Diffusion of Aqueous Solutions in Oxycarbosilane Nanoporous Thin Films during Processing of Interconnect Structures

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MATERIALS

Abstract:

For the microelectronics industry to begin manufacturing smaller and faster devices, thin films utilized as interconnect structures must have lower dielectric constants and increased thermo-mechanical stability. The introduction of nanoporosity is often used to fine-tune electrical properties of certain materials. Oxycarbosilane (OCS), an organosilicate spin-on glass, has shown not only an extremely low dielectric constant, but has also exhibited a high level of mechanical reliability in comparison to similar nanoporous thin film glasses. During integrated circuit fabrication, thin films are subjected to active chemical solutions which can diffuse into the material, adversely affecting device performance and reliability. The current study focuses on the extent to which different solutions diffuse into OCS thin films with varying porosity levels and pore size characteristics.

Introduction:

Two forms of OCS, a bridged precursor molecule, were studied. These variations of OCS, namely ethylene and methylene, are defined by the specific organic group acting as the bridging bond. Nanopores were created by introducing sacrificial porogen molecules coupled with post-deposition annealing to remove porogen remnants, leaving behind pores of various sizes. Previous x-ray diffraction tests have revealed an organized, symmetric structure of nanopores in certain OCS thin films and a completely random distribution of pores in others.

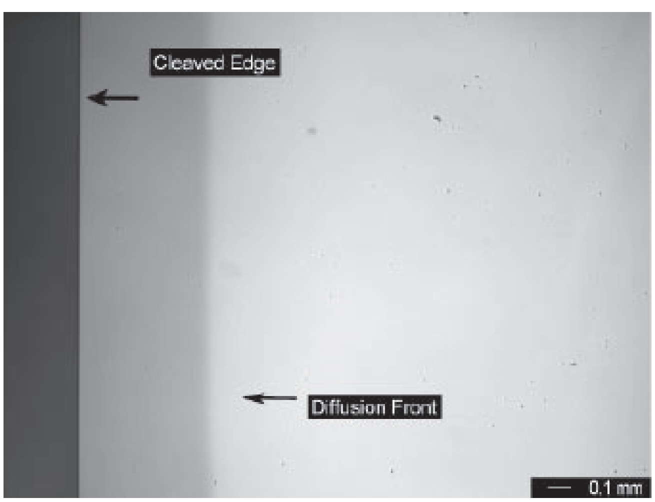

Figure 1: Photomicrograph of sample in solution showing a sharp diffusion front.

Organic groups present in organosilicate glasses typically result in highly hydrophobic materials. Experiments with similar nanoporous organosilicates have shown rapid diffusion in the presence of buffering solutions. For this reason, initial testing of OCS thin films was performed in concentrated buffer solutions of varying pH.

Procedure:

The OCS films were applied to silicon wafers using a spin-casting technique, resulting in film thicknesses of 500 nm. Various samples included two forms of OCS, three pore sizes, and two porosity percentages. All samples were capped with a 200 nm transparent layer of silicon nitride using a plasma enhanced chemical vapor deposition system.

Samples were cleaved into approximately 50 mm squares immediately before immersing the films into solution. Deionized water and two buffer concentrates of pH 3 and pH 11 were tested. Photomicrographs were taken with an optical microscope at 5x magnification [Figure 1] in order to measure diffusion distance. All data was analyzed using Fick's Law of Diffusion which represents a linear relationship between diffusion distance and the square root of time.

