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Determination of crystal polarities of piezoelectric thin film using scanning nonlinear dielectric microscopy

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Abstract

Using scanning nonlinear dielectric microscopy (SNDM), we determined the polarities of ZnO thin films on various substrates including polar materials. In conventional methods based on detecting the piezoelectric and pyroelectric responses, it is very difficult to determine the polarities of thin films, particularly in the case of growing these films on the polar substrates, because the detected signals from thin films are very small and those from the substrates are large. Our SNDM method, however, enables us to determine the polarities of thin films on polar substrates easily. We also determined experimentally that ZnO thin films grew with a sign opposite to the substrate polarity and it was suggested that pyroelectric effects mainly governed the polarity of ZnO films. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Scanning nonlinear dielectric microscopy; ZnO

1. Introduction

Recently, many types of polar thin films have been developed. Some types of films are used for ferroelectric RAMs and some are used for piezoelectric applications and surface acoustic wave (SAW) devices. It is very important to determine the film polarity, not only from the scientific viewpoint of understanding a film growth mechanism but also from an engineering viewpoint. For example, the electromechanical coupling property of SAW depends strongly on the combination of polarities of a thin film and the substrate.[1] However, it has been difficult to determine the polarity of a thin film by the conventional methods using pyroelectric and piezoelectric responses. In particular, for the configuration of a thin film on a polar substrate, determining the film polarity is quite difficult, because the signal from the film is masked by that from the substrate.

However, we have proposed and developed a new, purely electrical method for detecting the local crystal anisotropy of dielectric materials without using pyroelectric and piezoelectric effects. This method involves the measurement of point-to-point variations of the nonlinear dielectric constants of the specimen, and is termed "scanning nonlinear dielectric microscopy"(SNDM).[2–4]

In this paper, we demonstrate that our SNDM technology is very useful for determining the polarity of thin films deposited on polar and non-polar substrates. We selected ZnO thin films on several kinds of polar and non-polar substrates as samples and measured their polarities. From these, we successfully determined the polarities of ZnO thin films and obtained many important results. For example, we determined that a positive ZnO thin film can grow on a negative Z-cut $LiNbO_3$ and $LiTaO_3$ substrate by electron cyclotron resonance (ECR) sputtering method and that the opposite was also true. We also demonstrate a theoretical reason for determining the polarity of a thin film on polar substrate using SNDM.

2. Determination of the polarities of ZnO thin films on the non-polar substrates

To date, we have determined the polarities of polar materials by detecting their piezoelectric and pyroelectric responses. However, in these methods, as the

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thickness of thin film reduces, the signal, which is proportional to the thickness, becomes weaker. Therefore, it is very difficult to determine the polarity of thin film from piezoelectric and pyroelectric signals. On the other hand, it is generally known that the sign of the third rank tensor, such as nonlinear dielectric constant and piezoelectric constant, changes in accordance with polarity inversion. Therefore, we can easily determine the polarity of the specimen by measuring the nonlinear dielectric constant.

Here, we briefly describe the theory for detecting nonlinear dielectric constants. Detailed descriptions of the microscope principle have been reported elsewhere.[2,3]

Fig. 1 shows the system setup for SNDM using the lumped constant (LC) resonator probe.[3] In the figure, $C_s(t)$ denotes the capacitance of the specimen under the center conductor (the needle) of the probe. $C_s(t)$ is a function of time because of the nonlinear dielectric response under an applied alternating electric field $E_{p3} = E_p \cos\omega_p t$ ($\omega_p = 5$ kHz). The ratio of the alternating variation of capacitance $\Delta C_s(t)$ to the static value of capacitance C_{s0} without time dependence is given as[2]

$$\frac{\Delta C_s(t)}{C_{s0}} = \frac{\varepsilon_{333}}{\varepsilon_{33}} E_p \cos\omega_p t + \frac{\varepsilon_{3333}}{4\varepsilon_{33}} E_p^2 \cos 2\omega_p t, \quad (1)$$

where ε_{33} is a linear dielectric constant and ε_{333} and ε_{3333} are nonlinear dielectric constants.

