Journal of the European Ceramic Society 21 (2001) 2135–2139
www.elsevier.com/locate/jeurceramsoc

Theory of scanning nonlinear dielectric microscopy and application to quantitative evaluation

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Received 4 September 2000; received in revised form 2 November 2000; accepted 20 December 2000

Abstract

A theory for scanning nonlinear dielectric microscopy (SNDM) and its application to the quantitative evaluation of the linear and nonlinear dielectric constants of dielectric materials are described. A general theorem for the capacitance variation under an applied electric field is derived and a capacitance variation susceptibility S_{nl} is defined. The results show that the sensitivity of the SNDM probe does not change, even if a tip with a smaller radius is selected to obtain a finer resolution and that SNDM has an atomic scale resolution. Using the theoretical results and the data taken by SNDM, the quantitative linear and nonlinear dielectric properties of several dielectric materials were successfully determined.

Keywords: Dielectric properties; Ferroelectric properties; Scanning nonlinear dielectric microscopy; Tantalates

1. Introduction

Recently, we proposed and developed a new purely electrical technique for imaging the state of ferroelectric polarization and the local crystal anisotropy of dielectric materials, which involves the measurement of point-to-point variation of the nonlinear dielectric constant of a specimen, and is termed the "scanning nonlinear dielectric microscopy" (SNDM).[1–3] This is the first successful purely electrical method for observing the ferroelectric polarization distribution without the influence of the shielding effect by free charge. To date, its resolution has been improved down to one nanometer.[3] However, to understand the dielectric properties using SNDM more deeply, more precise theoretical investigation is required.

In this paper, we present theoretical studies on the image production mechanism for SNDM, and we clarify the reason why such high resolution can be easily obtained, even if a relatively thick needle is used for the probe. Secondly, we examine a depth sensitivity of SNDM and a lateral resolution of SNDM and show that the SNDM has an atomic scale resolution. Moreover, we show successful results of the quantitative measurement of linear and nonlinear dielectric constants of ferroelectric materials.

2. General theorem for the capacitance variation under an applied electric field

We derive a general theorem for the capacitance variation due to the nonlinear dielectric response of a material under an applied electric field. As shown in Fig. 1(a), we consider that a metal conductor with a charge Q and electrostatic potential V exists in the space where the dielectric materials with respective linear and nonlinear dielectric constants of ε^l_{ij} and $\varepsilon^l_{ijk} (l = 1, 2, 3 \ldots)$ are distributed.

Taking the nonlinear dielectric response of the materials into account, the relationship between the stored charge Q in the metal and its potential V can be generally expressed by the polynomial expansion as using the second-order coefficient C_{S0},

$$Q = C_{S0}\left(V + \frac{1}{2}\alpha V^2 + \frac{1}{6}\beta V^3 + \ldots\right) \quad (1)$$

where α and β are second and third order expansion coefficients, respectively.

