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DIELECTRIC RELAXATION ASSOCIATED WITH DIPOLAR DEFECT COMPLEX IN $PbZr_xTi_{1-x}O_3$ MULTILAYER

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Abstract: Dielectric behavior of $PbZr_{0.38}Ti_{0.62}O_3$ multilayer with alternating dense and porous $PbZr_{0.38}Ti_{0.62}O_3$ layers was investigated at 420K. Two distinct dielectric relaxation processes were observed in the frequency range from 10^2 Hz to 10^6 Hz. The relaxation at lower frequencies is attributed to the space charge polarization. The one at higher frequencies, with a thermal activation energy of 0.49 eV, might originate from the response of singly positive charged defect dipoles $V_0^{\cdot\cdot}-Ti^{3+}$ to ac electric fields. These dipoles are formed by the doubly ionized oxygen vacancies V_0 and trivalent titanium ions Ti^{3+} as indicated by the results of Auger electron spectrum and electron paramagnetic resonance spectrum.

Key words: $PbZr_{0.38}Ti_{0.62}O_3$ multilayer; dipolar defect complex; dielectric relaxation
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$PbZr_xTi_{1-x}O_3$多层膜中与极性缺陷复合体相关的介电驰豫

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摘要:研究了由致密$PbZr_{0.38}Ti_{0.62}O_3$和多孔$PbZr_{0.38}Ti_{0.62}O_3$膜层交替排列组成的多层膜在温度为420K时的介电行为.在$10^2\sim10^6$Hz的频率范围,观测到两种截然不同的介电驰豫.位于低频区的介电损耗峰归因于空间电荷极化.通过俄歇电子谱和电子顺磁共振谱分析,初步判定遵从Arrhenius律、热激活能为0.49 eV的高频介电驰豫则起源于氧空位$V_0^{\cdot\cdot}$和Ti^{3+}形成的极性缺陷复合体$V_0^{\cdot\cdot}-Ti^{3+}$对交变电场的响应.

关 键 词:$PbZr_{0.38}Ti_{0.62}O_3$多层膜;极性缺陷复合体;介电驰豫

Introduction

Processing-related lead and oxygen vacancies ($V_{Pb}^{\cdot\cdot}$, $V_0^{\cdot\cdot}$) are ubiquitous point defects in $PbZr_xTi_{1-x}O_3$ (PZT) material and have a remarkable influence on ferroelectric and dielectric properties of PZT material. For example, La-doping can effectively eliminate B-site deficiencies in $PbTiO_3$, which makes $PbTiO_3$ exhibit giant dielectric permittivity, lower loss, and excellent thermal stability[1]. Metal acceptor impurities (such as Pt, Fe, and Ni), substituting for Ti^{4+} ions in PZT, can couple with the nearby oxygen vacancies $V_0^{\cdot\cdot}$ to form dipolar defect complexes. These defect dipoles act as domain wall pinning agents, giving rise to the polar-

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ization fatigue and imprint. They can rearrange themselves under a dc field at an elevated temperature via V_O hopping between nonequivalent sites in a unit cell[2~5]. The $Ti^{3+}-V_O^{..}$ defect center was first observed by Scharfschwerdt *et al.* both in pure and reduced $BaTiO_3$ single crystal and in $BaTiO_3$ thin films[6,7]. Ti^{3+} ions could also be present in PZT as proved by Robertson and Nagaraj et al[8,9]. Therefore, the study on the behavior and electronic structure of Ti^{3+} ions has been of great interest to condensed matter physics and materials science.

In the past several years, to promote application of multifunctional PZT material in photonic band-gap engineering, we developed a simple method for constructing one-dimensional periodic PZT multilayers based on phase separation using one single chemical solution. The building block of PZT multilayer is a bilayer consisting of dense and porous PZT layers. Besides good performance as dielectric reflectors and optical cavities, the prepared multilayer stacks exhibit excellent electric properties, such as low leakage current density, high remanent polarization, and large dielectric permittivity, etc[10,11].

