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# Molecular design of ultralow-*k* insulator materials[*]

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Dielectric materials with low permittivity (low *k*) are required for insulation to reduce the interconnect *RC*-delay in deep submicron integrated circuits. Combinations of classical and quantum-theoretical approaches for the assessment of the dielectric properties of fullerene-based materials with the goal to find ultralow-*k* dielectrics with suitable mechanical properties were used. We study the covalent linking of $C_{60}$ molecules and vary the length and chemical composition of the linker molecule as well as the linkage geometry. The (static) electric permittivities, *k*, and elastic bulk moduli, *B*, of the proposed materials are in the range of 1.7–2.2 and 5–23 GPa, respectively.

Key words: *ultralow-k dielectrics; interlayer dielectrics; molecular design; dielectric properties; mechanical properties; fullerene-based dielectrics; microelectronics*

## 1. Introduction

The continuous shrinking of device dimensions of ultra-large-scale integrated (ULSI) chips imposes strong demands on the backend of the line (BEoL) interconnect structures [1]. The higher wire resistance of smaller metal lines and the crosstalk between closely spaced metal increase the interconnect *RC* delay, crosstalk noise, and power dissipation of the interconnect structure. It has fuelled a frantic search for new insulator materials [2, 3]. In order to decrease the first term of the *RC* product, the traditionally used in interconnects Al, with a resistivity of 2.7 μΩ·cm, was replaced by Cu, whose resistivity is 1.8 μΩ·cm [4]. The electric permittivity of $SiO_2$ also cannot sufficiently prevent cross talk between closely spaced copper wires in the semiconductor devices [5]. Using dielectric materials with smaller permittivity values, referred to as low-*k* dielectrics, in turn, can reduce the value of *C*. A great deal of intensive research has been conducted in this area. The candidate materials include non-fluorinated polymers [6], inorganic-organic hybrids [7, 8], porous polymers [9], and silica [10, 3].

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The first generation of low-*k* dielectrics had a *k* value lower than that of $SiO_2$ ($k = 4.2$). Such materials included fluorinated $SiO_2$ (referred to as fluorosilicated glass, FSG), and hydrogen silsesquioxanes (HSQ). The first generation of low-*k* dielectrics has been successfully implemented in the manufacturing of integrated circuits (IC) with dimensions down to 0.25 μm. The second generation of low-*k* dielectrics mostly includes organic polymers [4].

In order to achieve low electric permittivity, it is necessary to reduce, for example, the material density. This means these dielectric materials will need to be produced in a porous form [11]. However, depending on the structural details, porosity can also adversely affect other properties crucial to chip performance, such as mechanical strength [12], electrical properties, and Cu diffusion into the insulator [5].

The primary consideration in selecting an interlayer dielectric material (ILD) for IC applications is the electric permittivity, *k*. But the *k* values need to be further reduced to 2.0 for the 45 nm technology node or bellow in the next few years [5, 13]. Although many materials have been studied, nowadays there is no material available with ultralow electric permittivity and sufficient mechanical properties.

Here we study a structure model for new ultralow-*k* materials proposed recently [14]. This model is generated as an ordered three-dimensional (3D) network consisting of two components: Fullerenes as nodes and bridge molecules as edges connecting the nodes. In the present study, simple cubic (sc) and diamond-like arrangements of fullerenes are considered where the fullerenes are connected by hydrocarbons and Teflon-like bridge molecules. The calculation of electronic and mechanical properties is rather complex, and, therefore, the theoretical tools used range from classical approaches to *ab-initio* quantum-mechanical methods.

## 2. Computational methods and model

### 2.1. Computational methods

We use molecular mechanics and density-functional based quantum chemical methods [15, 16] for structure optimization of the structural units and for calculation mechanical and dielectric properties. Considered structures were constructed by molecular mechanics as periodic arrangements of fullerenes and bridge molecules. For the construction the HyperChem 7.51 [16] program packet was used. The structures within the unit cell and the lattice parameters were optimized using either the conjugated gradient or the steepest descent method at the density functional tight binding (DFTB) level [17, 18]. Periodic boundary conditions were imposed on the polymers. The DFTB method is the density-functional based tight-binding method as described in [17]. This method is suitable for theoretical analyses of carbon-based clusters [19] and has been successfully applied to several problems of surfaces and interfaces of carbon structures [20].

