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Molecular modeling and synthesis of polymers for use in applications requiring a low-k dielectric

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Abstract

As integrated circuits have become more and more complex and with smaller and smaller feature sizes several limitations have become apparent. One of these is the need for low-k dielectric materials as insulating layers. Recent work has reported promising materials for such insulators that include some fluorinated polymers. These dielectric materials were further improved by introducing porosity into the polymer films. One of the key factors in the dielectric constant of a material is its density. As the polarization of the material is related to the number of bonds, the dielectric constant will scale with the density. In this paper a series of molecular modeling calculations were conducted on various fluorine substituted polymers in order to predict their densities. A surprising result of these calculations was the prediction that some of the polymers would have densities less than 1 g/cm^3. One of these polymers was synthesized and the density determined. The calculated density was in extremely good agreement with the experimental density. This paper will present the details of the molecular modeling technique as well as the synthesis and characterization of one of the polymers of interest.

Keywords: Low-k dielectrics; Polymer densities; Molecular modeling

1. Introduction

Over the past several decades there has been ongoing development of advanced ULSI integrated circuits. These devices have reached the point that one of the major limiting factors is the dielectric material separating the metallic connections. It is not uncommon to have devices with 6–7 layers of metallization separated by dielectric material that is less than 1 μm thick. The International Technology Roadmap for Semiconductors [1] has identified the need for dielectric film materials with dielectric constants of less than 2 as a limiting factor in lithographic production of devices at below the 100 nm size range. The ITRS, describes the need for materials with low dielectric constants in order to affect the capacitance (*C*) of the portion of the interconnect relay (*RC*) as transistors become smaller. This effect of reducing the *RC* delay is leading to the introduction of metals with lower resistivity (Cu) and the replacement of SiO_2 as the interlayer dielectric.

Silicon oxide has a dielectric constant of about 4 but is widely used because it exhibits a unique combination of properties including the ability to withstand the rigors of semiconductor manufacturing and exhibits very good thermal and mechanical stability. Further it has become routine to produce thick defect free films of this material. It is clear, however, that the dielectric constant is far too high for the next generation of devices. SiO_2 has been slowly being replaced by organic polymer dielectrics. The progress of this replacement has been slow due to the fact that these polymers cannot match all of the properties of SiO_2. Fluorinated silica glass comes very close to matching the properties of SiO_2, but its k value of 3.6 is only a small improvement over SiO_2 and is not sufficient at below the 130 nm node.

Work conducted by. Zhou, et al. [2] on fluorinated polymers has shown that dielectric constants of ∼2 can be produced. A review of the physical properties of a number of fluorinated polymers by Bruma, et al. [3] also reports low values for the dielectric constant for these type of polymers. Recent work on these materials has shown that even lower dielectrics can be made by forming porous foam films. This is accomplished by

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inducing a phase separation of solvent from the polymer on a microscale with subsequent removal of the solvent to leave voids. The dielectric constant of a material is given by the Debye equation [4] Eq. (1) below;

$$(\varepsilon_r - 1)/(\varepsilon_r + 2) = \rho P_m / M \tag{1}$$

where M is the molar mass and P_m the relative permitivity is given by Eq. (2);

$$P_m = \frac{N_A}{3\varepsilon_0(\alpha + \mu^2/3KT)} \tag{2}$$

And where; N_A, Avogadro's number; ε_0, is the permitivity of a vacuum; α, polarizability of the molecule; μ^2/KT, term arises from the thermal averaging of the dipole moments in the molecule under and applied field.

Rearranging the Debye equation we find the following relationship between ε_r and ρ in Eq. (3).

$$\varepsilon_r = \frac{(2\rho P_m/M + 1)}{(1 - \rho P_m/M)} \tag{3}$$

This shows that the dielectric constant of a material is very sensitive to the density of the material assuming molar mass and relative permitivity remain fairly constant across chemically similar compounds.

Given the relationship between density and dielectric constant it would be reasonable to expect that if the free volume of a low-k dielectric material could be increased then the dielectric of that material would also improve. It would be extremely useful to have a fast easy method to predict polymer densities prior to committing laboratory resources to synthesis of potential polymers of interest. The calculation of polymer density for dense polymers utilizing molecular modeling has been reviewed by Kremer and Muller–Plathe [5] and reported for selected dense polymers Curco and Aleman [6]. This paper reports the results of molecular modeling of the densities for a series of known density polymers utilizing commercially available software. The method was then followed by the prediction of densities for several fluorine substituted styrenic polymers that have the potential for low-k dielectric constants and low density due to steric hindrance. One of these polymers was synthesized and the density measured and comparisons made between measured and calculated densities. The effect of polarizability of the fluorinated polymers has been ignored in this study and could turn out to effect the dielectric substantially. This however, is thought not to be the case for several reasons. First, fluorines are least polarizable of atoms. Secondly any dipole moments in the family of polymers that were studied tend to be quite small due to the fact that the polymers tend to form helical structures that tend to cancel any dipoles. Thirdly, within the family of fluorinated styrenes the expected difference in permittivity would be very small across the whole family.

2. Experimental

2.1. Materials

The monomer 3,5-bis(trifluoromethyl styrene) was obtained from Aldrich. The inhibitor was removed by using *tert*-butylcatechol as a remover. The solvent, dimethyl sulfoxide, was obtained from Aldrich with 99.9% purity and used as recieved. The nitroxide and initiator azobis isobutyronitrile were obtained from Aldrich and used as received. Styrene, benzene and toluene were purchased from Aldrich and solvents anisole, ethyl acetate, tetra hydrofuran and diethyl ether were purchased from Fischer. All the solvents were used as received.

2.2. Molecular modeling

The molecular modeling was carried out utilizing the commercial Cerius 2 software package. All calculations were atomistic forcefield based and were conducted using the COMPASS forcefield reported by Sun and Ren [7] and Sun [8].. The monomers for all the polymers were produced using the 3D sketcher. The monomers were then assigned charges in the open forcefield setup module and minimized in open forcefield methods module [9–28]. The COMPASS forcefield was utilized in all calculations. The homopolymers were generated using polymer builder. The polymers generated were 10 units in length. The partial charges on the polymers were recalculated and were iterated through several cycles of minimization and molecular dynamics. In Crystal Builder a tetragonal unit cell of 12×12×30 Å was generated and converted to $P1$ symmetry. The polymer of interest was then imported to that cell. In visualizer a 4×4 cell array was created and converted to a super cell. This super cell now containing 16 molecules of the polymer of interest was taken through a series of minimizations and molecular dynamics until a minimum energy was reached. The cycles of molecular dynamics were conducted under NVE (constant moles, volume, and energy) conditions until the last few cycles at which time it was switched to NPT (constant moles, pressure, and temperature) conditions. The dynamics were run at 298 K and 0.1 GPa of pressure with 1000 steps of 0.001 ps per step.

2.3. Synthesis of poly(3,5-(bistrifluoromethyl)styrene)

The synthesis of poly(3,5-(bistrifluoromethyl)styrene) was accomplished as follows. Azobis isobutyronitrile (0.016 g) was dissolved in 5 ml of DMSO placed in a 25 ml round bottom flask with continuous argon purge. Purified monomer (3,5-bis trifluoromethyl styrene) 0.5 ml was injected via syringe into the round bottom flask with continuous argon purging. The round bottom flask was then placed in an oil bath maintained at 95 °C. After 36 h the solution was precipitated into methanol and the precipitate was filtered and dried overnight under vacuum at room temperature.