High Dielectric Constant due to the Strain-induced Phase Transition of $BaTiO_3$ nanocubes in an Ordered Assembly

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The dielectric constant of an ordered assembly of $BaTiO_3$ nanocubes (nanocrystals) fabricated using the dip-coating method has been experimentally reported as more than 4000 at 1 kHz for the thickness of the assembly of 290 nm [K.Mimura and K.Kato, Appl.Phys.Express 7, 061501 (2014), Jpn.J.Appl.Phys. 53, 09PA03 (2014)]. The dielectric constant is higher than the normal dielectric constant of a $BaTiO_3$ bulk crystal of about 2000 without any domain contribution [T.Tsurumi et al., Appl.Phys.Lett. 91, 182905 (2007)]. It is higher than that of the nanocrystalline $BaTiO_3$ ceramic which is less than 2000 at room temperature [M.T.Buscaglia et al., Phys.Rev.B 73, 064114 (2006)]. It is even higher than the recently reported high dielectric constant of 2940 at 1 kHz for a $BaTiO_3$ thin film fabricated by layer-by-layer electrohydrodynamic jet deposition of the $BaTiO_3$ nanopowder suspension [J.Liang et al., Materials 9, 61 (2016)]. Moreover, it is higher than the experimental estimates of the static dielectric constant of 2500-4000 for epitaxial $BaTiO_3$ thin films [T.Hamano et al., Appl.Phys.Lett. 83, 5274 (2003)].

In the present paper, the Gibbs function has been derived for a $BaTiO_3$ nanocube under three dimensional (3D) clamping in an ordered assembly taking into account the effect of misfit strain associated with a tilt angle of two attached crystal faces, and numerical calculations of the Gibbs function have been performed [K.Yasui et al., Jpn.J.Appl.Phys. (in press)]. It is assumed that 3D clamping is (nearly) rigid because each nanocube is tightly clamped by the surrounding nanocubes attached face-to-face with the top and bottom surfaces of the assembly fixed with Pt electrodes. It is different from normal nanocrystalline (polycrystalline) ceramics with elastic clamping. As a result, it is shown that a $BaTiO_3$ nanocube undergoes phase transition from the tetragonal to cubic crystal structures at a misfit strain at room temperature. As is already known for a $BaTiO_3$ single crystal under 3D clamping, the phase transition becomes second order rather than first order observed for a free-standing $BaTiO_3$ single-crystal. As a result, the dielectric constant nearly diverges at the phase transition. This is considered to be the reason for the high dielectric constant for an ordered assembly of $BaTiO_3$ nanocubes. In the actual assembly, a tilt angle of two attached crystal faces as well as the misfit strain has a wide distribution. Thus the dielectric constant of the total (the measured part of) assembly comprises of series and parallel connections of all the capacitors (nanocubes) in an assembly. The total capacitance (dielectric constant) dramatically decreases when there is a low capacitance in the series connections in the thickness direction. Thus thinner assembly can result in higher capacitance (dielectric constant) as the probability of the presence of a low capacitance in the thickness direction is lower. This agrees with the experimental observation that an assembly of 580 nm thickness has lower dielectric constant than that for an assembly of 290 nm thickness [K.Mimura and K.Kato, Appl.Phys.Express 7, 061501 (2014), Jpn.J.Appl.Phys. 53, 09PA03 (2014)].