The LC resonator is connected to an oscillator tuned to the resonance frequency of the resonator. The above-mentioned electrical parts (i.e. the needle, ring, inductance and oscillator) are assembled into a small probe for SNDM whose dimensions are $10\times5\times1$ mm^3. The oscillating frequency of the probe (or oscillator) (around 1.2 GHz) is modulated by the change of capacitance $\Delta C_s(t)$ due to the nonlinear dielectric response under an applied electric field. As a result, the probe

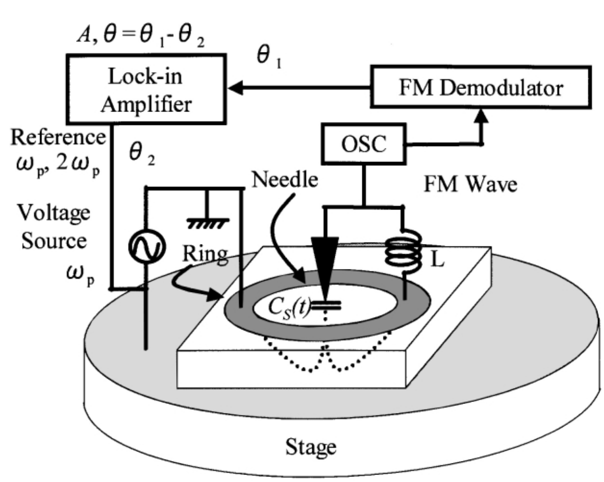

Fig. 1. Schematic diagram of SNDM.

(oscillator) produces a frequency modulated (FM) signal. By detecting this FM signal using the FM demodulator and lock-in amplifier, we obtain a voltage signal proportional to the capacitance variation. In Fig. 1, symbol A and θ denote the signal amplitude and the phase delay from reference signal, respectively. This phase delay shows the sign of nonlinear dielectric constant. Each signal corresponding to ε_{333} and ε_{3333} was obtained by setting the reference signal of the lock-in amplifier at the frequency ω_p of the applied electric field and at the doubled frequency $2\omega_p$, respectively.

Thus, using this microscopy system, we determined the polarities of *c*-axis oriented ZnO thin films on the various substrates, which were fabricated by ECR sputtering method (temperature of substrate: 200–500°C, gas pressure: 10^{-4} Torr).[5] We assumed that the ZnO films deposited on the metals were polycrystalline and the film on the sapphire substrate included both epitaxial and polycrystalline parts, because its thickness was very small. Table 1 presents the results. (In Tables 1 and 2, we show only those polarities of ZnO films which were clearly determined, without the values of the nonlinear dielectric constant, because a distribution of the

Table 1
Polarities of ZNO thin films on the various non-polar substrates

Substrate	Thickness of film (μm)	Polarities of film
NCA/glass	1.9	–
Au/NiCr/glass	1.9	–
NiCr/glass	1.9	–
Ti/glass	1.9	–
Al/glass	2.1	–
Ni/Ti/glass	2.1	–
Ta/glass	1.9	–
C-Plate (0001) sapphire	0.5	+

Table 2
Polarities of ZNO thin films on the various polar substrates

Substrates	Polarity of substrates	Thickness of film (μm)	Polarity of film
$LiNbO_3$			
Y-cut	+	1.6	–
128-cut	+	1.7	–
41-cut	+	1.7	–
Z-cut	+	6.3	–
Z-cut	–	6.3	+
Z-cut	+	1.48	–
Z-cut	–	1.48	+
Z-cut	+	1.7	–
$LiTaO_3$			
36-cut	+	5	–
36-cut	+	6.3	–
36-cut	–	6.3	–
Z-cut	+	6.3	–
Z-cut	–	6.3	+
Z-cut	+	1.48	–
Z-cut	–	1.48	+

values of nonlinear dielectric constant was observed. However, Fig. 5, which is also mentioned later, showed that the value of nonlinear dielectric constant of ZnO was about 30 times lower than that of $LiNbO_3$. The reported value of ϵ_{333} of $LiNbO_3$ is -2.91×10^{-19} F/V, hence the value of ZnO was estimated at about -8×10^{-21} F/V.)

Table 1 indicates that the polarities of ZnO thin films on metal films are negative, while its signal on sapphire is positive. However, we should note that the inversion of polarities of ZnO thin films on the metal / glass substrates was observed in some small areas.

