# Effect of Grain Size on Ferroelectric Films using Effective Medium Theory

## J. Thongsri*

*Research Unit on Mechanical Reliability Technology, College of Data Storage Innovation, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand*

*\*Corresponding author. E-mail: ktjatupo@kmitl.ac.th*

## ABSTRACT

*Based on effective medium theory, the temperature dependence of effective dielectric permittivity, $\varepsilon_e(T)$, on the core radius (a) and thickness (t) of non-ferroelectric dead layer (DL) on the surface of inhomogeneous grains of ferroelectric film made up of cylindrical ferroelectric grains was theoretically investigated. It was found that $\varepsilon_e(T)$ increases with increasing core radius and decreases with increasing DL thickness. In this study, an equation expressing the relationship among $\varepsilon_e$, a and t was derived. This equation is useful for preparing ferroelectric film to desired properties.*

**Keywords:** Effective medium Theory, Ferroelectric film, Dielectric permittivity

## INTRODUCTION

(Ba,Sr)TiO$_3$ (BST) thin film is a leading candidate among high dielectric materials for producing high-density, dynamic, random-access memory. The size of the dielectric constant of a thin ferroelectric film depends on its thickness. Since the tiny size of modern devices require films thinner than tens of nanometers, its dielectric constant is markedly suppressed, making it an apparently less attractive choice. This suppression phenomenon is referred to as effect of grain size. In order to explain this effect, a postulate of "dead layer" (DL) was proposed (Lee and Hwang, 2000). It was confirmed later by a study of a BST thin film based on a series capacitor model (Chen et al., 2004) that each of the film's grains has a ferroelectric core surrounded by a non-ferroelectric surface dead layer that drastically alters the effective permittivity of the film. Because this dependency is so important in making a decision whether to use this material, a more in-depth investigation of the effect of grain size on thin ferroelectric film is clearly warranted.

Based on an average field method, Vendik et al. (2007, 2008) theoretically studied the dependence of effective dielectric permittivity of a nanostructured ferroelectric film on the size of its spherical and elliptical grains and the thickness of these grains' DL. He found a similar dependency trend to a previous experiment (Vendik et al., 1997).

Effective medium theory (EMT) was originally proposed by Hashin (1968) in his study of effective properties of spherical two-phase composite materials. In one of our previous studies, we used his EMT to model a two-phase, strongly nonlinear, dielectric composite and to predict its effective nonlinear coefficients (Thongsee and Natenapit, 2007). We found that the modeling results were in good agreement with experimental results, confirming the reliability of the EMT.

In this study, the EMT was used to model, in two dimensions, a ferroelectric film having cylindrical grains in order to determine the effect of their size on the film. Additionally, the temperature dependence of effective permittivity on grain size and DL thickness was theoretically determined.

## MATERIALS AND METHODS

In an EMT model, a ferroelectric film is considered to be composed of cylindrical grains. Each grain has a ferroelectric core with radius $a$, surrounded by a concentric non-ferroelectric shell with radius $b$. All of the grains are embedded in a homogeneous medium. The permittivities of the core, the shell and the effective medium are $\varepsilon_c$, $\varepsilon_s$ and $\varepsilon_e$, respectively. Figure 1 shows a picture of a grain, modeled according to the EMT, with shell thickness $t = b\text{-}a$.
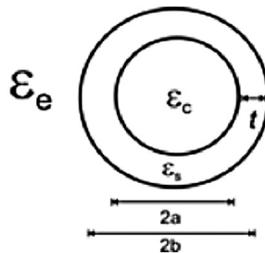


**Figure 1.** Schematic diagram of a grain modeled in the EMT.

To determine the effective permittivity of a ferroelectric film ($\varepsilon_e$), solutions of the following Laplace equations in cylindrical coordinate were solved for:

$$\phi_c(r,\theta) = Ar\cos\theta, \qquad 0 \leq r \leq a \tag{1}$$
$$\phi_s(r,\theta) = (Br + \frac{C}{r})\cos\theta, \quad a \leq r \leq b \tag{2}$$
$$\phi_e(r,\theta) = (-r + \frac{D}{r})\cos\theta, \quad b \leq r < \infty \tag{3}$$

where $\phi$ is the electric potential and the subscripts $c$, $s$ and $e$, refer to the core, the shell and the effective medium, respectively.

