physica status solidi a

phys. stat. sol. (a) **203**, No. 15, 3868–3872 (2006) / **DOI** 10.1002/pssa.200622312

Molecular design of fullerene-based ultralow-*k* dielectrics

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Received 29 June 2006, revised 1 September 2006, accepted 5 September 2006
Published online 20 October 2006

PACS 62.20.Dc, 68.60.Bs, 73.40.Rw, 77.22.Ch, 77.55.+f, 81.05.Tp

This paper presents results of a theoretical study of hypothetical insulating layers for semi-conducting circuits. The dielectric material consists of C_{60} fullerenes interconnected by bridge molecules. The structural optimisation is carried out using quantum-chemical methods. The predicted materials have ultralow values of the static dielectric constant of about $k = 1.5$ and good elastic bulk moduli of $B = 12$ to 17 GPa. These values meet the demands of future microelectronic devices.

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1 Introduction

Continuous miniaturisation of the device dimensions in semi-conducting circuits has led to improved performance due to increased clock rate and enhanced number of functions per unit area. This development is expressed in the International Technology Roadmap for Semiconductors [1]. Currently, the interconnect delay time and the power dissipation of semiconducting circuits both determined by the geometrical dimensions of the metallic wiring, the metal resistivity, and the dielectric constant of the insulating layers, appear as limiting factors of further improvements [2]. The delay time and the power dissipation can be diminished by introducing insulating materials with reduced dielectric constant, k. The k-value of the traditional interlayer dielectric silicon oxide is about $k = 4$, and solutions for $k = 2.7$ to 3.0 are known, but the production of high-performance circuits will require dielectrics with k-values below 2 in near future [1, 3–5]. Here we predict a new class of interlayer dielectrics using quantum-theoretical methods. The proposed materials are composed of fullerenes interconnected by bridge molecules and have dielectric constants of $k = 1.5$.

There are two ways to reduce the k-value of a material: Minimisation of the dipole polarisability using compounds with molecular units of lower molar refractivity than, e.g., the SiO_2 unit, and reduction of the number of dipoles per unit volume by introducing porosity into the material. Following these ideas several silicon-based and non-silicon-based low-k dielectrics have been explored during the past decade [2–4]. Currently, dielectric materials such as chemical vapor deposited carbon containing SiO_x, spin-on polymers, porous silicon oxide, and air gap architectures are under consideration [5]. In a recent paper, new low-k and ultralow-k nanoporous organosilicate dielectrics from blends of polymethylsilsesquioxane precursors with globular ethyl acrylate-terminated polypropylenimine dendrimers have been presented [6]. Besides experimental research and development, molecular design and theoretical prediction of properties of new materials may initiate progress in the field of low- and ultralow-k dielectrics.

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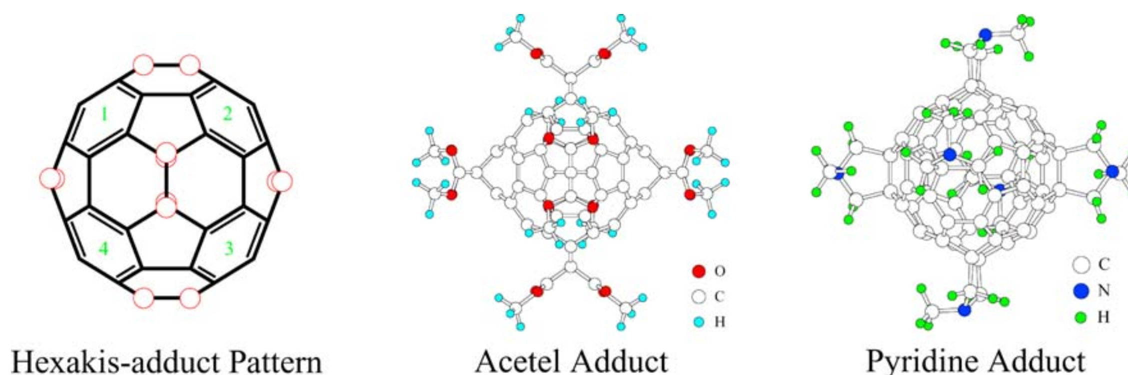

Fig. 1 (online colour at: www.pss-a.com) Hexakis adduct pattern of C_{60} and two examples. The open circles (left pattern) indicate the carbon atoms undergoing covalent bonding with an adduct atom. Numbers (1 to 4) denote hexagons of carbon atoms not bound to an adduct.

