Characterization of various low-k dielectrics for possible use in applications at temperatures below 160 °C

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Abstract: This study aims at the testing of various low-k insulators deposited at temperatures below approximately 160 °C for possible application in temperature-limited copper interconnects (e.g., in plastic electronics). Various polymers were tested such as the well-known poly(methyl methacrylate) (PMMA), a Polyhedral Oligomeric Silsesquioxane (POSS) based copolymer partially fluorinated (POSS-F) and the newly synthesized poly(2,2,2-trifluoroethyl methacrylate) (PFEMA) and poly(dimethyl-siloxane) (PDMS). The above materials were compared with conventional spin-on glasses (SOGs), purchased from Filmtronics with respect to their handling (application, curing, mechanical strength, patterning) and dielectric constant. It was shown that organic polymers containing C-F bonds (PFEMA), Si-O bonds (PDMS) and Si-O and C-F bonds (POSS-F) present considerable advantages (related to the value of k and to handling) for use in Cu/low-k interconnects compared with usual SOGs cured at low temperatures.

1. Introduction

The increasing need for faster ICs has resulted in the realization of higher-speed and higher-density semiconductor devices. For the last two decades, device feature size has decreased from 1 µm down to 90 nm, increasing the working frequency of the microprocessors from 66 MHz to 4GHz [1]. However, further decrease of feature sizes to values lower than 1 µm has introduced certain limitations such as the interconnection delay [2] which namely is the resistance-capacitance (RC) delay that a signal experiences during its propagation through the interconnection. In order to face the problem and bring down resistance and capacitance, architectures with Cu wirings have replaced Al which traditionally was used in interconnects (36% decrease in resistivity) and novel interlayer or interlevel dielectric materials have been introduced as alternatives to silicon dioxide. Silicon dioxide till recently appeared to be the standard insulating material with a dielectric constant about 3.9. However, to fulfill the requirements for Ultra Large Scale Integration materials with dielectric constants lower than 3.9 (so called low-k dielectrics) are necessary.

Generally speaking, a low-k material is an insulating material that exhibits weak polarization when subjected to an externally applied electric field. As a result, a capacitor with a dielectric medium of lower k will hold less electric charge at the same applied voltage or, in other words, its capacitance will be lower. There are several guidelines employed to the design of low-k materials. The most obvious one is to choose materials with chemical bonds of lower polarizability than Si-O. The IC industry has already moved to materials, which exhibit less polarizable bonds such as Si-F [3] or Si-C [4] in order to replace Si-O bonds. Additionally, by using materials, like organic polymers, with virtually non-polar bonds such as C-C or C-H
we can help out a more fundamental reduction in $k$ values. Another approach is to minimize the moisture content in the dielectric since water has extremely polar O-H bonds and a $k$ value close to 80. A low-$k$ dielectric needs to be as hydrophobic as possible to prevent deterioration of its $k$ value. Furthermore, since the air’s dielectric constant is equal to unity, dielectric materials can have lower effective $k$’s with the introduction of some porosity into their chemical structure. By introducing porosity, we manage to increase the free volume and as a result to decrease the density of a material. Generally, in order to create porosity in the films, the template material is thermally decomposed and the decomposition products will volatise and permeate through the main matrix during the thermal treatment. As a result, voids are created at sites occupied by the templates prior to the decomposition process. In most cases thermal treatment at high temperatures is necessary in order to render the material porous. Indeed, this is the case of spin-on glasses (SOGs). In the field of non-porous, organic materials polyimides and fluorinated polymers are the most promising candidates for use as low-$k$ dielectrics [5,6]. Such materials have received considerable attention lately [8, 9].

In order to be successfully integrated in IC manufacturing processes, a low-$k$ dielectric material must comply with five general requirements: a) to exhibit adequate thermal, mechanical and electrical characteristics; b) be able to operate with the rest of materials of the interconnect structure; c) be compatible with the processes used in the IC manufacturing (e.g., cleaning, etching, thermal treatments, chemical-mechanical polishing, etc); d) be available in high purity form, and at low cost; and e) be able to operate reliably over the life of the product under the specific device operation conditions.

This article deals with some newly synthesized, low-$k$ candidate, organic materials applied by spinning and cured at temperatures below 160 °C.

2. Experimental

Various possible candidate low-$k$ materials were tested. These materials are the well-known poly(methyl methacrylate) (PMMA), the poly(dimethyl-siloxane) (PDMS) and the newly synthesized POSS-F based copolymers and poly(2,2,2- trifluoroethyl methacrylate) (PFEMA). Two different batches of the POSS-F copolymer: POSS-F 61 and POSS-F 66 were used in order to examine the reproducibility of its behavior as low-$k$ material. Both POSS-F copolymer and PFEMA were synthesized with free-radical polymerization of their monomers. The above materials were compared with commercial spin-on glasses (SOGs) with respect to their handling (application, curing, mechanical strength, patterning) and dielectric constant. The dielectric layers were prepared by the standard spin coating procedure on p-type 3 in. Si wafers at speeds of 5000 (PMMA and PFEMA) and 3000 (PDMS and POSS-F copolymers) rotations per minute (RPM). SOGs tested were the 15A, 314 and 114 of Filmtronics Inc., which after spinning were cured at temperatures and times shown in Table 1. Post applying baking conditions for organic materials is shown in Table 2. After application of the various materials, trenches were formed on their surface by lithography and etching and their thickness was measured with a profilometer. The adhesion of films was also tested by the scotch-tape test. For the determination of the various dielectric constants, Metal-Insulator-Semiconductor (MIS) capacitors were formed using the materials under test and thermally evaporated aluminium as metal. Combinations of high frequency (100KHz, 1 MHz) Capacitance-Voltage (C-V) curves have been taken to extract the dielectric constant of each material.

