LEAD ZIRCONATE TITANATE (PZT) BASED THIN FILM CAPACITORS FOR EMBEDDED PASSIVE APPLICATIONS

By

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KIM, TAEYUN Lead Zirconate Titanate (PZT) Based Thin Film Capacitors For Embedded Passive Applications (Under the direction of Angus I. Kingon and Jon-Paul Maria)

Investigations on the key processing parameters and properties relationship for lead zirconate titanate (PZT, 52/48) based thin film capacitors for embedded passive capacitor application were performed using electroless Ni coated Cu foils as substrates. Undoped and Ca-doped PZT (52/48) thin film capacitors were prepared on electroless Ni coated Cu foil by chemical solution deposition. The effects of processing parameters on the phase evolution, microstructures, dielectric properties, and reliability were investigated. Electroless Ni coated Cu foil was selected as substrate for its low cost, oxidation resistance and lamination capability. When annealed at 450 $_{o}$C, electroless Ni coated Cu foil showed transformation from amorphous Ni to crystalline phase of Ni-P (mostly Ni_3P) and Ni metal.

For PZT (52/48) thin film capacitors on electroless Ni coated Cu foil, voltage independent (zero tunability) capacitance behavior was observed. Dielectric constant reduced to more than half of the identical capacitor processed on Pt/SiO_2/Si. Dielectric properties of the capacitors were mostly dependent on the crystallization temperature. Capacitance densities of almost 350 nF/cm$_2$ and 0.02 ~ 0.03 of loss tangent were routinely measured for capacitors crystallized at 575 ~ 600 $_{o}$C. Leakage current showed dependence on film thickness and crystallization temperature. It is speculated that space-charge limited conduction (SCLC) seems to be consistent with conduction mechanism in PZT thin films on electroless Ni. From a two-capacitor model, the existence of a low permittivity interface layer (permittivity ~ 30) was suggested. Also it is suggested a high concentration of traps exist inside the PZT capacitor. Interface reaction between PZT thin film and electroless Ni was suggested to be responsible for measured electrical properties.

The interfacial layer might be composed of unreacted oxide, phosphate, and phosphides possibly from phosphorous diffused from electroless Ni into PZT bulk.

For Ca-doped PZT (52/48) thin film capacitors prepared on Pt, typical ferroelectric and dielectric properties were measured up to 5 mol % Ca doping. Further addition up to 10 mol % changed the lattice parameter of the unit cell, and reduced dielectric properties were observed. The possibility of Ca acceptor doping is suggested. When Ca-doped PZT (52/48) thin film capacitors were prepared on electroless Ni coated Cu foil, phase stability was influenced by Ca doping and phosphorous content. Dielectric properties showed dependence on the crystallization temperature and phosphorous content. Capacitance density of ~ 400 nF/cm^2 was achieved, which is an improvement by more than 30 % compared to undoped composition. Ca doping also reduced the temperature coefficient of capacitance (TCC) less than 10 %, all of them were consistent in satisfying the requirements of embedded passive capacitor. Leakage current density was not affected significantly by doping. Interface control by controlled pO_2 crystallization was found to be not effective in interface layer mitigation. Phase purity, dielectric properties, surface microstructure, and pO_2 were found to have a correlated dependence. To tailor the dielectric and reliability properties, ZrO_2 was selected as buffer layer between PZT and electroless Ni. Only RF magnetron sputtering process could yield stable ZrO_2 layers on electroless Ni coated Cu foil. Other processes resulted in secondary phase formation, which supports the reaction between PZT capacitor and electroless Ni might be dominated by phosphorous component. Incorporation of ZrO_2 layers reduced maximum capacitance density by 10 % (~ 350 nF/cm^2) due to lower permittivity of ZrO_2 layer. Significantly improved leakage current densities were measured for PZT thin film capacitors on ZrO_2. For PZT thin film capacitors incorporating 100 nm thick ZrO_2 layer, leakage current density of 10^{-8} A/cm^2 was measured at 25 VDC, which is more than three orders of magnitude lower than those directly deposited on electroless Ni coated Cu foil. The complete set of experimental data provides validation and process conditions for the use of PZT thin films on low cost electroless Ni coated Cu foil substrate as embedded capacitors in high density printed circuit boards.