Results:

As illustrated in Figures 2 and 3, two general trends were confirmed by experiment. With regard to both forms of OCS, methylene and ethylene, smaller pores present a better barrier to diffusion. Figure 2 shows a steady decline in the diffusion coefficient as pore radius

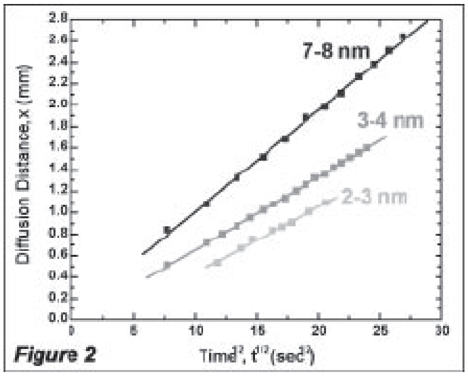

Figure 2: Comparison between different pore sizes of a specific film and solution.

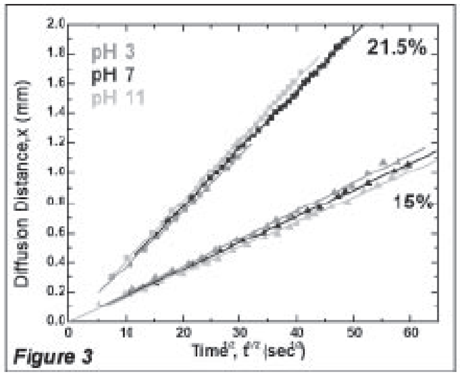

Figure 3: Comparison between porosity percentages of a given OCS film.

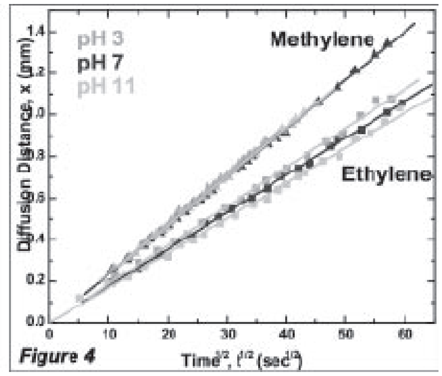

Figure 4: Rare occurrence in which methylene showed faster diffusion rates than an identical ethylene film.

decreases. Correspondingly, samples with the lowest porosity percentage exhibited the slowest diffusion rates, as depicted in Figure 3. In addition to the differences in porosity percentage, Figure 3 also demonstrates the relationship between the three solutions for a specific OCS thin film. The graph shows that porosity percentage has a much larger impact on diffusion rates than the solution. When comparing data for ethylene and methylene, as in Figure 4, all thin films and solutions showed faster diffusion rates in ethylene, with the exception of two methylene films. When considering nanopore organization alongside the data collected, nearly all ethylene samples displayed a “not organized” structure of nanopores, while most methylene thin films showed signs of organization. The two methylene films described as “not organized” were the same two films that exhibited the only occurrence of higher diffusion rates in methylene when compared to ethylene.

Additionally, an organosilicate glass similar in total composition and overall porosity created with a chemical vapor deposition (CVD) process was subjected to identical diffusion experiments. The main difference between the CVD glass and OCS was the placement of the organic groups, which are found as terminal bonds instead of bridging bonds in the CVD glass. No diffusion was observed for the samples tested.

Conclusion:

Although oxycarbosilane nanoporous thin films are ultra low-κ materials with a high level of mechanical reliability, OCS displays extremely low resistance to diffusion of any aqueous solution tested. This process seems to be further enhanced by a lack of nanopore organization. If experimentation could be performed on OCS thin films exhibiting different organization levels, the mechanism responsible for alignment of the nanopores may be isolated and understood. This could result in future materials being manufactured with highly symmetric porous structures which may ultimately lead to drastically reduced diffusion rates. With respect to the lack of diffusion seen in the CVD glass, the placement of the organic groups obviously lends to the overall hydrophobicity of the material. Such a drastic difference in diffusion rates between the two organosilicate glasses may also mean that the organic groups used in OCS are possibly of more importance than other factors mentioned.

Because of the large amount of different OCS thin films and solutions used in this project, time permitted only one series of experiments for each specimen and testing condition. To be sure of the general trends discussed, these diffusion experiments should be repeated to ensure reproducibility.

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References:

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