

Molecular Caulking

A Pore Sealing CVD Polymer for Ultralow k Dielectrics

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Porosity has been introduced in existing low-*k* interlayer dielectrics to further reduce their dielectric constant. It is desirable to deposit a metallic layer on top of the porous dielectric by chemical vapor deposition (CVD). However this presents the challenge of preventing the precursor from penetrating into the porous dielectric and depositing metal within this insulating layer. In the present paper a low-*k* CVD polymer capping (Molecular CaulkingTM) is deposited at room temperature onto the porous ultralow *k* dielectric methyl silesequioxane. Experiments show that the Molecular Caulking prevents precursor penetration during subsequent metallorganic CVD. In addition, while the Molecular Caulking itself slightly penetrates into the methyl silesequioxane, it does not appreciably increase surface roughness or film dielectric constant. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1751195] All rights reserved.

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In future gigascale integrated circuits (ICS) resistive-capacitive (RC) delay is an increasingly important issue.¹ Carbon-doped oxides and aromatic polymers are examples of materials being investigated to replace SiO₂ as the interlayer dielectric (ILD).² Both materials possess lower dielectric constants and will lower the contribution to RC delay. In order to reduce the dielectric constant further, it is generally accepted that the ILD will contain some amount of porosity. The introduction of porosity results in a number of other undesirable properties such as a reduction in mechanical strength and susceptibility to penetration of chemicals. Most importantly, during chemical vapor deposition (CVD) exposure of the porous dielectric to gaseous precursors that are expected to infiltrate an open pore film or even a closed pore film if the pore wall thickness in the nanoscale dimensions³⁻⁶ cause degradation of film properties. CVD will typically have a reactive sticking coefficient much less than one in order to have good conformal coverage. Indeed, one way to reduce this penetration would be to increase the reactive sticking coefficient, e.g., by increasing the deposition temperature. However, this would reduce the conformality of the deposition. Clearly porosity and conformal CVD on high aspect ratio substrates are fundamentally at odds.

Several methods have been studied recently to solve this problem. A recent review details some of the currently proposed strategies to seal porous dielectrics.7 A new sealing layer, Molecular Caulking, is presented here. MC films are deposited by CVD at room temperature using a free radical polymerization process. Preliminary results are promising. The approach taken was to measure the new sealant's ability to prevent penetration of metal precursors (copper, cobalt) during CVD. The depth distribution of deposited metals were measured by Rutherford backscattering spectrometry (RBS). In addition, changes in the dielectric constant as a result of MC, were determined by metal insulator semiconductor (MIS) capacitance measurements. Deposited film thickness was determined by both ellipsometry and ion beam backscattering using the 5.75 MeV ⁴He elastic nuclear resonance of ¹²C. Finally, the effect of MC deposition on surface topology was measured by atomic force microscopy (AFM).

Experimental

The porous methyl silsesquioxane (MSQ) film was deposited by spin coating and went through a series of baking stations before the final cure in an N₂ ambient at 420°C. The resulting films contain 50% porosity, and the pores are interconnected. Pore size ranges from 0.5-4 nm, with an average pore size of 1.5 nm. MSQ has a nominal stoichiometry of $SiO_{1.5}(CH)_{0.5}$.⁸

Copper CVD experiments were done via $Cu^{II}(tmhd)_2$ and H_2 in a vertical, low pressure, warm-wall reactor. The precursor bubbler was held at a constant temperature of $127.5 \pm 0.6^{\circ}C$ and delivered with 15 sccm of argon carrier gas. The substrate was kept at 217 \pm 5°C and the chamber walls and precursor transfer lines all held at 150 \pm 5°C. The total pressure of argon, H₂, and precursor, was approximately 2 Torr. The deposition time was 30 min for all experiments. Bare MSQ and several MC/MSQ films of varying MC thickness were placed side-by-side on the substrate heater in each experiment. For further details on the copper CVD process employed in this study, we refer to an earlier publication.⁶

Cobalt deposition experiments were performed in a vertical, low pressure, warm-wall reactor. $Co_2(CO)_8$ was sublimed at room temperature. The substrate was kept at $60 \pm 2^{\circ}C$ and the deposition time was 2 min. No carrier or purge gas was used, and deposition pressure was approximately 18 mTorr. Bare MSQ and several MC/MSQ films of varying MC thickness were placed side-by-side on the substrate heater in each experiment.

