

Organofluorosilicate Glass Interlayer Dielectric Material and Integration Study

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Abstract

Organofluorosilicate glass (OFSG) films of the composition Si:O:C:H:F were deposited via plasma enhanced chemical vapor deposition (PE-CVD). This material, in which essentially all fluorine is bonded to silicon, provides superior electrical and mechanical properties, improved thermal and oxidative stability, and improved adhesive strength relative to a reference organosilicate glass (OSG) currently in production at a major manufacturer. OFSG has shown potential as a new interlayer dielectric material for a high yield Cu-Low k process.

Introduction

Interlayer dielectric (ILD) materials capable of surviving common IC processing schemes must balance materials properties, such as minimizing the dielectric constant and maximizing mechanical strength. Current leading low dielectric constant materials are evolutionary in nature. In fluorosilicate glass (FSG) and organosilicate glass (OSG) a portion of the oxygen atoms of the silicate network are replaced with species specifically aimed at reducing the dielectric constant. [1] While the introduction of Si-F species into an oxide film is highly effective at reducing the electronic polarization density, a major component of the dielectric constant, the effect is limited to ~ 5 atomic % F [2]. OSG materials are the leading candidates for interlayer dielectric (ILDs) for the 90 nm technology node. They contain a relatively large concentration of organic species and material's properties differ sufficiently from traditional insulators to present significant challenges for integration. For OSG materials the benefit of organic groups introduced to the silicate network reaches a point of diminishing returns when increases in organic content provide minimal further reduction in dielectric constant yet dramatically diminish the mechanical strength of the material. Organic groups are also prone to thermal and oxidative instability. As a result the implementation of new low dielectric constant materials has been much slower than anticipated just a few years ago.

Our molecular modeling work suggests that synergy may exist between the introduction of inorganic fluorine and organic groups to a silicate network. Herein we describe organofluorosilicate glass (OFSG), a new material that captures the synergy of Si-F and organic groups. The

addition of SiF₄ effects the replacement of more weakly bound and chemically susceptible organic species with Si-F groups. Replacing a small portion of organic groups with fluorine atoms decreases disruptions to the silicate network. This provides a denser material with improved mechanical, electrical, and thermal properties at similar dielectric constants.

Experimental

Films were deposited on 200 mm Si wafers in an Applied Materials DxZ chamber. Design of experiment methodologies were used to define parameter space for stable plasma and uniform deposition conditions as well as for optimization of films' electrical and mechanical properties. Blanket films produced from optimized processes were tested for dielectric constant and hardness by mercury probe and MTS nanoindenter, respectively. Thickness and refractive index were measured by reflectometry and ellipsometry. Film composition and bonding structure were assessed by X-ray Photoelectron Spectroscopy (XPS), Rutherford Backscattering / Hydrogen Forward Scattering (RBS/HFS), transmission FT-IR, Secondary Ion Mass Spectrometry (SIMS), and carbon-13 and silicon-29 Nuclear Magnetic Resonance (NMR). X-ray Reflectivity (XRR) measurements were used to determine material density. Thermal stability was tested by Thermogravimetric Analysis (TGA), and adhesion by stud pull testing. Three-level copper structures were produced to test integratability, electrical performance and reliability.

Blanket Film Properties

The properties of OFSG and reference OSG films are compared in Figure 1. The data show OFSG provides superior mechanical and electrical properties compared to OSG, with essentially no difference in throughput as determined by relative deposition and etch rates. For the particular materials properties targeted for OFSG, the optimum balance between dielectric constant and hardness is achieved from gaseous mixtures of organosilicon precursor:SiF₄:O₂ in the approximate ratio 10:5:3.

Compositional analyses of representative OFSG materials indicate approximately 2 atomic percent fluorine is present within the film. The addition of fluorine primarily affects the carbon content of the OFSG films, with silicon

Figure 1. Comparison of optimum OSG and OFSG films.

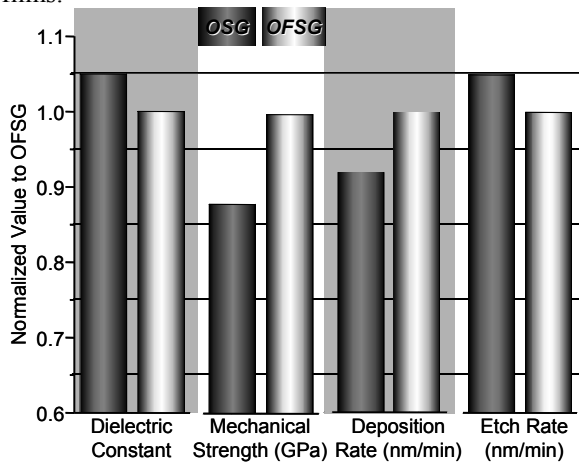


Figure 2. Leakage current for OFSG and OSG.