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PII: S0955-2219(01)00188-1

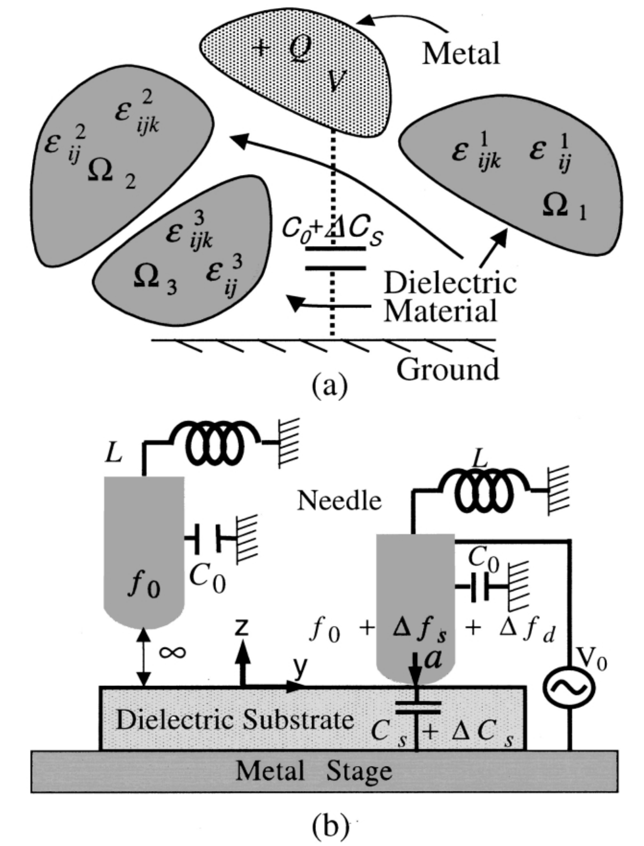

Fig. 1. Models of calculations: (a) capacitance variation under an applied electric field; (b) needle tip of a SNDM.

Further, C_{S0} can be given by

$$C_{S0}\alpha = \sum_l \int_{\Omega_l} \frac{\varepsilon^l_{ijk} E_i E_j E_k}{V^3} \mathrm{d}v \tag{2}$$

where $E_i\,(i = 1, 2, 3 \ldots)$ is the electric field in the material. We also consider the situation in which a relatively large voltage V_0 is applied to the metal, producing a change in its differential capacitance from the nonlinear dielectric response. To measure the differential capacitance variation, a small high frequency voltage $\tilde{V}$ is also superposed on V_0.[2] We substitute $V = V_0 + \tilde{V}$ into Eq. (1) and calculate the relationship between the small high frequency voltage $\tilde{V}$ and the small high frequency charge $\tilde{Q}$ induced by $\tilde{V}$. As the ratio of $\tilde{Q}$ to $\tilde{V}$ gives the differential capacitance $\tilde{C}$, we obtain

$$\tilde{C} = \tilde{Q}/\tilde{V} = C_{s0} + C_{s0}\alpha V_0 + \ldots = C_{s0} + \Delta C_S + \ldots \tag{3}$$

where ΔC_S denotes the first-order differential capacitance variation. Thus, we obtain the final formula which gives the first-order capacitance variation as

$$\frac{\Delta C_S}{V_0} = \sum_l \int_{\Omega_l} \frac{\varepsilon^l_{ijk} E_i E_j E_k}{V^3} \mathrm{d}v. \tag{4}$$

This equation indicates that the first-order variation of differential capacitance per unit applied voltage in a system with arbitrarily shaped boundaries can be precisely calculated as the stored energy per unit applied voltage which is attributable to the nonlinear dielectric constant ε^l_{ijk}. Therefore, Eq. (4) gives the general theorem for the capacitance variation under an applied electric field.

3. Theoretical calculation for SNDM image

Applying Eq. (4) to a model of the tip of the needle of a SNDM probe as shown in Fig. 1(b), we consider the SNDM image theoretically. Like in many papers on scanning probe microscopy, we also modeled the needle tip as a spherical conductor with radius a assuming that the thickness of the sample is much larger than the radius of the pointed end of the needle.[4] Generally, the nonlinear dielectric constant ε^l_{ijk}, which is a third-rank tensor, exists in anisotropic material and there is no ε^l_{ijk} in a material with a center of symmetry. For this calculation, however, we use an isotropic approximation for simplicity, assuming the relationship between the field strength of the electric displacement D and that of the electric field E as

$$D = \varepsilon_{33} E + \frac{1}{2}\varepsilon_{333} E^2 + \ldots \tag{5}$$

where ε_{33} and ε_{333} are the linear and nonlinear dielectric constants defined in the Z-direction. From Eqs. (4) and (5), the first-order capacitance variation in this model is obtained as

$$\frac{\Delta C_S}{V_0} = \varepsilon_{333} \int \left(\frac{E}{V}\right)^3 \mathrm{d}v \equiv \varepsilon_{333} S_{\mathrm{nl}}(\varepsilon_{33}) \tag{6}$$

where the parameter $S_{\mathrm{nl}}(\varepsilon_{33})$ is the quantity giving the capacitance variation per unit nonlinear dielectric constant ε_{333} and we name this $S_{\mathrm{nl}}(\varepsilon_{33})$ the "capacitance variation susceptibility".