### 2.2. Molecular design

We have developed the next model for investigations of the properties of dielectric materials. We consider spherical molecules and connect them by bridge molecules forming an ordered 3D network. Our model is based on the well-known $C_{60}$ fullerene molecules which are used as spherical molecules. Pure fullerene molecule can also be modified, for example, by decorating with different number of fluorine atoms to change its electronic properties [21]. The detailed researches of influence of the fluorine atoms on the electronic properties of $C_{60}$ molecules are presented in [21]. The bridge molecules are realized by hydrocarbon chains $C_nH_{2n}$ and Teflon-like structures ($C_nF_{2n}$). The distance between $C_{60}$ molecules can be modified by using bridge molecules with various lengths covalently bound to the fullerenes. Fullerenes connected by bridge molecules are used as structural units for the construction of the 3D network.

Introduction of bridge molecules with various lengths between neighbouring $C_{60}$ molecules reduces the density of the material. It can be also considered as incorporation of pores with mono-disperse pore size distribution on the scale of 1 nm.

Pure $C_{60}$ fullerenes deposited on a substrate arrange in a face centred cubic (fcc) lattice. The lattice can be theoretically expanded. Bridging next-nearest fullerene neighbours by chain molecules one obtains a possible realization of 3D networks of connected fullerenes. In the fcc lattice, each fullerene molecule has 12 next-nearest neighbours. Other networks may be generated, for example, according to the sc lattice, where each fullerene molecule has 6 next-nearest neighbours, or the diamond lattice, where each $C_{60}$ molecule has 4 next-nearest neighbours. An example of the 3D network of the fullerene with the diamond like symmetry is shown in Fig. 1.

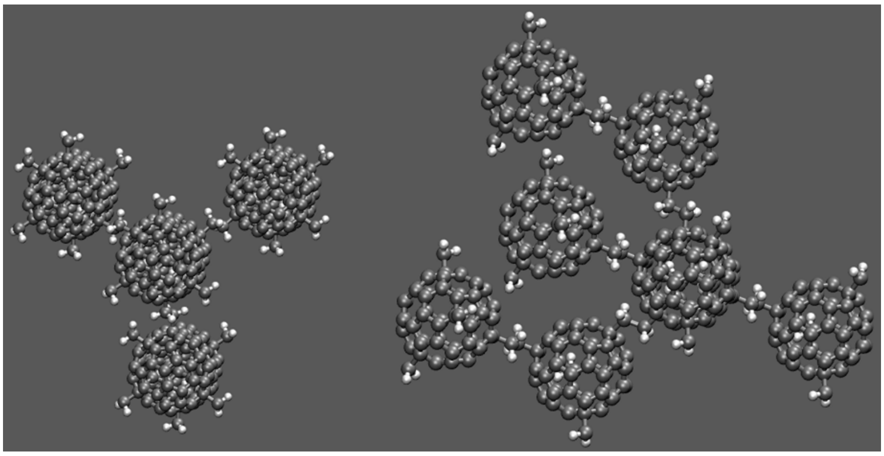

Fig. 1. Arrangement of $C_{60}$ fullerenes into an ordered 3D network
with a diamond like symmetry interconnected by hydrocarbon molecules $C_2H_4$

Fullerene chemistry has shown that it is possible to attach fullerene to existing polymers by covalent bonds [22, 23]. One of the possible reactions results in $C_{60}$

fullerene decorated with four $CH_3$ groups. By combining fourfold decorated fullerenes it should be possible to generate a diamond like lattice, where the lattice sites occupied by fullerenes and the bonds between them are arranged tetrahedrally by $C_nH_{2n}$ or by other chemical groups. This is the experimental background of the present model which consists of fullerenes situated at the sites of a lattice and of bridge molecules connecting next-nearest fullerene neighbours.

Expansion of the fullerene lattice as described would lead to reduction of the density and to the formation of a nanoporous material. The pore size would be of the order of the length of the bridge molecules. Varying the length of the bridge molecules, its chemical realization and the topology of the 3D network (sc, fcc, and diamond like symmetry), the properties of the material can be modified and various process requirements adopted. Such materials can be classified as hybrid materials tailoring the properties of $C_{60}$ together with the properties of polymeric linker molecules.

## 3. Results and discussion

### 3.1. Dielectric properties

The static electric permittivity of materials is an important issue for microelectronics. The calculation of this parameter for a solid material is a non-trivial task. The electric permittivity, $k$, depends on the polarizability of materials under the influence of an external electric field. The electronic, ionic, and dipolar components of the polarizability contribute to the electric permittivity of dielectric materials. Reduction of the polarizability lowers the electric permittivity. One of the ways to reduce the polarizability is to introduce hydrogen, carbon and fluorine atoms in dielectric materials [24].

