JOURNAL OF MATERIALS SCIENCE **34** (1999) 4129–4132

Preparation and characterization of preferred oriented PZT films on amorphous substrates

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The (001) preferred orientation of Nb-doped $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin films was successfully realized on amorphous glass substrate with $LaNiO_3$(LNO) as electrode by rf-sputtering method. It was found that the LNO film greatly promotes formation of the PZT film with pervoskite phase on amorphous substrate and the preferred orientation of the PZT film depends strongly on the process of preparation. The experimental results show that the dielectric constant and loss of the PZT films with the (001) preferred orientation are 1308 and 0.042, respectively, at 1 kHz, 0.05 V. The remanent polarization (P_r), saturation polarization (P_s) and coercive field (E_c) are 34.5, 43 μC/cm^2 and 105 kV/cm, respectively. The PZT films also show a 33 kV/cm internal bias field due to its (001) preferred orientation. The piezoelectric coefficient d_{33} of the PZT film without the poled treatment is about 15 pC/N due to its (001) preferred orientation. The effect of the foreign stress on the piezoelectric voltage response of the PZT/LNO/glass was investigated. The results make us consider using the PZT film as an artificial skin to realize the self-diagnosis of amorphous materials under the action of stress. © *1999 Kluwer Academic Publishers*

1. Introduction

The $Pb(Zr_xTi_{1-x})O_3$ ($x = 0.52$) thin films are attractive materials for various sensors and actuators because of their excellent dielectric, pyroelectric, piezoelectric, and optical properties. These properties depend strongly on their crystallographic orientation and microstructures. Various single crystal materials (such as $SrTiO_3$, MgO, and silicon) were chosen as substrates to obtain preferred orientation or epitaxial thin film [1, 2, 3], but there are very few reports about PZT thin films deposited on glass substrates due to large mismatch in structure. Chang Jung Kim and coworkers reported the fabrication and microstructure of PZT thin films with (100) and (111) preferred orientation on Pt/Ti/glass substrates using Sol-Gel method [4], but they did not describe the electrical properties of PZT films on glass substrates.

As part of the research on self-diagnosis materials and systems, we aim to create piezoelectric thin film on amorphous and polycrystalline substrates instead of single crystal to make the film behave like a sensitive skin on these substrates. Firstly, we must realize the structure assembly between PZT thin films and amorphous glass substrates, then obtain the PZT thin films with preferred orientation, and finally make these films posses better properties.

The lanthanum nickel oxide (LNO) is a metallic oxide with a pervoskite-like structure. In order to solve structural mismatch problem between film and substrate, the LNO film was employed as electrode and buffer layer of the ferroelectric thin film simultaneously. According to some reports, the dielectric loss of $PbTiO_3$ thin film with LNO as electrode on MgO single crystal substrate reached 0.06 and showed better ferroelectric and dielectric properties [5], but the PZT thin film on LNO/Si substrate did not exhibit a good hysteresis loop [6]. However, we strongly believe that we could achieve a preferred orientation of the PZT films when deposited on amorphous glass substrate with LNO as a buffer layer and a bottom electrode. To our knowledge, the PZT thin film with a good dielectric and ferroelectric properties with LNO as bottom electrode has not been successfully achieved so far, even using a single crystal substrate.

2. Experimental

The LNO precursor solution was synthesized by the aqueous method. The pervoskite-like structure LNO thin film was fabricated on micro slide glass by spin coating and thermally annealing process. The details of the preparation technique have been described in literature [7]. The thickness of the LNO thin films was about 400 nm and its resistivity was about $2 \times 10^{-3}\ \Omega \cdot$cm. The PZT thin films were prepared by rf-sputtering technique. The target composition was 0.4 at % Nb-doped $Pb_{1.15}(Zr_{0.52}Ti_{0.48})O_3$. Excess Pb (0.15 mol %) was added to compensate for evaporation loss of lead during sputtering process. The sputtering condition is summarized in Table I. Two kinds of post thermal treatment are discussed here: one is the removal of the sample

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TABLE I Sputtering condition for preparation of PZT thin films

rf power density	1.9 W/cm^2
Target diameter	10 cm
Target-substrate distance	4.5 cm
Sputtering gas	Ar
Gas pressure	2 Pa
Substrate temperature	650 °C
Sputtering time	3 h

from the growth chamber and treating it in a tube furnace in air; the other method is the *in situ* treatment of the sample in growth chamber in vacuum. Effect of substrate on microstructure of PZT thin film was also investigated.