One possible explanation suggested as the determining factor for the polarities on sapphire and metals, is the charging up phenomena caused by argon ion collision on the substrate. That is, when positive argon ions collide with a substrate during the ZnO deposition, the metal film does not charge up because it is connected to the ground. On the other hand, the sapphire substrate charges up positively. Thus, the polarity of ZnO film on the sapphire substrate becomes positive, because ZnO film grows by attraction to this positive voltage (similar to the case of polar substrates mentioned later.) However, some other reports show that the polarity of ZnO film on metal film is positive and that on sapphire is negative.[6,7] These results differ from our results. However, the polarity of the polar film is strongly dependent on the film production conditions. Therefore depending on the conditions of film production, it is necessary to determine the polarity of polar film.

3. Determination of polarities of ZnO thin films on the polar substrates

On the contrary to the above-mentioned determination of polarity of polar films on the non-polar substrates, it is more difficult to determine the polarity of polar thin films deposited on polar substrates. By conventional methods of detecting piezoelectric and pyroelectric responses, the output signal is proportional to the thickness of polar materials so that the signal from the film is masked by that from the substrate.

On the other hand, from theoretical calculations,[8] we have found that the radius of the pointed end of the probe needle and the dielectric constant of the specimen determine the sensitivity in the depth direction of SNDM. Fig. 2 shows the sensitivity in the depth direction of SNDM.

In Fig. 2, the horizontal axis shows the depth normalized by the radius of the pointed end of the probe needle a, the vertical axis shows the signal strength of the SNDM arising from the area between the surface and the point at depth H, which was normalized by the entire signal strength from the material (i.e. $H \rightarrow \infty$). This is the function of the dielectric constant of the material. For example, when we measure a sample with a relative dielectric constant of 300, the output signal is saturated at the point where the normalized depth is 0.1. This means that SNDM is not sensitive to the material which lies below the depth of $H=0.1$a. In other words, this means that SNDM only has sensitivity to the area from the surface to the depth of $H=0.1$a. Thus, in measuring ZnO thin film whose relative dielectric constant is about 10, SNDM has sensitivity to the area up to the depth equivalent to the radius of the pointed end of the probe needle. Accordingly, by using the probe needle whose radius of pointed end is smaller than the thickness of thin film, we can determine the polarity of only the ZnO thin film, even if the substrate also has polarity.

Initially, to confirm that we could measure the polarities of the thin film and substrate, separately, one-dimensional scanning was performed as shown in Fig. 3, where the specimen was ZnO thin film with a thickness of 6.3 μm on Z-cut $LiTaO_3$ substrate with the thickness of 480 μm. In this study, we used the probe needle with a tip radius of 1 μm so that SNDM has sensitivity only for an area from surface to the depth 1 μm. The result is shown in Fig. 4. From this, it is clear that the polarity of the substrate was positive and that of the thin film was negative. As we have found that SNDM has the ability

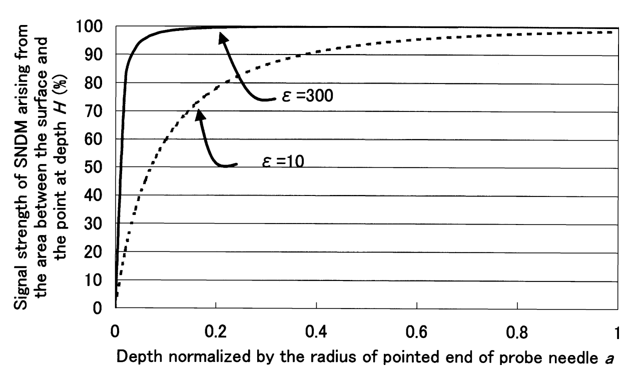

Fig. 2. Sensitivity of SNDM along depth direction.

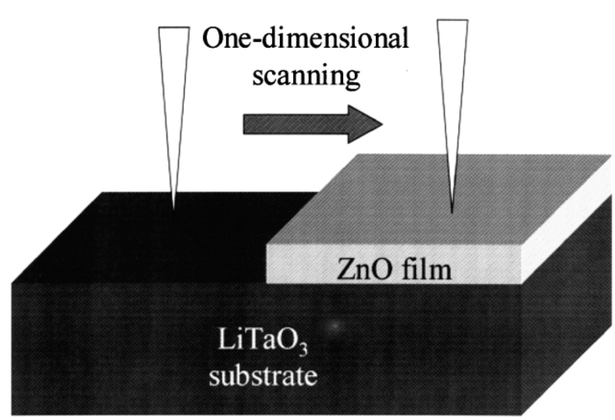

Fig. 3. Measurement of one-dimensional polarity distribution using SNDM.