The constants $A$, $B$, $C$ and $D$ in equations (1) - (3) are determined by using the boundary condition of continuity at the core and the shell surfaces. Under this condition, the expression of A becomes:

$$A = \frac{-4b^2 \varepsilon_s \varepsilon_e \hat{E}_0}{v_c(\varepsilon_c - \varepsilon_s)(\varepsilon_s - \varepsilon_e) + (\varepsilon_c + \varepsilon_s)(\varepsilon_s + \varepsilon_e)}, \tag{4}$$

where $E_0$ is an external electric field and $v_c = a^2 / b^2$.

The effective permittivity of a medium with volume $V$ was defined by Hashin (1968) as:

$$\varepsilon_e \langle E \rangle = v_c \varepsilon_c \langle E_c \rangle + v_s \varepsilon_s \langle E_s \rangle, \tag{5}$$

where $\langle E \rangle = (1 / V) \int_V |E| \, dV$. $v_c$ and $v_s$ are the volume packing fractions of the core and the shell, respectively, constrained by $v_s = 1 - v_c$.

It was stipulated that the volume average of the electric field inside the medium is uniform throughout (Hashin, 1968) with a solution $\langle E \rangle = E_0$. This stipulation leads to an expression:

$$v_c \langle E_c \rangle + v_s \langle E_s \rangle = E_0. \tag{6}$$

Combining equations (5) and (6) yields:

$$\varepsilon_e E_0 = \varepsilon_s E_0 + v_c (\varepsilon_c - \varepsilon_s) \langle E_c \rangle. \tag{7}$$

From the stipulated volume average of the electric field inside the core, an expression $\langle E_c \rangle = -A$ is formed. Substituting expression (4) into (7), the terms were rearranged so that the effective permittivity of the ferroelectric film is expressed as:

$$\varepsilon_e = \varepsilon_s \left[ 1 + \frac{v_c}{\frac{\varepsilon_s}{\varepsilon_c - \varepsilon_s} + \frac{v_s}{2}} \right]. \tag{8}$$

This equation is well known in the study of effective linear coefficients of two-phase cylindrical composite materials (Hashin, 1968). An alternate expression for $\varepsilon_e$ is given by:

$$\varepsilon_e = \varepsilon_s \left[ \frac{\varepsilon_c(b^2 + a^2) + \varepsilon_s(b^2 - a^2)}{\varepsilon_c(b^2 - a^2) + \varepsilon_s(b^2 + a^2)} \right]. \tag{9}$$

Substituting $b = a + t$ into equation (9) and neglecting the second power of small values of $t$, as well as approximating $b^2 \cong a^2 + 2at$, an expression of the effective permittivity of a ferroelectric film as a function of the size of its grains ($a$) and the thickness of the grains' dead layer ($t$) was found to be:

$$\varepsilon_e = \varepsilon_c \left( 1 + \frac{t}{a} + \frac{\varepsilon_s}{\varepsilon_c} \frac{t}{a} \right) \Big/ \left( 1 + \frac{t}{a} + \frac{\varepsilon_c}{\varepsilon_s} \frac{t}{a} \right). \tag{10}$$