The microstructure of the PZT film was examined using X-ray Diffraction (XRD) technique and their surface morphologies were investigated by a Scanning Electron Microscopy (SEM). To measure the electrical properties of PZT thin films, gold was deposited as the top electrode in the form of dot matrix with 1 mm diameter by DC sputtering method. The dielectric constant and loss of the PZT thin films were measured using NF 2330A LCZ meter (NF Electronic Instruments, Japan). The signal voltage was 0.05 V. The hysteresis loops were observed by a Sawyer-Tower circuit.

The piezoelectric coefficient d_{33} of the PZT films was measured by the static load method using the direct piezoelectric effect [10]. The stress was exerted perpendicularly to the surface of the sample, and could be measured by a pressure gauge. The diameter of the tip was about 1 mm, which was just equal to the diameter of a gold dot in the surface of the sample. The surface of the tip was manufactured carefully to ensure the uniformity of the stress on the sample. Using this method, the piezoelectric effect was determined by increasing or decreasing the stress, which results in the reversible voltage response. Here, the d_{33} does not represent the truly free piezoelectric coefficient of the PZT film since it is clamped to stiff substrate.

3. Results and discussion

Fig. 1 shows the surface morphology of the PZT thin film. It is observed that the fine sub micron grains uniformly distributed across the surface of the film after post thermally treated *in situ* at 650 °C for 2 h. Very small pinholes were seen on the surface of the thin film due to the evaporating of PbO. The size of pinholes is about 20 nm, far smaller than the grain size (the average size of which is on the order of 70 nm). To prolong the post thermally treated time would make the pinholes disappear due to the densification of the PZT film at high temperature after the extra PbO is evaporated. Fig. 1c presents a dense and uniform PZT film treated for 3 h. The two kinds of post thermally treated processes showed a little difference in SEM micrographs. The surface of the film post thermally treated in the tube furnace at 650 °C for 2 h still had some impure PbO phase (as shown in Fig. 1b). It is consistent with the result of XRD below.

As shown in Fig. 2a, after sputtering, the PZT film with LNO as electrode on glass substrate showed a mixture of a pervoskite phase and an impure PbO phase. In order to remove the impure phase, the film was subjected to a post thermal treatment. Fig. 2b shows the PbO peak decreased after treatment in a tube furance in air atmosphere, but it still exists. The PZT thin films treated in a tube furance showed no preferred

