of polarization that is classified into orientation polarization, ionic polarization, and electronic polarization.[35] Thus, when we discuss the reduction mechanism, it is necessary to separate polarization into its various components. Some studies have reported the mechanism of reduced dielectric constant of SiO_2 films by fluorination. Y. Nakasaki et al. reported that replacing Si-O in the SiO_2 matrix with Si-F reduced electronic polarization.[36, 37] S. Lim et al. reported that each polarization could be separated by calculating the electronic polarization from the refractive index and ionic polarization by using Kramers-Kronig transformation of infrared absorption index.[38,39] They attributed the reduction of the dielectric constant to the reduction of the orientation polarization generated by the Si-OH component in the SiO_2 matrix.

We can use a C-V measurement to measure the overall dielectric constant due to the orientation, ionic, and electronic polarizations. The dielectric constant ε_r, due to electronic polarization, can be calculated from the refractive index n by using Eq. (1). The dielectric constant due to ionic polarization can be determined by calculating the refractive index n by using the Kramers-Kronig transformation as described in Eq. (2) and by using Eq. (3). In these equations, n_i is the refractive index at wave number $\nu=\nu_i$, n_∞ is the refractive index at $\nu=\nu_\infty$, k is the absorption index, and *P* means that the principal value of the integral must be taken since there is a singularity at $\nu=\nu_i$.

$$\varepsilon_r = n^2 \qquad (1)$$

$$n_i = n_\infty + \frac{2}{\pi} P \int_0^\infty \frac{\nu k(\nu)}{\nu^2 - \nu_i^2} d\nu \qquad (2)$$

$$\varepsilon_r = n^2 - k^2 \qquad (3)$$

Figure 7 shows the electronic and ionic polarization of some low-k materials. The ionic polarization of SiO_2 is the highest because of the ionic nature of the Si-O bond due to the difference in electron negativity. By introducing an organic component we can observe the reduction in the ionic component because of the substitution of Si-O for the $Si\text{-}CH_3$ bond. To further decrease the dielectric constant, introducing pores in the dielectric decreases both electronic and ionic polarization effectively. On the other hand, the dielectric behavior of low-k polymers is completely different from SiO_2 based materials with the dielectric constant mostly consisting of electronic polarization. This can be explained by the covalent bonding nature of polymer.

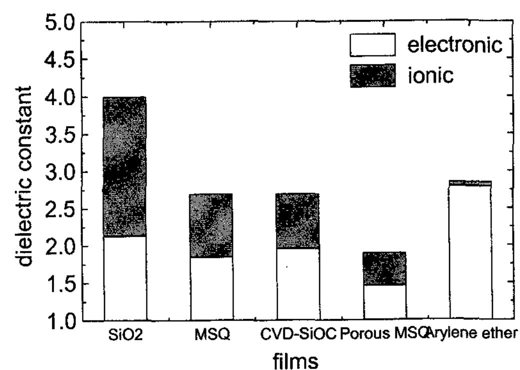

Fig. 7. Contribution of electronic and ionic polarization to dielectric constant.

4 Barrier low-k films

Because of the increasing difficulty in introducing a low-k dielectric with much lower dielectric constant, it is becoming increasingly important to reduce the dielectric constant of not only the inter-metal layer but also the etch-stop and Cu passivation layer as shown in fig. 8 to reduce the effective dielectric constant. Previous reports show the reduction of an effective dielectric constant by introducing an organic component in the film and replacing SiN (k=7) to a series of SiC materials with a dielectric

constant of around 5.[40] However, the way to further reduce the dielectric constant of the etch-stop/passivation layer is still under discussion. As the passivation dielectric is placed directly onto the Cu, it is important to ensure adhesion characteristics to obtain high resistance against electro-migration (EM) and time-dependent dielectric breakdown (TDDB) of the interconnects.[41, 42, 43] The organic component such as CH_3 group in the film terminates the chemical bond at the interface and decreases adhesion energy. It is thus very important to reduce the dielectric constant of the passivation layer without increasing CH_3 group in the film.

The recent study has demonstrated the reduction of the effective dielectric constant by introducing a new low-k barrier dielectric using trimethlvinylsilane (TMVS) without increasing the CH_3 group in the film. This is done instead of using conventional trimethylsilane (3MS).[44] This can be explained as due to the vinyl group in the film with only CH and CH_2 groups that helps to increase the adhesion on the substrate. 5% reduction of parasitic capacitance was observed. Furthermore, tolerance against electromigration (EM) and the time dependent dielectric breakdown (TDDB) is the highest amongst the interconnects with new barrier films from TMVS. The new dielectrics are thus candidates for reducing the effective dielectric constant without major changes to fabrication

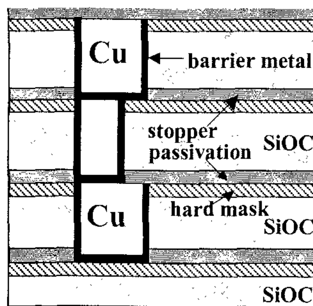

Fig. 8. Schematic cross-section of Cu interconnects

4 Conclusions

From the early 90's many low-k dielectrics have been investigated intensively and films with dielectric constants around 3 have been widely used in production. However, it is becoming more and more difficult to integrate low-k films with much lower dielectric constants due to the weak mechanical characteristics. Further improvements in film characteristic and in fabrication processes are required. Other approaches to decreasing the effective dielectric constant of interconnects are thus very important. Consequently, new low-k etch-stop and passivation dielectrics were successfully demonstrated using TMVS as a new precursor.

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