Comparative Study of Phase Transitions in Polycrystalline and Epitaxial BaTiO$_3$ Thin Films by Means of Specific Heat Measurements

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At the last decade the number of works concerned with the study of the size effects in ferroelectrics increased essentially. The fundamental size effect for films, whiskers and small-size particles are under theoretical and experimental investigations because of its importance for ferroelectric nanoscale device applications and “critical size” question to be solved. In this report we give the short review of the finite-size effects in nanostructured ferroelectrics; in our study the main attention is given to the specific heat measurements of BaTiO$_3$ thin films by the dynamical 3ω-method for both polycrystalline and epitaxial thin films sputtered on the massive substrate. The phase transition temperature, transition smearing, excess entropy and spontaneous polarization can be determined from these data, giving the comprehensive characterization of the phase transition in the films. The thickness limitation for the method is 30-50 nm; in fact sometimes the specific heat temperature dependence gives the more reliable information about the electric properties of the films than the direct measurements of the spontaneous polarization reversal.

It is shown that the thermal properties of the fine particles [1], nanostructured ceramics [2] and polycrystalline BaTiO$_3$ films on SiO$_2$ substrate [3] in the linear size range 50-1000 nm are very similar and support the existence of the fundamental finite-size effect in all these cases; the difference became apparent only for the value of the critical size of the particles (grains) obtained by extrapolation of the transition temperature to zero against the reciprocal linear size. There are two characteristic sizes for the polycrystalline films – that is the film thickness and the average grain size. Therefore we studied thermal properties of two groups of films - one with nearly constant grain size and variable thickness and another with constant thickness and variable grain size. The critical sizes were estimated in the both cases as 2.6 nm for the film thickness and 8 nm for the grain size.

The results of specific heat measurements for the epitaxial films (BaTiO$_3$+MgO) in the range of thicknesses 50-450 nm are quite different (fig. 1). The maximum of the diffused specific heat anomaly was found to be shifted to higher temperatures, the larger shift for thinner films. This effect is in agreement with the theory taking into account misfit mechanical strains which are sufficiently relaxed due to arising of the misfit dislocations. The possibility of the existence of the critical thickness in this case will be discussed.

Fig. 1 Temperature dependences of the specific heat of epitaxial BaTiO$_3$ films on a MgO substrate.

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References