

**Development of barrierless dielectrics and their integration with
copper for nanodevice wiring.**

by

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ABSTRACT

Future generation integrated circuits require the development and integration of new low dielectric permittivity (e.g., $\kappa \ll 2.5$) materials with copper wiring such that the chemical and mechanical stability of the metal-dielectric interface are preserved. Introducing pores and/or including low electronic polarizability bonds such as Si-C, C-C and C-H are promising strategies to lower κ dielectrics. Presently, 5-10 nm interfacial layers comprised of inorganic materials are used to inhibit metal and water intake into the dielectric, and enhance metal-dielectric adhesion. Recent work has shown that these features can be achieved using ultrathin (<2 nm) molecular nanolayers, but integrating them with device processing schemes, or devising strategies to eliminate the interfacial layer altogether remain challenges.

This thesis investigates strategies to obviate the use of a separate barrier/glue layer for integrating low-k dielectrics with metals. This is a problem of fundamental importance because low polarizability groups in low-k materials bond poorly with metals, and lead to rapid metal diffusion. We study two approaches, namely, incorporating metal-/water-blocking and adhesion enhancing moieties in the dielectric during synthesis or processing, or exploiting interfacial reaction between the dielectric and the metal to inhibit copper diffusion and enhance adhesion. Mesoporous silica and carbosilane polymer serve as model systems for our investigations of the two approaches. This understanding provides insights that could enable the design of a new class of “barrierless” low- κ materials with inherent resilience to metal and water uptake, and provide good adhesion with copper without the use of a separate interfacial layer.

Functionalizing mesoporous silica (MPS) with organosilanes having different chemical moieties can be utilized to tailor the chemical stability of MPS and Cu/MPS structures against water uptake and copper diffusion. We show that MPS functionalized with trimethyl and tetrasulfide organosilanes inhibit copper diffusion as well as water uptake, and increase the time for dielectric breakdown. The hydrophobic trimethyl termini inhibit moisture uptake while the use bis[3-(triethoxysilyl)propyl] tetrasulfide BTPTS is efficient in decreasing Cu-induced leakage currents. Our studies also show that the sequence of organosilane treatments can have a significant bearing on the roles of the individual organosilanes due to steric and chemical effects. For example, MPS films treated by trimethyl-chloro-silane(TMCS) followed by BTPTS organosilane treatment results in a film with a lower relative dielectric constant and one that is more stable against moisture-induced instabilities, compared with films functionalized in the reverse sequence. Our results reveal that surface passivation induced physical blocking of Cu ions is the dominant mechanism for copper immobilization by longer organosilane in MPS. The chemical moieties in the organosilane also contribute to copper immobilization but that contribution is significantly lower.

Incorporating organosilanes into MPS during synthesis of the dielectric by sol-gel processing can enhance the chemical and mechanical stability. For example, incorporating cyanide-terminated 2-cyano-ethyl-trimethoxysilane (CTS) organosilane into MPS during dramatically improves the time-to-failure of the CTS-MPS films and enhances both the hardness and the modulus of the film. The reduced water uptake due to hydrophobic tails combined with surface passivation and chemical interaction by

cyanide moieties improves the copper immobilization and enhances the electrical stability. Thus, a one step functionalization MPS by an organosilane with a suitable backbone and chain length by in-situ or post deposition technique can be utilized to enhance the diffusion barrier properties and/or mechanical properties of mesoporous silica films.

Another key finding in this thesis is that Cu oxide surface catalyzes the crosslinking of cyclolinear polycarbosilane (CLPCS), a low- κ polymeric precursor, containing disilacyclobutane rings, leading to a thermoset film adherent to the copper surface. Additionally, crosslinking occurs at a higher rate at lower temperatures ~ 160 °C compared to those on oxidized Si or Al surfaces, providing a means to selectively form the dielectric on copper. Air curing of the CLPCS polymer on copper results in excellent interfacial toughness due to PCS-O-Cu bridges formed by the catalytic opening of disilacyclobutane rings in PCS by oxygen bound to the copper surface. Vacuum curing also promotes catalytic ring opening and crosslinking, but the formation of metallic Cu(0) by surface oxide reduction precludes the covalent anchoring of the opened moieties to the metal surface. These results, combined with earlier studies showing low- κ values of the CLPCS films, their impermeability to copper intake and aggressive chemical treatments offer attractive possibilities for integrating carbosilane-based dielectrics directly with copper, without a diffusion barrier or adhesion layer. The results from this thesis are of importance for developing low- κ materials with intrinsic/inherent diffusion barrier and/or adhesion properties.