3. Results and discussion

From the C-V measurements, and knowing film thickness, the values of $k$ were obtained. In the case of

| SOG  | Cure (°C) | Thickness (nm) | $k$  |
|------|-----------|----------------|------|
| 314  | 75 °C, 2 min+ | 230           | > 5  |
| 114  | 140 °C, 2 min+ | 105           | > 5  |
| 15A  | 240 °C, 2 min | 118           | > 5  |
SOGs when cured at temperatures up to 240 °C (see Table 1) their dielectric constant was found, in all cases, above 5 rendering them unsuitable for use as low-k dielectrics when cured at such temperatures. The high k value at low curing temperatures is consistent with the operating instructions provided by their manufacturer, where it is noted that these SOGs must be cured at 425 °C for 1 h. SOGs are mainly composed of Si and O atoms and also contain C and H atoms. Curing above 425 °C eliminates the bonds C-O, C-H and O-H, the material becomes porous and the dielectric constant drops to values lower than SiO₂. Indeed after curing at 150 °C for 60 min followed by a curing at 425 °C for 60 min the dielectric constant of SOGs was found to drop at 3.97

In Figure 1 FTIR Transmission spectra for a 314 SOG film prebaked at various temperatures are shown. It is evident that as the prebake temperatures increase peaks corresponding to SiO₂, such as those at wavenumbers 1080 and 1200 cm⁻¹ (asymmetric stretching of Si-O bond) and 810 cm⁻¹ (symmetric stretching of the Si-O-Si bridge) increase. Peaks at 1107 cm⁻¹ (corresponding to the C-O stretching mode), 940 cm⁻¹ (C-H asymmetric stretching) and the broad peak of O-H bond at 3400 cm⁻¹ decreases.

![Figure 1. FTIR transmission spectra within the range 2800-3600 and 700-1300 cm⁻¹ (inset) of a 314 SOG film baked at various temperatures.](image)

![Figure 2. Typical C-V characteristics taken at 100 KHz on MIS capacitors using as insulator a PFEMA film.](image)

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**Table 2. Low-k polymers tested.**

| Material | Cure (°C)/time (min) | Thickness (nm)/rot. speed (RPM) | k | Mech. Strength | Patterning |
|----------|----------------------|--------------------------------|---|----------------|------------|
| PMMA     | 150/2                | 495/5000                        | 3.2 | Very good     | With e-beam |
| PFEMA    | 150/2                | 248/5000                        | 2.8 | Very good     | "          |
| PDMS     | 100/2                | 35/3000                         | 2.8 | Good          | With standard optical resists |
| POSS-F 61| 130/2                | 85/3000                         | 2.5 | Good          | With deep UV lithography |
| POSS-F 66| 130/2                | 57/3000                         | 2.35 | Good         | With deep UV lithography |

From the above observations it is concluding that the removal of C-H and O-H bonds, probably in the form of hydrocarbons and water respectively, is connected with the formation of a porous material with low dielectric constant. This process starts at temperatures much higher than 160 °C and this is why SOGs cured below this temperature cannot be used as low-k dielectrics.
Typical C-V measurements at 100 KHz and 1 MHz were made for a PMMA, PFEMA (figure 2), PDMS (figure 3) and POSS-F copolymers (figures 4 and 5) films. From the C-V and thickness measurements the value of k was obtained for each material and reported in Table 2. It can be observed that the values of k of all polymers are below that of SiO₂ (3.9). PMMA, which is a methacrylate polymer used in e-beam lithography, was used as a reference because it mainly has C-H bonds. On the other hand, PFEMA is newly synthesized fluorinated methacrylate polymer, which contains three C-F bonds per polymer unit.

PDMS is a siloxane type polymer, highly hydrophobic due to the repeating units of –O–Si(CH₃)₂– groups. Moreover the C-H and Si-O bonds that exhibit a small polarizability result in a rather low k. POSS-F 61 and 66 are copolymers containing C-F bonds and silsesquioxane type groups and demonstrate reduced k values because of the decreased material’s density, which derives from the way that Si and O atoms are arranged in the silsesquioxane elementary unit. POSS-F copolymers showed a considerably low dielectric constant. Neither PDMS nor POSS-F films exhibit any hysterisis in the C-V curves, while for PFEMA film a slight hysterisis is observed.

4. Conclusions
It was shown that considerable reduction of the dielectric constant can be achieved by introducing organic polymers containing C-F (PFEMA), Si-O (PDMS), Si-O and C-F bonds (POSS-F) which also present considerable advantages related to handling for use in Cu/low-k interconnects when cured at temperatures below 160 °C. Such materials can contribute to domains such as plastic electronics. Work on the field of low-temperature low-k dielectrics continues.

5. References
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