We reported previously the investigations on dielectric and ferroelectric properties of a 2.1μm thick $PbZr_{0.38}Ti_{0.62}O_3$ multilayer (PZTM) with 24 pairs of dense and porous PZT layers, which was grown on Si wafer buffered with a 200 nm conductive metallic oxide $LaNiO_3$ (LNO) layer[11]. Figure 1 displays the dielectric loss tanδ spectrum measured on the PZTM at 420 K (solid line). The peak at lower frequencies originates mainly from space charge polarization, as identified in Ref. 11. The dielectric relaxation at higher frequencies follows the Arrhenius law and is thermally activated with activation energy of 0.49 eV[11]. The dielectric relaxation behavior seems to be sample dependent, with some of samples having a pronounced shoulder and some showing very weak above-mentioned relaxation properties (see Fig. 1). Although it was suggested that the high-frequency dielectric relaxation occurring in the PZTM was closely related to oxygen vacancy at that time, the underline mechanism was still unclear.

The work presented here tries to determine the fundamental electric polarization species corresponding

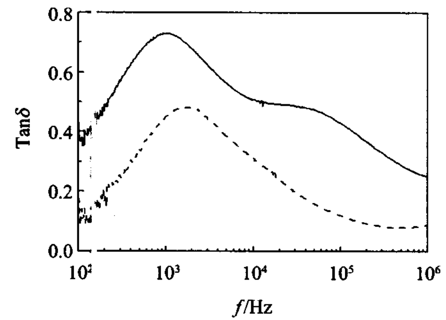


Fig. 1 Dielectric loss spectra measured on the two multilayers at 420K, the solid line corresponds to the $PbZr_{0.38}Ti_{0.62}O_3$ multilayer investigated in the Ref. 11, and the dashed line denotes the one with a little of Ti^{3+} ions.
图1 两个$PbZr_{0.38}Ti_{0.62}O_3$多层膜在420K时的介电损耗谱，实线对应文献11中的样品，虚线对应Ti^{3+}很难被探测到甚至无Ti^{3+}的样品

to the high-frequency dielectric relaxation (HFDR) observed in the PZTM. The response of singly positive charged defect dipoles ($V_O^{..}-Ti^{3+}$) formed by doubly ionized oxygen vacancies $V_O^{..}$ and trivalent titanium ions Ti^{3+} to ac electric fields is considered as the origin of the HFDR.

1 Experiment

The average thickness of a single bilayer in the PZTM is ~ 90 nm, and crystallization time at 700℃ is 480s for the $PbZr_{0.38}Ti_{0.62}O_3$ gel layer. For comparison, another PZT multilayer with a nominal Zr/Ti ratio of 40/60 was also grown on silicon substrate with $LaNiO_3$ buffer layer. The fabricating process for the $PbZr_{0.4}Ti_{0.6}O_3$ multilayer with 14 pairs of dense and porous $PbZr_{0.4}Ti_{0.6}O_3$ layers was similar to that for the PZTM. The average thickness of a pair of dense and porous $PbZr_{0.4}Ti_{0.6}O_3$ layers is ~ 112nm, and annealing time at 700℃ for the $PbZr_{0.4}Ti_{0.6}O_3$ gel layer is 300s. The detailed sample preparation was described elsewhere[10]. Dielectric dispersion spectra were measured using an HP4194A impedance analyzer under a 0.5 V ac driving voltage in a background vacuum of 10^{-2} Pa. Electron paramagnetic resonance (EPR) measurements were performed using an EPR spectrometer (ERUKER EMX-8/2.7) working in the X-band (9.865GHz). Auger electron spectroscopic (AES) measurement, followed by Ar ion etching, was repeatedly conducted on the PZTM sample.

2 Results and Discussion

Figure 2 shows the depth profile of atomic concentration, measured on the as-grown PZTM. From Fig. 2, it can be seen that there is a ~10 nm thick defect layer or dead layer with a high concentration of oxygen vacancies below the free-surface of the PZTM. Since the dead layer thickness is much thinner than that of the bulk of the PZTM (~2.1μm), the measured total dielectric spectra at higher frequencies are mainly contributed by the bulk of the PZTM according to the dielectric equivalent circuit model, i. e., the influence of the defect layer on the dielectric response of the PZTM can be ignored.

There are four known possible polarization mechanisms in a dielectric medium which can give rise to dielectric relaxations. They are electronic, ionic, dipolar, and space charge polarizations[12]. Electronic and ionic relaxations appear typically at frequencies above 10^{10} Hz, and thus are not observed in our studies. Because the low-frequency dielectric relaxation has been identified as the space charge polarization[11], the observed HFDR with a single relaxation time in the PZTM is most likely originated from dipolar polarization.