Defining a structural unit, the polarizability of this unit and its response to the electric field at the position of this unit must be considered. Unfortunately, the strength of the local field acting on the polarizable unit can differ considerably from that of the applied external field. This is one of the main problems: a given structural unit in the material is not polarized by the mean of an internal electric field but by the macroscopic one present at the structural unit (local field corrections). Therefore, it is important not only to count the local polarizabilities but also to consider the influence of the environment of a local dipole. A recent review of methods for the calculation of the polarizability of atoms, molecules and clusters is given in [25]. The treatment of extended systems has been re-formulated in the past decade with the result that the information about the polarization is not in the electronic density but in the phases of the wave functions [26–28]. A simple approach to describe the complex interplay of external field, local field and polarizability of a local unit is the Clausius–Mossotti model (see [29]). The Clausius–Mosotti model is a continuum theoretical approach to the interaction of a molecule and a polarizable environment [30].

In a recent theoretical paper [31], this approach was applied to calculate the electric permittivity of low-*k* materials consisting of chemical groups such as Si–H, Si–$CH_3$, Si–O, where the polarizability of the groups was calculated using the density functional theory (DFT). Chemical bonds of this type appear as structural components in hydrogen silsesquioxane (HSQ) and methyl silsesquioxane (MSQ) low-*k* materials.

Replacing the neighbouring molecular units by a polarizable continuum with a spherical cavity where the unit under consideration is situated, the Clausius–Mossotti model applies [29, 30, 32–37]:

$$k=\frac{1+2c\alpha}{1-c\alpha},\qquad c=\frac{4\pi}{3}\frac{N}{V},$$

where $N/V$ is the number density of molecular units and $\alpha$ is the molecular polarizability.

The quantity $N/V$ is a geometrical parameter determined from the structures. The molecular polarizability can be calculated by means of several methods [38].

According to the model presented here, the electric permittivity of the fullerene solid is supposed to be reduced by creating cross-linkage between the fullerene monomers, increasing the $C_{60}$–$C_{60}$ distance and, consequently, by decreasing the number of dipoles per the unit volume. Choosing the sc lattice as a skeleton for the fullerene network, the density for $n = 4$ takes the value $\rho = 0.621$ g/cm$^3$. It leads to the value of electric permittivity $k = 1.7$. The diamond lattice is even more efficient with respect to the reduction of the *k* value. In this case, *k* values below 1.5 are possible for $n > 4$. The results of calculation of *k* for the structures with diamond like symmetry with different *n* are shown in the Table 1.

Table 1. Lattice constant $a$, mass density $\rho$, and electric permittivity $k$ for fullerene networks with $C_nH_{2n}$ bridge molecules

| $n$ | Sc like | | | Diamond like | | |
|---|---|---|---|---|---|---|
| | $a$ [nm] | $\rho$ [g/cm$^3$] | $k$ | $a$ [nm] | $\rho$ [g/cm$^3$] | $k$ |
| 2 | 1.14 | 0.905 | 2.18 | 2.60 | 0.586 | 1.68 |
| 4 | 1.33 | 0.620 | 1.72 | 3.08 | 0.378 | 1.41 |

### 3.2. Mechanical properties

The bulk modulus *B* was calculated for fullerene 3D networks described above with sc and diamond symmetry. To calculate the mechanical properties, three-dimensional periodic boundary conditions were applied to the 3D network of interconnected $C_{60}$. The lattice parameters are the results of the DFTB structure optimization procedure. The bulk modulus *B* was determined from the relation $B = V_0(\partial^2E/\partial V^2)$, where *E* is the DFTB energy per unit cell at hydrostatic strain of the elementary cell. Volume $V_0$ applies for the strain-free state. All atoms have been fully relaxed for given cell parameters and the moduli were obtained for the equilibrium structures by a polynomial fitting method.

Firstly we consider the sc symmetry. The lattice constants of the sc model structures with $C_nH_{2n}$ as bridge molecules increase monotonously with increasing length $n$ of the hydrocarbon molecules (Table 1). For $n = 2$ and 4, the lattice constant takes the value of 1.136 nm and 1.335 nm, respectively. The corresponding electric permittivities are $k = 2.2$ ($n = 2$) and 1.8 ($n = 4$). The structures with $n = 2$ show robust and stable behaviour ($B = 5.0$ GPa), while for $n = 4$ fluctuations of energy appear, pointing to possible instabilities ($B = 0.4$ GPa). This means that increasing length of hydrocarbon bridge molecules decreases $k$-values but also deteriorates mechanical properties. Nevertheless, the sc model with $C_2H_4$ bridge molecules shows already a very good combination of dielectric and mechanical properties.