The electric fields in this model are obtained by the image charge method found in the standard textbooks of electromagnetic theory. Defining the normalized coordinates with respect to the radius a of the tip of the needle as $x/a = X$, $y/a = Y$ and $z/a = Z$, the three components of the electric field E_x, E_y and E_z are given by

$$E_i(x, y, z) \equiv \frac{V}{a}\bar{E}_i(X, Y, Z) \quad (i = 1, 2, 3). \tag{7}$$

The newly defined normalized electric field components, $\bar{E}_x$, $\bar{E}_y$ and $\bar{E}_z$, are functions of the linear dielectric constant ε_{33} and the normalized coordinates X, Y and Z only and are independent of the radius a and the voltage V. Thus the capacitance variation susceptibility

$S_{nl}(\varepsilon_{33})$ is given by

$$S_{nl}(\varepsilon_{33}) = \int_{-\infty}^{0}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(\bar{E}_x^2 + \bar{E}_y^2 + \bar{E}_z^2\right)^{\frac{3}{2}} dX dY dZ. \quad (8)$$

$S_{nl}(\varepsilon_{33})$ is a function of ε_{33} only and does not depend on the tip radius a. This implies that the probe sensitivity or signal strength of SNDM does not change even if we choose a probe needle with a smaller tip radius to obtain a finer resolution. In other words, in principle, we can use an infinitely thin probe needle and obtain a clearly resolved image without degradation of the signal to noise ratio of the SNDM signal. This is a beneficial feature of SNDM for observing very small ferroelectric domains and local crystal anisotropy. We calculated $S_{nl}(\varepsilon_{33})$ as a function of the relative dielectric constant of the specimen and obtained the result shown in Fig. 2. $S_{nl}(\varepsilon_{33})$ is almost constant (~0.3) above $\varepsilon_{33}/\varepsilon_0 = 10$.

An application of $S_{nl}(\varepsilon_{33})$ to SNDM imaging is to estimate what depth information can be obtained using SNDM. We calculated the depth sensitivity of SNDM by integrating the region from the sample surface to the position $Z = -H = (-h/a)$.

$$DS_{nl}(\varepsilon_{33}, H) \equiv \frac{\int_{-H}^{0}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(\bar{E}_x^2 + \bar{E}_y^2 + \bar{E}_z^2\right)^{\frac{3}{2}} dX dY dZ}{S_{nl}(\varepsilon_{33})}. \quad (9)$$

$DS_{nl}(\varepsilon_{33}H)$ gives the ratio of the signal arising from the region between the surface $Z = 0$ and the position $Z = -H$ to the whole signal strength of the SNDM From the calculated results shown in Fig. 3, it is clear that the SNDM is sensitive in the very shallow areas,

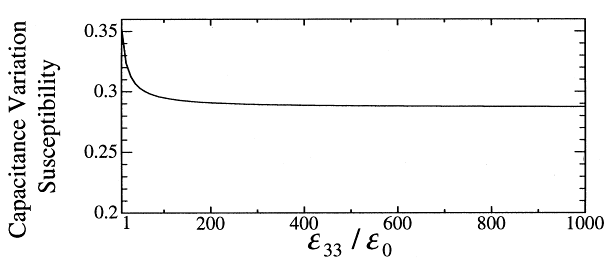

Fig. 2. Capacitance variation susceptibility S_{nl} as a function of linear relative dielectric constant.

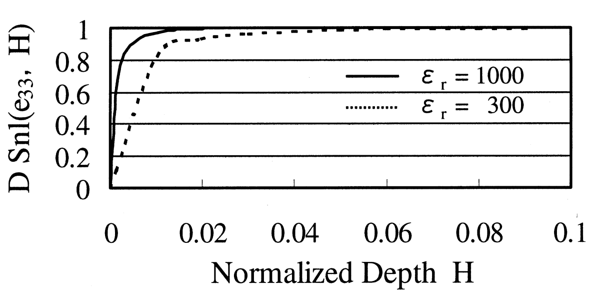

Fig. 3. Depth sensitivity of the SNDM. H denotes the depth normalized to the tip radius a.