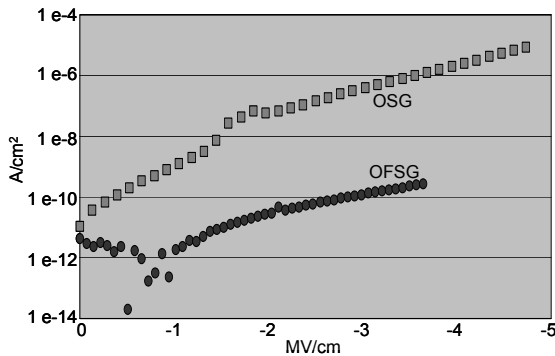
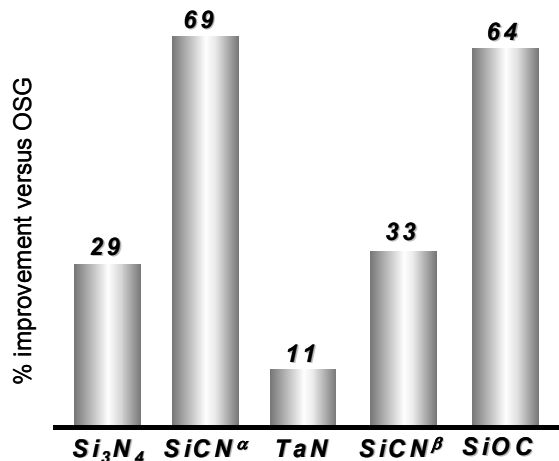


Figure 3. Relative adhesive strength for OFSG and OSG as determined by stud pull analysis.



and oxygen concentrations being very similar to OSG. The C:H ratio of both materials is approximately 0.6, suggesting that in addition to terminal methyl groups, carbon is also incorporated as network forming methylene and methyne groups. The ^{29}Si -NMR spectrum of OFSG indicates a

dominant peak assigned to Si-CH₃ at ~ 0 ppm with slight asymmetry on its downfield shoulder likely arising from networked carbon groups (eg. Si-CH₂-, Si-CH-). Neither NMR nor XPS provide evidence for C-F bonds within OFSG. FT-IR spectra reflect the structural similarities of the films. Only a slight blue-shift of the Si-O absorption reveals the presence of Si-F bonds in the OFSG, as Si-C absorptions mask direct determination.

X-ray reflectivity measurements indicate an approximate 10% increase in density of OFSG relative to OSG. This increased density is mostly likely the result of Si-F bonds occupying approximately 50% less volume than Si-CH₃ groups [3]. Increases in density typically increase dielectric constant because polarizable atoms are substituted for void space; however, the Pauling estimates of the polarizabilities of fluorine and carbon show that fluorine is significantly less polarizable [4]. The reduction in free volume is balanced by decreased polarizability, thus retaining the low- κ dielectric properties while significantly increasing the mechanical strength of the material.

The electrical performance of OFSG was superior to OSG in all cases. Leakage current measurements in Figure 2 indicate very low leakage by OFSG, less than OSG by approximately 3 orders of magnitude (~2e-11 A/cm² for OFSG versus ~ 5e-8 A/cm² for OSG at 2MV/cm). Breakdown voltage for OFSG also indicated a measurable increase over those determined for OSG.

Thermal stability measurements for representative OFSG and OSG materials indicate excellent thermal stability to > 500 °C. Both materials experience weight loss < 0.1 wt%/hr under inert environments during isothermal tests at 425 °C. Introduction of air to the test chamber resulted in instantaneous weight loss of approximately 2% for OSG materials, while no measurable change in weight was seen for OFSG. Dielectric measurements of OFSG and OSG samples after air exposure at 425 °C indicate an increase of up to 0.5 in κ value for OSG with no measurable increase in κ for OFSG.