In ABO_{3-y} perovskite oxides, a common and processing-related point defect is doubly ionized oxygen vacancy $V_O^{\cdot\cdot}$ which plays an important role both in electric conduction and in dielectric response. The activation energy E_a of oxygen vacancy $V_O^{\cdot\cdot}$ is closely related to the concentration of oxygen deficiency y, and can be written as:[13]

$$E_a(y) = 2^{1-20y}(eV) \quad (1)$$

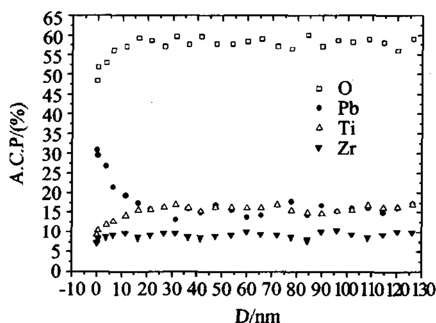
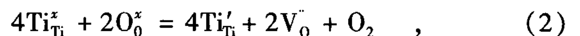


Fig. 2 Atomic concentration percentage (A. C. P.) verses the depth of the PZTM D

图 2 PZTM 中各元素的百分比含量随溅射深度 D 的变化

As shown in Fig. 2, except for a thin defect layer below the free-surface of the PZTM, lead and oxygen deficits occur simultaneously in the film, and the average percentage of oxygen atomic concentration in the bulk of the PZTM is ~58%, corresponding to a mean oxygen atom number of 2.9 or an oxygen deficiency parameter $y = 0.1$ in the unit cell of PZT. The E_a value of 0.5eV can be calculated by substituting $y = 0.1$ into Eq. (1), consistent with that determined using Arrhenius law. Thus, it is reasonable to conclude that the oxygen vacancy $V_O^{\cdot\cdot}$ may be involved in the high-frequency dielectric relaxation of PZTM.

According to the defect chemistry analysis, Ti^{3+} ions can be found in PZT due to oxygen loss process as follows:[9]



$$4Ti_{Ti}^{x} + 2O_O^{x} = 4Ti_{Ti}' + 2V_O^{\cdot\cdot} + O_2 \quad , \quad (2)$$

where the Kröger-Vink notation is employed, $(S_p)^C$ represents the structural element, S is the species, P is the crystallographic position, C is the charge state of the species relative to the site that it occupies, and x is for neutral. As elucidated by Eq. (2), Ti^{4+} ionizing to Ti^{3+} is accompanied by the creation of $V_O^{\cdot\cdot}$, and the ionization energy of Ti^{4+} to Ti^{3+} is estimated to be ~0.5 eV[9]. On the other hand, Robertson *et al.* have demonstrated that it is reliable to determine valences of elements in PZT power by measuring EPR spectra, and provided a substaintial evidence of existence of Ti^{3+} ions in PZT[8]. Figure 3 shows the EPR measurements for the two specimens. As rendered by the dashed line in Fig. 3, a very strong first harmonic signal of Ti^{3+} ion is detected near the magnetic filed of 3500 gauss (corresponding to a g-factor value of 2.000), agreeing well with the observations by Robertson *et al.* However, Ti^{3+} signal is very weak in the $PbZr_{0.4}Ti_{0.6}O_3$ multilayer with 14 bilayers consisting of dense and porous $PbZr_{0.4}Ti_{0.6}O_3$ layers (denoted by the solid line in the Fig. 3), correspondingly, in which the HFDR was hardly observed. For comparison, fig. 1 also shows the spectra of dielectric loss measured on the $PbZr_{0.4}Ti_{0.6}O_3$ multilayer with a little of Ti^{3+} ions at 420 K. Only a dielectric loss peak locating at lower frequencies is remarkably visible in the investigated frequency range. This evidences that the observed HFDR in the PZTM is also related to the Ti^{3+} ions.