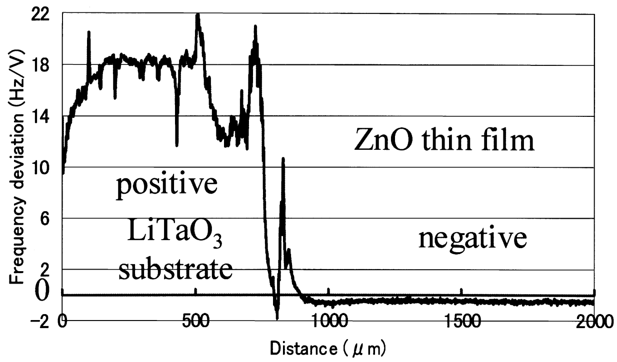

Fig. 4. One-dimensional image scanning on the film edge of ZnO thin film on the $LiTaO_3$ substrate.

to determine the polarity of the polar material clearly, we investigated the polarities of ZnO thin films deposited on $LiNbO_3$ and $LiTaO_3$ substrates varying the combinations of polarization directions of polar substrates and thicknesses of films. The samples in this study were also prepared by the ECR sputtering method[5] and were *c*-axis oriented. Table 2 summarizes the results.

From the data presented in Table 2, we found that positive ZnO thin film grew on the negative Z-cut substrate and the negative one grew on the positive Z-cut substrate. In the case of Y-cut and rotated Y-cut substrates, the tendency was not clear. From the above results, we can explain the polarity of ZnO on the $LiNbO_3$ and $LiTaO_3$ assuming that pyroelectric voltage causes this phenomenon. Fig. 5 shows a film production process.

When ZnO thin film is deposited, the temperature of substrate rises so that the voltage with the sign opposite to the polarity of the substrate is generated at the substrate surface by the pyroelectric effect. Consequently, the ZnO film with the same polarity as the surface voltage grows, because a dipole moment of ZnO is attracted by the pyroelectric electric field. In other words, a

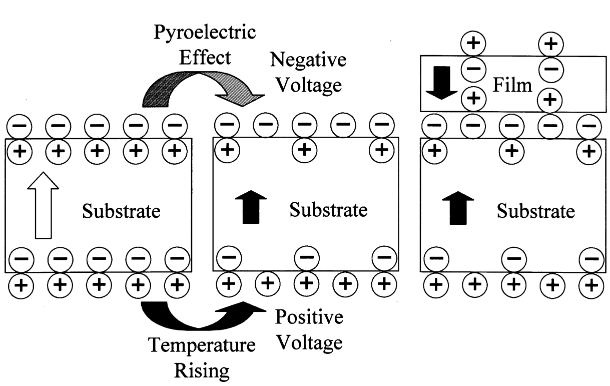

Fig. 5. Schematic illustration of the film growth process.

negative dipole moment on the substrate with the negative voltage is attracted. The authors, however, must point out that ZnO thin film produced under another film growth condition may have another polarity, because the growth mechanism is governed by the electric field around the substrate, and the polarity of the electric field may be different under another film growth condition.

4. Conclusions

Using scanning nonlinear dielectric microscopy (SNDM), we determined the polarities of ZnO piezoelectric thin films on various substrates. We showed that SNDM had the ability to determine the polarity accurately even if the film was extremely thin and was prepared on polar substrate. We also performed basic investigations on growth mechanism of ZnO thin film. From these investigations, we concluded that ZnO thin film with a sign opposite to the polarity of substrate grew on the polar substrate due to pyroelectric effects. However, we have to mention that ZnO thin film produced under other film growth conditions may have other polarities, because the growth mechanism is governed by the electric field around the substrate, and the polarity of the electric field may be different under other film growth conditions. Therefore, depending on the condition of the film production, it is necessary to determine the polarities of polar thin films using our SNDM, each time.

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