MC thin films were deposited using the Gorham method.9 The reactor consisted of a sublimation furnace, a pyrolysis furnace, and a bell-jar-type deposition chamber. Base pressure in the deposition chamber was at mid 10^{-6} Torr. During growth the deposition chamber pressure was in the low mTorr range and deposition rates were between 0.09-0.14 Å/s. A detailed description of the reactor and deposition process has been described elsewhere.^{10,11} Briefly, the precursor [2.2]-paracyclophane was sublimed at a temperature of 155°C. The sublimed precursor flew into a high-temperature region (650°C) of the reactor inlet where it was quantitatively cleaved into two p-xylylene monomers by vapor-phase pyrolysis. These reactive intermediates were then transported to a room temperature deposition chamber where upon condensation, spontaneous polymerization took place. Linear chains of poly(p-xylylene) with unterminated end groups were formed. Bulk poly(p-xylylene) has a k value of approximately 2.65 perpendicular to the plane of the film.¹² In this work ultrathin films (1-5 nm) were deposited. Si(100) 50 Ω cm substrates were rinsed in ethanol, followed by deionized water, blown dry with nitrogen, and then placed side-by-side with the porous MSQ in the deposition reactor. Ultrathin poly(p-xylylene) films (1-5 nm) are low molecular weight and more oligomeric than polymeric. Molecular weight increases with film thickness. Annealing thin poly(p-xylylene) films has shown indications of conversion

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from low polymer to high polymer.¹³ It is advantageous to have the pore sealant to be a high polymer since it possesses more robust chemical bonds. In addition, unreacted monomers or larger oligimers that are volatile at higher temperatures will diffuse out of the film upon annealing. Therefore after deposition, samples were annealed in forming gas at 250°C for 30 min.

The deposited film thickness was measured by a variable angle spectroscopy ellipsometer (VASE, J. A. Wollam, Lincoln, NB) on the silicon samples. VASE measurement interpretation is difficult on MSQ films, so thickness measurements were used from the silicon wafers and assumed similar growth on the MSQ films. The thickness of MC was determined by using the Cauchy coefficients of poly(p-xylylene) ($A_n = 1.6, B_n = 0.01$) or an index of refraction of 1.458 at 634.1 nm.

Copper growth was characterized by RBS with the 4.0 MV Dynamitron accelerator at the Ion Beam Laboratory, Department of Physics, University at Albany. Measurements were made with 2.0 MeV ⁴He particles. The RBS-determined areal density was converted into an equivalent thickness by dividing by the bulk atomic density of copper 8.45×10^{22} atom/cm³. Spectra were collected with a 20 mm² area beam spot, 2-4 μ C of charge, and with 3 nA of current. Ion beam backscattering using the 5.75 MeV ⁴He elastic nuclear resonance of ¹²C was done at the same facility.

Two samples were chosen for extraction of the *k* value, 540 nm MSQ/5 nm SiO₂/Si (control sample) and 250°C annealed 3.7 nm MC/540 nm MSQ/5 nm SiO₂/Si. Top aluminum dots of 0.5, 1, and 1.5 mm diam were electron-beam evaporated via a shadow mask. In order to get good ohmic contact at the back side of the silicon wafer, 300 nm of aluminum was sputter deposited. The capacitance-voltage (*C*-*V*) characteristics of the Al/low- κ (stack)/5 nm SiO₂/Si structures were measured with a HP 4280A 1 MHz capacitance meter/CV plotter. At least five measurements were performed for each capacitor size for each sample.