especially when the dielectric constant is large. These results are quite understandable, because the electric field under the needle is more highly concentrated with larger dielectric constant. Next, we calculated one-dimensional images of the 180° c–c domain boundary lying at $Y = 0$. These images is obtained by calculating the following equations,

$$I_m(\varepsilon_{33}, Y_0) = \frac{1}{S_{nl}(\varepsilon_{33})}\left(\int_{-\infty}^{Y_0} f(Y)dY - \int_{Y_0}^{\infty} f(Y)dY\right) \quad (10)$$

and

$$f(\varepsilon_{33}, Y) \equiv \int_{-\infty}^{0}\int_{-\infty}^{\infty}\left(\bar{E}_x^2 + \bar{E}_y^2 + \bar{E}_z^2\right)^{\frac{3}{2}} dX dZ \quad (11)$$

where Y_0 is the tip position normalized to the tip radius a. Fig. 4 shows the calculated results. The resolution of the SNDM image is heavily dependent on the dielectric constant of the specimen. For example, for the case of $\varepsilon_{33}/\varepsilon_0 = 1000$ and $a = 10$ nm (a needle tip with a radius of 10 nm is easily obtainable.), the resolution is about 0.1 nm. Thus, we conclude that an atomic scale image can be obtained by SNDM.

4. Quantitative measurement of linear and nonlinear dielectric constant

We describe a quantitative method for measuring linear and nonlinear dielectric constants using SNDM with a LC lumped constant resonator probe. A conceptual figure, describing the measurement of the linear and nonlinear dielectric constant is also shown in Fig. 1(b). In this figure, L and C_0 show the inductance and the stray capacitance (which inevitably exists between the needle and the electrical circuit of the probe), respectively. f_0 is the carrier frequency of the probe when the probe needle is far from the specimen. Δf_s denotes the frequency shift from f_0 when the needle makes contact with the specimen. C_s is the static capacitance variation from C_0 by the tip contact and is much smaller than C_0 and can also be calculated using the image charge method. Thus, we obtain

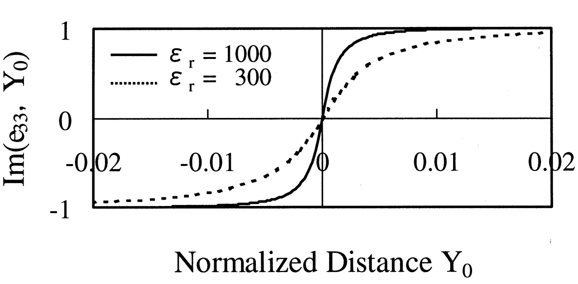

Fig. 4. Calculation for the one-dimensional image of the 180° c–c domain boundary.

$$\frac{\Delta f_S}{f_0} = -2\pi\varepsilon_0 \frac{a}{C_0}\left(\frac{\ln\frac{1}{1-b}}{b} - 1\right). \quad (12)$$

where $b = (\varepsilon_{33} - \varepsilon_0)/(\varepsilon_{33} + \varepsilon_0)$.[4] Eq. (12) indicates that we can obtain the linear dielectric constant of the specimen by a relative measurement using a standard sample, even if the values of the stray capacitance C_0 and the tip radius a are unknown. To check the above results, we measured the carrier frequency shift Δf_S of several dielectric materials. The results are shown in Fig. 5 with the theoretical curve (solid line) adjusted to the data of the standard sample (PZT, $\varepsilon_{33}/\varepsilon_0 = 2000$). Given that both theoretical and experimental data agree well, it is clear that we can determine the absolute value of the linear dielectric constant by a relative measurement using a standard sample.