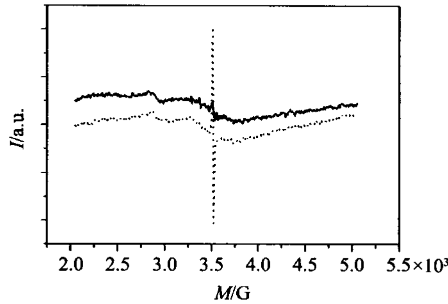


Fig. 3 Electron paramagnetic resonance spectra measured on the two PZT multilayers. The dashed line corresponds to the PZTM in which a HFDR has been detected, and the solid line to the $PbZr_{0.38}Ti_{0.62}O_3$ multilayer in which only a low-frequency loss peak has been observed.

图3 两个PZT多层膜的电子顺磁共振谱,虚线对应能观测到高频损耗峰的样品,实线对应只出现一个低频损耗峰的样品,其中横坐标是磁场 M,纵坐标是强度 I

Other possible point defects in the PZTM include lead vacancies, metallic atoms, as well as trivalent acceptor impurities. Lead and oxygen vacancies could not form energetically stable dipolar defect complexes, as demonstrated by Pöykkö and Chadi from the first principle calculation analysis[14]. Extensive studies have shown that metallic atoms and trivalent acceptor impurities such as Pt, Ni^{3+}, Fe^{3+} (they substitute for Ti^{4+} ions), and Ti^{3+} tend to couple with V_O forming dipolar defect pairs in Ti-based perovskite compounds[2~5]. However, the results of AES measurements show no signatures of other metallic atoms and trivalent acceptor impurities in the PZTM. V_O is considered to be the most mobile defect in this kind of oxides. When a V_O moves close to a Ti^{3+} ion, the strong electrostatic interaction between them leads to the creation of a polar defect association[2]. Based on the above analysis, we conclude that the microscopic entity responsible for the dielectric relaxation centered at 49kHz is defect dipoles $V_O^{\cdot\cdot}-Ti^{3+}$, similar to those observed in $BaTiO_3$ material system[6,7].

The maximum value of the dielectric loss, due to the dipolar polarization with a single relaxation time τ, takes[15]

$$(\tan\delta)_{\max} = \frac{\varepsilon_s - \varepsilon_\infty}{2\sqrt{\varepsilon_s\varepsilon_\infty}} \propto \frac{N_d\mu^2}{3kT} \quad , \tag{3}$$

at $\omega\tau \sim 1$, where ε_s is static permittivity, ε_∞ the permittivity at optical frequencies, N_d the dipole concentration, μ the dipolar moment, k the Boltzmann constant, and T the absolute temperature. Thus, $(\tan\delta)_{\max}$ is proportional to N_d. At given temperature, the dielectric relaxation associated with the dipolar polarization is measurable within the resolution limit of the impedance analyzer only when N_d is large enough. ERP result shows that the concentration of Ti^{3+} ions in the $PbZr_{0.4}Ti_{0.6}O_3$ multilayer is very low, thus the number of the $V_O^{\cdot\cdot}-Ti^{3+}$ dipolar defects is expected to be very low. As a result, its contribution of the relaxation to the dielectric loss is negligible.

Both creation and concentration of oxygen vacancy in perovskite oxides are closely related to processing conditions and doping. The formation of oxygen vacancy is accelerated with increasing crystallization time and temperature[16,17]. The oxygen loss is always accompanied by the formation of lead vacancies or Ti^{3+} ions for charge compensation. We believe that the discrepancy in the concentration of Ti^{3+} ions observed in the two investigated PZT multilayers is due to the different sample crystallization time.

3 Conclusion

In summary, we have observed an abnormal high-frequency dielectric relaxation in the PZTM. The relaxation is found due to the dipolar defect complex $Ti^{3+}-V_O^{\cdot\cdot}$ formed through a Ti^{4+} ion becoming Ti^{3+} via loosing a hole or capturing an electron and then coupling with a nearby $V_O^{\cdot\cdot}$.

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$\times 30mm^2 \times 4$ 碲镉汞垂直液相外延工艺的可重复性,外延材料的组分控制能力做到了 ±0.005,$40 \times 30mm^2$材料组分面分布的相对均方差在 1.3×10^{-3} 以内,片与片之间组分和厚度的差异分别小于0.001和1μm,经热处理后所获得汞空位p型碲镉汞材料具有较高的空穴迁移率.碲镉汞垂直液相外延技术在组分控制能力、厚度均匀性和表面平整性方面均优于水平推舟技术,其大批量生产能力及提供大面积性能完全相同材料的能力也明显优于水平推舟技术.

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