Surface morphology was measured using an atomic force microscope (AFM, AutoProbe CP) made by Park Scientific Instruments, TM Microscope. A triangular silicon cantilever with silicon conical tip (Veeco Metrology Group) was used in noncontact mode to measure the surface topography. The tip radius of curvature is <10 nm and had a half apex angle of 12° .

Results and Discussion

From previous work, copper was shown to deposit inside the porous dielectric rather than on the surface during CVD.⁶ The copper precursor penetrated the interconnected porous MSQ and selectively deposited at the interface between the MSQ film and the silicon substrate. This was observed by RBS and scanning electron microscopy (SEM). RBS can be used to measure the amount of penetrated material quantitatively down to monolayer levels. The SEM only has a sensitivity of several nanometers, so RBS was used to see small amounts of precursor that penetrated through the MC sealant. To illustrate this, Fig. 1 shows RBS spectra after copper deposition on bare MSQ/SiO₂/Si and a 1.1 nm MC/MSQ/SiO₂/Si sample. The arrows labeled surface copper and surface silicon show the kinematic energy of backscattering from copper and silicon, respectively, at the surface. The observed peak at about 1400 KeV shows that copper is deposited at the interface between the MSQ and the SiO₂/Si substrate.

Figure 2 is a plot of the amount of RBS-determined copper deposited by CVD at this MSQ/SiO_2 interface as a function of MC thickness. Data from two separate experiments are shown in Fig. 2 (circles and triangles). The data in Fig. 2 show that a MC film thickness of only 1.1 nm resulted in a 96% reduction in copper penetration during CVD. After 3.5 nm MC, the copper penetration goes below the 0.05 nm detection limit of RBS. Reactor modifications, including precursor and purge gas inlet lines, resulted in different growth rates of the two experiments, but the MC liner thickness sufficient to prevent penetration was consistent.



Figure 1. RBS spectra showing penetration of copper into the interface on bare $MSQ/SiO_2/Si$ and 1.1 nm thick $MC/MSQ/SiO_2/Si$. The double arrows show the thickness of the MSQ film as determined by the width of the silicon signal in MSQ. The double arrow length also corresponds with the signal peak of penetrated copper.

If MC deposition passivates the MSQ/SiO₂ interface, there would be no deposition to signify the penetration of the copper precursor. A nonselective metal precursor $Co_2(CO_8)$ was chosen to provide further evidence that MC/MSQ/SiO₂/Si physically blocks the pores. Cobalt CVD is nonselective and readily grows on MC. Deposition was approximately 0.5 nm/min at 60°C, a temperature where cobalt deposition is surface-reaction controlled and thus expected to grow at the surface and penetrate the porous MSQ. Figure 3 shows RBS spectra of the three samples, Co/2.7 nm MC/MSQ/SiO₂/Si, Co/2.7 nm MC/MSQ/SiO₂/Si, and Co/bare MSQ/SiO₂/Si. The bare MSQ shows penetration of cobalt supported by the long tail of the cobalt surface peak, while the other samples have only surface deposition. The width of penetrated co-



Figure 2. RBS is used to determine the equivalent thickness of copper deposition on/in MC/MSQ/SiO₂ /Si as a function of MC thickness. Two data sets: circles and triangles are from experiments before and after reactor alterations, respectively. Data point size is larger than error bars.



Figure 3. RBS spectra of cobalt on 2.7 nm MC/Si, 2.7 nm MC/MSQ/SiO₂/Si, and bare $MSQ/SiO_2/Si$. Cobalt penetration is only observed on the bare $MSQ/SiO_2/Si$ substrate. The 2.7 nm MC/Si and 2.7 nm MC/MSQ/SiO₂/Si samples show cobalt deposition only at the surface.

balt is consistent with the silicon width (thickness) in MSQ and shows that cobalt penetrates completely through the MSQ film without MC sealing.

Figure 4 shows a schematic representation of how the MC layer may be sealing the pores in MSQ. MSQ films used here have a pore size distribution of 0.5-4 nm. From Fig. 4, one expects that significant blocking of pores would require a MC thickness on the order of the average pore diameter, consistent with our result of 1.1 nm in Fig. 2.