## RESULTS AND DISCUSSION

In this study, a few important results reported in the literature were used as the basis for analysis. Vendik et al. (2007) has reported a temperature dependence of the permittivity of a homogeneous ferroelectric film of $Ba_{0.65}Sr_{0.35}TiO_3$ (BST) with a structural quality factor of $\xi_s = 0.9$, based on a phenomenological model. Their result is shown in Figure 2. Another study by Chen et al. (2004) stated that a

shell exhibits non-ferroelectric properties when its thickness (*t*) is about 3 nm, the permittivity of its DL ($\varepsilon_s$) is in the order of 40, and the permittivity was assumed to be temperature dependent. Using the permittivity of the core as reported by Vendik et al. in figure 2 and the permittivity of the DL as reported by Chen et al. cited above, the temperature dependence of the effective permittivity of the ferroelectric film for several sizes of core radius were determined, as shown in Figures 3 and 4.
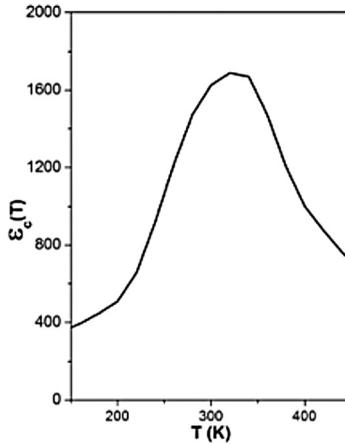
**Figure 2.** The temperature dependence of the permittivity of ferroelectric core ($\varepsilon_c$) based on phenomenological model (Vendik et al., 1997).
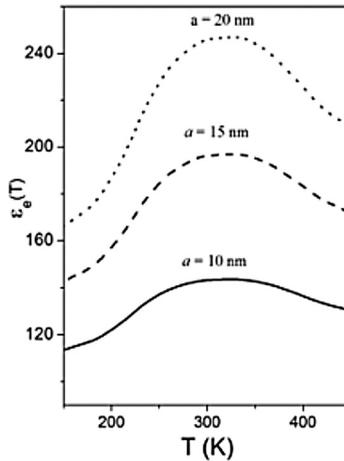
**Figure 3.** The temperature dependence of the effective permittivity ($\varepsilon_e(T)$) of ferroelectric film for a DL thickness *t=3* nm at three sizes of core radius (a).
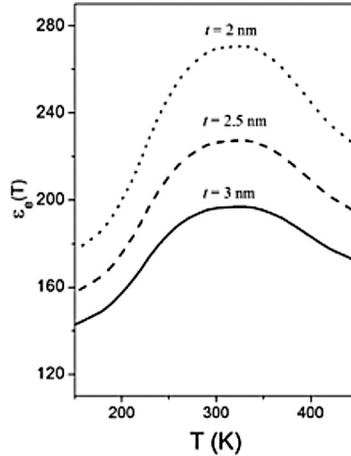
**Figure 4.** The temperature dependence of the effective permittivity ($\varepsilon_e(T)$) of ferroelectric film for a core radius of $a=15$ nm at three different sizes of DL thickness ($t$).

Figure 4 shows the temperature dependence of the effective permittivity ($\varepsilon_e(T)$) for a core radius $a=15$ nm at three sizes of DL thickness. It can be seen that $\varepsilon_e(T)$ increases with decreasing DL thickness. Since the permittivity of the shell is less than that of the core, decreasing the size of the DL thickness increases the $\varepsilon_e$ of a ferroelectric film.

By comparing the reported size of $\varepsilon_c(T)$ of the monocrystalline ferroelectric film shown in Figure 2 with those determined by this paper's analysis shown in Figures 3 and 4, it can be deduced that the existence of DL reduces the effective permittivity of the ferroelectric film. This trend is similar to the trend reported by Berge et al. (2007) in their study of the nanostructure of BTO thin film grown on multilayer metal electrode by pulsed laser deposition, whose growth was controlled by varying the growth temperature.

Furthermore, we also applied the EMT to investigate the temperature dependence of effective permittivity ($\varepsilon_e(T)$) in the study of effective permittivity of a nanostructure ferroelectric film consisting of the spherical grains. The results are consistent with those reported in the study of Vendik et al. (2007) using average field method, since the electric fields inside the ferroelectric film are uniform. However, the result of our study in this case is not reported in this article, but also confirms the reliability of the EMT.

