MnO_2 Thin Film Electrodes for Enhanced Reliability of Thin Glass Capacitors

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Many dielectric thin films for energy storage capacitors fail by thermal breakdown events under high-field drive conditions. The lifetime of the device can be improved under conditions where the current path within the defect regions in dielectrics is eliminated. Self-healing electrodes were developed by depositing a manganese dioxide (MnO_2) thin film between the glass substrate and an aluminum film. For this purpose, thin films of MnO_2 on boroaluminosilicate glass were fabricated via chemical solution deposition and heat-treated at temperatures in the range 500°C–900°C. The α-MnO_2 structure was stabilized by Ba^{2+} insertion to form the hollandite structure. The phase transition temperature of α-MnO_2 to Mn_2O_3 is strongly dependent on the Ba concentration, with transition temperatures of 600°C and 675°C with Ba concentrations of [Ba]/[Mn] = 0.04 and 0.1, respectively. The electrical resistivity increased from 4.5 Ω·cm for MnO_2 to 10^5 Ω·cm for Mn_2O_3. Both dielectric breakdown strength and the associated cleared aluminum electrode area increased with an MnO_2 interlayer between Al electrodes and the borosilicate glass. The enhancement in dielectric strength was related with self-healing. The associated redox reaction between MnO_2 and Mn_2O_3 was also proved by RAMAN spectroscopy following dielectric breakdown.