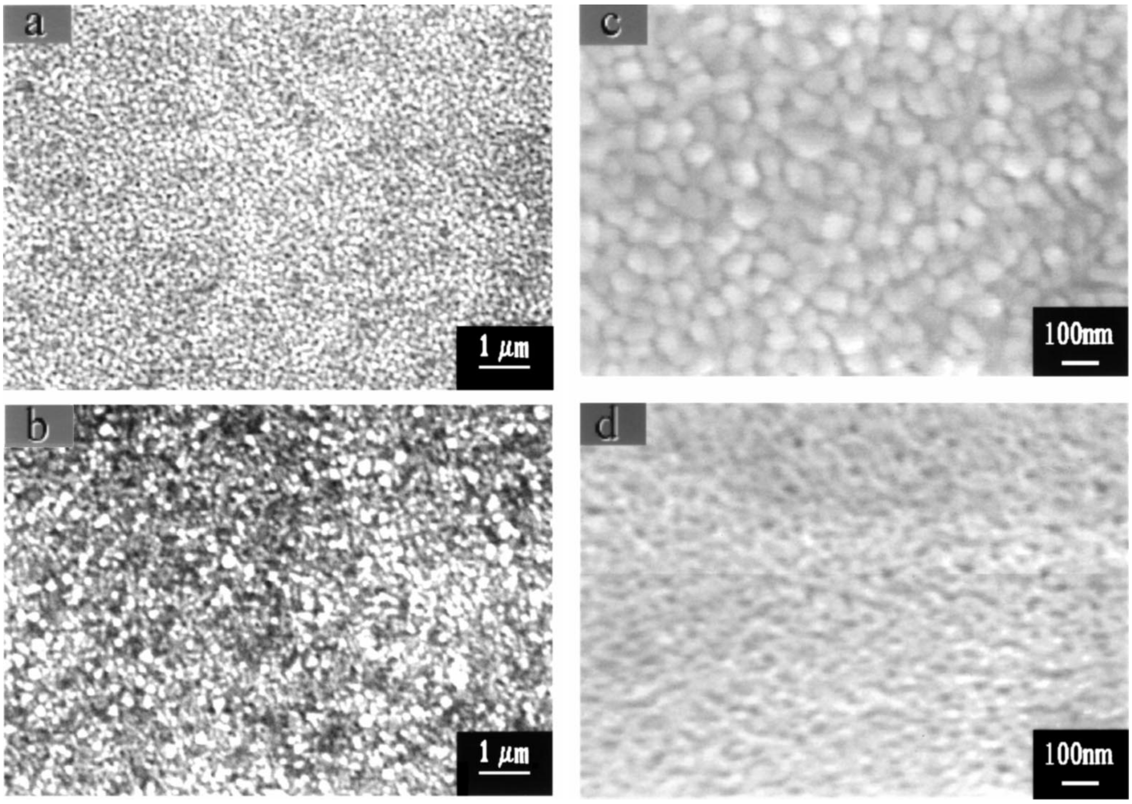

Figure 1 SEM micrographs of the PZT films on LNO/glass under various post thermal treatments: (a) *In situ* at 650 °C for 2 h; (b) In tube furnace at 650 °C for 2 h; (c) *In situ* at 650 °C for 3 h; and (d) SEM micrograph of the LNO film on glass.

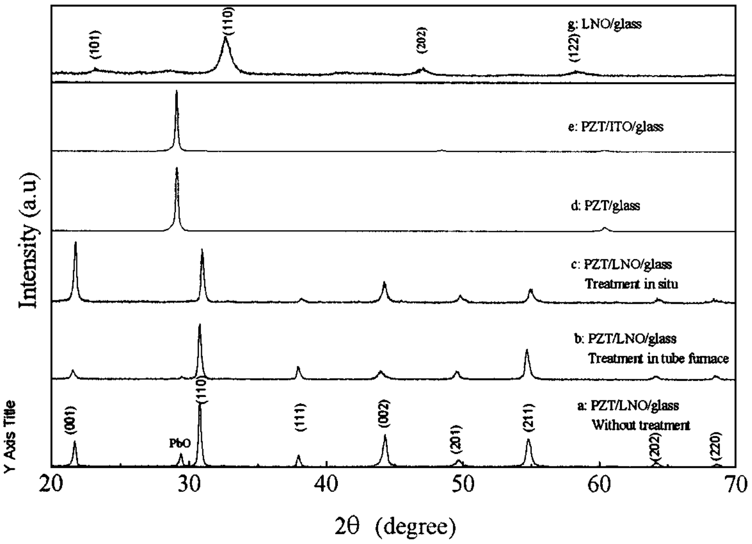

Figure 2 XRD patterns of the PZT films on glass substrates.

orientation. However, after treated in the growth chamber in vacuum (5×10^{-4} Pa), the impure PbO phase basically disappeared and the (001) peak of the PZT film notably enhanced (as shown in Fig. 2c), in which, the (001) direction was determined by multipeaks-separating technique. Generally, the (001) orientation (N) of thin film could be evaluated by formula

$$N = \frac{I(001)/[I(001) + I(110)]}{I_0(001)/[I_0(001) + I_0(110)]}$$

Here, the I_0 is the standard peak intensity of the PZT powder, and the I is the measured intensity. When $N = 1$, it indicates no orientation and $1 < N < 12.5$, there is preferred orientation. Correspondingly, we get $N = 8.6$ for PZT thin films treated *in situ*. This illustrates that the preferred orientation of PZT film on LNO/glass depends more strongly on the process condition, especially, post thermal treatment process.