2 Model

Inspired by recent progress in fullerene chemistry [7, 8] we consider the following model: C_{60} fullerenes are situated on a regular lattice. Next-nearest C_{60} neighbours are connected by bridge molecules that are covalently bound to the fullerenes. Here we chose six bridge molecules per one fullerene arranged on the C_{60} molecule according to the hexakis-adduct pattern shown in Fig. 1. Structures with two different types of bridge molecules and two different local configurations were constructed by molecular mechanics as periodic arrangements of fullerenes and bridge molecules. The structure within the unit cell and the lattice parameters were optimised using either the conjugate gradient or the steepest decent method at the density functional tight binding (DFTB) level [9]. This method is a simplified DFT scheme, based on the LCAO (Linear Combination of Atomic Orbitals) representation of the Kohn–Sham (KS) wave functions. The two-center Hamiltonian matrix elements are considered. (For review of the method see, e.g., [10].) The weak interactions in the systems were considered with a recently developed extension of the DFTB method for the treatment of the dispersion interactions [11]. Periodic boundary conditions were imposed. All structure relaxations involved were performed at the energy gradient level of less than 10^{-6}. The accuracy and reliability of the method is illustrated by the results for the optimised C_{60} molecule: The DFTB (experimental [12]) result for the C=C bond length is 1.3971 Å (1.3909 Å), for C–C it is 1.4478 Å (1.4527 Å), and for the C_{60} diameter 7.0849 Å (7.0893 Å) was obtained.

The calculation of the dielectric constant of a material is a non-trivial task. One of the main problems is caused by the fact that a given structural unit in the material is not polarised by the mean internal electric field but by the microscopic one present at the structural unit (local field corrections). Therefore, it is important not only to count the local polarisabilities but also to consider the influence of the environment of a local dipol. An overview of the experimental and theoretical methods for the determination of the polarisability of finite systems is given in [13]. The treatment of extended systems has been reformulated in the past decade with the result that the information about the polarisation is not in the electronic density but in the phases of the wavefunctions [14–16]. The present work is concentrated on structures that can approximately be considered in the Clausius–Mossotti limit of localised polarisable units with non-overlapping charge densities. The Clausius–Mosotti model (CMM) is a continuum theoretical approach to the interaction of a molecule and a polarisable environment [17].

In a recent theoretical paper [18] this approach was applied to calculate the dielectric constant of low-k materials consisting of chemical groups such as SiH, Si–CH_3, Si–O, where the polarisability of the groups was calculated using density functional theory. Chemical bonds of this type appear as structural components in hydrogen silsesquioxane (HSQ) and methyl silsesquioxane (MSQ) low-k materials.

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Table 1 Molar refractivities of atoms taken from [19, 20].

atom type	R (cm^3)	atom type	R (cm^3)
C_{sp^3}	2.8158	H	0.9155
C_{sp^2}	3.8278	O<	1.6351
C_{sp}	3.8974	O=	1.7956
C_{Ar}	3.5090	Si[a]	8.4321
C=X	3.0887	Si[b]	7.087

[a] estimated from SiO_2-type compounds, [b] taken from [21]. X – heteroatom, Ar – Aryl group.

As far as the compounds to be treated here are concerned, orientational and ionic contributions to the molar polarisability can be neglected. So only the electronic polarisations contribute significantly to the *k*-value of the material. In this case the frequency dependence of the *k*-value can be neglected and the static *k*-value can be calculated from the molar refractivities of the material using the CMM expression in the form

$$k = \frac{V_M + 2R_M}{V_M - R_M}\,, \tag{1}$$

where $V_M = M/\rho$ is the molar volume with M being the molar mass and ρ the bulk density. The molar refractivity, R_M, of a compound can be obtained from the sum of either atom or bond refractivities R by

$$R_M = \sum_i a_i R(i)\,, \tag{2}$$

where a_i is the molar fraction of the i-th atom or bond in the compound. Table 1 shows the molar refractivities as used in this paper [19–21].

3 Results and discussion

For a single C_{60} molecule one obtains from Eq. (2) $R_M = 60 \times 3.8278$ cm^3 $= 229.7$ cm^3. Application to the face-centred cubic C_{60} crystal with the molar volume of $V_M = 431.1$ cm^3 yields $k = 4.421$ which is in excellent agreement with the experimental value of 4.4 ± 0.2 [22].

One may argue that the validity of CMM could be violated by the introduction of bridge molecules covalently bound to the fullerenes. Indeed, the present structure model does not comply exactly with the requirements of the CMM. A related problem was discussed in a recent paper [23] on the polarisability of partially fluorinated ($C_{60}F_n$) fullerenes. The calculations were done using the finite field method and the modified neglect of diatomic overlap (MNDO) approach. There are two interesting results: (i) The additivity model (see Eq. (2) in the present paper) is approximately valid for $C_{60}F_n$. (ii) The polarisability of $C_{60}F_n$ is increased only weakly by about 1% (for $n = 2$) and 0.5% ($n = 20$ to 48) per F atom relating to the value for $n = 0$. Transferring these results qualitatively to the present situation the conclusion is justified that both expressions (1) and (2) give reasonable approximations for the considered systems.

According to the model presented here, the dielectric constant of the fullerene solid is supposed to be reduced by creating cross-linkage between the fullerene monomers, increasing the fullerene-fullerene distance and, consequently, by decreasing the number of dipoles per unit volume. Additionally, the mechanical properties of the material can be modified by this means.