Next, using $S_{nl}(\varepsilon_{33})$, we can measure the nonlinear dielectric constant quantitatively. We consider the situation in which a relatively large alternating voltage V_0 is applied to the capacitor C_0, producing a change in the capacitance ΔC_S resulting from the nonlinear dielectric response.[1–3] In this situation, the ratio of the frequency deviation Δf_d caused by the applied voltage to the carrier frequency $f_s = (f_0 + \Delta f_s)$ is given by

$$\frac{\Delta f_d}{f_S} = -\frac{1}{2}\frac{\Delta C_S}{(C_0 + C_S)} \approx -\frac{1}{2}\frac{\Delta C_S}{C_0}. \quad (13)$$

From Eqs. (13) and (12), it is apparent that if the tip radius a and the linear dielectric constant ε_{33} are known, we can directly measure the nonlinear dielectric constant (absolute measurement) because C_0 can be calculated using Eq. (12). Moreover, even if the radius a is unknown, we can determine the nonlinear dielectric constant from a relative measurement using a standard sample and the following equation

$$\varepsilon_{333}^{ui} = \varepsilon_{333}^{st}\frac{S_{nl}\left(\varepsilon_{33}^{st}\right) f_S^{st}}{S_{nl}\left(\varepsilon_{33}^{ui}\right) f_S^{ui}}\frac{\Delta f_d^{ui}}{\Delta f_d^{st}} \quad (14)$$

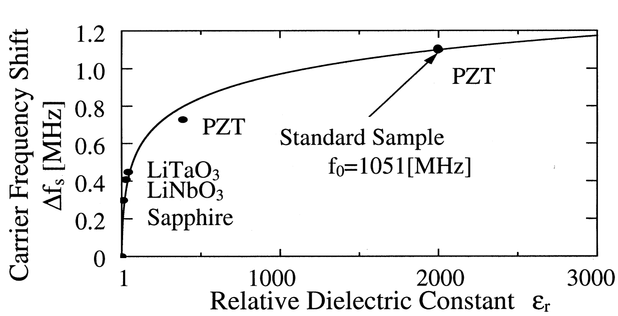

Fig. 5. Carrier frequency shift vs. relative dielectric constant.

Table 1
Nonlinear dielectric constants obtained by SNDM

Sample	ε_{333} by SNDM (F/V)		ε_{333} by the dynamic method (F/V)
	Absolute	Relative	
$LiNbO_3$	-1.65×10^{-19}	-1.12×10^{-19} (standard data)	-1.12×10^{-19}
$LiTaO_3$	-2.79×10^{-19}	-2.80×10^{-19}	-2.26×10^{-19}

where the superscript *st* and *ui* mean "standard sample" and "under investigation", respectively. Δf_d^{ui} and Δf_d^{si} are the measured frequency deviations under the same applied voltage V_0.

Based on the results, we performed an absolute measurement of the nonlinear dielectric constants of Z-cut $LiNbO_3$ and Z-cut $LiTaO_3$ substrates. The tip radius was 12.5 μm. The values of ε_{333} obtained from the absolute measurement by SNDM are given in Table 1 with standard values determined by another accurate standard method termed the "dynamic measuring method of capacitance variation with alternating electric field".[5] The data show good agreement with each other, although the exact evaluation of the tip radius a is fairly difficult. Of course, the relative measurement for ε_{333} is easier and more accurate than the absolute measurement. Thus, we also performed the relative measurement of the nonlinear dielectric constant ε_{333} of Z-cut $LiTaO_3$ using the Z-cut $LiNbO_3$ as the standard sample. In this measurement, we used a probe needle with an unknown tip radius. The result is also shown in Table 1. From the relative measurement, the value of the nonlinear dielectric constant of $LiTaO_3$ was 1.8 times larger than that of $LiNbO_3$. In comparison with the standard value of $\varepsilon_{333}$of $LiTaO_3$ which is 2.0 times larger than that of $LiNbO_3$, both values from the relative measurement and the standard values of the nonlinear dielectric constants show good agreement.

5. Conclusion

We have described the theory of SNDM and its application to the quantitative evaluation of the linear and nonlinear dielectric properties of ferroelectric and piezoelectric materials. From the calculation of the depth sensitivity and one-dimensional images of SNDM, it was shown that the resolution and the depth sensitivity of SNDM are functions of the dielectric constant of the specimen and the tip radius a. For example, in the case of $\varepsilon_{33}/\varepsilon_0 = 1000$ and $a = 10$ nm, atomic scale resolution is obtainable. Moreover, we successfully determined the linear and nonlinear dielectric constants of dielectric materials using SNDM.

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