On the other hand, the PZT thin film deposited on glass and ITO/glass substrate without LNO film showed very strong impure PbO phase without pervoskite structure. Even though these films were post thermally treated *in situ* at the same treatment condition, they still have no pervoskite structure (as shown in Fig. 2d and e). It indicates the LNO film greatly promotes formation of the PZT film with pervoskite phase on glass substrate. Fig. 2g shows the microstructure of the LNO film on glass substrate, in which, the LNO film possesses rhombohedral structure with lattice parameter $a = 3.84$ Å, which is near the pervoskite structure. In terms of the Volmer-weber (island-mode) mechanism [11], a lot of nuclei are very important for the epitaxial growth of the film, that means, there should be a large amount of nuclei in the surface of the LNO film to induce the growth of the PZT film along this pervoskite-like structure. From the SEM micrographs shown in Fig. 1d, the LNO film consists of a large amount of grains with small size, which nucleated, promoting the formation of the PZT film with the pervoskite phase. For the ITO/glass and glass substrate, there were no nuclei with the pervoskite phase, making it difficult to form the PZT film with the pervoskite phase.

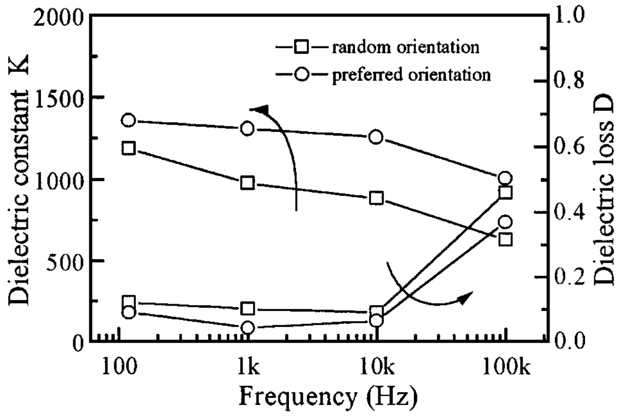

Figure 3 Dielectric-frequency property of the PZT films on LNO/glass substrates.

Fig. 3 shows the dielectric properties of the PZT thin films with the (001) preferred and random orientations. The dielectric constant and loss of the PZT film with the (001) preferred orientation are 1308 and 0.042, respectively, at 1 kHz, 0.05 V. The dielectric constant of the PZT thin film with (001) preferred orientation is so high that it approaches the maximum value of the (001) oriented PZT thin film reported for single crystal substrates. The dielectric loss was lower than the value reported in the literatures [8, 9]. These results demonstrate that the PZT thin film without orientation gives lower dielectric constant and higher loss than that of the oriented films.

The PZT thin film with (001) preferred orientation on LNO/glass substrate shows excellent P-E hysteresis loop, as shown in Fig. 4. The remanent polarization (P_r), saturation polarization (P_s) and coercive field (E_c) are 34.5 μC/cm^2, 43 μC/cm^2 and 105 KV/cm at $f = 60$ Hz, respectively. The remanent polarization P_r of the PZT film on LNO/glass is near to the value of PZT film on the single crystal substrate [8, 9]. The PZT film shows the higher coercive field E_c due to large stress in the film caused by the mismatch between film and amorphous substrate in structure. Its hysteresis loop has clear deviation along the X-axis, that is, $E_{c_+} \neq E_{c_-}$. This can

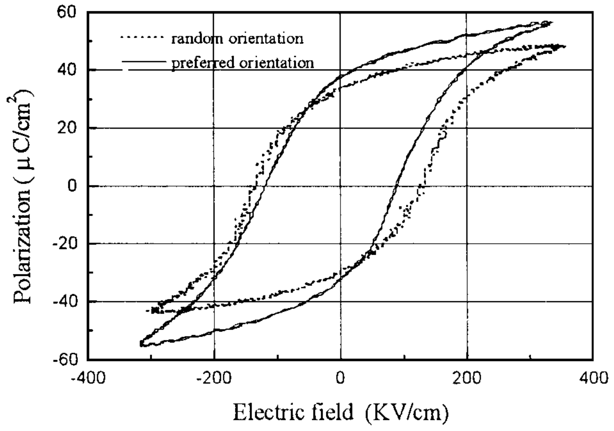

Figure 4 The P-E hysteresis loops of the PZT films on the LNO/glass substrates ($f = 60$ Hz).