The residual stress for OFSG is ~ 20 MPa (tensile), significantly less than the ~ 50 MPa (tensile) for OSG. Stress hysteresis measurements for OFSG indicated very stable profiles through the first and second scan from ambient to 400 °C. A hysteresis of 0.6 MPa was measured for OFSG relative to 1.5 MPa for OSG. The change in stress from ambient to 400 °C was also substantially reduced for OFSG, changing by ~ 25 MPa over the entire scan. Comparatively, OSG stress-temperature profiles indicate a large swing in residual stress from ~50 MPa tensile at ambient temperatures to ~50 MPa compressive at 400 °C.

Adhesive strength to various commercial barrier layer materials were performed by stud pull analysis (Figure 3). The adhesion of OFSG was found to be superior in all cases. For SiOC and SiCN^a the significantly larger adhesive strength determined for OFSG reflects a catastrophic failure of the OSG material at the interface. The types of layered

materials and their respective process conditions have a dramatic effect upon adhesive strength and failure location. It was found that plasma pretreatment of interfaces prior to OSG deposition improved adhesion to most materials, approaching that determined for OFSG. Similar pretreatments were found to have little effect upon measured adhesive strength for OFSG. Minimization of residual stress, stress hysteresis and changes in stress with temperature may minimize interfacial forces that can cause delamination.

The stability of fluorine to migration from OFSG was compared to PE-FSG and HDP-FSG materials. Sandwich structures of the ILDs between layers of silicon oxide were exposed to a representative copper alloy cycle process (7 x 400°C / 30 minutes / N₂) to determine the degree of fluorine migration. Dynamic SIMS analysis of OFSG structure indicated that fluorine had migrated 500 Å into the oxide layer, for HDP-FSG the fluorine migrated ~1200 Å into the oxide, and for PE-FSG fluorine was detected throughout the entire 2000 Å oxide layer. The reduction in fluorine migration for OFSG is likely the result of lower F content versus FSG and that the nature of the OFSG material may allow for internal gettering of fluorine. This reduction in fluorine migration should alleviate some of the integration issues that were experienced with FSG processes.

Integrated Structures

A via-first dual damascene process scheme was used to create a three level metal structure with 180 nm feature sizes for both OFSG and OSG. Via performance were comparable for both OFSG and OSG materials, with OFSG structures showing reduced line-to-line leakage current.

Films deposited from the OFSG process typically provides a film that has a slight center-thick profile, with percent non-uniformity measured at < 2%. This center thick profile matches better with common Cu-CMP processes which tend to be center-fast, and may ultimately provide better overall planarity in integrated structures.

A scanning electron micrograph cross-section for Cu-OFSG structure is shown in Figure 4. Excellent feature profiles are made, with no indication of adhesive failure, or fluorine corrosion issues. For these structures a fluorine-gettering liner layer was not employed.

Conclusions

A new material is defined, Organofluorosilicate glass, which provides superior materials property performance versus a leading organosilicate currently being used in production at the 130 nm generation. OFSG was successfully integrated into a copper-based process, showing good material performance and potential for high yield Cu-low k dual-damascene processing scheme.

Our presentation will focus on the latest integration information for OFSG in Cu-based process scheme. Electrical performance and reliability for OFSG versus this reference OSG material will be provided.

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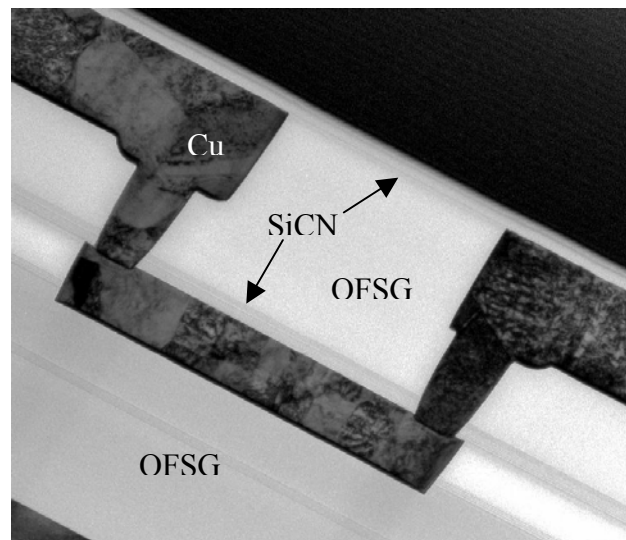


Figure 4. SEM cross-section of copper interconnect structure using OFSG.