Fluorination of materials is one of possible ways to reduce the electric permittivity $k$. In order to obtain low-$k$ materials many new fluorine containing polymers such as fluorinated silicate glass [39, 40], fluoromethylene cyanate ester, fluoroaromatic triallyl ether copolymer [41], etc., were developed and researched in the last few years. The C–F bond is the bond with one of the lowest polarizabilities. That is why the fluorination is one of the promising methods to improve the dielectric properties of the materials. We replaced in the previous model with $n = 2$ the hydrogen atoms of the bridge molecules by fluorine. The results for the series $C_{60}(CH_2)_6$, $C_{60}(CF_2)_2(CH_2)_4$ and $C_{60}(CF_2)_6$ are collected in Table 2. The $k$-value is slightly reduced (5%) and the bulk modulus is enhanced by about 20% compared to the data for the $C_2H_4$ sc model. Therefore, we conclude that the transition from hydrocarbon to Teflon-like bridge molecules in the sc basic structure improves gradually the properties of the hypothetical low-$k$ dielectric material.

Table 2. Properties of sc structures with $C_2X_4$ bridge molecules, X = H, (H, F), F

| Molecule | $C_{60}(CH_2)_6$ | $C_{60}(CF_2)_2(CH_2)_4$ | $C_{60}(CF_2)_6$ |
|---|---|---|---|
| Lattice constant, $a$ [nm] | 1.14 | 1.15 | 1.16 |
| Mass density, $\rho$ [g/cm$^3$] | 0.906 | 0.967 | 1.087 |
| Electric permittivity, $k$ | 2.18 | 2.16 | 2.11 |
| Bulk modulus $B$ (GPa) | 5.0 | 5.1 | 6.1 |

The results of the structure optimization of the models with fullerenes situated at the lattice sites of a diamond like elementary cell and hydrocarbon bridge molecules $C_nH_{2n}$ are given in Table 1. As expected, the lattice constant increases with growing length $n$, of the hydrocarbon molecule which results in a reduced mass density. Accordingly, the electric permittivity scales down and reaches extremely low values of $k < 1.5$ for $n \geq 4$.

Regarding the mechanical properties of the diamond-like network, we expect improved results as compared to the sc model with equal bridge molecules because of the different topology. Indeed, the simulated hydrostatic deformation of the $C_{60}(CH_2)_4$ model (equilibrium lattice constant 2.602 nm) and the fitting of the energy values by a parabola gives the value of 23 GPa. The statistical error due to deviations of the data from the ideal parabolic shape is of the order of 30%. The electric permittivity *k* is 1.7. These results suggest that diamond like $C_{60}$-based networks are excellent candidates for future ultralow-*k* dielectric materials.

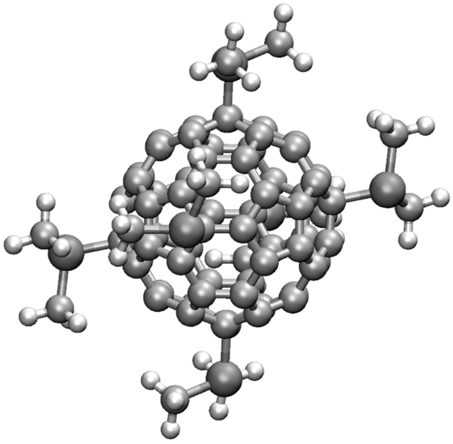

Fig. 2. Atomic structure of a $C_{60}(SiC_2H_6)_6$ unit optimized for periodic boundary conditions. Large spheres represent Si atoms, middle size – carbon atoms, and small ones are hydrogen atoms

Further improvements could include the use of Teflon-like or even other bridge molecules. Figure 2 shows an example of the fullerene network with methylsilane like bridge molecules, as an example of the further theoretical investigation. Another structures with Si-containing bridge molecules was presented in [42].

## 4. Conclusion

Molecular design was applied to generate models for new insulating materials with extremely low electric permittivities and good mechanical properties. The models are mosaic structures with fullerenes at the nodes and bridge molecules along the edges of the mosaic cells. The interior of a mosaic cell represents a pore on the 1 nm scale. Promising candidates based on sc and diamond-like lattices and hydrocarbon or Teflon-like bridge molecules were generated. The search for model structures with low electric permittivity *k* and sufficient elastic bulk modulus *B* started with the sc structure and $C_2H_4$ bridge molecules. The strategy of improving the properties by structural modification included three options: (i) change of the bridge molecules from $C_2H_4$ to $C_nH_{2n}$, $n > 2$, for sc fullerene arrangement with variable lattice constant; (ii) replacement of hydrogen by fluorine in the bridge molecules $C_2X_4$, X = H, F for the sc structure; (iii) transition from sc to diamond-like arrangement of fullerenes with $C_nH_{2n}$ bridge molecules.

At the moment, property combinations with electric permittivity of $k = 1.7$ and elastic bulk modulus of about 20 GPa are achieved. Strategies for further improvement of the materials are discussed.

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