be attributed to the internal bias field caused by the preferred orientation of the PZT thin films. The internal bias field is about 33 kV/cm. The hysteresis loop of the random film looks fatter than that of the oriented film because of higher dielectric loss. Apparently, the P_r and P_s values of the randomly oriented films are lower than those of the oriented films, and the E_c is larger than that of the oriented films due to the larger energy required to reverse the direction of the domain in the randomly oriented films.

The piezoelectric coefficient d_{33} of PZT films is about 15 pC/N without poled treatment due to its preferred orientation. After the film poled using 5 V DC voltage for 3 min at room temperature, the d_{33} becomes 23 pC/N. The PZT film was clamped to the stiff substrate, therefore, the d_{33} value does not represent the true piezolectric coefficient. Usually, we call it as the effective piezoelectric coefficient, which is far lower than that of bulk and film without clamping.

The piezoelectric response of stress acted on PZT/LNO/glass was discussed in Fig. 5. With the increasing of the stress, the piezoelectric voltage response of the PZT film increased almost linearly. When the stress exerted on the sample exceeded the elastic limit of glass, the cracks of glass substrate were observed and correspondingly, the first peak appeared in the response curve. With the propagation of the cracks under the action of the stress, the response has a little decrease. Accompanying with the appearance of fracture in the sample, the second peak appeared in the response again and then the response dropped down rapidly with the increasing of stress. According to the aforementioned discussion, the response curve reflects the force behavior of the sample. From this primary experiment, since the PZT film has been successfully deposited on amorphous substrate, we believe that the PZT film could be used as a kind of artificial skin, in which, the self-diagnosis of force behavior of amorphous substrate can be realized in the future. The study in this field is in progress in our institute.

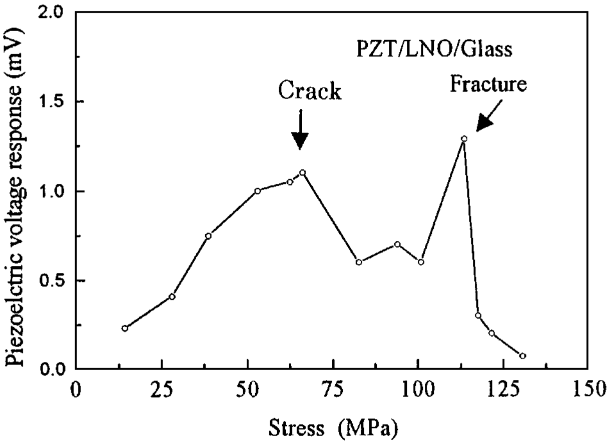

Figure 5 The piezoelectric voltage response of the PZT film under the action of stress.

4. Conclusion

In summary, the (001) preferred orientation of Nb-doped Pb($Zr_{0.52}Ti_{0.48}$) O_3 (PZT) thin film was successfully realized on amorphous glass substrate with LNO as electrode by rf-sputtering method. It was found that the LNO film greatly promotes formation of the PZT film with pervoskite phase on amorphous substrate and the preferred orientation of PZT film depends strongly on the process of preparation. The PZT films with the (001) preferred orientation on LNO/glass substrates show better dielectric, ferroelectric and piezoelectric properties. Moreover, the piezoelectric voltage response of the PZT film displayed effect of the stress on substrate. It makes us consider using the PZT film as an artificial skin of amorphous materials to realize the self-diagnosis of materials under the action of stress.

Acknowledgement

This research work is supported by AIST, MITI, Japan as part of the Synergy Ceramics Project under the Industrial Science and Technology Frontier (ISTF) Program.

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Received 8 December 1998
and accepted 15 March 1999