One may start with exohedral fullerenes of the type illustrated in Fig. 1. The figure shows a pattern of hexakis-adducts of C_{60} as well as two monomers that have been synthesised experimentally by the regioselective mild Bingel reaction or tether-directed remote functionalisation [24–27]. Monomers of this type could be polymerised. One possible way is, e.g., the reaction (A)

$$n C_{60}[C(COOH)_2]_6 + 6n HOCH_2CH_2OH \rightarrow \{C_{60}[C(COOCH_2)_2]_6\}_n + 12n H_2O\,.$$

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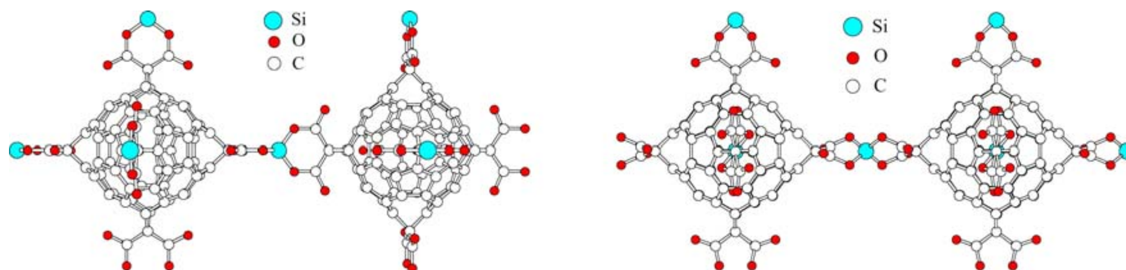

Fig. 2 (online colour at: www.pss-a.com) Fullerene dimers. Configuration 1 (left) and 2 (right) of a dimer that is the basic unit of the fullerene polymer $\{C_{60}[C(COO)_2Si_{0.5}]_6\}_n$.

Since, in recent years, several silica- and silsesquioxane-based low-k materials have been explored, it seems promising to include structural units of those dielectrics in fullerene-based polymers. The synthetic methodology for different types of silicon-containing exohedral fullerene molecules is described in [28]. For creating silicon-containing C_{60} polymers, the following reaction (B) may be used:

$$nC_{60}[C(COOH)_2]_6 + 3nSiX_4 \rightarrow \{C_{60}[C(COO)_2Si_{0.5}]_6\}_n + 12nHX \; (X = Cl, OH) .$$

For reaction B, two possible configurations of dimers are possible as shown in Fig. 2. The polymer is created by placing the fullerenes on the sites of a simple cubic lattice and connecting next-nearest fullerene neigbours by bridge molecules according to one of the reactions A, B. The resulting crystal symmetry is simple cubic (sc) for reaction A and for reaction B with configuration 2, and it is face-centred cubic (fcc) for reaction B with configuration 1 (Fig. 2). The properties of the three fullerene polymers described are compiled in Table 2. The lattice parameters are the result of the DFTB structure optimisation procedure. Bulk modulus, B, and stiffness constant, C_{11}, were determined from the relations $B = V_0\, \partial^2 E/\partial V^2$ and $C_{11} = (1/a_0)\, \partial^2 E/\partial a^2$ where E is the DFTB energy per unit cell at hydrostatic strain (for the determination of B) and at deformation in the direction of the a-axis of the elementary cell (C_{11}). Volume V_0 and lattice parameter a_0 apply for the strain-free state. For reaction B, the fcc structure is more stable than the sc one by an energy difference of about 2.4 eV per monomer.

4 Conclusion

The results show that cross-linking of C_{60} fullerenes by suitable bridge molecules is an efficient way to construct materials with extremely low dielectric constant. One of the significant advantages of such polymers is that it contains uniformly distributed porosity with a pore size of about 1 nm. Experimental

Table 2 Properties of fullerene polymers.

formula of monomer	$C_{60}[C(COO)_2Si_{0.5}]_6$		$C_{60}[C(COOCH_2)_2]_6$
crystal symmetry	fcc	sc	sc
cell parameter (Å)	31.8023	15.7453	16.7164
volume (cm^3/mol)	2421.23	2350.71	2813.11
molecular weight	1405.08	1405.08	1489.14
density (g/cm^3)	0.580	0.598	0.529
band gap (eV)	1.655	1.622	1.657
refractivity (cm^3/mol)	337.95	337.95	368.41
dielectric constant*	1.487	1.504	1.452
bulk modulus, B (GPa)	16.62	12.44	13.95
stiffness constant, C_{11} (GPa)	42.45	32.98	36.20

* The dielectric constant of the silicon-containig structures was calculated using the value 8.4321 cm^3 for the molar refractivity of Si (Table 1).

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preparation of the proposed materials should be possible according to the reactions suggested above. We conclude that the $C_{60}[C(COO)_2Si_{0.5}]_{6n}$ fcc-polymer with a dielectric constant of $k = 1.5$ and reasonable elastic properties represents a promising candidate of a new class of ultralow-k dielectric materials for application in future high-performance semiconducting cicuits.

Acknowledgements This work was supported by the European Fund ERFE and the Saxonian Government (Germany). The authors are grateful to M. Taut (IFW) for critical comments on dielectric properties, to E. Zschech (AMD LLC & Co.) for discussions on technological aspects, and to G. Thomas (SAB Saxony).

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