Electrical and mechanical properties of molecularly functionalized mesoporous silica thin films

by

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ABSTRACT

Mesoporous silica (MPS) thin films are attractive for achieving low relative dielectric permittivity (low-κ) interlayer isolation in integrated circuit wiring, but are susceptible to instabilities in electrical behavior due to water uptake and copper diffusion. This work investigates the electrical, chemical, and thermal instabilities, Cu diffusion, and adhesion of these materials for evaluating and enabling their use for applications as interlayer insulators in nanodevice wiring.

Upon annealing Al/MPS/Si(001)/Al capacitors between 80 to 200 °C, the flat-band voltage first increases, reaches a maximum, and then decreases. Concurrently, the initially observed deep depletion behavior is replaced by strong inversion. Subsequent air-exposure restores the preanneal C-V characteristics. Kinetics analyses reveal two thermally activated processes: proton generation through fissure of silanol bonds (activation energy E_{a1} = 0.42 ± 0.04 eV) and proton-induced depassivation of dangling bond traps (E_{a2}=0.54 ± 0.05 eV) at the MPS/Si interface. We present an empirical model correlating these processes with the C-V characteristics.

Further, we show that capping MPS films with a trimethyl-terminated organosilane irreversibly suppresses moisture-induced capacitance instabilities, and decreases the relative dielectric permittivity and Cu-induced leakage currents. Analysis of capacitance-voltage and current-voltage characteristics along with infrared spectroscopy shows that the trimethyl organosilanes inhibit hydrogen bonding of water molecules by rendering the dielectric surfaces hydrophobic.

Fracture behavior and mechanical properties of pristine (i.e., un-functionalized MPS) and silylated mesoporous silica (SMPS) films were studied by four-point bend

tests and nanoindentation measurements. Four-point bend measurements on Si/epoxy/Ti/Cu/MPS/Si stacks show that structures with un-silylated MPS films fracture at ~3 J/m^2, while those with SMPS films show a ~50% lower fracture energy. X-ray photoelectron spectroscopy (XPS) of fracture surfaces reveal that for both cases, fracture occurs inside the MPS films, but closer to the Cu overlayer. These measurements, along with nanoindentation, thin film stress and Fourier transform infrared (FTIR) spectroscopy measurements further reveal that silylation modifies the mechanical properties of the MPS films. Analysis of fracture surface chemistry using variable take-off angle X-ray photoelectron spectroscopy (ARXPS) and depth profiling shows that the fracture pathway is governed by the depth of metal penetration into the MPS layer during vapor-deposition. Similar changes in mechanical properties were observed in MPS films functionalized with cyanide- (CTS-MPS) and mercaptan-terminated (MPTS-MPS) organosilanes.

Thermal stability of CTS-MPS and MPTS-MPS was studied by annealing the films at temperatures up to 500 °C in vacuum, nitrogen and air. XPS and Auger electron spectroscopy analyses indicate that the molecules are attached to the external surfaces of the films as well as the pores inside the films. The cyanide-functionalized MPS films are stable up to 500 °C in vacuum, N_2 and air ambient. In contrast, mercaptan-functionalized MPS films are stable only up to 400 ^{o}C in vacuum due to the higher reactivity of mercaptan with oxygen.

Another key finding of this thesis is that the pore structure in MPS films is a crucial factor that governs their electrical and mechanical properties. MPS films with ordered pores oriented parallel to the substrate (2D-hexagonal) exhibit more than a 4-

fold enhancement in Cu-induced dielectric breakdown time in comparison to pores organized in a cubic fashion (3D-cubic). Additionally, upon silylation there is more than 50% decrease in elastic modulus of 2-D hexagonal MPS films in comparison to 20% in 3D-cubic MPS films. Four-point bend measurements on Si(100)/epoxy/Ti/Cu/MPS/Si(001) stacks show that MPS films with 2D-hexagonal MPS films exhibit a lower fracture toughness of ~2.5 J/m^2, than the 3D-cubic MPS films, which show ~3.5 J/m^2. Electron spectroscopy of fracture surfaces reveals that fracture occurs closer to the interface in 2D-hexagonal pore structures due to lesser density of surface open pores. Our findings are important to tailor electrical and mechanical properties of MPS low-κ dielectrics for future nanodevice components.