Capacitance measurements showed that the dielectric constant of a MSQ/SiO₂/Si film covered with 3.7 nm of MC had essentially the same dielectric constant as the bare MSQ/SiO₂/Si film. The effective dielectric constant of the low *k* stack was calculated from the slope of the measured accumulation capacitance *vs.* capacitor area. The measured dielectric constant of porous MSQ was 2.26, this increased to 2.30 after an annealed MC coating. The ~1.7% increase in dielectric constant after annealing at 250°C was less than the sample-to-sample variation in capacitor area.

The MC thickness as determined by ellipsometry on SiO_2 is an indirect method, but was meant for quantitative comparison due to



Figure 4. Illustration of possible MC deposition behavior in the connected pore structure of porous MSQ.



Figure 5. ⁴He 5.75 MeV ion beam backscattering spectra of MC/MSQ/SiO₂/Si and bare MSQ/SiO₂/Si samples. View has been expanded to show only the carbon region of spectra, and the silicon substrate contribution has been subtracted from both spectra to emphasize relative carbon content in each sample.

the complexity of measuring the thickness deposited on MSQ/SiO₂/Si. Given that during CVD, precursor gases can diffuse into the porous material, some penetration of the MC layer was expected. The quantitative measure of deposited film content in/on the porous MSQ/SiO₂/Si was determined by adding a stoichiometric atomic percentage of hydrogen (C8H8) to the measured carbon content as determined by ⁴He ion beam backscattering analysis at 5.75 MeV. ¹²C exhibits a strong (α, α) elastic scattering resonance in the energy region between 5.5-5.8 MeV. In this energy region the cross section is more than 100 times the Rutherford cross section. The resonance is sufficiently broad to enable depth profiling over depths on the order of micrometers. Essentially ion beam analysis at these energies is similar to RBS at 2 MeV, providing there is accurate absolute cross section data available at the energies used. Davies et al.¹⁴ have measured the non-Rutherford cross sections in the energy region of 5.5-5.8 MeV.

Measurements of carbon content were made on bare MSQ/SiO₂/Si and 3.5 nm MC/MSQ/SiO₂/Si samples. Amorphous carbon (H-Square, Ca) was used as a standard. Amorphous carbon is dense and has a mirror smooth surface. No detectable bulk contamination was determined by RBS, and hydrogen depth profiling showed no bulk contamination of hydrogen at a detection limit of ~0.1%. Given that bare MSQ/SiO₂/Si and MC/MSQ/SiO₂/Si are approximately the same thickness, the carbon content of MC/MSQ/SiO₂/Si was obtained by comparing the carbon contents in both films using the backscattering geometry and cross-sectional data determined by the amorphous carbon standard. An increase in carbon content of 1.54×10^{17} atom cm² was found for the 3.5 nm MC/540 nm MSQ/SiO₂/Si film. Adding a stoichiometric quantity of hydrogen (C₈H₈) brings the total areal density to 3.08×10^{17} atom cm². The bulk density of MC is 1.02×10^{23} atom cm³, so an equivalent MC thickness of approximately 30 nm was deposited in/on MSQ/SiO₂/Si. Figure 5 shows the substrate subtracted ion beam backscattering spectra. Qualitatively it can be seen that the carbon content of the front two-thirds of the film has a statistically significant increase in carbon content. To estimate the increase in dielectric constant, a uniform penetration of the MC layer was assumed. The MSQ films are 540 nm thick and contain 50% porosity, so an MC equivalent thickness of 30 nm evenly distributed through



Figure 6. AFM measurements: (a) bare $MSQ/SiO_2/Si$, (b) $MC/MSQ/SiO_2/Si$, (c) plot of rms roughness as a function of MC thickness, and (d) lateral correlation length as a function of MC thickness.