This study has produced several useful results. The most important result is the derived equation expressing the relationship among $\varepsilon_e(T)$, $a$ and $t$ [equation (10)]. This equation is useful for finding the right parameters for preparing a ferroelectric film to a desired property. For instance, if we want to make a film having $\varepsilon_e(T) \approx 220$, and we know that $\varepsilon_s = 40$, we need to prepare the film at 300 K with a core size $a = 15$ and a dead layer thickness of 2.5 nm. Another useful result is that the temperature dependence of effective permittivity determined in this study can be used to predict the best temperature range for film preparation.

For example, a (Ba,Sr)TiO$_3$ (BST) film is an essential component in the production of dynamic random-access memory (DRAM). The film's dielectric constant needs to be high, and this property depends strongly on its effective permittivity $\varepsilon_e(T)$. The temperature dependence curves in Figures 3 and 4 indicate that a film with the highest $\varepsilon_e(T)$ can be achieved at the preparation temperature range of 300-350 K.

## CONCLUSION

In this study, effective medium theory was used to model a ferroelectric film made up of cylindrical grains and its effective permittivity ($\varepsilon_e(T)$) was investigated in two dimensions. The temperature dependence of effective permittivity ($\varepsilon_e(T)$) was determined as a function of grain size ($a$) and DL thickness. It was found that $\varepsilon_e(T)$ increases as core radius increases at a DL thickness of $t$=3 nm. Furthermore, for a core radius of $a$=15 nm, $\varepsilon_e(T)$ increases with decreasing DL thickness. It can be concluded that the existence of DL reduces the effective permittivity of a ferroelectric film. These results are useful for characterizing a thin ferroelectric film and for improving its permittivity property.

## ACKNOWLEDGEMENTS

## REFFERENCES

Lee, B. T., and C. S. Hwang. 2000. Influences of interfacial intrinsic low-dielectric layers on the dielectric properties of sputter (Ba,Sr)TiO$_3$ thin films. Appl. Phys. Lett. 77: 124-126.

Chen, B., H. Yang, L. Zhao, J. Miao, B. Xu, X. G. Qiu, and B. R. Zhao. 2004. Thickness and dielectric constant of dead layer in Pt/(Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$/YBa$_2$Cu$_3$O$_{7-x}$ capacitor. Appl. Phys. Lett. 84: 583-585. DOI :10.1063/1.1644342

Vendik, O.G., N. Yu. Medvedeva, and S. P. Zubko. 2007. Size effect in nanostructured ferroelectric films, Tech. Phys. Lett. 33: 231-234. DOI: 10.1134/S1063785007030145

Vendik, O.G., N. Yu. Medvedeva, and S. P. Zubko. 2008. Effective permittivity of a nanostructured film consisting of elliptic ferroelectric grains. Tech. Phys. Lett. 34: 323-326. DOI: 10.1134/S1063785008040160

Vendik, O. G., and S. P. Zubko. 1997. Modeling the dielectric response of incipient ferroelectrics, J. Appl. Phys., 82: 4475-4483. Doi: 10.1063/1.366180

Hashin, Z. 1968. Assessment of the self-consistent scheme approximation: conductivity of particulate composites, J. Comp. Mat. 2: 284-300. DOI: 10.1177/002199836800200302

Thongsee, J., and M. Natenapit. 2007. Effective nonlinear coefficients of strongly nonlinear dielectric composites. J. Appl. Phys., 101: 024103-1-4. DOI: 10.1063/1.2404792

Berge, J., A. Vorobiev, and S. Gevorgian. 2007. The effect of growth temperature on the nanostructure and dielectric response of $BaTiO_3$ ferroelectric films. Thin Solid Films. 515: 6302-6308. DOI: 10.1016/j.tsf.2006.11.139