the MSQ film would fill 11.1% of the porosity. An upper bound to the calculation of the composite film dielectric constant can be found by adding the contribution of components in parallel¹⁵

$$k_{\rm tot} = k_1 P_1 + k_2 P_2 + k_3 P_3, \qquad [1]$$

where k_{tot} , k_1 , k_2 , and k_3 are the dielectric constants of the total film, air, MC, and the dense MSQ, respectively. P_1 , P_2 , and P_3 are the respective fractions of air, MC, and the dense MSQ. An increase of approximately 4% in the dielectric constant should be expected. Capacitance-determined dielectric constant increase of $1.5 \pm 3.3\%$ for a 3.7 nm thick MC/MSQ/SiO₂/Si is consistent with these results.

Roughness was measured by AFM and quantitative information about surface morphology was extracted from a height-height correlation function defined elsewhere.¹⁶ Figure 6a and b show the AFM images of bare MSO/SiO₂/Si and 5 nm MC/MSO/SiO₂/Si samples, respectively. At 4 nm, a suitable MC thickness to prevent penetration, the root mean square (rms) roughness is 0.62 nm greater than the bare MSQ/SiO₂/Si sample. The morphology after deposition shows an initial increase in roughness followed by an apparent smoothing as deposition proceeds (Fig. 6c). The lateral correlation length continues to increase with deposition thickness and increases from an initial 20 nm for the bare MSQ/SiO₂/Si to 44.6 nm in the 5 nm thick MC/SiO2 /Si coated sample. An increase in the lateral correlation length indicates that as the film grows there is some long range smoothing. The lateral correlation length is roughly the wavelength of fluctuation of the surface. The lateral correlation length changes are evident in the AFM images of bare MSQ (Fig. 6a) and 5 nm MC coated MSQ (Fig. 6b) by an overall increase in surface feature size

During deposition of *p*-xylylene monomer ($-C_8H_8$ -), two chemical reactions can occur at the surface, initiation, in which new polymer molecules/chains are generated, and propagation, in which existing polymer molecules are extended to higher molecular weight.¹⁷ It is, perhaps, this effect which results in the decrease in roughness,

whereas the lateral correlation length continues to increase. As the oligimer grows it tends to align itself parallel to the substrate surface.

Vaeth *et al.*¹⁸ showed inhibited polymer growth on a copper surface. 335 nm of polymer grew on a silicon substrate before any growth occurred on copper. Selectivity is a highly desired quality of the free radical polymerization process used here. For dual damascene structures in the back end of line processes there would be no growth on the underlying copper layer. Only the dielectric would be coated, and there would be no series contribution to ohmic contact from the MC film. This would alleviate the need to etch back the dielectric liner and therefore reduce the number of processing steps.

Thermal stability of poly(p-xylylene) films deposited with the reactor used in these studies has been studied previously.¹⁹ Thermal desorption studies (TDS) revealed the onset of decomposition at about 400°C. In addition, small thickness changes due to isothermal annealing in vacuum were detectable after 2 h at 410°C. Future work will test the thermal stability of poly(p-xylylene) films as used in this application.

Conclusions

A polymer liner as thin as 3.5 nm has been shown to prevent copper penetration during CVD. The liner has a low dielectric constant (2.65) and effectively seals the porous dielectric. The amount of liner penetration resulted in a negligible increase in dielectric constant as determined by capacitance measurements. AFM results show a 0.62 nm increase in rms roughness of the sealed MSQ surface. The sealant is a selective CVD process and will not deposit on the underlying Cu surface. Selective growth in this manner reduces the number of process steps by possibly eliminating the need to etch back the liner before further metallization steps in a via or trench structure.

The free radical polymerization film deposition process used here contains beneficial fundamental properties, such as, initial reactions of condensation followed by two to three orders of magnitude growth rate increase by subsequent propagation.¹⁷ The rapid growth rate after initiation should aid in quickly sealing off the top layers to

further penetration and thus result in a conformal low dielectric constant liner. In the future we will present results on alternative sealants including adhesion and thermal stability.

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